Structural studies of some heterocyclic compounds.

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Structural Studies of Some Heterocyclic Compounds.

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"If a man's education is finished, he is finished."

E.A.Filene, 1860-1937

Contents

Abstract

Single crystal X-ray analysis has been used to examine the solid state structures of a selection of heterocyclic compounds which fall into three categories:

1. Triazole and imidazole compounds

The activity of fungicides is highly dependent upon the predominant conformation adopted by the molecule. The crystal and molecular structures of five compounds showing fungicidal activity and provided by I.C.I. Plant Protection have been determined. The conformations of the compounds, which contain either a 1,2,4-triazol-1-yl or imidazol-1-yl ring have been compared. The most noteworthy feature is the significant difference in the conformation adopted by triadimefon compared with the other triazole compounds studied.

2. Macrocyclic metal compounds

Single crystal X-ray analyses of five macrocyclic complexes containing alkaline earth metal ions (calcium, strontium, and barium) have been completed. The relative sizes of the macrocyclic cavity and the metal ion play a crucial role in determining the structure adopted. Thus, in the complexes $M(NCS)_2(L).nH_2O$ (M = Ca, $n = 0$; M = Sr or Ba, $n = 1$) in which L is the macrocyclic ligand 3,25,21-triaza-6,9,12-trioxabicyclo(15.3.1)heneicosa-1(21), 2,15,17,19-pentaene; increasing size of the metal ion is accompanied by (i) a progressive displacement of the metal ion from the mean plane through the six donor atoms and (ii) an increase in the coordination number of the metal from eight (calcium) to nine (strontium and barium).

3. Phosphorus heterocyclic compounds

The structures of three phosphorus heterocycles have been

determined in an attempt to establish the importance of ring strain within the heterocyclic phosphonium ring systems. While the small endocyclic C-P-C angle of $94(1)^\circ$ found in 5-(p-bromo--benzyl)-5-phenyl-dibenzophospholium bromide is indicative of the presence of significant ring strain within the phosphorus heterocycle, such effects appear to be of much less importance in the six- and seven-membered ring systems studied, viz: 10-(4-bromobenzyl)-10-phenylphenoxaphosphonium bromide and 5-phenyl-10,11-dihydrobenzo(b,f)phosphepin-5-oxide.

Abbreviations

General

Me - methyl
Bu^t - tertiary butyl
R - hydrocarbon group
M - metal atom
L - neutral unidentate ligand
TCNQ - 7,7,8,8-tetra cyanoquinodimethane
Et - Ethyl
Ph - phenyl
M_r - relative molecular mass

Crystallographic

Å - Angströms
F_o - observed structure factor
F_c - calculated structure factor
I - intensity of a reflection
W - weighting function
$\mu(Mo\text{-}K\alpha)$ - absorption coefficient for molybdenum $K\alpha$ radiation
F(000) - number of electrons per unit cell
R - refinement factor
D_c - calculated density
D_m - measured density
Z - number of molecules per unit cell

Contents

1.1 Single Crystal X-ray Diffraction

W. L. Bragg[1] showed that X-rays are scattered by crystals in such a way that the process may be regarded as reflection from sets of planes within the crystal. The diffraction maxima are regarded as reflections from stacks of planes orientated at a suitable angle to the incident beam. The condition for diffraction is given by the equation

$$n\lambda = 2d\sin\theta \qquad (1.1)$$

where

n is the order of diffraction

λ is the wavelength of the incident X-ray beam

d is the interplanar distance

θ is the angle between the planes and the incident beam.

Each diffraction maximum occurs from reflection from the respective set of planes having Miller indices h, k, l (defined such that one of the set of planes intersects the three axes of the unit cell at a/h, b/k, c/l). The resultant of the j waves scattered in that direction by the j atoms within the unit cell is known as the structure factor (F_{hkl}). If the positions for all the atoms within a unit cell are known, then the structure factor F_{hkl} may be calculated from

$$F_{hkl} = \sum_{n=1}^{j} f_n \exp\left(-2\pi i(hx_n + ky_n + lz_n)\right) \qquad (1.2)$$

Where f_n is the scattering factor for the n^{th} atom and x_n, y_n and z_n are its fractional coordinates. The scattering power, f_n, can be shown to be independent of the position of the atom within the cell and, with the assumption that the atom is spherical, a function only of $(\sin\theta)/\lambda$. For $\theta = 0^{\circ}$, f_n is equivalent to the number of electrons of the atom located at the position of atomic nucleus. The scattering factor, f_n, is calculated on the assumption that the atom is stationary. Thermal motion causes the electron cloud to spread over a larger volume than would be found for such a stationary atom and, thus, the scattering power falls off more rapidly than for the stationary model due to the scattering from one part of the electron cloud being out of phase with scattering from another part. It has been found that the relationship

$$f_n = f_o \exp [- 8\pi^2 U \sin^2\theta / \lambda^2] \qquad (1.3)$$

where U = mean square amplitude of vibration isotropic temperature factor

f_o = scattering factor for a point atom

leads to a satisfactory description of isotropic thermal behaviour. A further refinement of the model allowing for anisotropic vibration is such that the atomic scattering factor is given by:

$$f_n = f_o \exp [- 2\pi^2 (U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}kl\, b^* c^* + 2U_{13}hl\, a^* c^* + 2U_{12}hk\, a^* b^*)].$$

The six parameters U_{ij} describe the direction and magnitude of a vibrational ellipsoid and are known as anisotropic temperature factors.

The assumption has been made in the above that the frequency of the X-ray radiation is widely different from the natural absorption frequency of the given atom. While this is true for light atoms it ceases to hold for atoms close in atomic number to the target source for the radiation. The scattering factor ceases to be a real function and is now represented by the complex expression for anomalous scattering:

$$f_o^{anom} = f_o + \Delta f' + i\Delta f'' = f' + i\Delta f'' \qquad (1.4)$$

where f' and f'' are the real and complex components of the anomalous dispersion. Corrections for anomalous dispersion are virtually independent of $\sin\theta$.

1.2 Data Collection and Data Processing

Preliminary photographs were taken of suitably sized crystals to determine that the crystal was suitable for further investigatory work and to determine possible space groups and unit cell dimensions. Preliminary photographs were taken on Weissenberg and precession X-ray goniometers. Intensity measurements were made with a Stoe Stadi-2 two circle diffractometer using a stationary counter - rotating crystal technique with background scans made at either extremity of the intensity scan for each reflection.

The raw data collected has inherent errors which are independent of molecular structure. Both the graphite crystal used to monochromate the X-ray beam and the crystal under investigation will cause slight polarisation of the X-ray beam, thus reducing the measured intensity. Correction for polarisation due to the crystal itself is given by equation 1.5 but the overall expression is more complex.

$$p = (1 + \cos^2 2\theta)/2 \qquad (1.5)$$

Further correction for the Lorentz factor, L, is needed to compensate for the beam passing through the diffracting positions for different reflections at different velocities. L is dependent on the method of data collection: for equi-inclination Weissenberg geometry, L is given by:

$$L = \sin\theta/(\sin 2\theta[\sin^2\theta - \sin^2\mu]^{\frac{1}{2}}) \qquad (1.6)$$

The corrected observed structure factor amplitude, $|F_o|_{hkl}$, is given by

$$|F_o|_{hkl} = \sqrt{\frac{KI_{hkl}}{Lp}} \qquad (1.7)$$

where K is a constant dependent on several physical variables including crystal size, absorption effects and beam intensity^2 and I_{hkl} is given by:

$$I_{hkl} = I - \frac{(b_1 + b_2).\ t_s}{2t_b} \qquad (1.8)$$

The significance of each reflection, (I), was calculated from

$$\sigma(I) = \sqrt{I + \frac{(b_1 + b_2)}{4}.\ \frac{t_s^2}{t_b^2}} \qquad (1.9)$$

where b_1, b_2 = the intensities of the background scans respectively before and after reflection scan

t_s = time for reflection scan

t_b = time for each background scan

I = scan count

Before proceeding in attempts to find a preliminary solution, it is necessary to correct the intensity data for the effects of thermal motion. Wilson[3] showed that this could be done by use of statistical relations between the atomic scattering factors and the intensities. By assuming that the atomic distribution in a cell is random (this assumption is sufficiently accurate for most structures, though not all), the absolute intensities (Ia) are related to the measured intensities (Io):

$$Ia = KIo \qquad (1.10)$$

where K is the required scale factor and

$$\langle Ia \rangle = \sum_{n=1}^{j} f_n^2 \qquad (1.11)$$

Hence, allowing for thermal motion,

$$K \langle Io \rangle = \exp(-2B \sin^2\theta/\lambda^2) \sum_{n=1}^{j} f_n^2 \qquad (1.12)$$

where $B = 8\pi^2 U$

The Wilson plot[3,4] (the plot of $\ln(Io/\sum_{n=1}^{j} f_n^2)$ v. $\sin^2\theta/\lambda^2$) allows K to be calculated from the intercept by the line of best fit with the $\ln Io(\sum_{n=1}^{j} f_n^2)$ axis and hence correction may be made via (1.10).

1.3 Structure Solution

1.3.1 The Patterson function[5]

One of the basic problems in single crystal X-ray analysis arises from the total absence of experimental information relating to the phase of each reflection[6,7,8]. This ceases to be a major problem if the position of sufficient of the scattering material is known for the phases may be signed by use of equation 1.2. The Patterson function is widely used to overcome 'the phase problem' and is particularly suited to compounds containing a heavy atom. Patterson showed that the function (1.13) represented the sum

$$P(u,v,w) = \frac{1}{V} \sum_h \sum_k \sum_l \left| F_{hkl} \right|^2 \exp\left(-2\pi i\ (hu + kv + lw)\right) \qquad (1.13)$$

where V = Volume of unit cell

$\left|F_{hkl}\right|$ = structure amplitude (known experimentally)

of the electron density product of all sets of points in the unit cell separated by the vector (u,v,w). Clearly, when the vector represents the distance between two atoms, a peak will be given of size proportional to the product of the scattering factors of the two atoms. Unfortunately, it also follows that a unit cell containing N atoms will give N(N-1) peaks in addition to the origin peak. Thus, the complexity of the three dimensional Patterson map rapidly increases with increase in N. The poor resolution of the function further inhibits interpretation so that, in practice, only the peaks formed by the relatively heavy atoms can be readily found although this is usually sufficient to allow the detection of the remainder of the structure using subsequent Fourier techniques.

Knowing the structure factors, the electron density at any point (x,y,z) in the unit cell may be calculated from the Fourier series

$$\rho(x,y,z) = \frac{1}{V} \sum_h \sum_k \sum_l F_{hkl} \exp(-2\pi i\ (hx + ky + lz)) \qquad (1.14)$$

So long as sufficient structure factors are known, peaks will be found on the resultant 3D Fourier map which will correspond to atom positions. The type of atom can be identified from chemical knowledge of the structure and the new atomic positions used to further improve successive Fourier maps. In practice, truncation errors on the Fourier series result in slight errors in locating the position of peaks and 'diffraction ripples' around heavy atoms. A Fourier synthesis based on coefficients of calculated structure factor amplitudes (Fc) has similar truncation errors to those observed for (1.14). Hence, a series in which coefficients of (Fo - Fc) (where Fo is the observed structure factor modulus with the phase of Fc) are used (1.15) will have the properties of largely avoiding truncation errors and giving peaks that correspond to atoms not included in the phasing model. The series is known as a difference Fourier synthesis.

$$\Delta \rho(x,y,z) = \frac{1}{V} \sum_{h} \sum_{k} \sum_{l} (F_o - F_c) \exp\left(-2\pi i \left(hx + ky + lz\right)\right) \tag{1.15}$$

1.3.2 Direct methods

The direct determination of atomic positions from measured structure amplitudes, $|Fo|$, thereby overcoming the 'phase problem', is an attractive goal. However, it is more convenient to use E values (normalized structure factors), rather than direct application of measured structure factor amplitudes, which may be derived from (1.12):

$$|E_{hkl}|^2 = F_{hkl}^{\ 2} / \varepsilon \sum_{n=1}^{i} f_n^{\ 2} \tag{1.16}$$

where ε is an integer multiplicity factor which is usually 1 but may assume higher values for special reflections in certain space groups (especially those of higher orders of symmetry) e.g. $\varepsilon = 2$ in $P2_1/c$ for h0l and 0k0 reflections[9].

E statistics may be helpful in differentiating between centrosymmetric and non-centrosymmetric space groups. Theoretical values for E statistics based on a random molecule of similar atoms are shown overleaf.

	centrosymmetric	non-centrosymmetric
$<\lvert E\rvert^2>$	1.0	1.0
$<\lvert E\rvert>$	0.798	0.886
$<\lvert E^2 - 1\rvert>$	0.968	0.736
$\%\lvert E\rvert > 1$	31.7	36.8
$\%\lvert E\rvert > 2$	4.6	1.8
$\%\lvert E\rvert > 3$	0.3	0.01

The $\lvert E^2 - 1\rvert$ statistic is especially useful in this context.

The use of E values instead of F values as coefficients in Fourier systhesis leads to very sharp peaks which are equivalent to atom positions. Further, the effect of a few low angle reflections with high F values tend to dominate in calculations but this effect is avoided using E values. Conversely, many high angle reflections have low F values but relatively high E values.

Inequalities

(a) Harker-Kasper inequalities[10]

Inequalities may be established in such a way that direct information on the phases of some reflections may be deduced. The simplest inequality of $\lvert F_{hkl}\rvert^2 < F^2_{000}$ is trivial but the requirements of symmetry elements leads to further nontrivial inequalities. The requirement of centrosymmetry, for example, leads to the result:

$$F^2_{h,k,l} < F_{000} \left|\tfrac{1}{2}F_{000} + \tfrac{1}{2}F_{2h,2k,2l}\right| \qquad (1.17)$$

Dividing by F^2_{000} and defining $U_{hkl} = \dfrac{F_{hkl}}{F_{000}}$,

$$U^2_{hkl} < \tfrac{1}{2} + \tfrac{1}{2}U_{2h,2k,2l}$$

Since both the magnitude and sign (positive) of U^2_{hkl} are known, only the phase of $U_{2h,2k,2l}$ is unknown. Further $\lvert U_{hkl}\rvert < 1$ by definition so that the sign of $U_{2h,2k,2l}$ will have to be positive to satisfy (1.17) if the magnitudes of U_{hkl} and $U_{2h,2k,2l}$ are sufficiently large.

Other workers[11-23] have extended the work on equalities. Using the constraints imposed on the structure factors by the fact that the electron density function cannot be negative, Karle and Hauptman developed a set of inequalities expressing $F_{\underline{h}}$ in terms of $F_{\underline{h}}\ F_{\underline{h-k}}$ $\left[\underline{h}, \underline{k}\right.$ represent the Miller indices $(h_1k_1l_1)$ and $(h_2k_2l_2)$ and $\underline{h-k}$ is the triplet $\left.(h_1-h_2,\ k_1-k_2,\ l_1-l_2)\right]$. It has been shown that[24], subject to certain restrictions,

$$F_{hkl} = C_{hkl} \sum_{h'}\sum_{k'}\sum_{l'} F_{h'k'l'} \cdot F_{h-h',\, k-k',\, l-l'} \qquad (1.18)$$

where C_{hkl} is a calculable scaling constant. In order to calculate F_{hkl} from this relation, all pairs of structure factors $F_{h'k'l'}$ and $F_{h-h',\, k-k',\, l-l'}$ would have to be known. Sayre, however, pointed out that for strong reflections the series would have a marked tendency toward one direction (i.e. + or -). Thus, using the abbreviation of S for "the sign of " and $\approx$ for "is probably equal to", we have:

$$S(F_{hkl}) \approx S(F_{h'k'l'}) \cdot S(F_{h-h',\, k-k',\, l-l'}) \qquad (1.19)$$

It may be directly deduced from (1.19) that

$$S(F_{2h,\, 2k,\, 2l}) \approx S(F_{hkl}) \cdot S(F_{hkl}) \qquad (1.20)$$

and hence that $S(F_{2h,\, 2k,\, 2l})$ is probably positive. The variation of (1.19) using normalized structure factors (viz. $SE_{\underline{h}} = S \sum_{\underline{k}} E_{\underline{k}} E_{\underline{h-k}}$), the $\sum_2$ formula of Hauptman and Karle[25], is the main formula used for the initial solution of centrosymmetric crystals. The probability that the sign of $E_{\underline{h}}$ is positive, $P_+(\underline{h})$, is given by[11,26,27]:

$$P_+(\underline{h}) = \tfrac{1}{2} + \tfrac{1}{2} \tanh \left[(\sigma_3/\sigma_2^{3/2})\, \alpha' \right] \qquad (1.21)$$

where $\alpha' = \left| E_{\underline{h}} \right| \sum_{\underline{k}} E_{\underline{k}} E_{\underline{h-k}}$ and $\sigma_n = {}^{n}_{j=1} Z_j^n$ (z_j is the atomic number of the j^{th} atom).

A large and negative value for α' produces a value for $P_+(\underline{h})$ that tends to zero. This indicates that $S(F_{hkl})$ is negative with a probability tending to 1 as $P_+(\underline{h})$ tends to zero. The most reliable signs are associated with high $|E|$ values and a large number of consistent Σ_2 relations. This puts constraints on the starting set in addition to those discussed later.

For non-centrosymmetric space groups, the tangent formula[28], (1.22), is used where:

$$\tan\phi_{\underline{h}} \doteq \frac{\sum_{\underline{k}} \left|E_{\underline{k}} E_{\underline{h-k}}\right| \sin(\phi_{\underline{k}} + \phi_{\underline{h-k}})}{\sum_{\underline{k}} \left|E_{\underline{k}} E_{\underline{h-k}}\right| \cos(\phi_{\underline{k}} + \phi_{\underline{h-k}})} \qquad (1.22)$$

$\phi_{\underline{h}}$ is the phase angle associated with $F_{\underline{h}}$; i.e. the phase being determined. The reliability, $\alpha_{\underline{h}}$, of $\phi_{\underline{h}}$ is determined from:

$$\alpha^2_{\underline{h}} = \left[\sum_{\underline{k}} \kappa_{\underline{hk}} \cos(\phi_{\underline{k}} + \phi_{\underline{h-k}})\right]^2 + \left[\sum_{\underline{k}} \kappa_{\underline{hk}} \sin(\phi_{\underline{h}} + \phi_{\underline{h-k}})\right]^2 \qquad (1.23)$$

where $\kappa_{\underline{hk}} = 2\sigma_3\sigma_2^{-\frac{3}{2}} \left|E_{\underline{h}}E_{\underline{k}}E_{\underline{h-k}}\right|$ (1.24)

Higher values of $\alpha_{\underline{h}}$ indicating high reliability in $\phi_{\underline{h}}$.

In initial stages of phase determination, α will be zero as no phase information is available. To overcome this problem, an estimated value for $\alpha_{\underline{h}}$ ($\alpha_{\underline{h}}^{est}$) is used:

$$(\alpha_{\underline{h}}^{est})^2 = \sum_{\underline{k}} \kappa^2_{\underline{hk}} + 2\sum_{\underline{k}}\sum_{\underline{k}'} \kappa_{\underline{hk}}\kappa_{\underline{hk}'} \frac{I_1(\kappa_{\underline{hk}}) \cdot I_1(\kappa_{\underline{hk}'})}{I_o(\kappa_{\underline{hk}}) \cdot I_o(\kappa_{\underline{hk}'})} \qquad (1.25)$$

for $\underline{k} \neq k'$

where I_o and I_1 are modified Bessel functions.

1.3.3 Procedure for Phase Determination

The majority of centrosymmetric structures described in this thesis have been solved using an automatic approach available in the SHELX[29] X-ray package. Other structures, including non-centrosymmetric structures, were solved using MULTAN[30]. Each method requires an originfixing set of reflections whose phases are known. The phase of certain reflections (dependent upon space group) will be invariant for several possible origin definitions and as such must not be used for the starting set. The phases of such semi-invariants are functions of the structure itself and cannot be chosen at will. For non-centrosymmetric structures, it is also necessary to specify to which enantiomorphic form the derived phase set refers[31]. In the absence of anomalous dispersion, the magnitudes of the structure factors do not distinguish between the two possible enantiomorphs; for a phase angle of ϕ in one enantiomorph, the corresponding phase angle in the other enantiomorph is $-\phi$. This is overcome by arbitrarily specifying the phase (or more accurately, an approximation to the phase which may be corrected during structure determination) to fix the particular chirality.

For centrosymmetric structures, a sign expansion is carried out using $\sum_2$ relationships and the known (+) phases of the origin determining reflections. The $\sum_2$ relationship is a more general form of (1.19) and is defined as

$$S(E_{\underline{h}}) \approx S(\sum E_{\underline{k}}\, E_{\underline{h-k}}) \qquad (1.26)$$

$\underline{h}$,$\underline{k}$ are, respectively, the Miller indices (h,k,l), (h′,k′,l′) and $\underline{h-k}$ is the triplet (h-h′, k-k′, l-l′). A multisolution symbolic addition approach is used to determine phases not otherwise found. The n (usually $\leqslant 12$) reflections chosen are given phase angles of 0° or 180° (i.e. + or -) and this leads to 2^n sets of phases. The resulting sets of phases are progressively reduced during the expansion pathway by using two rejection tests - M(min) and gt(max). The M(min) test is based on the M(abs) formula (1.27) of Germain, Main and Woolfson[33].

$$M(abs) = \frac{\sum_{\underline{h}} \alpha_{\underline{h}} - \sum_{\underline{h}} \alpha_{\underline{h}}^{rand.}}{\sum_{\underline{h}} \alpha_{\underline{h}}^{est.} - \sum_{\underline{h}} \alpha_{\underline{h}}^{rand.}} \qquad (1.27)$$

$$\text{where } (\alpha_{\underline{h}}^{rand.})^2 = \sum_{\underline{k}} K^2_{\underline{h}\,\underline{k}} \qquad (1.28)$$

and $\alpha_{\underline{h}}$ and $\alpha_{\underline{h}}$ are respectively defined in (1.23) and (1.25).

The gt(max) test is based on Giacovazzo[32]'s formula for the probability of reliance on the sign relationship:

$$P_+ = \tfrac{1}{2} + \tfrac{1}{2}\tanh \frac{1}{2N} \left| E_3E_4 \right| (2E_1^2\ E_2^2 - E_1^2 - E_2^2) \qquad (1.29)$$

where P_+ is the probability that the phase is positive.

N is the number of atoms in the unit cell (an assumption is made that they are all of the same type)

$E_1 = E_{\underline{h}}$

$E_2 = E_{\underline{k}}$

$E_3 = E_{\underline{h}-\underline{k}}$

$E_4 = E_{\underline{h}+\underline{k}}$

and $$P_- = \tfrac{1}{2} - \tfrac{1}{2}\tanh \frac{1}{2N} \left| E_3E_4 \right| (2E_1^2\ E_2^2 - E_1^2 - E_2^2) \qquad (1.30)$$

where P_- is the probability that the phase is negative. By using the rejection tests during the phase expansion, the number of surviving permutations is progressively reduced so that few sets of phases remain at the end of the systematic computation. The number is reduced still further using information from reflections having low $|E|$ values. For each of the surviving sets, a figure of merit, called PARACHOR, is calculated and is based on the M(abs) and gt tests.

An initial trial solution may be expected to be found in the E maps calculated from the phase sets having the highest parachor values. These E maps use $|E_{hkl}|$ as the Fourier coefficients and ϕ_{hkl} as the phases found from the direct methods solution. In contrast with the method using the Patterson synthesis, the direct method solution usually locates approximately all (or nearly all) the non-hydrogen atoms.

For non-centrosymmetric structures discussed in this work (and for particularly stubborn centrosymmetric structures), the MULTAN X-ray package has been utilised. Because of this and the similarity between the SHELX (multisolution tangent refinement method) and MULTAN methods, the following discussion is confined to the MULTAN approach. $\sum_2$ relationships are first formed and those having a κ value (c.f. 1.24) below a given value (a default setting of 0.6 was used with MULTAN) are rejected $\alpha_{\underline{h}}^{est}$ (c.f. 1.25) is calculated for all remaining reflections. The reflection with the lowest α value is placed at the bottom of the convergence list. It, together with all $\sum_2$ relationships in which it is involved, is then removed from the set of remaining reflections. $\alpha_{\underline{h}}^{est}$ is then recalculated for all remaining reflections and again the lowest is removed and placed in the convergence list. The process is continued until all reflections have been ordered[33]. The origin set, the enantiomorphic determining reflection and a limited number of reflections for the multisolution set are chosen from reflections at the top of the convergence list. Starting from the top of the list, phases are determined using the weighted tangent formula (1.31).

$$\tan\phi_{\underline{h}} = \frac{\sum_{\underline{k}} W_{\underline{k}} W_{\underline{h}-\underline{k}} \left| E_{\underline{k}} - E_{\underline{h}-\underline{k}} \right| \sin(\phi_{\underline{k}} + \phi_{\underline{h}-\underline{k}})}{\sum_{\underline{k}} W_{\underline{k}} W_{\underline{h}-\underline{k}} \left| E_{\underline{k}} - E_{\underline{h}-\underline{k}} \right| \cos(\phi_{\underline{k}} + \phi_{\underline{h}-\underline{k}})} = \frac{T_{\underline{h}}}{B_{\underline{h}}} \qquad (1.31)$$

$$\text{where } W_{\underline{h}} = \tanh\left[\sigma_3 \sigma_2^{-\frac{3}{2}} \left| E_{\underline{h}} \right| (T_{\underline{h}}^2 + B_{\underline{h}}^2)^{\frac{1}{2}}\right] \qquad (1.32)$$

Reflections used for the multisolution set are allowed symbolic phases of 45°, 135°, 225° and 315°.

The weighting allows all reflections to be used, as poorly determined phases have little effect on the determination of other phases. MULTAN calculates phases for the top 100 reflections in the convergence list. Multisolution reflections are held constant until the tangent formula has been used to refine other reflections, then they are allowed to refine in a final cycle.

As with the centrosymmetric method, the tangent multisolution method may produce a number of phase sets and figures of merit are again used to order the phase sets of phases. E-maps are then produced for a limited number of the surviving sets. MULTAN uses three figures of merit (FOM) and a combined overall FOM. The first of these, ABSFOM - the absolute figure of merit is defined in 1.22.

For a good phase set, ABSFOM is marginally greater than 1.

The PSIZERO (ψ_o) figure[34], is defined by:

$$\psi_o = \sum_{\underline{h}} \left| \sum_{\underline{k}} E_{\underline{k}} E_{\underline{h-k}} \right| \qquad (1.32)$$

where the terms in the outer summation are those for which $|E_{\underline{h}}|$ is small, while the inner summation is over the determined phases. Thus, for a good phase set, ψ_o should be close to zero.

The third figure is the residual FOM, RESID, defined by:

$$\text{RESID} = \frac{100 \sum_{\underline{h}} \left| S \alpha_{\underline{h}}^{est} - \alpha_h \right|}{\sum_{\underline{h}} \alpha_{\underline{h}}^{est}} \qquad (1.33)$$

where S is a scale factor. It is a measure of how well the Σ_2 relationships have followed the statistical expectation. For a correct set of phases this should be a minimum. MULTAN generates a combined figure of merit (CFOM):

$$\text{CFOM} = W_1 \left(\frac{A - A_{min}}{A_{max} - A_{min}} \right) + W_2 \left(\frac{\psi_{o\,max} - \psi_o}{\psi_{o\,max} - \psi_{o\,min}} \right) + W_3 \left(\frac{R_{max} - R}{R_{max} - R_{min}} \right) \qquad (1.34)$$

where W_1, W_2, W_3 are weights (default setting of 0.6, 1.2, 1.2 respectively) and A - ABSFOM
R - RESID

max. and min., respectively, represent the highest and lowest values of the variable for the sets of phases calculated.

1.4 Refinement of Trial Solution

The methods previously discussed (1.3.1 and 1.3.2) for obtaining trial solutions give only approximate atomic positions. A least squares technique is used to refine the parameters by minimising the function:

$$D = \sum_{hkl} W_{hkl} (|F_o| - c|F_c|)^2 \qquad (1.35)$$

$$= \sum w\Delta^2$$

where W_{hkl} is the weight applied to each $|F_o|$ and c is a scale factor to put F_o and F_c on the same scale. While W = 1 (unit weighting) is used in the early stages of refinement, the final stages employ non-unit weights of the form:

$$W = a/\left[\sigma^2(|F_o|) + b(|F_o|^2)\right] \qquad (1.36)$$

where a and b are refined to minimise the variation of $W\Delta^2$ over ranges of $|F_o|$. For each parameter, minimisation is obtained by partial differentiation and equating the derivatives to zero. The non-linearity of the functional form of F_c renders the equation set unsolvable by direct algebraic methods. Hence F_c is approximated by a Taylor series using only terms up to degree 1. The resultant equation set may be put into the matrix form $[A][p] = [V]$ (1.37)

where: $$a_{ij} = \sum_{hkl} W_{hkl} \frac{k^2\partial|F_c|}{\partial p_i} \cdot \frac{\partial|F_c|}{\partial p_j} \qquad (1.38)$$,

$\Delta p_{ij} = p_{ij} - a_{ij}$ (1.39)(p_{ij} is the parameter under refinement and a_{ij} is the approximate initial value) and

$$v_{ij} = \sum_{hkl} W_{hkl} \Delta F \cdot \frac{c\partial|Fc|}{\partial p_{ij}} \qquad (1.40)$$

c and k are constants.

Only those reflections having $I/\sigma(I) \geqslant n$ (usually 2.5 - 3.0) are used in the refinement process.

As there is, inevitably, some degree of interdependence between parameters, correlation coefficients are calculated:

$$r_{ij} = b_{ij}/(b_{ii})^{\frac{1}{2}}(b_{jj})^{\frac{1}{2}} \qquad (1.41)$$

where b_{rs} is an element of the matrix $[A^{-1}]$, A as defined in 1.37. Estimated errors in the parameters are expressed in terms of the estimated standard deviation of error, σ, given by:

$$\sigma = (b_{ii} \sum_{hkl} w_{hkl} \Delta F^2)/(m-n)^{\frac{}{2}} \qquad (1.42)$$

where m is the number of reflections used in the refinement and n is the number of parameters.

A reliability index (R) for a specific model of the structure is calculated by:

$$R = \frac{\sum_{hkl} \left| |F_o| - |F_c| \right|}{\sum_{hkl} |F_o|} \qquad (1.43)$$

where Fo and Fc are on the same scale. Where non-unit weights are employed, a further reliability index, Rw, is calculated:

$$Rw = \frac{\sum \sqrt{w} \left| |Fo| - |Fc| \right|}{\sum \sqrt{w} \; |Fo|} \qquad (1.44)$$

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Chapter 2

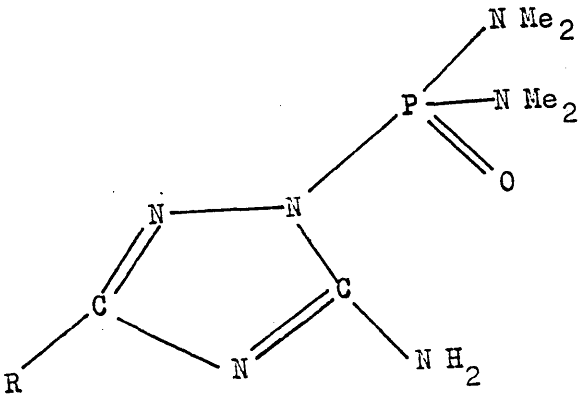
Comparative Study of the Structures of Related Triazole and Imidazole Compounds and the Relation to Systemic Fungicidal Activity

Contents

2.1 The relationship between structure and systemic fungicidal activity

Accepting the broad definition of a fungicide as an agent that kills or inhibits the development of fungus spores or mycelium; fungicides may be classified into three broad categories, viz: protectants, eradicants and systemic fungicides. Protectants are applied to the plant prior to infection and may be general cell poisons, selectivity arising through inability to penetrate the host plant (e.g. use as seed coatings, soil treatment prior to sowing). Eradicants are used to kill or inhibit the growth of established fungal infections at the site of application. Systemic fungicides are absorbed into the host plant where they, in situ, destroy or inhibit the fungus and thus are less susceptible to losses by leaching or photo-degradation. Most systemic fungicides have specific modes of action and are highly toxic to particular fungi whilst being relatively non-toxic to the host plant.

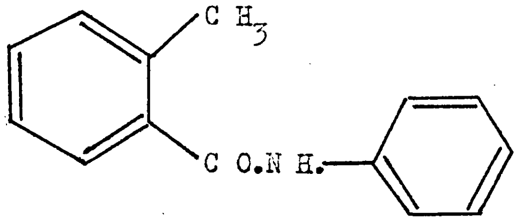
An apparent small change in molecular configuration can radically effect the action on the host or the fungus. Thus the reaction product (1) of 3-amino-1,2,4-triazole[1,2,3,4] and bis(dimethylamido) phosphoryl chloride is used under the common name "triamiphos" (R = phenyl or cyclohexyl) to control mildew on roses.



R = H,phenyl,cyclohexyl, $(CH_2)_{10}\cdot CH_3$

1.

With R = H, the compound is a good fungicide with low phytotoxicity; however, when R is a long-chained hydrocarbon group (e.g. R = $(CH_2)_{10}.CH_3$) the fungicidal properties are significantly reduced but the compound has high phytotoxicity. Again, with R = Ph, high fungicidal activity is found but very little activity is found for the benzyl derivative; in neither case is there phytotoxicity. While 'triamiphos' is widely used to control mildew on roses it cannot be used on apple trees due to its phytotoxicity, illustrating the further effect of specificity to the host as well as to the fungus.



2.

In 2-toluanilide mebenil (2), fungicidal activity can be radically altered by changing the position of the methyl group or by suitable substitution. While activity remains high if the 2-methyl group is replaced by trifluoromethyl, chloro, bromo, nitro or amino groups, it is greatly reduced if a hydroxy or methoxy group is substituted or if the methyl group is in the 3- or 4-positions[5]. Similar substituent effects have been reported in oxathiins (carboxin analogues), thiosemicarbazides and a large and diverse range of other compounds[5].

Fungicidal activity is affected by several major variables including:

(i) metabolism by host and resultant effects

(ii) translocation in host from site of absorption to site of activity

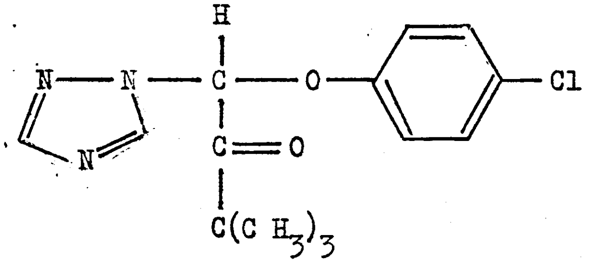
(iii) metabolism in fungus

(iv) intrinsic activity at site of action.

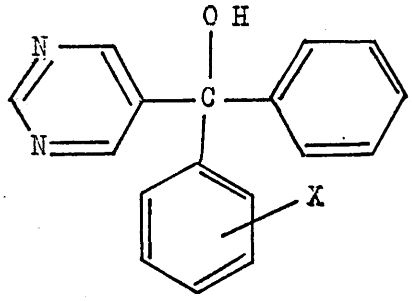
Thus, in attempting to relate structural features of the fungicide to fungicidal activity, it is helpful to study processes (i) - (iv) separately. Some fungicides are found to be ineffective in laboratory experiments with the test fungus but work efficiently in vivo, thus suggesting that the fungicide does not act directly but reacts in the host to produce a secondary product that itself kills the fungus. Rimocidin and pimaricin[6] which are extracted from treated plants and are known to be effective fungicides in vivo, fail to kill fungus grown on cultures. The fungicide may cause additional effects to the principal action which may then lead to increased activity. Evidence will be discussed later for the illustrative case of a pyrimidine derivative (triarimol) where several side effects have been noted, all of which could inhibit fungi development. Finally, variations are found between rates of uptake and fungicidal effects (e.g. imidazoles have greater general inhibitory effect in vitro than triazoles but the tendency is reversed in vivo. It is suggested that this is due to varying rates of uptake and retention by the host plant. (Note: Imidazoles tend to be retained by soil particles and hence are only suitable as leaf sprays).

Absorption may be regarded as a passive process and the translocation of fungicide to the site of action may be considered as a set of partitions between, say, soil solids and soil water, soil water and root tissue, root tissue and xylem vessels, xylem vessels and stem leaf[7,8]. Thus the distribution will depend on the lipid - water distribution coefficient for each of the above partitions. It has been shown[9], for example, that the root uptake of some oximecarbamates and phenylureas is proportional to log P, where P is the octanol - water distribution coefficient. For the structures discussed in 2.2 to 2.5 and eleven other closely related structures, the correlation between fungicidal activity and log P was 0.7 . Such results suggest that log P, when considered cautiously in conjunction with data on related compounds, may act as a guide to likely fungicidal activity.

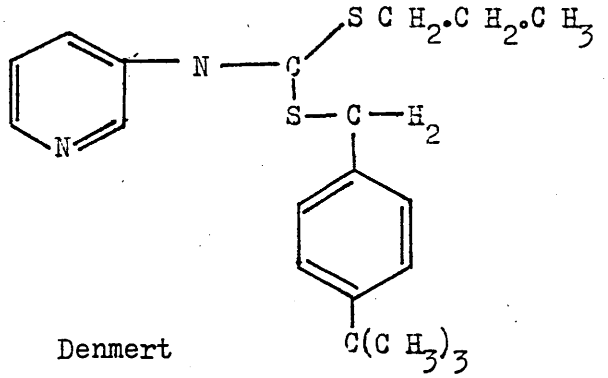
Despite the difficulties discussed above, a high degree of success can be obtained in relating structure to activity for specific groups of compounds and specific fungi. Most systemic fungicides act specifically on one biosynthetic pathway or enzyme. Several series of compounds are known to have an effect on the formation of ergosterol from lanosterol (part of the process of producing ergosterol from acetates - see scheme 2.1); commercially successful fungicides illustrative of these series are:-



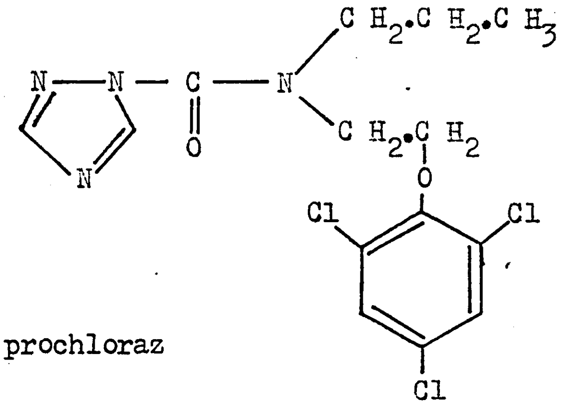
Triadimefon



Fenarimol X = 2-Chloro
Triarimol X = 4-Chloro



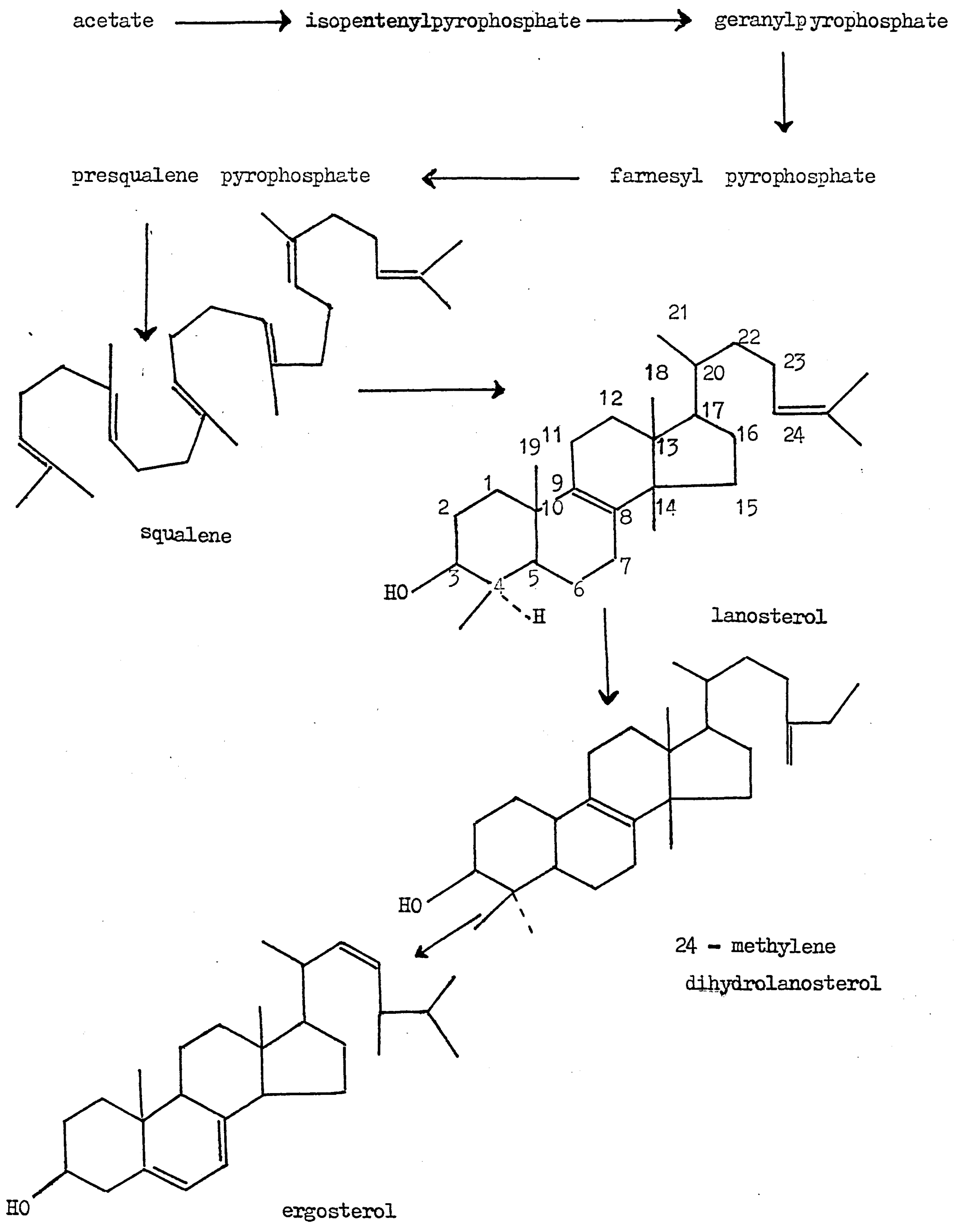
Denmert



prochloraz

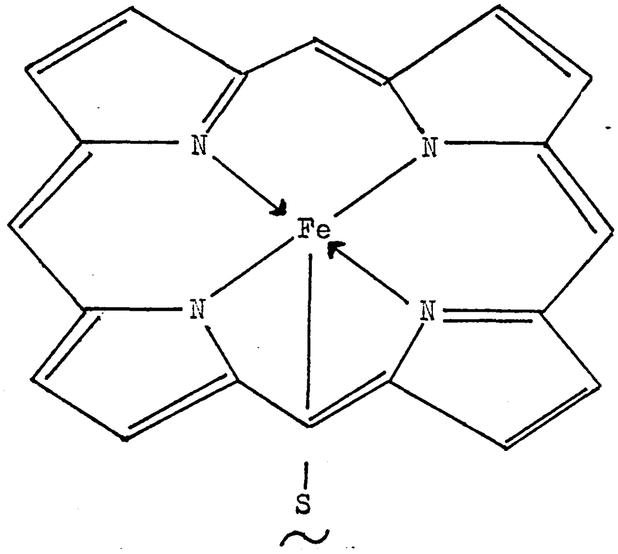
3.

Each contains a nitrogen atom in a heterocyclic ring and it has been suggested that the primary action of the fungicide results from interaction of this nitrogen with the iron of cytochrome P450 (a haem protein of molecular weight in the region of 48,000 containing a single polypeptide chain). The protein contains one molecule of protohaem



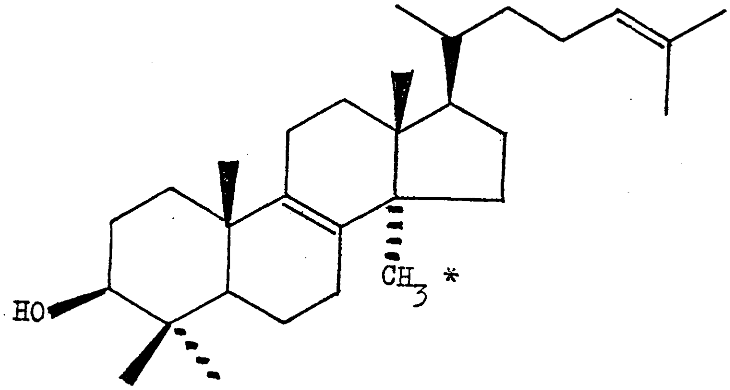
Scheme 2.1 Fungal biosynthesis of ergosterol.

as a prosthetic group and the porphyrin ring of this group binds to an iron atom (which is also coordinated with a protein sulphydryl group (4).



4.

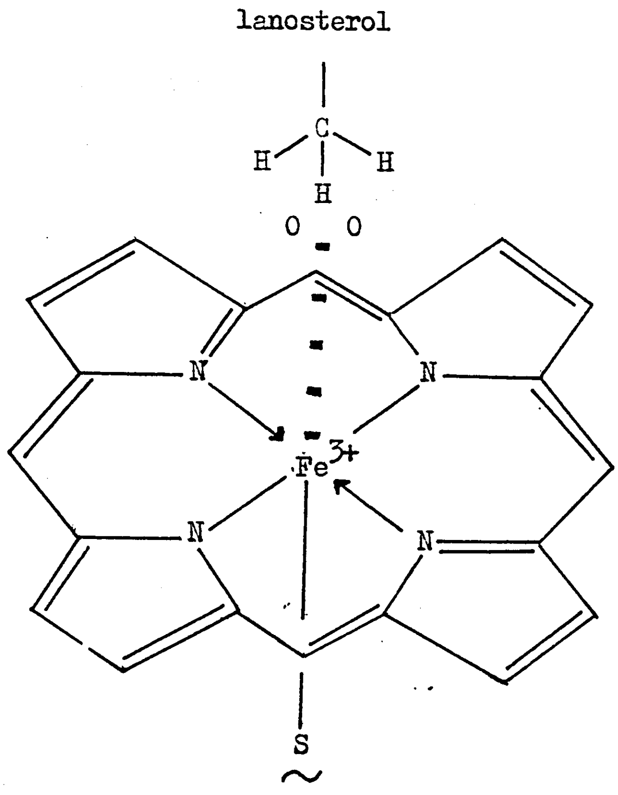
The cytochrome P450 inhibited by the azole fungicides appears to be that involved in the oxidative removal of the 14α-methyl group (5) of lanosterol (schemes 2.1 and 2.2) although some inhibition of the oxidase involved in the removal of the C4 methyl groups has also been suggested[11].



* 14α methyl

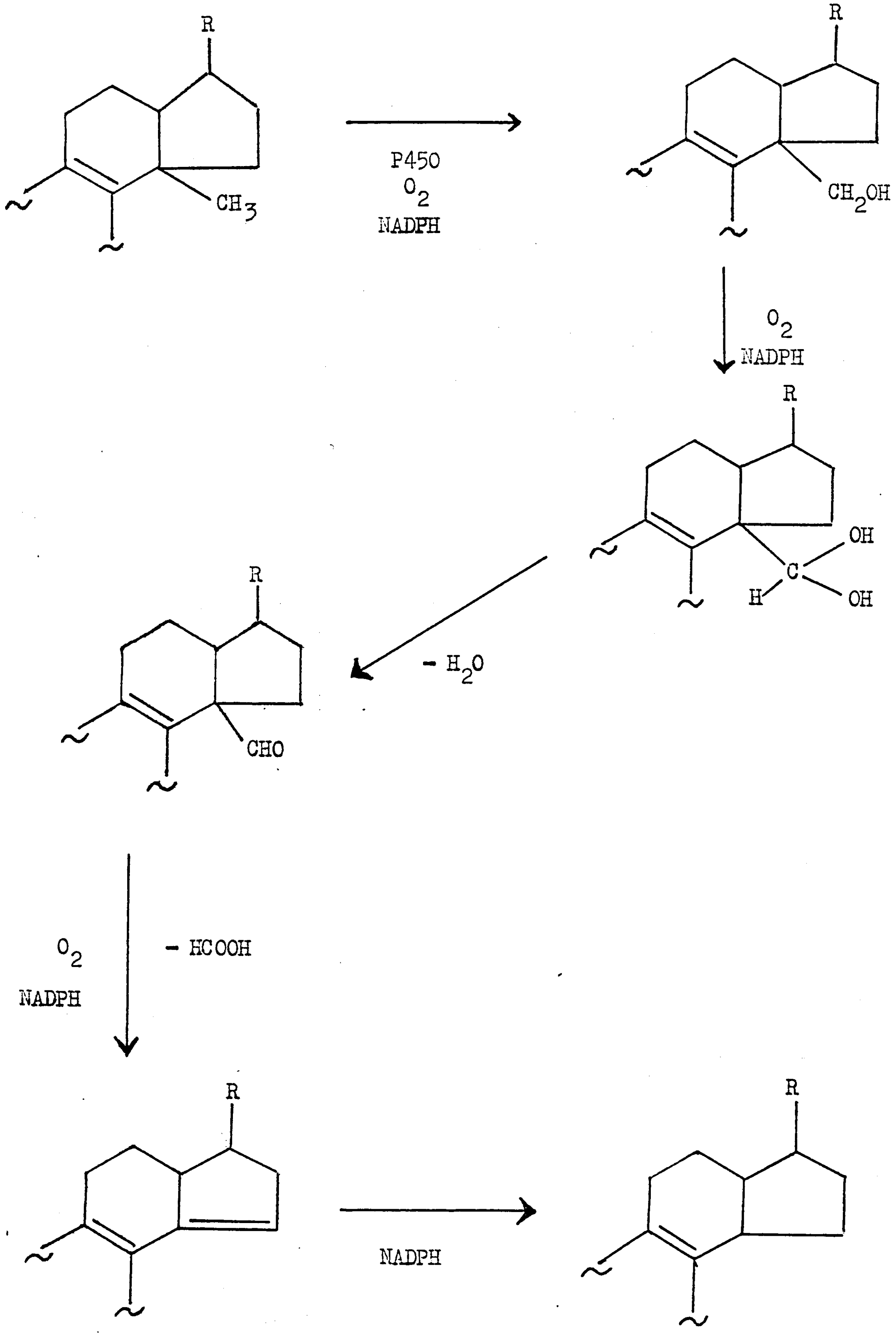
5.

In the presence of P450 as catalyst, oxygen and NADPH, the methyl group is initially hydroxylated. The oxygen molecule is activated via coordination with the iron of (4), thereby promoting its reaction with the methyl group (6).



6.

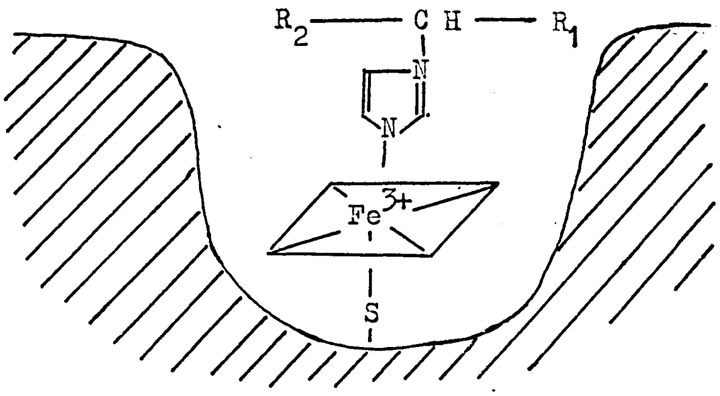
Schematically, the demethylation reaction at C14 proceeds as in scheme 2.2.


R
CH3
P450
O2
NADPH
CH2OH
O2
NADPH
OH
C
H
OH
- H2O
CHO
O2
NADPH
- HCOOH
NADPH

Scheme 2.2

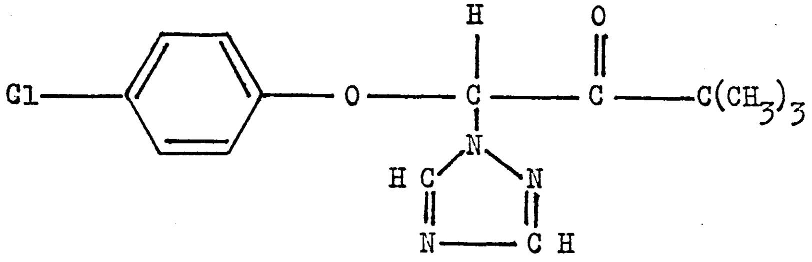
Triadimenol and related fungicides are thought to block the first step by coordinating with the iron of the porphyrin ring through the nitrogen containing heterocyclic group[10]. Ragsdale and Sisler[12,13,14] showed triarimol (3) affects ergosterol biosynthesis in <u>Ustilago maydis</u>. They noted an excessive quantity of ergosterol percursors (in the chain of biosynthesis from acetate to lanosterol) and a major reduction in ergosterol levels. The latter would have a major effect on the fungal cells since ergosterol is responsible for stabilization of biological membranes.

More detailed studies of inhibition of cytochrome P450 based oxidases have been conducted on those contained in rat liver microsomes, since they are readily prepared. Experiments with imidazole[12] showed the molecule to be identically located in binding to both P-450$_{LM2}$ and P-450$_{LM4}$ obtained from rat liver[15] with the imidazole strongly bonded to the iron atom via a nitrogen atom. It has been deduced[16] that the porphyrin ring resides in a "well" (7) with surrounding substrates and that acetanilide is too bulky to "fit" comfortably in the well as judged from nmr longitudinal relaxation studies[15]. The fungicidal activity of imidazole, triazole and other nitrogen - heterocycle containing compounds lies primarily in the ability of the azole group to "fit" into the well of the fungal P450 and bond strongly to the iron atom.



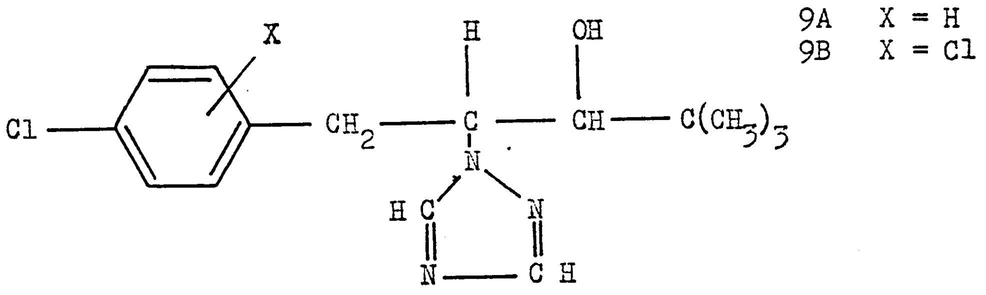
7.

Successful binding also depends on the nature of the groups R_1 and R_2 (7), the specificity depending on the source of the oxidase. The relationship between size of the side group and binding energy to rat liver enzyme has been investigated using primary alcohols[15]. A complex pattern resulted but it was shown that binding effects of side groups were limited to a specific region around the porphyrin ring. Beside purely steric factors, binding appears to be predominantly hydrophobic[16].



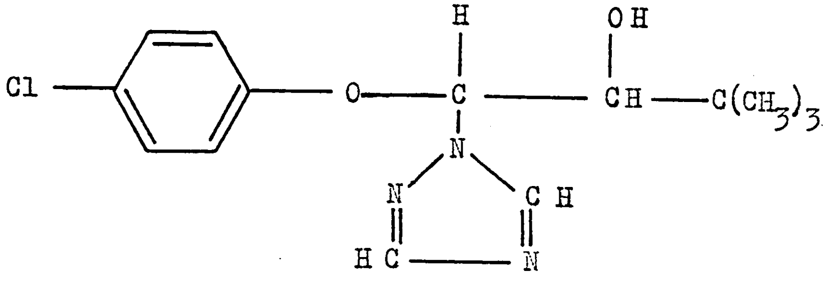
8.

The fungicide triadimefon (8), the active compound of the commercial fungicide Bayleton, is highly toxic to a broad range of fungi from the families Ascomycetes (including powdery mildews), Deutoromycetes (including rusts and smuts) and Basidomycetes[17,18,19]. Levels of fungicide needed vary according to the crop but, for example, a dressing (foliar spray) of 125g/hectare gives total control of mildew on barley[20,21]. Triadimefon and related fungicides only affect the host plant at much higher concentrations than those needed for fungicidal control when stunting is observed. This is probably due to inhibition of giberellic acid (GA) biosynthesis since ICI experimental growth regulator, paclobutrazol(9A), a close analogue of the fungicide (9B), has been shown to inhibit GA synthesis in Giberella fujikoira[10] and is believed to act in the same way in plants[10A].



9.

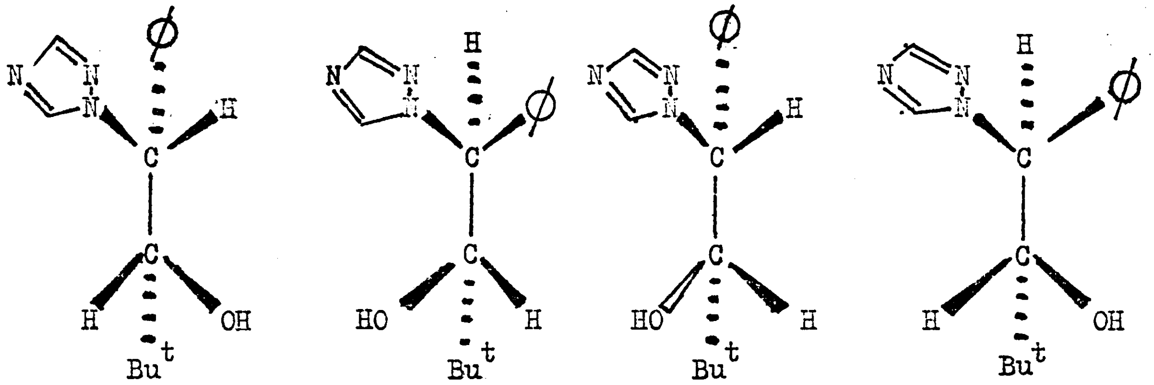
Studies on the action of tridimefon have shown that it is metabolised by both host and fungus to the alcohol, triadimenol (10), which is itself the active fungicide[22,23,24,25]. Gaszontyi and Josepovits have



10.

shown that triadimefon is not metabolised by fungi resistant to it whereas the same fungi are sensitive to action by triadimenol[26].

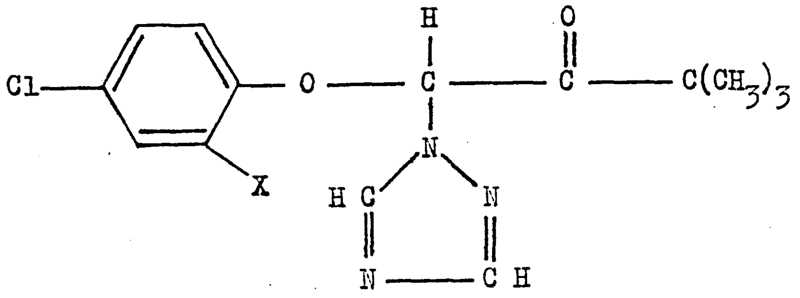
Triadimenol exists as four optically isomeric structures.



11.

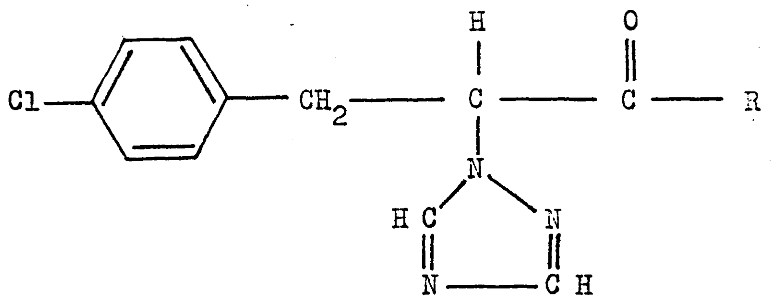
While the RR/SS diastereoisomer is the active mixture against yeast, it is the RS/SR pair that is active with rat liver demethylation of lanosterol[11].

Structure - activity relationships have been investigated in triadimefon analogues[20,20A]. For 2-substituted compounds (12), the order of fungicidal activity is Cl > F > NO_2 with the 2-Cl compound being ca. X10 more active than the 2-NO_2 analogue.



12.

High activity is associated with a tertiary butyl group on one side chain. For example, in (13), R = Bu^t was more active by a factor of 3 than for R = Ph[10].



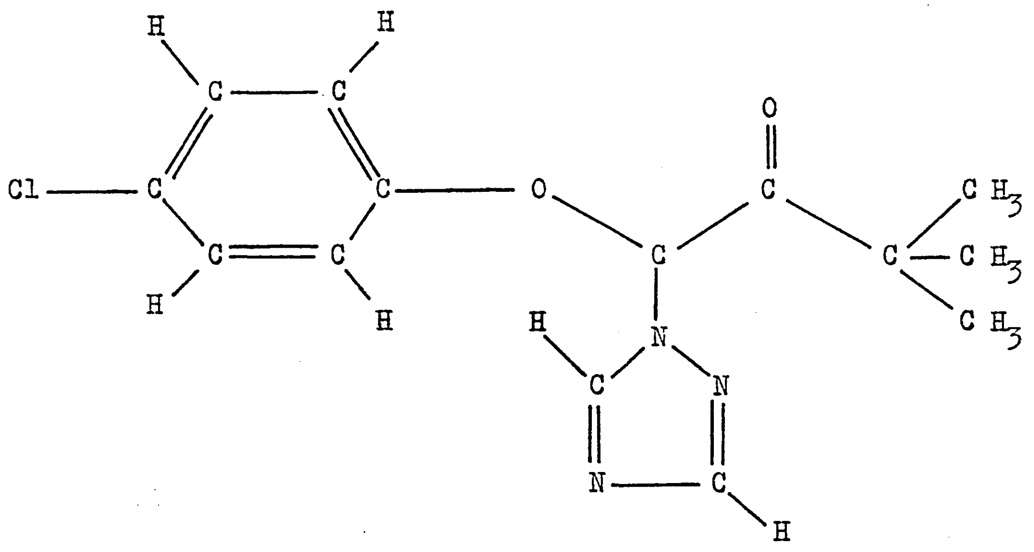
13.

However, replacement of both side chains with Bu^t groups led to low activity which suggests that the active site is asymmetrical.

At the start of the investigations described here, it was thought that both ketones (e.g. 12, 13) and alcohols (e.g. 9, 10) were active *per se*, but subsequent studies of metabolism, referred to above, imply that the latter are largely responsible for fungicidal activity. Thus knowledge of crystal structures of the ketones is relevant to the activation process in the host or fungus and the structures of the alcohols are of value in determining features required for binding to cytochrome P450. Furthermore, a comparison of alcohol and ketone structures could help to explain the lack of intrinsic activity in the latter.

It is sometimes argued that crystal conformations are not related to those in solution, or to that of the molecule bound to the active site. However, in compounds where the major barriers to rotation are intramolecular, as for the major torsion axes in the compounds examined here, the positions of conformational minima are not, in general, expected to be greatly affected by the environment of the molecule. Conformational studies by nmr[33] and calculation[10] tend to support this view. The present study includes the single crystal X-ray analysis of five compounds showing fungicidal activity and provided by I.C.I. Plant Protection, Ltd..

2.2 The crystal and molecular structure of 1 - (4 -chlorophenoxy) -3, 3 -dimethyl - 1 - (1, 2, 4 -triazol -1 -yl) - 2 -butanone



1. - R85827

2.2.1 Crystal data:

$C_{14}H_{16}N_2O_2Cl$.	$M_r = 293.8$	Monoclinic
$a = 8.076(3)$	$b = 20.317(8)$	$c = 9.307(3)$ Å
$\beta = 97.43(5)^\circ$	$D_c = 1.29$ Mg m^{-3}	$D_m = 1.31$ Mg m^{-3}
$Z = 4$	$F(000) = 616$	$\mu(Mo - K\alpha) = 0.21$ cm^{-1}

Systematic absences: h0l, h+l = 2n+1, 0k0, k = 2n+1; uniquely define the crystals as belonging to the space group $P2_1/n$.

2.2.2 Data collection and refinement:

An opaque crystal, approximately 0.20 x 0.24 x 0.35 mm, was mounted about the b axis. 11 layers, 0kl $\rightarrow$ 10kl, were collected; 2773 independent reflections were recorded of which 1023 having $I/\sigma(I) \geqslant 2.5$ were used for subsequent analysis. Reflections having $E \geqslant 1.2$ were utilized for direct methods trial solution which allowed all non-hydrogen atoms to be located. The structure was refined by full-matrix least squares techniques and the hydrogen atoms were located from successive difference Fourier syntheses and were included in positions calculated from the geometry of the structure (C-H = 1.08Å). The non-hydrogen atoms were given anisotropic temperature factors in the later stages of refinement. The hydrogen atoms were given isotropic temperature factors; H7 was refined to a final value of 0.049(20)Å^2 while the common isotropic temperature factor applied to the methyl hydrogens refined to 0.081(7)Å^2. The remaining hydrogen atoms were given a common temperature factor whose final value was 0.082(10)Å^2. A weighting scheme of $w = 0.8614/[\sigma^2(|F_o|) + 0.0016(|F_o|)^2]$ was adopted and gave final reliability values of R = 0.058 and Rw = 0.064. The highest residue peak from a final difference Fourier synthesis was 0.47eÅ^{-3}. Bond lengths and angles are given in Tables 2.2.1 and 2.2.2 and Fig. 2.2.3; final positional and thermal parameters, mean plane data, torsion angles and structure factors are contained in Appendices A1.1, A2.1, A3.1 and A4.1 respectively.

2.2.3 Description of structure:

The phenyl ring (C71 → C76) (Figure 2.2.1) is effectively planar with C1 and O2 also in the plane (Appendix (A3,1). Mean plane data also show C5, C4, O1 and C31 to be planar as, also, is the triazole ring; C5 is effectively in the plane of the triazole ring (deviation 0.06Å).

While the C-C bonds in the phenyl ring were shorter, on average, than expected (1.377 for the structure; 1.393Å for benzene[27]), none was outside statistical limits(all less than 3σ from benzene value).

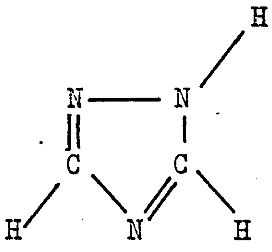
The triazolyl ring is effectively planar with C5 showing the maximum deviation from the best mean plane (0.061(7)Å) (table A2.1). Although the C1 - N1 and C2 - N3 distances are somewhat larger than those for

C1 - N3 and C2 - N2, in keeping with the uncharged canonical valence form (see below), all four distances are shorter than the normal single bond distance (C-N = 1.47Å). A comparison of bond lengths with those for 1, 2, 4 - triazole itself[28] is shown in Table 2.1.

bond	Value (Å) in Triazole	Value (Å) in R85827
N1 - N2	1.359(3)	1.349(8)
N2 - C2	1.323(3)	1.310(13)
C2 - N3	1.359(3)	1.338(12)
C1 - N3	1.324(3)	1.332(9)
N1 - C1	1.331(3)	1.321(11)

Table 2.1

The values for triazole represent the low temperature results which confirmed the room temperature structure deduced from earlier work[29]. The bond length data coupled to the planar nature of the three atoms bonded to N1 suggests considerable electron delocalisation within the triazolyl ring in R85827. The resonance forms for 1, 2, 4 -triazole are shown below with percentage contributions as given by Goldstein et al[28].



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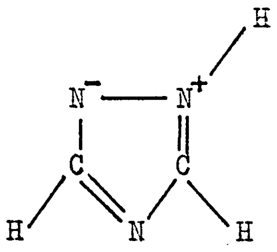

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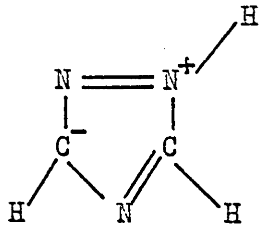

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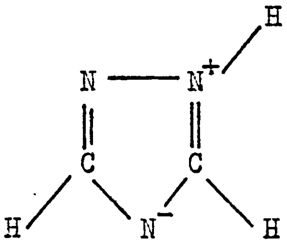

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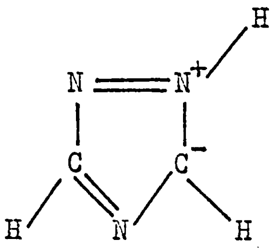

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The triazole ring is inclined at an angle of 61.8° to the plane through C31, C4, O1, C5 and at 73.1° to the phenyl ring. The overall configuration is such that N1 and N2 are closely approached by the ortho hydrogen, H72, giving N ... H distances (N1 .... H = 2.63Å and N2 .... H = 2.68Å) within the sum of the van der Waals' radii of nitrogen and hydrogen (Fig 2.2.2). The accompanying distortion of the exocyclic angles at C71 (O2 - C71 - C72 = 124.2(7)° and O2 - C71 - C76 = 114.7(6)°) may well reflect an attempt by the chlorophenyl ring to adopt a sterically most acceptable position. It is noticeable that Cl is almost equidistant from the two oxygen atoms (Cl - O1 = 2.99Å, Cl - O2 = 3.02Å). A further noticeable feature of the structure is the asymmetry of the exocyclic angles at N1 (119.5(6) and 130.7(6)°) which appears to be a property of the triazolyl ring itself and not caused by any intermolecular interactions. This will be discussed further in section 2.5.

The C31, C4, C5, O2, C71 backbone is rather compressed, resulting in the main from the orientation of the t-butyl group, with the C31 - C4 - C5 - O2 torsion angle being only 100.1(7)° (Appendix A3.1).

No significant intermolecular interaction is present; the intermolecular distance being 2.37Å (between N3 and H5′ where H5′ is related to H5 by the symmetry transformation -0.5 + x, 1.5-y, -0.5+z). The crystal structure is shown in Fig 2.2.4.

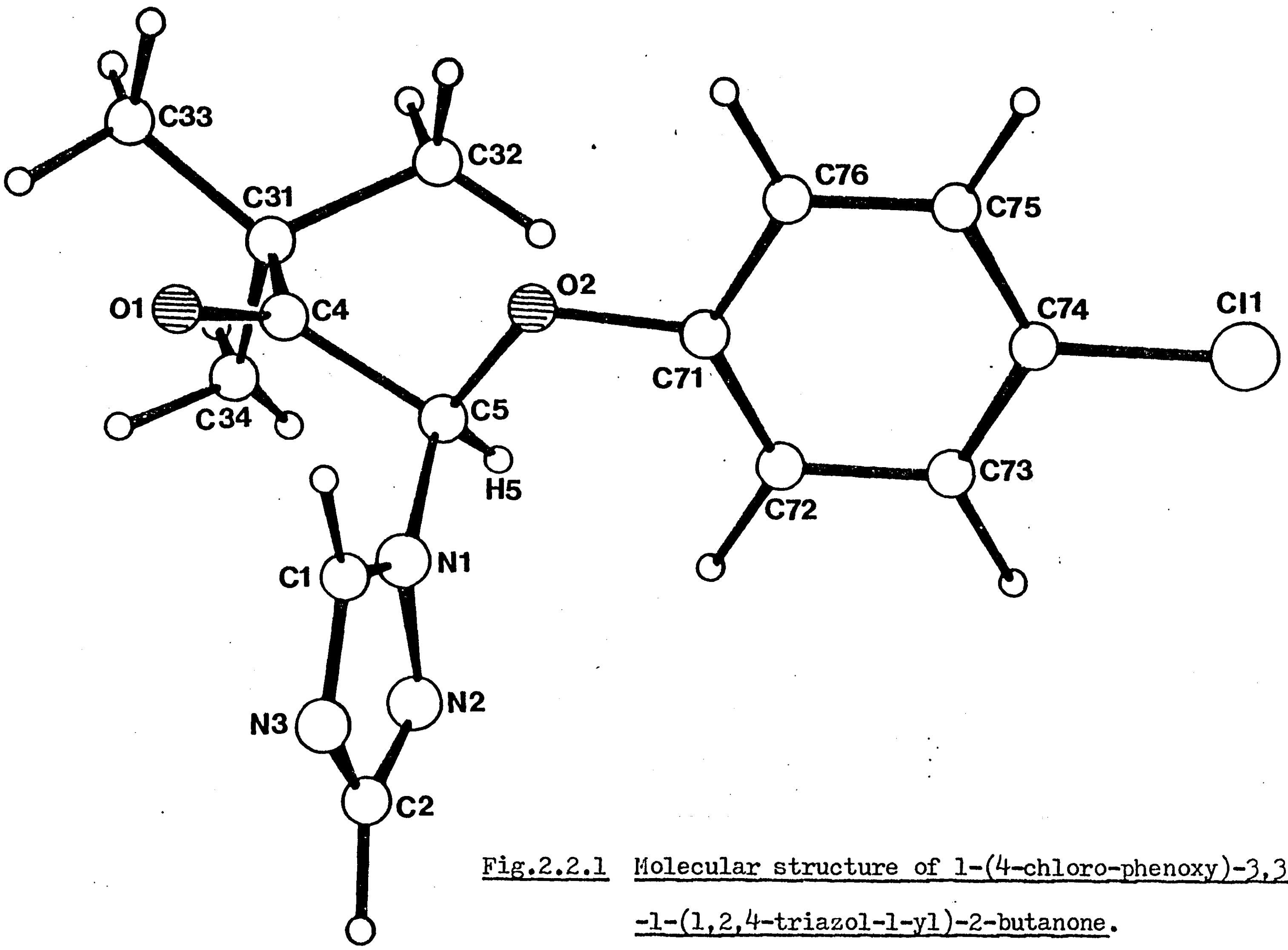


Fig.2.2.1 Molecular structure of 1-(4-chloro-phenoxy)-3,3-dimethyl -1-(1,2,4-triazol-1-yl)-2-butanone.

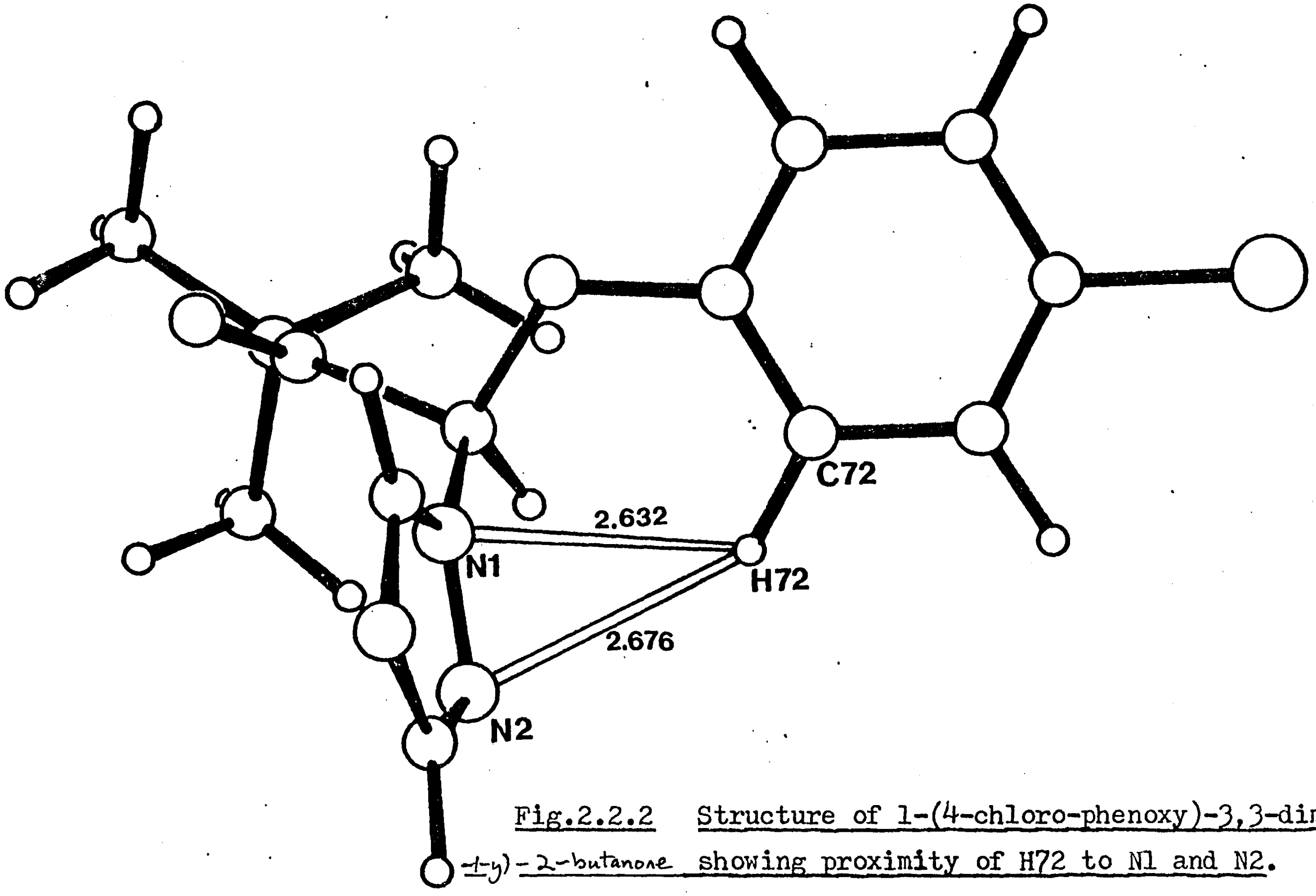


Fig.2.2.2 Structure of 1-(4-chloro-phenoxy)-3,3-dimethyl-1-(1,2,4-tria
-1-y)-2-butanone showing proximity of H72 to N1 and N2.

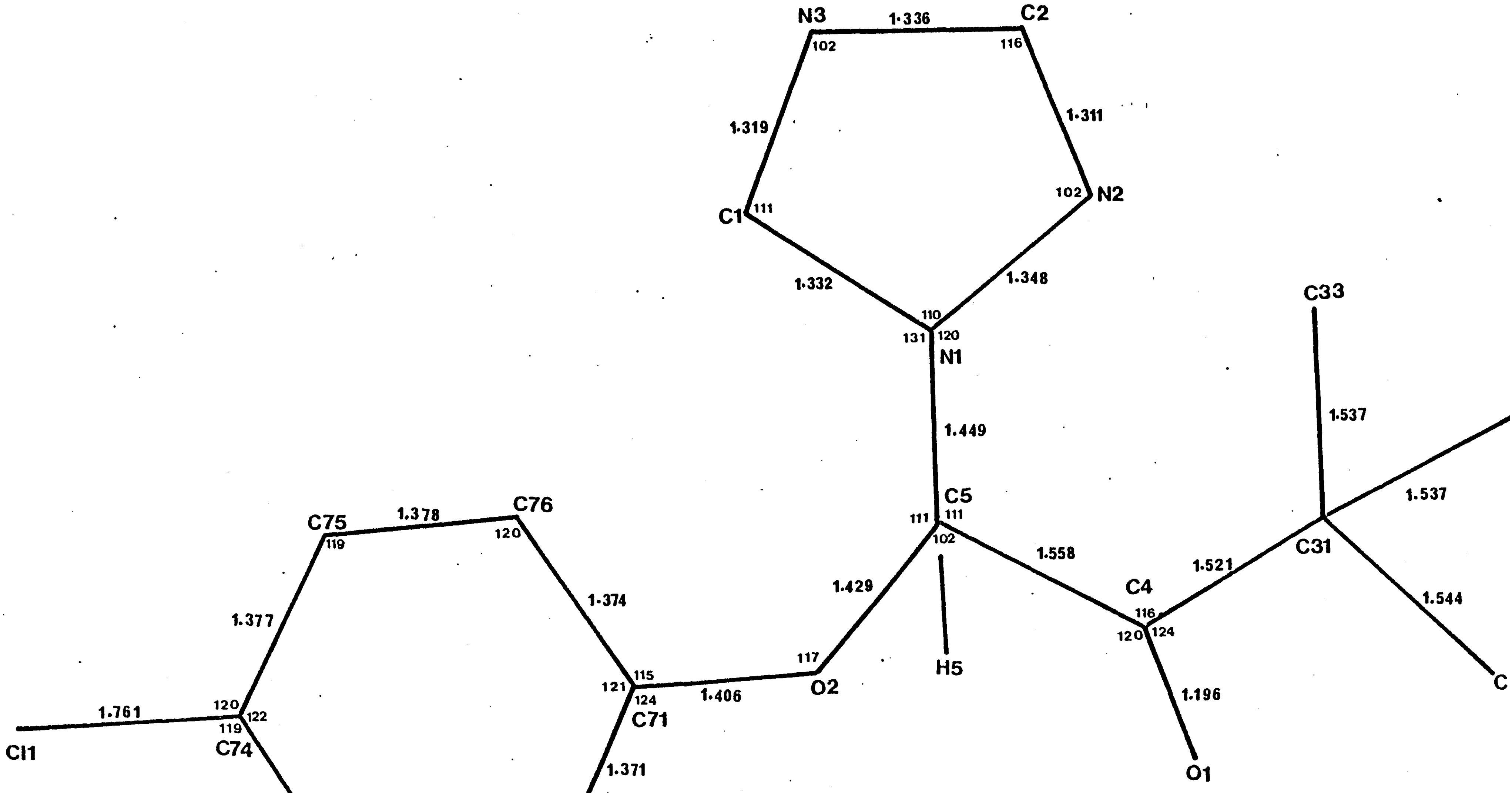


Fig.2.2.3 Bond lengths and angles for 1-(4-chloro-phenoxy)-3,3-dimethyl-1-(1,2,4-triazol-1-yl)-2-butanone.

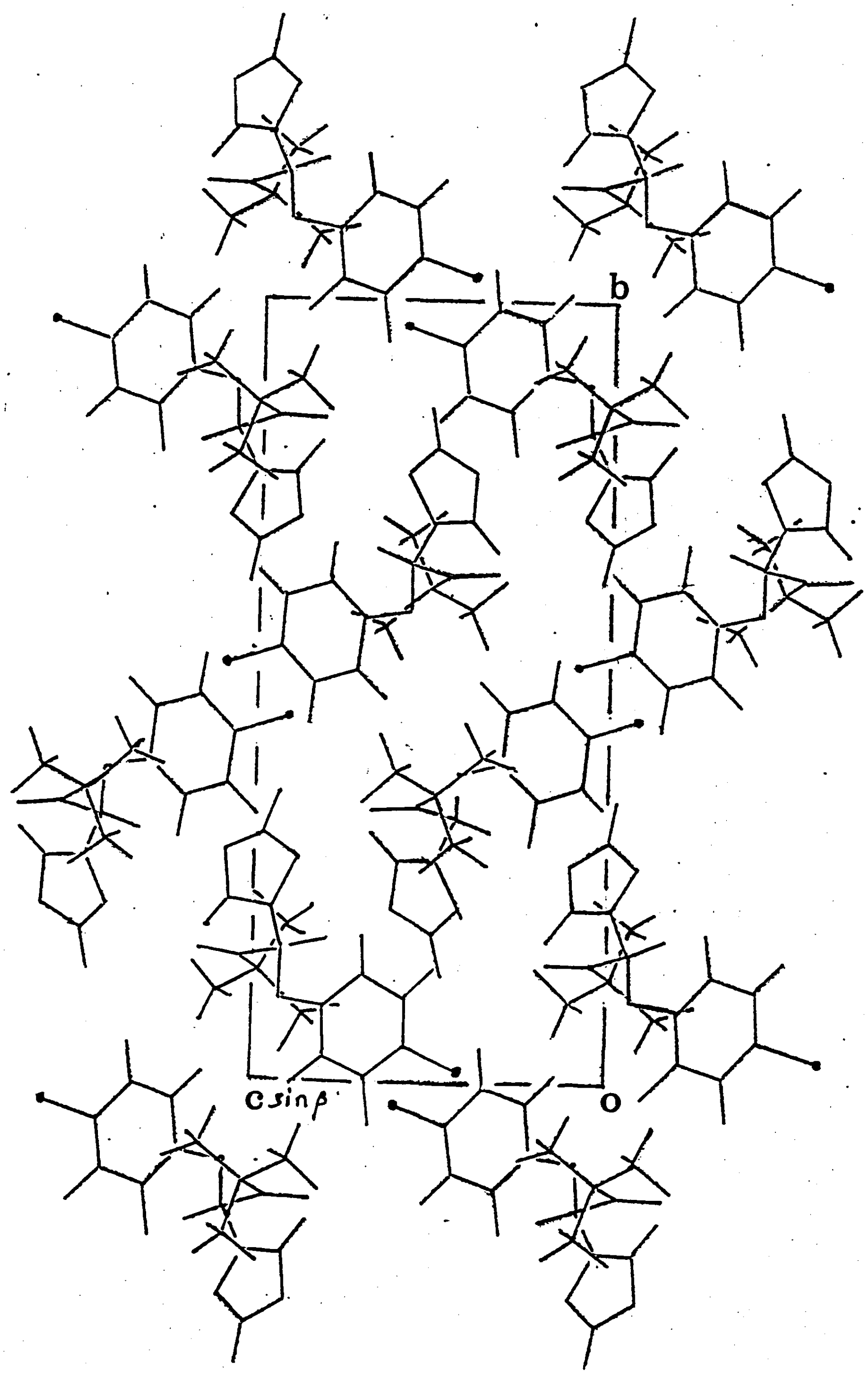


Fig.2.2.4. The crystal structure of 1-(4-chloro-phenoxy)-3,3-dimethyl-1-(1,2,4-triazol-1-yl)-2-butanone.

Projection down the a axis.

Table 2.2.1 Bond distances, with estimated standard deviation of errors in parentheses, for 1-(4-chlorophenoxy)-3,3-dimethyl-1-(1,2,4-triazol-1-yl)-2-butanone

Distances in Angströms

N1 - N2 = 1.348(8)
N1 - C1 = 1.332(10)
N2 - C2 = 1.311(13)
C2 - N3 = 1.336(12)
N3 - C1 = 1.319(11)
N1 - C5 = 1.449(9)
C4 - C5 = 1.558(11)
C5 - O2 = 1.429(9)
C4 - O1 = 1.196(8)
C4 - C31 = 1.521(11)
C31 - C32 = 1.537(10)
C31 - C33 = 1.537(12)
C31 - C34 = 1.544(10)
O2 - C71 = 1.406(9)
C71 - C72 = 1.371(11)
C71 - C76 = 1.374(11)
C72 - C73 = 1.399(12)
C73 - C74 = 1.363(14)
C74 - C75 = 1.377(13)
C75 - C76 = 1.378(13)
C74 - Cl = 1.761(9)

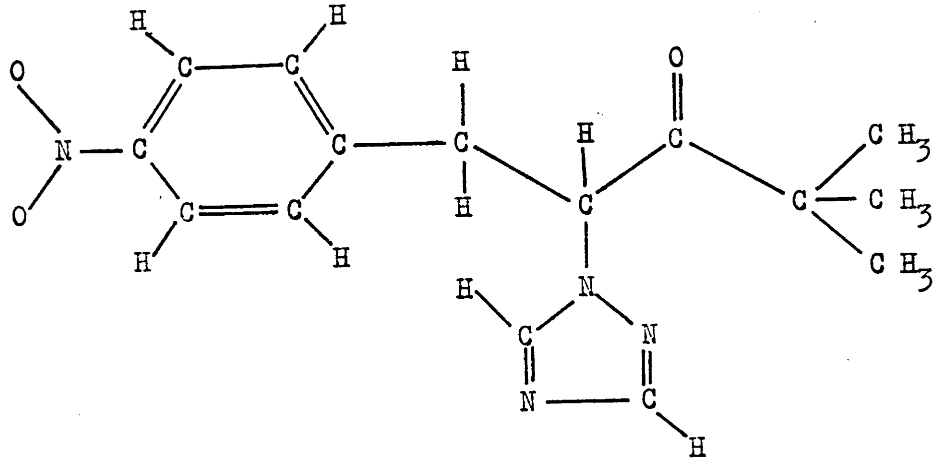
Table 2.2.2 Bond angles, with estimated standard deviation of errors in parentheses, for 1-(4-chlorophenoxy)-3,3-dimethyl-1-(1,2,4-triazol-1-yl)-2-butanone

Angles in degrees

C5 - N1 - N2 = 119.5(6)
C5 - N1 - C1 = 130.7(6)
C1 - N1 - N2 = 109.7(6)
N1 - N2 - C2 = 101.6(6)
N2 - C2 - N3 = 116.3(8)
C1 - N3 - C2 = 101.8(7)
N1 - C1 - N3 = 110.5(7)
N1 - C5 - C4 = 111.3(5)
N1 - C5 - O2 = 110.7(6)
C5 - C4 - O1 = 119.6(7)
C5 - C4 - C31 = 116.4(6)
O1 - C4 - C31 = 124.0(7)
C4 - C31 - C32 = 110.4(7)
C4 - C31 - C33 = 109.7(6)
C4 - C31 - C34 = 105.9(6)

C32 - C31 - C33 = 111.4(6)
C32 - C31 - C34 = 110.2(6)
C33 - C31 - C34 = 109.1(7)
C5 - O2 - C71 = 117.4(5)
O2 - C71 - C72 = 124.2(7)
C72 - C71 - C76 = 121.1(7)
C71 - C72 - C73 = 119.5(8)
O2 - C71 - C76 = 114.7(6)
C72 - C73 - C74 = 118.7(8)
C73 - C74 - C75 = 121.8(8)
C73 - C74 - Cl = 118.5(7)
Cl - C74 - C75 = 119.6(7)
C74 - C75 - C76 = 119.3(8)
C75 - C76 - C71 = 119.5(7)

2.3. The crystal and molecular structure of 1-(4-nitrophenyl)-4,4-dimethyl-2-(1,2,4-triazol-1-yl)-pentan-3-one.



2. - R79386

2.3.1 Crystal Data:

$C_{15}H_{18}O_3N_4$ $M_r = 302.335$ Monoclinic

$a = 5.835(5)$ $b = 13.645(11)$ $c = 19.860(16)$Å

$\beta = 91.91(5)^\circ$

$D_m = 1.30$ Mg. m^{-3} (by flotation) $D_c = 1.27$ Mg. m^{-3}

$Z = 4$ $F(000) = 640$ $\mu(Mo - K\alpha) = 0.55$ cm^{-1}

Systematic absences: 0k0, k = 2n + 1; h0l, l = 2n + 1.

These absences uniquely define the crystals as belonging to the space group $P2_1/c$.

2.3.2 Data collection and refinement:

An opaque crystal, approximately 0.44 x 0.32 x 0.20 mm, was mounted about the a - axis. Seven layers, 0kl → 6kl, were collected; 2241 independent reflections were recorded of which 960, having

$I/\sigma(I) \geqslant 1.5$, were used for structure refinement. An initial solution was obtained by direct methods using reflections having $E \geqslant 1.2$; this yielded all non-hydrogen atoms. Full-matrix least square refinement was used and hydrogen atoms were found from difference Fourier syntheses. These atoms were inserted in subsequent stages of refinement in positions calculated from ideal geometry using a fixed C-H bond length of 1.08Å. In the final stages of refinement all non-hydrogen atoms were given anisotropic temperature factors and a weighting scheme of

$$w = 0.5210 / (\sigma^2|F_o| + 0.001523|F_o|^2)$$

led to a value of $\underline{R} = 0.064$ and $\underline{R}_w = 0.064$. At this stage, the highest residue peak from a Fourier difference synthesis was 0.23 e Å^{-3}.

Confirmation of the correct designation to the atoms of the triazole ring was achieved by:

(a) consideration of relative heights of peaks on a Fourier difference synthesis with relevant atoms from the triazole ring removed from the structure. The atoms N_2, N_3, C1 and C2 showed peaks of 4.73, 4.65, 4.23, 4.02 e Å^{-3} respectively.

(b) attempted refinement by interchanging N2 and C1 (with attached H1), N_3 and C2 (with attached H2). The resultant structure was refined to a final value of R = 0.0800.

(c) The ring was investigated by difference Fourier synthesis with the H atoms removed from the structure. Peaks for these hydrogens suggested the chosen configuration. Although this was not too convincing in differentiating between N3 and C2, differentiation between C1 and N2 was conclusive.

Bond lengths and angles are shown in Tables 2.3.1 and 2.3.2 and Fig. 2.3.2. Structural and thermal parameters, mean planes, torsion angles and structure factors are given in Appendices A1.2, A2.2, A3.2 and A4.2. A general view of the molecule is given in Fig. 2.3.1.

2.3.3 Description of the structure:

The phenyl ring (C71 → C76) is effectively planar (Appendix A2.2) with C6 and N4 coplanar to the ring. The mean plane through N4, O41, O42 is inclined at angel of 3° to the phenyl ring. Both the triazolyl ring and the group C5, C4, O1, C31 are effectively planar. C5 shows identical deviation (0.06Å) from the mean plane of the triazolyl ring as found for R85827; with very similar bond angles and lengths in the triazolyl rings of the two structures, the same degree of electron delocalisation in the two rings may be expected. The variation in exocyclic angles about N1 is again observed with a 9° difference between C5-N1-C1 (129.2(7)°) and C5-N1-N2 (120.3(6)°). The triazolyl ring is inclined at 54° to the phenyl ring and at 83° to the plane through C5, C4, O1, C31. The resultant configuration is very close to that predicted from theoretical calculations designed to show minimum energy configuration[10].

The closest intermolecular distance is 2.24Å between O1 and H2′ (where H2′ is related to H2 by the symmetry relation 2.0-x, -0.5+y, 0.5-z).

Although this distance is within the sum of the van der Waals' radii for oxygen and hydrogen, it is not possible to be definitive about the nature of the interaction. The packing of the four molecules within the unit cell is shown in Fig. 2.3.3.

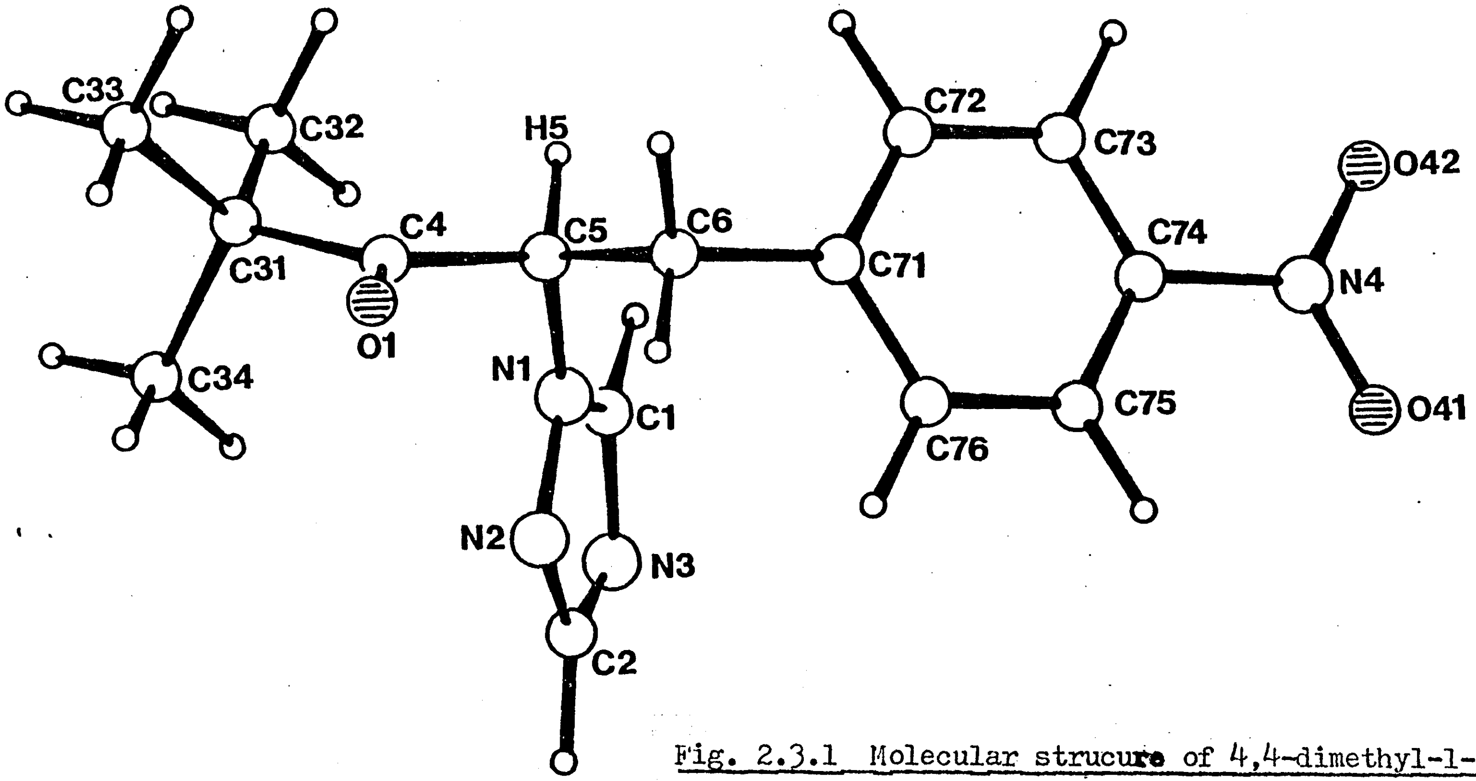


Fig. 2.3.1 Molecular strucure of 4,4-dimethyl-1-(4-nitrophenyl) -2-(1,2,4-triazol-1-yl)-pentan-3-one.

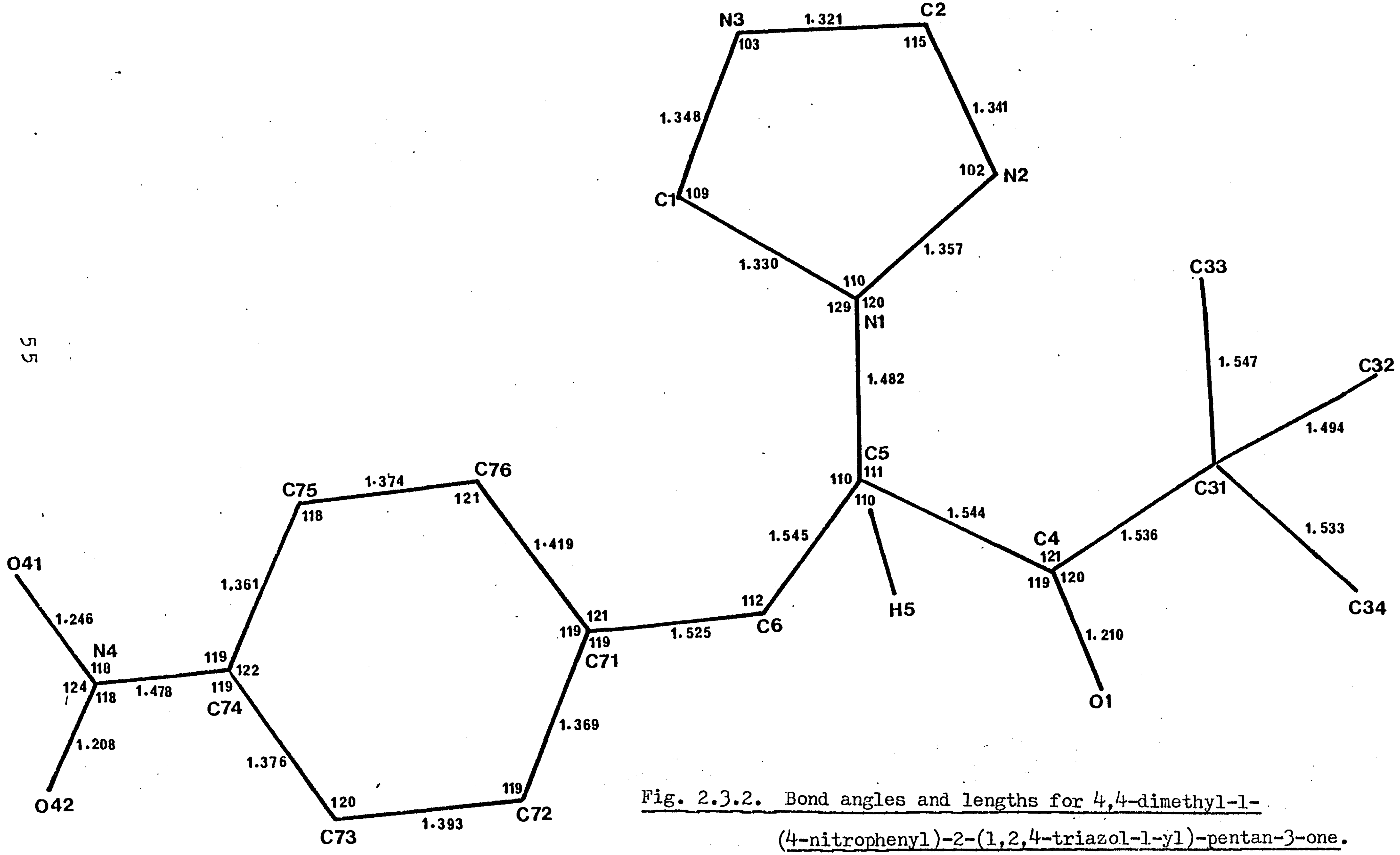


Fig. 2.3.2. Bond angles and lengths for 4,4-dimethyl-1-(4-nitrophenyl)-2-(1,2,4-triazol-1-yl)-pentan-3-one.

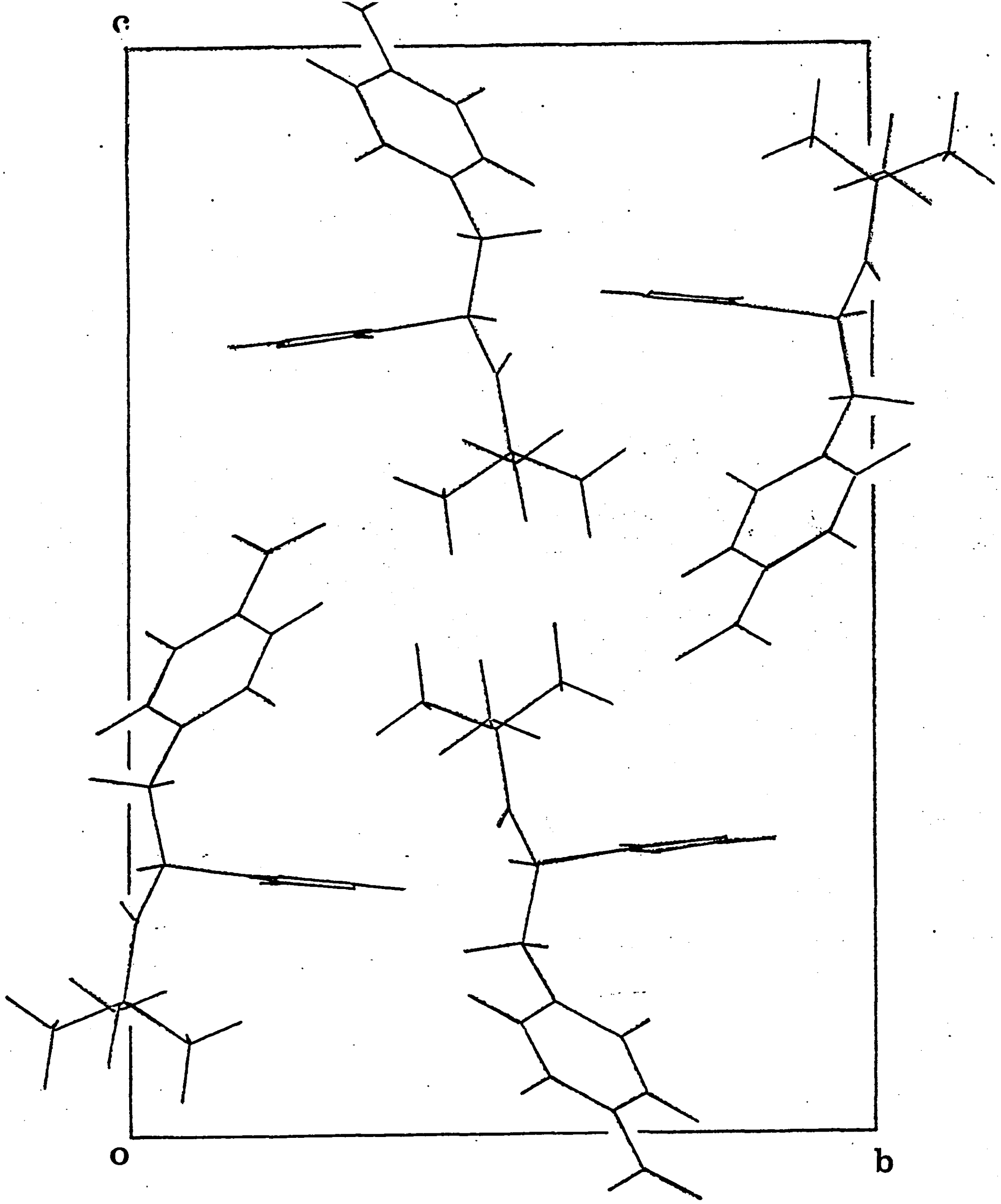


Fig.2.3.3 Crystal structure of 1-(4-nitrophenyl)-4,4-dimethyl-2-(1,2,4-triazol-1-yl) pentan-3-one

Projection down the a axis.

Table 2.3.1 Bond lengths, with estimated standard deviation of errors in parentheses, for 1-(4-nitrophenyl)-4,4-dimethyl-2-(1,2,4-triazol-1-yl)-pentan-3-one.

Distances in Å.

N4 - O41 = 1.247(13)
N4 - O42 = 1.205(14)
N4 - C74 = 1.477(12)
C74 - C73 = 1.359(14)
C72 - C73 = 1.375(12)
C72 - C71 = 1.418(11)
C71 - C76 = 1.367(11)
C75 - C76 = 1.392(11)
C74 - C75 = 1.377(12)
C71 - C6 = 1.527(10)
C6 - C5 = 1.545(8)
N1 - C5 = 1.480(8)

N1 - C1 = 1.331(12)
C1 - N3 = 1.348(13)
N3 - C2 = 1.320(18)
C2 - N2 = 1.343(12)
N1 - N2 = 1.356(10)
C5 - C4 = 1.547(9)
C4 - C31 = 1.537(9)
C4 - O1 = 1.208(10)
C31 - C32 = 1.492(13)
C31 - C33 = 1.542(14)
C31 - C34 = 1.527(13)

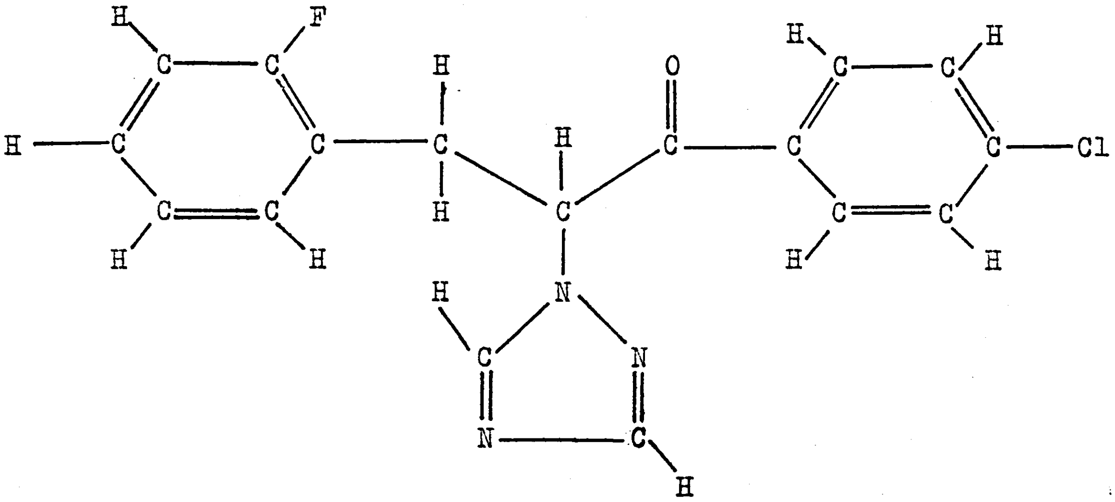
Table 2.3.2 Bond angles, with estimated standard deviation of errors in parentheses, for 1-(4-nitrophenyl)-4,4-dimethyl-2-(1,2,4-triazol-1-yl)-pentan-3-one.

Bond angles in degrees

O41 - N4 - O42 = 123.6(9)
O41 - N4 - C74 = 118.1(9)
O42 - N4 - C74 = 118.3(9)
N4 - C74 - C75 = 119.1(8)
N4 - C74 - C73 = 118.8(8)
C74 - C73 - C72 = 120.3(8)
C73 - C72 - C71 = 119.0(8)
C72 - C71 - C76 = 119.4(7)
C71 - C76 - C75 = 121.2(7)
C76 - C75 - C74 = 118.0(8)
C75 - C74 - C73 = 122.1(8)
C72 - C71 - C6 = 119.3(7)
C76 - C71 - C6 = 121.4(6)
C71 - C6 - C5 = 112.2(6)
C6 - C5 - C4 = 109.3(6)
C33 - C31 - C34 = 109.1(7)
C32 - C31 - C34 = 111.7(8)

C6 - C5 - N1 = 110.3(5)
C5 - N1 - C1 = 129.2(7)
C5 - N1 - N2 = 120.3(6)
N1 - C1 - N3 = 109.4(9)
C1 - N3 - C2 = 103.2(9)
N3 - C2 - N2 = 115.4(9)
C2 - N2 - N1 = 101.6(8)
C1 - N1 - N2 = 110.4(7)
N1 - C5 - C4 = 107.6(5)
C5 - C4 - O1 = 119.0(6)
C5 - C4 - C31 = 121.0(6)
O1 - C4 - C31 = 119.9(6)
C4 - C31 - C32 = 112.7(6)
C4 - C31 - C33 = 107.8(7)
C4 - C31 - C34 = 106.6(7)
C32 - C31 - C33 = 108.9(8)

2.4 The crystal and molecular structure of 1-(4-chlorophenyl)-3-(2-fluorophenyl)-2-(1,2,4-triazol-1-yl)propan-1-one



3. - R110043

2.4.1 Crystal data:

$C_{17}H_{13}N_3O$ F Cl   Mr = 329.76   monoclinic

a = 11.687(4)   b = 5.895(3)   c = 12.443(4)Å

β = 113.55(5)° D_c = 1.39 Mg. m^{-3} D_m = 1.40 Mg. m^{-3}

Z = 2   F(000) = 340 μ(Mo-Kα) = 2.15 cm^{-1}

Systematic absences: 0k0, k = 2n + 1

These systematic absences do not distinguish between the space groups $P2_1$ or $P2_1/m$. $P2_1$ was assumed for initial analysis and was confirmed as the correct space group by subsequent structure refinement.

2.4.2 Data collection and refinement:

A transparent crystal, approximate dimensions 0.23 x 0.20 x 0.12 mm, was mounted about the b axis. 16 layers, h0l → h15l were collected; 1880 independent reflections were recorded of which 1088 having $I/\sigma(I) \geqslant 5.0$ were used for subsequent structure refinement. An initial solution was obtained by direct methods using the 366 reflections having $E \geqslant 1.2$. A convergence map was generated from which the reflections

- 3 0 1, -7 0 2 and -4 1 6 were selected, conforming to space group and parity considerations, as defining the origin. The enantiomorph was specified by the reflection -3 5 6. The generation of a series of E maps yielded a trial solution from which non-hydrogen atoms were located. Subsequent refinement and Fourier difference syntheses yielded all hydrogen atoms which were placed in positions calculated from the geometry of the molecule (C - H = 1.08Å) for later stages of refinement. The structure was refined by full-matrix least squares techniques and non-hydrogen atoms were given anisotropic temperature parameters. The phenyl hydrogen atoms and those associated with the triazolyl ring were given isotropic temperature factors which were common for each ring but allowed to vary from ring to ring. The remaining hydrogen atoms were given isotropic temperature factors that were allowed to refine independently. Attempts were made to solve the structure as the R-isomer and as the S-isomer (by changing all coordinates from x,y,z to -x,-y,-z) but it was not possible to differentiate between the two possible structures. The S-isomer refined to give R = 0.0566 and R_w = 0.0674 with a final weighting scheme of $W = 8.5369/(\sigma^2(F_o) + 0.000197F_o^2)$ while the R-isomer refined to give R = 0.0565 and Rw = 0.0674 under a weighting scheme of $w = 8.4929/(\sigma^2(F_o) + 0.000195\ F_o^2)$. Disorder was found for the fluorine atom; a site occupation factor of 0.17 was obtained for fluorine bonded to C76. In the final refinement, the hydrogen bonded to C76 was omitted and the appropriately weighted fluorine atom was considered as bonded to C76 and C72 respectively. The highest residue peak on the final Fourier difference synthesis was 0.41 e $Å^{-3}$. Bond lengths and bond angles are shown in Tables 2.4.1 and 2.4.2 respectively and are given for the R-isomer; structural and thermal parameters, mean plane data, torsion angles and structure factors are given in Appendices A1.3, A2.3, A3.3 and A3.4 respectively. A general view of the molecule is shown in Fig.2.4.1, bond lengths and angles are summarised in Fig.2.4.2.

2.4.3 Discussion of structure:

The two phenyl rings are both essentially planar with C4, Cl and F, C6 being effectively in the plane of the C31 → C36 and C71 → C76 rings respectively. The triazolyl ring is planar: C5 is, however, more displaced (0.174Å) from the plane of the ring than for any of the other triazole compounds studied in the present work. Also, the N1-N2 bond is found to be identical in length with the C1-N1 bond (1.335(11) and 1.335(9)Å respectively). This is in contrast to all other related triazoles studied, where the N1-N2 distance is, on average, 0.025Å larger than the C1-N1 distance. The exo-cyclic angles about N1 show the characteristic asymmetry. The difference in C5-N1-N2/C1 angles being 10°. The triazole ring is inclined at an angle of approximately 90° to the chlorophenyl ring and to the C4,C5,O1,C6 grouping (Appendix A2.3). This arrangement keeps the triazolyl ring at the most favourable steric position from the afore mentioned groups. The plane through C4,C5,O1,C6 is inclined at 20° to the chlophenyl ring. The resultant close proximity of O to H32 probably explains the unequal exocyclic angles about C31 (C4-C31-C32 = 123°; C4-C31-C36 = 117°) with the phenyl ring "bending away" from the carbonyl group.

The fluorophenyl ring is inclined at an angle of 43° to the triazolyl ring. Energy calculations[30] show that there is only a small energy difference ($<$1KJ) between the two positions adopted by the discovered fluorine atom and that the energy barrier against rotation of the fluorophenyl ring about the C6-C71 bond is also very small.

No significant intermolecular interactions were found; the shortest distance being 1.993Å between H74 and H2′ where H2′ is related by the symmetry relation x-1.0,y,z-1.0 to H2 (Fig.2.4.3).

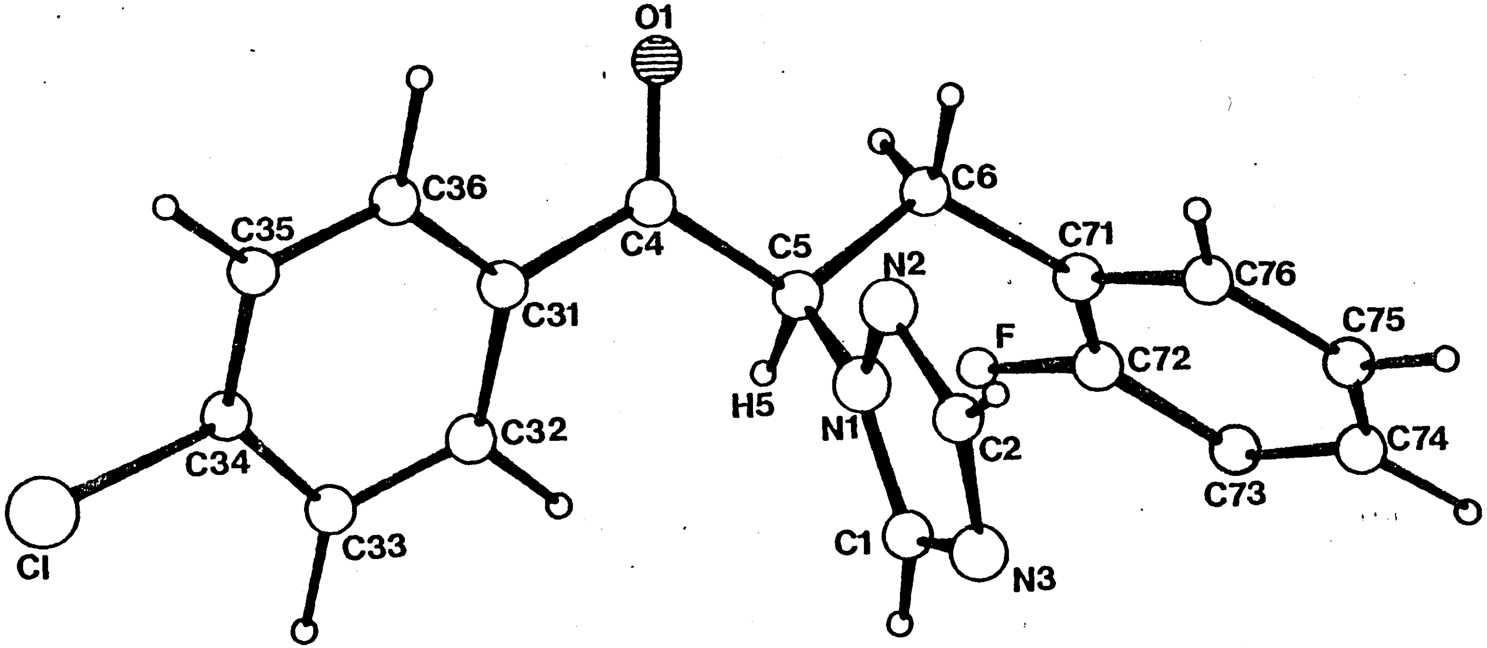


Fig.2.4.1.

Molecular structure for 1-(4-chlorophenyl)-3-(2-fluorophenyl)-2-(1,2,4-triazol-1-yl)-propan-1-one.

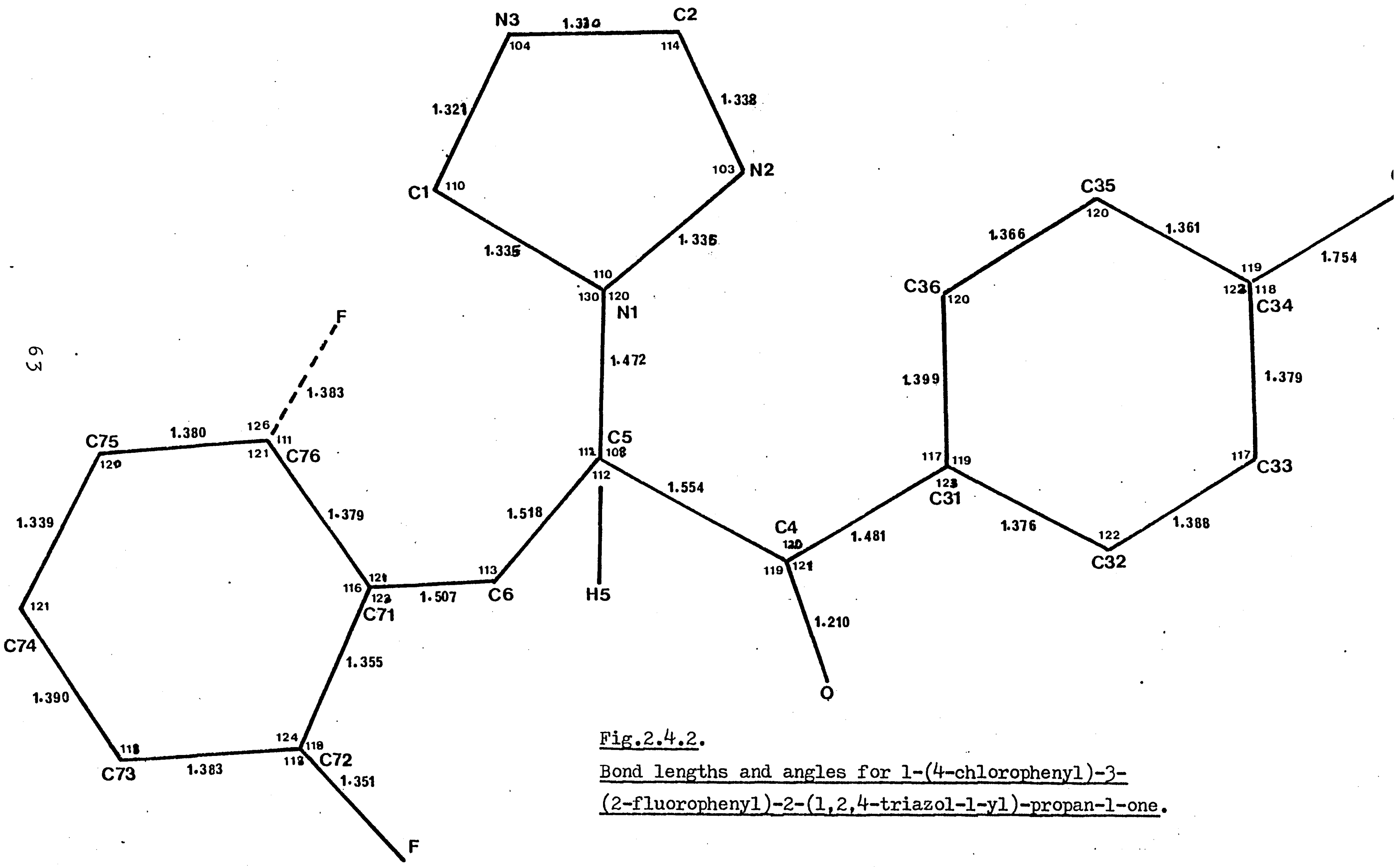


Fig.2.4.2.

Bond lengths and angles for 1-(4-chlorophenyl)-3-(2-fluorophenyl)-2-(1,2,4-triazol-1-yl)-propan-1-one.

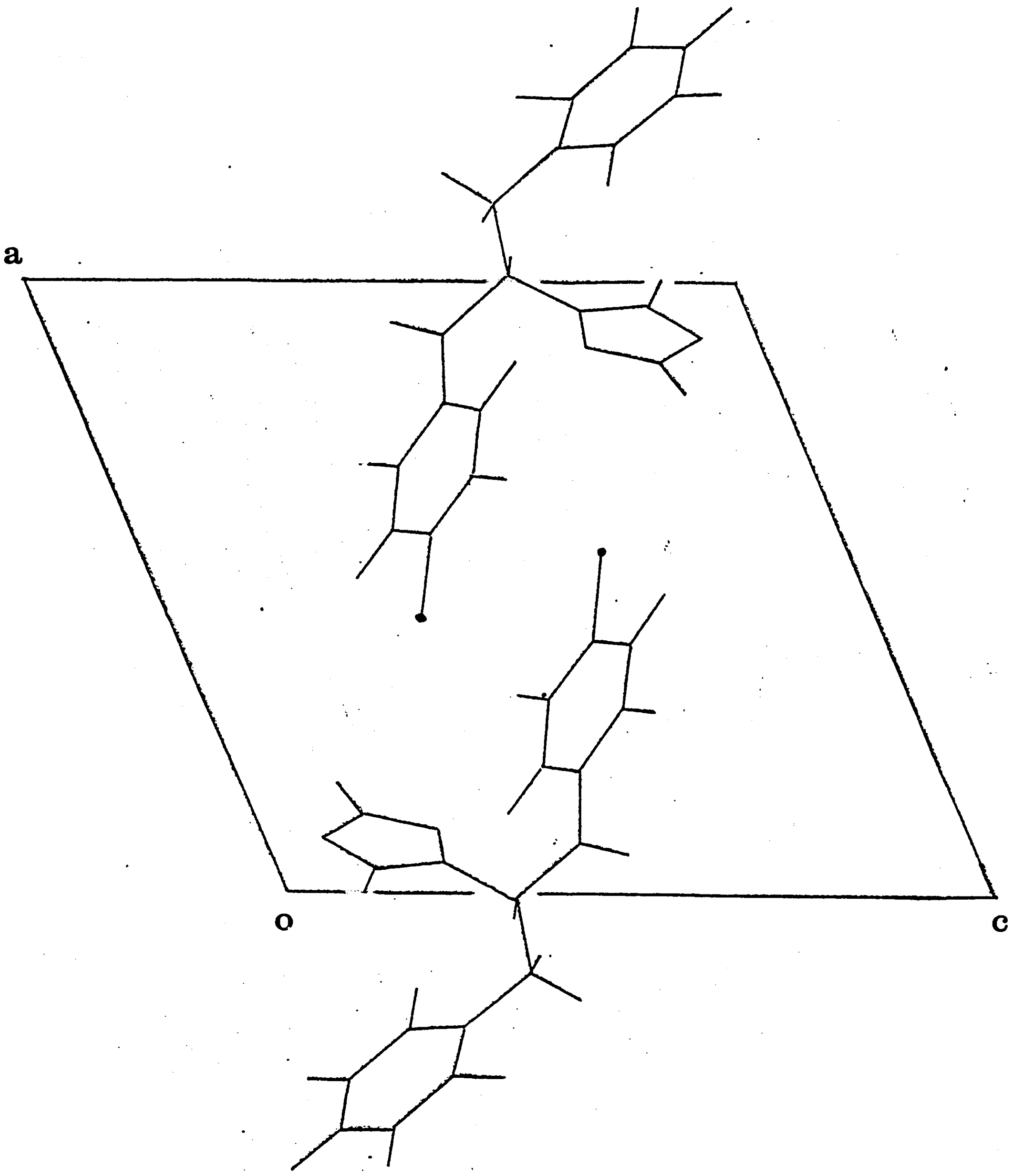


Fig.2.4.3.

Crystal structure of 1-(4-chlorophenyl)-3-(2-fluorophenyl) - 2 - (1,2,4-triazol - 1 - yl)-propan -1 -one.

Projection down the b axis.

Table 2.4.1

Bond lengths,with estimated standard deviations of error in parentheses, for 1-(4-chlorophenyl)- 3 -(2-fluorophenyl) - 2 -(1,2,4-triazol-1-yl)-propan - 1 - one.

Distances in Å

C1 - N1 = 1.335(9)
C1 - N3 = 1.321(12)
C2 - N3 = 1.330(13)
C2 - N2 = 1.338(10)
N1 - N2 = 1.335(11)
N1 - C5 = 1.472(9)
C4 - C5 = 1.554(7)
C4 - O = 1.210(8)
C4 - C31 = 1.481(8)
C31 - C32 = 1.376(8)
C32 - C33 = 1.388(8)
C33 - C34 = 1.379(7)
C34 - Cl = 1.754(6)

C34 - C35 = 1.361(8)
C35 - C36 = 1.366(7)
C31 - C36 = 1.399(8)
C5 - C6 = 1.518(10)
C6 - C71 = 1.507(7)
C71 - C72 = 1.355(7)
C72 - C73 = 1.383(9)
C73 - C74 = 1.390(9)
C74 - C75 = 1.339(8)
C75 - C76 = 1.380(9)
C71 - C76 = 1.379(9)
C72 - F72 = 1.351(14)
C76 - F76 = 1.383(25)

H74 .... H2' 1.993

where H2' is related to H2 by the symmetry relation

x - 1, y, z - 1

Table 2.4.2

Bond angles, with estimated standard deviations of error in parentheses, for 1-(4-chlorophenyl) - 3 - (2-fluorophenyl) - 2 - (1,2,4-triazol -1 -yl)-propan - 1 - one.

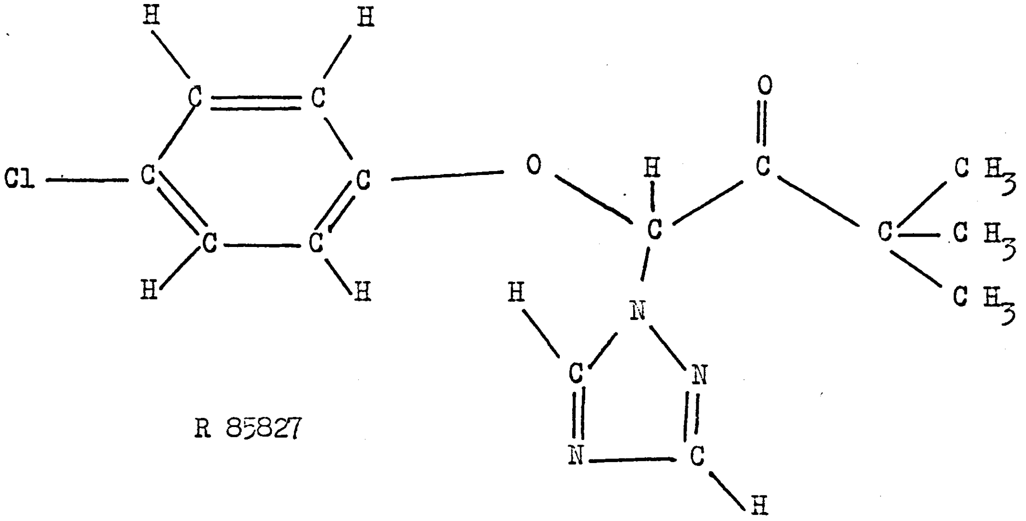
Angles (°)

C1 - C34 - C33 = 119.4(4)
C1 - C34 - C35 = 117.9(4)
C31 - C32 - C33 = 122.0(5)
C32 - C33 - C34 = 116.9(5)
C33 - C34 - C35 = 122.7(5)
C34 - C35 - C36 = 119.7(5)
C35 - C36 - C31 = 119.9(5)
C36 - C31 - C32 = 118.8(5)
C4 - C31 - C32 = 123.1(5)
C4 - C31 - C36 = 117.4(5)
C5 - C4 - C31 = 119.9(5)
C5 - C4 - O = 118.6(5)
C31 - C4 - O = 121.4(5)
C4 - C5 - N1 = 108.0(5)
C4 - C5 - C6 = 112.1(5)
N1 - C5 - C6 = 111.7(4)
C5 - N1 - C1 = 129.5(5)
C5 - N1 - N2 = 119.5(5)

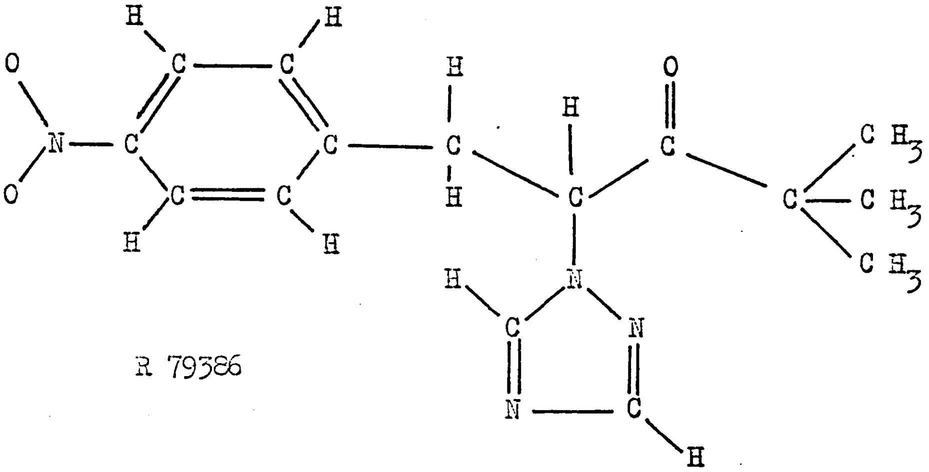
N1 - C1' - N3 = 109.6(5)
C1 - N3 - C2 = 104.4(6)
N3 - C2 - N2 = 114.2(6)
C2 - N2 - N1 = 102.8(5)
N2 - N1 - C1 = 111.3(6)
C5 - C6 - C71 = 112.6(5)
C6 - C71 - C72 = 122.7(5)
C6 - C71 - C76 = 120.6(5)
C71 - C72 - C73 = 124.1(6)
C72 - C73 - C74 = 117.8(5)
C73 - C74 - C75 = 120.5(6)
C74 - C75 - C76 = 119.6(6)
C75 - C76 - C71 = 121.4(5)
C76 - C71 - C72 = 116.4(5)
C71 - C72 - F72 = 117.9(5)
C73 - C72 - F72 = 117.9(5)
C71 - C76 - F76 = 110.6(21)
C75 - C76 - F76 = 126.1(22)

2.5 Comparative study of selected triazoles

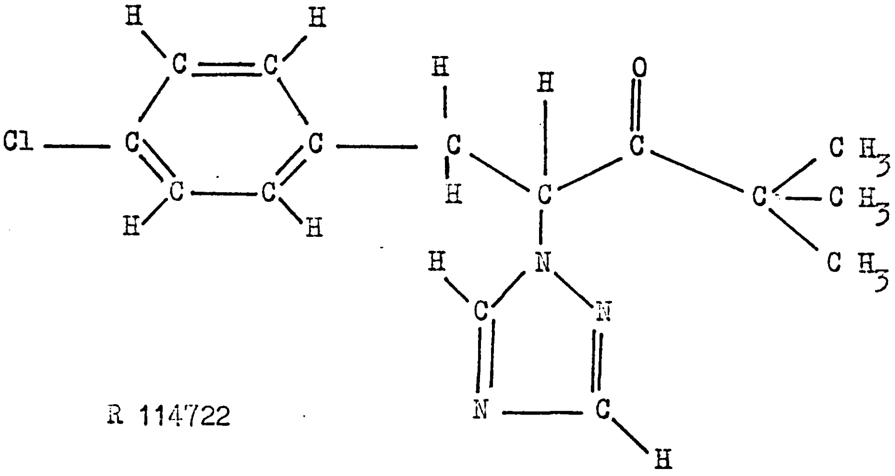
A comparative analysis of the three structures discussed (3.2 to 3.4) with other related structures (in particular, R113295 and R114722) highlights many similarities (with the exception of R85827) between the configurations.



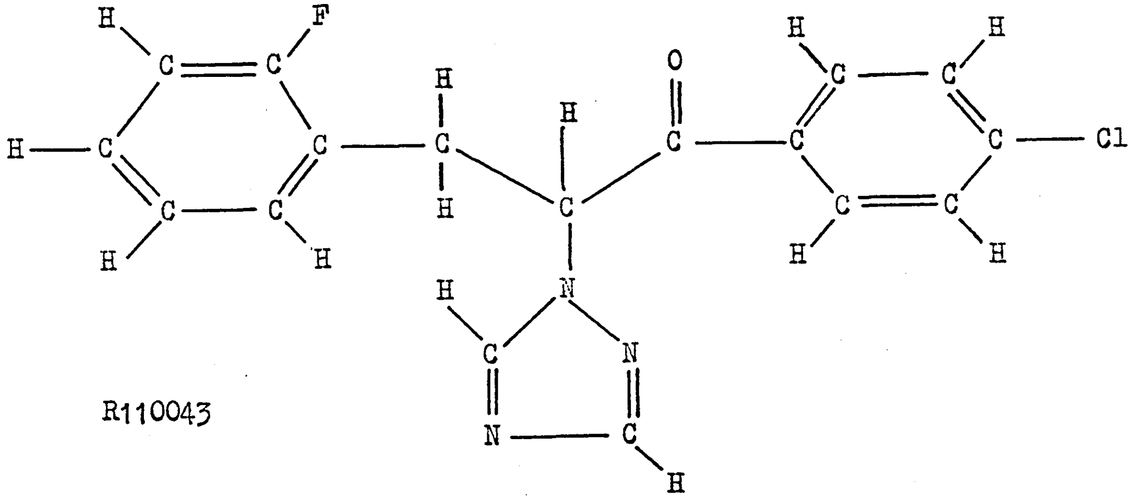
R 85827



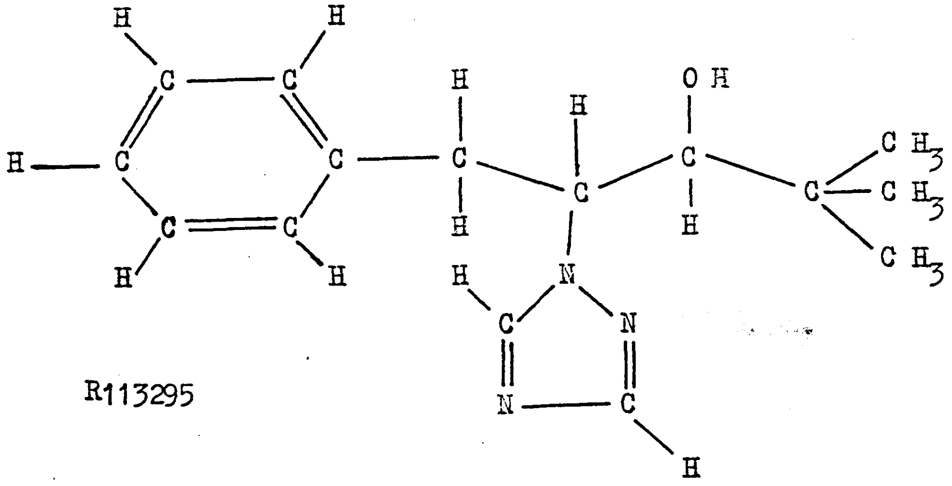
R 79386



R 114722



R110043



R113295

All the structures have at least one asymmetric carbon atom and hence are capable of existing as optical isomers. R79386 and R85827 give rise to racemic crystals: although R110043 give enantiomorphic crystals it was not possible from the crystallographic data to differentiate between the two isomers. R113295 with two asymmetric carbon atoms, crystallised to give the enantiomorphic pair RR and SS. R114722, however, crystallised in a non-centrosymmetric space group ($P2_12_12_1$) and statistical methods showed the S-isomer to be present in the crystals studied[32].

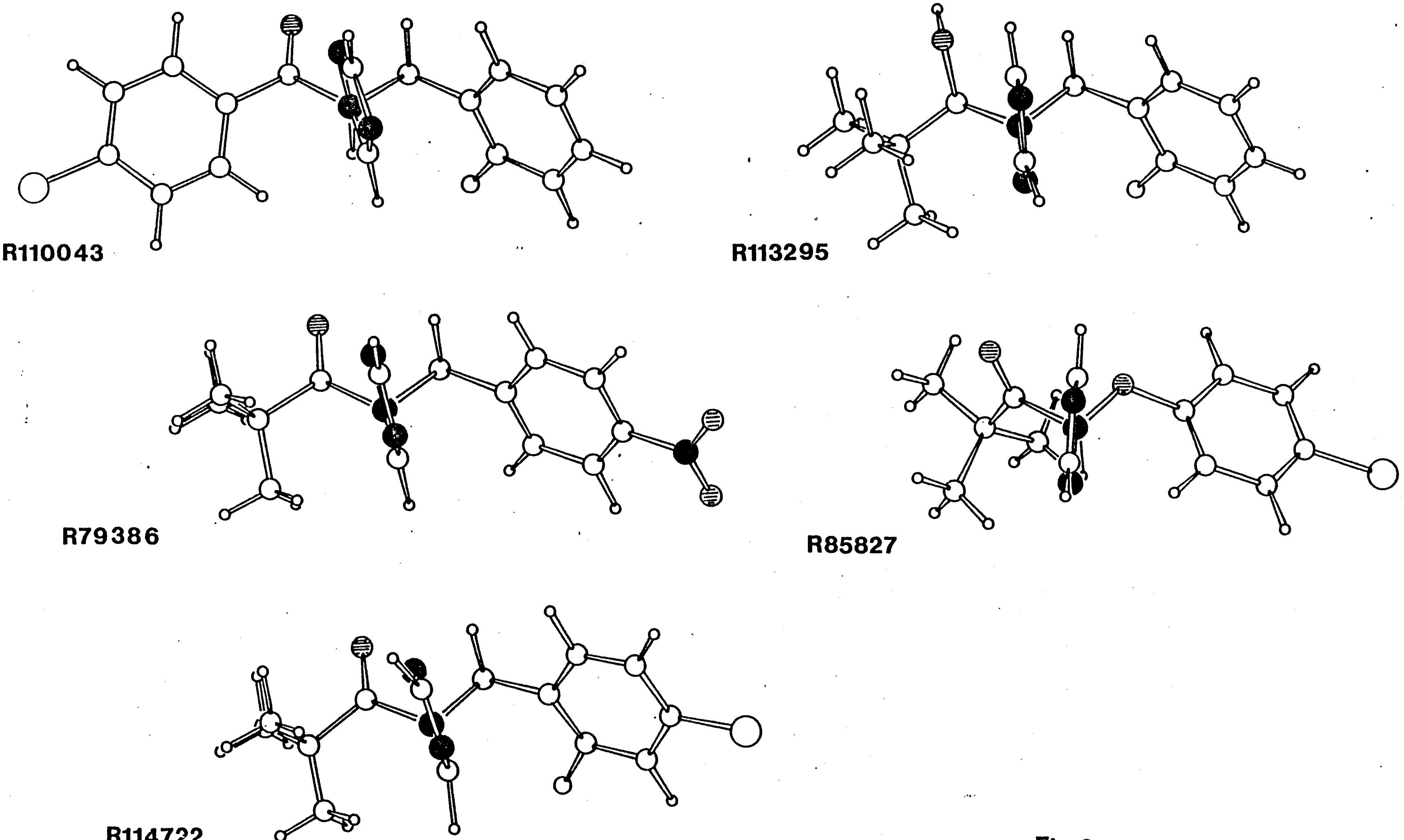
Conformations adopted by the five compounds are dominated by the relative orientation of the triazole ring, the phenyl ring at C71 and the group (phenyl or tertiary butyl) at C31 both to each other and to the aliphatic chain (C31-C4-C5-X-C71; X = O, C6). Relevant torsion angles are tabulated below. Projection down the N1-C5 (figs 3, 4a, 4b) and C4-C5 bonds (figs 5, 6a, 6b) indicate that R79386 and R114722 adopt very similar conformations. Replacement of the NO_2 group by a chlorine atom at C74 appears to have very little effect on the conformation adopted.

	R79386	R114722	R113295
O - C4 - C5 - C6	-19.4(8)	-11	-65
C31 - C4 - C5 - C6	163.8(6)	165	169
C31 - C4 - C5 - N1	-76.2(7)	-73	-67

Many of the similarities between R79386 and R114722 are preserved in R110043 (figs 3, 4a - c, 5, 6a - c). The p-chlorophenyl group is orientated such that C32 lies in the same orientation as the C32 methyl groups in R79386 and R114722. Also, C36 of the phenyl ring bisects the positions occupied by the C33 and C34 methyl groups in the comparative structures (figs 7, 8a, 8b, 8c). R113295 is also analogous to the above three structures in that projection down the C31-C4 bond (fig 7, 8a - d) shows the -OH group taking up a similar position to the carbonyl group in R79386, R114722 and R110043, (being trans to C32). The -OH group in R113295 does show some differences in orientation with the corresponding group in R114722 as shown by the N1-C5-C4-O1 torsion angle (108° in R114722 but only 59° in R113295). Whilst the orientation of the triazolyl ring in R113295 is very similar to that of the other three structures it differs in that the ring is rotated through approximately 180° in respect to the other triazolyl rings.

In striking contrast to the above structures, R85827 has a fundamentally different conformation - as is readily seen from figs 3, 5, 7 and 9. The triazolyl ring is rotated by 180° to the arrangement found in R110043, R79386 and R114722 and the orientation of the tertiary butyl group and the phenyl ring is quite different. The dihedral angle between the phenyl ring and the triazolyl ring (86°) is far larger than for any of the other structures (table 2.5.4). This results in H72 approaching N1 and N2 (fig 2.2.2) such that the distances N1 .... H72 and N2 .... H72 (2.632 and 2.676Å respectively) fall with the sum of the van der Waals' radii for nitrogen and hydrogen. This feature is not found in any related structure. There is an accompanying distortion in the exocyclic angles about C71 (115° and 124°), which is also absent in the other structures (Table 2.5.2). The differing orientation of the aromatic ring at C71 in R85827 may be a reflection of greater ease of rotation about the ether linkage (O2) compared with the CH_2 group found in the other structures. The different orientation of the tertiary butyl group with respect to the aliphatic chain can be seen in the projection down the C31-C4 bond (fig 7, 8a - e) and the C4-C5 bond (fig 5, 6a - e). The C31-C4-C5-N1 torsion angle is -142° in R85827 compared to a range of -62° to -76° for the comparative structures. In addition, a far smaller value of 37° for the O1-C4-C5-N1 torsion angle is found than in the comparative range of 100° to 116°. The overall effect of these differences is to produce a far more "compact" conformation in R85827 than the full extended aliphatic chain for the other four structures (fig 3, 4a - 4f).

All five structures exhibit asymmetric exocyclic angles at N1 (C5-N1-N2 and C5-N1-C1 with the latter always the larger). This appears to be a function of the triazolyl ring and not a result of steric hinderance. The effect is independent of the orientation of the ring and is not observed in imidazolyl systems (see 2.6).



R110043

R113295

R79386

R85827

R114722

Fig.3

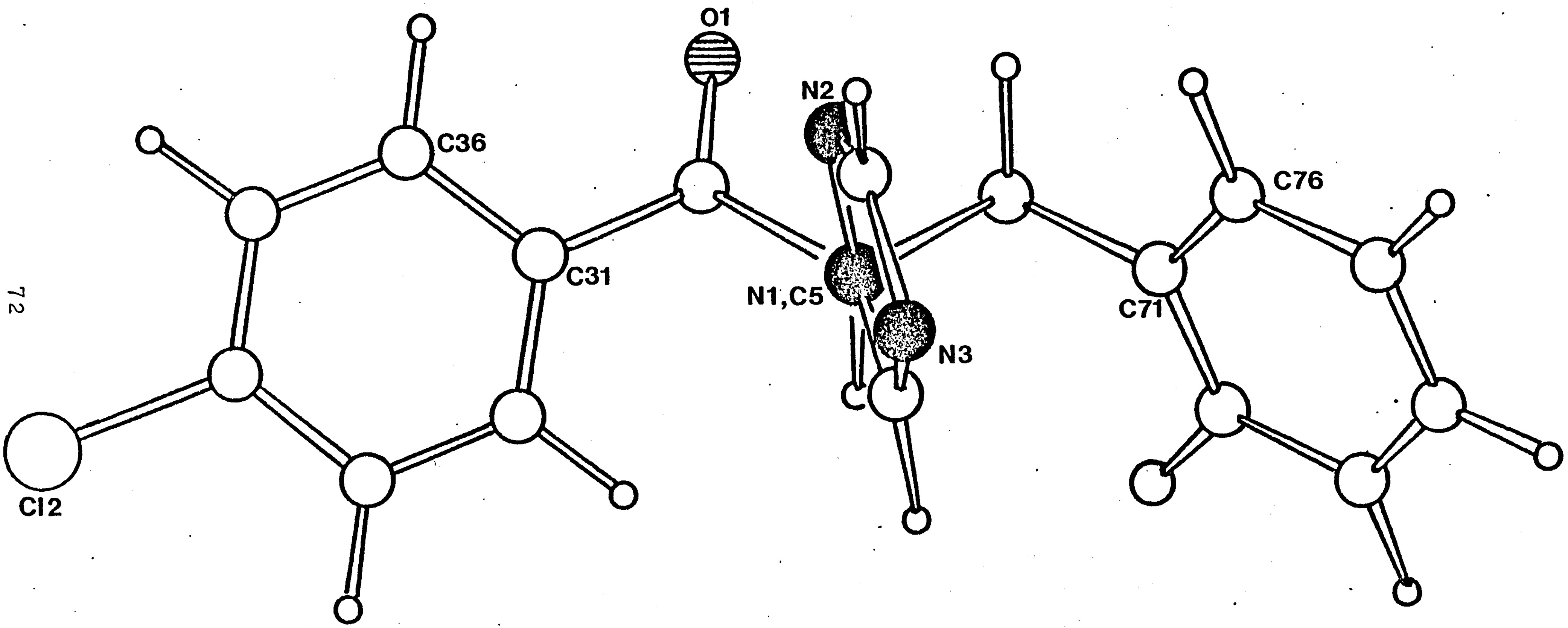


Fig. 4a R110043

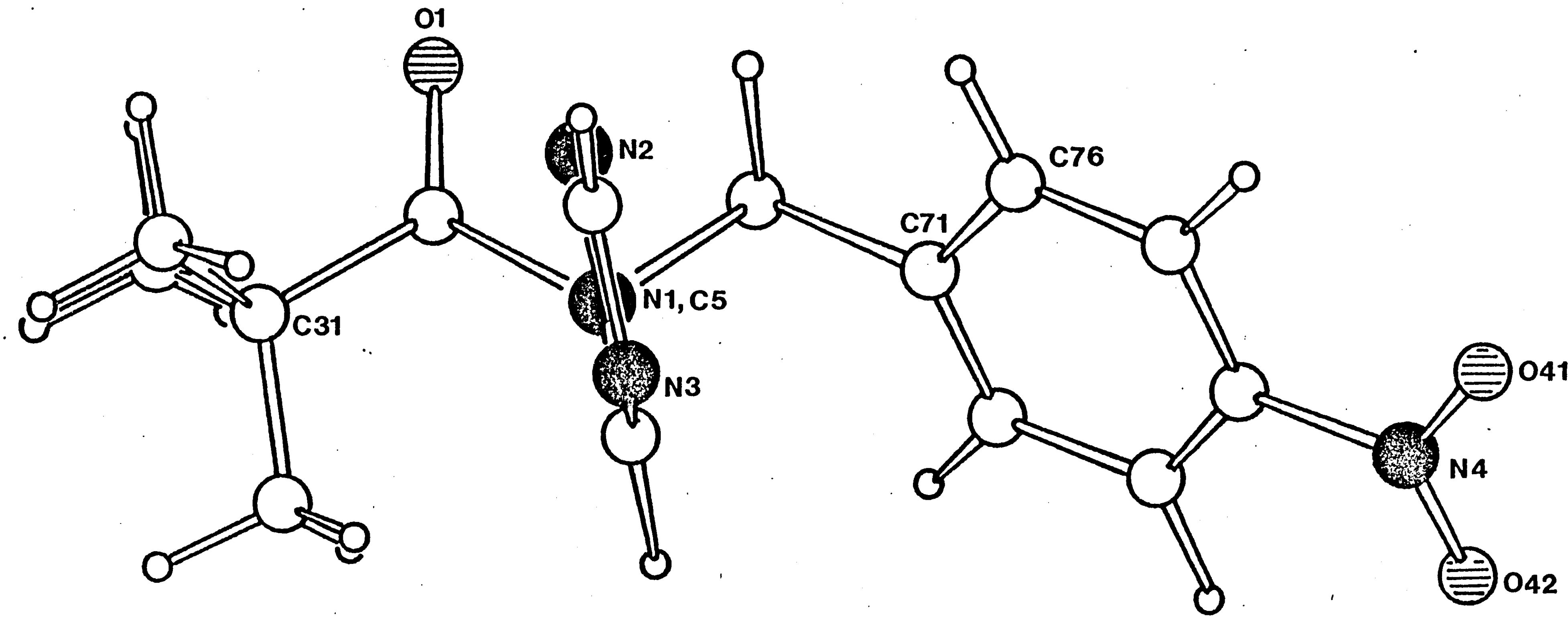


Fig. 4b R79386

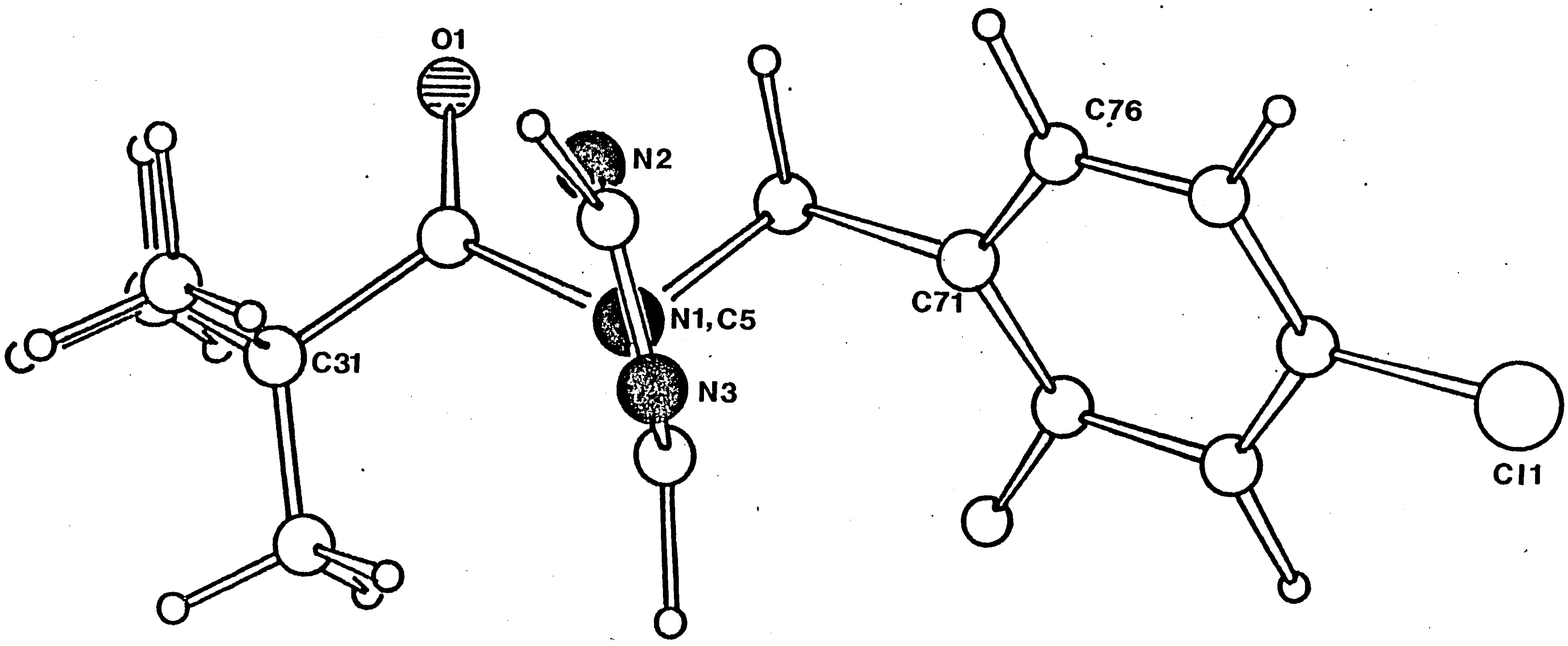


Fig.4c R114722

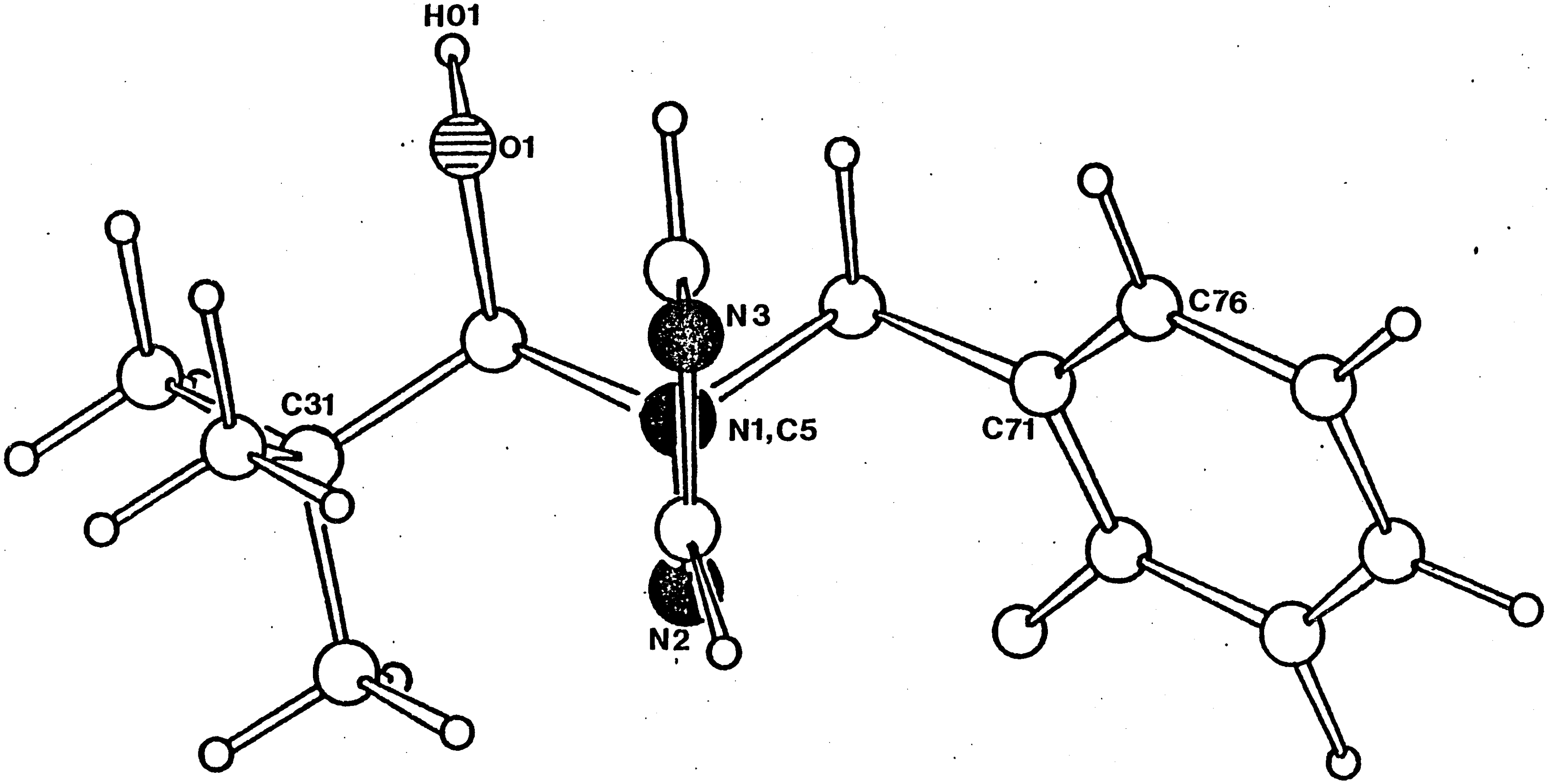


Fig. 4d R113295

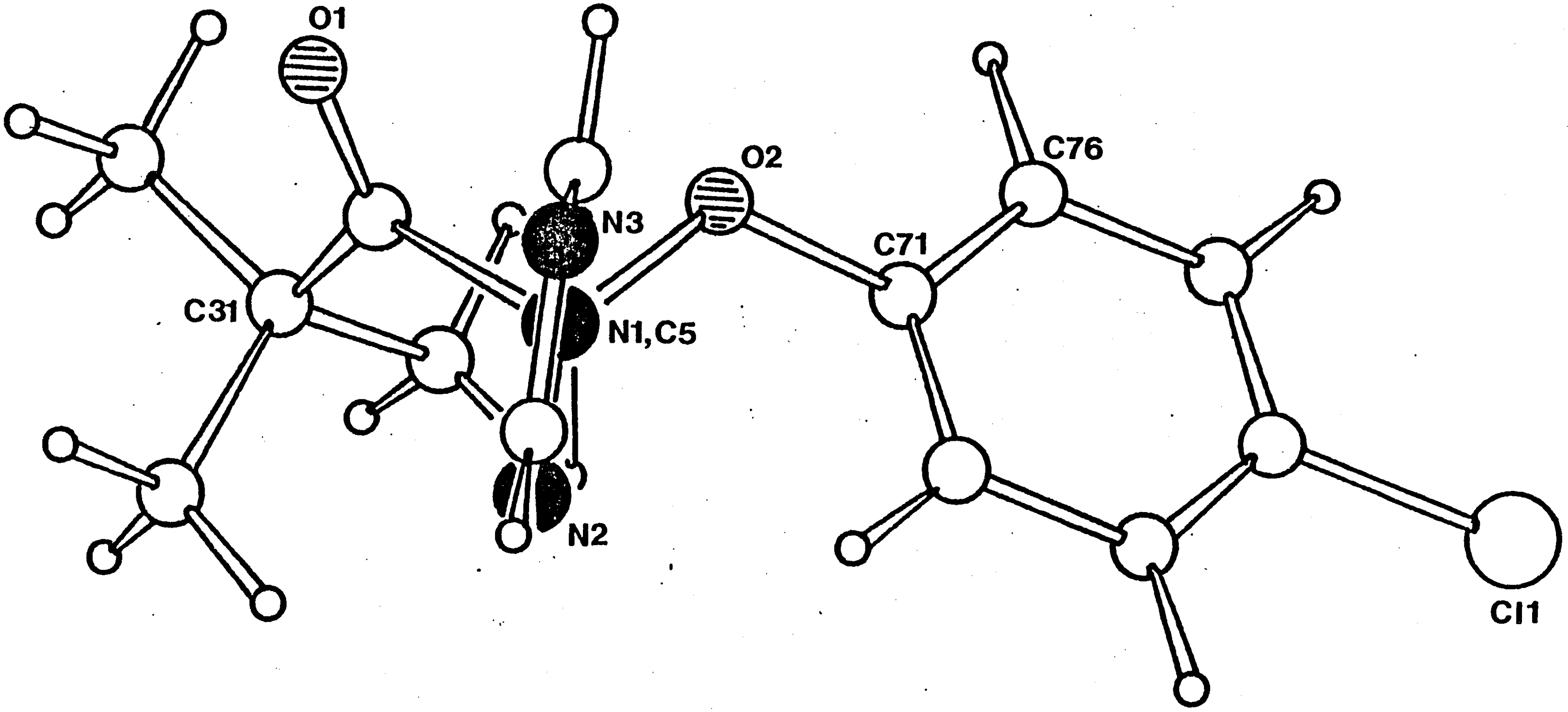


Fig.4e R85827

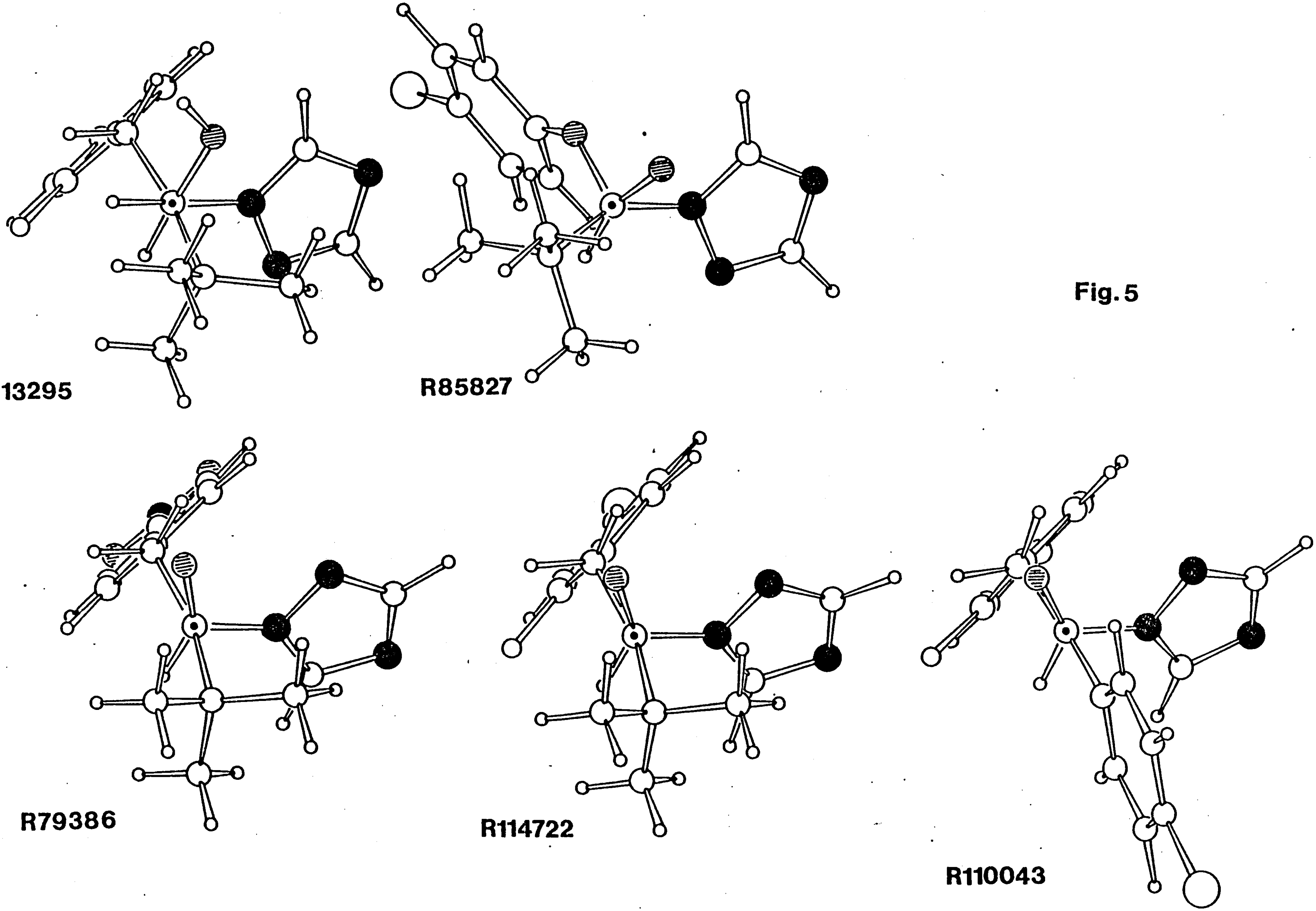


Fig. 5

R113295

R85827

R79386

R114722

R110043

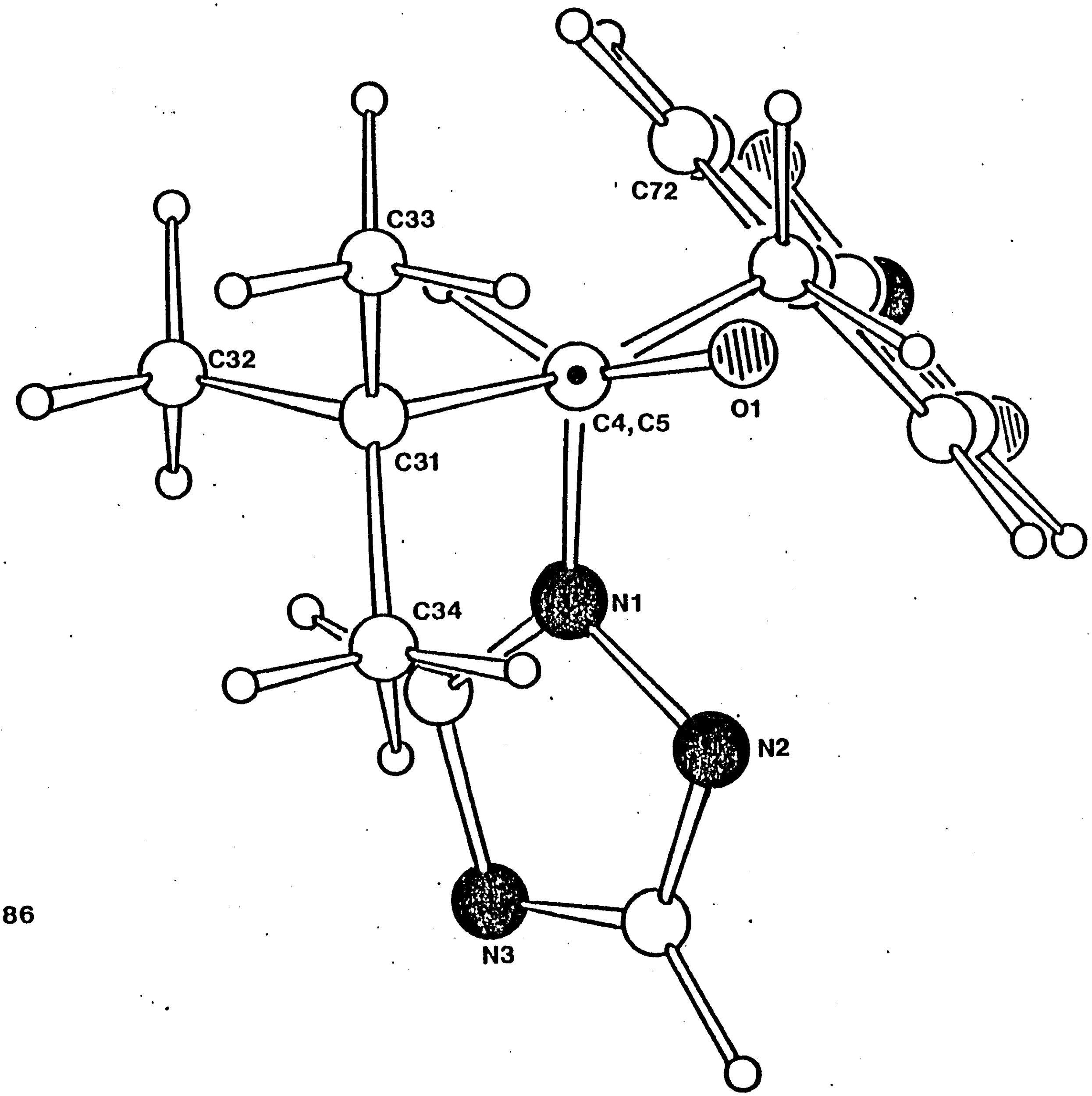


Fig. 6a R79386

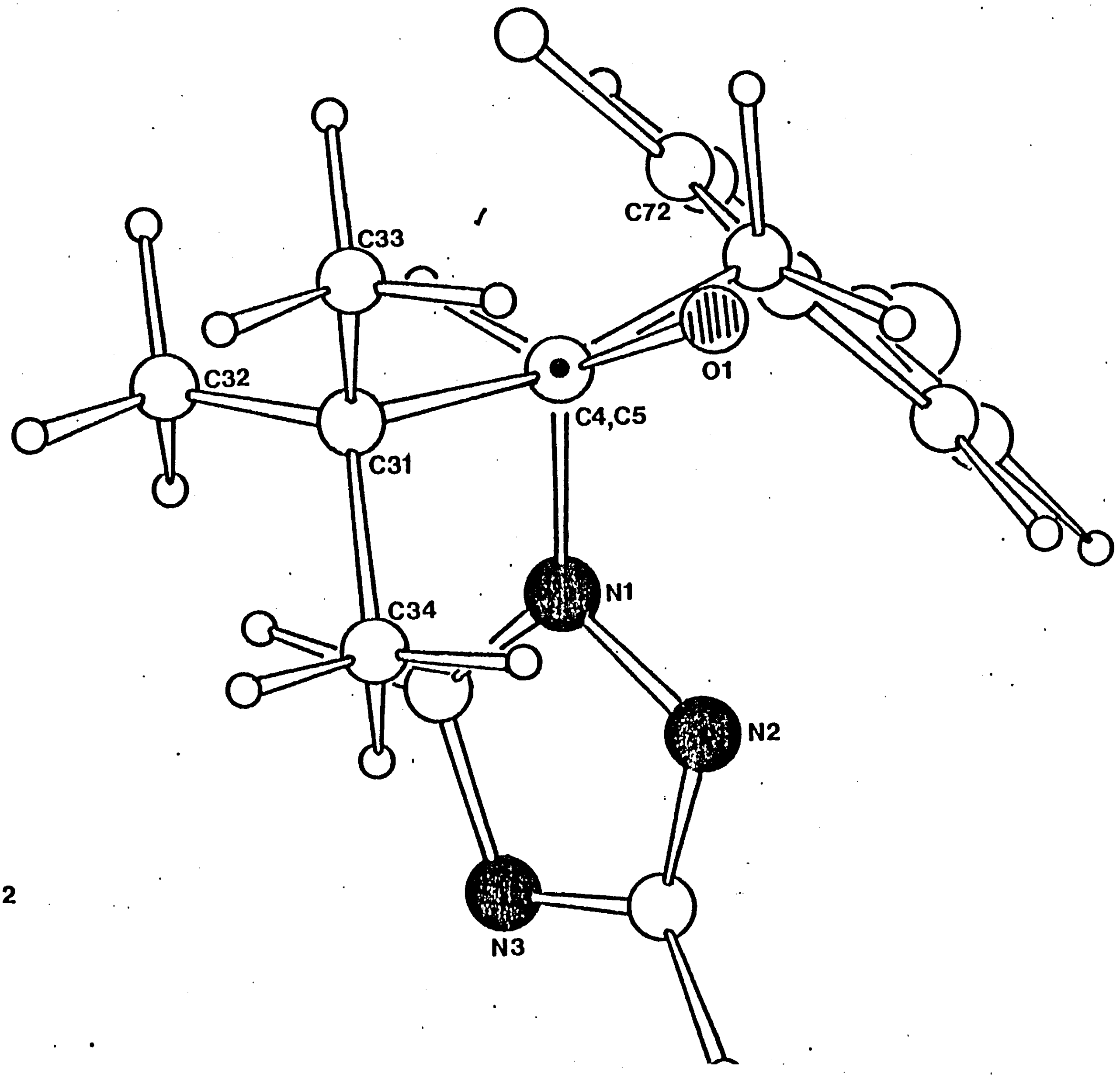


Fig.6b R114722

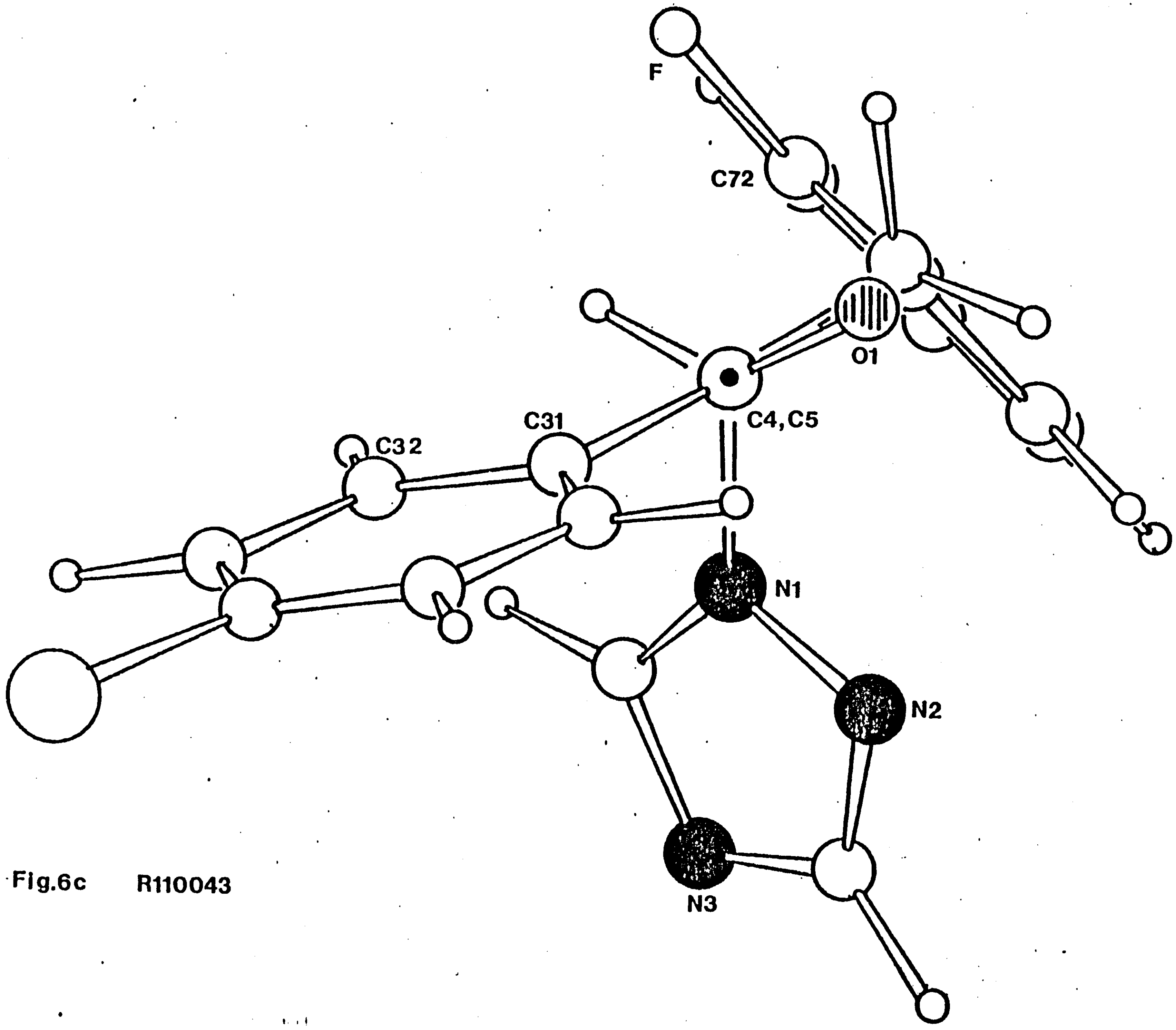


Fig.6c R110043

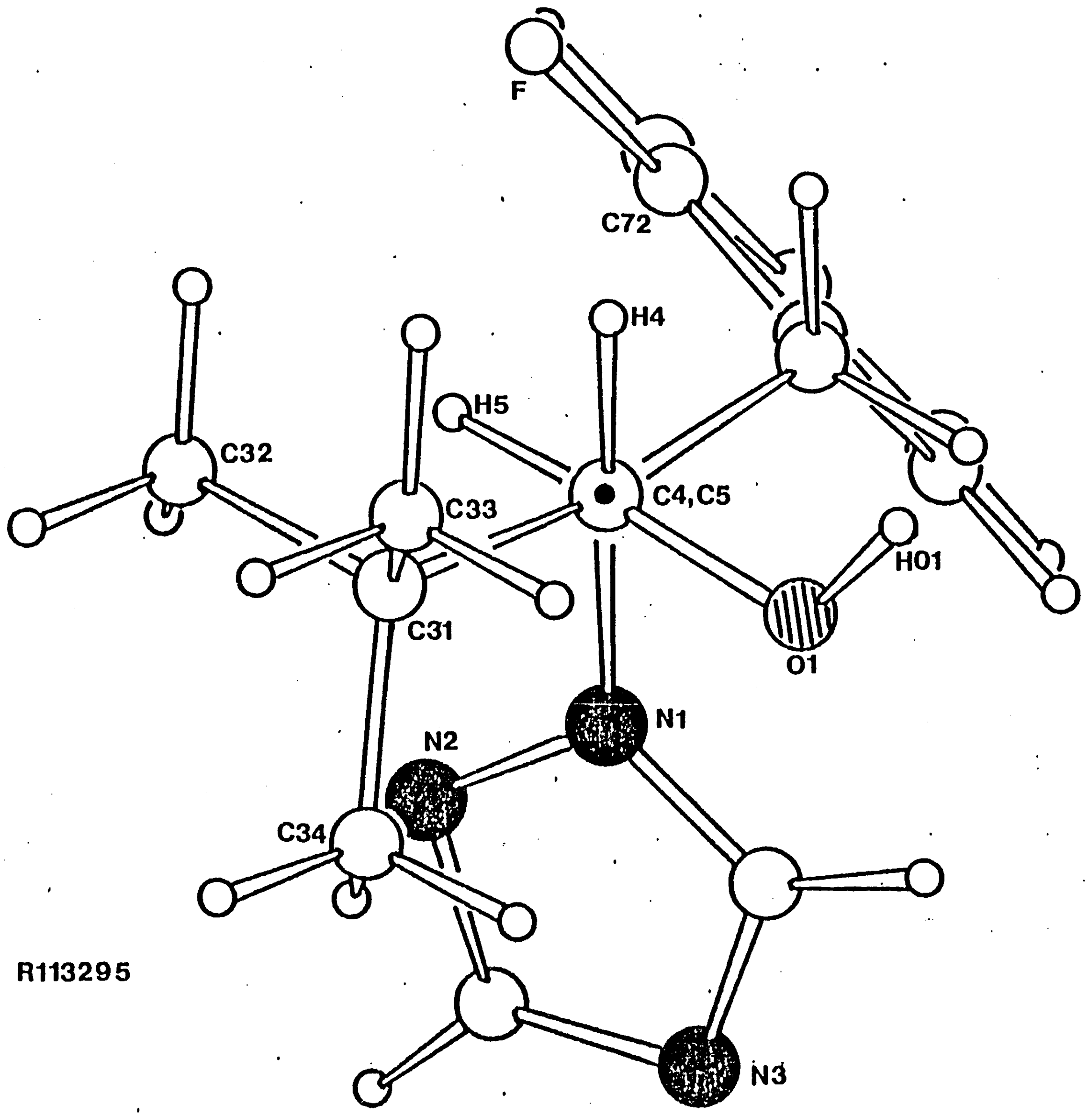


Fig.6d R113295

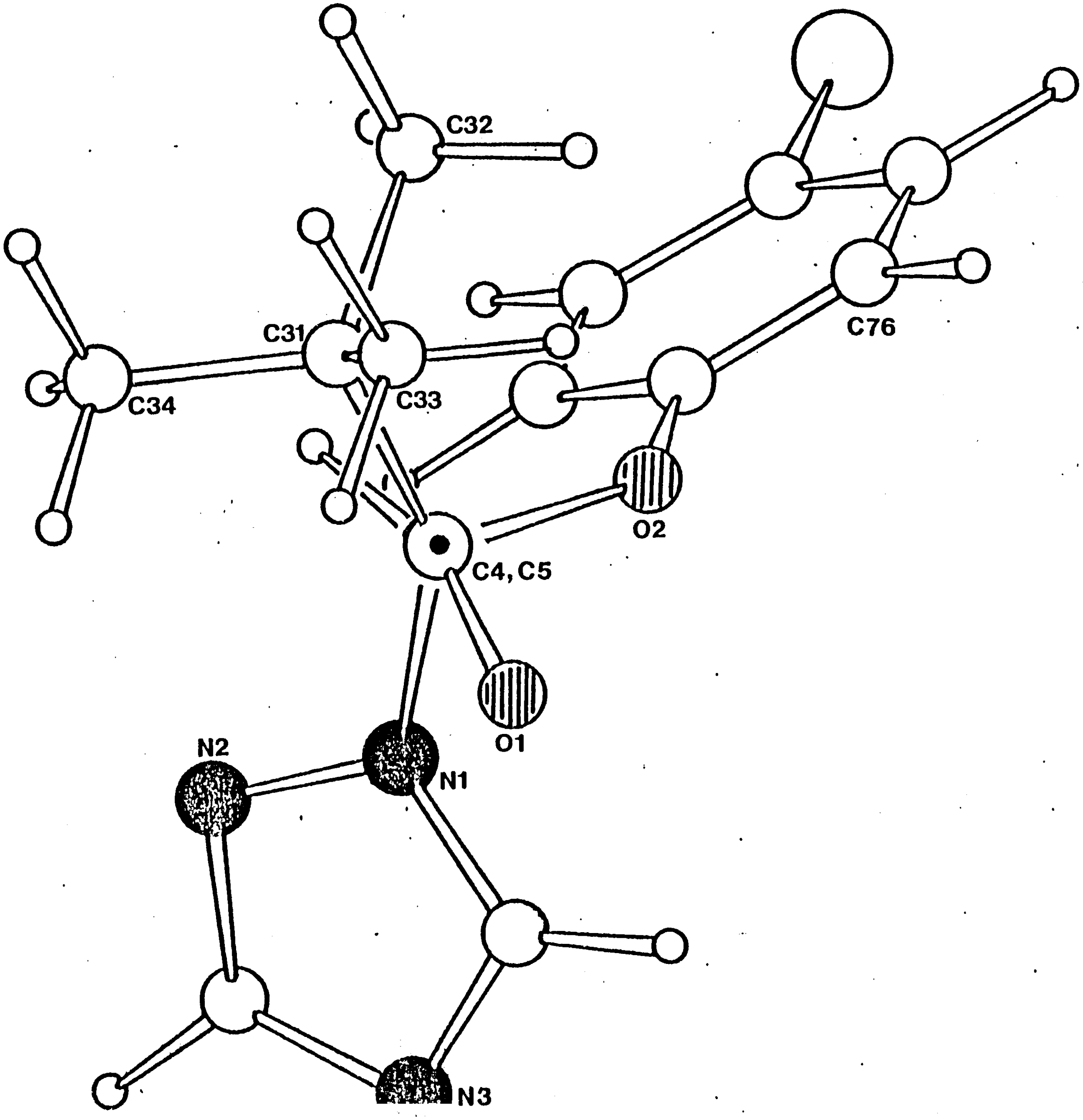


Fig.6e R85827

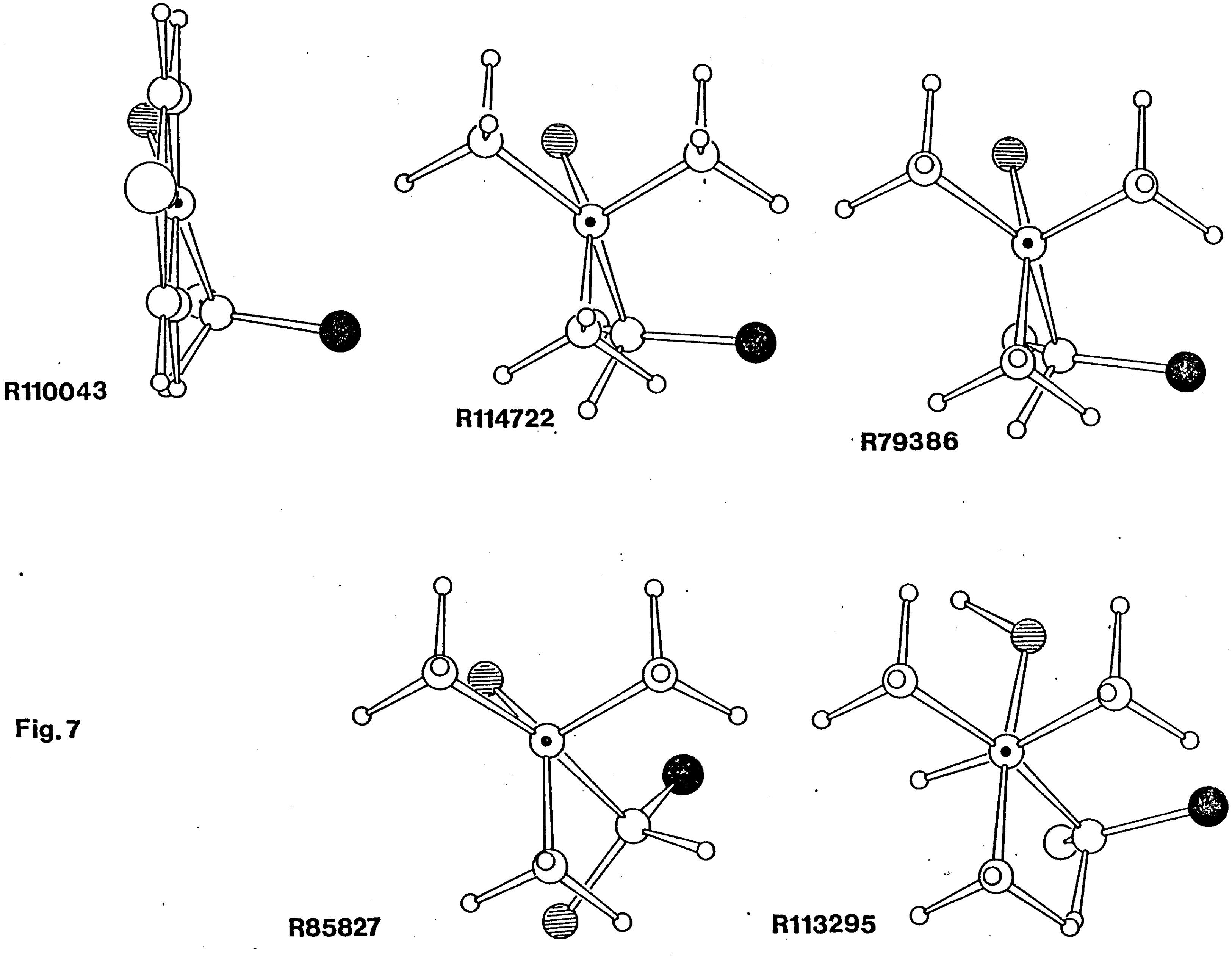


Fig. 7

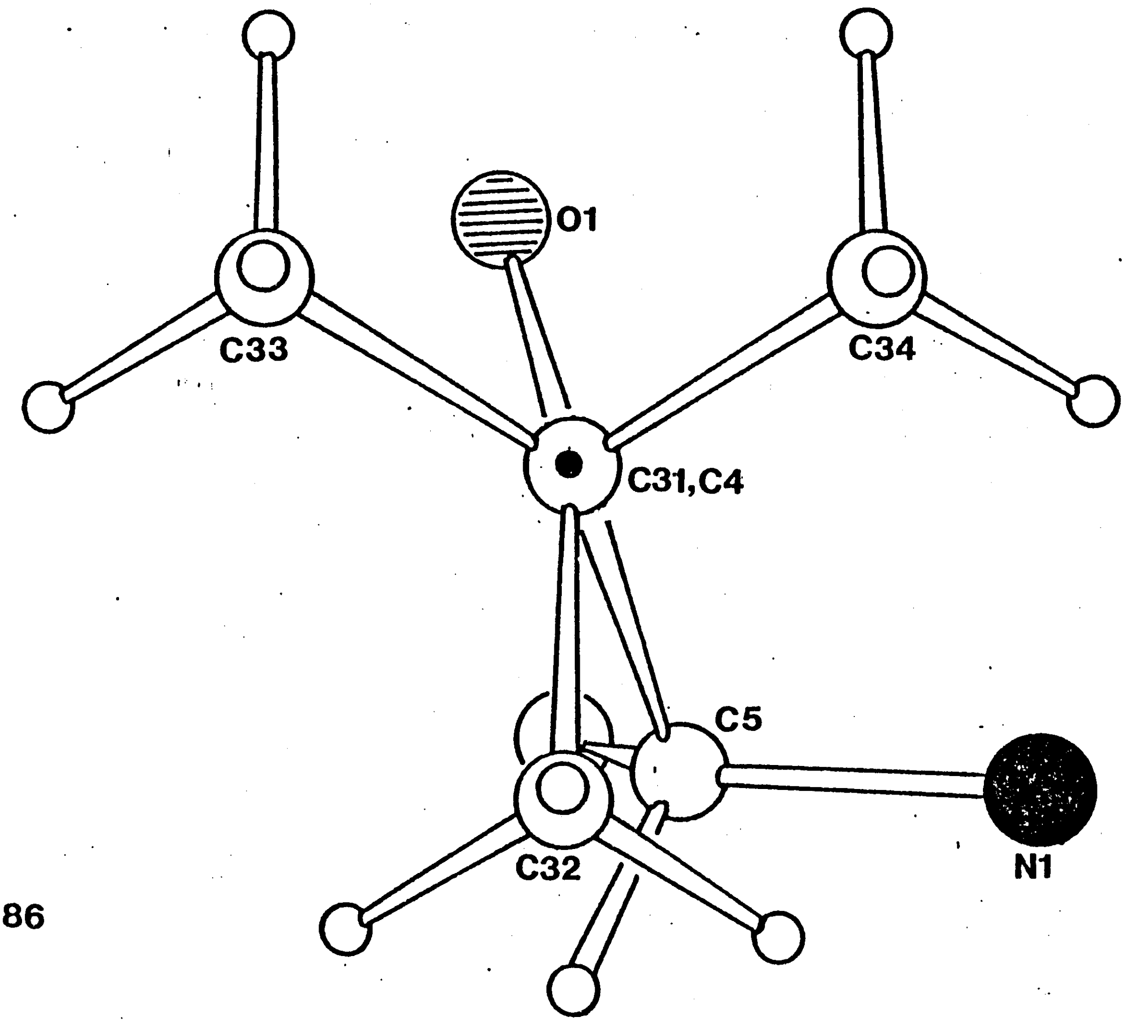


Fig.8a R79386

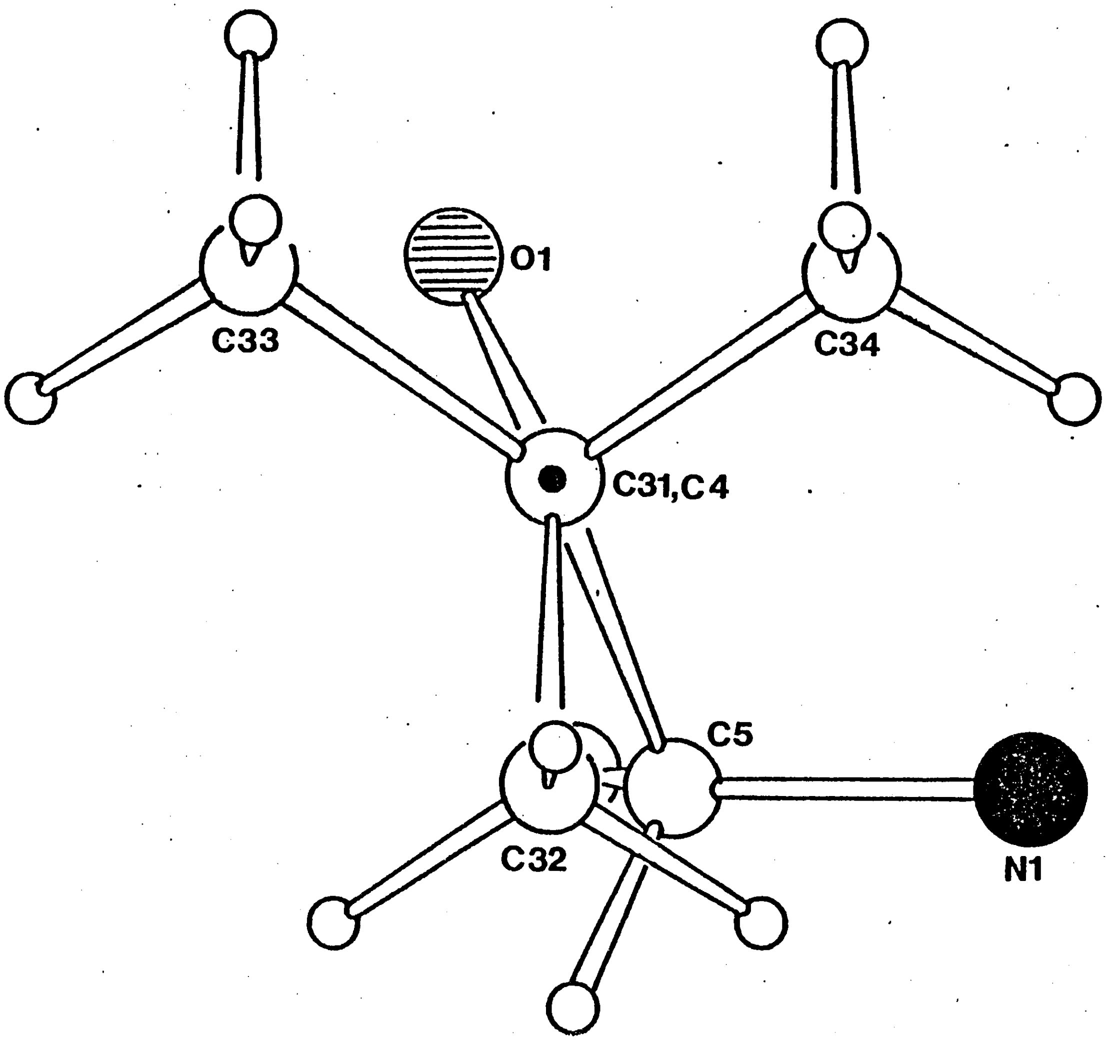


Fig.8b R114722

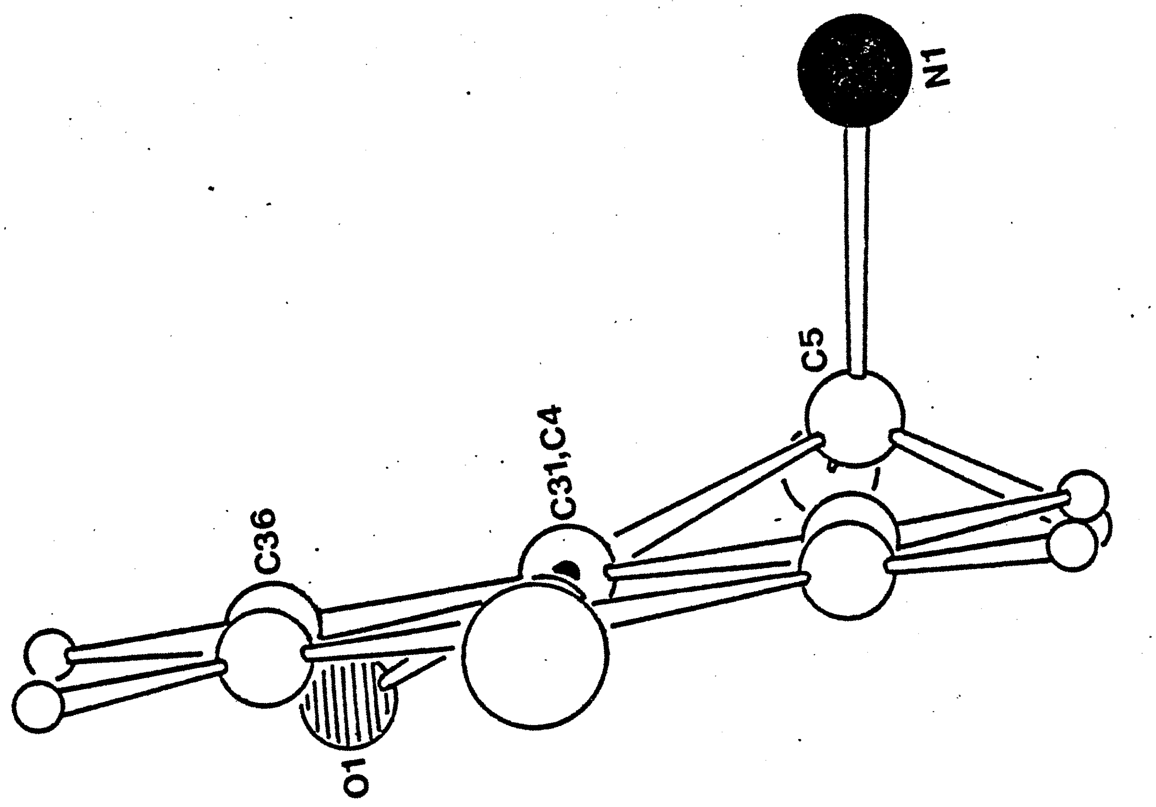


Fig.8c R110043

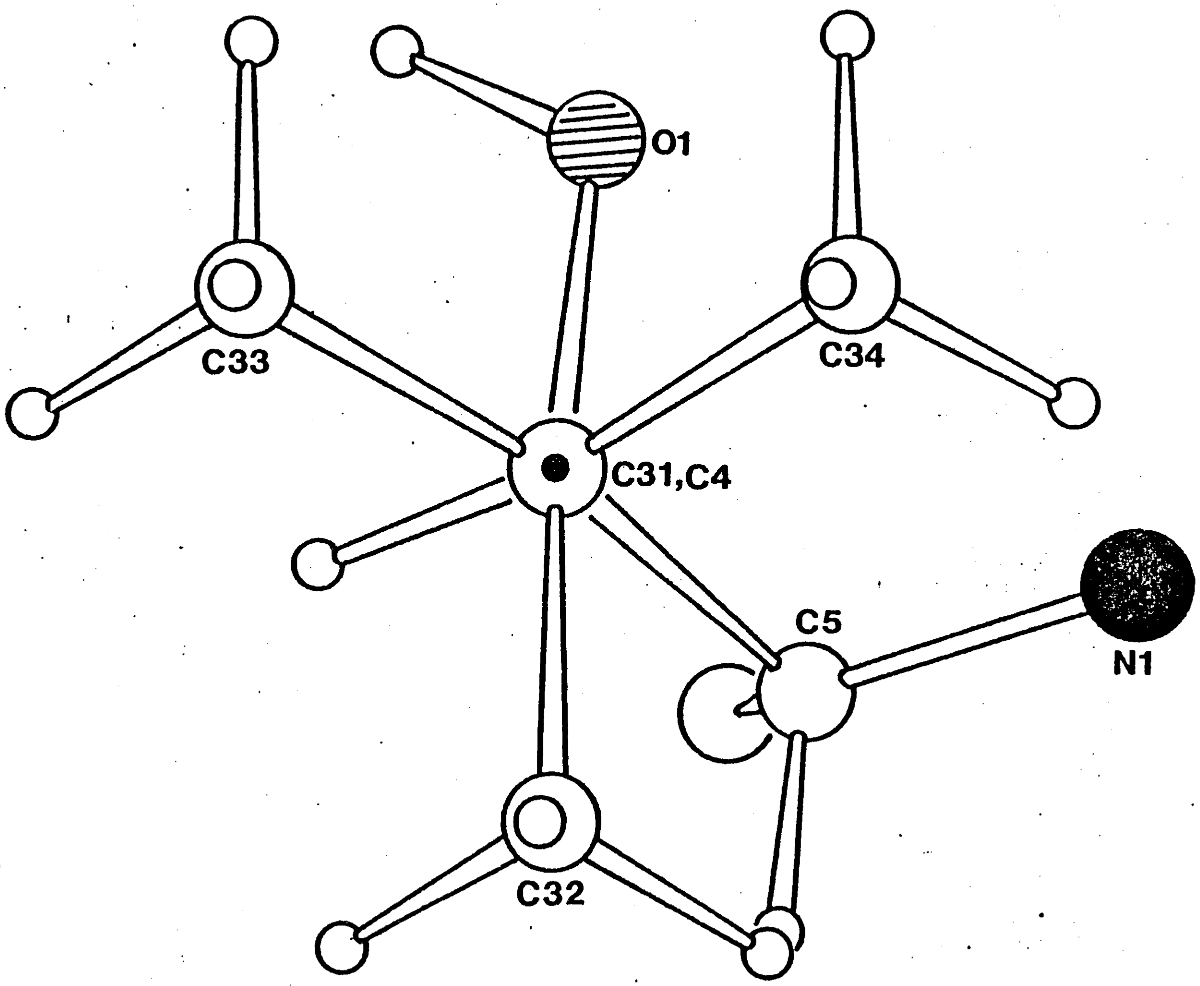


Fig.8d R113295

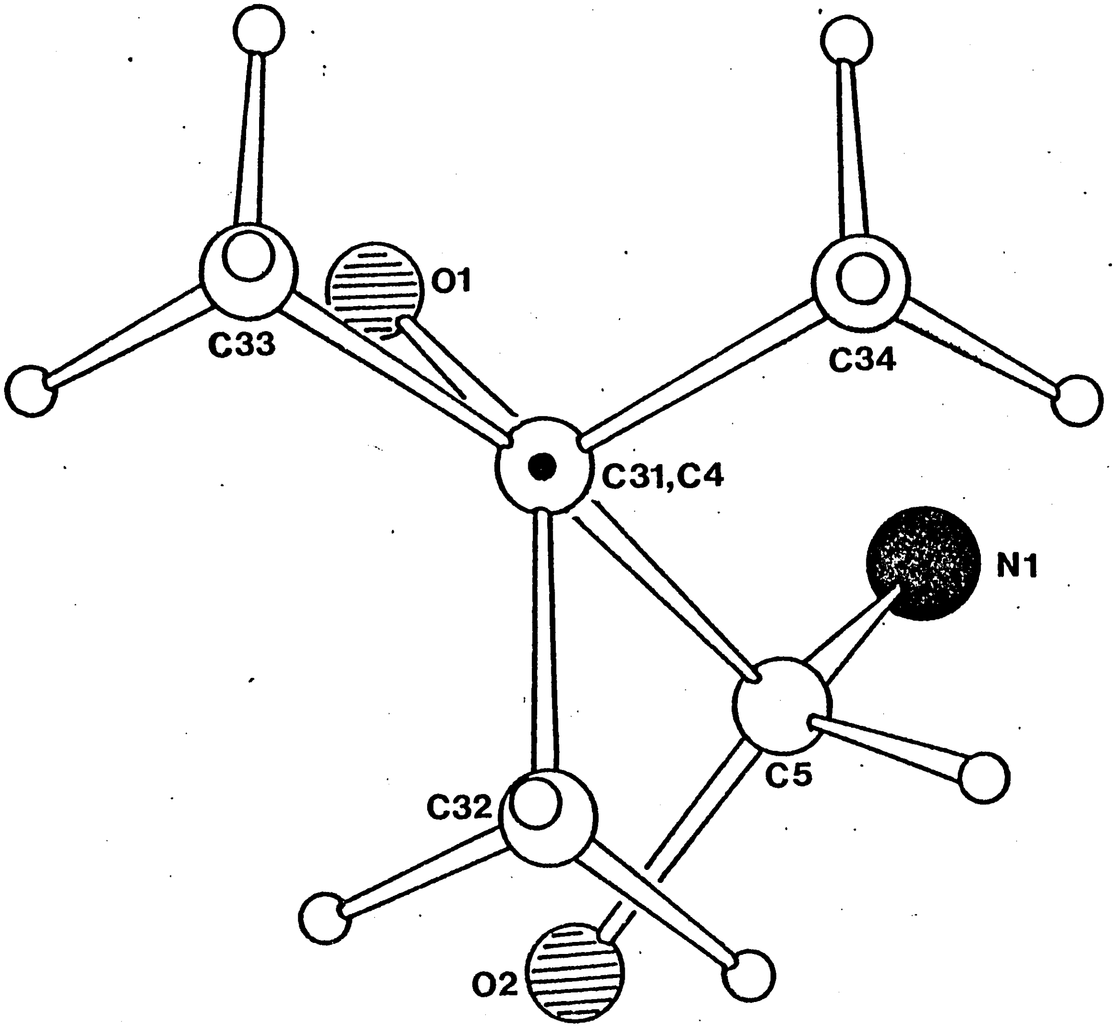
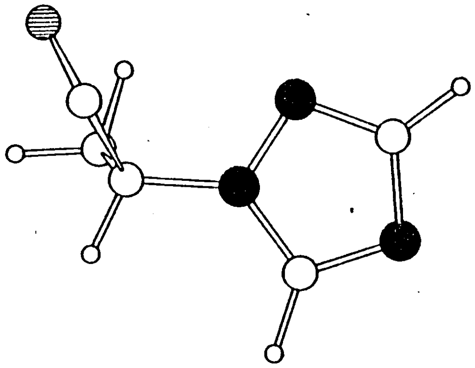
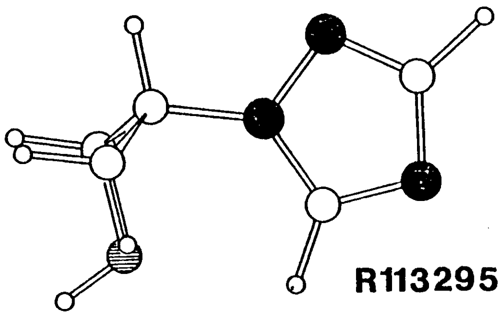


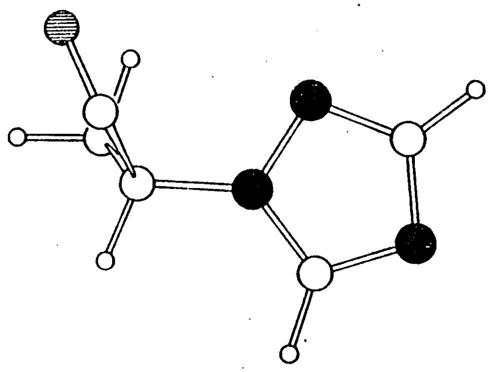
Fig.8e R85827



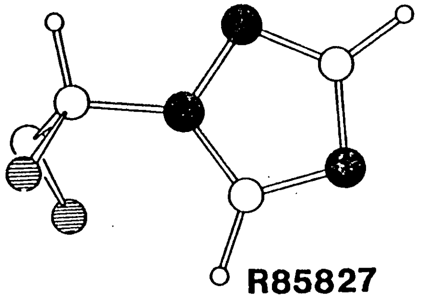
R110043



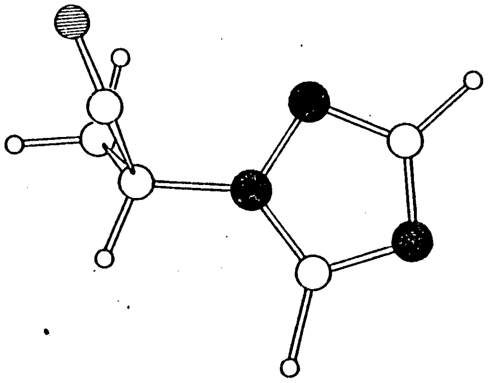
R113295



R79386



R85827



R114722

Fig. 9

Table 2.5.1

Summary of selected bond distances

Distance (Å)	R85827	R114722	R110043	R79386	R113295
N1-N2	1.348(8)	1.371(18)	1.336(11)	1.357(9)	1.355(4)
N1-C1	1.332(10)	1.318(22)	1.334(9)	1.330(11)	1.335(5)
N2-C2	1.311(13)	1.339(20)	1.339(10)	1.341(11)	1.308(6)
C2-N3	1.336(12)	1.293(28)	1.329(13)	1.321(16)	1.344(5)
C1-N3	1.319(11)	1.335(20)	1.320(12)	1.348(12)	1.317(6)
N1-C5	1.449(9)	1.475(14)	1.472(8)	1.482(8)	1.455(5)
C4-C5	1.558(11)	1.536(20)	1.554(6)	1.544(9)	1.528(4)
C4-O1	1.196(8)	1.201(23)	1.210(9)	1.210(9)	1.429(4)*
C31-C33	1.537(12)	1.567(24)	-	1.547(13)	1.536(6)
C31-C32	1.537(10)	1.392(34)	-	1.494(12)	1.538(5)
C31-C34	1.544(10)	1.578(23)	-	1.533(12)	1.532(6)

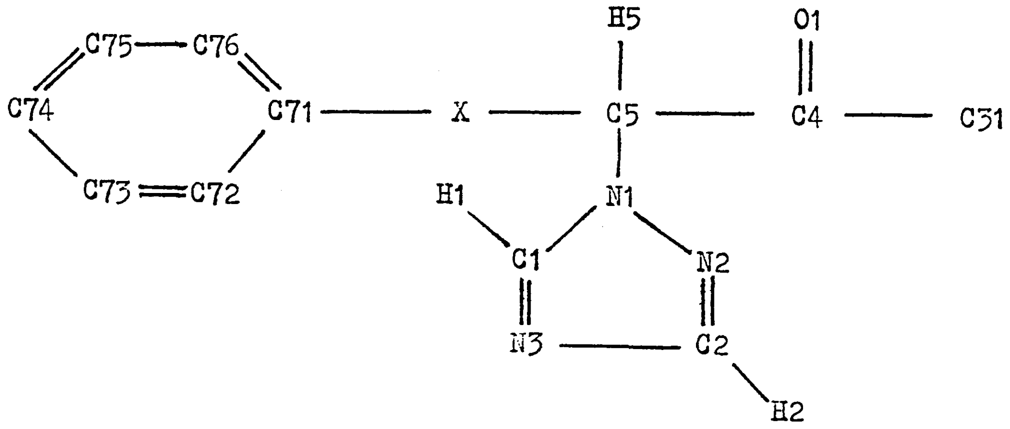
* C - O(H)

Table 2.5.2

Summary of selected bond angles(°)

	R85827	R114722	R110043	R79386	R113295
C5-N1-N2	119.5(6)	119.4(12)	119.6(6)	120.2(6)	120.6(3)
C5-N1-C1	130.7(6)	130.7(14)	129.6(7)	129.3(7)	129.9(3)
C1-N1-N2	109.7(6)	109.9(11)	110.0(6)	110.4(6)	109.4(3)
N1-N2-C2	101.6(6)	100.7(13)	102.5(7)	101.6(7)	102.0(3)
N2-C2-N3	116.3(8)	115.8(15)	113.9(9)	115.4(8)	115.8(4)
C2-N3-C1	101.8(7)	104.0(15)	103.8(7)	103.1(8)	102.3(4)
N1-C1-N3	110.5(7)	109.4(17)	109.7(9)	109.4(8)	110.4(3)
N1-C5-C4	111.3(5)	106.7(9)	107.3(5)	111.0(6)	112.6(2)
N1-C5-X	110.7(6)	110.2(8)	111.2(6)	110.3(5)	110.4(3)
C4-C5-X	102.3(5)	110.3(12)	111.8(6)	109.5(1)	110.1(3)
C5-C4-O1	119.6(7)	118.7(12)	118.7(6)	118.9(5)	108.9(3)
C5-C4-C31	116.4(6)	121.2(16)	118.9(6)	121.2(6)	117.0(3)
O1-C4-C31	124.0(7)	120.0(14)	122.5(4)	119.9(6)	110.3(2)
C5-X-C71	117.4(5)	111.1(12)	113.4(6)	112.3(6)	112.4(3)
X-C71-C72	124.2(7)	121.6(11)	121.7(8)	121.3(6)	121.1(4)
X-C71-C76	114.7(6)	120.5(15)	121.9(7)	119.4(7)	122.7(3)
C72-C71-C76	121.1(7)	117.7(12)	116.2(6)	119.3(7)	116.1(3)
C71-C72-C73	119.5(8)	123.8(11)	124.4(10)	121.2(7)	124.6(4)
C72-C73-C74	118.7(8)	115.8(15)	116.9(10)	117.9(8)	117.5(4)
C73-C74-C75	121.8(8)	121.3(13)	120.5(7)	122.3(8)	120.5(4)
C74-C75-C76	119.3(8)	120.6(13)	120.6(11)	120.1(8)	119.8(5)
C75-C76-C71	119.5(7)	120.7(15)	121.3(10)	119.1(8)	121.5(4)
F -C72-C71	-	120.5(10)	118.9(6)	-	117.8(3)
F -C72-C73	-	115.6(13)	116.6(10)	-	117.6(4)
F -C76-C71	-	123.0(20)	111.4(14)	-	-
F -C76-C75	-	116.2(19)	126.3(17)	-	-
Cl -C74-C73	118.5(7)	117.6(14)	-	-	-
Cl -C74-C75	119.6(7)	121.1(10)	-	-	-
C4 -C31-C33	109.7(6)	106.9(13)	-	107.7(6)	-
C4 -C31-C32	110.4(7)	114.0(14)	-	112.7(6)	109.8(3)
C4 -C31-C34	105.9(6)	106.3(13)	-	106.5(6)	112.6(3)
C33-C31-C32	111.4(6)	110.9(17)	-	109.0(7)	
C34-C31-C33	109.1(7)	106.2(14)	-	109.1(7)	
C34-C31-C32	110.2(6)	112.0(18)	-	111.7(7)	

Table 2.5.3 Summary of angles between mean planes



X = O2, R85827; X = C6, R79386, R110043

Plane A: N1,N2,N3,C1,C2

Plane B: C71 → C76

Plane C: C4,C5,O1,C31

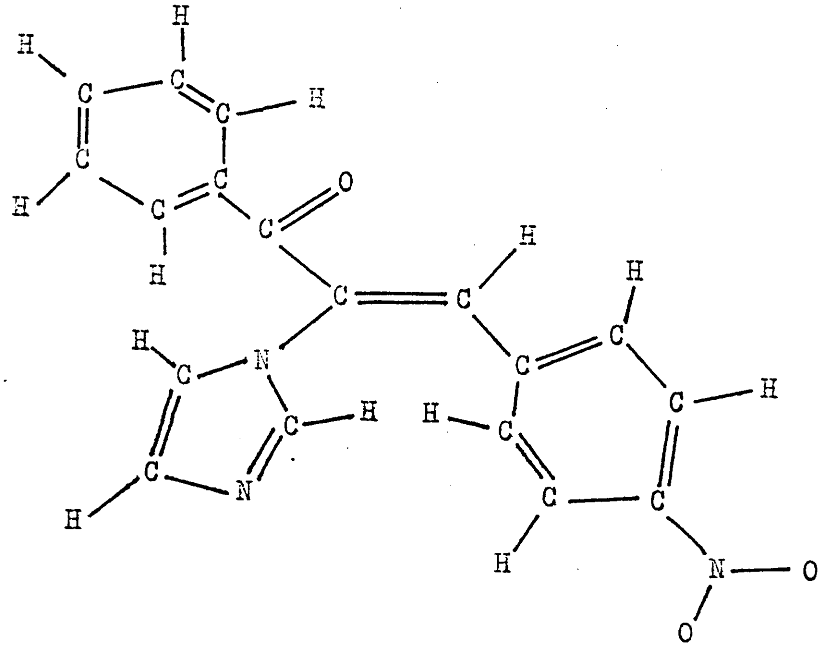
Angle ($^{\circ}$) between planes		R85827	R79386	R110043
A	B	54.1	43.1	42.9
A	C	82.6	89.2	89.4
B	C	57.4	73.1	73.1

Table 2.5.4 Summary of selected torsion angles (in degrees) with estimated standard deviations in parentheses

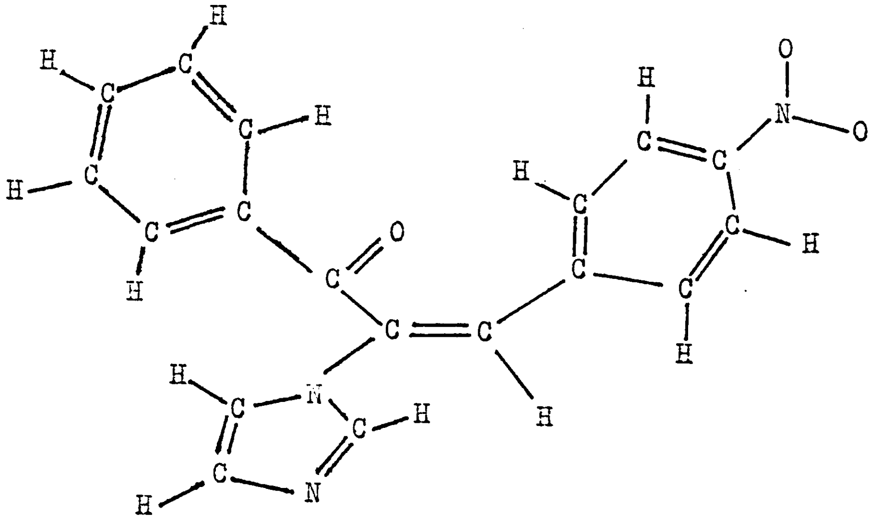
Torsion angle	R85827	R79386	R110043	R114722	R113295
N2-N1-C5-X	-136.4(7)	65.9(7)	70.9(8)	68	-120.8(3)
N2-N1-C5-C4	110.6(7)	-53.6(7)	-51.7(8)	-50	115
O1-C4-C5-N1	37.3(9)	100.6(7)	116.4(7)	108	58.7(4)
O1-C4-C5-X	-80.9(8)	-19.4(8)	-5.8(9)	-11	-65
C31-C4-C5-N1	-141.6(6)	-76.2(7)	-64.8(7)	-73	-67.3(4)
C31-C4-C5-X	100.1(7)	163.8(6)	173.0(6)	165	69.1(3)
C71-X-C5-N1	86.0(7)	57.9(7)	52.7(8)	-	59.8(4)
C71-X-C5-C4	-155.4(6)	176.3(5)	172.7(6)	-	-
C72-C71-X-C5	-17.6(10)	76.9(8)	80.2(9)	-	78.0(4)
C5-C4-C31-C32	-44.8(8)	-20.5(9)	-	-23	-49.1(4)
C5-C4-C31-C33	-167.8(6)	-140.7(7)	-	-145	-170
C5-C4-C31-C34	74.6(8)	102.3(7)	-	102	73
O1-C4-C31-C32	136.3(8)	162.7(7)	-	155	-174
O1-C4-C31-C33	13.3(10)	42.5(9)	-	30	72
O1-C4-C31-C34	-104.3(8)	-74.5(8)	-	-81	-51

Where estimated errors are not shown, the values were calculated from best available data and may be assumed to have estimated errors of the same order as shown for other angles for that structure. Errors for R114722 are of the order of 1°.

2.6 The Crystal and Molecular Structures of the E- and Z-isomers of 3- (4-nitrophenyl) -1-phenyl-2- (imidazol-1-yl) -prop-2-en -1-one



Z-isomer



E - isomer

2.6.1 Crystal data:

$C_{18}H_{13}N_3O_3$ M_r = 319.33 monoclinic

	Z -isomer	E-isomer
a/Å	9.822(8)	11.921(10)
b/Å	13.378(11)	14.154(12)
c/Å	12.095(10)	18.726(15)
β/°	94.26(5)	97.05(5)

$D_m/\mathrm{Mg.m^{-3}}$	1.36	1.36
$D_c/\mathrm{Mg.m^{-3}}$	1.34	1.35
Z	4	8 (two independent molecules)
F(000)	664	1328
$\mu(\mathrm{M_o}\text{-}K_\alpha)/\mathrm{cm^{-1}}$	0.56	0.37

systematic absences for both isomers:

0k0, k = 2n + 1; h0l, l = 2n + 1; uniquely define both isomers as belonging to the space group $P2_1/c$.

2.6.2 Data Collection and Analysis

For the E -isomer, a transparent crystal, approximate dimensions 0.40 x 0.30 x 0.24 mm, was mounted about the a axis. Thirteen layers, 0kl → 12kl, were collected and 3379 independent reflections were recorded of which 1866 having $I/\sigma(I) \geqslant 2.5$ were used for structure analysis.

For the Z -isomer, a transparent crystal, approximate dimensions 0.42 x 0.26 x 0.16 mm, was mounted about the b axis. Fifteen layers, h0l → h14l, were collected and 2386 independent reflections were recorded of which 1487 having $I/\sigma(I) \geqslant 2.5$ were used for structure analysis.

Corrections for Lorentz and polarisation factors were applied. For both structures, reflections having $E \geqslant 1.2$ were used for direct methods analysis. All non-hydrogen atoms were located; hydrogen atoms were located from successive difference Fourier syntheses. Refinement was by full-matrix least squares techniques with hydrogen atoms placed in positions calculated from the geometry of the molecule (C-H = 1.08Å). The non-hydrogen atoms were given anisotropic temperature factors and the hydrogen atoms were given common isotropic temperature factors of 0.0971 for the E -isomer and of 0.0988 for the Z -isomer. A weighting scheme of $w = 1.000/[\sigma^2(F_o) + 0.005492(F_o)^2]$ for the E -isomer gave final values of R = 0.056 and Rw = 0.065, with the highest residue peak from a Fourier synthesis of 0.31 $e\text{Å}^{-3}$. For the Z-isomer, a weighting scheme of $w = 1.1596/[\sigma^2(F_o) + 0.004455(F_o)^2]$ gave final values of a Fourier synthesis of 0.37 eÅ^{-}. Bond distances and angles are given in Tables 2.6.1 - 2.6.4; molecular and crystal structures are shown in Figs. 2.6.1 - 2.6.6; final positional and thermal parameters, torsion angles, mean plane data and structure factors are contained in Appendices A1.4, A1.5, A2.4, A2.5, A3.4, A3.5, A4.4, A4.5.

2.6.3 Discussion of structures:

The two asymmetric molecules for the E -isomer are almost identical and hence discussion will be confined to molecule 1, except where significant differences arise. Each of the three ring systems for both the E- and Z-isomers are effectively planar (Appendix A2.4 and A2.5). Although the conformations adopted (especially in the Z -isomer) suggested the possibility of conjugation involving the carbonyl group and the unsaturated C7-C8 bond, no evidence for this was observed in the bond distances. Indeed, all the relevant bond distances were found to be almost identical to idealised values. As with the triazole ring, the imidazole ring shows evidence of delocalisation (e.g. C10-C11 is close in length to the idealised value for a benzene ring) though the C9-N2 length is consistently shorter than the other C-N distances (Tables 2.6.1 and 2.6.2).

The principal feature of the structures is the relative orientation of the three rings to the ethylenic grouping. In the E -isomer, there may well be steric interactions between the nitrophenyl ring and the carbonyl group which is relieved by the adoption of large values for the bond angles C7-C8-C12 (128°) and C4-C7-C8 (128°) and a particularly small C12-C8-N1 angle of 113°. With the Z -isomer, similar interactions appear to be present between the nitro phenyl ring and the imidazole ring resulting in a large value for the C4-C7-C8 angle (128°) and a small value for the C12-C8-N1 angle of only 114°. The orientation of the rings to achieve favourable steric positions is further reflected in the dihedral angles between the rings (Appendix A2.4 and A2.5) and in the values of the torsion angles. This is well illustrated by the orientation adopted by the imidazole ring with respect to the ethylene grouping. Thus, while in the E -isomer, the C9-N1-C8-C7 torison angle is -41°, in the Z -isomer the analogous angle is 63.5°.

The asymmetry of the exocyclic angles about N1 found for the triazole structures studied is not found in the present imidazole rings. This further strengthens the contention that this feature is a function of the triazole ring itself.

The nitro-group tends to be orientated slightly out of the plane of the attached phenyl ring /the dihedral angle between the phenyl and nitro planes is 1.2° and 11.4° (E -isomer) and 12.5° (Z -isomer)/.

No significant intermolecular interactions were found for either isomer.

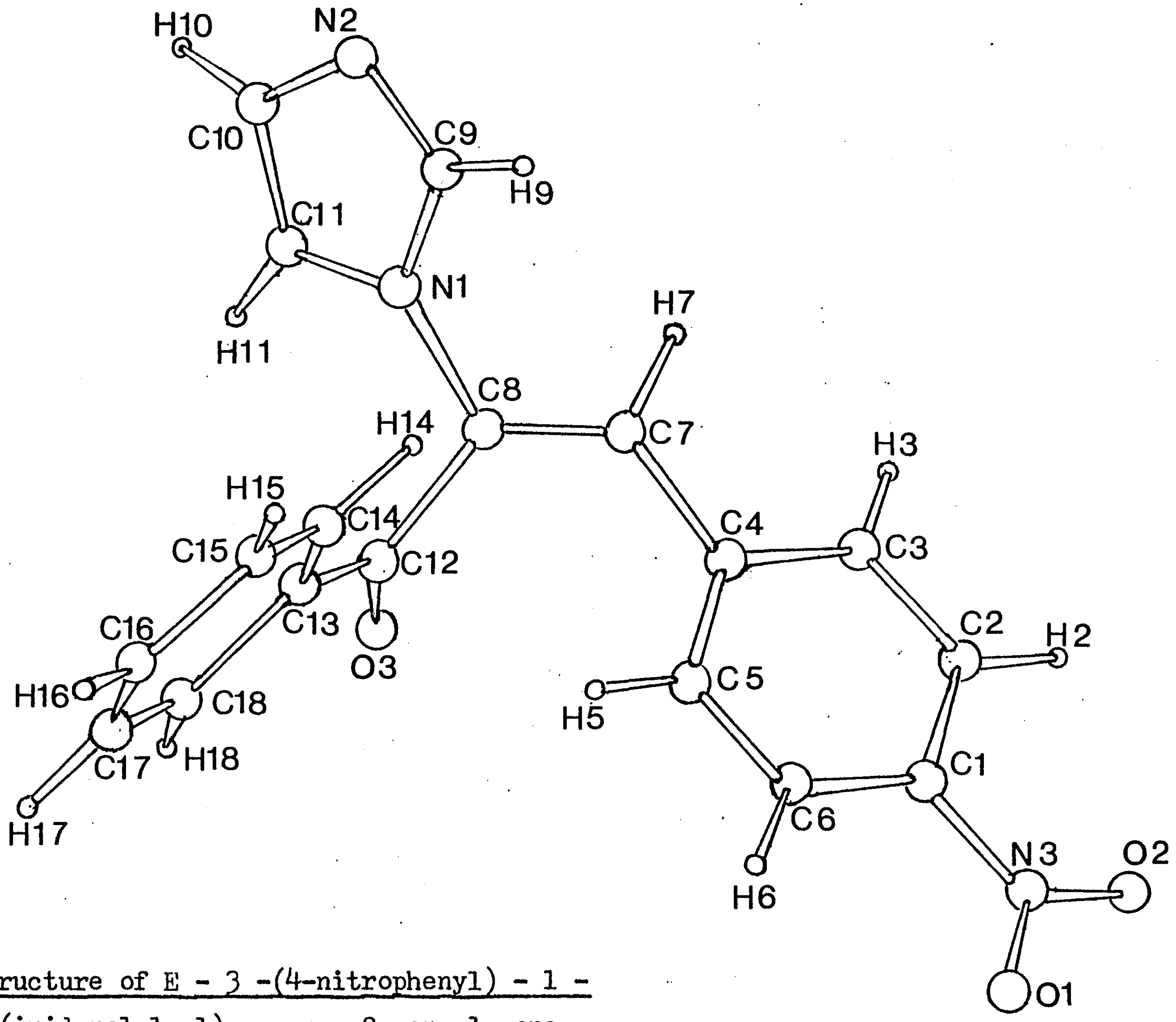


Fig.2.6.1.

Molecular structure of E - 3 -(4-nitrophenyl) - 1 - phenyl - 2 -(imidazol-1-yl) - prop -2 -en -1 -one.

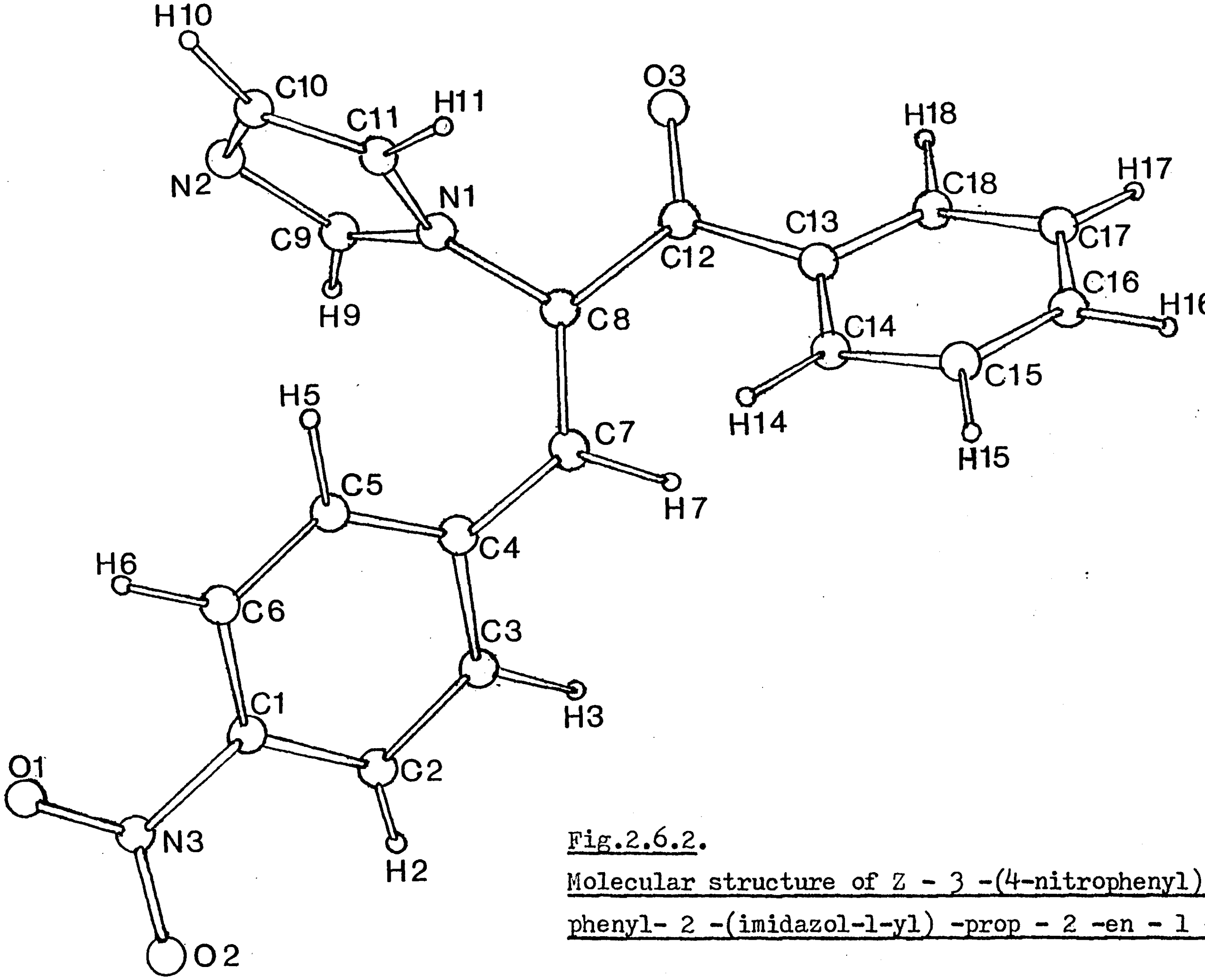


Fig.2.6.2.

Molecular structure of Z - 3 -(4-nitrophenyl) - 1 - phenyl- 2 -(imidazol-1-yl) -prop - 2 -en - 1 -one.

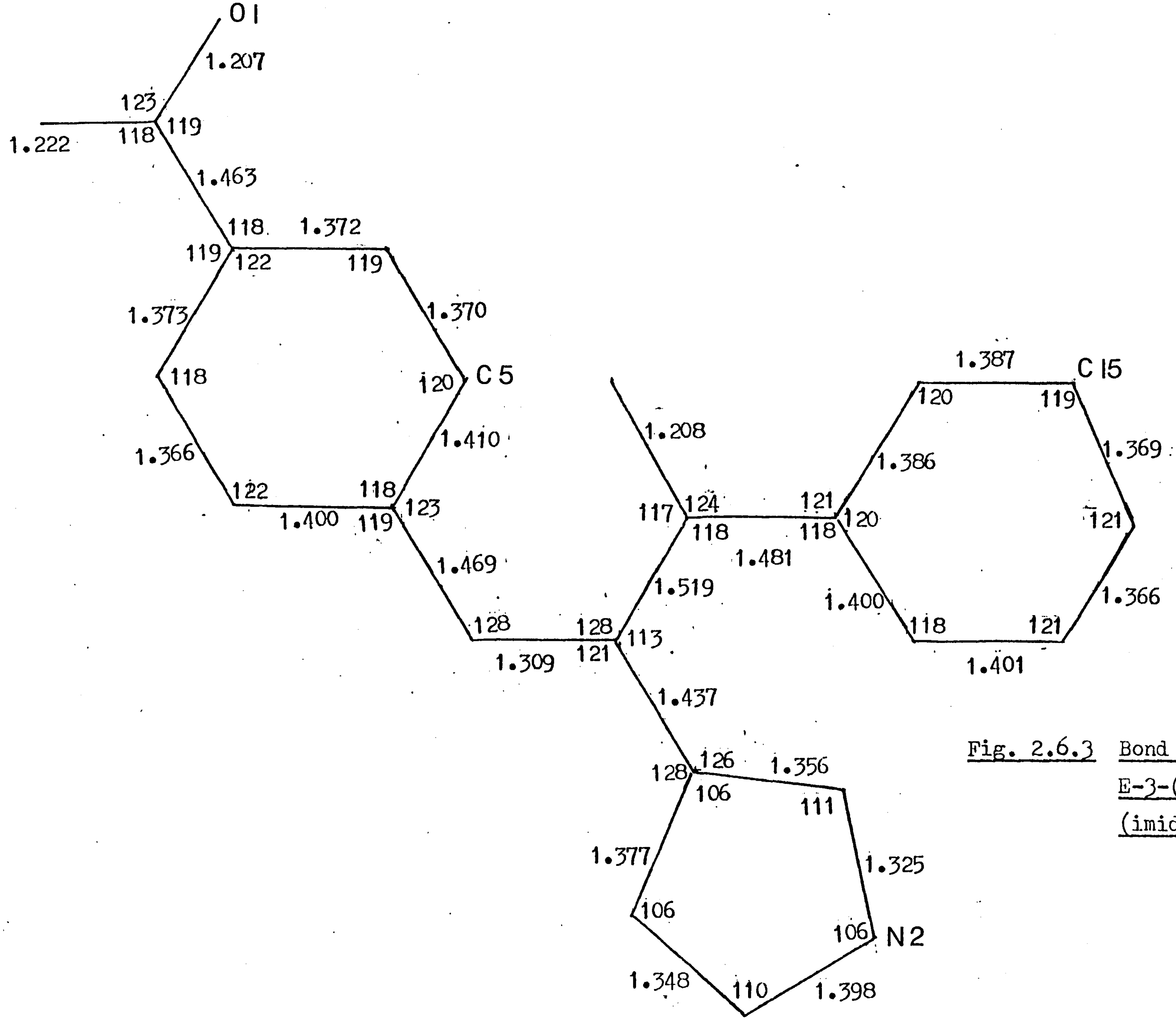


Fig. 2.6.3 Bond lengths and angles for E-3-(4-nitrophenyl)-1-phenyl- (imidazol-1-yl)-prop-2-en-1-o

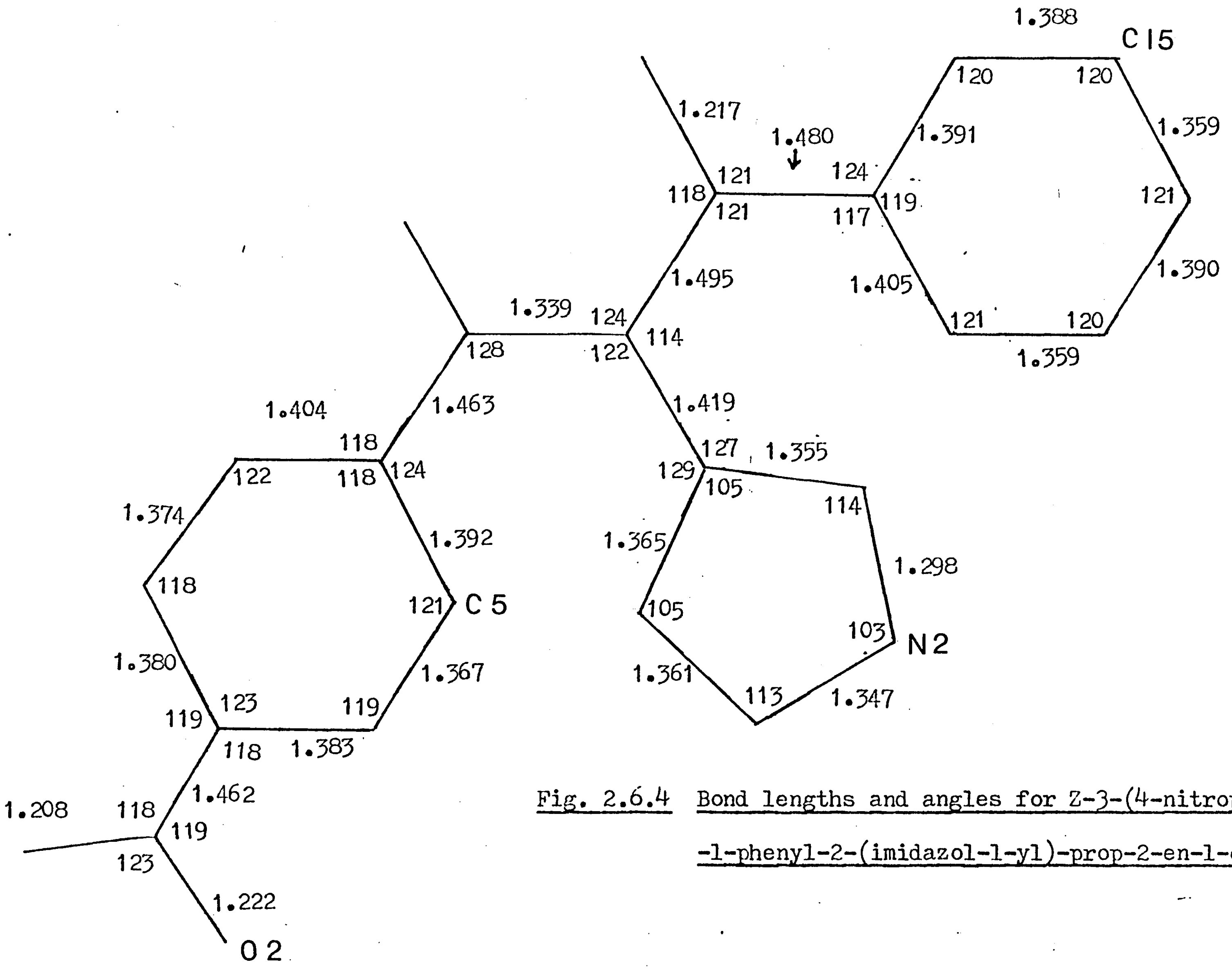


Fig. 2.6.4 Bond lengths and angles for Z-3-(4-nitrophenyl) -1-phenyl-2-(imidazol-1-yl)-prop-2-en-1-one.

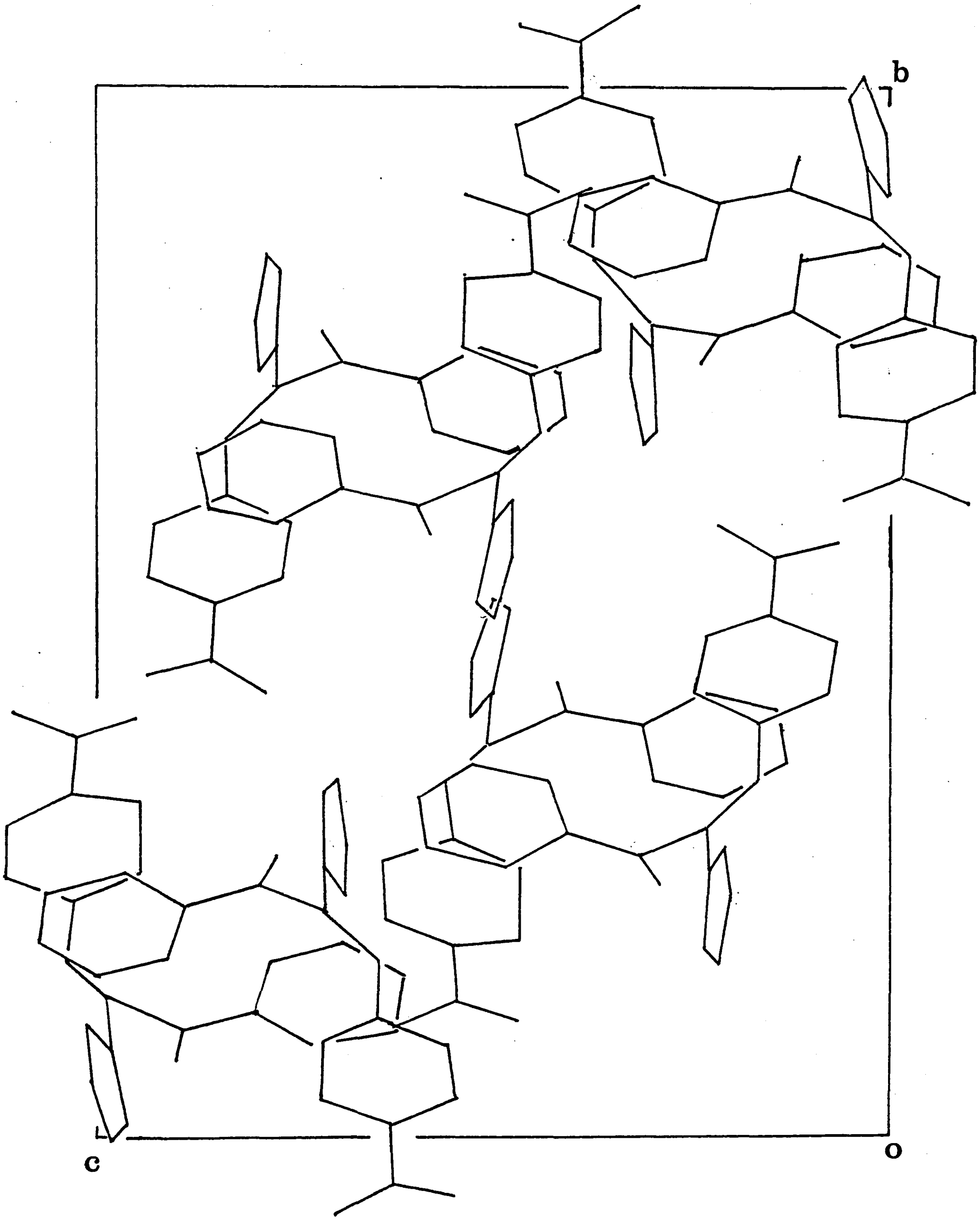


Fig.2.6.5 Crystal structure for E-3-(4-nitrophenyl)-1-phenyl-2-(imidazol-1-yl)-prop-2-en-1-one.

Projection down the a axis.

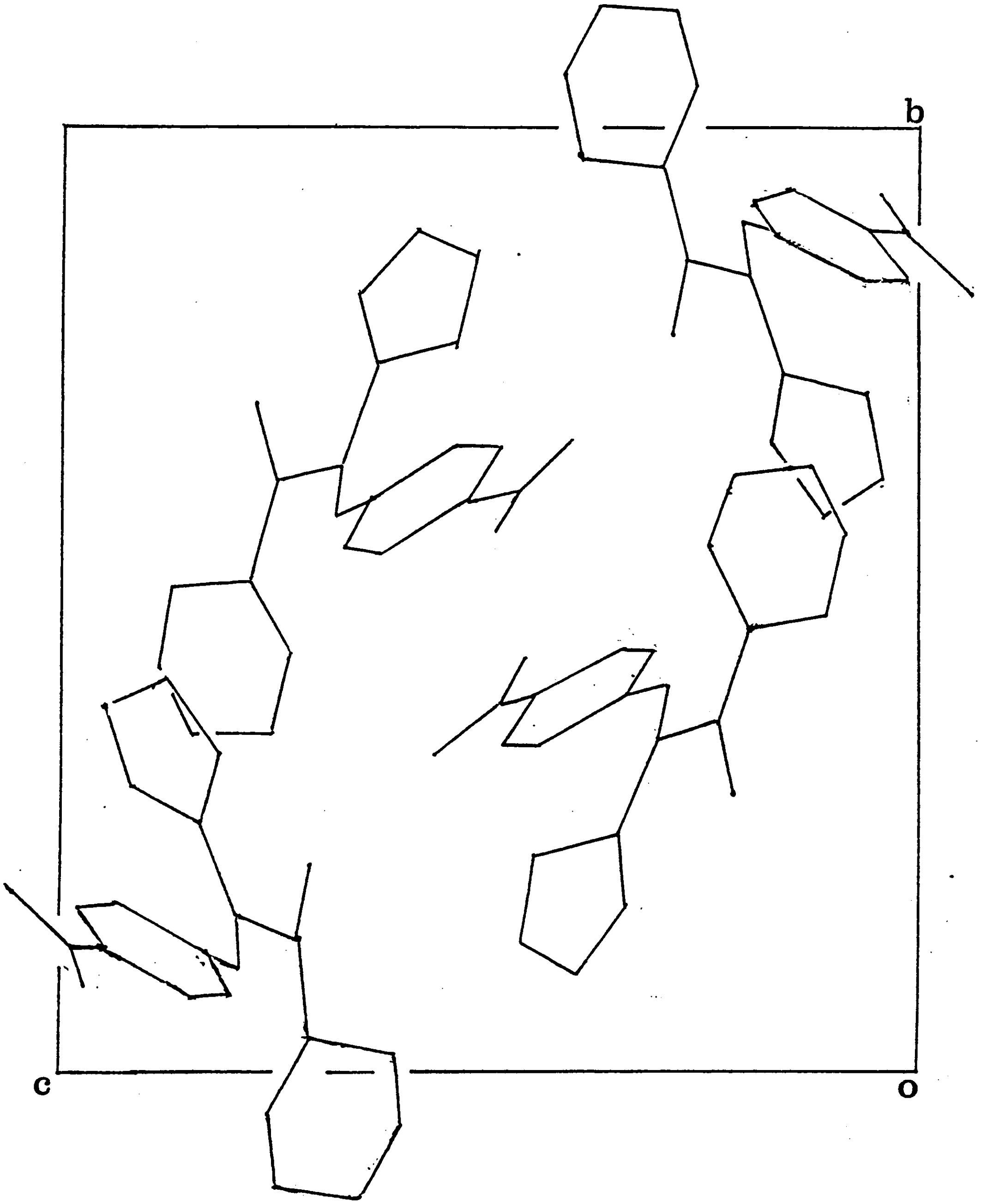


Fig.2.6.6 Crystal structure for Z-3-(4-nitrophenyl)-1-phenyl-2-(imidazol-1-yl)-prop-2-en-1-one.

Projection down the a axis.

Table 2.6.1 Bond lengths, with estimated standard deviation of error in parentheses, for Z-3-(4-nitrophenyl)-1-phenyl-2-(imidazol-1-yl)-prop-2-en -1-one

Distances in Å

N3 - O1 = 1.208(6)
N3 - O2 = 1.222(6)
N3 - C1 = 1.462(6)
C1 - C2 = 1.380(6)
C2 - C3 = 1.374(6)
C3 - C4 = 1.404(6)
C4 - C5 = 1.392(6)
C5 - C6 = 1.367(6)
C1 - C6 = 1.383(6)
C4 - C7 = 1.463(6)
C7 - C8 = 1.339(6)
C8 - C12 = 1.495(6)
C12 - O3 = 1.217(6)
C12 - C13 = 1.480(7)
C14 - C13 = 1.391(7)
C14 - C15 = 1.388(8)
C15 - C16 = 1.359(10)
C16 - C17 = 1.390(10)
C17 - C18 = 1.359(9)
C18 - C13 = 1.405(7)
C8 - N1 = 1.419(6)
N1 - C9 = 1.355(7)
C9 - N2 = 1.298(7)
N2 - C10 = 1.347(8)
C10 - C11 = 1.361(9)
N1 - C11 = 1.365(6)

Table 2.6.2 Bond angles, with estimated standard deviation of error in parentheses, for Z-3-(4-nitrophenyl)-1-phenyl-2-(imidazol-1-yl)-prop-2-en -1-one

Bond angles in degrees

O1 - N3 - O2 = 122.9(4)
O1 - N3 - C1 = 118.4(4)
O2 - N3 - C1 = 118.7(4)
N3 - C1 - C6 = 118.2(4)
N3 - C1 - C2 = 119.3(4)
C1 - C2 - C3 = 117.8(4)
C2 - C3 - C4 = 121.6(4)
C3 - C4 - C5 = 118.0(4)
C4 - C5 - C6 = 121.4(4)
C5 - C6 - C1 = 118.5(4)
C6 - C1 - C2 = 122.6(4)
C3 - C4 - C7 = 118.3(4)
C5 - C4 - C7 = 123.6(4)
C4 - C7 - C8 = 128.2(4)
C7 - C8 - C12 = 123.8(4)
C7 - C8 - N1 = 122.0(4)
C8 - C12 - O3 = 118.0(4)
C13 - C12 - O3 = 120.9(4)

C8 - C12 - C13 = 121.0(4)
C12 - C13 - C14 = 123.5(4)
C12 - C13 - C18 = 117.3(4)
C14 - C15 - C16 = 119.9(6)
C15 - C16 - C17 = 120.9(6)
C16 - C17 - C18 = 119.8(6)
C17 - C18 - C13 = 120.5(5)
C18 - C13 - C14 = 118.7(4)
C13 - C14 - C15 = 120.1(5)
C8 - N1 - C11 = 127.8(4)
C8 - N1 - C9 = 126.8(4)
C12 - C8 - N1 = 113.8(4)
N1 - C9 - N2 = 114.3(5)
C9 - N2 - C10 = 103.0(5)
N2 - C10 - C11 = 112.6(5)
C10 - C11 - N1 = 104.8(5)
C11 - N1 - C9 = 105.3(4)

Table 2.6.3 Bond lengths, with estimated standard deviation of error in parentheses, for E-3-(4-nitrophenyl)-1-phenyl-2-(imidazol-1-yl)-prop-2-en-1-one

Distances in Å

	Molecule 1	Molecule 2
N3 - O2	1.222(14)	1.219(11)
N3 - O1	1.207(13)	1.208(11)
N3 - C1	1.463(12)	1.441(11)
C1 - C2	1.373(12)	1.380(11)
C2 - C3	1.366(13)	1.373(11)
C3 - C4	1.400(12)	1.385(12)
C4 - C5	1.410(11)	1.405(11)
C5 - C6	1.370(12)	1.386(10)
C1 - C6	1.372(13)	1.382(12)
C4 - C7	1.469(12)	1.468(11)
C7 - C8	1.309(10)	1.329(9)
C8 - N1	1.437(11)	1.402(11)
C8 - C12	1.519(10)	1.509(10)
N1 - C9	1.356(12)	1.352(12)
C9 - N2	1.325(12)	1.302(12)
N2 - C10	1.398(12)	1.350(12)
C10 - C11	1.348(12)	1.357(15)
N1 - C11	1.377(9)	1.409(9)
O3 - C12	1.208(10)	1.199(10)
C12 - C13	1.481(10)	1.494(8)
C13 - C14	1.386(10)	1.385(9)
C14 - C15	1.387(11)	1.403(9)
C15 - C16	1.369(11)	1.380(11)
C16 - C17	1.366(14)	1.370(15)
C17 - C18	1.401(12)	1.370(11)
C13 - C18	1.400(10)	1.410(10)

Table 2.8.4 Bond angles, with estimated standard deviations of error in parentheses, for E-3-(4-nitrophenyl)-1-phenyl-2-(imidazol-1-yl)-prop-2-en -1-one

Angles in degrees

	Molecule 1	Molecule 2
O1 - N3 - O2	123.4(9)	122.4(9)
O1 - N3 - C1	119.1(10)	118.9(8)
O2 - N3 - C1	117.5(9)	118.7(7)
N1 - C1 - C2	119.1(8)	119.8(7)
N1 - C1 - C6	118.2(8)	118.0(7)
C1 - C2 - C3	118.0(8)	118.7(7)
C2 - C3 - C4	122.0(8)	121.1(7)
C3 - C4 - C5	117.8(8)	119.0(7)
C4 - C5 - C6	120.3(8)	120.0(7)
C5 - C6 - C1	119.2(8)	119.0(7)
C6 - C1 - C2	122.6(8)	122.1(8)
C3 - C4 - C7	118.8(7)	119.1(7)
C5 - C4 - C7	123.4(7)	121.7(6)
C4 - C7 - C8	128.3(7)	127.9(7)
C7 - C8 - N1	119.7(7)	121.7(7)
C7 - C8 - C12	128.0(8)	124.5(7)
N1 - C8 - C12	112.3(6)	113.7(6)
C8 - N1 - C9	125.7(6)	126.0(7)
C8 - N1 - C11	127.6(7)	127.9(6)
N1 - C9 - N2	111.1(7)	111.8(8)
C9 - N2 - C10	106.0(8)	106.6(9)
N2 - C10 - C11	108.6(7)	110.9(8)
C10 - C11 - N1	107.7(8)	104.6(8)
C9 - N1 - C11	106.6(7)	106.1(7)
C8 - C12 - O3	117.1(6)	119.8(6)
C13 - C12 - O3	124.6(6)	122.7(6)
C8 - C12 - C13	118.2(6)	117.6(6)
C12 - C13 - C14	122.4(6)	120.3(6)
C12 - C13 - C18	117.2(6)	119.0(6)
C13 - C14 - C15	120.0(7)	119.9(6)
C14 - C15 - C16	119.0(8)	119.1(8)
C15 - C16 - C17	122.4(8)	120.2(7)
C16 - C17 - C18	119.4(8)	122.4(8)
C17 - C18 - C13	118.7(7)	117.9(8)
C18 - C13 - C14	120.4(6)	120.5(6)

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Chapter 3

Aspects of the Structure and Coordination Chemistry of Macrocyclic Compounds

Contents

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3.1 Aspects of the coordination chemistry of macrocyclic compounds

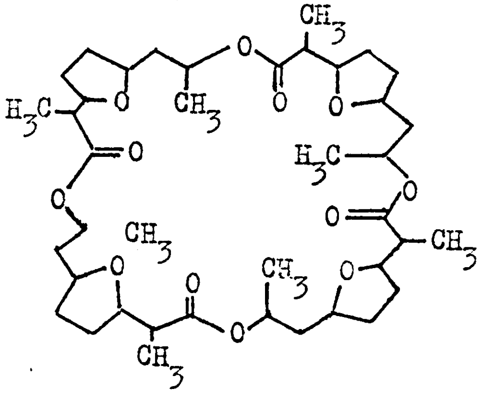
The coordination chemistry of macrocyclic compounds increased rapidly following the gradual realization (ca. 1967) that such compounds behaved as models for certain naturally occurring substances having important biological effects. Several antibiotics were discovered that are capable of selective movement of group IA and IIA ions across cell membranes and are referred to as "ionophores". They all bear certain common features, not always apparent from the structure of the free antibiotic, which gives rise to their ability to transport ions. Each has several oxygen atoms available for potential binding to cations. In bonded form, the antibiotic usually forms a ring conformation, presenting a hydrophobic exterior and masking the ion from the lipid molecules. Hydrogen bonding is a common feature of such metal - antibiotic complexes, helping to hold the complexes in more or less rigid configuration. Selectivity is dependent on several factors of which three are of special structural importance, viz:-

(i) ionic radius of the cation

(ii) preferred coordination number of the ion

(iii) preference for donor atoms.

These features will be discussed below. It is convenient to distinguish two classes of ionophoric antibiotics, viz:- neutral (e.g. valinomycin, enniatins and nonactin) and antibiotics with one or more carboxylic acid groups (e.g. monensic acid and nigericin).



1.

Valinomycin (1), a cyclic dodecadepsipeptide containing D-valine, D-hydroxyvaleric acid, L-valine, L-lactic acid groups repeated three times in sequence, is a well studied neutral antibiotic [1,2,3,4,5,6]. In solution, three major possible configurations are known (and other states have been revealed by ultrasonic techniques); schematically, the equilibrium between the states may be represented as in Fig 3.1.1.

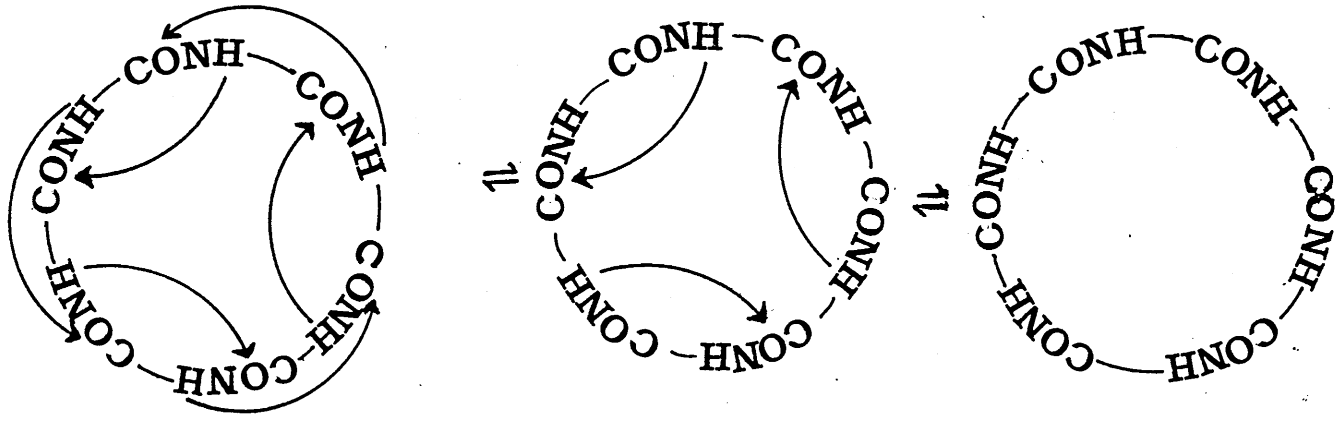


Fig 3.1.1

The dominance of any one state is solvent dependent[4]. Even in the solid state, two different (though similar) conformations have been found by single crystal X-ray studies. The differences in conformation are sufficient, however, to give rise to different crystal systems: while one form crystallizes to give a triclinic space group, the other form has a monoclinic space group.

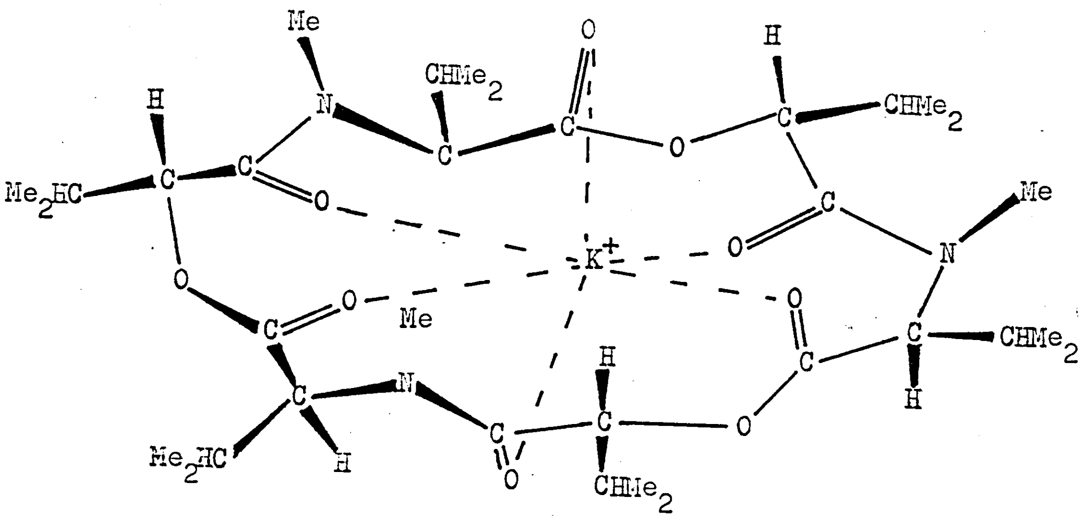
Although valinomycin forms complexes with Na^+, K^+, Rb^+ and Cs^+, interest has been centred on the potassium complex [1,2,3,4,6]. The K^+ ion is coordinated to six carbonyl oxygens of the valine residues, with the valinomycin folding to form a bracelet-like shape about the ion; internal hydrogen bonding stabilises the structure. Although the cavity within the bracelet is large enough to accommodate a hydrated ion, single crystal X-ray analysis has shown the complex to be free of water molecules. The Na^+ complex, in comparison, is less stable. The smaller Na^+ ion is unable to interact with the six carbonyl oxygens simultaneously.

This has been confirmed by Ovchinnikov and Ivanov[2,4] who showed the non-equivalence of the carbonyl oxygen atoms from infra red spectra. Clearly, the high degree of selectivity of valinomycin for K^+ ions is closely related to the relative ionic radii of the cations but it is noticeable, however, that selectivity is also dependent upon the anion present. Thus, potassium picrate is transported across membranes in preference to potassium aurichloride. It therefore appears that an anion-cation pair is transported. The mechanism for complex formation is believed to be by stepwise loss of hydration of the cation followed by bonding to the carbonyl oxygens[4].

The mode of transport across the cell membrane has not yet been conclusively elucidated, though two possible mechanisms have been suggested. The antibiotic could act as a single carrier or the ions could be passed in relay from one molecule to another across the membrane. The latter would require an intermediate state of a 2:1 complex (or 3:2, etc.) of antibiotic : metal ion. Ovchinnikov and Ivanov report evidence of a 2:1 antibiotic : K^+ complex[3]. Such evidence does not support a relay mechanism, however, but only indicates that such a mechanism is possible. A carrier mechanism is supported by Eyal and Redhmitz[7] who carried out studies on selectivity over a range of temperatures. Although a gradual drop in ion transport with drop in temperature to freezing point would be expected, selectivity would be maintained if the "stacking" theory is correct. It was found that the K^+ to Na^+ selectivity from a phenyl ether solution through a liquid membrane of valinomycin-phenyl ether solution at 5°C (at this temperature the membrane was freezing) was in a ratio of ca. 2:1 compared to a ratio of ca. 1000:1 at room temperature. Further, all ion transport was greatly reduced. This strongly suggests a carrier mechanism with the complex losing most of its mobility in the frozen membrane. Similar and confirmatory results were found by

Ciani, Eisenmann and Szabo[8] working with the actins.

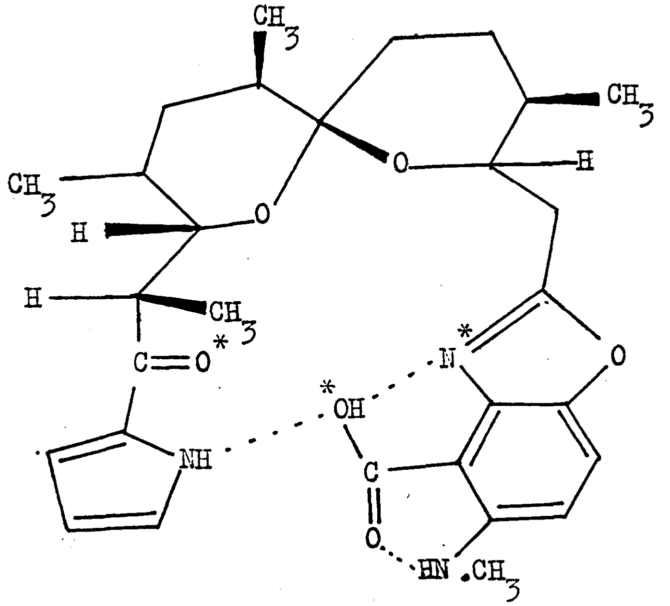
Strong evidence for a relay mechanism of transport is found for the enniatin B antibiotic. This cyclohexadepsipeptide forms a complex with potassium iodide (2) which, in the solid state, appears to "stack"[1,9]. Solution studies show the existence



2.

of 2:1 and 3:2 antibiotic : metal complexes, so that a relay mechanism appears probable, the more so as no contradictory evidence has been found. K^+/Na^+ selectivity is lower than for valinomycin although the 2:1 complexes have greater selectivity towards potassium than do the 1:1 complexes. Enniatin B has six oxygen atoms available as donor atoms for complex formation which is ideal for group IA ions but insufficient for the preferred coordination number for group IIA ions, hence accounting for selectivity of enniatin B for group IA[3,10].

Antibiotics with one or more carboxylic acid groups readily form salts wherein the metal atom is again shielded from external environment. Thus, for example, A23187 is an open chain carboxylic acid antibiotic (3)



------ hydrogen bond

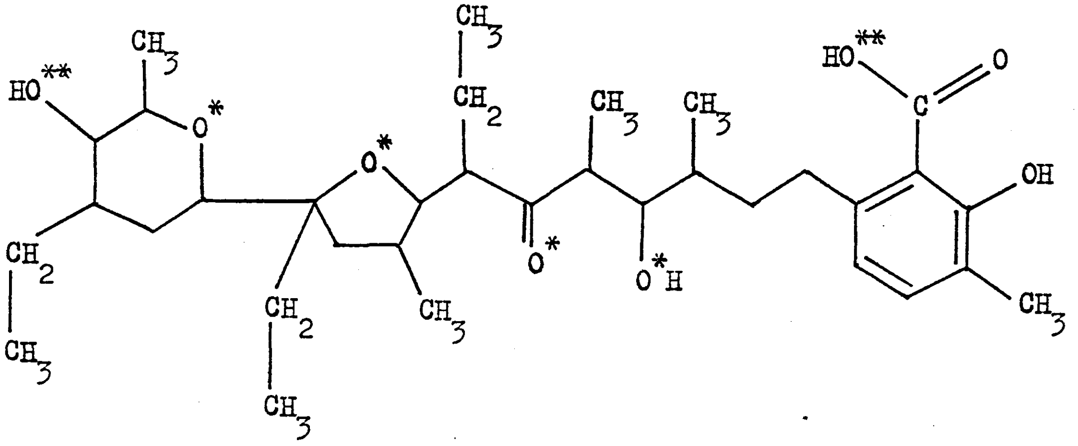
starred atoms bonded
to calcium in calcium
complex

3.

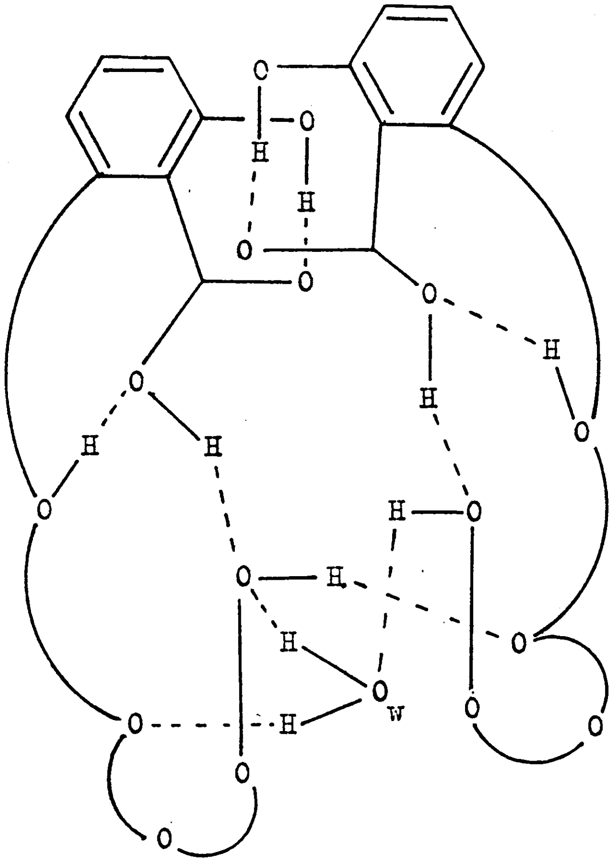
although X-ray analysis[11,12,13] has shown that two molecules are held together in the solid state "head to tail" by hydrogen bonding to give a macrocyclic conformation. The polar groups are found within the macrocyclic cavity so that the closed structure can be expected to prevail in non-polar solvents but that an open conformation is expected in aqueous solution. The alkali metals are only weakly bonded but 2 : 1 ligand : metal complexes are formed with divalent cations. A stability sequence of $Mn^{2+} \gg Ca^{2+} \approx Mg^{2+} \gg Sr^{2+} > Ba^{2+}$ is found[13]: this appears to be related to ionic radius. With these divalent cations, the 2 : 1 complexes are neutral and probably can be easily transported across the non polar lipid membranes. With only three available donor atoms, it is unlikely that 1 : 1 complexes could be formed with the group 1A metal ions whilst 2 : 1 complexes would carry a net negative charge which would be unfavourable for transporting across a membrane.

A23187[14] crystallizes from Streptomyces Chartreusensis as the mixed Mg/Ca salt. The pure calcium complex has a 2 : 1 ligand : metal stoichemistry, in which the atom interacts with three donor atoms of each A23187 molecule (3). The calcium atom achieves a coordination number of seven by further interaction with a water molecule.

Similarly, X-537A(4)[14,15] crystallizes as a dimer, enclosing a water molecule, only here the molecules are arranged in a "head to head" manner (5). Although X-ray analysis failed to locate all the hydrogen atoms, the bonding scheme is believed to be as shown in (5). However, hydrogen bonding is not found in the Ba^{2+} [16] or Ag^{+} salts which show the two X-537A ligands united in a "head to tail" manner in the solid state. The overall coordination number of nine for the barium in the Ba^{2+} salt is achieved by bonding to all six starred oxygen atoms in one ligand and only to the two double starred oxygen atoms on the other: the ninth bond is to a water molecule. The low solubility in water and the ease of solution in organic solvents is again accounted for by the absence of oxygen atoms on the exterior of the complex and the general hydrophobic nature of the surface. Unlike A-23187, which selectively transports calcium and magnesium



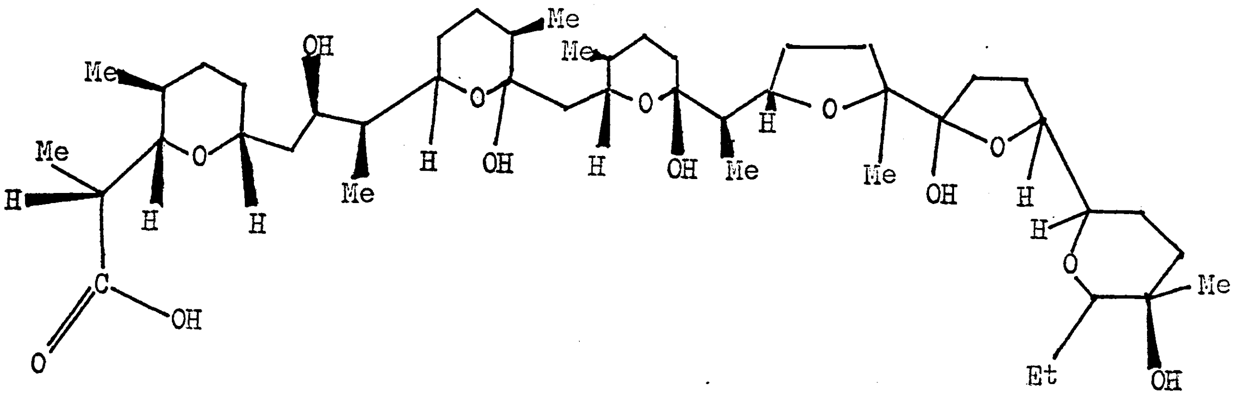
4.



Schematic view
with only oxygen
atoms and hydrogen
atoms involved
in bonding shown.
Carbon atom chain
is represented
by solid lines.

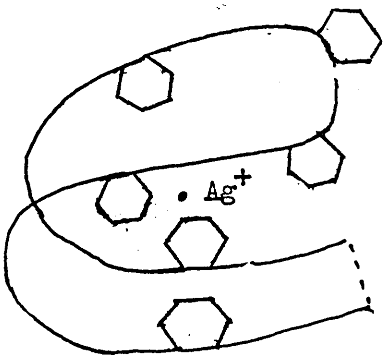
ions, X-537A inhibits the transport of both groups IA and IIA cations across membrances: the alkali metals forming dimeric complexes with the antibiotic of the form $(M^+ X^-)_2$.

Where the antibiotic is sufficiently large, it may be able to form complexes without recourse to dimerizing. Thus, in order of increasing size, monensic acid[17,18], nigericin[19] and X-206[20] are all known to form 1:1 complexes. As the three are so similar, discussion will be limited to X-206 (6).



6.

X-206[21] forms a silver salt in which the ligand forms an exaggerated U-shape which is then wrapped around the centre silver ion analogously to the seams of a tennis ball (7).



7.

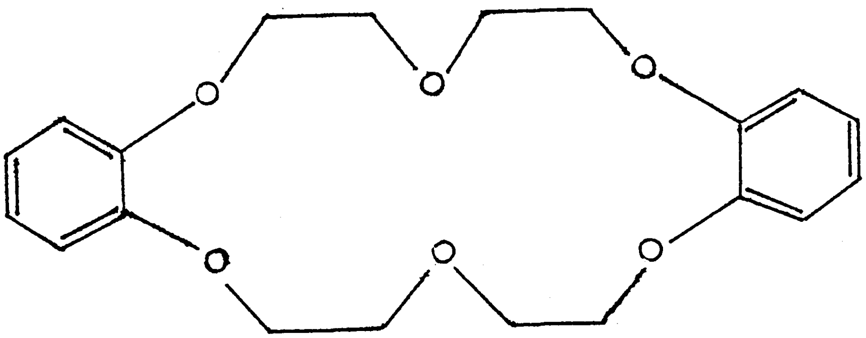
The relative rigidity of the structure in solution is achieved by nine intramolecular hydrogen bonds in addition to the Ag - O interactions;

the silver is unsymmetrically coordinated to six oxygen atoms, bonding distances ranging from 2.5 to 2.8Å.

Although the similarities between the neutral antibiotics and synthetic cyclic polyethers (the "crown" ligands) are strong (both sets are neutral with an interior cavity ringed by oxygen atoms and have hydrophobic exteriors), interest in the crown complexes spreads beyond using members as models for biological systems. To date, the emphasis on using the crown ligands as model systems has been very low: the main concentration has been on the coordination chemistry of the crown ethers for their own intrinsic value and it is this aspect which is now considered. Firstly, however, it is helpful to establish a simplified system of nomenclature. In place of the I.U.P.A.C. naming, "crown" ligands are described, in order, by

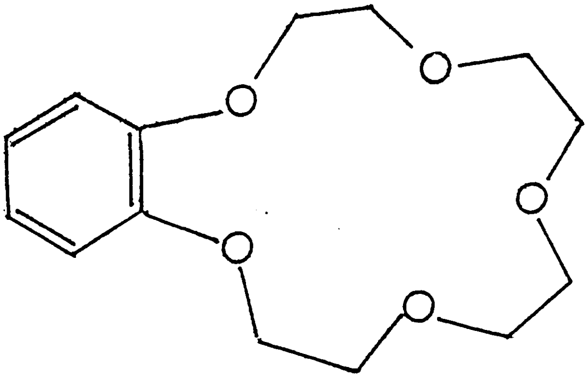
1. the number and kind of substituent groups on the ring,
2. the total number of atoms in the polyether ring,
3. the class name of "crown" and
4. the number of oxygen atoms in the polyether ring.

Since Pedersen's first preparation[22] of a crown ether in 1962, a proliferation of crown complexes have been isolated - indeed, Petersen himself has isolated over fifty[23] - with any number of oxygen atoms from four to twenty in the macrocyclic ring. The early crown complezes had 1:1 stoichemistry but it was later found[24] that in cases where the size of ring cavity was too small for the cation to fit into the macrocyclic cavity, a 2:1 ligand : cation complex was formed. Thus, while dibenzo - 18 - crown - 6(8) forms stable 1:1 complexes with barium thiocyanate,



8.

the same salt forms a 2:1 ligand : cation complex with the smaller (in terms of macrocyclic cavity) benzo - 15 - crown - 5(9).



9.

Parsons et al have prepared[25] a series of alkali tetraphenylborate complexes with a variety of benzyl crown ethers containing five to ten oxygen atoms. While mostly 1:1 complexes were obtained, sodium, potassium and caesium complexes of benzo - 18 - crown - 6 were prepared of the form L_2MBPh_4 (L = crown ligand). Benzo - 15 - crown - 5 gave 1:1 complexes only with $NaBPh_4$. With dibenzo - 30 - crown - 10, on the other hand, both

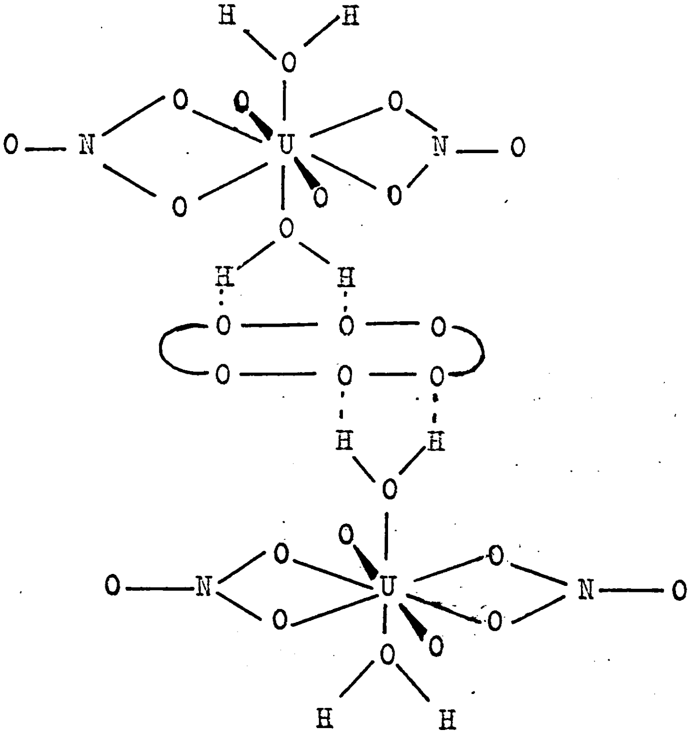
LNaX and $L(NaX)_2$ were obtained. In the latter case, the crystals contained water molecules despite being prepared in anhydrous solvents. Solvent molecules, especially water, are common in the crystalline state and, although truly anhydrous complexes exist, extremely rigorous exclusion of water is necessary if they are to be successfully prepared[26]. The water molecules often are present to satisfy the coordination number of the metal ion.

The relative stability of various complexes depends on a number of mutually independent factors. Although cavity size of the ring is prominently discussed in much of the literature, too simplistic a view is obtained if other factors are neglected. Indeed, cavity size within the ring is only of any importance for rings containing 6 or 7 ether oxygen atoms. For - 12 - crown - 4 complexes, the cavity is too small to hold even a Mg^{2+} ion in the plane of the ring and - 15 - crown - 5 is too small for Na^+ (cavity size is best considered to be a circle of diameter obtained from a regular arrangement of the oxygen atoms in a plane: from this measurement, correction is made for the Van der Waals' radius of the oxygen atoms) whilst for crown - 8 and larger crown ethers, the cavity size is so large that the ring has to be distorted to allow coordination between donor atoms and the cation. The effect of cavity size is most pronounced with the - 18 - crown - 6 complexes.

Consideration of the complexes formed by Group IA and IIA salts and 18 - crown - 6 shows greatest stability with K^+ and Ba^{2+} ions. Further, a progression is noted in each series between stability and closeness of fit of metal ion to cavity diameter. For the series $K^+ > Rb^+ > Cs^+ > Na^+$, a corresponding series of ionic radius of 1.38, 1.49, 1.70, 1.02Å results in a progression of absolute difference from the cavity radius of 1.40Å of .02, .09, .30, .38Å. Similarly, with the group IIA cations. It is worthy of note that with both group IA and IIA there is an ion which almost exactly matches the cavity (K^+ - 1.38Å, Ba^{2+} - 1.36Å). Relatively high stability is also found for other ions that have similar ionic radii (e.g. Ag^+, Tl^+, Pb^{2+}, Hg^{2+}). If the ionic radius of the cation and the cavity radius differ too greatly, then the cation is either situated out of the plane of the ring (e.g. with the caesium thiocyanate complex of 4 - nitrobenzo-18 - crown - 6[27]) or the ring is distorted with unequal M-O distances (e.g. sodium complex of 18 - crown - 6[28]). The dominance given to the issue of cavity size is probably due to the great majority of the early crown ethers being of the 18 - crown - 6 type.

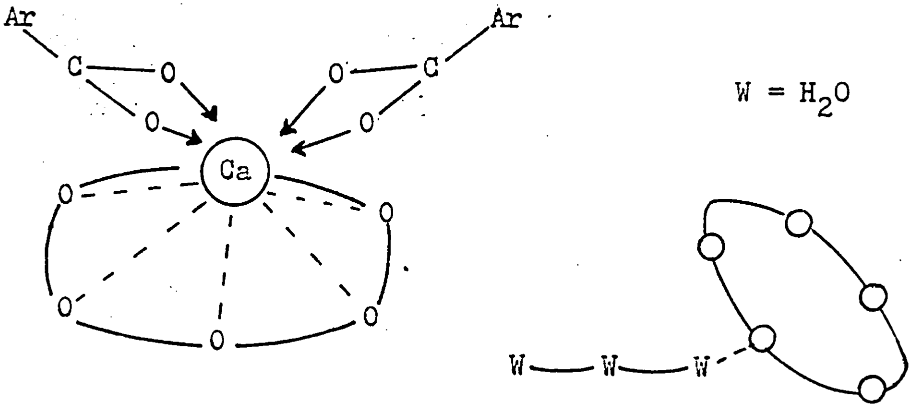
In addition to cavity size, four other factors may influence the stability of complexes (indeed, they may determine whether a complex can actually be formed). There is often an interplay between hydration energy and complex formation which may, in turn, be influenced by the second factor, the nature of the anion present. Thirdly, certain coordination numbers are more favourable to the cation than others. Complex formation may not occur, for example, in the absence of sufficient donor atoms. Favourable (or desired) coordination number is often reached by bonding to one or more water molecules. Finally, substitution of differing groups into the macrocycle will effect complex formation.

The cavity size of 4 - and 5 - crown ligands is too small to satisfactorily accommodate a Mg^{2+} ion whilst the cavity is much larger than the ion for 6 - crown ligands. With such unfavourable ionic radius: cavity size ratio, magnesium complexes are only found where other factors are favourable to complex formation. Attempts to form complexes using ortho-nitrophenolates ($Mg(ONP)_2$), dinitrophenolates ($Mg(DNP)_2$) and picrates ($Mg(Pic)_2$) by either direct synthesis or by reacting the crown compound with $MgCl_2 .6H_2O$ and the parent acid yielded interesting results[29]. Using direct methods, no complex was formed with $Mg(ONP)_2$ though complexes were formed with the other anions present. By indirect synthesis, $Mg(ONP)_2$ and $Mg(DNP)_2$ both gave 1:1 complexes but $Mg(Pic)_2$ yielded a 2:1 complex ($Mg(Pic)_2 (crown)_2 .2H_2O$) even when the reactants were in a 1:1 ratio. The yield of this complex was found to increase as the proportion of water in the reaction media was increased from 25 to 50%. Unlike the 1:1 complex, the 2:1 complex was soluble in organic solvents such as benzene and carbon tetrachloride. The results may be explained by noting that the ONP anion is a strong nucleophile and deters the crown from complexing with magnesium. In contrast, both the DNP and picrate ions are relatively delocalised systems and can allow complexing to occur. The 2:1 magnesium picrate complex is unusual in that its apparent sandwich structure (infra red spectrum suggests both crown ligands are complexed and its low solubility in water suggests a hydrophobic exterior) contradicts the view that sandwich structures are not formed where the cation is larger than the cavity. Unfortunately, no X-ray crystal structure determination has been reported and so the above conclusions must be treated with some caution. The dangers inherent in drawing conclusions without the evidence of an X-ray crystal determination are well illustrated by the erroneous conclusions drawn by Costes et al[30,31] from infra red data on $UO_2 (NO_3)_2 .18$ - crown - 6. $4H_2O$. The authors assumed that this was a 'true complex' with the cation located in the ring cavity. However, a X-ray crystal structure determination of the dihydrate[32] showed the $UO_2 (NO_3)_2 .2H_2O$ and the crown species to be stacked alternately with no direct interactions between the cation and the crown ether (10). Only weak hydrogen bonding was found to exist between the water molecules (attached to the uranium atom) and two oxygen atoms in the crown ligands (10).



10.

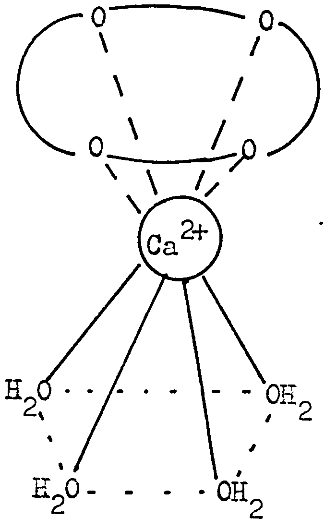
Further, apparent 2:1 complexes are known which show, on X-ray examination, that interaction is limited to only one of the crown ligands present. Thus, the calcium dinitrobenzoate complex formed with benzo - 15 - crown - 5[33] crystallizes as shown schematically in (11). Calcium is coordinated to nine oxygen atoms (this in itself is



11.

unusual, calcium rarely having a coordination number greater than 8), five from the crown ether and four from two different dinitrobenzoate anions. The second crown molecule is hydrogen bonded to a chain of three water molecules.

No success has yet been met in obtaining crown - 4 complexes of magnesium in which the metal ion is coordinated to the crown ligand. Attempts to complex magnesium chloride hexahydrate with 12 - crown - 4 produced a 1:1 complex but X-ray analysis revealed that the macrocyclic ligand does not replace any of the water molecules in the solvation sheath around the cation. The cation was found to be similarly bonded as in the uncomplexed $MgCl_2 \cdot 6H_2O$. The crown molecules are held in the lattice by hydrogen bonds between the water molecules and the ether oxygens[34]. In comparison, the hydration energy for the calcium chloride is lower and the crown ligand is able to replace two water molecules from the sheath around the metal ion to form a true complex[35]. The calcium ion is located well outside the macrocyclic ring but is bonded to all four ether oxygens. The coordination number of 8 is reached by bonds to four water molecules to form a distorted square antiprism (four other water molecules are present in the structure but not bonded to the calcium) (12).



12.

It is thus clear that in these complexes it is the magnitude of the hydration energy that determines whether a complex is formed and not the size of the ring cavity.

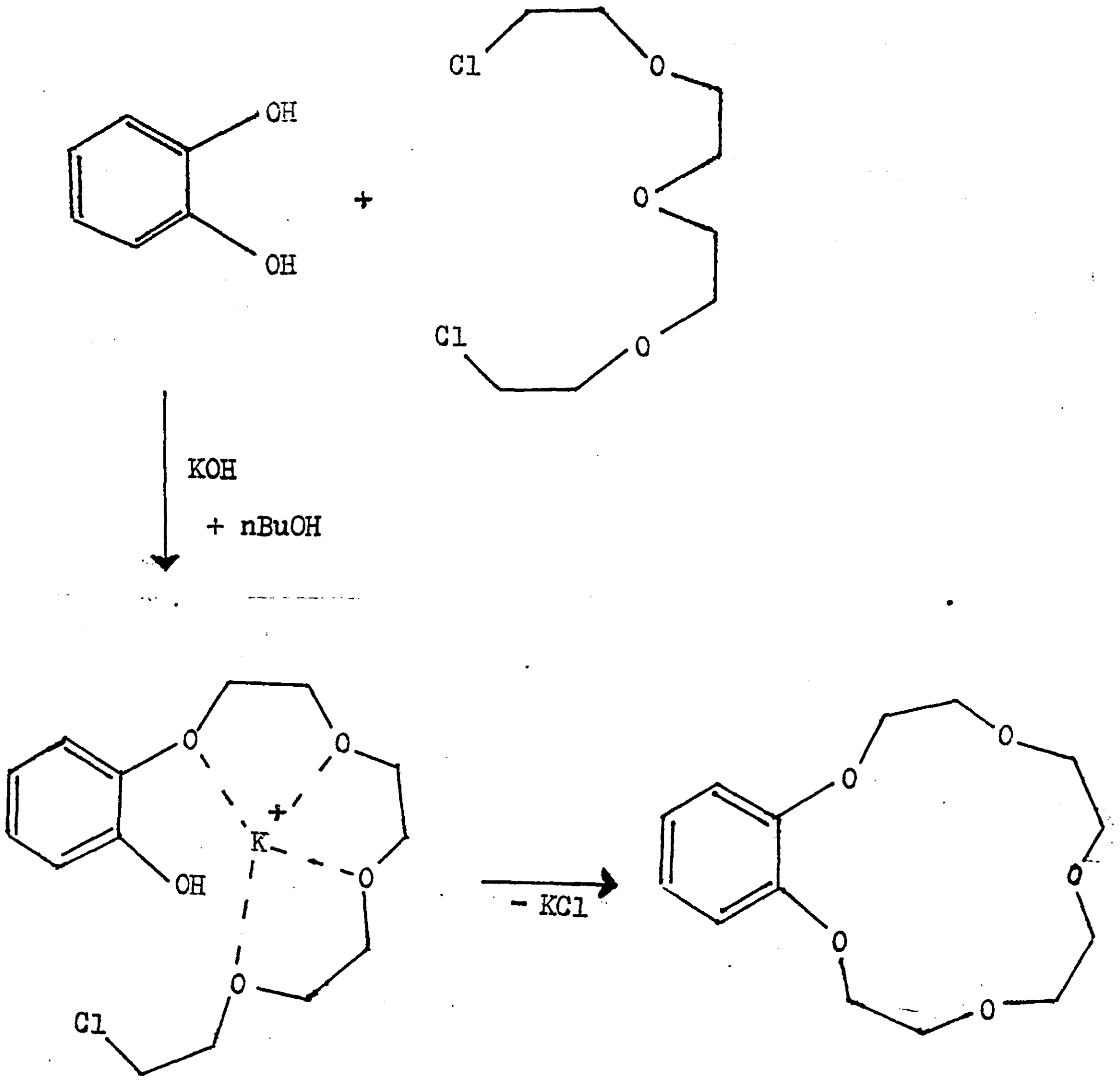
A wide range of coordination numbers are formed for many metal ions in their reactions with crown ligands. For example, potassium is 6 coordinate in the planar 18 - crown - 6 complex (but a higher coordination is attained if the complex is not rigorously excluded from water during preparation[26]) and in its valinomycin complex (octahedral configuration); 8 coordinate in the dibenzo - 24 - crown - 8 complex and in its nonactin complex (cubic); 9 coordinate in the dibenzo - 27 - crown - 9 complex and 10 coordinate in the dibenzo - 30 - crown - 10 complex[36]. There are no stereo-chemical reasons for the variation; in each case, the ligand is providing an electronically basic environment to replace all or part of the cation's solvation shell. Nevertheless, there is a tendency to favour higher states by coordinating to water molecules. Exclusion of water by preparation in methanol or pyridine can lead to these molecules being included into the structure of the complex as Parsons and Wingfield[37] found in preparing the calcium thiocyanate complex of benzo - 15 - crown - 5 in these media.

The addition of side groups to the macrocyclic ring may alter both the stability and the selectivity of the ether towards various cations. Thus, while the formation constant of the Ba^{2+} complex of 18 - crown - 6 is larger than that for the K^+ complex by a factor of 10, the situation is almost exactly reversed[38] for the corresponding complexes with dibenzo - 18 - crown - 6. While substitution into a "cyclohexo" group has only limited effect on stability with various cations, more marked effects are noted with substitution into a "benzo" group. Thus, the dinitro derivative (substituted in the p- position) of dibenzo - 18 - crown - 6 has a markedly reduced affinity for Na^+ [38] (compared to the unsubstituted dibenzo - 18 - crown - 6) whilst the analogous amino substitution gives a slightly more stable complex[39]. This may be explained in terms of electron withdrawal by the nitro group which may in turn produce delocalization of electrons from the donor oxygen atoms. Conversely, the amino group has an electron donating function. A factor of nearly 20 is involved in relative stability between the two species with Na^+. Further, selectivity is altered; Pannell et alia[40] found that the selectivity of dibenzo - 18 - crown - 6 for K^+ over Na^+ in methylene chloride was reversed with nitro substitution in the ring. Selectivity is also solvent dependent: thus, for example, K^+ over Na^+ selectivity is found for dicyclohexyl - 18 - crown - 6 in oxetan but is reversed in tetrahydrofuran[41]. Arnett and Moriarity[42] reported that stability of complexes of large cations is less effected by solvent than for small cations. It is suggested[42] that greatest selectivity will occur in strongly solvating media which will have a greater affinity for the smaller cations and thus inhibit complexing to the macrocyclic ligand. In less polar media, the effect of the solvent is very low and factors such as cavity size dominate.

The metal ions outside groups IA and IIA do not tend to form crown complexes easily. Although complexes of the lanthanoid and actinoid elements have been reported[43,44], the transition metals find polyethers to be poor ligands and reported complexes are few and not particularly stable. Of these, only the Cu(II) complex of 12 - crown - 4 has been shown by X-ray analysis to be a coordination complex[45]. There is much inherent danger in assuming true complexes have been formed without the confirmation of X-ray analysis. Thus, for example, both the $UO_2(NO_3)_2$. 18 - crown - 6 . $4H_2O$ structure already cited[32] and the apparent complex of manganese nitrate with the same ligand

$\{(Mn(NO_3)(H_2O)_5)\ NO_3 \cdot 18 - crown - 6 \cdot H_2O\}$[46] contains metal ions which are not coordinated to the crown ether. However, the substitution of some or all of the oxygen atoms by either nitrogen or sulphur atoms produces macrocyclic complexes with most metal ions. Unlike the corresponding crown ethers, these macrocyclic ligands often cannot exist in the free state and are only found in metal ion complexes. Replacement of oxygen by nitrogen atoms decreases the affinity of the group IA and IIA cations for the ligand while leaving unchanged (or even enhancing) the stability of late transition metal ions, e.g. Ag^+. Substitution of sulphur atoms for oxygen atoms has a very marked effect. The configuration of the crown is fundamentally altered with the sulphur atoms being directed away from the ring cavity. No structures of sulphur substituted crowns have been found without the metal ion being coordinated to other ligands. Indeed, a very high incidence of 2:1 ligand : metal ion complexes have been reported. For sulphur substituted crown complexes, the stability increases greatly for Hg^{2+} and Ag^+ complexes whilst Pb^{2+} and Tl^+ form much less stable compounds than the corresponding crown ether complexes.

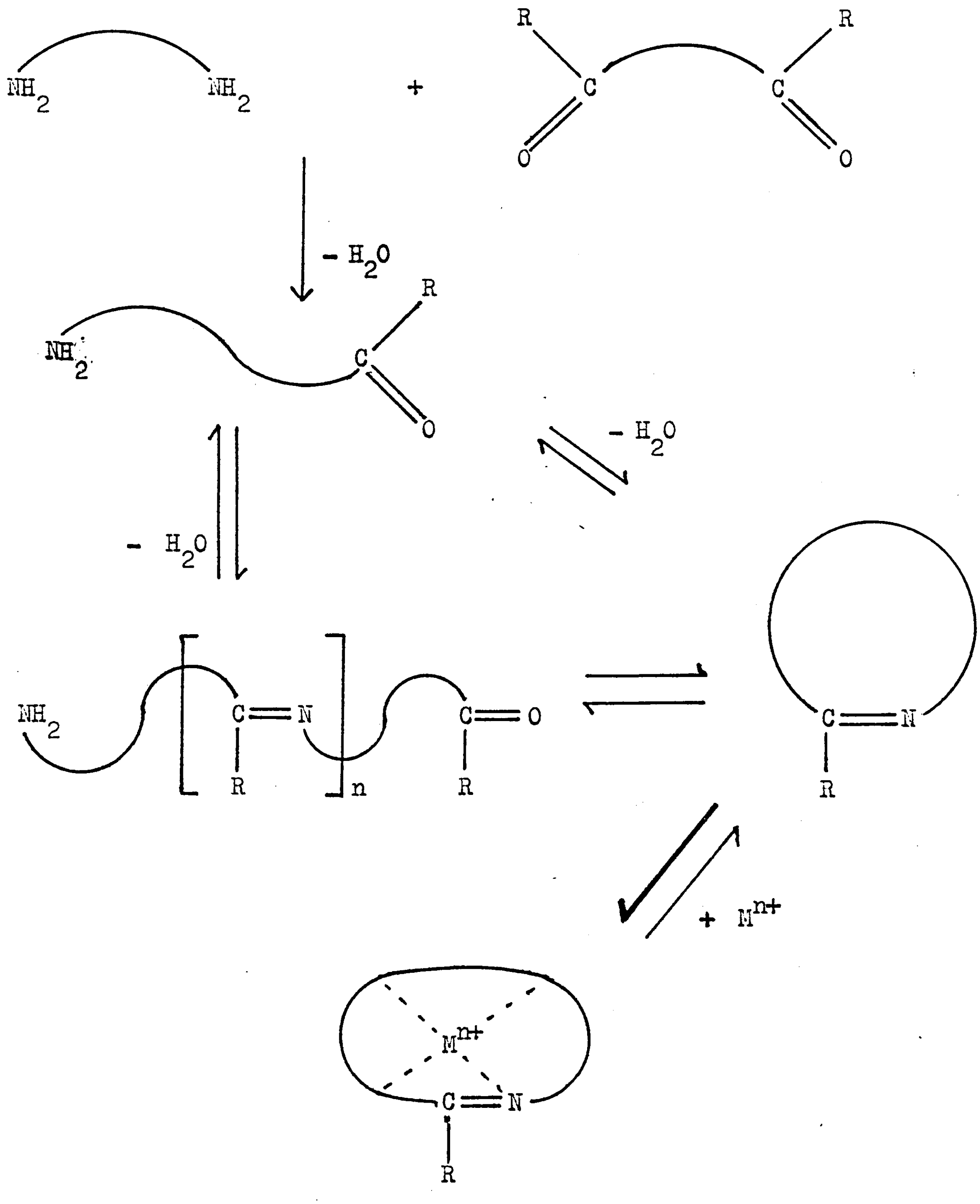
The classic preparation used for producing large polyether rings is to work at high dilution. However, at an early stage, Pedersen[22] found that the addition of potassium or sodium hydroxide gave much increased yields of the desired crown. This was still true at fairly high concentration. Conversely, if a base such as tetra n-butyl ammonium hydroxide was used then the yield was drastically reduced. It was postulated that the metal ion was acting as a template about which intermediatory products formed such that cyclisation was encouraged; the bulky units (e.g. tetra n-butyl ammonium hydroxide) proving too large to allow cyclisation. It appears that the nature of the metal ion is relatively unimportant: it is the effect of a geometrically acceptable cationic centre that determines the quantity of the end product. Thus, the preparation of benzo - 15 - crown - 5 may be represented schematically by:-



Yields of crown complexes as high as 93% are obtained by such methods whereas only 2% yields are expected with high dilution techniques without complex-aiding ions.

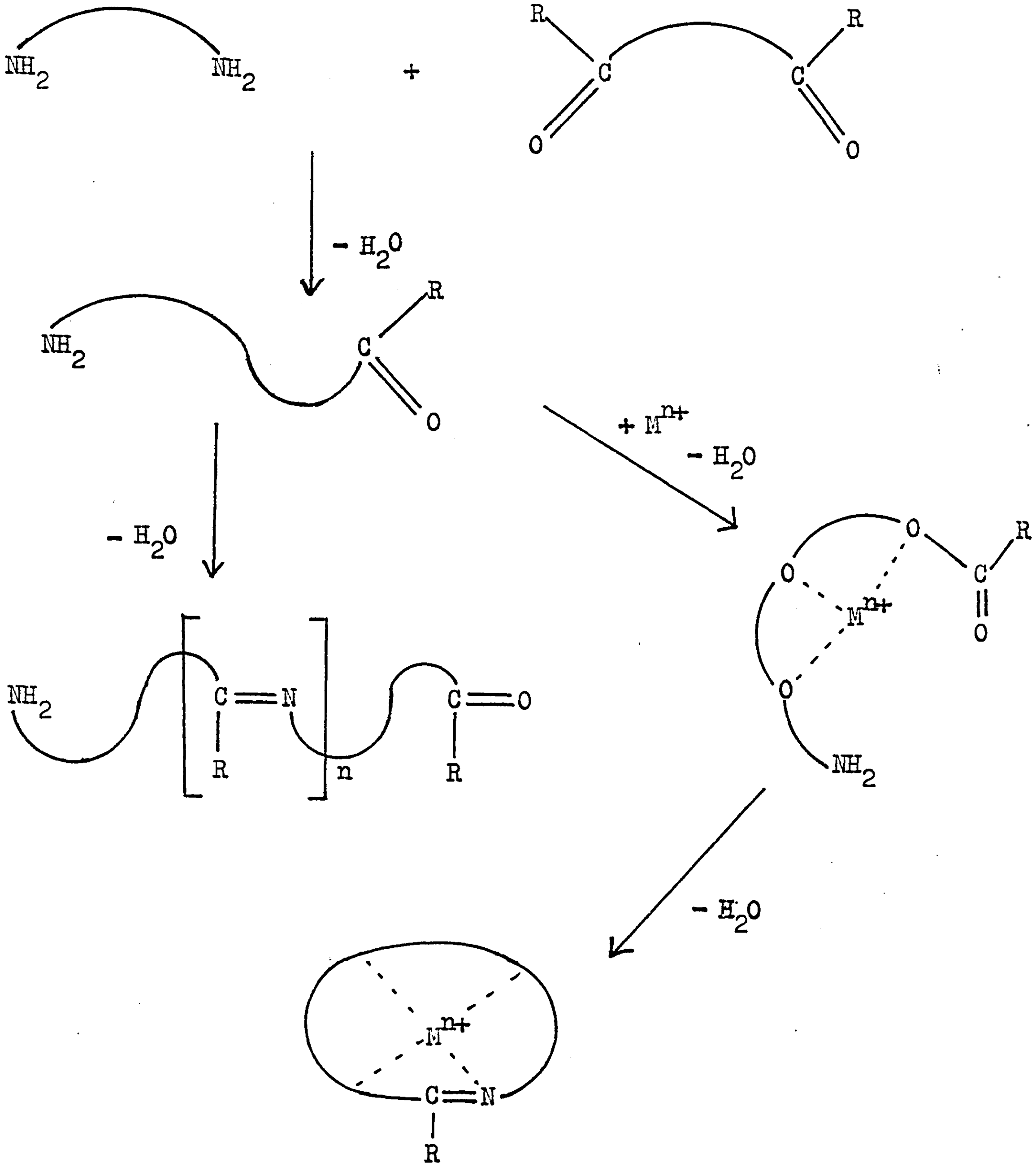
Both kinetic and thermodynamic factors have been considered to be important in considering the mechanisms for crown formation. Where the metal ion controls the stepwise reactions, the kinetic effect is considered to be dominant but, where a metal ion perturbs an equilibrium causing preferential coordination, a thermodynamic template effect exists. The stepwise reaction is such that the metal ion, by complexing with half-cyclised intermediate products orientates the ligand in such a way as to significantly increase the rate of formation of the closed macrocycle. In a thermodynamic template effect, the metal ion complexes with the organic reactants to remove the macrocycle from equilibrium, thus encouraging further complex formation. Most in situ syntheses of macrocyclic ligands involve a kinetic effect. However, the role of the metal ion is not always clear and hence a firm conclusion cannot be always made as to which effect dominates. The schematic mechanisms are shown in schemes 1 and 2.

Thermodynamic template mechanism.



Scheme 1.

Kinetic template mechanism.



Scheme 2.

Coordination via a kinetic template effect lowers the free energy of the transition state of the reaction whereas, for a thermodynamic effect, the free energy of the product is lowered by complexing. Hinz and Margerum[47] made a detailed study of the thermodynamic properties of the Ni^{2+} complexes of a series of tetramine ligands in water. The results are summarised in Table 3.1.1.

Thermodynamic data relating to formation of Ni^{2+} complexes (with suitable anions) with various ligands

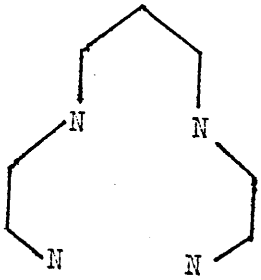
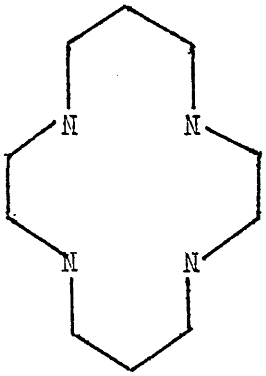
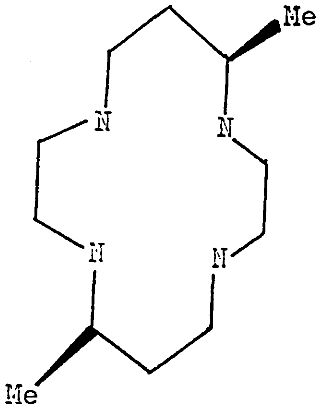
ligand	log K	ΔH (k J mol^{-1})	$T\Delta S$ (k J mol^{-1})
 (2,3,2 - tet)	64.0	-70.3	17.2
 cyclam	92.9	-129.8	2.5
 Me_2 cyclam	91.7	-117.2	10.0

Table 3.1.1

It is seen that enthalpy contributions dominate in confering increased stability in the ring complexes over the open chain structure. Indeed, entropy changes are even in opposition to the stability of the macrocyclic forms. However, in a similar study[48] involving the Cu^{2+} ions, the kinetic effect dominated. The corresponding table (Table 3.1.2) shows that now ΔH has a destabilizing effect while $T\Delta S$ is responsible for the increased stability of the macrocyclic ligand.

Theremodynamic data relating to the formation of Cu^{2+} complexes (with suitable anions) with various ligands

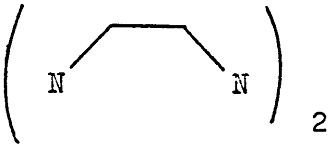
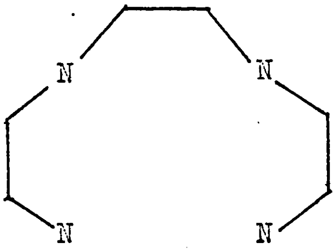
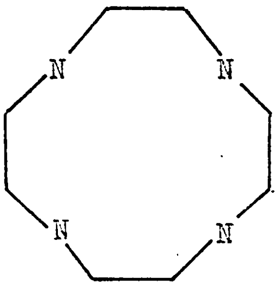
ligand	log K	ΔH (k J mol^{-1})	$T\Delta S$ (k J mol^{-1})
 (en)	82.5	-105.5	7.1
 (2,2,2 - tet)	84.1	-90.4	24.3
 (cyclen)	103.8	-76.6	64.0

Table 3.1.2

The apparent contradictory nature of the sets of data render simplistic explanations (as put forward in the two studies) of dubious value. As the cavity of the cyclen is too small to accommodate the Cu^{2+} ion but can contain the Ni^{2+} ion, different formation mechanisms are likely and hence the two studies do not appear to be measuring the same effect. Even apparent minor structural changes can upset predictions as Lamb[49] illustrates by reference to a series of cyclic polyethers with various cations(Table 3.1.3). With the ligands (a), (b), (c), a progressive stabilisation is noted for the Na^+, K^+ and Ba^{2+} complexes (the Na^+ complex of (a) was not reported) in moving from (a) to (c).

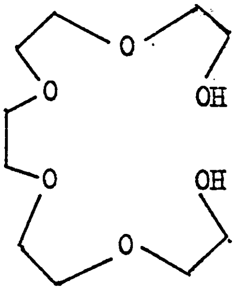
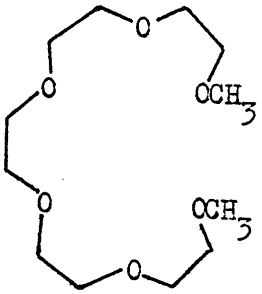
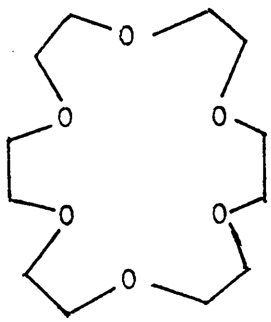
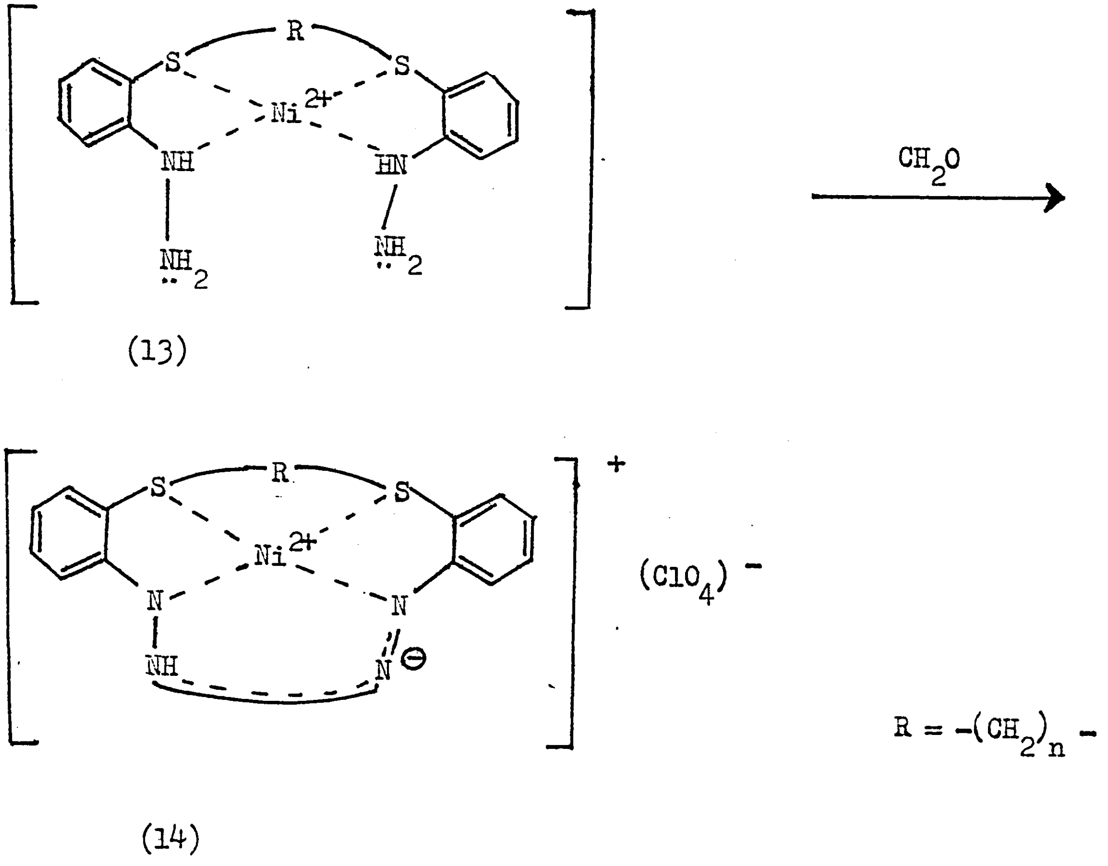
ligand	cation	log K	ΔH (kJ mol^{-1})	TΔS (kJ mol^{-1})
 (a)	K^+	8.6	-26.7	-14.7
	Ba^{2+}	16.6	-28.1	-5.5
 (b)	Na^+	4.2	-38.3	-32.2
	K^+	9.5	-34.2	-21.2
	Ba^{2+}	10.5	-23.6	-9.3
 (c)	Na^+	18.1	-34.0	-9.2
	K^+	25.3	-55.3	-20.8
	Ba^{2+}	29.3	-43.5	-3.5

Table 3.1.3

Stabilization for the sodium complexes is almost totally due to the entropy term whilst the potassium complexes owe progressive stability through the series mostly to the enthalpy factor: the barium series receives about equal contribution to both factors. The explanation would appear to lie in the adoption of differing conformations, the exact nature being dependent on the cation present. Thus, the crown ligand is wrapped around the Na^+ ion while the ligand is effectively flat for the K^+ ion (and probably for the Ba^{2+} ion as it is approximately the same radius as the K^+ ion)[50].

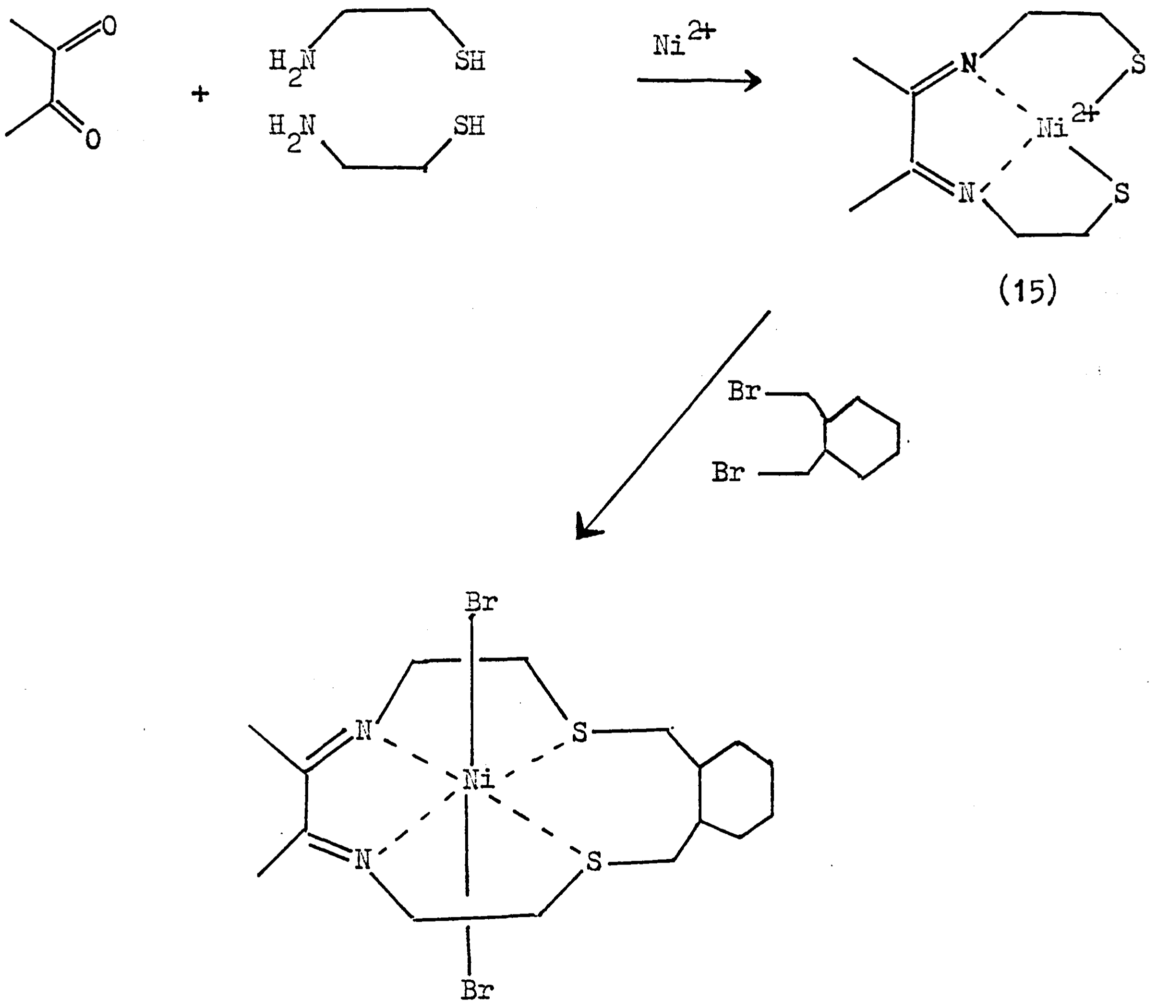
Tasker et alia[51] tried to distinguish between the kinetic and thermodynamic effects by using ligands derived from the condensation of the dihydrazine derivative (13) [Scheme 3] as its nickel complex with formaldehyde.



Scheme 3

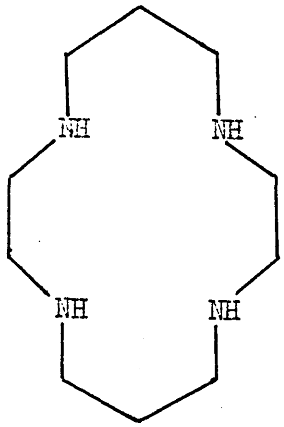
The square planar nickel complex (13) can be preformed but because there are lone pairs of electrons on the nitrogen atoms still available for a Schiff base condensation reaction, then it is possible that a kinetic template process is involved. The same reaction carried out in the absence of nickel salts yielded a mixture of oils from which the nickel complex (14) could not be extracted by subsequent digestion with nickel (II) perchlorate. This supports the inference that the nickel ions participate in a kinetic template process.

In the templating effect of nickel (II) acetate on condensations between α-diketones and β-mercaptoamines[52] (Scheme 4), the first reaction in the sequence may be regarded as a thermodynamic template process as the Schiff base (15) may be isolated without the metal ions being present but the yield is greatly increased by their addition. In the second step of the reaction, a kinetic template effect is more likely as the nickel ion tends to hold the half-cyclised intermediatery in a position favourable for completion of the ring.

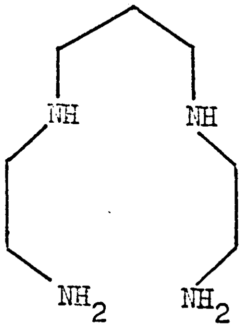


Scheme 4

The enhanced stability of the macrocycle over the analogous open chain system is found despite the fact that a more restricted geometry may be forced on the macrocycle. Both Paoletti et al[49] and Cabbiness and Margerum[53] observed that the copper (II) complex of the macrocyclic amine (16) is 10^6 times more stable than the analogous acyclic complex (17).



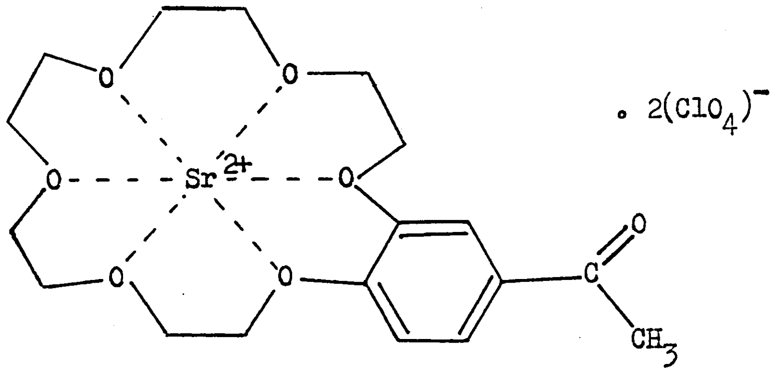
(16)



(17)

The enhanced stability of the macrocyclic effect has been termed "multiple ju~~s~~xtapositioned fixedness" by Buesch et alia[52] who suggested that the stability is due to very slow rates of decomposition. Paoletti et alia[49] suggested that the macrocyclic effect involved a more favourable enthalpy term which overcomes the less favourable entropy changes. Macrocyclic complex formation may be associated with a more favourable enthalpy[52,54,55], not via the donor-metal bond strengths (which do not differ markedly between cyclic and acyclic analogues) but from decreased solvation of the macrocyclic ligand compared to the acyclic analogue. As there is less solvent to be displaced on complexation by a macrocyclic ligand, ΔH for complexation will be more negative than for the acyclic complex which, because of its openness, can be postulated as having greater solvation in its uncomplexed form.

3.2 The crystal and molecular structure of 4'-aceto-2,3-benzo-1,4,7,10,13,16 - hexa oxa cyclooctadeca - 2 - ene,strontium perchlorate.



3.2.1. Crystal data

$C_{18}H_{26}Cl_2O_{15}Sr$ $M_r = 640.91$ triclinic ($P\bar{1}$)

$a = 17.174(15)$ $b = 9.036(9)$ $c = 19.959(16)$ Å

$\alpha = 87.42(5)$ $\beta = 124.82(7)$ $\gamma = 96.07(5)^\circ$

$D_m = 1.77$ Mg. m^{-3} $D_c = 1.75$ Mg. m^{-3} $Z = 4$

$F(000) = 1304$ $\mu(\text{Mo} - K\alpha) = 2.34\ mm^{-1}$

3.2.2. Data collection and structure analysis

The crystals were prone to deterioration in air and it was necessary to seal the crystals in epoxy resin prior to data collection. A crystal of approximate dimensions 0.16 x 0.22 x 0.31 mm was eventually found to be suitable for data collection and was mounted about the a axis. 20 layers, 0kl → 19kl, were collected; 5299 independent reflections were recorded of which 2054, having $I \geqslant 4\sigma(I)$ were used for structure analysis. Corrections for Lorentz and polarization effects were applied but no corrections were made for absorption.

The positions of two independent strontium atoms were determined from a three dimensional Patterson synthesis. The apparent translation of a/2 between the atoms led to investigation to find a higher symmetry space group. However, a Delaunay cell reduction[56] did not produce a higher symmetry unit cell and the structure was solved initially in space group $P\bar{1}$ with two independent molecules in the cell. Subsequent refinement and location of non-hydrogen atoms from a series of Fourier difference syntheses revealed small but significant differences between the apparent a/2 relationship between the two molecules. The pseudo relationship resulted in high correlation between some sets of refined parameters in the full-matrix least squares refinement. Within each macrocyclic ligand, two sets of positions were found for the acetyl group (being attached to C20 and C21) suggesting that the true space group was P1 with four independent molecules in the cell. This was the only interpretation possible to avoid the unrealistically short intermolecular distances between the acetyl oxygen atoms (<1.5Å).

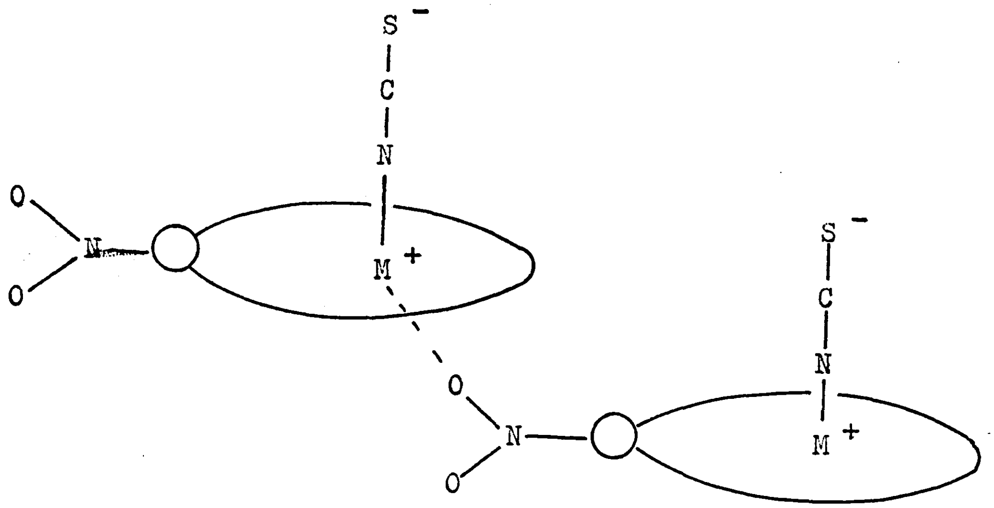
An attempt was made to refine the structure in P1 but the extent of the correlation problems between parameters was so great as to inhibit a satisfactory refinement. In view of such difficulties and the apparent correctness of the centrosymmetric space group for all but the acetyl groups, the final refinement stages were conducted in $P\bar{1}$ with the acetyl groups being statistically disordered (each of the four groups being given 0.5 site occupation factors).

All the non-hydrogen atoms were given anistropic temperature factors and a weighting scheme of $w = 4.1767 / [\sigma^2(F_o) + 0.0034\ (F_o)^2]$ was used to give a final R value of 0.103 and $R_w = 0.103$. The final Fourier difference synthesis revealed the presence of all the hydrogen atoms excluding those associated with the acetyl group and C20 and C21. However, the size limitation of the SHELX program made the full inclusion impossible and, hence, no hydrogen atoms were included in the refinement. The highest residue peak was 1.50 e Å^{-3} found in close proximity to one of the strontium atoms.

Bond distances and bond angles are given in Tables 3.2.3 and 3.2.4 respectively; positional and temperature parameters, structure factors, mean planes and torsion angles are given in Appendices A1.6, A4.6, A2.6 and A3.6 respectively.

3.2.3. Description of the Structure

The crystallographic difficulties in refining this structure preclude a detailed discussion but some general features may be noted. The overall arrangement about the strontium ion is the same in each independent molecule, with the metal ion interacting with both perchlorate groups and the six macrocyclic oxygen atoms (Figures 3.2.1 and 3.2.2). There is no evidence that the acetyl group is involved in bonding to the metal ion. This contrasts with the rubidium and caesium thiocyanate complexes of 4'-nitrobenzo-18-crown-6 where intermolecular bonding of the alkali ion to a nitro oxygen is observed[27,57]:-



The estimated radius of the macrocyclic cavity of an 18-crown-6 is 1.3 - 1.6Å and is such that the strontium ion would be expected to fit easily into the cavity (ionic radius of strontium is 1.25Å[3]). This appears to be the case for, in both molecules, the strontium ion is essentially planar with the weighted mean plane through the six donor atoms of the ring. This contrasts with the related Rb^+ and Cs^+ complexes cited where the ion lies well outside the cavity (Table 3.2.1).

Complex	Distance of metal ion from best mean plane of donor atoms in macrrocyclic ring (Å)
4'-nitrobenzo-18-crown-6.RbNCS	1.17
4'-nitrobenzo-18-crown-6.CsNCS	1.46
4'-acetobenzo-18-crown-6.$Sr(ClO_4)_2$	0.01

Table 3.2.1

The combined effect of shielding of the strontium atom by the sterically large ClO_4^- ion (in contrast to the NCS^- ion) and by the macrocyclic ring may well inhibit the close approach of a neighbouring acetyl oxygen atom though the differing natures of the nitro and acetyl groups may be a contributing factor to the lack of intermolecular bonding.

The Sr-O (macrocycle distances vary from 2.611(16) to 2.782(21)Å with the Sr-O2, O17 values being substantially greater than the remaining values. The mean Sr-O (macrocycle) distance of 2.679Å lies close to the sum of the van der Waals' radius of oxygen and the ionic radius of the strontium ion (2.65Å). While there are similarities between the conformations of the major portion of the macrocycles for each independent molecule, there are striking differences in the O14 portion of the ring and the torsion angles about C12-C13 and O14-C15 (Table A3.6 shows all the torsion angles in the macrocyclic ring but an extract is given in Table 3.2.2.

	Molecule I	Molecule II
C7-O8-C9-C10	170	160
O8-C9-C10-O11	67	60
C9-C10-O11-C12	179	167
C10-O11-C12-C13	171	164
O11-C12-C13-O14	-59	36
C12-C13-O14-C15	-166	-174
C13-O14-C15-C16	-97	-168
O14-C15-C16-O17	-60	-74

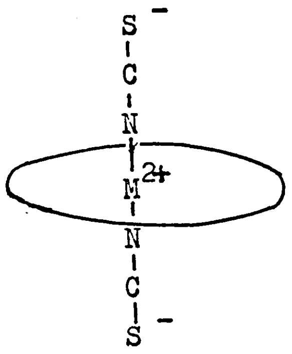
Table 3.2.2

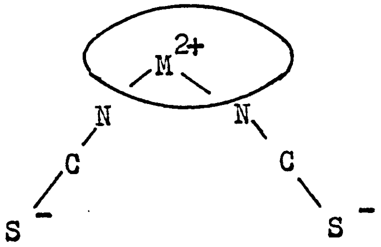
Torsion angles (^{o}) for the two independent molecules

The torsion angles may be taken as an approximate guide to strain within the ring. A strain free macrocyclic ring would have idealized angles of 180^{o} about C-O bonds and $\pm 60^{o}$ about C-C bonds. As Appendix A3.6 shows, most angles do in fact lie close to these expected values. However, the angle about O14-C15 in molecule I (-97^{o}) deviates most noticeably from the expected value and other deviations of up to 120^{o} are found (e.g. about O8-C9 in molecule II). It is difficult to give definitive reasons for such deviations but they may be caused by the macrocyclic ring cavity being slightly larger than the size of the strontium ion. This phenomenon is observed in section 3.3 with the calcium complex discussed therein.

The C-C bond distances within the ring would be expected to be close to the theoretical value of 1.54Å for C-C bonds involving sp^3-sp^3 hybridization. The average bond length found in the present structure of 1.48Å is, however, significantly less than 1.54Å but still consistent with results reported in many related structures [27, 3, 6, 41, 58, 59, 60, 61, 62, 63, 64 et alia]. Indeed, a range of average C-C distances varying from as low as 1.42Å [36] to 1.56Å [64] have been found for differing macrocyclic crown complexes. While it has been suggested that these unexpected C-C bond lengths can be attributed to systematic errors in data collection and structure refinement, Goldberg[60] has found the same tendency for the shortening of the C-C bonds to occur in data collected at low temperatures. This strongly suggests that the shortening of the C-C bond is a real effect, a view supported by Truter et alia[41,58], but no explanation is offered by these writers.

Interest also centres on the role of the anions. With the thiocyanate ion, it is possible for two ions to be positioned on the same side of the ring or on different sides of the ring; i.e.

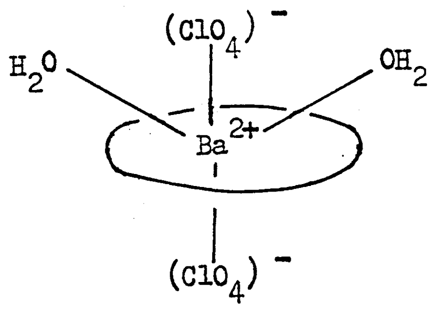




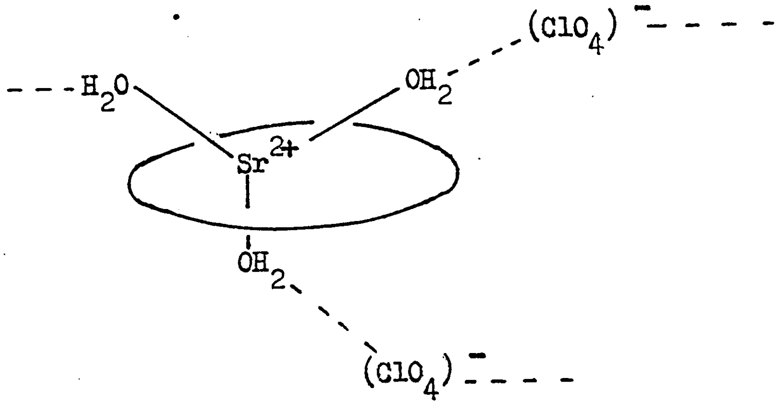
Both arrangements are found and these will be discussed in later sections. However, the perchlorate ion is sterically less able to bond with both ions on the same side of the ring though variations are possible (e.g. one ion uncoordinated). Unfortunately, while perchlorate complexes of calcium have been prepared, these are not well characterized.

The barium and strontium perchlorate complexes formed with benzo-18-crown-6 have also been investigated[58] and both are found to be hydrated. The barium complex is analogous to the structure reported here in having the perchlorate ions situated on either side of the ligand ring.

However, barium reaches a coordination number of ten by bonding to the oxygen atoms in the macrocyclic ring and to the oxygens of both perchlorate groups and to two water molecules in the following manner:



In contrast, in the strontium complex, $SrL.(ClO_4)_2.3H_2O$, the strontium ion achieves a coordination number of nine by interaction with the six oxygen atoms in the ring and to three water molecules. The two perchlorate ions are not directly involved with the strontium ion but are hydrogen bonded to the water molecules:



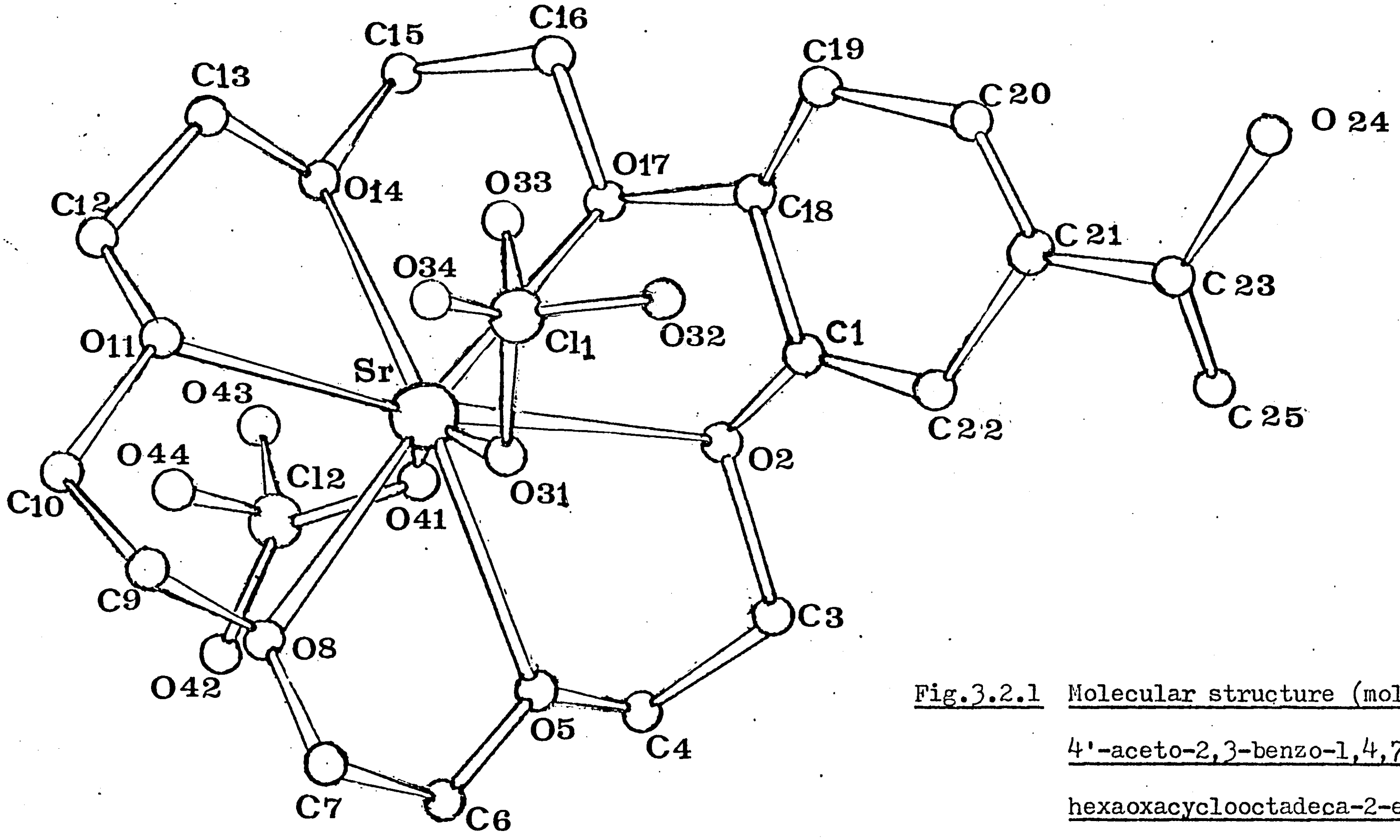


Fig.3.2.1 Molecular structure (molecule 1) for 4'-aceto-2,3-benzo-1,4,7,10,13,16-hexaoxacyclooctadeca-2-ene, strontium perchlorate.

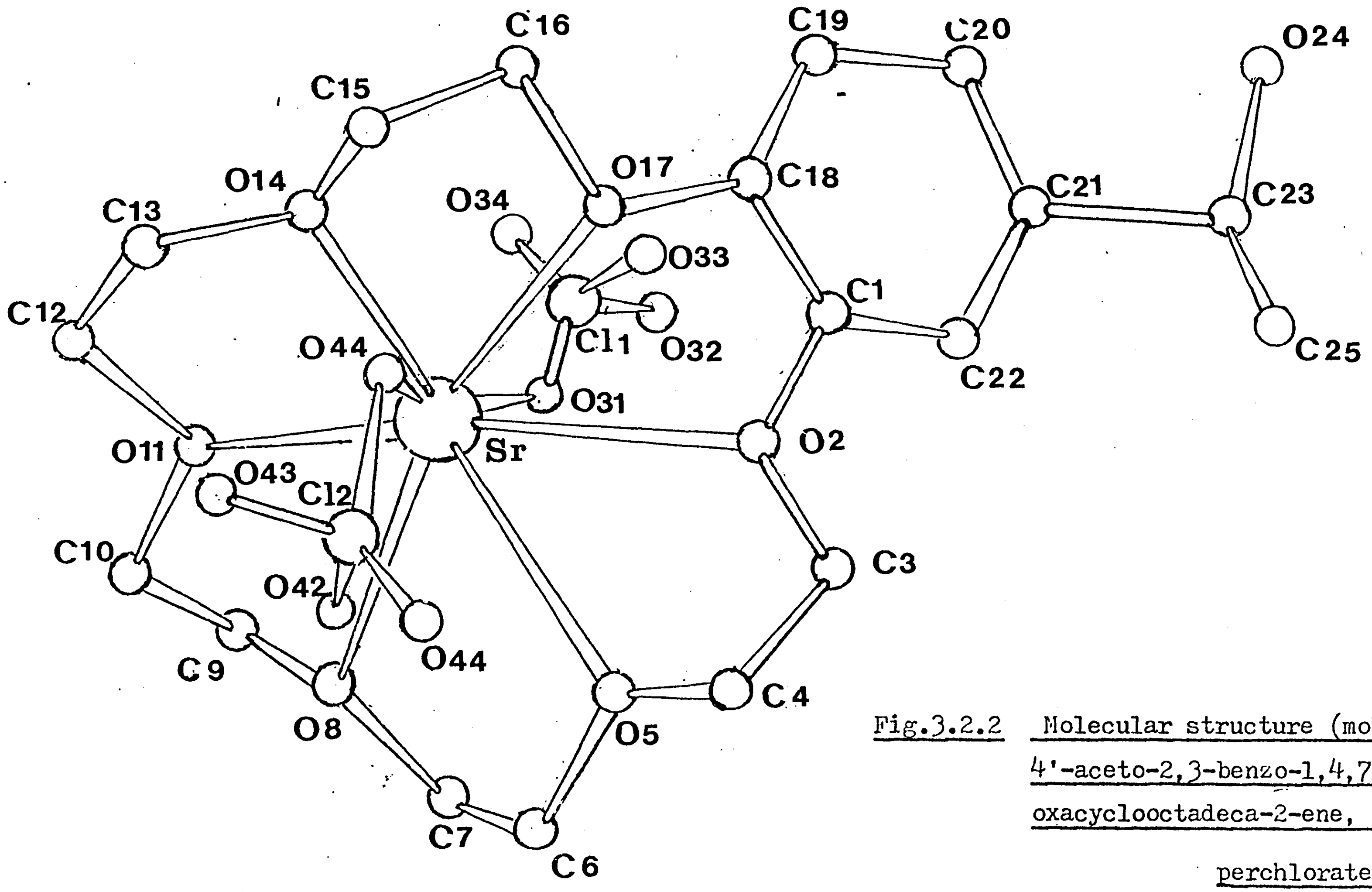


Fig.3.2.2 Molecular structure (molecule 2) for 4'-aceto-2,3-benzo-1,4,7,10,13,16-hexaoxacyclooctadeca-2-ene, strontium perchlorate.

Table 3.2.3.

Bond distances, with estimated standard deviation of errors in parentheses, for 4'-aceto-2,3-benzo-1,4,7,10,13,16-hexaoxacyclooctadec-2-ene, strontium perchlorate.

Distances in Angstroms.

	Molecule 1	Molecule 2.
Sr - O2	2.75(2)	2.75(1)
Sr - O5	2.66(3)	2.64(3)
Sr - O8	2.63(2)	2.63(2)
Sr - O11	2.68(2)	2.61(2)
Sr - O14	2.62(3)	2.68(3)
Sr - O17	2.78(2)	2.72(2)
Sr - O31	2.69(3)	2.72(3)
Sr - O41	2.55(3)	2.63(4)
Cl1 - O31	1.37(3)	1.39(3)
Cl1 - O32	1.47(2)	1.36(3)
Cl1 - O33	1.45(3)	1.42(3)
Cl1 - O34	1.40(2)	1.41(2)
Cl2 - O41	1.47(2)	1.53(3)
Cl2 - O42	1.39(4)	1.44(3)
Cl2 - O43	1.33(3)	1.37(3)
Cl2 - O44	1.41(3)	1.34(4)
C1 - O2	1.28(5)	1.27(6)
O2 - C3	1.46(5)	1.47(5)
C3 - C4	1.51(5)	1.52(6)
C4 - O5	1.42(5)	1.42(5)
O5 - C6	1.40(6)	1.41(5)
C6 - C7	1.49(5)	1.46(5)
C7 - O8	1.39(6)	1.42(5)
O8 - C9	1.58(5)	1.56(5)
C9 - C10	1.43(4)	1.43(5)
C10 - O11	1.49(5)	1.49(4)
O11 - C12	1.41(5)	1.42(5)
C12 - C13	1.43(5)	1.42(4)

Table 3.2.3 continued.

	Molecule 1	Molecule 2
C13 - O14	1.43(5)	1.45(5)
O14 - C15	1.42(5)	1.42(5)
C15 - C16	1.54(5)	1.52(5)
C16 - O17	1.46(6)	1.51(5)
O17 - C18	1.41(5)	1.40(6)
C18 - C19	1.28(6)	1.34(7)
C19 - C20	1.45(6)	1.40(5)
C20 - C21	1.44(6)	1.41(6)
C21 - C22	1.37(6)	1.36(6)
C1 - C22	1.43(6)	1.43(6)
C21 - C23	1.63(7)	1.46(7)
C23 - O24	1.11(6)	1.31(6)
C23 - C25	1.57(7)	1.58(7)

Table 3.2.4

Bond angles, with estimated standard deviation of errors in parentheses, for 4'-aceto-2,3-benzo-1,4,7,10,13,16-hexaoxacyclooctadec-2-ene, strontium perchlorate.

Angles in degrees.

	Molecule 1	Molecule 2
O2 - Sr - O5	61.9(7)	62.1(6)
O5 - Sr - O8	60.1(6)	60.9(6)
O8 - Sr - O11	66.0(7)	59.9(8)
O11 - Sr - O14	63.4(7)	60.6(7)
O14 - Sr - O17	60.8(6)	62.6(6)
O2 - Sr - O17	59.7(6)	58.1(6)
O31 - Sr - O2	83.2(7)	75.1(6)
O31 - Sr - O5	76.0(9)	79.2(8)
O31 - Sr - O8	76.0(7)	73.6(8)
O31 - Sr - O11	87.3(7)	104.1(7)
O31 - Sr - O14	122.5(7)	118.4(8)
O31 - Sr - O17	99.5(7)	91.7(7)
O41 - Sr - O2	79.4(7)	77.6(7)
O41 - Sr - O5	79.4(9)	117.8(8)
O41 - Sr - O8	97.5(7)	95.3(10)
O41 - Sr - O11	122.9(7)	103.1(8)
O41 - Sr - O14	81.8(8)	73.2(9)
O41 - Sr - O17	85.3(7)	71.2(8)
O31 - Sr - O41	154.5(8)	152.6(6)
O31 - Cl1 - O32	110(1)	110(2)
O31 - Cl1 - O33	109(2)	107(2)
O31 - Cl1 - O34	115(2)	105(1)
O32 - Cl1 - O33	106(2)	110(2)
O32 - Cl1 - O34	111(2)	112(2)
O33 - Cl1 - O34	106(2)	113(2)
O41 - Cl2 - O42	103(2)	111(2)
O41 - Cl2 - O43	114(2)	113(2)
O41 - Cl2 - O44	109(2)	96(2)
O42 - Cl2 - O43	130(2)	116(2)
O42 - Cl2 - O44	107(2)	100(2)
O43 - Cl2 - O44	93(2)	119(3)

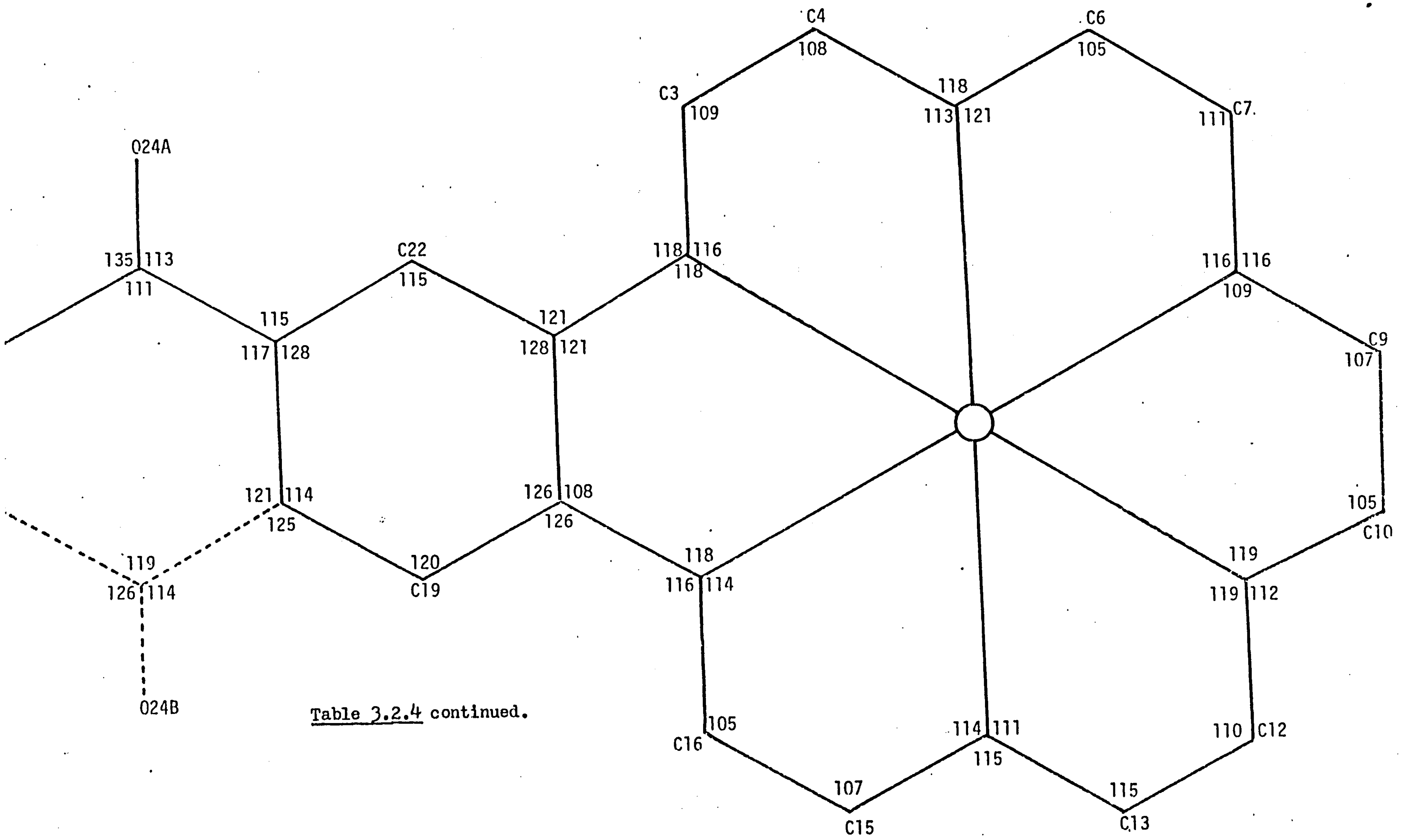
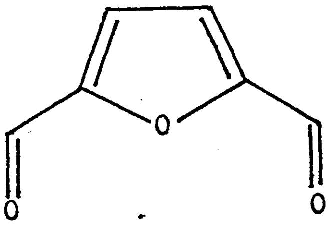


Table 3.2.4 continued.

3.3 The crystal and molecular structures of four related macrocyclic complexes.

3.3.1 Introduction.

Investigatory work[29] was conducted into the formation of macrocyclic complexes from α,ω-amino-ethers with furan-2, 5-dicarbaldehyde (18) and pyridine-2, 6-dicarbaldehyde (19) in the presence of alkaline earth metal cations.



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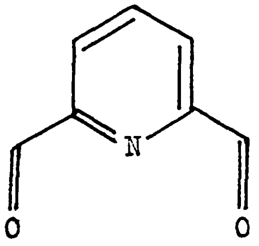

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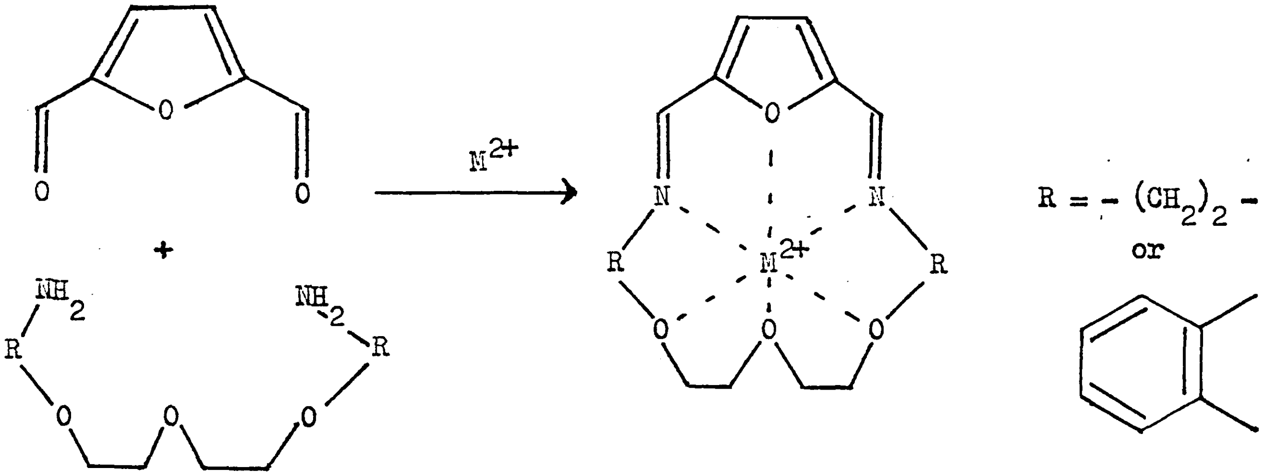
The reaction



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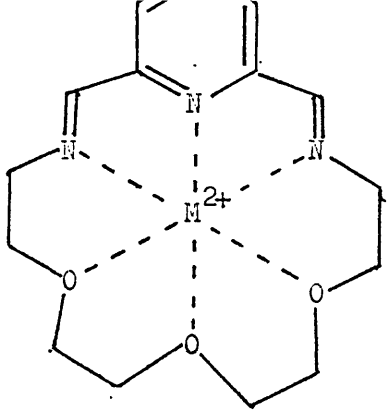
and the analogous reaction with (19) yielded a series of complexes with M = Ca, Sr, Ba but attempts to synthesise either the Mg^{2+} complex or the free macrocycle without the presence of metal ions failed. In order to fully compare the analogous complexes, a series of single crystal X-ray analyses were conducted on the following:

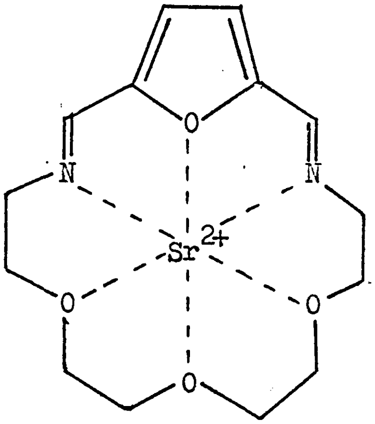
(i)



2 $NCS^-.nH_2O$

	(I)	(II)	(III)
M	Ca	Sr	Ba
n	0	1	1

(ii)



2 $NCS^-.H_2O$ (IV)

3.3.2 Crystal data

	(I)	(II)	(III)	(IV)
formula	$C_{17}H_{21}CaN_5O_3S_2$	$C_{17}H_{23}N_5O_4S_2Sr$	$C_{17}H_{23}BaN_5O_4S_2$	$C_{16}H_{22}N_4O_5S_2Sr$
M_r	447.6	513.2	562.9	502.1
a(Å)	9.624(2)	13.660(4)	13.626(4)	13.556(4)
b(Å)	26.103(7)	9.124(2)	9.355(2)	9.130(2)
c(Å)	8.636(2)	10.070(2)	9.999(2)	9.895(2)
α(°)	90.0	108.50(4)	109.28(4)	107.81(4)
β(°)	90.25(3)	108.42(4)	108.50(4)	109.10(4)
γ(°)	90.0	83.11(3)	82.75(3)	84.01(3)
D_c (Mg. m^{-3})	1.37	1.51	1.64	1.51
D_m (Mg. m^{-3})	1.40	1.50	1.66	1.58
Z	4	2	2	2
F(000)	936	524	560	512
μ(Mo-Kα)(cm^{-1})	4.53	25.35	18.2	25.98
systematic absences	0k0, k=2n+1; h0l, l=2n+1	-	-	-
crystal system	monoclinic	triclinic	triclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$

The space group for the three triclinic crystals was assumed to be $P\bar{1}$ and this was confirmed by subsequent structure solution.

3.3.3 Data collection and structure analysis

All crystals were white and opaque and details of data collection are summarised in Table 3.3.1. All crystals were mounted about the a axis of the Stöe Stadi 2 two circle diffractometer.

	(I)	(II)	(III)	(IV)
Crystal dimensions (mm.)	0.24x0.36x0.44	0.18x0.22x0.38	0.14x0.26x0.36	0.26x0.16x0.33
No. of layers collected	11(0kl→10kl)	17(0kl→16kl)	17(0kl→16kl)	11(0kl→10kl)
No. of independent reflections	3700	4670	4795	5011
No. of reflections used for structure analysis with minimum value of $I/\sigma(I)$ ratio in parenthesis	2084 (3)	1999 (4)	4061 (4)	3285 (4)

Table 3.3.1

Corrections were made for Lorentz and polarisation factors but not for absorption. Initial trial solutions were obtained using direct methods. Initially, reflections having $E \gg 1.2$ were included but the SHELX direct methods package automatically raised the value to 1.4 for the strontium structures (II and IV) and to 1.5 for the barium structure (III). The E-statistics (as discussed in section 1.3.2) confirmed the centrosymmetric nature of the triclinic crystals. In all cases, the trial solution showed the position of the metal ion, the sulphur atoms and most of the non-hydrogen atoms in the macrocyclic ring. All remaining atoms, including hydrogen atoms, were located from successive Fourier difference syntheses. Refinement was by least square full-matrix techniques with non-hydrogen atoms given anisotropic temperature factors in the later stages of refinement. Hydrogen atoms were given ideal positions with C-H distances of 1.08Å and O-H distances (except for (IV)) of 1.04Å: a common isotropic temperature factor was used for the hydrogen atoms (Table 3.3.2). For structure IV, the hydrogen atoms attached to the oxygen atom of the water molecule were refined independently, giving an average O-H distance of 1.07Å. In the final stages of refinement, a weighting scheme of the form $w = a/\left[\sigma^2(F_o) + b(F_o)^2\right]$ was used. Values for a, b, the final values for R and R_w and the highest residue peak on the final Fourier synthesis are given in Table 3.3.2.

	I	II	III	IV
a	0.0534	0.4970	2.1299	1.4695
b	0.0555	0.0903	0.0005	0.0044
R	0.0384	0.0474	0.0311	0.0568
R_w	0.0501	0.0538	0.0307	0.0590
Common isotropic temperature factor for hydrogen atoms (Å) (errors in parentheses)	0.1109	0.0734	0.1025	0.0862
Highest residue peak on final Fourier synthesis	0.56	0.68	1.30*	1.03*

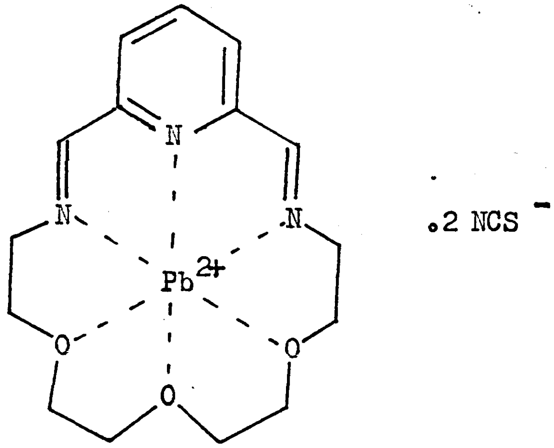
* Peak located within 1Å of metal ion

Table 3.3.2

Hydrogen bonding was found to be present in the two strontium structures (II), (IV). The closest intermolecular distances for the remaining structures, (I) and (III), (both being H .... H distances) are, respectively, 2.53 and 2.42Å. Tables of final positional parameters and temperature factors, mean planes, torsion angles and structure factors are given, respectively in Appendices A1.7-10, A2.7-10, A3.7-10, A4.7-10. Figures showing molecular structures (and crystal structure for (I)), tables of bond angles and lengths are contained at the end of 3.3.4.

3.3.4 Description of structures

There is a progressive displacement of the metal ion from the mean plane containing the macrocyclic donor atoms, the extent of the displacement reflecting the relative sizes of the ions. The effect is further illustrated by the analogous lead complex (21)[66] - the lead (II) ion having an ionic radius between that of the calcium and strontium ions.



(V in tables and discussion below)

21.

The displacements are also illustrated by the X1-M-O2 bond angles (I-III, V, X=N; IV, X=O) and results are shown in Table 3.3.3.

	I	II	III	IV	V
Distance of metal ion below plane of donor atoms (Å)	0.01	0.53	0.86	0.56	0.41
X1-M-O_2 bond angle (°), (I-III, V, X=N; IV, X=O)	175.6	146.0	139.4	144.7	143.8

Table 3.3.3.

The heterocyclic ring in all structures is so inclined that the metal ion is close to the mean plane through the ring: the aromatic ring progressively making a larger angle with the best mean plane of the donor atoms as the metal ion size increases (Table 3.3.4).

	I	II	III	IV	V
Angle (°) between donor atom plane and heterocyclic ring	9.3	17.1	18.6	18.2	19.9
Distance (Å) of M^{2+} from the heterocyclic ring plane	0.11	0.015	0.09	0.04	0.01

Table 3.3.4.

Average M-O(ring) and M-N(ring) distances for the five structures are shown in Table 3.3.5.

	I	II	III	IV	V
Av. M-O(ring) distance (Å)	2.64	2.78	2.84	2.74	3.06
Av. M-N(ring) distance (Å)	2.64	2.78	2.85	2.79	2.62

Table 3.3.5.

It is clear from the table that there is no effective preference of the metal ion for either oxygen or nitrogen in Structures I to IV but that the lead ion shows a strong preference for the N atoms. While there is indication of some covalent character to the Pb-N bonds, the Pb-O interactions would appear to be essentially electrostatic.

In (I), calcium is found to be 8-coordinate with trans bonding to the N atoms of the thiocyanate groups completing the coordination of the six macrocyclic donor atoms. The larger strontium and barium ions are both able to attain higher coordination numbers than calcium (Figure 3.3.1). Both attain a coordination number of nine by interaction with the six donor atoms of the ring, two thiocyanate nitrogen atoms and with one water molecule situated on the opposite side of the ring to the two thiocyanate ions (Figures 3.3.3, 3.3.4 and 3.3.5). In both cases, the water molecule is strongly bonded to the metal ion with the Sr-O(water) and Ba-O(water) distances being significantly shorter (2.59Å in II; 2.79Å in III; 2.58Å in IV) than the M-O(ring) distances, (Table 3.3.5).

The apparent strain-free nature of the macrocyclic ring in II, III and IV may be seen by examination of the torsion angles. Thus, torsion angles about the C-O and C-C bonds lie close to the expected values of 180° and ±60° respectively (Appendices A3.8, A3.9, A3.10). In (I), however, there would appear to be considerable strain within the macrocyclic ring for the torsion angle about O3-C13 is only -132° and several other angles show more than 10° variations from ideal values (Appendix A3.7).

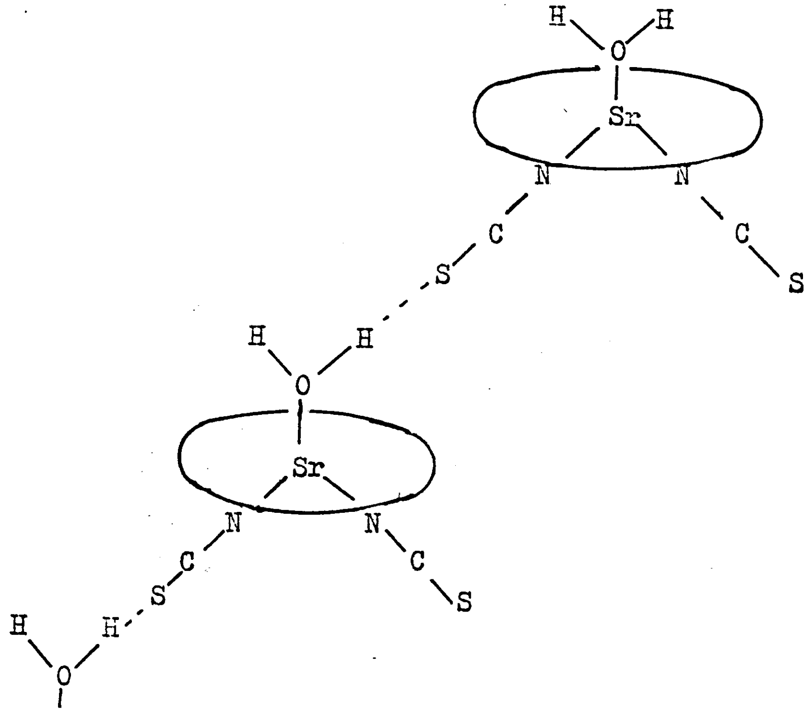
The characteristic shortening of the C-C distances in the macrocyclic rings (cf. 3.2.2) is found for structures (I) to (IV). The average C-C (macrocyclic ring) distances are shown in Table 3.3.6.

	I	II	III	IV
Average C-C distance in macrocyclic ring (Å)	1.467	1.478	1.493	1.500

Table 3.3.6.

It is noticeable that the shortest C-C(ring) distances correspond to the structure with the greatest apparent ring strain whilst the largest C-C(ring) distances are found in the barium complex (III) wherein few torsion angles deviate by more than 5° from expected values (similar results are recorded for (IV) - Appendix A3.9). While it is difficult to see any theoretical reason for such shortening of the C-C distances or any relationship with ring strain, the data in the present complexes suggest that such a link exists. A similar relationship is found for the strontium and barium complexes of benzo-18-crown-6[58]. There, the strontium complex has the longer C-C (ring) distances and the torsion angles deviate less from expected values than for the barium complex.

The very close similarity between the two strontium complexes((II) and (IV)) is illustrated in the tables of bond lengths and angles. This indicates that the substitution of a furanyl for a pyridinyl grouping in the transition from (II) to (IV) has no noticeable effect on the configuration of the macrocyclic ring: in particular, the substitution of an oxygen donor atom for a nitrogen atom did not affect the bonding of the strontium ion to the macrocyclic ring. In (II) and (IV), the complexes are linked together in chains by hydrogen bonding involving the water molecule of one complex with the sulphur atom of a neighbouring thiocyanate group:



No similar bonding was found in the barium complex (III).

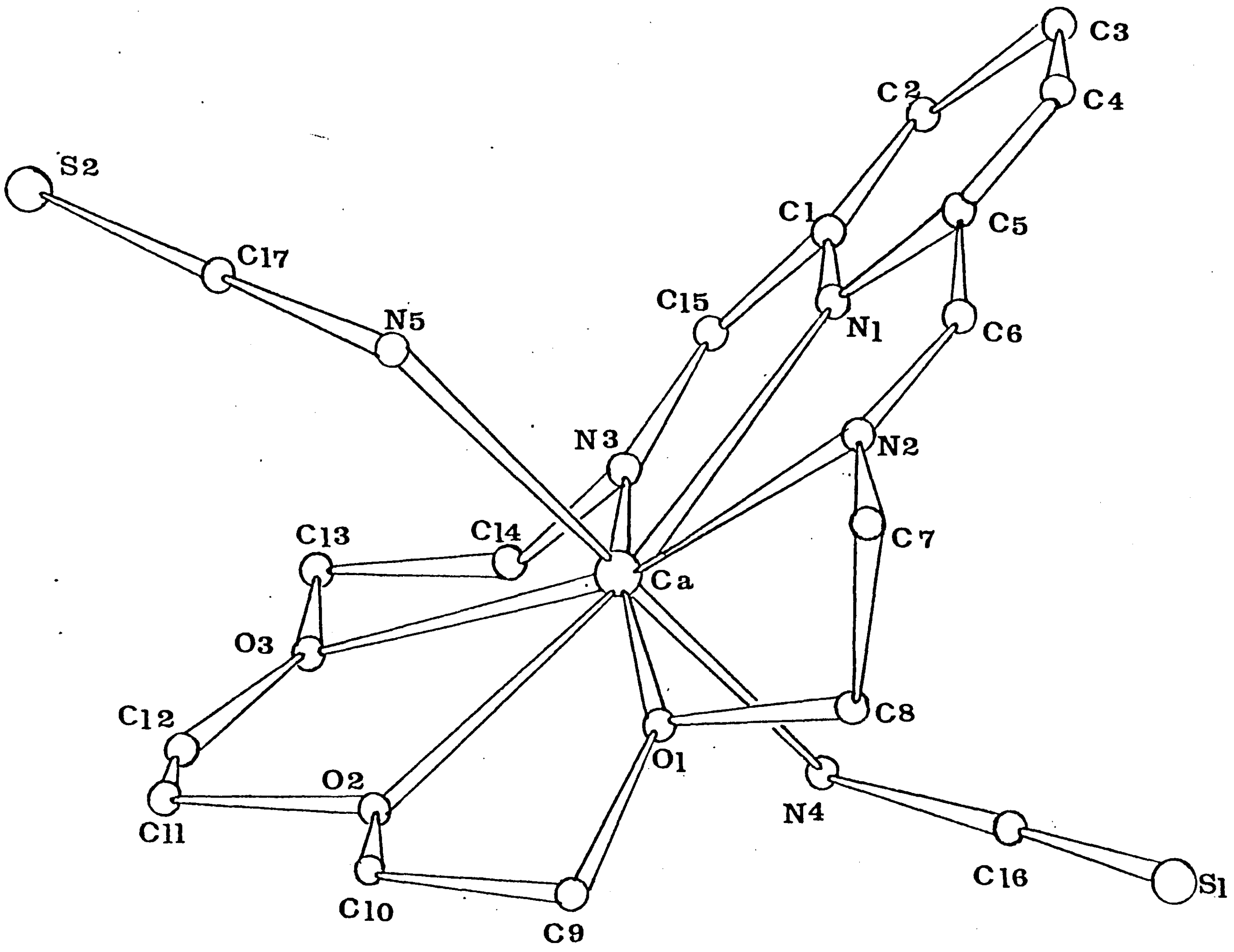


Fig. 3.3.1 Molecular structure of isothiocyanato(3,15,21-triaza-6,9,12-trioxabicyclo(15.3.1) heneicosa-1(21),2,15,17,19-pentaene) calcium (II).

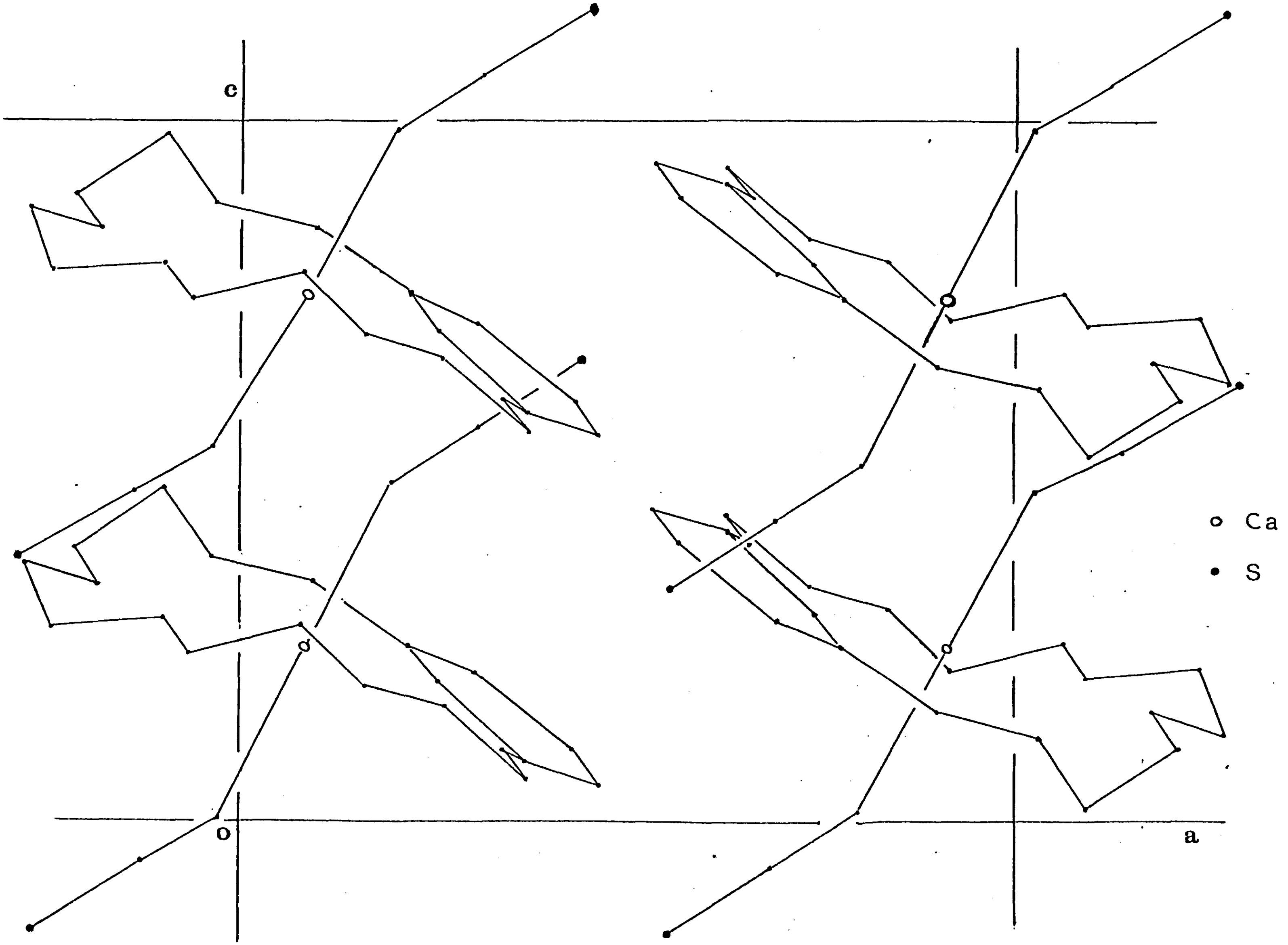


Fig. 3.3.2 Crystal structure of isothiocyanato(3,15,21-triaza-6,9,12-trioxabicyclo(15.3.1)heneicosa-1(21),2,15,17,19-pentaene) calcium (II).

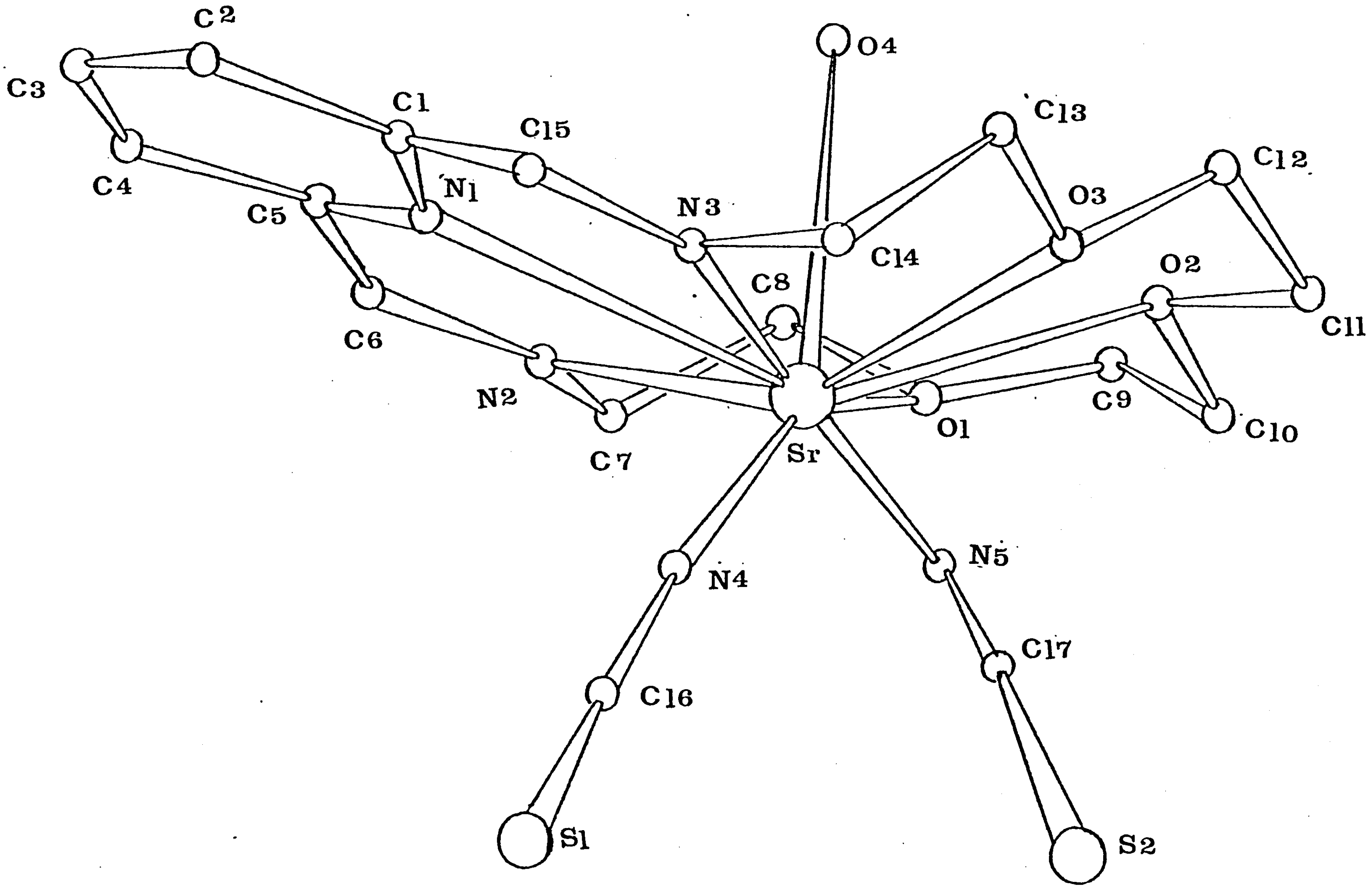


Fig. 3.3.3 Molecular structure of aqua-di-isothiocyanato(3,15,21-triaza-6,9,12-trioxabicyclo(15.3.1) heneicosa-1(21),2,15,17,19-pentaene) strontium (II).

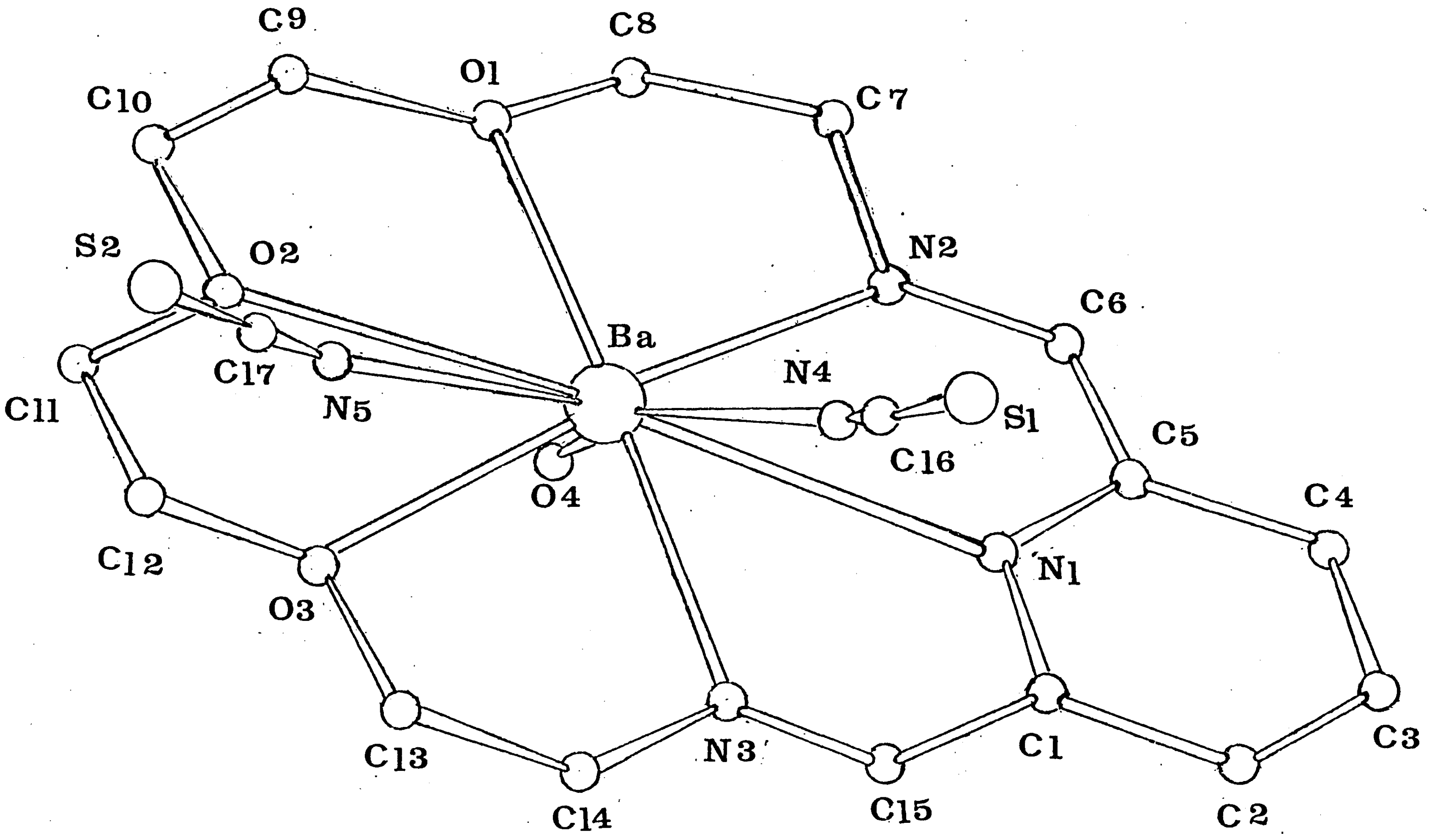


Fig. 3.3.4 Molecular structure of aqua-di-isothiocyanato(3,15,21-triaza-6,9,12-trioxabicyclo(15.3.1) heneicosa-1(21),2,15,17,19-pentaene) barium (II).

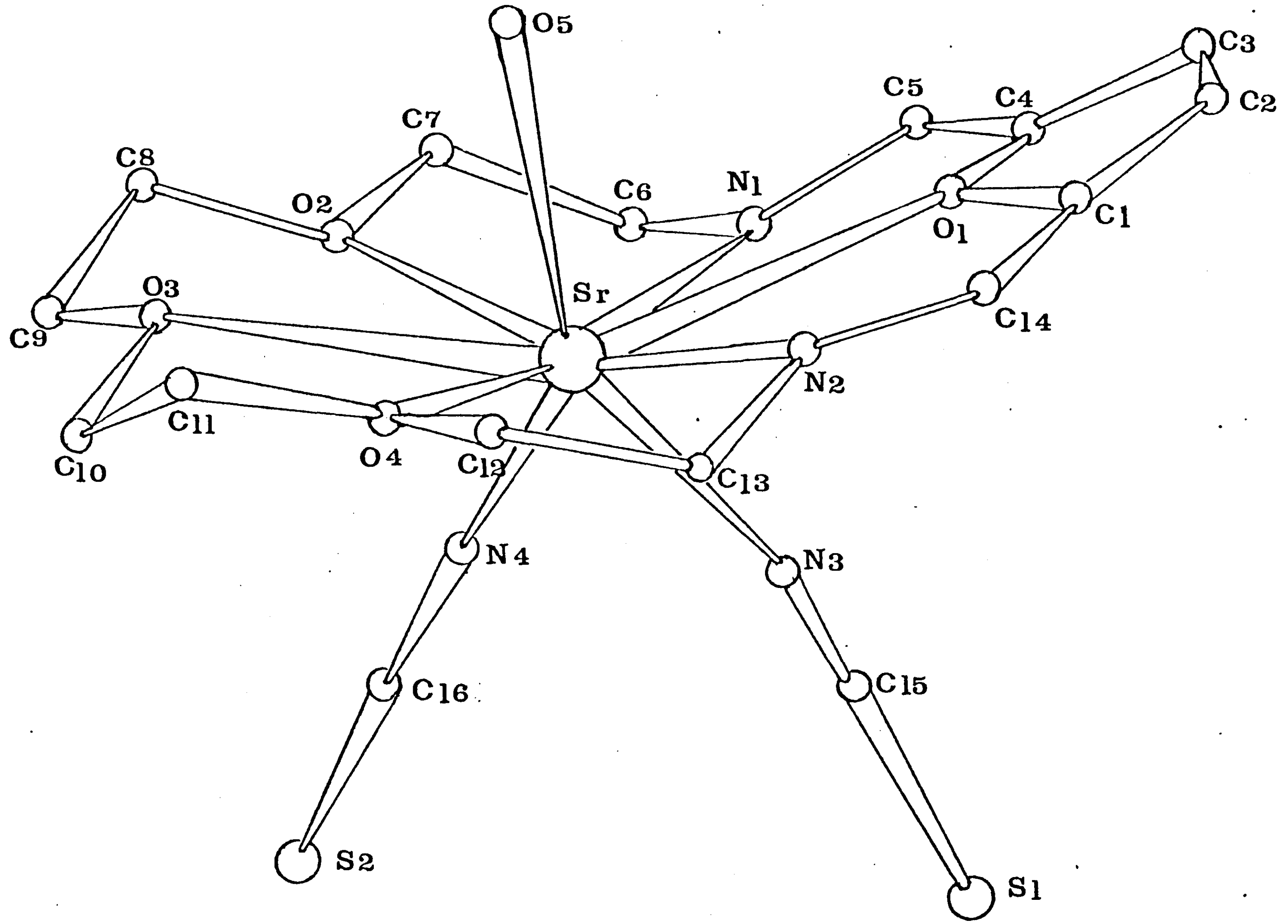


Fig. 3.3.5 Molecular structure of aqua-di-isothiocyanato(3,15-diaza-6,9,12,20-tetraoxabicyclo (15.2.1)eicosa-2,15,17,19-tetraene) strontium (II).

Table 3.3.7 Bond distances, with standard deviations of errors in parentheses, for $Ca(NCS)_2.L$ (I); $Sr (NCS)_2.H_2O.L$ (II) and $Ba(NCS)_2.H_2O.L$ (III) where L is the ligand 3,5,21-triaza-6,9,12-trioxabicyclo (15.3.1) heneicosa-1(21), 2,15,17,19-pentaene

Distances in Å

	I (M = Ca)	II (M = Sr)	III (M = Ba)
M - N1	2.656(3)	2.824(9)	2.886
M - N2	2.634(4)	2.750(12)	2.817
M - N3	2.625(4)	2.759(7)	2.856
M - N4	2.392(4)	2.653(8)	2.823
M - N5	2.363(5)	2.638(13)	2.821
M - O1	2.614(3)	2.790(7)	2.863(5)
M - O2	2.615(4)	2.742(8)	2.806(4)
M - O3	2.701(5)	2.800(8)	2.844(5)
M - O4	-	2.583(8)	2.793(6)
N1 - C1	1.341(5)	1.351(11)	1.350(5)
N1 - C5	1.324(6)	1.320(16)	1.331(7)
C1 - C2	1.400(7)	1.387(16)	1.376(7)
C2 - C3	1.362(10)	1.357(20)	1.367(9)
C3 - C4	1.386(8)	1.393(16)	1.383(7)
C4 - C5	1.400(8)	1.357(17)	1.373(7)
C1 - C15	1.451(7)	1.472(19)	1.451(8)
C5 - C6	1.469(7)	1.502(13)	1.490(6)
C6 - N2	1.252(6)	1.248(16)	1.239(7)
N2 - C7	1.463(6)	1.478(13)	1.467(6)
C7 - C8	1.493(8)	1.462(17)	1.497(6)
C8 - O1	1.419(8)	1.421(20)	1.411(9)
O1 - C9	1.429(7)	1.427(15)	1.431(6)
C9 - C10	1.459(7)	1.471(25)	1.473(10)
C10- O2	1.428(7)	1.440(12)	1.434(5)
O2 - C11	1.426(8)	1.411(7)	1.424(8)
C11- C12	1.439(11)	1.481(15)	1.501(7)
C12- O3	1.343(9)	1.435(11)	1.432(5)
O3 - C13	1.428(8)	1.424(11)	1.431(5)
C13- C14	1.478(10)	1.498(13)	1.510(6)
C14- N3	1.430(8)	1.427(18)	1.447(8)
N3 - C15	1.260(6)	1.262(16)	1.249(7)

	I (M = Ca)	II (M = Sr)	III (M = Ba)
S1 - C16	1.620(5)	1.645(9)	1.630(4)
C16 - N4	1.155(7)	1.139(12)	1.146(6)
S2 - C17	1.616(5)	1.636(13)	1.624(6)
C17 - N5	1.165(7)	1.174(17)	1.141(8)
Hydrogen bond			
S_1 - H_{w2}		2.392(11)	
H5A .... H'8B			2.417
H33 .... H'131	2.353		

Table 3.3.8. (IV)

Bond distances for aqua-di-isothiocyanato(3,15-diaza-6,9,12,20-tetraoxabicyclo(15.2.1)eicosa-2,15,17,19-tetraene)strontium(II). Standard deviations of errors in parentheses. Distances in Å.

Sr - 01 = 2.723(6)

Sr - 02 = 2.762(6)

Sr - 03 = 2.701(5)

Sr - 04 = 2.756(6)

Sr - 05 = 2.583(6)

Sr - N1 = 2.797(9)

Sr - N2 = 2.792(6)

Sr - N3 = 2.622(7)

Sr - N4 = 2.651(10)

N3 - C15 = 1.172(10)

S1 - C15 = 1.640(7)

N4 - C16 = 1.152(13)

S2 - C16 = 1.636(10)

05 - HW1 = 0.964(8)

05 - HW2 = 1.174(6)

C1 - C2 = 1.360(16)

C2 - C3 = 1.430(18)

C3 - C4 = 1.365(13)

C1 - 01 = 1.380(9)

01 - C4 = 1.360(13)

C4 - C5 = 1.449(13)

C5 - N1 = 1.271(12)

N1 - C6 = 1.460(11)

C6 - C7 = 1.486(13)

C7 - 02 = 1.429(16)

02 - C8 = 1.428(11)

C8 - C9 = 1.489(11)

C9 - 03 = 1.436(9)

03 - C10 = 1.414(13)

C10 - C11 = 1.496(12)

C11 - 04 = 1.425(9)

04 - C12 = 1.430(9)

C12 - C13 = 1.530(11)

C13 - N2 = 1.458(14)

N2 - C14 = 1.278(12)

C1 - C14 = 1.446(15)

H bond

HW1 - S1′ = 2.323.

Table 3.3.9 Bond angles, with standard deviations of errors in parentheses for Ca (NCS)$_2$.L (I); Sr (NCS)$_2$.H$_2$O.L (II) and Ba (NCS)$_2$.H$_2$O.L (III) where L is the ligand 3,5,21-triaza-6,9,12 -trioxabicyclo (15.3.1) heneicosa - 1(21),2,17,19 - pentaene

Angles in degrees

	I (M = Ca)	II (M = Sr)	III (M = Ba)
N1 - M - N2	60.5(1)	57.6(2)	57.3(2)
N1 - M - N3	60.5(1)	58.6(3)	56.3(2)
N1 - M - N4	89.2(1)	73.9(3)	76.3(2)
N1 - M - N5	90.4(1)	141.1(3)	145.2(3)
N1 - M - O1	121.7(1)	116.0(3)	112.9(2)
N1 - M - O2	175.6(1)	146.0(2)	139.4(2)
N1 - M - O3	116.8(1)	113.0(2)	109.6(2)
N1 - M - O4	-	77.2(3)	74.5(2)
N2 - M - N3	120.4(1)	116.1(3)	113.6(3)
N2 - M - N4	89.6(1)	72.7(3)	75.4(2)
N2 - M - N5	87.4(2)	125.6(3)	129.5(3)
N2 - M - O1	61.5(1)	60.2(3)	58.3(2)
N2 - M - O2	123.0(1)	115.7(2)	112.4(2)
N2 - M - O3	168.2(1)	159.1(2)	153.4(2)
N2 - M - O4	-	83.6(3)	81.3(2)
N3 - M - N4	96.8(1)	87.5(3)	90.9(2)
N3 - M - N5	85.9(1)	102.1(3)	106.2(3)
N3 - M - O1	167.4(1)	167.9(3)	159.2(2)
N3 - M - O2	116.4(1)	118.1(2)	115.6(2)
N3 - M - O3	59.9(1)	59.2(2)	58.0(2)
N3 - M - O4	-	85.7(3)	80.5(2)
N4 - M - N5	176.7(2)	71.8(3)	74.1(3)
N4 - M - O1	95.6(1)	101.5(3)	104.1(2)
N4 - M - O2	88.2(1)	139.1(3)	143.0(2)
N4 - M - O3	78.8(2)	124.9(3)	126.8(2)
N4 - M - O4	-	149.4(4)	149.4(2)
N5 - M - O1	81.8(1)	88.4(3)	91.9(2)
N5 - M - O2	92.3(1)	71.9(3)	74.0(2)
N5 - M - O3	104.3(2)	74.1(3)	75.3(2)
N5 - M - O4	-	138.8(3)	136.5(2)
O1 - M - O2	62.2(1)	59.4(2)	59.0(2)
O1 - M - O3	121.2(1)	119.5(2)	119.3(2)

	I (M = Ca)	II (M = Sr)	III (M = Ba)
O1 - M - O4	-	82.4(3)	79.3(2)
O2 - M - O3	59.2(1)	60.1(2)	60.4(2)
O2 - M - O4	-	68.9(3)	64.9(2)
O3 - M - O4	-	75.9(3)	72.6(2)
N1 - C1 - C2	122.3(5)	122.6(12)	122.7(5)
N1 - C1 - C15	115.2(4)	115.8(10)	117.4(4)
N1 - C5 - C4	123.3(4)	123.6(10)	122.4(4)
N1 - C5 - C6	115.9(4)	114.4(9)	117.1(4)
C1 - C2 - C3	119.4(5)	119.6(9)	118.1(4)
C2 - C3 - C4	118.9(6)	117.3(12)	119.9(5)
C3 - C4 - C5	118.2(6)	119.9(14)	118.4(6)
C4 - C5 - C6	120.8(5)	122.0(12)	120.5(5)
C5 - C6 - N2	119.4(5)	120.6(12)	120.9(5)
C6 - N2 - C7	118.1(4)	118.9(12)	119.2(5)
N2 - C7 - C8	108.6(5)	110.2(10)	108.7(4)
C7 - C8 - O1	106.4(4)	109.8(11)	107.9(5)
C8 - O1 - C9	113.0(4)	112.3(10)	111.7(4)
O1 - C9 - C10	106.6(5)	108.0(11)	108.1(5)
C9 - C10 - O2	108.2(5)	107.8(11)	108.5(5)
C10 - O2 - C4	113.7(5)	111.5(9)	113.5(4)
O2 - C11 - C12	116.6(6)	108.5(8)	109.0(5)
C11 - C12 - O3	111.9(6)	109.5(8)	109.3(4)
C12 - O3 - C13	115.7(6)	112.9(7)	110.8(3)
O3 - C13 - C14	108.9(6)	106.5(7)	108.2(3)
C13 - C14 - N3	108.0(5)	110.1(9)	107.6(4)
C14 - N3 - C15	118.6(4)	118.9(8)	118.3(4)
N3 - C15 - C1	120.2(4)	121.8(9)	120.7(4)
C15 - C1 - C2	122.5(4)	121.5(9)	119.9(4)
C1 - N1 - C5	117.9(4)	116.8(9)	118.4(4)
S1 - C16 - N4	179.9(1)	179.2(10)	179.2(4)
S2 - C17 - N5	178.7(4)	179.1(12)	179.5(5)
M - N4 - C16	148.3(4)	167.5(11)	163.0(4)
M - N5 - C17	150.0(4)	166.8(10)	163.2(4)
H_{w2} - C4 - H_{w2}	-	116.1(12)	109.5(5)
O4 - H_{w2} - S1'	-	148.0(11)	-

Table 3.3.10. (IV)

Bond angles for aqua-di-isothiocyanato(3,15-diaza-6,9,12,20-tetraoxabicyclc(15.2.1)eicosa-2,15,17,19-tetraene)strontium(II). Standard deviations of errors in parentheses.

Angles in degrees.

01 - Sr - 02 = 113.6(2)
01 - Sr - 03 = 144.7(2)
01 - Sr - 04 = 112.1(2)
01 - Sr - 05 = 76.4(2)
01 - Sr - N1 = 56.1(2)
01 - Sr - N2 = 56.7(2)
01 - Sr - N3 = 72.5(2)
01 - Sr - N4 = 142.8(2)
02 - Sr - 03 = 60.6(2)
02 - Sr - 04 = 122.2(2)
02 - Sr - 05 = 81.3(2)
02 - Sr - N1 = 59.4(2)
02 - Sr - N2 = 164.6(2)
02 - Sr - N3 = 103.3(2)
02 - Sr - N4 = 87.2(3)
03 - Sr - 04 = 61.6(2)
03 - Sr - 05 = 68.4(2)
03 - Sr - N1 = 115.9(2)
03 - Sr - N2 = 119.0(2)
03 - Sr - N3 = 141.8(2)
03 - Sr - N4 = 72.0(2)
04 - Sr - 05 = 76.9(2)
04 - Sr - N1 = 158.4(2)
04 - Sr - N2 = 59.5(2)
04 - Sr - N3 = 123.1(3)
04 - Sr - N4 = 76.9(2)
05 - Sr - N1 = 82.5(2)
05 - Sr - N2 = 84.5(2)
05 - Sr - N3 = 147.7(3)
05 - Sr - N4 = 139.4(2)
N1 - Sr - N2 = 112.8(2)
N1 - Sr - N3 = 73.2(3)
N1 - Sr - N4 = 123.9(3)
N2 - Sr - N3 = 85.7(2)
N2 - Sr - N4 = 107.6(3)
N3 - Sr - N4 = 72.9(3)
C1 - 01 - C4 = 107.4(7)
01 - C4 - C3 = 109.8(9)
C2 - C3 - C4 = 106.7(10)
C1 - C2 - C3 = 106.5(9)
01 - C1 - C2 = 109.6(9)
01 - C4 - C5 = 113.6(8)
C4 - C5 - N1 = 118.1(10)
C5 - N1 - C6 = 118.7(9)
N1 - C6 - C7 = 109.1(8)
C6 - C7 - 02 = 108.8(9)
C7 - 02 - C8 = 111.6(8)
02 - C8 - C9 = 108.3(8)

Table 3.3.10 continued.

Angles in degrees.

C8 - C9 - O3 = 107.2(8)
C9 - O3 - C10 = 112.9(7)
O3 - C10 - C11 = 108.9(8)
C10 - C11 - O4 = 109.1(7)
C11 - O4 - C12 = 110.6(6)
O4 - C12 - C13 = 107.9(6)
C12 - C13 - N2 = 107.3(7)
C13 - N2 - C14 = 117.7(7)
N2 - C14 - C1 = 118.1(7)
C2 - C1 - C14 = 135.9(8)
O1 - C1 - C14 = 114.4(8)
C3 - C4 - C5 = 136.6(11)
Sr - N4 - C16 = 167.2(7)
Sr - N3 - C15 = 163.6(7)
N3 - C15 - S1 = 177.5(6)
N4 - C16 - S2 = 178.2(7)
HW1 - O5 - HW2 = 105.8(7)
O5 - HW2 - S1' = 93.4

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Chapter 4

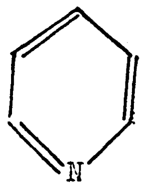
The Structure and Reactivity of Heterocyclic Phosphorus Ring Systems

Contents

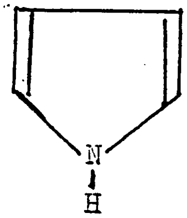
4. Structure and Reactivity of Heterocyclic Phosphorus Ring Systems.

4.1 Introduction

While pyrrole, pyridine, indole, carbazole



pyridine



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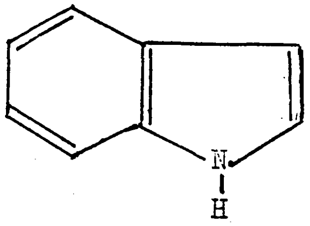
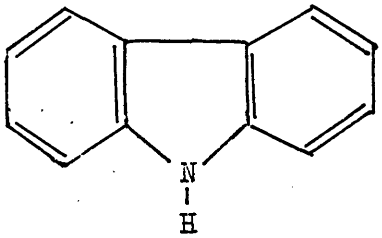
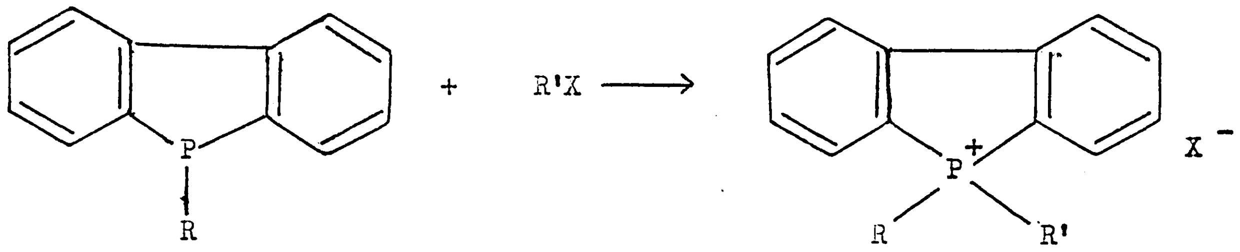


indole



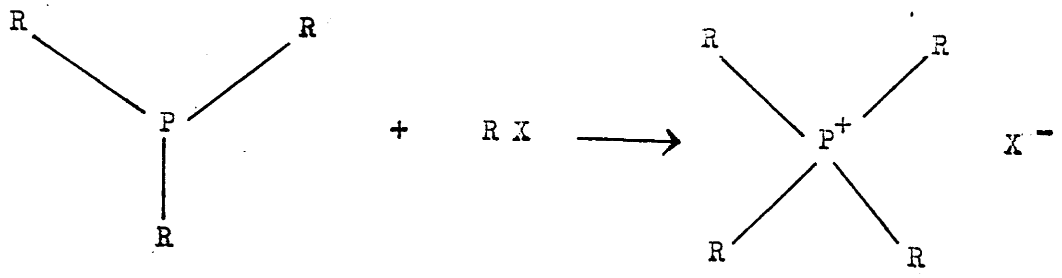
carbazole

and other N-substituted derivatives are extensively delocalised, the extent to which the analogous phospholes and their benzologues have aromatic character is a subject of controversy. Much data have been obtained in experiments aimed at assessing the degree of delocalisation in the phosphole system[1-8]. Much of the work which has been reported as indicating some degree of delocalisation of the lone pair in dibenzophospholes is based on either the conversion of a quaternary derivative to the parent dibenzophosphole or the reverse process of the formation of quaternary derivatives. Thus, the typical quaternisation reaction of the type:



(1) R = Ph

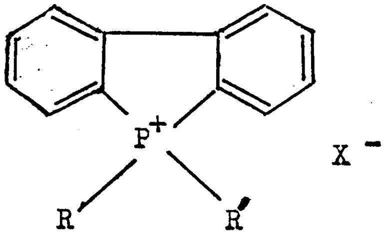
is far slower than for the analogous reaction with the acyclic phosphine:



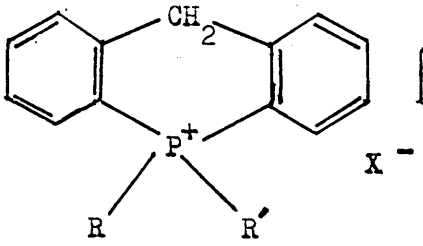
The differing speeds of the two reactions have been interpreted[2-6] as implying that the lone pair on phosphorus is less available in the phosphole, due to delocalisation, than it is in the acyclic phosphine. Doubt has been cast on this interpretation and Schäfer et alia, for example, have suggested[7] that the lone pair takes no part in five-membered ring conjugation. It is also found that, while 5-phenyldibenzophosphole (1) undergoes quaternization approximately five times more slowly than triphenylphosphine, the energy of activation is roughly similar[8]. Further, the phosphole (1) undergoes many reactions that are typical of a normal tertiary phosphine suggesting that any delocalisation is clearly small[1].

An alternative interpretation of much of the kinetic data may be offered in terms of ring strain in the heterocyclic ring. The very rapid rate of nucleophilic attack at the phosphonium centre of dibenzophospholium salts[9,10] may be associated with relief of ring strain attending formation of trigonal bipyramidal intermediates. The increase in predicted ring strain in passing from the parent dibenzophosphole (1) (in which, by analogy to the reported structure of 1 - benzylphosphole[11], a bond angle of ca. 90° for the endocyclic angle at P is expected) to the quaternary derivative may well account for the reduced rate of quaternisation of 5 - phenyldibenzophosphole relative to triphenylphosphine[12].

In order to investigate the extent of ring strain within phospholium ring systems, it was proposed to examine the crystal structures of the related quaternary systems (2), (3) and (4).



(2)



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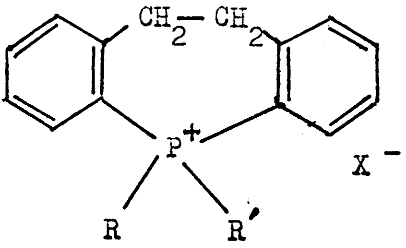
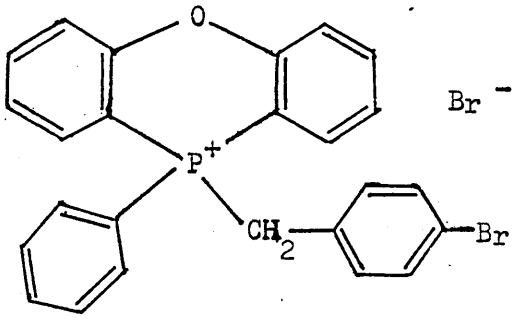


(4)

While suitable crystals were available for the phospholium salt (2) [R = phenyl; R′ = CH_2.  Br; X = Br], no crystals suitable for single crystal studies could be obtained for the six- and seven-membered ring systems. However, crystals of the related systems (5), (6) were suitable for crystallographic study and single crystal analyses were undertaken.



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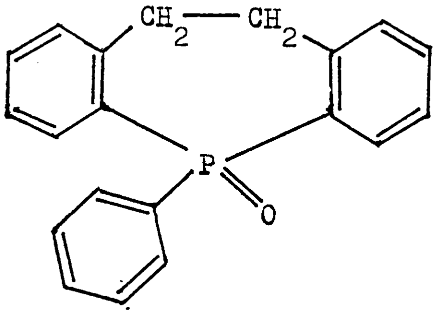
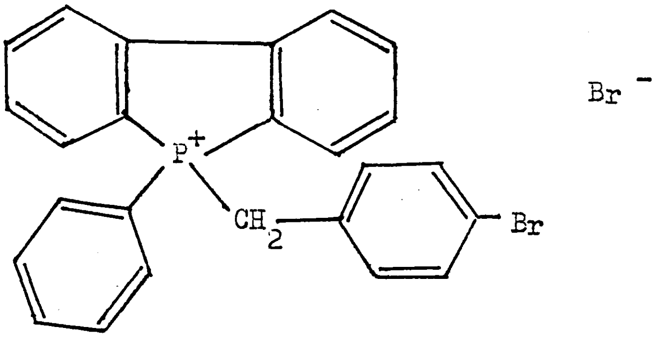


(6)

4.2 The Crystal and Molecular Structure of 5 - (p-Bromobenzyl) - 5 - phenyl - dibenzophospholium bromide



(7)

4.2.1 Crystal data:

$C_{25}H_{19}Br_2P.0.5H_2O$	$M_r = 519.2$	monoclinic
$a = 25.685\ (15)$	$b = 10.444\ (6)$	$c = 18.818\ (11)$ Å
$\beta = 119.18\ (5)^\circ$	$D_m = 1.56\ Mg.m^{-3}$	$D_c = 1.57\ Mg.m^{-3}$
$Z = 8$	$F(000) = 2080$	$\mu(M_o - K\alpha) = 36.6\ cm^{-1}$

Systematic absences:

hkl, $h + k = 2n + 1$; h0l, $l = 2n + 1$ $(h = 2n + 1)$.

These systematic absences do not distinguish between the space groups Cc and C2/c but the centrosymmetric C2/c was assumed and shown by subsequent analysis to be correct.

4.2.2. Data collection and structure refinement:

A colourless crystal of approximate dimensions 0.18 x 0.26 x 0.34 mm was mounted about the b axis . 12 layers, h0l → h11l were collected; 2773 independent reflections were recorded of which 992, having $I / \sigma(I) \geqslant 2.5$, were used for structure solution. Lorentz and polarization factors were applied but no absorption corrections were made. The positions of the bromine atoms were determined from a three dimensional Patterson synthesis and the remaining atoms (including hydrogen atoms) were located from successive Fourier synthesis difference maps. The structure was refined by full-matrix least squares methods; hydrogen atoms were given a common isotropic temperature factor (which refined to a final value of $U = 0.034\text{Å}^2$) and placed in positions calculated from the geometry of the molecule (C-H= 1.08Å). Non-hydrogen atoms were given anisotropic temperature factors in the final stages of refinement and a weighting scheme of the form:

$$w = 0.1277/[\sigma^2(F_o) + 0.046\,(F_o)^2]$$ was used.

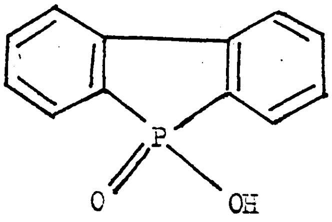
A final convergence to $R = 0.063$ and $R_w = 0.064$ was achieved with the highest residual peak on the Fourier difference map being 1.08 e/Å^{-3} (this peak was in close proximity to the bromine atom). The four oxygen atoms were found to occupy positions along 2-fold axes at $0,\ y,\ \frac{1}{4};\ 0,\ y,\ \frac{3}{4};\ \frac{1}{2},\ \frac{1}{2} + y,\ \frac{1}{2};\ \frac{1}{2},\ \frac{1}{2} - y,\ \frac{3}{4};\ [y = -\,0.1561]$.

Bond angles are given in Table 4.2.1 and bond lengths in Table 4.2.2. A pictorial representation of a molecule is shown in Figure 4.1. Data on mean planes, positional and temperature parameters and structure factors is given, respectively, in A2.11, A1.11 and A4.11.

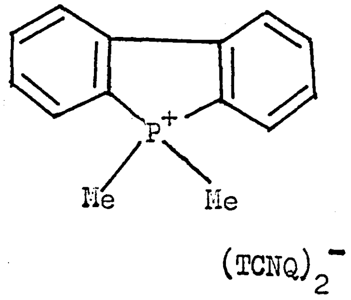
4.2.3 Description of the structure:

The four carbon atoms of the five-membered heterocyclic ring are effectively planar (plane A, Appendix A2.11) with the phosphorus atom 0.159Å out of the plane (Figure 4.1). The best mean planes through the fused phenyl rings (C14 → C19, C20 → C25) attached to the five membered ring are inclined to this plane A at angles of 2.60° and 2.84° respectively. However, theoretical energy calculations[14] show a totally planar fused system to leave a still lower energy than the arrangement in the crystal structure. This suggests that the slight distortion from planarity found in the solid state may well be due to packing effects and may not be present in the solution phase cation. The phenyl rings C1 → C6 and C8 → C13 are effectively planar and the best mean planes through the rings make angles of 72.8° and 73.0° respectively with plane A and 44.4° with each other. Again, from energy calculations, such non-orthogonality would seem to reflect intermolecular interactions present in the solid state rather than intramolecular interactions.

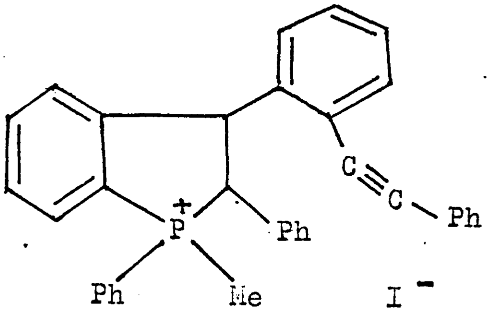
While the exocyclic bond angles at phosphorus (110-117°) lie close to the ideal tetrahedral value, the endocyclic angle (C14 - P - C20) is only 93.9(9)°. This agrees closely with the endocyclic angles of 93.4, 95.4 and 95.6° found for the phosphinic acid[15] (8) and the phospholium salts[16,17] (9), (10).



(8)



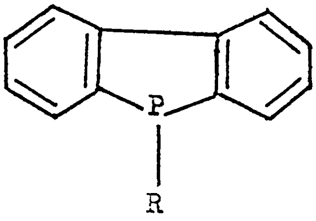
(9)



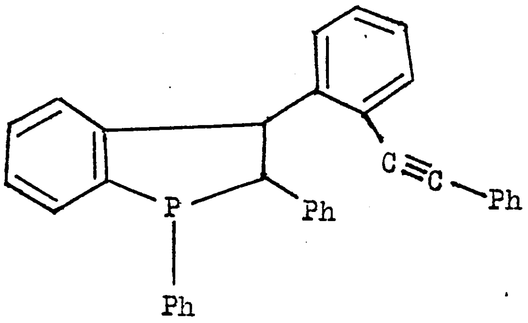
(10)

This would seem to be indicative of considerable deformation of bond angles for a quaternary phosphonium centre compared with an acyclic phosphonium salt. Thus, for the Ph_3P^+Me cation, the smallest angle about P is 105°. Hence, it is reasonable to suppose that there is appreciable ring strain in the phospholium ring, as a result of the deformation of bond angles at phosphorus, which would be relieved on formation of a quinquecovalent trigonal bipyramidal phosphorane, in which the endocyclic C - P - C angle would theoretically be 90°, assuming that the phospholium ring occupies apical-equatorial positions. Apical bond-cleavage or migration of the apical substituent to an equatorially disposed site then leads to either ring opening or ring expansion respectively with the formation of a relatively strain-free structure. The above deductions account for the increased rate of nucleophilic attack at phosphorus in dibenzophospholium salts over acyclic phosphonium salts[18].

The simplest phosphole crystallographically characterised, 1 - benzylphosphole[11] (11, $R = CH_2Ph$), has an endocyclic C - P - C angle of $90.7(2)^{\circ}$ while a value of $88.1(4)^{\circ}$ is reported for the phenylphosphole (12)[19]. These values are close to the values found for acyclic phosphines. Bond angle strain at phosphorus would, however, be introduced on quaternisation and this factor may well account for the reduced rate of quaternisation of 5 - phenyldibenzophosphole relative to triphenylphosphine.[8]



(11)



(12)

Similarly, the increased rate of retrocyanoethylation of cyanoethyldibenzophospholium salts[6] and the ease of electrochemical reduction of dibenzophospholium salts[20], compared to corresponding acyclic systems, can be explained on the basis of ring strain relief attending conversion of the quaternary derivative to the parent phosphole.

Figure 4.2 shows the packing of the ions and water molecules in the unit cell. Pairs of bromide ions, related by two-fold axes, are separated along the (0 1 0)direction by water molecules. The final Fourier difference map indicated the presence of hydrogen atoms at positions suitable for bonding to the oxygen atoms (O - H distance of 1.02Å, H peak of 0.24 e $Å^{-3}$) and for hydrogen bonding to bromide ions (Br^-..... H = 2.38Å).

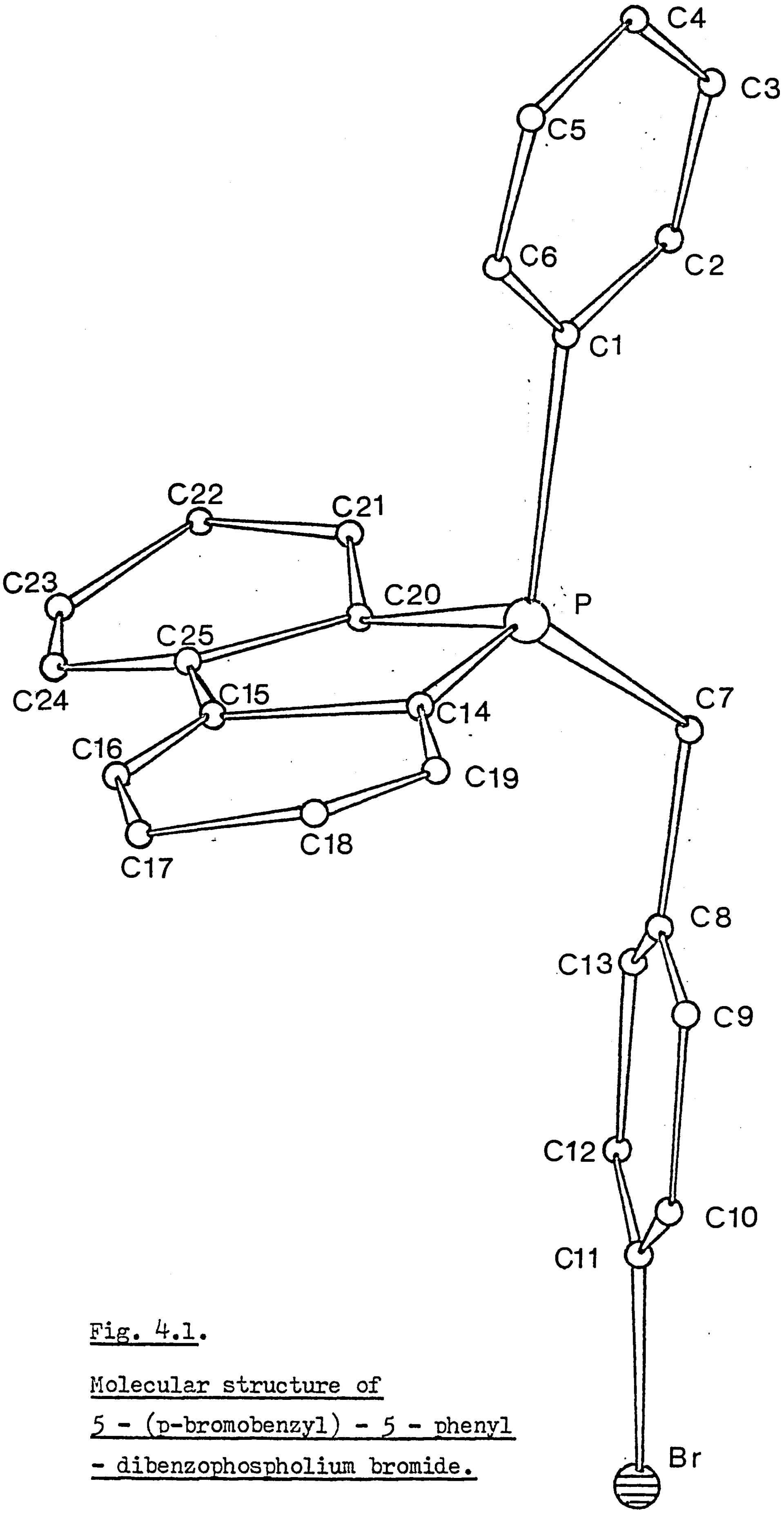


Fig. 4.1.

Molecular structure of
5 - (p-bromobenzyl) - 5 - phenyl
- dibenzophospholium bromide.

Projection down the b axis.

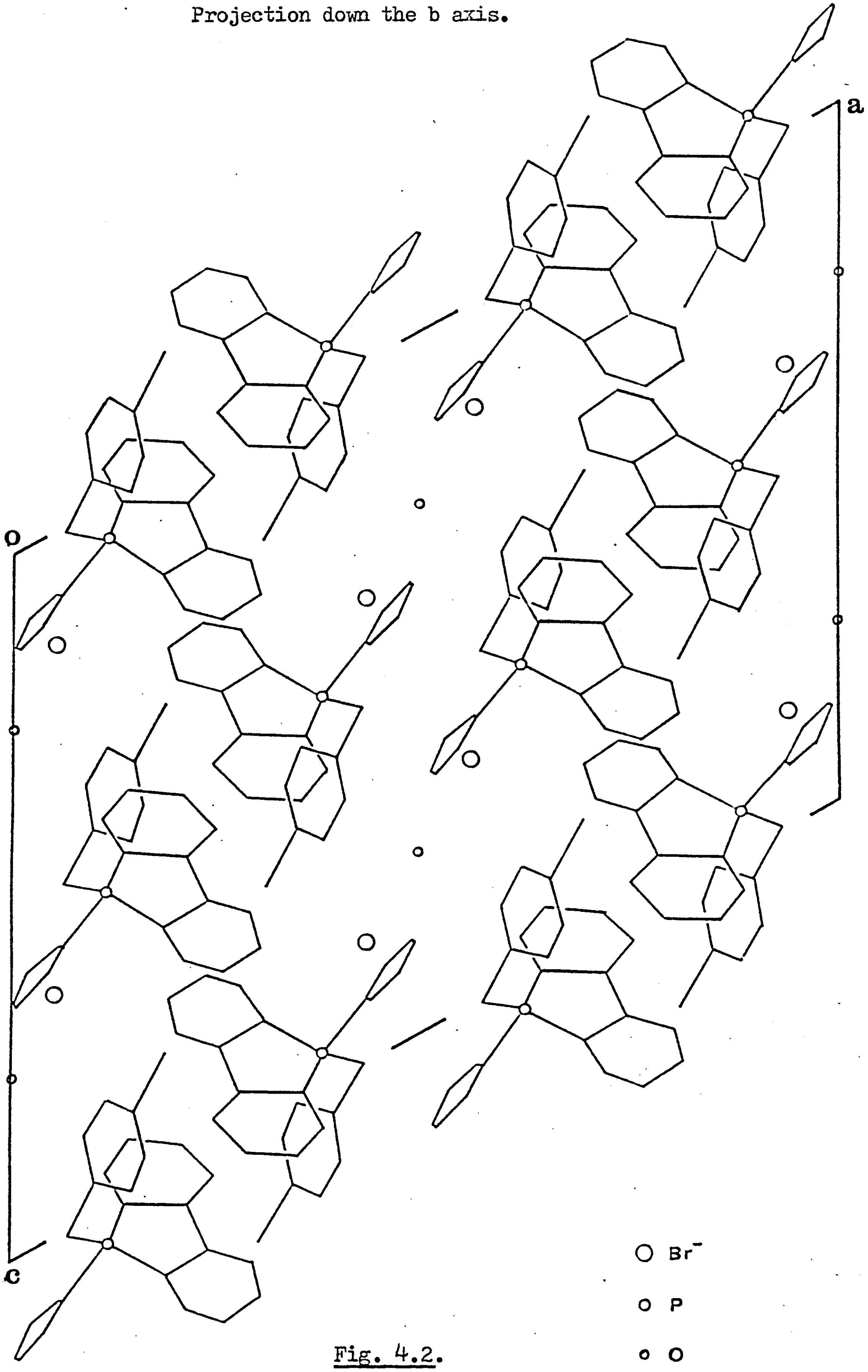


Fig. 4.2.

Crystal structure of 5 - (p-bromobenzyl) - 5 - phenyl-dibenzophospholium bromide.

Table 4.2.1

Bond lengths (Å) for 5 - (p-bromobenzyl) - 5 - phenyl - dibenzophospholium bromide. Estimated standard deviation of errors in parentheses.

Distances in Angströms

P - C1 = 1.80(3)
P - C7 = 1.77(2)
P - C14 = 1.74(3)
P - C20 = 1.79(2)
C1 - C2 = 1.44(4)
C2 - C3 = 1.42(4)
C3 - C4 = 1.29(4)
C4 - C5 = 1.40(4)
C5 - C6 = 1.40(4)
C1 - C6 = 1.36(3)
C7 - C8 = 1.52(4)
C8 - C9 = 1.37(3)
C8 - C13 = 1.39(3)
C9 - C10 = 1.40(4)
C10 - C11 = 1.35(3)
C11 - C12 = 1.41(3)
C12 - C13 = 1.41(4)
C11 - Br = 1.91(3)
C14 - C15 = 1.39(3)
C15 - C16 = 1.41(4)
C16 - C17 = 1.35(3)
C17 - C18 = 1.39(3)
C18 - C19 = 1.35(4)
C14 - C19 = 1.45(3)
C15 - C25 = 1.51(3)
C20 - C21 = 1.37(3)
C21 - C22 = 1.34(3)
C22 - C23 = 1.41(4)
C23 - C24 = 1.34(4)
C24 - C25 = 1.37(2)
C20 - C25 = 1.40(3)

Table 4.2.2

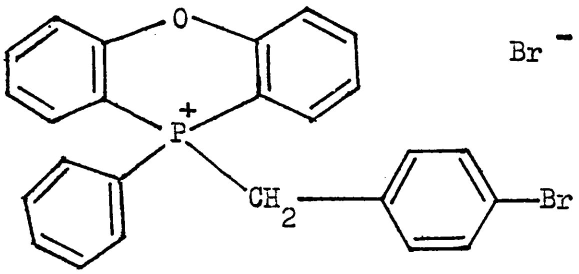
Bond angles (°) for 5 - (p-bromobenzyl) - 5 - phenyl-dibenzophospholium bromide. Estimated standard deviations of errors in parentheses.

Angles (°)

C1 - P - C7 = 110(1)
C1 - P - C14 = 109(1)
C1 - P - C20 = 112(1)
C7 - P - C14 = 117(1)
C7 - P - C20 = 114(1)
C14 - P - C20 = 94(1)
P - C1 - C2 = 117(2)
P - C1 - C6 = 122(2)
C1 - C2 - C3 = 116(2)
C2 - C3 - C4 = 121(3)
C3 - C4 - C5 = 125(3)
C4 - C5 - C6 = 116(3)
C5 - C6 - C1 = 121(2)
C6 - C1 - C2 = 121(2)
P - C7 - C8 = 115(2)
C7 - C8 - C9 = 119(2)
C7 - C8 - C13 = 119(2)
C8 - C9 - C10 = 120(2)
C9 - C10 - C11 = 120(2)
C10 - C11 - C12 = 123(2)
C10 - C11 - Br = 120(2)
C12 - C11 - Br = 117(2)
C11 - C12 - C13 = 118(2)

C12 - C13 - C8 = 119(2)
C13 - C8 - C9 = 122(2)
P - C14 - C15 = 112(2)
P - C14 - C19 = 130(2)
C14 - C15 - C16 = 121(2)
C15 - C16 - C17 = 118(2)
C16 - C17 - C18 = 122(3)
C17 - C18 - C19 = 121(2)
C18 - C19 - C14 = 119(2)
C19 - C14 - C15 = 119(2)
C14 - C15 - C25 = 112(2)
C16 - C15 - C25 = 127(2)
C15 - C25 - C24 = 127(2)
C15 - C25 - C20 = 114(1)
P - C20 - C25 = 108(1)
P - C20 - C21 = 131(2)
C20 - C21 - C22 = 119(3)
C21 - C22 - C23 = 120(2)
C22 - C23 - C24 = 121(2)
C23 - C24 - C25 = 120(2)
C24 - C25 - C20 = 119(2)
C25 - C20 - C21 = 121(2)

4.3 The Crystal and Molecular Structure of 10- (4-bromobenzyl)- 10 - phenylphenoxa - phosphonium bromide



(5)

4.3.1 Crystal data

$C_{25}H_{19}Br_2OP$ $M_r = 526.2$ orthorhombic

$a = 18.954(11)$ $b = 25.715(14)$ $c = 9.322(5)Å$

$D_m = 1.55\ Mg.m^{-3}$ $D_c = 1.54\ Mg.m^{-3}$ $Z = 8$.

$\mu(Mo - K\alpha) = 35.5\ cm^{-1}$ $F(000) = 2104$

Systematic absences:

0kl, k = 2n + 1; h0l, l = 2n + 1; hk0, h = 2n = 1;

The absences uniquely define the space group to be Pbca.

4.3.2 Data Collection and Refinement

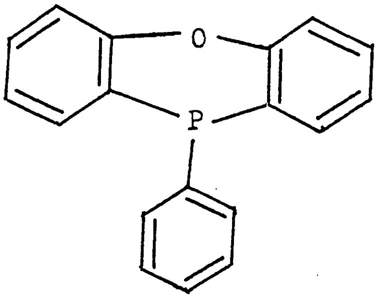
A colourless crystal, of approximate dimensions 0.26 x 0.28 x 0.44 mm, was mounted about the c axis. 10 layers, hk0 → hk9, were collected; 4171 independent reflections were recorded of which 1505 had $I/\sigma(I) \geqslant 2.5$ and were used for structure refinement. Corrections for Lorentz and polarisation factors were applied but no correction was made for absorption. The two bromine atoms and the phosphorus atom were located by multisolution direct methods. All remaining atoms (including hydrogen) were located from successive Fourier difference syntheses and the structure was refined by full matrix least squares techniques. Once located, hydrogen atoms were included in theoretical positions calculated from the geometry of the molecule and given a common isotropic temperature factor final value, $U = 0.072Å^2$. All non-hydrogen atoms were given anisotropic temperature factors in the final stages of refinement.

A weighting scheme of

$$w = 0.5239 / \left[\sigma^2(F_o) + 0.0025(F_o)^2\right]$$ was used to give a final convergence at R = 0.045 and Rw = 0.050. The final difference map showed no peak greater than 0.47 e $Å^{-3}$. Bond lengths and bond angles are given in Tables 4.3.2 and 4.3.3 and data on mean planes, positional and temperature parameters and structure factors are in Appendices A2.12, A1.12 and A4.12 respectively. The molecular configuration is shown in Fig 4.3 and the crystal structure is shown in Fig 4.4.

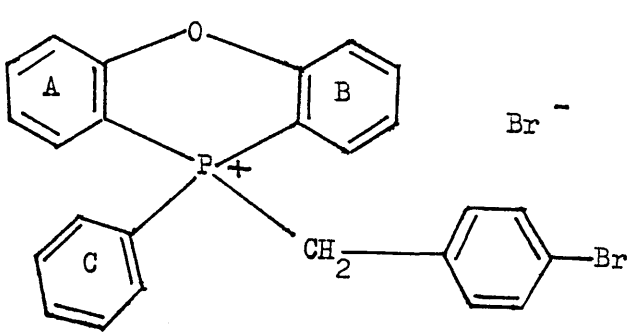
4.3.3 Description of the Structure:

As with the parent cyclic phosphine[21] (13), the fused ring system of the phosphonium cation is not planar. The central heterocyclic ring adopts a boat-like configuration with the oxygen and phosphorus atoms displaced from the effectively co-planar carbon atoms by 0.07 and 0.14Å respectively.

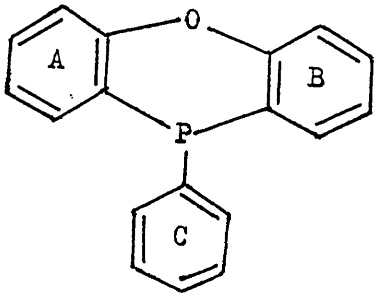


(13)

The fused phenyl rings are inclined at an angle of 4.1° though this may result from packing forces within the crystal lattice for theoretical calculations[14] show a totally planar arrangement of the outer rings to be the minimum energy arrangement. In comparison, the parent phosphine (13) has a more pronounced boat-like conformation to the heterogeneous ring and a higher dihedral angle in the fused ring system as illustrated in table 4.3.1.



(5)



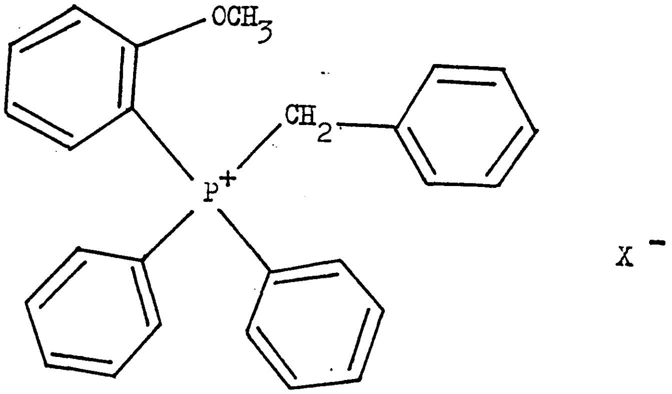
(13)

	(5)	(13)
Distance (Å) of P from plane of heterogeneous ring	0.14	0.17
Distance (Å) of O from plane of heterogeneous ring	0.07	0.22
Angle (^{o}) between planes A and B	4.1	15.0
Angle (^{o}) between planes A and C	76.7	87.0
Endocyclic C-P-Cangle(^{o})	98.0	103.1
Average exocyclic C-P-C angle (^{o})	101.0	110.7

Table 4.3.1

Quaternisation produces significant changes in the bond angles about the phosphorus atom; the endocyclic and average exocyclic C-P-C angles increase from 98.0^{o} to 101.0^{o} in (5) to 103.1 to 110.7^{o} in (13). There is also a change in the angle between planes A and C (Table 4.3.1) though the mean plane of the p-bromobenzyl ring is similarly inclined to the fused ring system (angles of 69.7 and 49.2^{o} respectively with planes A and B) as the analogous group in the dibenzophospholium salt (7) (angles of 73.0 and 44.4° respectively).

The P .... O distance in both (5) and (13) (3.11 and 3.20Å respectively) lies within the sum of van der Waals' radii for phosphorus and oxygen (3.30Å) but these values are significantly larger than the value of 2.88Å found in the salt formed by the reaction between o-methoxyphenyldiphenylphosphine and benzyl bromide (14); X = Br.



(14)

The analogous quaternisation reaction with benzyl chloride proceeds four times faster than the corresponding reaction with the methoxy substituent in the para position and seven times faster than with triphenylphosphine. It has been suggested that, in the formation of (14), the overlap of a pair of 2p electrons of the o-methoxy group with a 3d (or hybrid orbital) of the phosphorus in a transition state stabilises the developing phosphonium centre. Supporting evidence for such interaction has been adduced from spectroscopic studies of the parent phosphines and related phosphonium salts[22,23]. With heterocyclic systems, the phosphorus and oxygen atoms are not as flexible as in (14), accounting for the larger P .... O distance found in this study. Thus, phosphorus - oxygen interactions seem unlikely to be significant in the phenoxaphosphonium system and the predominant effect of the oxygen atom appears to be electron-withdrawal from the phosphorus atom. This is supported by studies of rates of quaternisation[22,23,24] and this effect is also, doubtlessly, responsible for the greatly increased rate of alkaline hydrolysis of phenoxaphosphonium salts compared to related acyclic salts[9,25].

It is further felt that data on rates of quaternization cannot be explained in terms of bond angle strain about the phosphorus. Although the C-P-C endocylic angle of 103.1° in (5) is some way from the ideal strain-free angle of 109.5° for a phosphonium salt, it compares favourably with the smallest C-P-C angle (105°) in the cation $Ph_3\overset{+}{P}Me$[26]. (This may be considered as an acyclic analogue of (5) suggesting that there is little significant deformation of bond angle in (5) and hence little strain).

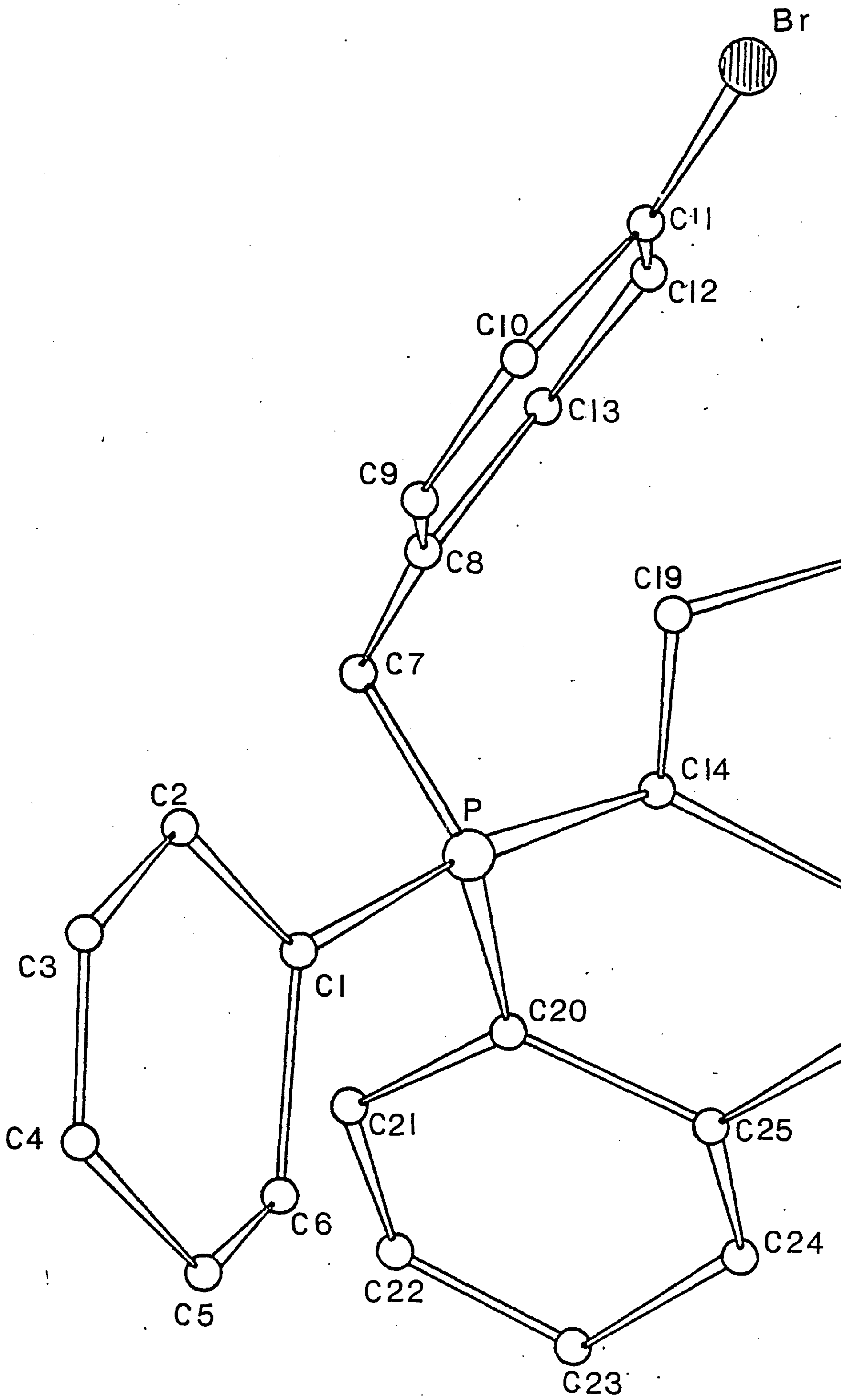


Fig.4.3 Molecular structure of 10- (4-bromobenzyl) -10- phenylphenoxaphosphonium bromide.

Projection down the c axis.

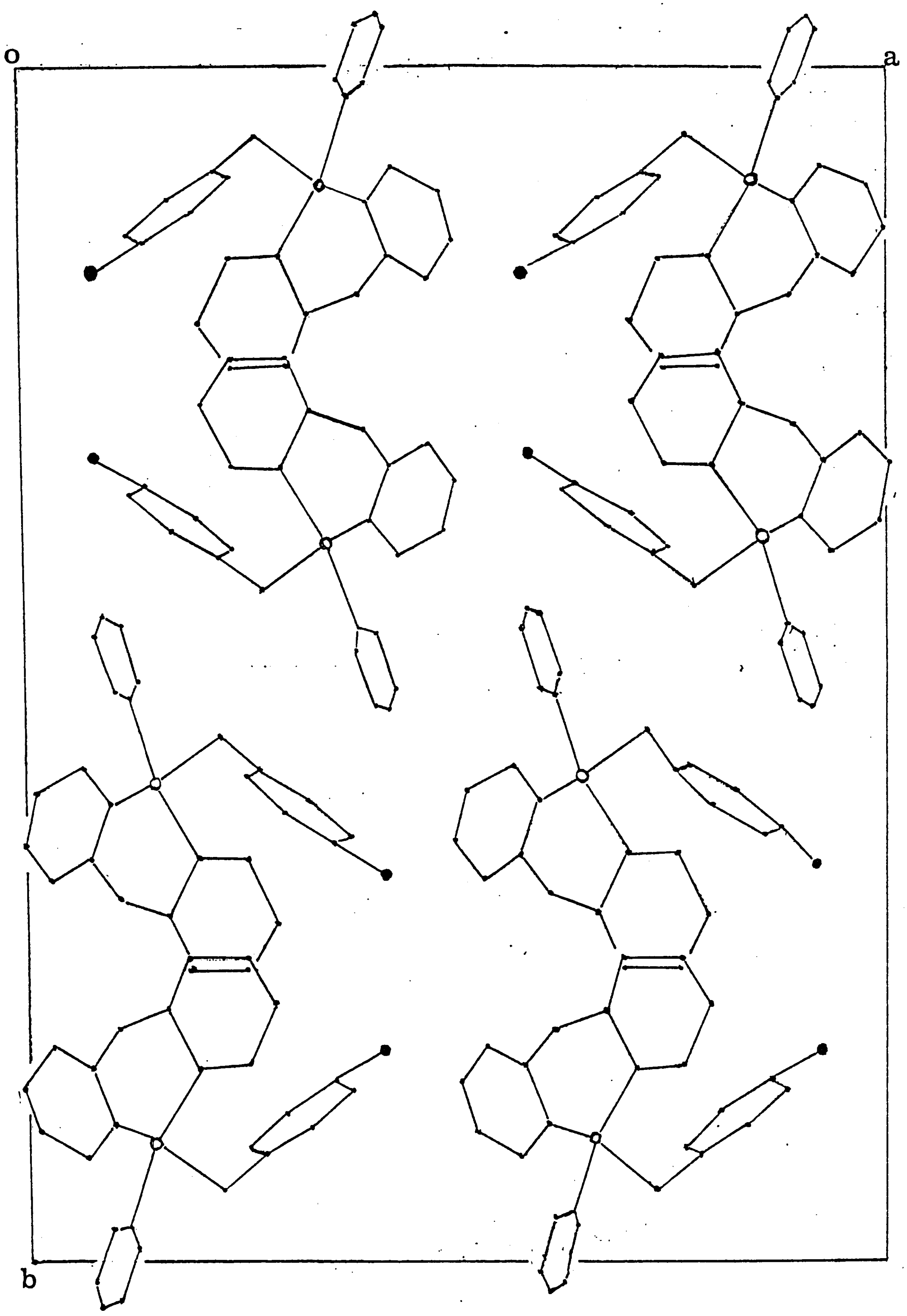


Fig. 4.4 Crystal structure of 10-(4-bromobenzyl)-10-phenylphenoxaphosphonium bromide.

Table 4.3.2 Bond lengths (Å) for 10-(4-bromobenzyl)-10-phenylphenoxaphosphonium bromide. Estimated standard deviation of errors in parentheses.

Distances in Angströms

P - C1 = 1.80(1)
P - C7 = 1.81(1)
P - C14 = 1.78(1)
P - C20 = 1.79(1)
C1 - C2 = 1.39(2)
C1 - C6 = 1.38(2)
C2 - C3 = 1.39(2)
C3 - C4 = 1.35(2)
C4 - C5 = 1.37(2)
C5 - C6 = 1.37(2)
C7 - C8 = 1.50(1)
C8 - C9 = 1.39(2)
C8 - C13 = 1.39(2)
C9 - C10 = 1.40(2)
C10 - C11 = 1.39(2)
C11 - Br = 1.91(1)

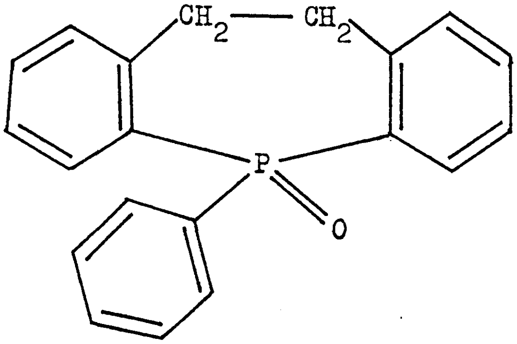
C11 - C12 = 1.37(2)
C12 - C13 = 1.39(2)
C14 - C15 = 1.40(2)
C14 - C19 = 1.38(2)
C15 - O = 1.36(2)
C15 - C16 = 1.39(2)
C16 - C17 = 1.33(2)
C17 - C18 = 1.39(2)
C18 - C19 = 1.40(2)
C20 - C21 = 1.40(2)
C20 - C25 = 1.38(1)
C21 - C22 = 1.40(2)
C22 - C23 = 1.38(2)
C23 - C24 = 1.39(2)
C24 - C25 = 1.36(2)
C25 - O = 1.37(1)

Table 4.3.3 Bond angles (°) for 10-(4-bromobenzyl) - 10 - phenylphenoxa-phosphonium bromide. Estimated standard deviation of errors in parentheses.

Angles in degrees.

C1 - P - C7 = 108.3(5)
C1 - P - C14 = 109.6(5)
C1 - P - C20 = 111.0(5)
C7 - P - C14 = 111.8(5)
C7 - P - C20 = 113.0(5)
C14 - P - C20 = 103.1(5)
P - C1 - C2 = 120(1)
P - C1 - C6 = 120(1)
C2 - C1 - C6 = 120(1)
C1 - C2 - C3 = 120(1)
C2 - C3 - C4 = 119(1)
C3 - C4 - C5 = 122(1)
C4 - C5 - C6 = 121(1)
C1 - C6 - C5 = 119(1)
P - C7 - C8 = 113(1)
C7 - C8 - C9 = 120(1)
C7 - C8 - C13 = 122(1)
C9 - C8 - C13 = 118(1)
C8 - C9 - C10 = 121(1)
C9 - C10 - C11 = 118(1)
Br - C11 - C10 = 117(1)
Br - C11 - C12 = 120(1)
C10 - C11 - C12 = 123(1)
C11 - C12 - C13 = 116(1)
C8 - C13 - C12 = 123(1)
P - C14 - C15 = 121(1)
P - C14 - C19 = 120(1)
C15 - C14 - C19 = 119(1)
O - C15 - C14 = 125(1)
O - C15 - C16 = 116(1)
C14 - C15 - C16 = 119(1)
C15 - C16 - C17 = 121(1)
C16 - C17 - C18 = 121(1)
C17 - C18 - C19 = 119(1)
C14 - C19 - C18 = 121(1)
P - C20 - C21 = 118(1)
P - C20 - C25 = 120(1)
C21 - C20 - C25 = 121(1)
C20 - C21 - C22 = 117(1)
C21 - C22 - C23 = 122(1)
C22 - C23 - C24 = 119(1)
C23 - C24 - C25 = 121(1)
O - C25 - C20 = 126(1)
O - C25 - C24 = 114(1)
C15 - O - C25 = 124(1)
C20 - C25 - C24 = 120(1)

4.4 The Crystal and Molecular Structure of 5-phenyl-10,11-dihydrodibenzo(b,f) phosphepin 5-oxide



(6)

4.4.1 Crystal data:

$C_{20}H_{17}PO$	Mr = 304.33	triclinic
a = 8.533(5)	b = 11.106(2)	c = 8.815(5)Å
α = 107.83(6)	β = 104.99(6)	γ = 81.30(5)°
Z = 2	D_m = 1.33 g cm^{-3}	D_c = 1.32g cm^{-3}
F(000) = 320	μ(Mo - Kα) = 1.36 cm^{-1}	

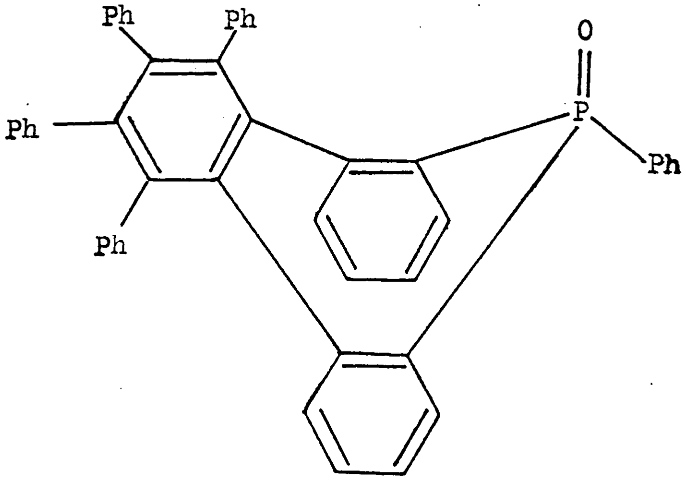
The structure was assumed to crystallize in the centrosymmetric space group P$\bar{1}$ and this was confirmed by subsequent structure analysis.

4.4.2 Data Collection and Structure Refinement:

A colourless crystal, approximate dimensions 0.24 x 0.30 x 0.45 mm, was mounted about the a axis. 10 layers, Okl → 9Kl, were collected; 3100reflections were recorded of which 1753 had $I/\sigma(I) \geqslant 4.0$ and were used in structure analysis. Corrections for Lorentz and polarization factors were applied but no correction for absorption was made. The structure was solved by multisolution direct methods yielding the positions of all non-hydrogen atoms. Refinement was by full-matrix least squares methods. Hydrogen atoms were located from successive Fourier syntheses and were included in subsequent refinement in positions calculated from the geometry of the molecule. Non-hydrogen atoms were given anisotropic temperature factors while the hydrogen atoms were given a common isotropic factor (refined to a final value of $U = 0.082\text{Å}^2$). A weighting scheme of $w = 2.0396/(\sigma^2(F_o) + 0.0037(F_o)^2)$ led to a value of $R = 0.081$ and $R_w = 0.090$. The largest residue peak from the final Fourier synthesis was 0.63 e Å^{-3}. Bond lengths and angles are given in Tables 4.4.1 and 4.4.2 respectively. The molecule is represented in Fig. 4.5. Data on structural and thermal parameters, mean planes and structure factors is given in Appendices A1.13, A2.13 and A4.13 respectively.

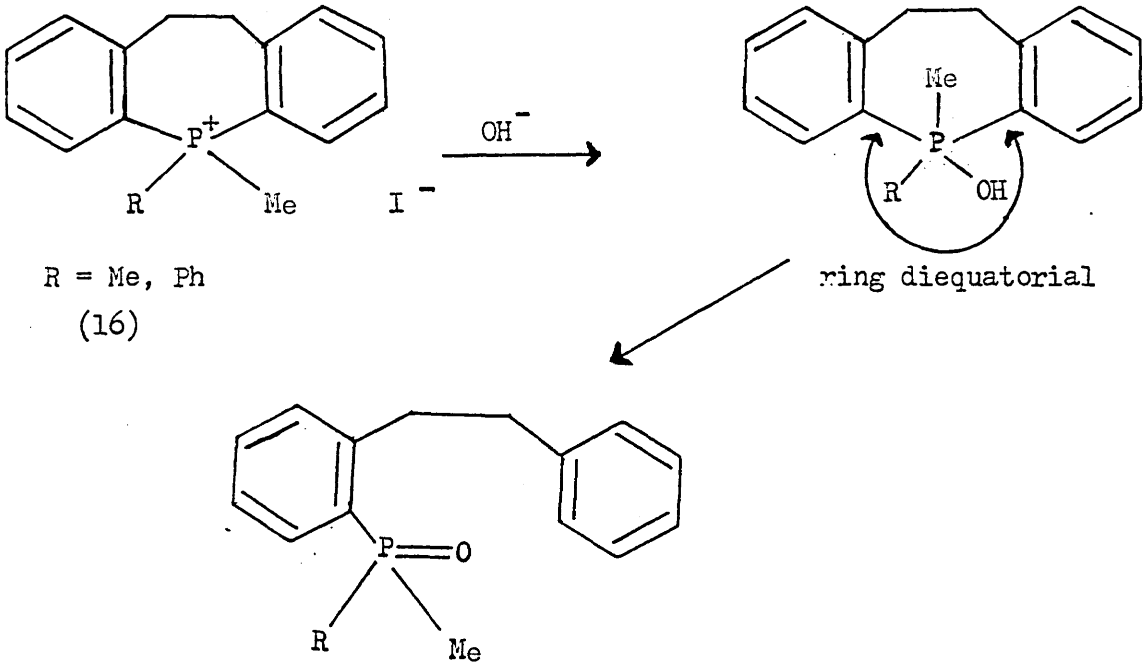
4.4.3 Discussion of Structure:

The six-membered rings, C1→C6 and C9→C14, are effectively planar (Appendix A2.13) and adopt a butterfly configuration with an inclination of 56.8° to each other. C7 is approximately planar with ring A and, similarly, C8 is near-planar to ring B. The phenyl ring, C15 C20, is inclined at 80.2° and 74.9° respectively to rings A and B. The phosphorus atom lies approximately at the intersection of the three planes (-0.060, -0.108 and 0.165Å respectively from the best mean planes). The butterfly arrangement found here contrasts with the compound (15) where the seven-membered ring adopted a boat conformation[27].



(15)

The presence of the substituted phenyl group at the positions equivalent to C7 and C8 in 5-phenyl-10,11-dihydrodibenzo (b,f) phosphepin 5-oxide (6) would seem to account both for the major conformational differences and for the apparent ring strain within the seven-membered ring in (15). Thus, while the C6-C7 and C8-C9 bonds in (6) adopt a staggered arrangement with respect to the C7-C8 direction (the torsion angle C6-C7-C8-C9 = 67.4°), in (15), the equivalent bonds are effectively eclipsed (the corresponding torsion angle is 3.3°). In (15), the endocyclic C-P-C angle is unexpectedly small being only $99.0(5)^{\circ}$, while in (6) it hardly deviated from the regular tetrahedral value being $107.2(3)^{\circ}$. Further the exocyclic angles about phosphorus are in the range $106.5\text{-}111.9(3)^{\circ}$. Allen et alia[28] showed that alkaline hydrolysis of the seven-membered ring systems (16) occur at a very much slower rate than for analogous five-membered rings and suggest that a diequatorial position is favoured in the formation of intermediatory phosphoranes (ideal endocyclic C-P-C angle of 120°), viz:-



R = Me, Ph
(16)

This contrasts with the five-membered ring spanning an apical-equatorial position in the trigonal bipyramidal intermediatory (this requires an endocyclic C-P-C angle of 90°). Clearly, there would be less bond angle deformation for (6) in passing from the quaternary derivative in the former scheme than in the latter, though some caution needs to be exercised in considering the data. Allen et alia[28] discussed compounds with a nominally charged phosphorus atom whilst the phenyl phosphepin (6) has an uncharged phosphorus atom so that the analogy may be more apparent than real.

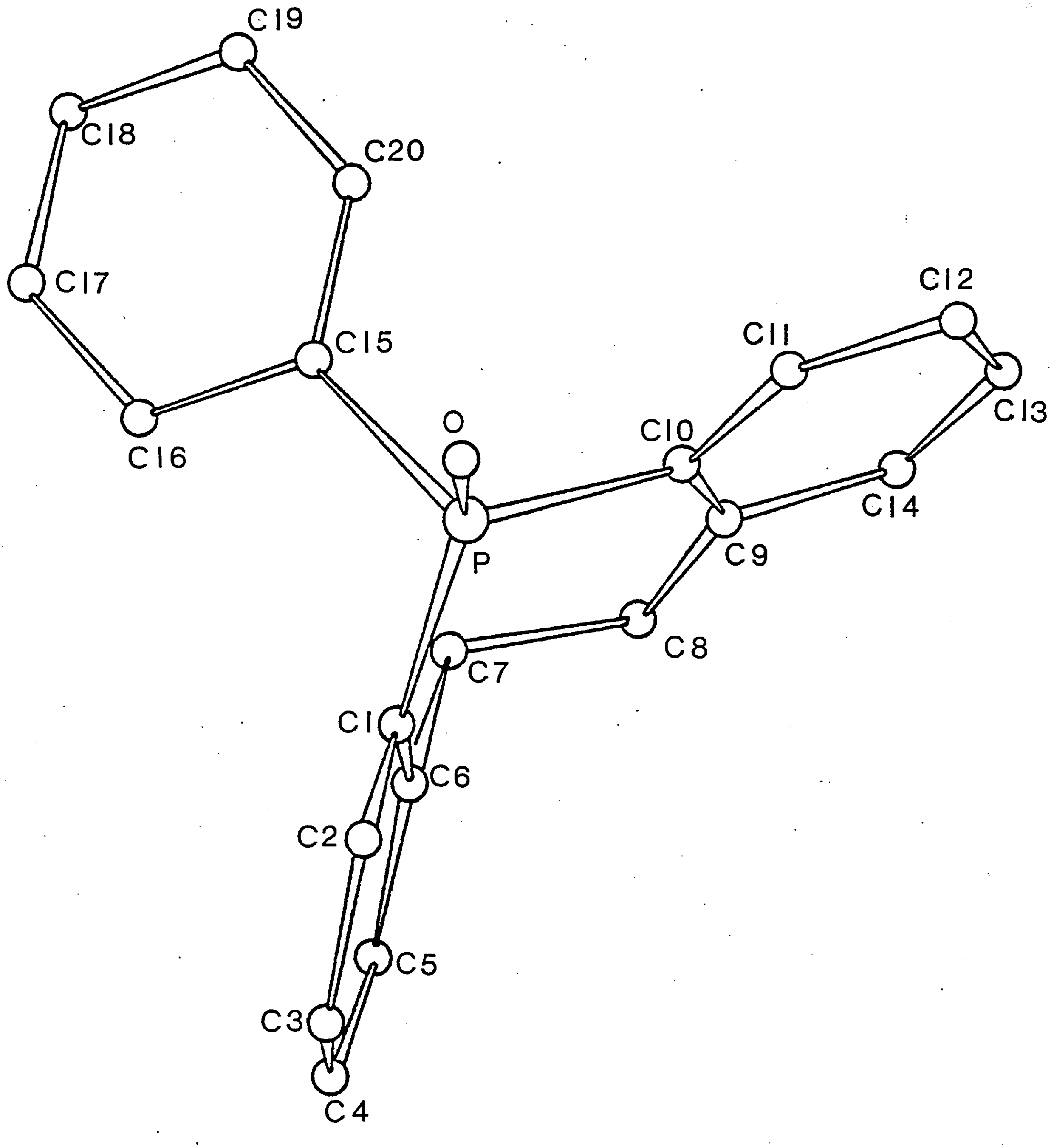


Fig.4.5.

Molecular structure of 5 - phenyl-10,11-dihydrobenzo (b,f)-phosphepin - 5 - oxide.

Table 4.4.1 Bond distances (Å) for 5-phenyl-10,11-dihydrodibenzo (b,f)-phosphepin-5-oxide. Standard deviations of errors in parentheses

Distances in Å

P - O = 1.506(4)
P - C1 = 1.793(7)
P - C10 = 1.815(5)
P - C15 = 1.797(8)
C1 - C2 = 1.384(9)
C1 - C6 = 1.416(8)
C2 - C3 = 1.388(11)
C3 - C4 = 1.369(10)
C4 - C5 = 1.393(12)
C5 - C6 = 1.381(12)
C6 - C7 = 1.517(10)
C7 - C8 = 1.512(9)
C8 - C9 = 1.528(10)
C9 - C10 = 1.404(8)
C9 - C14 = 1.408(8)
C10 - C11 = 1.403(10)
C11 - C12 = 1.382(9)
C12 - C13 = 1.392(11)
C13 - C14 = 1.363(11)
C15 - C16 = 1.403(9)
C15 - C20 = 1.381(11)
C16 - C17 = 1.388(13)
C17 - C18 = 1.387(14)
C18 - C19 = 1.391(11)
C19 - C20 = 1.390(14)

Table 4.4.2 Bond angles (°) for 5-phenyl-10,11-dihydrodibenzo(b,f)-phosphepin-5-oxide. Standard deviations of errors in parentheses

Angles in degrees

O - P - C1 = 111.3(3)
O - P - C10 = 111.9(3)
O - P - C15 = 109.9(3)
C1 - P - C10 = 107.2(3)
C10 - P - C15 = 106.5(3)
C10 - P - C15 = 109.9(3)
P - C1 - C2 = 117.7(4)
P - C1 - C6 = 122.2(5)
C2 - C1 - C6 = 120.0(6)
C1 - C2 - C3 = 121.1(6)
C2 - C3 - C4 = 119.3(7)
C3 - C4 - C5 = 119.9(8)
C4 - C5 - C6 = 122.2(7)
C1 - C6 - C5 = 117.4(6)
C1 - C6 - C7 = 120.4(6)
C5 - C6 - C7 = 122.2(6)
C6 - C7 - C8 = 114.6(7)
C7 - C8 - C9 = 120.3(5)

C8 - C9 - C10 = 127.8(5)
C8 - C9 - C14 = 114.3(6)
C10 - C9 - C14 = 117.8(6)
P - C10 - C9 = 128.3(5)
P - C10 - C11 = 113.1(4)
C9 - C10 - C11 = 118.6(5)
C10 - C11 - C12 = 121.9(6)
C11 - C12 - C13 = 119.5(7)
C12 - C13 - C14 = 119.1(6)
C13 - C14 - C9 = 123.0(6)
P - C15 - C16 = 121.9(6)
P - C15 - C20 = 119.8(5)
C16 - C15 - C20 = 117.8(7)
C15 - C16 - C17 = 121.2(7)
C16 - C17 - C18 = 119.7(7)
C17 - C18 - C19 = 120.0(9)
C18 - C19 - C20 = 119.5(9)
C15 - C20 - C19 = 121.8(7)

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Summary and suggestions for future work.

Single crystal X-ray analyses have been carried out on three distinct groups of heterocyclic compounds:

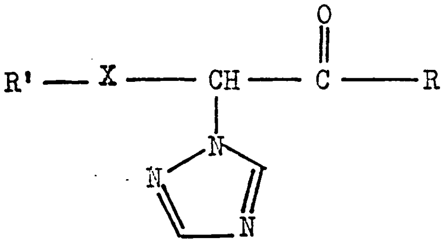
1. Triazole and imidazole compounds
2. Macrocyclic metal complexes
3. Phosphorus heterocyclic compounds.

In each case, data have been collected on a two-circle diffractometer and trial solutions obtained using Patterson and direct methods techniques. Least squares refinement linked to Fourier syntheses were used to establish the final structure.

1. Triazole and imidazole compounds.

Five compounds having fungicidal activity were provided by the Plant Protection Division of I.C.I. and contained either a 1,2,4-triazol-1-yl or an imidazol-1-yl ring:

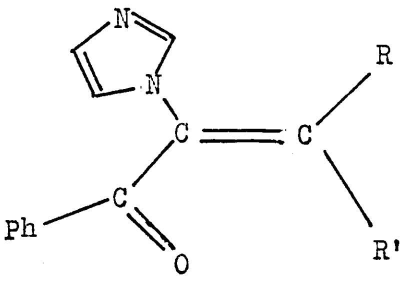
(i) Triazole compounds.



	R'	X	R
R85827	4-Cl-phenyl	O	Bu^t
R79386	4-NO_2-phenyl	CH_2	Bu^t
R110043	2-F-phenyl	CH_2	4-Cl-phenyl

The conformations adopted are dominated by the relative orientations of the ring systems and the tertiary butyl group (if present) with respect both to each other and also to the central backbone. Triadimefon (R85827) adopts a significantly different conformation compared to the other two compounds. In particular, the central backbone is far more compact with the R(C) - C(O) - CH(triazole) - X(R') torsion angle being only 100.1(7)° compared with values of 163.8(6) and 173.0(6)° found for R79386 and R110043 respectively which are indicative of fully extended structures. The C - N and N - N bond lengths found within the triazole rings reflect the presence of considerable delocalisation within the heterocyclic ring. Of particular note is the extent of asymmetry found at the triazole nitrogen atom bonded to the carbon backbone. The average exocyclic angles found for the three compounds are 120° (C - N - N) and 130° (C - N - C) and appear to be a property of the 1,2,4-triazole ring itself rather than due to any inter- or intramolecular interactions. It would be of interest to establish, using energy calculations, whether such an asymmetric arrangement at the nitrogen atom is, in fact, the lowest energy conformation.

(ii) Imidazole compounds.

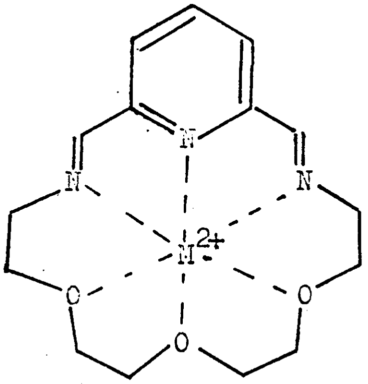


	R	R'
Z-isomer	4-NO_2-phenyl	H
E-isomer	H	4-NO_2-phenyl

The conformations adopted by the cis- and trans-isomers reflects a compromise between electronic factors which would favour the planarity of the groupings attached to the ethylenic fragment and steric factors. Unlike the triazole compounds studied, no asymmetry of the exocyclic angles at nitrogen is found.

The data available from the present work as regards conformations, bond angles and torsion angles are particularly useful in understanding the activity of the compounds. Although activity is dependent upon the structure adopted in solution, the X-ray structure may well be close to that found in solution and, nevertheless, the data on bond angles and distances are still relevant no matter what conformation is adopted. To gain a far better understanding of the relation between the structure and the activity of such compounds, a more systematic study of conformation in solution is needed, for which n.m.r. techniques using lanthanide shift reagents looks promising.

2. Macrocyclic metal complexes.



$2SCN^{-}.nH_2O$

M = Ca; n = 0

M = Sr,Ba; n = 1

The structures of the three macrocyclic complexes shown above have been established and reveal the importance of the relative sizes of the metal ion and the macrocyclic cavity upon the nature of the structure adopted. Thus, it is found that as the size of the metal ion increases so the metal ion is progressively displaced from the plane of the six donor atoms (Ca, 0.01; Sr,0.53; Ba,0.86Å). In addition, the coordination number of the metal ion increases from eight (calcium) to nine for strontium and barium. In the calcium complex, the coordination about the metal ion is effected by the six donor atoms within the macrocycle and by the two nitrogen-bonded thiocyanate ligands. For the strontium and barium complexes, the coordination number is increased to nine by the inclusion of a water molecule within the coordination sphere. Replacement of the pyridine ring by a furanyl ring appears to make very little difference upon the structure adopted. The strontium ion is similarly below the mean plane of the six donor atoms in the macrocycle.

4'-aceto-2,3-benzo-1,4,7,10,13,16-hexaoxacyclooctadec-2-ene, strontium perchlorate has also been structurally characterised. Of prime interest was the possible intermolecular interaction between the aceto group on one molecule and a neighbouring metal centre. Coordination about strontium comprises six oxygens from the macrocyclic ring and one oxygen from each of the perchlorate anions; no intermolecular interactions are present in the crystal structure.

The resulting coordination of eight is thus less than that found in the macrocyclic complexes discussed on the previous page and may reflect the presence of the sterically more demanding perchlorate groups which inhibit the inclusion of a water molecule within the coordination sphere.

While a considerable body of structural data has been established on macrocyclic complexes, there is still need for a systematic study of the influence upon the structure adopted by such factors as (i)role of anion; (ii)influence of solvent molecules; (iii)effect of changing the type of donor atom. It would be of particular interest to examine the structures of macrocyclic complexes containing phosphorus atoms for which little structural work has been reported.

3. Phosphorus heterocyclic compounds.

The crystal and molecular structures of three compounds containing 5, 6 and 7- membered heterocyclic phosphorus ring systems have been determined, in an attempt to establish the importance of ring strain within phosphonium ring systems. The structure of 5-(p-bromobenzyl)-5-phenyl-dibenzophospholium bromide reveals an endocyclic C - P - C angle of only 94(1)° and is indicative of the presence of considerable ring strain. The very rapid rate of nucleophilic attack at the phosphonium centre of dibenzophospholium salts may be interpreted as involving the relief of such ring strain upon formation of trigonal bipyramidal intermediates.

X-ray analysis of 10-(4-bromobenzyl)-10-phenylphenoxaphosphonium bromide shows the endocyclic angle within the six membered PC_4O ring to be 103.1(5)°. Although the latter angle is significantly smaller than a regular tetrahedral angle, it compares favourably with the smallest C - P - C angle (105°) in the acyclic cation Ph_3P^+Me and suggests there is little ring strain in this six-membered ring system. The increased rate of alkaline hydrolysis of phenoxaphosphonium salts compared to related acyclic salts is attributed to the presence of the oxygen atom which appears to be withdrawing electron density from phosphorus.

The endocyclic C - P - C angle in 5-phenyl-10,11-dihydrodibenzo-(b,f)phosphepin-5-oxide hardly deviates from the regular tetrahedral value, being 107.2(3)°. Thus, there appears to be little evidence of ring strain within the seven-membered PC_6 ring and it is likely that the related phosphonium ring system is also strain free.

Contents.

Value for n.

1. 1-(4-chlorophenoxy)-3,3-dimethyl-1-(1,2,4-triazol-1-yl)-2-butanone.

2. 1-(4-nitrophenyl)-4,4-dimethyl-2-(1,2,4-triazol-1-yl)-pentan-3-one.

3. 1-(4-chlorophenyl)-3-(2-fluorophenyl)-2-(1,2,4-triazol-1-yl)-propan-1-one.

4. Z-3-(4-nitrophenyl)-1-phenyl-2-(imidazol-1-yl)-prop-2-en-1-one.

5. E-3-(4-nitrophenyl)-1-phenyl-2-(imidazol-1-yl)-prop-2-en-1-one.

6. 4'-aceto-2,3-benzo-1,4,7,10,13,16-hexaoxacyclooctadec-2-ene, strontium perchlorate.

7. isothiocyanato(3,15,21-triaza-6,9,12-trioxabicyclo(15.3.1)heneicosa-1(21),2,15,17,19-pentaene) calcium (II).

8. aqua-di-isothiocyanato(3,15,21-triaza-6,9,12-trioxabicyclo(15.3.1)heneicosa-1(21),2,15,17,19-pentaene) strontium (II).

9. aqua-di-isothiocyanato(3,15,21-triaza-6,9,12-trioxabicyclo(15.3.1)heneicosa-1(21),2,15,17,19-pentaene) barium (II).

10. aqua-di-isothiocyanato(3,15-diaza-6,9,12,20-tetraoxabicyclo(15.2.1)eicosa-2,15,17,19-tetraene) strontium (II).

11. 5-(p-bromobenzyl)-5-phenyl-dibenzophospholium bromide.

12. 10-(4-bromobenzyl)-10-phenylphenoxa-phosphonium bromide.

13. 5-phenyl-10,11-dihydrodibenzo(b,f)-phosphepin-5-oxide.

Table A1.1.

Final positional parameters (fractional) and thermal parameters for the structure of 1-(4-chloro-phenoxy)-3,3-dimethyl-1-(1,2,4-triazol -1-yl) -2-butanone.

Atom	X/A	Y/B	Z/C	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl	-0.2893	0.9666	0.5907	0.0755	0.1517	0.0839	-0.0530	0.0305	0.0057
	0.0004	0.0002	0.0003	0.0023	0.0025	0.0016	0.0017	0.0014	0.0020
C74	-0.1961	0.9439	0.4370	0.0406	0.0943	0.0549	-0.0245	0.0074	0.0117
	0.0012	0.0005	0.0008	0.0067	0.0068	0.0045	0.0045	0.0044	0.0055
C73	-0.1521	0.8797	0.4223	0.0625	0.0796	0.0554	0.0003	0.0158	0.0088
	0.0013	0.0004	0.0008	0.0082	0.0058	0.0045	0.0040	0.0047	0.0052
H73	-0.1725	0.8438	0.5038	0.0779					
	0.0013	0.0004	0.0008	0.0080					
C72	-0.0802	0.8612	0.2994	0.0583	0.0564	0.0564	0.0017	0.0167	0.0130
	0.0012	0.0004	0.0008	0.0065	0.0044	0.0043	0.0036	0.0042	0.0045
H72	-0.0465	0.8105	0.2840	0.0779					
	0.0012	0.0004	0.0008	0.0080					
C71	-0.0526	0.9080	0.1990	0.0347	0.0668	0.0384	-0.0099	0.0008	0.0042
	0.0011	0.0004	0.0007	0.0055	0.0051	0.0034	0.0034	0.0033	0.0041
C76	-0.0962	0.9727	0.2160	0.0513	0.0372	0.0706	-0.0175	0.0044	0.0019
	0.0012	0.0004	0.0008	0.0063	0.0038	0.0046	0.0035	0.0043	0.0041
H76	-0.0744	1.0089	0.1355	0.0779					
	0.0012	0.0004	0.0008	0.0080					
C75	-0.1678	0.9910	0.3367	0.0546	0.0486	0.0845	-0.0283	-0.0030	0.0124
	0.0012	0.0004	0.0010	0.0067	0.0045	0.0059	0.0044	0.0051	0.0047
H75	-0.2015	1.0418	0.3519	0.0779					
	0.00 2	0.0004	0.0008	0.0080					
O2	0.0185	0.8950	0.0718	0.0491	0.0461	0.0482	0.0077	0.0100	0.0076
	0.0007	0.0002	0.0005	0.0044	0.0028	0.0025	0.0021	0.0025	0.0028
C5	0.1074	0.8345	0.0655	0.0356	0.0441	0.0468	-0.0035	0.0037	-0.0039
	0.0010	0.0003	0.0007	0.0052	0.0037	0.0034	0.0029	0.0035	0.0038
H5	0.1699	0.8131	0.1689	0.0779					
	0.0010	0.0003	0.0007	0.0080					
N1	-0.0052	0.7815	0.0150	0.0391	0.0441	0.0414	-0.0003	0.0097	-0.0012
	0.0009	0.0003	0.0006	0.0042	0.0033	0.0029	0.0025	0.0029	0.0032
N2	0.0106	0.7225	0.0817	0.0929	0.0535	0.0666	0.0074	-0.0162	-0.0307
	0.0011	0.0003	0.0007	0.0073	0.0039	0.0040	0.0034	0.0043	0.0046

Table A1.1 continued.

Atom	X/A	Y/B	Z/C	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C2	-0.1046	0.6879	0.0035	0.1198	0.0456	0.0682	0.0017	0.0081	-0.0361
	0.0016	0.0004	0.0010	0.0098	0.0043	0.0050	0.0040	0.0057	0.0057
H2	-0.1273	0.6369	0.0268	0.0779					
	0.0016	0.0004	0.0010	0.0080					
N3	-0.1930	0.7193	-0.1075	0.0546	0.0808	0.0554	-0.0070	0.0026	-0.0177
	0.0010	0.0004	0.0007	0.0056	0.0050	0.0035	0.0036	0.0035	0.0045
C1	-0.1262	0.7788	-0.0965	0.0466	0.0636	0.0503	-0.0102	0.0028	-0.0008
	0.0012	0.0004	0.0007	0.0062	0.0050	0.0040	0.0035	0.0042	0.0046
H1	-0.1640	0.8194	-0.1681	0.0779					
	0.0012	0.0004	0.0007	0.0080					
C4	0.2291	0.8504	-0.0467	0.0404	0.0511	0.0470	-0.0029	0.0126	-0.0063
	0.0010	0.0003	0.0007	0.0052	0.0042	0.0038	0.0029	0.0036	0.0035
O1	0.1800	0.8481	-0.1737	0.0622	0.1273	0.0441	-0.0053	0.0068	-0.0288
	0.0008	0.0003	0.0005	0.0048	0.0051	0.0027	0.0029	0.0028	0.0040
C31	0.4078	0.8675	0.0144	0.0497	0.0393	0.0565	-0.0106	0.0175	-0.0100
	0.0011	0.0003	0.0007	0.0057	0.0034	0.0038	0.0032	0.0039	0.0038
C33	0.5000	0.8963	-0.1059	0.0600	0.0651	0.0793	0.0029	0.0195	-0.0171
	0.0013	0.0004	0.0009	0.0069	0.0051	0.0052	0.0042	0.0047	0.0049
H331	0.6296	0.9060	-0.0673	0.0779					
	0.0013	0.0004	0.0009	0.0080					
H332	0.4396	0.9415	-0.1449	0.0779					
	0.0013	0.0004	0.0009	0.0080					
H333	0.4919	0.8609	-0.1931	0.0779					
	0.0013	0.0004	0.0009	0.0080					
C32	0.4094	0.9153	0.1428	0.0641	0.0635	0.0755	-0.0174	0.0063	-0.0054
	0.0014	0.0004	0.0009	0.0073	0.0049	0.0050	0.0040	0.0047	0.0048
H321	0.5391	0.9272	0.1759	0.0779					
	0.0014	0.0004	0.0009	0.0080					
H322	0.3525	0.9000	0.2361	0.0779					
	0.0014	0.0004	0.0009	0.0080					
H323	0.3453	0.9582	0.0948	0.0779					
	0.0014	0.0004	0.0009	0.0080					

Table A1.1 continued.

Atom	X/A	Y/B	Z/C	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C34	0.4908	0.8017	0.0675	0.0480	0.0604	0.0755	0.0004	0.0138	0.0061
	0.0012	0.0004	0.0008	0.0062	0.0047	0.0050	0.0039	0.0043	0.0046
H341	0.6139	0.8125	0.1096	0.0779					
	0.0012	0.0004	0.0008	0.0080					
H342	0.4878	0.7701	-0.0260	0.0779					
	0.0012	0.0004	0.0008	0.0080					
H343	0.4307	0.7773	0.1499	0.0779					
	0.0012	0.0004	0.0008	0.0080					

Table A1.2.

Final positional parameters (fractional) and thermal parameters for the structure of 1-(4-nitrophenyl)-4,4-dimethyl-2-(1,2,4-triazol-1-yl)-pentan-3-one.

Atom	X/A	Y/B	Z/C	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C74	0.3617	0.1450	0.4797	0.0601	0.0827	0.0380	0.0081	0.0104	0.0154
	0.0016	0.0006	0.0003	0.0072	0.0058	0.0039	0.0042	0.0038	0.0052
C75	0.5570	0.1919	0.4624	0.0907	0.0700	0.0505	-0.0153	-0.0040	0.0110
	0.0018	0.0006	0.0004	0.0087	0.0059	0.0045	0.0041	0.0047	0.0053
H75	0.6107	0.2575	0.4888	0.1042					
	0.0018	0.0006	0.0004	0.0146					
C76	0.6857	0.1560	0.4112	0.0759	0.0693	0.0438	0.0001	-0.0031	0.0110
	0.0016	0.0006	0.0003	0.0069	0.0053	0.0039	0.0040	0.0038	0.0049
H76	0.8376	0.1943	0.3961	0.1042					
	0.0016	0.0006	0.0003	0.0146					
C71	0.6164	0.0679	0.3785	0.0557	0.0601	0.0325	0.0086	-0.0055	0.0120
	0.0014	0.0005	0.0003	0.0061	0.0046	0.0033	0.0034	0.0032	0.0042
C72	0.4189	0.0226	0.3971	0.0710	0.0634	0.0409	0.0062	0.0015	-0.0142
	0.0015	0.0006	0.0003	0.0067	0.0051	0.0037	0.0037	0.0035	0.0045
H72	0.3645	-0.0439	0.3717	0.1042					
	0.0015	0.0006	0.0003	0.0146					
C73	0.2867	0.0606	0.4481	0.0619	0.0917	0.0404	-0.0009	-0.0031	-0.0003
	0.0015	0.0006	0.0003	0.0066	0.0062	0.0039	0.0040	0.0036	0.0049
H73	0.1303	0.0249	0.4622	0.1042					
	0.0015	0.0006	0.0003	0.0146					
N 4	0.2278	0.1857	0.5350	0.0829	0.1210	0.0543	-0.0016	0.0046	0.0340
	0.0018	0.0008	0.0004	0.0081	0.0082	0.0047	0.0047	0.0045	0.0060
O 41	0.2954	0.2634	0.5620	0.1427	0.1379	0.0887	-0.0420	0.0280	0.0147
	0.0015	0.0006	0.0003	0.0083	0.0069	0.0049	0.0049	0.0043	0.0056
O42	0.0608	0.1410	0.5522	0.0919	0.1665	0.0693	-0.0111	0.0226	0.0225
	0.0016	0.0007	0.0003	0.0067	0.0073	0.0042	0.0046	0.0038	0.0058
C6	0.7634	0.0254	0.3235	0.0510	0.0576	0.0474	0.0030	0.0045	0.0032
	0.0014	0.0005	0.0003	0.0058	0.0046	0.0038	0.0034	0.0031	0.0038
H61	0.9316	0.0584	0.3275	0.0553					
	0.0014	0.0005	0.0003	0.0138					
H62	0.7784	-0.0528	0.3309	0.0553					
	0.0014	0.0005	0.0003	0.0138					

Table A12 continued.

Atom	X/A	Y/B	Z/C	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C5	0.6600	0.0449	0.2522	0.0472	0.0410	0.0306	-0.0008	-0.0017	0.0045
	0.0012	0.0004	0.0002	0.0051	0.0036	0.0032	0.0025	0.0026	0.0032
H5	0.4958	0.0085	0.2477	0.0607					
	0.0012	0.0004	0.0002	0.0196					
N1	0.6310	0.1516	0.2409	0.0452	0.0404	0.0510	0.0043	-0.0096	0.0000
	0.0011	0.0004	0.0002	0.0043	0.0030	0.0030	0.0027	0.0025	0.0033
C1	0.4392	0.2039	0.2346	0.0642	0.0479	0.0885	0.0000	-0.0063	0.0142
	0.0017	0.0006	0.0004	0.0072	0.0052	0.0056	0.0042	0.0043	0.0048
H1	0.2674	0.1745	0.2347	0.1042					
	0.0017	0.0006	0.0004	0.0181					
N3	0.4927	0.2995	0.2279	0.0948	0.0577	0.1357	-0.0004	-0.0361	0.0169
	0.0018	0.0006	0.0004	0.0085	0.0053	0.0072	0.0045	0.0056	0.0050
C2	0.7192	0.2992	0.2309	0.1084	0.0288	0.1084	0.0058	-0.0273	-0.0100
	0.0021	0.0006	0.0004	0.0097	0.0047	0.0071	0.0044	0.0062	0.0053
H22	0.8187	0.3656	0.2273	0.1042					
	0.0021	0.0006	0.0004	0.0181					
N2	0.8172	0.2109	0.2387	0.0583	0.0589	0.0755	0.0025	-0.0134	-0.0160
	0.0012	0.0005	0.0003	0.0053	0.0043	0.0041	0.0033	0.0033	0.0038
C4	0.8249	0.0061	0.1991	0.0401	0.0393	0.0490	0.0011	0.0001	-0.0012
	0.0012	0.0005	0.0003	0.0055	0.0039	0.0036	0.0031	0.0030	0.0036
O1	1.0237	-0.0080	0.2156	0.0422	0.0930	0.0584	-0.0023	0.0032	0.0195
	0.0009	0.0004	0.0002	0.0039	0.0041	0.0028	0.0029	0.0023	0.0032
C31	0.7437	-0.0096	0.1255	0.0475	0.0740	0.0390	-0.0082	0.0076	-0.0042
	0.0013	0.0006	0.0003	0.0055	0.0052	0.0032	0.0037	0.0029	0.0042
C32	0.4890	-0.0188	0.1176	0.0526	0.1883	0.0530	-0.0324	-0.0022	-0.0190
	0.0015	0.0009	0.0004	0.0066	0.0105	0.0041	0.0059	0.0038	0.0070
H321	0.4093	0.0475	0.1351	0.1506					
	0.0015	0.0009	0.0004	0.0132					
H322	0.4316	-0.0803	0.1469	0.1506					
	0.0015	0.0009	0.0004	0.0132					
H323	0.4419	-0.0303	0.0651	0.1506					
	0.0015	0.0009	0.0004	0.0132					
C33	0.8558	-0.1050	0.1004	0.0836	0.1321	0.0874	-0.0459	0.0063	0.0109
	0.0019	0.0008	0.0005	0.0089	0.0086	0.0063	0.0061	0.0053	0.0069
H331	1.0400	-0.0991	0.1059	0.1506					
	0.0019	0.0008	0.0005	0.0132					

Table A1.2 continued.

Atom	X/A	Y/B	Z/C	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
H332	0.8078	-0.1163	0.0479	0.1506					
	0.0019	0.0008	0.0005	0.0132					
H333	0.7975	-0.1663	0.1297	0.1506					
	0.0019	0.0008	0.0005	0.0132					
C34	0.8343	0.0774	0.0855	0.1225	0.1220	0.0525	0.0279	-0.0049	-0.0399
	0.0019	0.0007	0.0004	0.0098	0.0083	0.0047	0.0053	0.0049	0.0072
H341	0.7813	0.0698	0.0332	0.1506					
	0.0019	0.0007	0.0004	0.0132					
H342	1.0193	0.0789	0.0900	0.1506					
	0.0019	0.0007	0.0004	0.0132					
H343	0.7662	0.1448	0.1052	0.1506					
	0.0019	0.0007	0.0004	0.0132					

Final positional parameters (fractional) and thermal parameters for the structure of 1-(4-chlorophenyl)-3-(2-fluorophenyl)-2-(1,2,4-triazol-1-yl)-propan-1-one.

Atom	X/A	Y/B	Z/C	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	0.5502	0.3785	0.6444	0.0737	0.1013	0.0750	-0.0016	0.0154	0.0199
	0.0002	0.0	0.0001	0.0009	0.0023	0.0009	0.0013	0.0007	0.0014
C34	0.4151	0.5453	0.5830	0.0600	0.0669	0.0503	0.0059	0.0220	0.0119
	0.0005	0.0018	0.0005	0.0033	0.0071	0.0025	0.0036	0.0025	0.0041
C35	0.4093	0.7471	0.6337	0.0676	0.0840	0.0577	-0.0184	0.0136	-0.0098
	0.0007	0.0020	0.0005	0.0040	0.0086	0.0032	0.0041	0.0030	0.0048
H35	0.4876	0.8029	0.7109	0.1743					
	0.0007	0.0020	0.0005	0.0233					
C36	0.3044	0.8783	0.5875	0.0683	0.0550	0.0478	-0.0123	0.0157	-0.0024
	0.0005	0.0019	0.0004	0.0034	0.0059	0.0024	0.0036	0.0024	0.0046
H36	0.3004	1.0400	0.6267	0.1743					
	0.0005	0.0019	0.0004	0.0233					
C31	0.2033	0.8046	0.4975	0.0551	0.0393	0.0404	-0.0049	0.0226	-0.0114
	0.0005	0.0014	0.0004	0.0029	0.0051	0.0021	0.0027	0.0030	0.0031
C32	0.2120	0.6002	0.4378	0.0702	0.0452	0.0473	-0.0131	0.0259	-0.0144
	0.0006	0.0016	0.0005	0.0036	0.0056	0.0024	0.0035	0.0021	0.0039
H32	0.1343	0.5432	0.3603	0.1743					
	0.0006	0.0016	0.0005	0.0233					
C33	0.3174	0.4642	0.4851	0.0587	0.0427	0.0512	-0.0004	0.0187	-0.0044
	0.0005	0.0015	0.0004	0.0031	0.0056	0.0025	0.0032	0.0024	0.0037
H33	0.3228	0.3024	0.4467	0.1743					
	0.0005	0.0015	0.0004	0.0233					
C4	0.0894	0.9470	0.4456	0.0690	0.0425	0.0396	-0.0067	0.0265	-0.0063
	0.0005	0.0014	0.0004	0.0033	0.0057	0.0021	0.0027	0.0022	0.0035
O1	0.0695	1.0868	0.5072	0.0764	0.0597	0.0489	-0.0137	0.0242	0.0046
	0.0004	0.0012	0.0003	0.0025	0.0043	0.0019	0.0024	0.0019	0.0020
C5	-0.0097	0.9127	0.3186	0.0641	0.0444	0.0387	-0.0027	0.0247	-0.0069
	0.0005	0.0015	0.0004	0.0029	0.0059	0.0020	0.0027	0.0020	0.0035
H5	-0.0402	0.7381	0.3847	0.1743					
	0.0005	0.0015	0.0004	0.0233					

Atom	X/A	Y/B	Z/C	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N1	0.0488	0.9774	0.2380	0.0593	0.0422	0.0376	-0.0085	0.0219	-0.0047
	0.0004	0.0012	0.0003	0.0025	0.0043	0.0018	0.0023	0.0017	0.0028
C1	0.0401	0.8789	0.1385	0.0806	0.0555	0.0445	-0.0067	0.0286	0.0071
	0.0006	0.0020	0.0004	0.0036	0.0058	0.0024	0.0035	0.0024	0.0046
H1	-0.0003	0.7140	0.1004	0.0949					
	0.0006	0.0020	0.0004	0.0191					
N3	0.0932	1.0095	0.0852	0.1037	0.0713	0.0591	-0.0005	0.0532	0.0085
	0.0006	0.0016	0.0004	0.0042	0.0064	0.0026	0.0035	0.0029	0.0044
N2	0.1056	1.1783	0.2507	0.0791	0.0616	0.0530	-0.0117	0.0329	-0.0207
	0.0005	0.0015	0.0004	0.0034	0.0056	0.0025	0.0030	0.0024	0.0038
C2	0.1311	1.1895	0.1551	0.0853	0.0705	0.0589	0.0020	0.0417	0.0015
	0.0007	0.0020	0.0005	0.0044	0.0071	0.0033	0.0043	0.0033	0.0049
H2	0.1805	1.3299	0.1377	0.0949					
	0.0007	0.0020	0.0005	0.0191					
C6	-0.1267	1.0512	0.2955	0.0613	0.0637	0.0479	-0.0064	0.0242	0.0066
	0.0005	0.0018	0.0004	0.0032	0.0067	0.0024	0.0035	0.0023	0.0040
H61	-0.1720	0.9864	0.3497	0.0775					
	0.0005	0.0018	0.0004	0.0166					
H62	-0.1000	1.2258	0.3185	0.0775					
	0.0005	0.0018	0.0004	0.0166					
C71	-0.2183	1.0455	0.1694	0.0506	0.0601	0.0517	0.0015	0.0231	-0.0035
	0.0005	0.0017	0.0005	0.0029	0.0064	0.0026	0.0035	0.0023	0.0038
C76	-0.2226	1.2129	0.0909	0.0716	0.0568	0.0736	0.0099	0.0231	-0.0013
	0.0007	0.0020	0.0006	0.0042	0.0072	0.0038	0.0043	0.0034	0.0047
H76	-0.1595	1.3549	0.1224	0.1743					
	0.0007	0.0020	0.0006	0.0427					
C75	-0.3043	1.2045	-0.0250	0.0712	0.1117	0.0664	0.0189	0.0204	-0.0013
	0.0007	0.0026	0.0007	0.0042	0.0099	0.0038	0.0051	0.0033	0.0058
H75	-0.3057	1.3409	-0.0834	0.1560					
	0.0007	0.0026	0.0007	0.0259					
C74	-0.3829	1.0291	-0.0648	0.0746	0.0970	0.0602	-0.0028	0.0157	-0.0074
	0.0007	0.0023	0.0006	0.0042	0.0098	0.0035	0.0049	0.0032	0.0057
H74	-0.4475	1.0240	-0.1556	0.1560					
	0.0007	0.0023	0.0006	0.0259					
C73	-0.3815	0.8519	0.0095	0.0890	0.0760	0.0744	-0.0082	0.0142	-0.0269
	0.0008	0.0023	0.0006	0.0049	0.0086	0.0039	0.0054	0.0036	0.0064

Atom	X/A	Y/B	Z/C	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
H73	−0.4440	0.7090	−0.0216	0.1560					
	0.0008	0.0023	0.0006	0.0259					
C72	−0.2971	0.8681	0.1246	0.0846	0.0667	0.0677	0.0053	0.0354	−0.0184
	0.0007	0.0021	0.0006	0.0042	0.0073	0.0033	0.0048	0.0032	0.0057
F	−0.2994	0.7008	0.1976	0.1125					
	0.0006	0.0019	0.0006	0.0026					
FB	−0.1524	1.4039	0.1501	0.1125					
	0.0029	0.0105	0.0039	0.0026					

Table A1.4.

Final positional parameters (fractional) and thermal parameters for the structure Z-3-(4-nitrophenyl)-1-phenyl-2-(imidazol-1-yl)-prop-2-en-1-one.

Atom	X/A	Y/B	Z/C	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	-0.2335	0.3277	0.5775	0.0671	0.1396	0.0611	0.0611	0.0221	-0.0123
	0.0004	0.0004	0.0003	0.0023	0.0042	0.0022	0.0025	0.0018	0.0024
O2	-0.3204	0.4394	0.4677	0.0417	0.1163	0.0891	0.0045	0.0169	0.0052
	0.0004	0.0004	0.0003	0.0018	0.0037	0.0027	0.0024	0.0018	0.0020
N3	-0.2253	0.3864	0.5024	0.0450	0.0816	0.0480	-0.0152	0.0092	-0.0162
	0.0004	0.0004	0.0003	0.0022	0.0032	0.0022	0.0021	0.0018	0.0021
C1	-0.0969	0.3921	0.4487	0.0409	0.0546	0.0393	-0.0113	0.0086	-0.0115
	0.0004	0.0004	0.0003	0.0021	0.0030	0.0021	0.0019	0.0017	0.0019
C2	-0.0934	0.4430	0.3498	0.0393	0.0577	0.0499	-0.0026	0.0059	0.0007
	0.0004	0.0004	0.0004	0.0021	0.0033	0.0024	0.0021	0.0018	0.0019
H2	-0.1835	0.4793	0.3121	0.0988					
	0.0004	0.0004	0.0003	0.0083					
C3	0.0284	0.4461	0.3010	0.0485	0.0502	0.0488	0.0099	0.0048	-0.0016
	0.0004	0.0003	0.0004	0.0024	0.0030	0.0024	0.0020	0.0019	0.0020
H3	0.0399	0.4860	0.2238	0.0988					
	0.0004	0.0003	0.0004	0.0083					
C4	0.1460	0.3991	0.3492	0.0409	0.0382	0.0444	-0.0018	0.0064	-0.0028
	0.0004	0.0003	0.0003	0.0021	0.0025	0.0022	0.0018	0.0017	0.0017
C5	0.1370	0.3506	0.4502	0.0467	0.0534	0.0463	0.0057	0.0071	0.0068
	0.0004	0.0004	0.0003	0.0023	0.0031	0.0022	0.0021	0.0018	0.0020
H5	0.2269	0.3155	0.4898	0.0988					
	0.0004	0.0004	0.0003	0.0083					
C6	0.0170	0.3465	0.5004	0.0560	0.0488	0.0417	0.0026	0.0085	-0.0023
	0.0005	0.0004	0.0004	0.0025	0.0030	0.0021	0.0020	0.0018	0.0021
H6	0.0111	0.3084	0.5787	0.0988					
	0.0005	0.0004	0.0004	0.0083					
C7	0.2727	0.4082	0.2938	0.0432	0.0395	0.0455	0.0022	0.0078	0.0002
	0.0004	0.0003	0.0003	0.0021	0.0026	0.0022	0.0018	0.0017	0.0018
H7	0.2787	0.4712	0.2384	0.0988					
	0.0004	0.0003	0.0003	0.0083					
O3	0.5749	0.2917	0.2206	0.0652	0.0479	0.0823	-0.0070	0.0293	0.0085
	0.0004	0.0003	0.0003	0.0021	0.0024	0.0025	0.0018	0.0019	0.0017

Table A1.4 continued.

Atom	X/A	Y/B	Z/C	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C13	0.5490	0.4662	0.2098	0.0371	0.0444	0.0473	0.0039	0.0043	0.0019
	0.0004	0.0003	0.0003	0.0020	0.0029	0.0023	0.0020	0.0017	0.0018
C8	0.3823	0.3484	0.3029	0.0415	0.0401	0.0448	-0.0031	0.0042	-0.0034
	0.0004	0.0003	0.0003	0.0021	0.0028	0.0022	0.0019	0.0017	0.0019
N1	0.3827	0.2569	0.3623	0.0301	0.0213	0.0384	-0.0005	0.0094	-0.0015
	0.0004	0.0003	0.0003	0.0016	0.0022	0.0020	0.0015	0.0015	0.0015
C9	0.3033	0.1759	0.3378	0.1080	0.0772	0.0671	-0.0138	0.0125	-0.0111
	0.0006	0.0004	0.0004	0.0040	0.0039	0.0030	0.0028	0.0028	0.0031
H9	0.2269	0.1740	0.2688	0.0988					
	0.0006	0.0004	0.0004	0.0051					
N2	0.3272	0.1005	0.4040	0.0904	0.0335	0.0412	0.0041	0.0097	-0.0115
	0.0006	0.0004	0.0004	0.0037	0.0030	0.0024	0.0021	0.0024	0.0024
C10	0.4289	0.1343	0.4751	0.1133	0.0811	0.1007	0.0352	0.0331	0.0300
	0.0006	0.0005	0.0005	0.0042	0.0043	0.0042	0.0034	0.0036	0.0033
H10	0.4763	0.0904	0.5422	0.0988					
	0.0006	0.0005	0.0005	0.0051					
C11	0.4660	0.2298	0.4526	0.0590	0.0648	0.0669	0.0136	0.0069	-0.0012
	0.0005	0.0004	0.0005	0.0029	0.0040	0.0033	0.0027	0.0025	0.0026
H11	0.5439	0.2746	0.4965	0.0988					
	0.0005	0.0004	0.0005	0.0051					
C12	0.5073	0.3645	0.2418	0.0426	0.0423	0.0480	-0.0074	0.0065	0.0008
	0.0004	0.0003	0.0004	0.0022	0.0028	0.0024	0.0020	0.0018	0.0020
C14	0.5310	0.5507	0.2742	0.0466	0.0467	0.0632	0.0011	0.0041	-0.0005
	0.0005	0.0004	0.0004	0.0024	0.0031	0.0028	0.0023	0.0021	0.0021
H14	0.4684	0.5468	0.3438	0.0988					
	0.0005	0.0004	0.0004	0.0051					
C15	0.5934	0.6401	0.2491	0.0651	0.0449	0.0939	0.0031	0.0095	-0.0015
	0.0006	0.0004	0.0005	0.0031	0.0035	0.0040	0.0029	0.0029	0.0025
H15	0.5826	0.7051	0.3008	0.0988					
	0.0006	0.0004	0.0005	0.0051					

Table A1.4 continued.

Atom	X/A	Y/B	Z/C	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C16	0.6684	0.6459	0.1593	0.0611	0.0659	0.1147	0.0398	0.0105	-0.0104
	0.0006	0.0005	0.0006	0.0032	0.0043	0.0048	0.0040	0.0032	0.0029
H16	0.7172	0.7155	0.1403	0.0988					
	0.0006	0.0005	0.0006	0.0051					
C17	0.6833	0.5634	0.0914	0.0683	0.0731	0.0823	0.0208	0.0190	-0.0082
	0.0006	0.0005	0.0005	0.0033	0.0046	0.0039	0.0033	0.0028	0.0030
H17	0.7407	0.5697	0.0190	0.0988					
	0.0006	0.0005	0.0005	0.0051					
C18	0.6256	0.4747	0.1167	0.0460	0.0767	0.0540	0.0093	0.0093	-0.0006
	0.0005	0.0004	0.0004	0.0024	0.0040	0.0028	0.0026	0.0021	0.0025
H18	0.6385	0.4105	0.0644	0.0988					
	0.0005	0.0004	0.0004	0.0051					

Table A1.5.

Final positional parameters (fractional) and thermal parameters for the structure of E-3-(4-nitrophenyl)-1-phenyl-2-(imidazol-1-yl)-prop-2-en-1-one.

Atom	X/A	Y/B	Z/C	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O2	0.9815	0.7435	0.0514	0.0939	0.1093	0.0954	0.0104	0.0244	-0.0434
	0.0008	0.0006	0.0004	0.0084	0.0057	0.0054	0.0044	0.0050	0.0049
O1	0.9925	0.7658	0.1650	0.0528	0.0704	0.1170	-0.0313	0.0025	-0.0330
	0.0007	0.0006	0.0005	0.0067	0.0051	0.0063	0.0048	0.0046	0.0043
N3	0.9543	0.7253	0.1107	0.0418	0.0500	0.0971	-0.0121	0.0086	-0.0019
	0.0008	0.0005	0.0006	0.0064	0.0043	0.0063	0.0043	0.0047	0.0039
C1	0.8696	0.6513	0.1149	0.0396	0.0403	0.0779	-0.0148	0.0103	-0.0009
	0.0008	0.0005	0.0005	0.0062	0.0037	0.0056	0.0035	0.0041	0.0033
C2	0.8100	0.6183	0.0525	0.0525	0.0525	0.0554	0.0000	0.0174	0.0050
	0.0008	0.0005	0.0005	0.0070	0.0043	0.0050	0.0038	0.0044	0.0042
H2	0.8275	0.6442	0.0007	0.0971					
	0.0008	0.0005	0.0005	0.0101					
C3	0.7277	0.5525	0.0580	0.0480	0.0478	0.0600	-0.0054	0.0039	-0.0062
	0.0008	0.0005	0.0004	0.0069	0.0039	0.0047	0.0035	0.0040	0.0037
H3	0.6789	0.5272	0.0095	0.0971					
	0.0008	0.0005	0.0004	0.0101					
C4	0.7053	0.5169	0.1245	0.0390	0.0578	0.0451	-0.0056	0.0017	-0.0115
	0.0008	0.0006	0.0004	0.0061	0.0040	0.0040	0.0034	0.0035	0.0038
C5	0.7688	0.5533	0.1870	0.0526	0.0390	0.0475	0.0055	-0.0035	0.0041
	0.0008	0.0005	0.0004	0.0068	0.0036	0.0041	0.0033	0.0039	0.0037
H5	0.7543	0.5273	0.2393	0.0971					
	0.0008	0.0005	0.0004	0.0101					
C6	0.8490	0.6213	0.1817	0.0505	0.0409	0.0628	-0.0065	0.0017	0.0011
	0.0008	0.0005	0.0005	0.0072	0.0039	0.0053	0.0036	0.0044	0.0039
H6	0.8953	0.6512	0.2296	0.0971					
	0.0008	0.0005	0.0005	0.0101					
C7	0.6131	0.4483	0.1261	0.0497	0.0401	0.0497	-0.0005	0.0093	0.0018
	0.0007	0.0005	0.0004	0.0062	0.0037	0.0040	0.0031	0.0037	0.0033
H7	0.5443	0.4540	0.0831	0.0971					
	0.0007	0.0005	0.0004	0.0101					
C8	0.60300	0.3818	0.1735	0.0416	0.0496	0.0520	-0.0098	0.0045	0.0002
	0.0008	0.0005	0.0004	0.0064	0.0039	0.0044	0.0033	0.0037	0.0037

Table A1.5 continued.

Atom	X/A	Y/B	Z/C	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N2	0.4995	0.3291	0.1703	0.0291	0.0497	0.0475	-0.0090	0.0086	-0.0057
	0.0006	0.0004	0.0003	0.0050	0.0032	0.0033	0.0027	0.0028	0.0031
C11	0.4873	0.2327	0.1761	0.0706	0.0298	0.0374	0.0022	0.0097	-0.0005
	0.0009	0.0005	0.0004	0.0079	0.0032	0.0037	0.0027	0.0036	0.0037
H11	0.5541	0.1812	0.1869	0.0971					
	0.0009	0.0005	0.0004	0.0101					
C10	0.3759	0.2131	0.1648	0.0410	0.0607	0.0519	-0.0033	0.0091	-0.0068
	0.0009	0.0006	0.0004	0.0069	0.0046	0.0048	0.0035	0.0039	0.0043
H10	0.3384	0.1437	0.1658	0.0971					
	0.0009	0.0006	0.0004	0.0101					
N1	0.3165	0.2978	0.1519	0.0454	0.0947	0.0651	-0.0176	0.0105	-0.0160
	0.0008	0.0006	0.0004	0.0063	0.0055	0.0048	0.0039	0.0038	0.0045
C9	0.3939	0.3655	0.1568	0.0354	0.0536	0.0587	-0.0079	0.0066	-0.0098
	0.0008	0.0006	0.0005	0.0072	0.0039	0.0051	0.0036	0.0042	0.0041
H9	0.3749	0.4398	0.1503	0.0971					
	0.0008	0.0006	0.0005	0.0101					
C12	0.6896	0.3505	0.2353	0.0381	0.0438	0.0550	-0.0026	0.0119	-0.0007
	0.0007	0.0004	0.0004	0.0050	0.0032	0.0039	0.0028	0.0032	0.0030
O1	0.7726	0.3101	0.2199	0.0465	0.1021	0.0717	0.0008	0.0049	0.0226
	0.0005	0.0004	0.0003	0.0044	0.0042	0.0033	0.0030	0.0027	0.0034
C13	0.6693	0.3750	0.3095	0.0302	0.0466	0.0565	0.0104	-0.0042	-0.0011
	0.0006	0.0004	0.0004	0.0049	0.0032	0.0037	0.0027	0.0031	0.0028
C14	0.5866	0.4388	0.3238	0.0491	0.0538	0.0581	-0.0111	0.0067	-0.0017
	0.0007	0.0005	0.0004	0.0057	0.0035	0.0042	0.0032	0.0035	0.0035
H14	0.5327	0.4711	0.2800	0.0971					
	0.0007	0.0005	0.0004	0.0115					
C18	0.7401	0.3333	0.3660	0.0544	0.0473	0.0757	-0.0019	0.0011	-0.0112
	0.0007	0.0005	0.0004	0.0063	0.0035	0.0045	0.0033	0.0039	0.0034
H18	0.8056	0.2844	0.3554	0.0971					
	0.0007	0.0005	0.0004	0.0115					
C17	0.7240	0.3557	0.4369	0.0788	0.0820	0.0586	-0.0007	-0.0055	-0.0274
	0.0009	0.0006	0.0004	0.0080	0.0053	0.0048	0.0039	0.0043	0.0049
H17	0.7773	0.3235	0.4810	0.0971					
	0.0009	0.0006	0.0004	0.0115					
C16	0.6419	0.4189	0.4491	0.0791	0.0715	0.0543	-0.0140	0.0210	-0.0208
	0.0009	0.0006	0.0004	0.0077	0.0048	0.0044	0.0038	0.0046	0.0049

Atom	X/A	Y/B	Z/C	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
H16	0.6323	0.4360	0.5042	0.0971					
	0.0009	0.0006	0.0004	0.0115					
C15	0.5733	0.4613	0.3944	0.0679	0.0629	0.0647	-0.0264	0.0164	-0.0112
	0.0008	0.0005	0.0004	0.0072	0.00444	0.0045	0.0037	0.0043	0.0040
H15	0.5090	0.5106	0.4065	0.0971					
	0.0008	0.0005	0.0004	0.0115					

<u>Molecule 2.</u>

Atom	X/A	Y/B	Z/C	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O2	0.5787	0.1325	0.4676	0.1171	0.1177	0.0909	0.0269	0.0085	0.0648
	0.0009	0.0006	0.0004	0.0085	0.0066	0.0051	0.0049	0.0050	0.0060
O1	0.5488	0.1366	0.3528	0.0801	0.0795	0.0894	0.0038	0.0330	0.0304
	0.0007	0.0005	0.0004	0.0063	0.0042	0.0047	0.0036	0.0040	0.0037
N3	0.5286	0.1630	0.4113	0.0572	0.0615	0.0731	0.0151	0.0182	0.0093
	0.0007	0.0005	0.0004	0.0062	0.0042	0.0052	0.0039	0.0043	0.0038
C1	0.4478	0.2357	0.4145	0.0415	0.0523	0.0483	0.0098	0.0036	0.0092
	0.0008	0.0005	0.0004	0.0071	0.0044	0.0042	0.0033	0.0039	0.0039
C6	0.3883	0.2678	0.3495	0.0477	0.0476	0.0525	-0.0098	0.0168	0.0013
	0.0008	0.0005	0.0004	0.0069	0.0042	0.0046	0.0036	0.0040	0.0042
H6	0.4074	0.2406	0.2985	0.0855					
	0.0008	0.0005	0.0004	0.0138					
C5	0.3064	0.3343	0.3517	0.0414	0.0525	0.0378	0.0051	0.0086	-0.0017
	0.0007	0.0005	0.0004	0.0061	0.0042	0.0038	0.0032	0.0034	0.0038
H5	0.2588	0.3586	0.3023	0.0855					
	0.0007	0.0005	0.0004	0.0138					
C4	0.2812	0.3708	0.4175	0.0366	0.0461	0.0429	0.0050	0.0057	-0.0007
	0.0007	0.0005	0.0004	0.0061	0.0039	0.0043	0.0034	0.0035	0.0036
C3	0.3370	0.3357	0.4806	0.0630	0.0457	0.0378	-0.0005	0.0122	0.0117
	0.0008	0.0005	0.0004	0.0071	0.0041	0.0041	0.0033	0.0038	0.0040
H3	0.3136	0.3600	0.5314	0.0855					
	0.0008	0.0005	0.0004	0.0138					
C2	0.4226	0.2689	0.4799	0.0728	0.0535	0.0401	0.0206	-0.0010	0.0018
	0.0008	0.0005	0.0004	0.0082	0.0043	0.0044	0.0037	0.0041	0.0045
H2	0.4679	0.2440	0.5298	0.0855					
	0.0008	0.0005	0.0004	0.0138					
C7	0.1881	0.4395	0.4211	0.0475	0.0425	0.0333	-0.0014	0.0093	-0.0006
	0.0007	0.0005	0.0003	0.0061	0.0036	0.0034	0.0029	0.0032	0.0035
H7	0.1427	0.4344	0.4675	0.0855					
	0.0007	0.0005	0.0004	0.0138					

Table A1.5 continued.

Atom	X/A	Y/B	Z/C	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C8	0.1534	0.5060	0.3739	0.0317	0.0484	0.0372	-0.0042	0.0027	-0.0050
	0.0007	0.0005	0.0004	0.0057	0.0039	0.0037	0.0030.	0.0031	0.0034
N1	0.0544	0.5579	0.3795	0.0356	0.0487	0.0493	-0.0026	0.0072	0.0029
	0.0006	0.0004	0.0003	0.0052	0.0033	0.0033	0.0028	0.0029	0.0032
C9	-0.0450	0.5255	0.3976	0.0467	0.0633	0.0681	0.0004	0.0185	0.0105
	0.0008	0.0006	0.0004	0.0074	0.0051	0.0051	0.0040	0.0045	0.0050
H9	-0.0604	0.4530	0.4114	0.0855					
	0.0008	0.0006	0.0004	0.0138					
N2	-0.1205	0.5924	0.3959	0.0555	0.0641	0.0926	0.0022	0.0289	0.0087
	0.0007	0.0005	0.0004	0.0064	0.0045	0.0054	0.0037	0.0042	0.0040
C10	-0.0693	0.6730	0.3757	0.0544	0.0578	0.0724	-0.0050	0.0046	0.0123
	0.0009	0.0006	0.0005	0.0081	0.0049	0.0056	0.0043	0.0047	0.0049
H10	-0.1101	0.7412	0.3699	0.0855					
	0.0009	0.0006	0.0005	0.0138					
C11	0.0391	0.6546	0.3646	0.0574	0.0363	0.0611	-0.0054	0.0105	0.0020
	0.0009	0.0005	0.0004	0.0079	0.0037	0.0049	0.0033	0.0044	0.0037
H10	0.0995	0.7040	0.3475	0.0855					
	0.0009	0.0005	0.0004	0.0138					
O3	0.3047	0.5676	0.3194	0.0442	0.0749	0.0924	0.0191	0.0059	-0.0205
	0.0006	0.0004	0.0003	0.0047	0.0035	0.0043	0.0032	0.0032	0.0033
C12	0.2126	0.5334	0.3103	0.0441	0.0377	0.0525	0.0045	0.0056	-0.0022
	0.0008	0.0004	0.0004	0.0062	0.0032	0.0039	0.0028	0.0033	0.0035
C13	0.1520	0.5136	0.2368	0.0401	0.0439	0.0495	0.0149	0.0190	0.0091
	0.0007	0.0005	0.0004	0.0060	0.0032	0.0039	0.0028	0.0033	0.0035
C18	0.1906	0.5566	0.1765	0.0676	0.0697	0.0608	0.0209	0.0248	0.0164
	0.0009	0.0006	0.0004	0.0074	0.0051	0.0053	0.0042	0.0045	0.0045
H18	0.2585	0.6076	0.1833	0.0855					
	0.0009	0.0006	0.0004	0.0102					
C17	0.1399	0.5324	0.1098	0.0861	0.1134	0.0548	0.0305	0.0317	0.0360
	0.0011	0.0008	0.0005	0.0099	0.0082	0.0059	0.0055	0.0058	0.0071
H17	0.1688	0.5648	0.0631	0.0855					
	0.0011	0.0008	0.0005	0.0102					
C16	0.0538	0.4674	0.0999	0.0901	0.0937	0.0458	0.0033	0.0021	0.0383
	0.0010	0.0008	0.0004	0.0102					

Table A1.5 continued.

Atom	X/A	Y/B	Z/C	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
H16	0.0155	0.4503	0.0462	0.0855					
	0.0010	0.0008	0.0004	0.0102					
C15	0.0153	0.4238	0.1586	0.0735	0.0746	0.0476	-0.0070	0.0043	0.0116
	0.0009	0.0006	0.0004	0.0078	0.0050	0.0046	0.0039	0.0042	0.0046
H15	-0.0523	0.3726	0.1508	0.0855					
	0.0009	0.0006	0.0004	0.0102					
C14	0.0661	0.4480	0.2282	0.0458	0.0535	0.0543	-0.0017	0.0101	0.0045
	0.0007	0.0005	0.0004	0.0057	0.0039	0.0040	0.0031	0.0034	0.0035
H14	0.0372	0.4149	0.2745	0.0855					
	0.0007	0.0005	0.0004	0.0102					

Table A1.6.

Final positional parameters (fractional) and thermal parameters for the structure of 4'-aceto-2,3-benzo-1,4,7,10,13,16-hexaoxacyclooctadec-2-ene, strontium perchlorate.

Molecule 1.

Atom	X/A	Y/B	Z/C	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sr	0.7156	0.7992	0.7115	0.0433	0.0211	0.0502	0.0027	0.0306	0.0066
	0.0002	0.0004	0.0002	0.0013	0.0020	0.0014	0.0013	0.0011	0.0012
C1	0.9501	0.9249	0.8801	0.0587	0.0524	0.0475	0.0070	0.0226	0.0074
	0.0020	0.0032	0.0016	0.0041	0.0043	0.0041	0.0041	0.0038	0.0042
02	0.9025	0.8032	0.8427	0.0557	0.0532	0.0610	0.0033	0.0332	-0.0046
	0.0013	0.0026	0.0012	0.0039	0.0042	0.0039	0.0040	0.0035	0.0040
C3	0.9579	0.6815	0.8402	0.0554	0.0529	0.0573	-0.0079	0.0304	0.0119
	0.0019	0.0032	0.0016	0.0041	0.0043	0.0041	0.0042	0.0039	0.0042
C4	0.8916	0.5525	0.7938	0.0498	0.0569	0.0583	0.0055	0.0228	0.0010
	0.0019	0.0033	0.0017	0.0041	0.0043	0.0041	0.0042	0.0039	0.0042
05	0.8204	0.6005	0.7131	0.0453	0.0444	0.0414	-0.0071	0.0358	0.0116
	0.0016	0.0029	0.0014	0.0039	0.0042	0.0039	0.0040	0.0034	0.0040
C6	0.7811	0.4972	0.6519	0.0567	0.0446	0.0557	-0.0096	0.0262	0.0109
	0.0019	0.0032	0.0016	0.0040	0.0042	0.0040	0.0041	0.0038	0.0041
C7	0.7141	0.5671	0.5762	0.0494	0.0476	0.0566	-0.0029	0.0296	0.0031
	0.0018	0.0031	0.0016	0.0040	0.0042	0.0040	0.0041	0.0037	0.0041
08	0.6473	0.6320	0.5813	0.0612	0.0554	0.0527	-0.0115	0.0376	0.0111
	0.0013	0.0024	0.0011	0.0038	0.0042	0.0037	0.0038	0.0032	0.0039
C9	0.5689	0.7181	0.5007	0.0606	0.0555	0.0573	-0.0028	0.0294	0.0074
	0.0020	0.0032	0.0017	0.0041	0.0042	0.0040	0.0041	0.0038	0.0041
C10	0.4965	0.7529	0.5125	0.0638	0.0598	0.0556	-0.0064	0.0332	0.0063
	0.0019	0.0032	0.0016	0.0041	0.0042	0.0040	0.0041	0.0038	0.0041
O11	0.5458	0.8675	0.5819	0.0532	0.0557	0.0538	-0.0022	0.0230	0.0042
	0.0013	0.0025	0.0011	0.0039	0.0042	0.0038	0.0039	0.0035	0.0039
C12	0.4830	0.9131	0.5987	0.0512	0.0591	0.0601	-0.0059	0.0344	0.0020
	0.0018	0.0032	0.0016	0.0040	0.0042	0.0040	0.0041	0.0037	0.0041
C13	0.5401	1.0020	0.6737	0.0500	0.0483	0.0469	-0.0072	0.0296	0.0050
	0.0018	0.0031	0.0015	0.0040	0.0042	0.0040	0.0040	0.0036	0.0041
014	0.6099	0.9316	0.7421	0.0392	0.0442	0.0571	-0.0026	0.0239	0.0117
	0.0012	0.0024	0.0011	0.0037	0.0042	0.0038	0.0039	0.0033	0.0038

Table A1.6 continued.

Atom	X/A	Y/B	Z/C	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C15	0.6517	1.0019	0.8190	0.0517	0.0562	0.0579	-0.0031	0.0330	0.0091
	0.0019	0.0032	0.0016	0.0040	0.0042	0.0040	0.0041	0.0037	0.0041
C16	0.7391	1.0869	0.8446	0.0505	0.0536	0.0542	-0.0049	0.0279	0.0019
	0.0019	0.0032	0.0016	0.0040	0.0042	0.0040	0.0041	0.0037	0.0041
O17	0.8038	0.9812	0.8500	0.0533	0.0528	0.0537	-0.0071	0.0289	0.0019
	0.0013	0.0025	0.0011	0.0038	0.0042	0.0038	0.0039	0.0034	0.0039
C18	0.8984	1.0501	0.8817	0.0551	0.0530	0.0525	0.0081	0.0267	-0.0008
	0.0019	0.0032	0.0016	0.0041	0.0042	0.0040	0.0041	0.0038	0.0041
C19	0.9359	1.1729	0.9141	0.0542	0.0547	0.0535	0.0010	0.0206	0.0023
	0.0020	0.0033	0.0017	0.0041	0.0042	0.0041	0.0041	0.0039	0.0041
C20	1.0322	1.2166	0.9440	0.0585	0.0505	0.0529	0.0061	0.0249	0.0029
	0.0020	0.0033	0.0017	0.0041	0.0042	0.0041	0.0041	0.0038	0.0041
C21	1.0843	1.1139	0.9401	0.0568	0.0502	0.0511	-0.0009	0.0276	0.0095
	0.0019	0.0032	0.0016	0.0041	0.0042	0.0040	0.0041	0.0038	0.0041
C22	1.0444	0.9645	0.9101	0.0571	0.0508	0.0486	-0.0025	0.0266	0.0025
	0.0019	0.0032	0.0016	0.0041	0.0043	0.0041	0.0041	0.0038	0.0041
C23A	1.1898	1.1556	0.9807	0.0499	0.0487	0.0493	-0.0001	0.0277	0.0082
	0.0029	0.0039	0.0025	0.0042	0.0043	0.0042	0.0042	0.0041	0.0042
C23B	1.0803	1.3666	0.9882	0.0557	0.0511	0.0518	0.0021	0.0280	0.0039
	0.0029	0.0039	0.0026	0.0042	0.0043	0.0042	0.0042	0.0041	0.0042
O24A	1.2258	1.0570	0.9896	0.0554	0.0508	0.0587	0.0024	0.0210	0.0082
	0.0023	0.0036	0.0020	0.0042	0.0043	0.0042	0.0042	0.0040	0.0042
O24B	1.0283	1.4434	0.9994	0.0585	0.0513	0.0581	-0.0020	0.0223	0.0079
	0.0023	0.0036	0.0021	0.0042	0.0042	0.0041	0.0042	0.0040	0.0042
C25A	1.2302	1.3318	1.0077	0.0575	0.0557	0.0592	0.0029	0.0253	0.0023
	0.0030	0.0039	0.0027	0.0042	0.0043	0.0042	0.0042	0.0042	0.0042
C25B	1.1770	1.4244	0.9985	0.0549	0.0521	0.0540	-0.0009	0.0260	0.0038
	0.0029	0.0039	0.0026	0.0042	0.0043	0.0042	0.0042	0.0041	0.0042
Cl1	0.7928	1.0861	0.6476	0.0502	0.0658	0.0628	-0.0075	0.0410	-0.0008
	0.0005	0.0012	0.0005	0.0028	0.0038	0.0029	0.0030	0.0023	0.0029
Cl2	0.6115	0.5023	0.7587	0.0832	0.0972	0.0938	-0.0105	0.0609	0.0107
	0.0005	0.0015	0.0006	0.0033	0.0040	0.0033	0.0034	0.0027	0.0034
O31	0.7928	0.9371	0.6374	0.0724	0.0653	0.0688	-0.0003	0.0440	0.0026
	0.0015	0.0027	0.0012	0.0039	0.0042	0.0039	0.0040	0.0035	0.0040
O32	0.7344	1.1542	0.5673	0.0696	0.0576	0.0626	0.0056	0.0280	0.0024
	0.0015	0.0027	0.0012	0.0040	0.0042	0.0040	0.0040	0.0037	0.0041

Table A1.[illegible] continued.

Atom	X/A	Y/B	Z/C	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
033	0.7478	1.1058	0.6895	0.0560	0.0614	0.0665	0.0071	0.0329	0.0130
	0.0013	0.0026	0.0012	0.0039	0.0042	0.0039	0.0040	0.0035	0.0040
034	0.8838	1.1638	0.6953	0.0624	0.0613	0.0785	0.0050	0.0232	0.0061
	0.0015	0.0028	0.0013	0.0040	0.0042	0.0040	0.0041	0.0038	0.0041
041	0.7014	0.5988	0.7987	0.0710	0.0653	0.0746	0.0113	0.0356	0.0020
	0.0015	0.0027	0.0013	0.0040	0.0040	0.0040	0.0041	0.0037	0.0041
042	0.5810	0.5186	0.8088	0.0768	0.0782	0.0800	0.0068	0.0428	-0.0008
	0.0015	0.0028	0.0013	0.0040	0.0042	0.0040	0.0041	0.0037	0.0041
043	0.6111	0.3799	0.7237	0.0822	0.0747	0.0972	0.0053	0.0256	0.0111
	0.0017	0.0030	0.0015	0.0041	0.0043	0.0041	0.0042	0.0040	0.0041
044	0.5448	0.5643	0.6829	0.0971	0.0778	0.0875	0.0014	0.0191	0.0094
	0.0018	0.0030	0.0015	0.0041	0.0043	0.0041	0.0042	0.0040	0.0042

Molecule 2

Atom	X/A	Y/B	Z/C	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sr	0.2016	0.7889	0.6838	0.0381	0.0337	0.0569	-0.0042	0.0286	0.0051
	0.0002	0.0004	0.0002	0.0013	0.0022	0.0015	0.0014	0.0012	0.0013
C1	0.4167	0.9262	0.8634	0.0477	0.0386	0.0290	-0.0074	0.0194	0.0097
	0.0020	0.0032	0.0016	0.0039	0.0042	0.0039	0.0039	0.0035	0.0040
02	0.3801	0.7978	0.8275	0.0610	0.0335	0.0621	-0.0176	0.0447	0.0142
	0.0012	0.0022	0.0010	0.0037	0.0041	0.0037	0.0036	0.0031	0.0037
C3	0.4405	0.7008	0.8333	0.0588	0.0489	0.0572	-0.0128	0.0359	0.0216
	0.0018	0.0030	0.0016	0.0039	0.0042	0.0039	0.0040	0.0036	0.0040
C4	0.3796	0.5562	0.7833	0.0760	0.0717	0.0866	-0.0117	0.0516	0.0298
	0.0021	0.0033	0.0019	0.0040	0.0042	0.0040	0.0041	0.0038	0.0040
05	0.3158	0.5934	0.7018	0.0537	0.0580	0.0798	0.0093	0.0347	0.0066
	0.0014	0.0026	0.0013	0.0038	0.0041	0.0039	0.0040	0.0035	0.0039
C6	0.2875	0.4853	0.6384	0.0423	0.0281	0.0493	-0.0109	0.0139	0.0149
	0.0017	0.0029	0.0015	0.0039	0.0041	0.0040	0.0039	0.0036	0.0039
C7	0.2301	0.5756	0.5612	0.0881	0.0833	0.0915	-0.0068	0.0533	0.0158
	0.0023	0.0035	0.0020	0.0041	0.0042	0.0041	0.0041	0.0039	0.0041
08	0.1553	0.6314	0.5562	0.0653	0.0723	0.0672	-0.0059	0.0489	-0.0082
	0.0014	0.0026	0.0012	0.0038	0.0041	0.0038	0.0039	0.0033	0.0039
C9	0.0888	0.7188	0.4787	0.0627	0.0581	0.0574	-0.0048	0.0305	0.0090
	0.0020	0.0032	0.0017	0.0040	0.0042	0.0040	0.0041	0.0038	0.0041
C10	0.0032	0.7182	0.4728	0.0601	0.0565	0.0553	0.0060	0.0286	-0.0055
	0.0020	0.0032	0.0016	0.0040	0.0042	0.0040	0.0041	0.0038	0.0041
011	0.0322	0.7924	0.5480	0.0568	0.0611	0.0709	-0.0031	0.0322	-0.0047
	0.0014	0.0026	0.0012	0.0039	0.0042	0.0039	0.0040	0.0035	0.0040

Table A1.6 continued.

Atom	X/A	Y/B	Z/C	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C12	-0.0464	0.8328	0.5457	0.0471	0.0574	0.0699	-0.0081	0.0314	0.0091
	0.0018	0.0032	0.0017	0.0040	0.0042	0.0041	0.0041	0.0038	0.0041
C13	-0.0232	0.8667	0.6240	0.0517	0.0662	0.0823	0.0136	0.0335	-0.0008
	0.0020	0.0033	0.0019	0.0040	0.0042	0.0041	0.0041	0.0039	0.0041
O14	0.0728	0.9417	0.6784	0.0491	0.0717	0.0719	-0.0082	0.0382	0.0086
	0.0013	0.0026	0.0012	0.0037	0.0042	0.0039	0.0039	0.0033	0.0039
C15	0.1000	0.9611	0.7601	0.0621	0.0663	0.0628	-0.0011	0.0405	0.0040
	0.0019	0.0032	0.0017	0.0040	0.0042	0.0040	0.0041	0.0037	0.0041
C16	0.1980	1.0773	0.7997	0.0702	0.0570	0.0730	-0.0044	0.0324	0.0130
	0.0021	0.0033	0.0018	0.0041	0.0040	0.0041	0.0041	0.0039	0.0041
O17	0.2652	0.9827	0.8091	0.0492	0.0365	0.0605	-0.0096	0.0309	0.0176
	0.0012	0.0023	0.0011	0.0037	0.0041	0.0038	0.0038	0.0033	0.0038
C18	0.3613	1.0322	0.8555	0.0518	0.0409	0.0489	-0.0069	0.0305	0.0112
	0.0018	0.0030	0.0015	0.0039	0.0042	0.0039	0.0040	0.0036	0.0040
C19	0.3929	1.1708	0.8865	0.0644	0.0552	0.0499	-0.0072	0.0326	0.0044
	0.0019	0.0032	0.0016	0.0040	0.0042	0.0040	0.0041	0.0037	0.0041
C20	0.4959	1.2195	0.9334	0.0661	0.0559	0.0514	-0.0004	0.0291	-0.0044
	0.0020	0.0032	0.0017	0.0041	0.0042	0.0040	0.0041	0.0038	0.0041
C21	0.5490	1.0912	0.9411	0.0564	0.0502	0.0495	0.0072	0.0274	0.0119
	0.0018	0.0031	0.0016	0.0040	0.0042	0.0040	0.0040	0.0037	0.0040
C22	0.5219	0.9550	0.9120	0.0748	0.0694	0.0602	-0.0005	0.0396	0.0025
	0.0021	0.0033	0.0017	0.0040	0.0042	0.0040	0.0041	0.0038	0.0041
C23A	0.6730	1.1275	0.9984	0.0496	0.0477	0.0474	0.0038	0.0239	0.0053
	0.0029	0.0038	0.0025	0.0041	0.0042	0.0041	0.0042	0.0040	0.0042
C23B	0.5445	1.3516	0.9768	0.0535	0.0496	0.0487	0.0003	0.0003	0.0042
	0.0029	0.0039	0.0025	0.0042	0.0042	0.0042	0.0042	0.0042	0.0042
O24A	0.7137	1.0311	1.0061	0.0599	0.0551	0.0592	0.0016	0.0218	0.0042
	0.0024	0.0036	0.0021	0.0041	0.0042	0.0041	0.0041	0.0040	0.0041
O24B	0.4890	1.4413	0.9766	0.0684	0.0617	0.0646	-0.0021	0.0209	0.0064
	0.0025	0.0036	0.0021	0.0042	0.0042	0.0042	0.0042	0.0041	0.0042
C25A	0.6927	1.2893	1.0183	0.0566	0.0506	0.0549	0.0001	0.0276	0.0066
	0.0029	0.0038	0.0026	0.0042	0.0042	0.0042	0.0042	0.0041	0.0042
C25B	0.6541	1.3900	1.0183	0.0604	0.0563	0.0594	-0.0015	0.0257	0.0025
	0.0030	0.0039	0.0027	0.0042	0.0042	0.0042	0.0042	0.0041	0.0042
Cl1	0.2986	1.0793	0.6375	0.0588	0.0843	0.0701	0.0105	0.0462	0.0213
	0.0005	0.0013	0.0005	0.0029	0.0039	0.0030	0.0031	0.0024	0.0031

Table A1.6 continued.

Atom	X/A	Y/B	Z/C	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C12	0.1134	0.5071	0.7527	0.0808	0.0638	0.0816	-0.0045	0.0534	0.0165
	0.0006	0.0013	0.0006	0.0032	0.0038	0.0032	0.0031	0.0026	0.0031
O31	0.3200	0.9325	0.6473	0.0669	0.0591	0.0940	-0.0109	0.0520	-0.0002
	0.0015	0.0027	0.0013	0.0038	0.0041	0.0039	0.0040	0.0035	0.0040
O32	0.2739	1.1285	0.5628	0.0870	0.1000	0.0768	0.0185	0.0601	0.0066
	0.0016	0.0028	0.0013	0.0039	0.0042	0.0039	0.0040	0.0035	0.0040
O33	0.2202	1.0812	0.6435	0.0597	0.0700	0.0767	0.0156	0.0458	0.0058
	0.0014	0.0026	0.0012	0.0038	0.0041	0.0039	0.0039	0.0034	0.0039
O34	0.3818	1.1587	0.7019	0.0582	0.0633	0.0849	-0.0078	0.0314	-0.0048
	0.0015	0.0027	0.0013	0.0039	0.0042	0.0040	0.0040	0.0037	0.0040
O41	0.1662	0.6618	0.7861	0.1164	0.1041	0.1098	0.0050	0.0553	0.0058
	0.0020	0.0032	0.0017	0.0041	0.0042	0.0041	0.0041	0.0039	0.0041
O42	0.0136	0.5094	0.7173	0.0846	0.1039	0.1333	0.0096	0.0499	0.0082
	0.0018	0.0031	0.0017	0.0040	0.0042	0.0041	0.0041	0.0039	0.0041
O43	0.1576	0.3949	0.8064	0.1396	0.1016	0.1202	0.0045	0.0360	0.0136
	0.0022	0.0033	0.0019	0.0041	0.0042	0.0041	0.0041	0.0041	0.0042
O44	0.1123	0.5147	0.6847	0.1292	0.1171	0.1259	-0.0004	0.0643	-0.0015
	0.0021	0.0033	0.0018	0.0041	0.0042	0.0041	0.0041	0.0040	0.0041

Table A1.7.

Final positional parameters (fractional) and thermal parameters for the structure of isothiocyanato(3,15,21-triaza-6,9,12-trioxabicyclo(15.3.1) heneicosa-1(21),2,15,17,19-pentaene)calcium(II).

Atom	X/A	Y/B	Z/C	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ca	0.0896	0.3821	0.2521	0.0329	0.0396	0.0459	-0.0035	-0.0002	-0.0014
	0.0001	0.0000	0.0001	0.0011	0.0003	0.0004	0.0003	0.0003	0.0003
S1	-0.2572	0.3479	-0.1635	0.0451	0.1066	0.0697	-0.0051	-0.0064	-0.0076
	0.0002	0.0001	0.0002	0.0013	0.0010	0.0008	0.0007	0.0006	0.0008
C16	-0.1167	0.3585	-0.0648	0.0466	0.0467	0.0430	-0.0035	0.0062	0.0067
	0.0005	0.0001	0.0005	0.0035	0.0019	0.0020	0.0015	0.0020	0.0019
N4	-0.0165	0.3661	0.0058	0.0639	0.0731	0.0549	-0.0141	-0.0099	0.0074
	0.0006	0.0002	0.0005	0.0038	0.0023	0.0022	0.0017	0.0022	0.0021
S2	0.4455	0.4230	0.6535	0.0538	0.0841	0.0994	-0.0195	-0.0146	-0.0046
	0.0002	0.0001	0.0002	0.0014	0.0009	0.0010	0.0008	0.0008	0.0007
C17	0.3060	0.4103	0.5559	0.0617	0.0414	0.0481	-0.0047	0.0075	0.0027
	0.0006	0.0001	0.0005	0.0040	0.0019	0.0021	0.0016	0.0023	0.0019
N5	0.2044	0.4006	0.4880	0.0776	0.0707	0.0652	-0.0123	-0.0235	0.0024
	0.0006	0.0002	0.0005	0.0041	0.0024	0.0023	0.0019	0.0024	0.0023
N1	0.2590	0.3035	0.2041	0.0445	0.0415	0.0459	0.0038	-0.0020	0.0043
	0.0004	0.0001	0.0004	0.0029	0.0015	0.0017	0.0013	0.0016	0.0015
C1	0.2254	0.2562	0.2521	0.0524	0.0416	0.0539	0.0008	-0.0091	0.0005
	0.0005	0.0001	0.0005	0.0036	0.0018	0.0021	0.0016	0.0021	0.0018
C2	0.3063	0.2133	0.2166	0.0874	0.0444	0.0757	-0.0025	-0.0079	0.0102
	0.0008	0.0002	0.0006	0.0051	0.0022	0.0030	0.0021	0.0031	0.0024
H23	0.2748	0.1756	0.2542	0.1109					
	0.0008	0.0002	0.0006	0.0118					
C3	0.4251	0.2194	0.1333	0.0781	0.0672	0.0927	-0.0128	0.0054	0.0330
	0.0008	0.0002	0.0007	0.0054	0.0031	0.0038	0.0027	0.0035	0.0030
H33	0.4885	0.1867	0.1036	0.1109					
	0.0008	0.0002	0.0007	0.0118					
C4	0.4634	0.2682	0.0873	0.0563	0.0719	0.0874	-0.0039	0.0109	0.0216
	0.0007	0.0002	0.0007	0.0043	0.0031	0.0034	0.0025	0.0029	0.0027
H41	0.5586	0.2746	0.0243	0.1109					
	0.0007	0.0002	0.0007	0.0118					
C5	0.3756	0.3091	0.1252	0.0389	0.0611	0.0531	-0.0008	0.0044	0.0062
	0.0005	0.0002	0.0005	0.0036	0.0023	0.0022	0.0018	0.0021	0.0020

Table A1.7 continued.

Atom	X/A	Y/B	Z/C	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C6	0.4112	0.3618	0.0811	0.0344	0.0682	0.0673	0.0069	0.0104	0.0007
	0.0006	0.0002	0.0006	0.0037	0.0025	0.0028	0.0021	0.0023	0.0022
H61	0.5077	0.3697	0.0224	0.1109					
	0.0006	0.0002	0.0006	0.0043					
N3	0.3293	0.3975	0.1134	0.0373	0.0524	0.0667	0.0120	0.0065	-0.0053
	0.0004	0.0001	0.0004	0.0028	0.0018	0.0021	0.0015	0.0018	0.0017
C7	0.3690	0.4497	0.0708	0.0422	0.0665	0.0980	0.0255	0.0141	-0.0105
	0.0007	0.0002	0.0007	0.0040	0.0027	0.0036	0.0027	0.0029	0.0024
H71	0.4809	0.4529	0.0715	0.1109					
	0.0007	0.0002	0.0007	0.0043					
H72	0.3296	0.4586	-0.0433	0.1109					
	0.0007	0.0002	0.0007	0.0043					
C8	0.3094	0.4858	0.1868	0.0704	0.0493	0.0907	0.0122	-0.0081	-0.0226
	0.0007	0.0002	0.0007	0.0049	0.0024	0.0035	0.0023	0.0031	0.0026
H81	0.3287	0.5249	0.1516	0.1109					
	0.0007	0.0002	0.0007	0.0043					
H82	0.3548	0.4793	0.2997	0.1109					
	0.0007	0.0002	0.0007	0.0043					
O1	0.1643	0.4762	0.1900	0.0639	0.0415	0.0686	-0.0037	0.0035	-0.0049
	0.0004	0.0001	0.0004	0.0030	0.0014	0.0018	0.0012	0.0017	0.0015
C9	0.0886	0.5140	0.2745	0.1173	0.0398	0.0824	-0.0090	0.0313	0.0053
	0.0009	0.0002	0.0007	0.0067	0.0021	0.0036	0.0021	0.0037	0.0029
H91	0.1090	0.5099	0.3970	0.1109					
	0.0009	0.0002	0.0007	0.0043					
H92	0.1182	0.5520	0.2375	0.1109					
	0.0009	0.0002	0.0007	0.0043					
C10	-0.0582	0.5050	0.2419	0.0980	0.0708	0.0853	0.0131	0.0355	0.0444
	0.0009	0.0002	0.0007	0.0067	0.0030	0.0035	0.0027	0.0038	0.0035
H101	-0.0771	0.5078	0.1188	0.1109					
	0.0009	0.0002	0.0007	0.0043					
H102	-0.1205	0.5331	0.3017	0.1109					
	0.0009	0.0002	0.0007	0.0043					
O2	-0.0929	0.4549	0.2953	0.0606	0.0656	0.0797	-0.0078	0.0042	0.0184
	0.0005	0.0001	0.0004	0.0032	0.0019	0.0021	0.0015	0.0020	0.0017

Table A1.7 continued.

Atom	X/A	Y/B	Z/C	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C11	-0.2371	0.4430	0.2821	0.0500	0.1179	0.1265	-0.0055	-0.0034	0.0317
	0.0008	0.0003	0.0009	0.0049	0.0051	0.0052	0.0042	0.0031	0.0036
H111	-0.2971	0.4739	0.3311	0.1109					
	0.0008	0.0003	0.0009	0.0043					
H112	-0.2641	0.4385	0.1614	0.1109					
	0.0008	0.0003	0.0009	0.0043					
C12	-0.2684	0.3963	0.3633	0.0495	0.1171	0.1367	-0.0313	0.0213	0.0024
	0.0008	0.0003	0.0009	0.0049	0.0053	0.0053	0.0043	0.0038	0.0037
H122	-0.3691	0.3824	0.3267	0.1109					
	0.0008	0.0003	0.0009	0.0043					
H121	-0.2702	0.4042	0.4360	0.1109					
	0.0008	0.0003	0.0009	0.0043					
O3	-0.1734	0.3597	0.3364	0.0617	0.1029	0.1407	0.0263	0.0502	0.0215
	0.0005	0.0002	0.0006	0.0036	0.0028	0.0036	0.0026	0.0028	0.0024
C13	-0.2073	0.3098	0.3923	0.0704	0.1026	0.1453	0.0039	0.0568	-0.0251
	0.0008	0.0003	0.0009	0.0058	0.0045	0.0054	0.0041	0.0046	0.0039
H131	-0.2942	0.3122	0.4707	0.1109					
	0.0008	0.0003	0.0009	0.0043					
H132	-0.2341	0.2851	0.2963	0.1109					
	0.0008	0.0003	0.0009	0.0043					
C14	-0.0857	0.2886	0.4755	0.0777	0.0772	0.0870	0.0138	0.0383	-0.0119
	0.0008	0.0002	0.0007	0.0053	0.0031	0.0033	0.0027	0.0033	0.0031
H141	-0.1034	0.2489	0.5041	0.1109					
	0.0008	0.0002	0.0007	0.0043					
H142	-0.0673	0.3101	0.5804	0.1109					
	0.0008	0.0002	0.0007	0.0043					
N 2	0.0323	0.2929	0.3762	0.0617	0.0524	0.0564	0.0021	0.0190	-0.0165
	0.0005	0.0001	0.0004	0.0032	0.0019	0.0019	0.0015	0.0019	0.0018
C15	0.1014	0.2531	0.3465	0.0692	0.0435	0.0614	0.0042	-0.0032	-0.0095
	0.0006	0.0002	0.0005	0.0041	0.0020	0.0025	0.0017	0.0025	0.0021
H151	0.0676	0.2165	0.3915	0.1109					
	0.0006	0.0002	0.0005	0.0043					

Table A1.8.

Final positional parameters (fractional) and thermal parameters for the structure of aqua-di-isothiocyanato(3,15,21-triaza-6,9,12-trioxabicyclo(15.3.1)heneicosa-1(21),2,15,17,19-pentaene)strontium(II).

Atom	X/A	Y/B	Z/C	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sr	0.2409	0.6793	0.0078	0.0343	0.0333	0.0360	0.0106	0.0114	0.0011
	0.0001	0.0001	0.0001	0.0004	0.0004	0.0006	0.0003	0.0003	0.0002
S1	0.2245	0.0640	-0.2636	0.0707	0.0290	0.0421	-0.0005	0.0271	-0.0054
	0.0002	0.0003	0.0004	0.0017	0.0011	0.0020	0.0012	0.0015	0.0011
S2	0.3335	0.2717	0.3230	0.0692	0.0578	0.0714	0.0430	0.0050	-0.0056
	0.0003	0.0004	0.0005	0.0020	0.0017	0.0029	0.0019	0.0019	0.0014
C16	0.2263	0.2535	-0.1980	0.0388	0.0387	0.0216	0.0138	0.0135	-0.0029
	0.0007	0.0011	0.0012	0.0048	0.0050	0.0063	0.0044	0.0043	0.0036
N4	0.2265	0.3850	-0.1528	0.0680	0.0362	0.0438	0.0075	0.0126	-0.0066
	0.0008	0.0010	0.0013	0.0060	0.0045	0.0074	0.0043	0.0053	0.0039
C17	0.3035	0.4079	0.2426	0.0521	0.0350	0.0260	0.0067	0.0134	-0.0134
	0.0008	0.0011	0.0013	0.0048	0.0048	0.0068	0.0045	0.0045	0.0039
N5	0.2814	0.5068	0.1861	0.0764	0.0341	0.0456	0.0178	0.0105	-0.0065
	0.0008	0.0010	0.0013	0.0066	0.0042	0.0072	0.0046	0.0054	0.0040
O4	0.2321	0.9688	0.0226	0.0948	0.0316	0.0579	0.0122	0.0210	-0.0004
	0.0008	0.0008	0.0012	0.0059	0.0035	0.0065	0.0038	0.0049	0.0036
HW1	0.2652	1.0467	0.0817	0.0734					
	0.0008	0.0008	0.0012	0.0227					
HW2	0.2166	0.9575	0.9212	0.0734					
	0.0008	0.0008	0.0012	0.0227					
C1	0.0223	0.6962	-0.3169	0.0344	0.0298	0.0335	0.0112	0.0081	0.0003
	0.0006	0.0010	0.0012	0.0039	0.0040	0.0068	0.0041	0.0041	0.0030
N1	0.1261	0.6781	-0.2799	0.0290	0.0333	0.0277	0.0105	0.0040	-0.0068
	0.0006	0.0008	0.0010	0.0035	0.0035	0.0053	0.0033	0.0034	0.0027
C5	0.1695	0.6600	-0.3841	0.0362	0.0313	0.0207	0.0091	0.0062	-0.0114
	0.0007	0.0010	0.0012	0.0041	0.0039	0.0061	0.0037	0.0042	0.0032
C4	0.1153	0.6536	-0.5245	0.0635	0.0529	0.0279	0.0098	0.0178	-0.0131
	0.0010	0.0014	0.0015	0.0067	0.0060	0.0073	0.0051	0.0056	0.0050
H4	0.1550	0.6305	-0.6066	0.0734					
	0.0010	0.0014	0.0015	0.0227					
C3	0.0087	0.6772	-0.5625	0.0478	0.0400	0.0371	0.0227	0.0079	-0.0017
	0.0008	0.0011	0.0014	0.0049	0.0048	0.0077	0.0047	0.0052	0.0038

Table A1.8 continued.

Atom	X/A	Y/B	Z/C	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
H3	-0.0357	0.6781	-0.6720	0.0734					
	0.0008	0.0011	0.0014	0.0227					
C2	-0.0373	0.6988	-0.4559	0.0345	0.0343	0.0363	0.0185	0.0012	0.0048
	0.0007	0.0010	0.0013	0.0045	0.0041	0.0073	0.0043	0.0049	0.0034
H2	-0.1198	0.7179	-0.4794	0.0734					
	0.0007	0.0010	0.0013	0.0227					
C6	0.2850	0.6406	-0.3369	0.0417	0.0480	0.0346	0.0172	0.0252	-0.0089
	0.0008	0.0011	0.0013	0.0053	0.0049	0.0076	0.0048	0.0053	0.0040
H6	0.3260	0.6187	-0.4173	0.0734					
	0.0008	0.0011	0.0013	0.0074					
N2	0.3327	0.6468	-0.2070	0.0304	0.0450	0.0334	0.0142	0.0136	0.0110
	0.0006	0.0009	0.0011	0.0037	0.0039	0.0067	0.0039	0.0041	0.0030
C7	0.4463	0.6278	-0.1650	0.0401	0.0608	0.0478	0.0275	0.0222	0.0090
	0.0008	0.0014	0.0015	0.0055	0.0067	0.0084	0.0059	0.0054	0.0046
H7A	0.4750	0.6449	-0.2473	0.0734					
	0.0008	0.0014	0.0015	0.0074					
H7B	0.4663	0.5120	0.1571	0.0734					
	0.0008	0.0014	0.0015	0.0074					
C8	0.4926	0.7409	-0.0240	0.0291	0.0838	0.0626	0.0297	0.0150	-0.0122
	0.0008	0.0016	0.0016	0.0047	0.0086	0.0100	0.0073	0.0055	0.0049
H8A	0.4777	0.8565	-0.0339	0.0734					
	0.0008	0.0016	0.0016	0.0074					
H8B	0.5748	0.7182	0.0077	0.0734					
	0.0008	0.0016	0.0016	0.0074					
O1	0.4524	0.7241	0.0846	0.0372	0.0503	0.0320	0.0012	0.0111	-0.0073
	0.0005	0.0008	0.0010	0.0032	0.0041	0.0054	0.0037	0.0033	0.0028
C9	0.5024	0.8208	0.2276	0.0375	0.0721	0.0687	-0.0069	0.0157	-0.0199
	0.0008	0.0016	0.0019	0.0049	0.0073	0.0113	0.0072	0.0059	0.0048
H9A	0.5840	0.7931	0.2591	0.0734					
	0.0008	0.0016	0.0019	0.0074					
H9B	0.4912	0.9396	0.2263	0.0734					
	0.0008	0.0016	0.0019	0.0074					
C10	0.4504	0.8036	0.3289	0.0395	0.0656	0.0330	-0.0056	-0.0010	-0.0151
	0.0008	0.0014	0.0015	0.0048	0.0065	0.0078	0.0055	0.0049	0.0044
H10A	0.4886	0.8689	0.4403	0.0734					
	0.0008	0.0014	0.0015	0.0074					
H10B	0.4526	0.6824	0.3209	0.0734					
	0.0008	0.0014	0.0015	0.0074					

Table A1.8 continued.

Atom	X/A	Y/B	Z/C	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O2	0.3448	0.8556	0.2831	0.0394	0.0415	0.0250	0.0073	0.0070	-0.0047
	0.0005	0.0008	0.0009	0.0036	0.0035	0.0047	0.0032	0.0033	0.0027
C11	0.2967	0.8817	0.3939	0.0575	0.0491	0.0213	0.0070	0.0160	-0.0024
	0.0008	0.0013	0.0013	0.0056	0.0055	0.0067	0.0046	0.0049	0.0043
H11A	0.2964	0.7759	0.4202	0.0734					
	0.0008	0.0013	0.0013	0.0074					
H11B	0.3373	0.9690	0.4910	0.0734					
	0.0008	0.0013	0.0013	0.0074					
C12	0.1894	0.9367	0.3399	0.0687	0.0366	0.0292	0.0010	0.0239	-0.0042
	0.0009	0.0011	0.0015	0.0063	0.0046	0.0079	0.0047	0.0057	0.0042
H12A	0.1904	1.0413	0.3119	0.0734					
	0.0009	0.0011	0.0015	0.0074					
H12B	0.1506	0.9598	0.4230	0.0734					
	0.0009	0.0011	0.0015	0.0074					
O3	0.1339	0.8197	0.2133	0.0293	0.0366	0.0329	0.0022	0.0120	0.0036
	0.0005	0.0007	0.0009	0.0031	0.0033	0.0049	0.0032	0.0032	0.0025
N3	0.0281	0.6952	-0.0772	0.0269	0.0349	0.0333	0.0081	0.0125	-0.0047
	0.0005	0.0009	0.0010	0.0034	0.0040	0.0055	0.0036	0.0037	0.0028
C13	0.0274	0.8589	0.1615	0.0388	0.0341	0.0484	0.0126	0.0247	0.0053
	0.0007	0.0010	0.0013	0.0049	0.0041	0.0076	0.0043	0.0049	0.0035
H13A	-0.0091	0.8795	0.2467	0.0734					
	0.0007	0.0010	0.0013	0.0074					
H13B	0.0201	0.9616	0.1274	0.0734					
	0.0007	0.0010	0.0013	0.0074					
C14	-0.0206	0.7237	0.0351	0.0294	0.0367	0.0574	0.0105	0.0187	-0.0007
	0.0007	0.0011	0.0014	0.0043	0.0045	0.0083	0.0048	0.0049	0.0034
H14A	-0.1006	0.7532	-0.0101	0.0734					
	0.0007	0.0011	0.0014	0.0074					
H14B	-0.0159	0.6232	0.0718	0.0734					
	0.0007	0.0011	0.0014	0.0074					
C15	-0.0246	0.7113	-0.2001	0.0214	0.0384	0.0361	0.0108	-0.0009	0.0026
	0.0007	0.0009	0.0014	0.0041	0.0039	0.0080	0.0043	0.0047	0.0031
H15	-0.1067	0.7320	-0.2198	0.0734					
	0.0007	0.0009	0.0014	0.0074					

Table A1.9

Final positional parameters (fractional) and thermal parameters for the structure of Ba(L)(NCS)$_2$.H$_2$O.

Atom	X/A	Y/B	Z/C	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ba	0.2414	0.1590	0.0079	0.0294	0.0290	0.0223	0.0101	0.0085	0.0023
	0.0000	0.0000	0.0000	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
S1	0.2291	-0.4617	-0.2626	0.0876	0.0371	0.0484	0.0022	0.0381	-0.0050
	0.0001	0.0001	0.0002	0.0009	0.0005	0.0009	0.0005	0.0007	0.0005
C16	0.2282	-0.2771	-0.2058	0.0377	0.0431	0.0228	0.0080	0.0067	-0.0022
	0.0003	0.0003	0.0005	0.0019	0.0019	0.0023	0.0016	0.0016	0.0014
N4	0.2265	-0.1472	-0.1671	0.0749	0.0392	0.0540	0.0084	0.0120	-0.0028
	0.0004	0.0005	0.0006	0.0029	0.0021	0.0032	0.0020	0.0023	0.0019
S2	0.3374	-0.2442	0.3324	0.0719	0.0659	0.0788	0.0508	0.0006	-0.0031
	0.0001	0.0002	0.0002	0.0009	0.0008	0.0013	0.0009	0.0008	0.0006
C17	0.3075	-0.1081	0.2583	0.0455	0.0397	0.0380	0.0129	0.0120	0.0002
	0.0003	0.0005	0.0006	0.0021	0.0021	0.0029	0.0019	0.0019	0.0016
N5	0.2863	-0.0119	0.2070	0.0877	0.0519	0.0555	0.0314	0.0189	0.0062
	0.0004	0.0005	0.0007	0.0035	0.0023	0.0037	0.0023	0.0028	0.0022
O4	0.2276	0.4645	0.0276	0.1074	0.0438	0.0473	0.0236	0.0237	0.0002
	0.0004	0.0004	0.0005	0.0032	0.0017	0.0025	0.0016	0.0022	0.0018
HW1	0.2686	0.5064	-0.0277	0.1025					
	0.0004	0.0004	0.0005	0.0072					
HW2	0.1554	0.5274	0.0273	0.1025					
	0.0004	0.0004	0.0005	0.0072					
N1	0.1238	0.1715	-0.2838	0.0352	0.0315	0.0249	0.0090	0.0067	-0.0011
	0.0002	0.0004	0.0004	0.0015	0.0014	0.0020	0.0013	0.0013	0.0011
C1	0.0200	0.1935	-0.3207	0.0357	0.0308	0.0311	0.0073	0.0058	-0.0027
	0.0003	0.0004	0.0005	0.0018	0.0016	0.0024	0.0015	0.0016	0.0013
C2	-0.0386	0.1979	-0.4595	0.0436	0.0416	0.0333	0.0161	-0.0026	-0.0004
	0.0003	0.0005	0.0006	0.0021	0.0020	0.0028	0.0018	0.0019	0.0016
H2	-0.1211	0.2196	-0.4842	0.1025					
	0.0003	0.0005	0.0006	0.0072					
C3	0.0107	0.1745	-0.5649	0.0560	0.0488	0.0269	0.0153	-0.0015	-0.0070
	0.0004	0.0006	0.0006	0.0027	0.0024	0.0028	0.0019	0.0021	0.0020
H3	-0.0329	0.1771	-0.6751	0.1025					
	0.0004	0.0006	0.0006	0.0072					

Table A1.9 continued.

Atom	X/A	Y/B	Z/C	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C4	0.1175	0.1486	-0.5295	0.0563	0.0420	0.0270	0.0115	0.0083	-0.0088
	0.0004	0.0005	0.0006	0.0024	0.0022	0.0028	0.0019	0.0020	0.0018
H4	0.1573	0.1511	-0.3870	0.1025					
	0.0004	0.0005	0.0006	0.0072					
C5	0.1708	0.1511	-0.3870	0.0405	0.0312	0.0246	0.0095	0.0075	-0.0049
	0.0003	0.0004	0.0005	0.0018	0.0017	0.0023	0.0015	0.0016	0.0014
C6	0.2857	0.1315	-0.3416	0.0391	0.0471	0.0285	0.0151	0.0118	-0.0006
	0.0003	0.0005	0.0006	0.0019	0.0023	0.0028	0.0020	0.0018	0.0016
H6	0.3265	0.1081	0.4234	0.1025					
	0.0003	0.0005	0.0006	0.0037					
N2	0.3349	0.1410	-0.2115	0.0330	0.0455	0.0302	0.0121	0.0130	0.0028
	0.0003	0.0004	0.0005	0.0015	0.0019	0.0023	0.0016	0.0015	0.0013
C7	0.4482	0.1254	-0.1704	0.0324	0.0764	0.0395	0.0199	0.0158	0.0108
	0.0003	0.0007	0.0007	0.0020	0.0036	0.0031	0.0026	0.0019	0.0021
H7A	0.4712	0.0146	-0.1578	0.1025					
	0.0003	0.0007	0.0007	0.0037					
H7B	0.4757	0.1386	-0.2556	0.1025					
	0.0003	0.0007	0.0007	0.0037					
C8	0.4928	0.2447	-0.0265	0.0351	0.0811	0.0438	0.0214	0.0124	-0.0110
	0.0004	0.0007	0.0007	0.0020	0.0032	0.0034	0.0026	0.0020	0.0020
H8A	0.4690	0.3556	-0.0384	0.1025					
	0.0004	0.0007	0.0007	0.0037					
H8B	0.5763	0.2347	0.0056	0.1025					
	0.0004	0.0007	0.0007	0.0037					
O1	0.4557	0.2222	0.0815	0.0350	0.0544	0.0340	0.0079	0.0084	-0.0057
	0.0002	0.0004	0.0004	0.0014	0.0017	0.0021	0.0015	0.0013	0.0012
C9	0.5024	0.3224	0.2261	0.0435	0.0700	0.0396	0.0009	0.0085	-0.0146
	0.0004	0.0007	0.0007	0.0023	0.0032	0.0035	0.0026	0.0022	0.0021
H9A	0.5836	0.2923	0.2614	0.1025					
	0.0004	0.0007	0.0007	0.0037					
H9B	0.4942	0.4384	0.2251	0.1025					
	0.0004	0.0007	0.0007	0.0037					

Table A1.9 continued.

Atom	X/A	Y/B	Z/C	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C10	0.4509	0.3042	0.3284	0.0373	0.0600	0.0332	0.0051	0.0012	-0.0013
	0.0003	0.0006	0.0006	0.0020	0.0026	0.0028	0.0021	0.0018	0.0018
H10A	0.4894	0.3711	0.4403	0.1025					
	0.0003	0.0006	0.0006	0.0037					
H10B	0.4538	0.1865	0.3226	0.1025					
	0.0003	0.0006	0.0006	0.0037					
O2	0.3450	0.3542	0.2852	0.0408	0.0458	0.0271	0.0107	0.0100	-0.0003
	0.0002	0.0004	0.0004	0.0015	0.0016	0.0018	0.0013	0.0012	0.0012
C11	0.2938	0.3751	0.3945	0.0539	0.0578	0.0216	0.0075	0.0128	-0.0036
	0.0004	0.0006	0.0006	0.0025	0.0029	0.0025	0.0021	0.0019	0.0021
H11A	0.2930	0.2690	0.4151	0.1025					
	0.0004	0.0006	0.0006	0.0037					
H11B	0.3340	0.4580	0.4960	0.1025					
	0.0004	0.0006	0.0006	0.0037					
C12	0.1845	0.4290	0.3387	0.0494	0.0458	0.0339	0.0007	0.0193	0.0006
	0.0004	0.0006	0.0006	0.0023	0.0023	0.0029	0.0020	0.0020	0.0018
H12A	0.1844	0.5283	0.3063	0.1025					
	0.0004	0.0006	0.0006	0.0037					
H12B	0.1476	0.4566	0.4254	0.1025					
	0.0004	0.0006	0.0006	0.0037					
O3	0.1290	0.3115	0.2133	0.0411	0.0386	0.0286	0.0087	0.0147	0.0048
	0.0002	0.0003	0.0004	0.0014	0.0014	0.0019	0.0013	0.0013	0.0011
C13	0.0238	0.3584	0.1584	0.0438	0.0448	0.0401	0.0151	0.0217	0.0105
	0.0003	0.0005	0.0006	0.0022	0.0023	0.0030	0.0020	0.0020	0.0017
H13A	-0.0137	0.3856	0.2444	0.1025					
	0.0003	0.0005	0.0006	0.0037					
H13B	0.0216	0.4568	0.1238	0.1025					
	0.0003	0.0005	0.0006	0.0037					
C14	-0.0308	0.2289	0.0288	0.0359	0.0536	0.0422	0.0151	0.0176	0.0042
	0.0003	0.0005	0.0006	0.0019	0.0023	0.0032	0.0021	0.0019	0.0017
H14A	-0.1108	0.2604	-0.0144	0.1025					
	0.0003	0.0005	0.0006	0.0037					

Table A1.9 continued.

Atom	X/A	Y/B	Z/C	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
H14B	-0.0270	0.1296	0.0628	0.1025					
	0.0003	0.0005	0.0006	0.0037					
N3	0.0210	0.1974	-0.0841	0.0326	0.0472	0.0330	0.0135	0.0146	0.0034
	0.0002	0.0004	0.0005	0.0015	0.0018	0.0022	0.0015	0.0014	0.0012
C15	-0.0296	0.2132	-0.2068	0.0302	0.0391	0.0344	0.0121	0.0061	0.0015
	0.0003	0.0005	0.0005	0.0017	0.0019	0.0026	0.0017	0.0016	0.0014
H15	-0.1113	0.2415	-0.2285	0.1025					
	0.0003	0.0005	0.0005	0.0037					

Table A1.10.

Final positional parameters (fractional) and thermal parameters for the structure of aqua-di-isothiocyanato(3,15-diaza-6,9,12,20-tetraoxabicyclo (15.2.1)eicosa-2,15,17,19-tetraene)strontium (II).

Atom	X/A	Y/B	Z/C	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sr	0.2378	0.1747	0.0063	0.0344	0.0302	0.0357	0.0119	0.0115	0.0035
	0.0000	0.0001	0.0001	0.0003	0.0003	0.0004	0.0002	0.0002	0.0002
S1	0.2237	0.5655	-0.2696	0.0702	0.0321	0.0425	0.0020	0.0324	0.0004
	0.0002	0.0002	0.0003	0.0014	0.0009	0.0013	0.0008	0.0011	0.0008
S2	0.3396	-0.2379	0.3220	0.0614	0.0521	0.0668	0.0408	0.0073	0.0022
	0.0002	0.0003	0.0004	0.0013	0.0013	0.0018	0.0013	0.0012	0.0010
N3	0.2128	-0.1125	-0.1597	0.0686	0.0360	0.0466	0.0095	0.0154	-0.0025
	0.0007	0.0009	0.0010	0.0048	0.0036	0.0051	0.0032	0.0038	0.0032
N4	0.2860	0.0008	0.1900	0.0699	0.0346	0.0502	0.0199	0.0053	-0.0007
	0.0007	0.0009	0.0010	0.0048	0.0035	0.0051	0.0034	0.0038	0.0032
C15	0.2195	-0.2467	-0.2035	0.0315	0.0362	0.0227	0.0046	0.0051	-0.0092
	0.0005	0.0008	0.0008	0.0030	0.0033	0.0038	0.0027	0.0025	0.0024
C16	0.3085	-0.0962	0.2467	0.0473	0.0365	0.0246	0.0101	0.0075	0.0034
	0.0006	0.0009	0.0009	0.0039	0.0037	0.0041	0.0030	0.0030	0.0029
O5	0.2329	0.4618	0.0176	0.0851	0.0291	0.0386	0.0111	0.0160	-0.0089
	0.0006	0.0006	0.0008	0.0045	0.0025	0.0038	0.0024	0.0032	0.0026
H1	0.2278	0.4589	-0.0826	0.0862					
	0.0006	0.0006	0.0008	0.0185					
H2	0.3086	0.5321	0.0956	0.0862					
	0.0006	0.0006	0.0008	0.0185					
O1	0.1290	0.1757	-0.2786	0.0422	0.0413	0.0261	0.0143	0.0043	0.0058
	0.0004	0.0006	0.0006	0.0026	0.0028	0.0030	0.0022	0.0021	0.0021
C1	0.0223	0.1943	-0.3335	0.0399	0.0411	0.0339	0.0116	-0.0049	0.0028
	0.0006	0.0009	0.0010	0.0037	0.0040	0.0046	0.0033	0.0032	0.0029
C4	0.1684	0.1581	-0.3926	0.0654	0.0332	0.0308	0.0122	0.0089	-0.0032
	0.0007	0.0009	0.0010	0.0050	0.0035	0.0046	0.0031	0.0037	0.0032
C2	-0.0047	0.1914	-0.4793	0.0670	0.0568	0.0410	0.0261	-0.0108	-0.0076
	0.0009	0.0012	0.0012	0.0060	0.0053	0.0058	0.0045	0.0046	0.0045
H22	-0.0824	0.2036	-0.5519	0.0862					
	0.0009	0.0012	0.0012	0.0185					
C3	0.0898	0.1684	-0.5176	0.0814	0.0478	0.0265	0.0127	0.0018	-0.0138
	0.0009	0.0011	0.0011	0.0066	0.0048	0.0048	0.0037	0.0042	0.0044

Table A1.10. continued

Atom	X/A	Y/B	Z/C	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
H3	0.0976	0.1613	-0.6247	0.0862					
	0.0009	0.0011	0.0011	0.0185					
O2	0.4494	0.2210	0.0808	0.0350	0.0451	0.0436	0.0098	0.0183	-0.0009
	0.0004	0.0007	0.0007	0.0025	0.0030	0.0035	0.0025	0.0023	0.0021
O3	0.3418	0.3511	0.2820	0.0324	0.0362	0.0314	0.0103	0.0087	0.0027
	0.0004	0.0006	0.0006	0.0023	0.0025	0.0030	0.0021	0.0020	0.0019
O4	0.1267	0.3093	0.2021	0.0326	0.0351	0.0334	0.0076	0.0144	0.0043
	0.0004	0.0006	0.0006	0.0023	0.0025	0.0030	0.0022	0.0020	0.0019
N1	0.3301	0.1436	-0.2158	0.0484	0.0376	0.0367	0.0105	0.0234	0.0049
	0.0005	0.0008	0.0008	0.0035	0.0032	0.0040	0.0027	0.0029	0.0026
N2	0.0204	0.1962	-0.0976	0.0303	0.0379	0.0383	0.0060	0.0093	0.0048
	0.0005	0.0007	0.0008	0.0027	0.0032	0.0038	0.0027	0.0024	0.0023
C6	0.4431	0.1207	-0.1727	0.0470	0.0705	0.0556	0.0287	0.0336	0.0172
	0.0007	0.0012	0.0012	0.0045	0.0059	0.0061	0.0048	0.0042	0.0040
H61	0.4615	0.0064	-0.1608	0.0862					
	0.0007	0.0012	0.0012	0.0077					
H62	0.4724	0.1343	-0.2575	0.0862					
	0.0007	0.0012	0.0012	0.0077					
C5	0.2806	0.1355	-0.3514	0.0608	0.0426	0.0418	0.0226	0.0241	0.0096
	0.0007	0.0010	0.0011	0.0049	0.0039	0.0051	0.0036	0.0038	0.0034
H51	0.3126	0.2220	-0.3790	0.0862					
	0.0007	0.0010	0.0011	0.0077					
H52	0.2953	0.0227	-0.4185	0.0862					
	0.0007	0.0010	0.0011	0.0077					
C7	0.4925	0.2363	-0.0280	0.0374	0.0658	0.0642	0.0248	0.0271	0.0024
	0.0007	0.0012	0.0013	0.0038	0.0057	0.0069	0.0049	0.0040	0.0036
H71	0.4765	0.3504	-0.0410	0.0862					
	0.0007	0.0012	0.0013	0.0077					
H72	0.5758	0.2175	0.0076	0.0862					
	0.0007	0.0012	0.0013	0.0077					
C8	0.4999	0.3200	0.2259	0.0399	0.0650	0.0514	0.0030	0.0125	-0.0114
	0.0007	0.0013	0.0013	0.0041	0.0057	0.0063	0.0046	0.0039	0.0039
H81	0.5815	0.2893	0.2619	0.0862					
	0.0007	0.0013	0.0013	0.0077					

Table A1.10. continued

Atom	X/A	Y/B	Z/C	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
H82	0.4928	0.4380	0.2230	0.0862					
	0.0007	0.0013	0.0013	0.0077					
C13	-0.0345	0.2193	0.0118	0.0285	0.0506	0.0571	0.0103	0.0209	0.0025
	0.0006	0.0010	0.0011	0.0031	0.0044	0.0059	0.0039	0.0033	0.0028
H131	-0.1151	0.2490	-0.0350	0.0862					
	0.0006	0.0010	0.0011	0.0077					
H132	-0.0307	0.1158	0.0444	0.0862					
	0.0006	0.0010	0.0011	0.0077					
C9	0.4482	0.3016	0.3312	0.0323	0.0507	0.0371	0.0032	0.0006	0.0008
	0.0006	0.0010	0.0010	0.0035	0.0044	0.0047	0.0035	0.0031	0.0030
H91	0.4868	0.3713	0.4432	0.0862					
	0.0006	0.0010	0.0010	0.0077					
H92	0.4508	0.1823	0.3294	0.0862					
	0.0006	0.0010	0.0010	0.0077					
C10	0.2907	0.3748	0.3908	0.0479	0.0616	0.0271	0.0086	0.0136	0.0040
	0.0007	0.0011	0.0010	0.0044	0.0053	0.0044	0.0037	0.0034	0.0037
H101	0.2896	0.2685	0.4167	0.0862					
	0.0007	0.0011	0.0010	0.0077					
H102	0.3315	0.4615	0.4909	0.0862					
	0.0007	0.0011	0.0010	0.0077					
C11	0.1812	0.4273	0.3301	0.0492	0.0513	0.0330	0.0010	0.0234	0.0045
	0.0007	0.0011	0.0010	0.0044	0.0046	0.0047	0.0036	0.0035	0.0034
H111	0.1822	0.5306	0.2991	0.0862					
	0.0007	0.0011	0.0010	0.0077					
H112	0.1426	0.4507	0.4142	0.0862					
	0.0007	0.0011	0.0010	0.0077					
C12	0.0197	0.3514	0.1473	0.0403	0.0379	0.0480	0.0080	0.0228	0.0109
	0.0006	0.0009	0.0011	0.0037	0.0037	0.0053	0.0035	0.0035	0.0029
H121	-0.0168	0.3703	0.2333	0.0862					
	0.0006	0.0009	0.0011	0.0077					
H122	0.0145	0.4553	0.1147	0.0862					
	0.0006	0.0009	0.0011	0.0077					

Table A1.10. continued

Atom	X/A	Y/B	Z/C	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C14	-0.0327	0.2066	-0.2275	0.0320	0.0336	0.0531	0.0131	0.0013	0.0061
	0.0006	0.0009	0.0011	0.0033	0.0036	0.0054	0.0034	0.0033	0.0026
H141	-0.0903	0.1163	-0.2765	0.0862					
	0.0006	0.0009	0.0011	0.0077					
H142	-0.0715	0.3172	-0.2127	0.0862					
	0.0006	0.0009	0.0011	0.0077					

Final positional parameters (fractional) and thermal parameters for the structure of 5-(p-bromobenzyl)-5-phenyl-dibenzophospholium bromide.

Atom	X/A	Y/B	Z/C	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br^-	0.0623	0.3298	0.6617	0.0465	0.0274	0.0667	0.0141	0.0186	0.0038
	0.0001	0.0003	0.0002	0.0021	0.0031	0.0029	0.0029	0.0021	0.0029
Br	0.1872	0.2220	0.3328	0.0899	0.0506	0.0563	0.0064	0.0504	0.0177
	0.0001	0.0003	0.0002	0.0040	0.0042	0.0034	0.0037	0.0031	0.0040
P	0.1165	0.6690	0.5608	0.0267	0.0156	0.0289	-0.0017	0.0118	-0.0018
	0.0002	0.0006	0.0003	0.0039	0.0049	0.0038	0.0042	0.0033	0.0043
C1	0.0719	0.7578	0.5939	0.0380	0.0323	0.0355	-0.0027	0.0076	-0.0055
	0.0009	0.0023	0.0012	0.0069	0.0073	0.0067	0.0071	0.0064	0.0072
C2	0.0426	0.6859	0.6295	0.0481	0.0374	0.0393	0.0020	0.0117	0.0019
	0.0008	0.0024	0.0010	0.0072	0.0073	0.0071	0.0071	0.0070	0.0072
H2	0.0440	0.5840	0.6320	0.0334					
	0.0008	0.0024	0.0010	0.0057					
C3	0.0084	0.7598	0.6540	0.0577	0.0446	0.0437	-0.0035	0.0221	- 0.0014
	0.0009	0.0027	0.0010	0.0071	0.0073	0.0070	0.0072	0.0067	0.0072
H3	-0.0167	0.7129	0.6798	0.0334					
	0.0009	0.0027	0.0010	0.0057					
C4	0.0077	0.8900	0.6520	0.0447	0.0519	0.0618	-0.0041	0.0260	0.0000
	0.0010	0.0027	0.0017	0.0071	0.0073	0.0073	0.0072	0.0070	0.0072
H4	-0.0177	0.9346	0.6737	0.0334					
	0.0010	0.0027	0.0017	0.0057					
C5	0.0369	0.9558	0.6189	0.0417	0.0414	0.0561	-0.0067	0.0076	0.0079
	0.0010	0.0026	0.0015	0.0069	0.0073	0.0073	0.0073	0.0071	0.0071
H5	0.0328	1.0606	0.6147	0.0334					
	0.0010	0.0026	0.0015	0.0057					
C6	0.0702	0.8899	0.5893	0.0349	0.0397	0.0463	0.0051	0.0326	-0.0010
	0.0008	0.0023	0.0012	0.0071	0.0073	0.0073	0.0072	0.0069	0.0071
H6	0.0922	0.9393	0.5628	0.0334					
	0.0008	0.0023	0.0012	0.0057					
C7	0.0749	0.5360	0.5009	0.0405	0.0385	0.0324	0.0015	0.0180	-0.0075
	0.0008	0.0021	0.0012	0.0071	0.0073	0.0070	0.0071	0.0069	0.0071
H7A	0.0332	0.5739	0.4534	0.0334					
	0.0008	0.0021	0.0012	0.0057					
H7B	0.0669	0.4728	0.5393	0.0334					
	0.0008	0.0021	0.0012	0.0057					

Atom	X/A	Y/B	Z/C	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C8	0.1055	0.4596	0.4615	0.0358	0.0350	0.0224	0.0053	0.0228	-0.0084
	0.0009	0.0023	0.0011	0.0069	0.0073	0.0069	0.0070	0.0063	0.0071
C9	0.0967	0.5019	0.3851	0.0378	0.0351	0.0389	-0.0013	0.0191	0.0011
	0.0010	0.0023	0.0014	0.0071	0.0073	0.0071	0.0072	0.0068	0.0072
H9	0.0692	0.5830	0.3565	0.0334					
	0.0010	0.0023	0.0014	0.0057					
C10	0.1209	0.4314	0.3471	0.0376	0.0386	0.0438	0.0127	0.0190	0.0042
	0.0009	0.0021	0.0012	0.0071	0.0073	0.0073	0.0073	0.0072	0.0072
H10	0.1141	0.4575	0.2884	0.0334					
	0.0009	0.0021	0.0012	0.0057					
C11	0.1550	0.3287	0.3862	0.0453	0.0435	0.0403	0.0090	0.0276	-0.0035
	0.0009	0.0025	0.0012	0.0071	0.0073	0.0071	0.0072	0.0067	0.0072
C12	0.1650	0.2848	0.4619	0.0378	0.0348	0.0417	0.0043	0.0201	0.0090
	0.0009	0.0024	0.0014	0.0069	0.0073	0.0071	0.0072	0.0065	0.0071
H12	0.1891	0.1962	0.4891	0.0334					
	0.0009	0.0024	0.0014	0.0057					
C13	0.1416	0.3570	0.5008	0.0505	0.0425	0.0287	0.0058	0.0128	-0.0048
	0.0008	0.0024	0.0011	0.0071	0.0073	0.0072	0.0072	0.0070	0.0072
H13	0.1480	0.3322	0.5609	0.0334					
	0.0008	0.0024	0.0011	0.0057					
C14	0.1459	0.7727	0.5166	0.0535	0.0402	0.0404	0.0004	0.0209	0.0060
	0.0008	0.0023	0.0010	0.0057	0.0058	0.0057	0.0057	0.0054	0.0057
C15	0.2066	0.7871	0.5656	0.0434	0.0333	0.0476	-0.0034	0.0286	0.0001
	0.0009	0.0023	0.0012	0.0054	0.0058	0.0057	0.0057	0.0055	0.0057
C16	0.2401	0.8751	0.5467	0.0458	0.0328	0.0521	-0.0022	0.0262	0.0050
	0.0009	0.0024	0.0013	0.0057	0.0058	0.0057	0.0057	0.0055	0.0057
H16	0.2870	0.8854	0.5837	0.0334					
	0.0009	0.0024	0.0013	0.0057					
C17	0.2092	0.9400	0.4734	0.0616	0.0387	0.0453	-0.0006	0.0298	0.0029
	0.0010	0.0021	0.0013	0.0057	0.0058	0.0057	0.0057	0.0054	0.0057
H17	0.2333	1.0067	0.4578	0.0334					
	0.0010	0.0021	0.0013	0.0057					
C18	0.1484	0.9201	0.4212	0.0684	0.0487	0.0349	0.0117	0.0314	0.0129
	0.0011	0.0028	0.0012	0.0056	0.0058	0.0054	0.0057	0.0051	0.0057

Atom	X/A	Y/B	Z/C	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
H18	0.1281	0.9756	0.3669	0.0334					
	0.0011	0.0028	0.0012	0.0057					
C19	0.1164	0.8395	0.4416	0.0461	0.0454	0.0495	0.0005	0.0445	-0.0039
	0.0008	0.0022	0.0012	0.0055	0.0058	0.0055	0.0057	0.0050	0.0057
H19	0.0691	0.8279	0.4004	0.0334					
	0.0008	0.0022	0.0012	0.0057					
C20	0.1900	0.6249	0.6455	0.0329	0.0326	0.0363	-0.0100	0.0207	0.0123
	0.0008	0.0022	0.0012	0.0054	0.0058	0.0057	0.0057	0.0054	0.0056
C21	0.2031	0.5357	0.7073	0.0497	0.0417	0.0366	0.0019	0.0141	0.0055
	0.0007	0.0023	0.0011	0.0057	0.0058	0.0056	0.0057	0.0055	0.0057
H21	0.1702	0.4806	0.7090	0.0334					
	0.0007	0.0023	0.0011	0.0057					
C22	0.2614	0.5285	0.7652	0.0552	0.0523	0.0427	0.0007	0.0190	0.0132
	0.0010	0.0028	0.0012	0.0057	0.0058	0.0055	0.0057	0.0054	0.0057
H22	0.2739	0.4544	0.8102	0.0334					
	0.0010	0.0028	0.0012	0.0057					
C23	0.3062	0.6052	0.7615	0.0454	0.0483	0.0419	0.0012	0.0116	0.0085
	0.0009	0.0026	0.0013	0.0055	0.0058	0.0057	0.0058	0.0056	0.0057
H23	0.3505	0.5959	0.8069	0.0334					
	0.0009	0.0026	0.0013	0.0057					
C24	0.2917	0.6959	0.7008	0.0460	0.0464	0.0422	-0.0026	0.0146	0.0106
	0.0009	0.0025	0.0011	0.0056	0.0058	0.0055	0.0056	0.0054	0.0056
H24	0.3237	0.7505	0.6994	0.0334					
	0.0009	0.0025	0.0011	0.0057					
C25	0.2311	0.7031	0.6416	0.0291	0.0314	0.0407	-0.0036	0.0299	0.0018
	0.0007	0.0018	0.0010	0.0054	0.0058	0.0055	0.0056	0.0050	0.0055

Table A1.12.

Final positional parameters (fractional) and thermal parameters for the structure of 10-(4-bromobenzyl)-10-phenylphenoxa-phosphonium bromide.

Atom	X/A	Y/B	Z/C	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br^-	0.3526	0.5430	0.6040	0.0355	0.0522	0.0351	-0.0011	-0.0047	0.0034
	0.0001	0.0001	0.0001	0.0004	0.0006	0.0006	0.0006	0.0006	0.0007
Br	0.0796	0.1810	-0.1305	0.0756	0.0976	0.0657	-0.0225	0.0186	0.0318
	0.0001	0.0001	0.0002	0.0009	0.0011	0.0011	0.0008	0.0009	0.0010
P	0.3417	0.1079	0.3714	0.0262	0.0324	0.0273	-0.0021	0.0012	0.0007
	0.0001	0.0001	0.0003	0.0013	0.0013	0.0017	0.0010	0.0013	0.0013
O	0.3935	0.2198	0.3005	0.065	0.039	0.055	-0.007	0.009	0.002
	0.0004	0.0003	0.0009	0.005	0.005	0.007	0.004	0.005	0.004
C1	0.3875	0.0722	0.5091	0.032	0.028	0.034	0.000	-0.011	0.006
	0.0005	0.0004	0.0012	0.005	0.006	0.008	0.007	0.007	0.009
C2	0.3492	0.0444	0.6110	0.041	0.073	0.055	-0.008	-0.013	0.018
	0.0006	0.0005	0.0014	0.005	0.007	0.008	0.007	0.007	0.009
H2	0.2925	0.0414	0.6025	0.072					
	0.0006	0.0005	0.0014	0.013					
C3	0.3845	0.0205	0.7238	0.045	0.088	0.056	-0.017	-0.015	0.029
	0.0007	0.0005	0.0016	0.008	0.011	0.011	0.007	0.007	0.008
H3	0.3551	-0.0004	0.8047	0.072					
	0.0007	0.0005	0.0016	0.013					
C4	0.4554	0.0241	0.7314	0.070	0.050	0.064	0.009	-0.033	-0.001
	0.0007	0.0005	0.0018	0.009	0.008	0.011	0.006	0.008	0.008
H4	0.4827	0.0052	0.8188	0.072					
	0.0007	0.0005	0.0018	0.013					
C5	0.4935	0.0507	0.6303	0.044	0.098	0.057	-0.013	-0.029	0.007
	0.0006	0.0006	0.0016	0.006	0.011	0.010	0.007	0.007	0.010
H5	0.5502	0.0530	0.6394	0.072					
	0.0006	0.0006	0.0016	0.013					
C6	0.4603	0.0746	0.5172	0.032	0.065	0.056	0.003	-0.010	-0.006
	0.0006	0.0005	0.0015	0.006	0.009	0.010	0.006	0.006	0.007
H6	0.4907	0.0950	0.4369	0.072					
	0.0006	0.0005	0.0015	0.013					
C7	0.2703	0.0679	0.3056	0.023	0.021	0.039	-0.010	-0.003	0.004
	0.0005	0.0004	0.0012	0.005	0.005	0.007	0.004	0.004	0.005

Table A1.12 continued.

Atom	X/A	Y/B	Z/C	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
H71	0.2382	0.0558	0.3948	0.072					
	0.0005	0.0005	0.0007	0.013					
H72	0.2927	0.0340	0.2538	0.072					
	0.0005	0.0005	0.0007	0.013					
C8	0.2246	0.0954	0.1986	0.032	0.024	0.032	-0.011	0.001	-0.006
	0.0005	0.0004	0.0012	0.006	0.006	0.008	0.004	0.005	0.005
C9	0.1664	0.1234	0.2448	0.028	0.042	0.037	0.007	0.004	0.001
	0.0005	0.0004	0.0014	0.006	0.006	0.008	0.005	0.005	0.006
H9	0.1547	0.1254	0.3580	0.072					
	0.0005	0.0004	0.0014	0.013					
C10	0.1223	0.1489	0.1468	0.029	0.061	0.047	0.004	0.002	0.000
	0.0006	0.0005	0.0014	0.005	0.008	0.010	0.005	0.005	0.007
H10	0.0786	0.1724	0.3580	0.072					
	0.0006	0.0005	0.0014	0.013					
C11	0.1371	0.1433	0.0013	0.045	0.042	0.049	0.012	-0.016	0.009
	0.0006	0.0004	0.0015	0.007	0.007	0.009	0.006	0.006	0.006
C12	0.1929	0.1148	-0.0503	0.050	0.062	0.039	0.009	-0.001	-0.002
	0.0006	0.0005	0.0015	0.007	0.009	0.009	0.006	0.006	0.006
H12	0.2029	0.1111	-0.1639	0.072					
	0.0006	0.0005	0.0015	0.013					
C13	0.2356	0.0910	0.0513	0.040	0.051	0.030	0.007	0.001	-0.006
	0.0006	0.0005	0.0013	0.007	0.008	0.008	0.005	0.005	0.005
H13	0.2796	0.0679	0.0145	0.072					
	0.0006	0.0005	0.0013	0.013					
C14	0.3106	0.1677	0.4426	0.037	0.044	0.027	0.001	0.000	-0.004
	0.0005	0.0004	0.0012	0.006	0.007	0.007	0.005	0.005	0.005
C15	0.3401	0.2151	0.3977	0.052	0.047	0.041	-0.007	-0.014	-0.010
	0.0006	0.0004	0.0014	0.007	0.007	0.008	0.005	0.007	0.007
C16	0.3158	0.2612	0.4576	0.084	0.037	0.062	0.011	-0.015	-0.006
	0.0008	0.0005	0.0017	0.010	0.008	0.011	0.007	0.008	0.007
H16	0.3380	0.2976	0.4221	0.072					
	0.0008	0.0005	0.0017	0.013					
C17	0.2656	0.2612	0.5580	0.076	0.055	0.068	0.010	-0.007	-0.020
	0.0008	0.0006	0.0017	0.010	0.009	0.012	0.008	0.009	0.008

Table A1.12 continued.

Atom	X/A	Y/B	Z/C	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
H17	0.2492	0.2978	0.6045	0.072					
	0.0008	0.0006	0.0017	0.013					
C18	0.2345	0.2151	0.6034	0.064	0.076	0.046	0.005	0.004	-0.011
	0.0007	0.0005	0.0016	0.009	0.009	0.009	0.007	0.008	0.008
H18	0.1931	0.2154	0.6831	0.072					
	0.0007	0.0005	0.0016	0.013					
C19	0.2577	0.1682	0.5438	0.046	0.050	0.042	-0.004	-0.007	-0.007
	0.0006	0.0005	0.0013	0.006	0.008	0.008	0.006	0.006	0.006
H19	0.2342	0.1319	0.5771	0.072					
	0.0006	0.0005	0.0013	0.013					
C20	0.4010	0.1281	0.2332	0.018	0.046	0.034	0.001	-0.001	0.008
	0.0005	0.0004	0.0013	0.004	0.006	0.007	0.005	0.004	0.006
C21	0.4319	0.0899	0.1467	0.047	0.060	0.033	0.008	0.003	-0.002
	0.0006	0.0005	0.0014	0.006	0.007	0.008	0.006	0.006	0.006
H21	0.4178	0.0493	0.1575	0.072					
	0.0006	0.0005	0.0014	0.013					
C22	0.4819	0.1063	0.0463	0.050	0.102	0.046	-0.003	0.019	-0.011
	0.0007	0.0007	0.0016	0.008	0.012	0.010	0.008	0.007	0.008
H22	0.5064	0.0779	-0.0229	0.072					
	0.0007	0.0007	0.0016	0.013					
C23	0.5001	0.1579	0.0328	0.037	0.121	0.056	-0.013	0.008	0.028
	0.0007	0.0007	0.0017	0.007	0.014	0.011	0.009	0.007	0.010
H23	0.5394	0.1696	-0.0446	0.072					
	0.0007	0.0007	0.0017	0.013					
C24	0.4675	0.1945	0.1197	0.049	0.068	0.054	-0.013	0.008	0.014
	0.0006	0.0005	0.0016	0.007	0.009	0.009	0.006	0.008	0.008
H24	0.4807	0.2351	0.1081	0.072					
	0.0006	0.0005	0.0016	0.013					
C25	0.4193	0.1798	0.2201	0.036	0.040	0.041	-0.006	0.001	0.019
	0.0005	0.0004	0.0012	0.006	0.006	0.008	0.005	0.005	0.006

Table A1.13.

Final positional parameters (fractional) and thermal parameters for the structure of 5-phenyl-10,11-dihydrodibenzo(b,f)-phosphepin-5-oxide.

Atom	X/A	Y/B	Z/C	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
P	0.2234	0.2469	0.6771	0.0312	0.0379	0.0421	0.0071	0.0132	-0.0028
	0.0002	0.0001	0.0002	0.0008	0.0006	0.0007	0.0005	0.0006	0.0005
O	0.0953	0.2070	0.5217	0.0318	0.0603	0.0519	0.0077	0.0099	-0.0063
	0.0006	0.0004	0.0005	0.0027	0.0023	0.0023	0.0018	0.0019	0.0020
C16	0.5359	0.1400	0.6422	0.0288	0.0510	0.0612	0.0123	0.0149	0.0011
	0.0009	0.0006	0.0008	0.0036	0.0028	0.0033	0.0024	0.0028	0.0026
H16	0.5159	0.0686	0.6938	0.0822					
	0.0009	0.0006	0.0008	0.0090					
C15	0.4174	0.2410	0.6296	0.0430	0.0364	0.0406	0.0059	0.0132	-0.0034
	0.0009	0.0005	0.0006	0.0037	0.0022	0.0024	0.0018	0.0025	0.0023
C9	0.2427	0.4682	0.9594	0.0425	0.0386	0.0730	0.0083	0.0209	-0.0037
	0.0010	0.0005	0.0008	0.0041	0.0025	0.0038	0.0024	0.0032	0.0025
C10	0.1805	0.4092	0.7932	0.0386	0.0430	0.0597	0.0174	0.0248	0.0016
	0.0009	0.0005	0.0007	0.0039	0.0025	0.0032	0.0023	0.0028	0.0024
C11	0.0640	0.4784	0.7012	0.0616	0.0498	0.0613	0.0182	0.0215	0.0074
	0.0011	0.0006	0.0008	0.0053	0.0028	0.0034	0.0025	0.0034	0.0031
H11	0.0120	0.4327	0.5745	0.0822					
	0.0011	0.0006	0.0008	0.0090					
C12	0.0137	0.6034	0.7679	0.0674	0.0536	0.0904	0.0281	0.0315	0.0149
	0.0012	0.0007	0.0011	0.0064	0.0033	0.0050	0.0033	0.0045	0.0036
H12	-0.0716	0.6557	0.6925	0.0822					
	0.0012	0.0007	0.0011	0.0090					
C13	0.0739	0.6615	0.9330	0.0660	0.0418	0.0880	0.0154	0.0391	0.0057
	0.0011	0.0006	0.0010	0.0061	0.0027	0.0048	0.0029	0.0044	0.0031
H13	0.0343	0.7588	0.9873	0.0822					
	0.0011	0.0006	0.0010	0.0090					
C14	0.1834	0.5940	1.0248	0.0658	0.0442	0.0739	0.0027	0.0312	-0.0099
	0.0012	0.0006	0.0009	0.0059	0.0028	0.0041	0.0026	0.0040	0.0032
H14	0.2267	0.6392	1.1535	0.0822					
	0.0012	0.0006	0.0009	0.0090					
C17	0.6787	0.1303	0.5901	0.0417	0.0638	0.0689	0.0016	0.0214	0.0068
	0.0011	0.0007	0.0009	0.0044	0.0035	0.0040	0.0030	0.0034	0.0033

Table A1.13 continued.

Atom	X/A	Y/B	Z/C	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
H17	0.7693	0.0526	0.6024	0.0822					
	0.0011	0.0007	0.0009	0.0090					
C18	0.7042	0.2208	0.5217	0.0438	0.0842	0.0666	0.0051	0.0305	-0.0154
	0.0011	0.0008	0.0009	0.0051	0.0047	0.0041	0.0034	0.0036	0.0039
H18	0.8148	0.2135	0.4803	0.0822					
	0.0011	0.0008	0.0009	0.0090					
C19	0.5874	0.3209	0.5066	0.0553	0.0680	0.0663	0.0147	0.0230	-0.0200
	0.0011	0.0007	0.0009	0.0054	0.0037	0.0039	0.0030	0.0036	0.0036
H19	0.6071	0.3923	0.4549	0.0822					
	0.0011	0.0007	0.0009	0.0090					
C20	0.4448	0.3284	0.5585	0.0476	0.0550	0.0665	0.0196	0.0253	-0.0032
	0.0010	0.0006	0.0008	0.0046	0.0031	0.0035	0.0027	0.0032	0.0030
H20	0.3528	0.4046	0.5429	0.0822					
	0.0010	0.0006	0.0008	0.0090					
C1	0.2368	0.1482	0.8079	0.0340	0.0429	0.0532	0.0167	0.0171	0.0007
	0.0008	0.0005	0.0007	0.0034	0.0022	0.0028	0.0020	0.0024	0.0022
C2	0.1385	0.0480	0.7511	0.0429	0.0476	0.0592	0.0104	0.0219	-0.0030
	0.0009	0.0005	0.0008	0.0040	0.0026	0.0032	0.0023	0.0029	0.0026
H2	0.0618	0.0296	0.6292	0.0822					
	0.0009	0.0005	0.0008	0.0071					
C3	0.1365	-0.0291	0.8481	0.0550	0.0547	0.0716	0.0220	0.0235	-0.0092
	0.0010	0.0006	0.0009	0.0049	0.0031	0.0040	0.0028	0.0035	0.0031
H3	0.0615	-0.1084	0.8012	0.0822					
	0.0010	0.0006	0.0009	0.0071					
C4	0.2308	-0.0039	1.0040	0.0613	0.0645	0.0767	0.0352	0.0229	-0.0031
	0.0011	0.0006	0.0009	0.0053	0.0034	0.0041	0.0030	0.0036	0.0033
H4	0.2268	-0.0610	1.0823	0.0822					
	0.0011	0.0006	000009	0.0071					
C5	0.3320	0.0955	1.0613	0.0641	0.0635	0.0654	0.0277	0.0165	0.0015
	0.0011	0.0007	0.0009	0.0056	0.0035	0.0038	0.0030	0.0037	0.0035
H5	0.4076	0.1129	1.1837	0.0822					
	0.0011	0.0007	0.0009	0.0071					

Table A1.13 continued.

Atom	X/A	Y/B	Z/C	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C6	0.3387	0.1728	0.9670	0.0439	0.0496	0.0551	0.0184	0.0125	-0.0005
	0.0009	0.0005	0.0007	0.0040	0.0027	0.0031	0.0023	0.0028	0.0026
C7	0.4497	0.2805	1.0289	0.0397	0.0597	0.0648	0.0197	0.0052	-0.0039
	0.0009	0.0006	0.0008	0.0042	0.0032	0.0036	0.0027	0.0031	0.0029
H7A	0.5062	0.2792	0.9319	0.0822					
	0.0009	0.0006	0.0008	0.0071					
C8	0.3652	0.4108	1.0838	0.0594	0.0571	0.0599	0.0046	0.0082	-0.0106
	0.0011	0.0006	0.0008	0.0052	0.0031	0.0036	0.0026	0.0034	0.0033
H8A	0.3014	0.4069	1.1730	0.0822					
	0.0011	0.0006	0.0008	0.0071					
H8B	0.4595	0.4757	1.1420	0.0822					
	0.0011	0.0006	0.0008	0.0071					

Appendix 2

A2.1 Planes for 1-(4-chloro-phenoxy)-3, 3-dimethyl-1-(1,2,4-triazole-1-yl)-2-butanone.

Plane A: N1, C1, N3, C2, N2.

$0.7512x - 0.2781\ y - 0.5962\ z + 4.5433 = 0.$ $\chi^2 = 0.0175$

N1 = 0.000(7) C1 = 0.000(9) N3 = 0.000(8)

C2 = 0.000(11) N2 = 0.000(8) C5 = 061(7)

Plane B: C4, C5, O1, C31.

$0.2561\ x - 0.9664\ y - 0.0202\ z + 16.1969 = 0.$ $\chi^2 = 0.5097$

C5 = 0.002(6) C4 =-0.006(6)

O1 = 0.002(6) C31 = 0.002(6)

Plane C: C71, C72, C73, C74, C75, C76.

$-0.8494\ x - 0.1808\ y - 0.4958\ z + 3.6807 = 0.$ $\chi^2 = 1.4562$

C71 = -0.001(8) C72 = 0.004(9) C73 = -0.007(10)

C74 = 0.008(9) C75 = -0.005(10) C76 = 0.002(9)

Cl = 0.01(3) O2 = 0.011(5)

Angles (°) between planes:

A	B	61.8
A	C	73.1
B	C	88.1

A2.2 Planes for 1-(4-nitrophenyl)-4,4-dimethyl-2-(1,2,4-triazol-1-yl)-pentan-3-one

Plane A: N1, N2, C2, N3, C1

$$0.0422x - 0.1096y - 0.9931z + 4.8267 = 0 \qquad \chi^2 = 0.1025$$

N1 = 0.000(4) C2 = -0.002(8) C1 = -0.001(8)
N2 = 0.001(6) N3 = 0.002(8) C5 = -0.056(4)

Plane B: C71, C72, C73, C74, C75, C76

$$-0.5060x + 0.5411y - 0.6717z + 6.2295 = 0 \qquad \chi^2 = 5.9346$$

C71 = -0.008(7) C72 = -0.001(7) C73 = 0.007(7)
C74 = -0.002(8) C75 = -0.008(9) C76 = 0.013(8)
C6 = -0.041(7) N4 = -0.025(10)

Plane C: C5, C4, O1, C31

$$0.2423x + 0.9440y - 0.2240z - 0.3441 = 0 \qquad \chi^2 = 8.9270$$

C5 = 0.005(6) C4 = -0.017(7)
C31 = 0.005(8) O1 = 0.007(5)

Plane D: N4, O41, O42

$$-0.5496x + 0.5240y - 0.6506z + 6.1169 = 0$$

Angles between planes ($^\circ$)

A	B	54.1	B	C	57.4
A	C	82.6	B	D	2.9
A	D	55.6	C	D	59.5

A2.3

Planes for 1-(4-chlorophenyl)-3-(2-fluorophenyl)-2-(1,2,4-triazol-1-yl)-propan-1-ane.

Plane A: C31, C32, C33, C34, C35, C36

$0.6712x + 0.4606y - 0.5808z = 1.0752 = 0$ $\chi^2 = 3.5823$

C34 = -0.001(6)
C35 = 0.008(7)
C36 = -0.009(6)
C31 = 0.003(7)
C32 = 0.003(9)
C33 = -0.004(2)
C4 = -0.091(6)
Cl = -0.001(2)

Plane B: N1, N2, C2, N3, C1

$-0.7441x + 0.4460y - 0.4974z - 1.6805 = 0$ $\chi^2 = 3.3047$

N1 = -0.007(5)
N2 = 0.004(7)
C1 = 0.007(8)
N3 = -0.004(7)
C2 = 0.000(9)
C5 = 0.174(7)

Plane C: C4, C5, O1, C6

$0.6463x + 0.6930y - 0.3194z - 1.4828 = 0$ $\chi^2 = 0.4304$

C4 = -0.002(7)
C5 = 0.007(7)
O1 = -0.003(6)
C6 = -0.002(7)

Plane D: C71, C72, C73, C74, C75, C76

$0.8484x - 0.4770y - 0.2295z + 6.2373 = 0$ $\chi^2 = 3.3869$

C71 = -0.010(7)
C72 = .003(9)
C73 = .004(8)
C74 = -0.005(8)
C75 = -0.002(9)
C76 = 0.009(9)
C6 = 0.002(8)
F72 = -0.215(35)
F76 = -0.215(9)

Angles between the planes:

A	B	89.7°	B	C	89.2°
A	C	20.5°	B	D	43.1°
A	D	61.0°	C	D	73.1°

A2.4 Mean planes for Z-3-(4-nitrophenyl)-1-phenyl-21 (imidazol-1-yl)-prop-2-en -1-one

Plane A: C1, C2, C3, C4, C5, C6

$-0.2067x - 0.8452y - 0.4928z + 6.8297 = 0 \qquad \chi^2 = 13.60$

C1 = 0.009(5)
C2 = -0.004(5)
N3 = 0.025(5)
C7 = -0.031(4)
C3 = -0.005(4)
C4 = 0.010(4)
O1 = 0.273(5)
C5 = -0.005(5)
C6 = -0.004(5)
O2 = -0.181(5)

Plane B: C13, C14, C15, C16, C17, C18

$-0.7827x + 0.2543y - 0.5680z + 3.9116 = 0 \qquad \chi^2 = 30.78$

C13 = -0.013(4)
C14 = 0.017(6)
C12 = -0.236(4)
C15 = -0.005(6)
C16 = -0.010(6)
C17 = 0.013(6)
C18 = -0.001(5)

Plane C: N1, C9, N2, C10, C11

$0.7212x - 0.3457y - 0.6006z + 1.3326 = 0 \qquad \chi^2 = 0.7471$

N1 = -0.002(4)
C9 = 0.003(6)
N2 = -0.002(6)
C10 = 0.001(6)
C11 = 0.001(5)
C8 = 0.042(4)

Plane D: C4, C7, C8, N1, C12

$-0.3430x - 0.4940y - 0.7990z + 6.3799 = 0 \qquad \chi^2 = 146.9$

C4 = -0.007(4)
C7 = 0.023(4)
C8 = -0.036(4)
N1 = 0.013(4)
C12 = 0.007(5)

Plane E: N3, O1, O2

$0.2532x + 0.7101y + 0.6590z + 6.9770 = 0$

Angles (°) between planes

A	B	77	B	D	53
A	C	64	B	E	67
A	D	28	C	D	66
A	E	12.5	C	E	63
B	C	72	D	E	16

A2.5 Mean planes for E-3-(4-nitrophenyl)-1-phenyl-2-(imidazol-1-yl)-prop-2-en -1-one

Plane A: C1, C2, C3, C4, C5, C6

Molecule 1

$$0.6905x - 0.7219y - 0.0450z - 0.2182 = 0 \qquad \chi^2 = 8.283$$

C1 = 0.009(8)
C2 = 0.005(8)
N3 = -0.040(8)
C7 = -0.055(8)
C3 = -0.013(8)
C4 = 0.007(9)
O1 = -0.270(9)
C5 = 0.007(8)
C6 = -0.015(8)
O2 = 0.140(9)

Molecule 2

$$0.6893x + 0.7238y - 0.0319z - 5.1894 = 0 \qquad \chi^2 = 14.27$$

C1 = 0.011(8)
C2 = -0.009(8)
N3 = -0.063(8)
C7 = -0.050(8)
C3 = -0.006(8)
C4 = 0.019(8)
O1 = -0.085(10)
C5 = -0.018(8)
C6 = 0.003(8)
O2 = -0.041(8)

Plane B: C13, C14, C15, C16, C17, C18

Molecule 1

$$0.6602x + 0.7509y - 0.0150z - 8.7082 = 0 \qquad \chi^2 = 2.972$$

C13 = -0.005(6)
C14 = -0.003(8)
C12 = 0.027(7)
C15 = 0.006(8)
C16 = -0.002(10)
C17 = -0.006(10)
C18 = 0.009(8)

Molecule 2

$$0.6796x - 0.7324y - 0.0421z + 4.6402 = 0 \qquad \chi^2 = 0.4248$$

C13 = -0.004(8)
C14 = 0.001(8)
C12 = 0.111(8)
C15 = 0.002(10)
C16 = -0.002(12)
C17 = -0.001(12)
C18 = 0.004(10)

Plane C: N1, C9, N2, C10, C11

Molecule 1

$$0.1758x - 0.0899y - 0.9803z + 2.5504 = 0 \qquad \chi^2 = 3.620$$

N1 = 0.008(6)
C9 = -0.009(9)
N2 = 0.006(8)
C10 = -0.002(8)
C11 = -0.004(8)
C8 = 0.098(8)

Molecule 2

$$-0.1878x - 0.2104y - 0.9594z + 8.3865 = 0 \qquad \chi^2 = 0.4757$$

N1 = -0.003(6)
C9 = 0.001(8)
N2 = 0.001(8)
C10 = -0.002(9)
C11 = 0.003(28)
C8 = 0.028(8)

Plane D: C4, C7, C8, N1, C12

Molecule 1

$$0.4599x - 0.6419y - 0.6136z + 2.3378 = 0 \qquad \chi^2 = 117.0$$

C4 = -0.042(8)
C7 = 0.056(8)
C8 = 0.015(8)
N1 = -0.034(6)
C12 = 0.005(7)

Molecule 2

$$-0.4966x - 0.6481y - 0.5774z + 9.1250 = 0 \qquad \chi^2 = 165.1$$

C4 = 0.049(9)
C7 = -0.065(8)
C8 = -0.016(8)
N1 = 0.040(6)
C12 = -0.007(7)

Plane E: N3, O1, O2

Molecule 1

$$0.7248x - 0.6737y + 0.1442z - 0.8126 = 0$$

Molecule 2

$$0.6904x + 0.7233y - 0.0113z - 5.2883 = 0$$

Angles (°) between planes

		Molecule 1	Molecule 2
A	B	85	87
A	C	77	75
A	D	36	38
A	E	11	1
B	C	86	86
B	D	80	81
B	E	88	87
C	D	42	38
C	E	87	74
D	E	47	36

A2.6 Planes for 4'-aceto-2,3-benzo-1,4,7,10,13,16-hexaoxacyclooctadec-2-ene, strontium perchlorate.

Plane A: O2,O5,O8,O11,O14,O17.

Molecule 1.

$0.5508x + 0.7529y - 0.3602z - 2.9338 = 0$ $\chi^2 = 1246$

O2 = 0.237(24) O8 = 0.426(24) O14 = -0.257(24)
O5 = -0.543(21) O11 = -0.029(25) O17 = 0.166(24)

Molecule 2.

$0.5798x + 0.7338y - 0.3539z + 1.8793 = 0$ $\chi^2 = 442.5$

O2 = 0.029(21) O8 = 0.212(25) O14 = -0.279(24)
O5 = -0.258(25) O11 = 0.063(22) O17 = 0.234(22)

Sr = -0.010(4) - molecule 1; = 0.013(4) - molecule 2.

Plane B: C1,C18,C19,C20,C21,C22.

Molecule 2.

$0.4561x + 0.3171y - 0.8315z + 10.855 = 0$ $\chi^2 = 1.893$

C1 = 0.020(25) C19 = -0.013(29) C21 = -0.016(29)
C18 = -0.009(27) C20 = 0.043(31) C22 = -0.006(31)

Molecule 1.

$0.2620x + 0.3416y - 0.9026z + 8.8266 = 0$ $\chi^2 = 7.392$

C1 = -0.032(28) C19 = 0.026(31) C21 = -0.038(31)
C18 = -0.006(29) C20 = -0.007(29) C22 = 0.057(29)

Sr = 1.579(3) - molecule 1; = 1.401(4) - molecule 2.

Angle (°) between planes:

		Molecule 1	Molecule 2
A	B	43	38

A2.7 Mean planes for isothiocyanato(3,15,21-triaza-6,9,12-trioxa bicyclo (15,3,1)heneicosa-1(21),2,15,17,19-pentaene) calcium(II) with estimated standard deviations of errors in parentheses

Plane A: C1, C2, C3, C4, C5, N1

$$-0.5083x - 0.1329y - 0.8509z + 3.8273 = 0 \qquad \chi^2 = 22.3187$$

C1 = -0.012(4)   C3 = 0.010(7)   C5 = -0.000(5)

C2 = 0.001(6)   C4 = -0.010(6)   N1 = 0.011(4)

Plane B: N1, N2, N3, O1, O2, O3

$$-0.3643x - 0.1719y - 0.9153z + 4.0041 = 0 \qquad \chi^2 = 23390$$

N1 = 0.124(4)   N3 = -0.392(4)   O2 = -0.041(4)

N2 = 0.172(4)   O1 = -0.207(4)   O3 = 0.344(5)

Ca = -0.013(1)

Angle (°) between planes:

A   B   9.3

A2.8 Mean planes for aqua-di-isothiocyanato(3,15,21-triaza-6,9,12-trioxabicyclo (15.3.1) heneicosa-1(21),2,15,17,19-pentaene) strontium(II) with estimated standard deviations of error in parentheses

Plane A: C1, C2, C3, C4, C5, N1

$-0.1464x - 0.9568y - 0.2513z + 6.4848 = 0$ $\chi^2 = 10.565$

C1 = 0.015(10)
C3 = -0.007(11)
C5 = -0.019(10)
C2 = -0.011(10)
C4 = 0.022(13)
N1 = 0.000(8)
Sr = -0.015(3)

Plane B: N1, N2, N3, O1, O2, O3

$0.0553x + 0.9981y - 0.0282z - 6.8732 = 0$ $\chi^2 = 4446$

N1 = 0.306(8)
N2 = -0.060(9)
N3 = -0.273(9)
O1 = -0.217(9)
O2 = 0.252(8)
O3 = -0.007(7)
Sr = -0.534(1)

Plane C: Sr, N4, N5, O4

$-0.9964x + 0.0542y - 0.0650z + 3.6806 = 0$ $\chi^2 = 80.36$

Sr = 0.013(1)
N4 = -0.004(12)
N5 = -0.003(12)
O4 = -0.006(12)
C16 = -0.032(10)
C17 = -0.108(12)

Angles (°) between the planes:

A	B	17.1
A	C	83.7
B	C	90.0

A2.9.

Planes for aqua-di-isothiocyanato(3,15,21-triaza-6,9,12-trioxabicyclo(15.3.1) heneicosa-1(21),2,15,17,19-pentaene) barium (II).

Plane A: C1,C2,C3,C4,C5,N1.

$-0.1698x - 0.9468y - 0.2732z + 2.0670 = 0$ $\chi^2 = 28.13$

C1 = 0.011(4) C3 = -0.002(6) C5 = -0.012(4)
C2 = -0.010(5) C4 = 0.013(5) N1 = 0.000(4)
Ba = 0.086(0)

Plane B: N1,N2,N3,O1,O2,O3.

$0.057x + 0.9980y - 0.0260z - 2.3556 = 0$ $\chi^2 = 16490$

N1 = 0.287(4) N2 = -0.075(4) N3 = -0.217(4)
O1 = -0.200(4) O2 = 0.266(4) O3 = -0.060(3)
Ba = -0.711(0)

Plane C: Ba,N4,N5,O4.

$-0.9968x + 0.0458y - 0.0650z + 3.3752 = 0$ $\chi^2 = 814.2$

Ba = -0.004(0) N4 = 0.001(6)
N5 = 0.001(6) O4 = 0.002(6)

Angles (°) between planes:

A	B	18.6
A	C	81.7
B	C	89.5

A2.10 Planes for aqua-(3,15,diazo-6,9,12,20-tetra oxabicyclo (15.2.1) eicosa-2,15,17,19-tetraene) di-isothiocyanato strontium (II). Estimated standard deviations of errors in parentheses

Plane A: O1, O2, O3, O4, N1, N2

$0.0608x + 0.9976y - 0.0318z - 2.3288 = 0$ $\chi^2 = 6978$

N1 = -0.056(7) N2 = -0.209(7) O1 = 0.273(5)
O2 = -0.205(6) O3 = 0.2493(6) O4 = -0.053(6)
Sr = -0.5603(3)

Plane B: Sr, N3, N4, O5

$-0.9984x + 0.0550y - 0.0136z + 3.3016 = 0$ $\chi^2 = 5880$

Sr = 0.0230(3) N3 = -0.007(9) N4 = -0.006(9)
O5 = -0.010(7)

Plane C: C1, C2, C3, C4, O1

$-0.1408x - 0.9511y - 0.2749z + 1.9398 = 0$ $\chi^2 = 2.842$

C1 = 0.004(9) C2 = 0.000(12) C3 = -0.004(11)
O1 = 0.007(9) Sr = -0.0428(3)

Angle (°) between planes

A	B	89.7
A	C	18.2
B	C	84.7

A .11 Mean planes for 5-(p-bromobenzyl)-5-phenyl-dibenzophospholium bromide

Plane A: C14, C15, C20, C25

$0.4835x - 0.7168y - 0.5025z + 10.5202 = 0$ $\chi^2 = 1.591$

C14 = -0.009(21)
C15 = 0.016(23

C20 = 0.009(22)
C25 = -0.016(18)

P = -0.159(6)

Plane B: C14, C15, C16, C17, C18, C19

$0.4833x - 0.7419y - 0.4647z + 10.5202 = 0$ $\chi^2 = 3.589$

C14 = -0.023(21)
C15 = 0.028(23)

C16 = -0.010(24)
C17 = -0.012(24)

C18 = 0.018(26)
C19 = 0.000(22)

Plane C: C20, C21, C22, C23, C24, C25

$0.4701x - 0.6945y - 0.5447z + 10.8114 = 0$ $\chi^2 = 1.306$

C20 = 0.012(22)
C21 = -0.002(21)

C22 = -0.014(26)
C23 = 0.019(25)

C24 = -0.009(23)
C25 = -0.007(18)

Plane D: C8, C9, C10, C11, C12, C13

$-0.6930x - 0.5769y - 0.4324z + 5.0170 = 0$ $\chi^2 = 5.419$

C8 = 0.026(20)
C9 = -0.015(23)
C7 = 0.081(22)

C10 = 0.008(20)
C11 = -0.010(21)
Br = 0.100(1)

C12 = 0.020(22)
C13 = -0.028(19)

Plane E: C1, C2, C3, C4, C5, C6

$-0.4193x - 0.0547y - 0.9062z + 7.7753 = 0$ $\chi^2 = 3.895$

C1 = 0.011(23)
C2 = -0.027(21)

C3 = 0.030(23)
C4 = -0.015(28)

C8 = -0.002(26)
C6 = 0.003(22)

Angles between planes (°)

A	B	2.6	B	D	72.9
A	C	2.8	B	E	75.0
A	D	73.0	C	D	71.9
A	E	72.8	C	E	70.5
B	C	5.4	D	E	44.4

A .12 Mean planes for 10-(4-bromobenzyl)-10-phenylphenosa-phosphonium bromide

Plane A: C14, C15, C20, C25

$-0.7138x + 0.1067y - 0.6922z + 6.5878 = 0 \qquad \chi^2 = 3.643$

C14 = -0.009(10)   C20 = 0.009(10)   P = -0.135(2)
C15 = 0.011(12)   C25 = -0.011(10)   O = -0.071(8)

Plane B: C1, C2, C3, C4, C5, C6

$0.0821x - 0.8343y - 0.5452z + 3.5214 = 0 \qquad \chi^2 = 2.472$

C1 = -0.012(10)   C3 = 0.001(4)   C5 = -0.001(14)
C2 = 0.008(12)   C4 = -0.004(14)   C6 = 0.009(12)

Plane C: C8, C9, C10, C11, C12, C13

$-0.5751x - 0.8173y - 0.0347z + 4.5029 = 0 \qquad \chi^2 = 5.842$

C8 = -0.015(10)   C10 = -0.008(12)   C12 = 0.004(12)
C9 = 0.017(10)   C11 = -0.003(12)   C13 = 0.005(12)
C7 = 0.031(10)   Br = 0.210(2)

Plane D: C14, C15, C16, C17, C18, C19

$-0.6900x + 0.0768y - 0.7198z + 6.6925 = 0 \qquad \chi^2 = 1.287$

C14 = -0.007(11)   C16 = 0.008(15)   C18 = 0.002(13)
C15 = 0.001(12)   C17 = -0.009(15)   C19 = 0.006(12)

Plane E: C20, C21, C22, C23, C24, C25

$-0.7260x + 0.1211y - 0.6769z + 6.5913 = 0 \qquad \chi^2 = 0.989$

C20 = 0.000(10)   C22 = 0.001(15)   C24 = 0.009(13)
C21 = 0.003(12)   C23 = -0.005(15)   C25 = -0.007(10)

Angles between planes (°)

A	B	77	B	D	74
A	C	70	B	E	78
A	D	3	C	D	69
A	E	1	C	E	70
B	C	49	D	E	4

A2.13

Planes for 5-phenyl-10,11-dihydrodibenzo(b,f)-phosphepin-5-oxide

Plane A: C1, C2, C3, C4, C5, C6

$0.7669\,x - 0.5350\,y - 0.3543\,x + 1.8444 = 0.$ $\chi^2 = 7.5336$

C1 = -0.009(7)
C2 = -0.001(7)
C3 = 0.012(8)
C4 = -0.012(9)
C5 = 0.001(9)
C6 = 0.009(7)
P = -0.108(2)
C7 = 0.033(9)

Plane B: C9, C10, C11, C12, C13, C14

$0.8856\,x + 0.4013\,y - 0.2340\,z + 0.1066 = 0.$ $\chi^2 = 10.2368$

C9 = 0.011(8)
C10 = 0.005(8)
C11 = -0.017(9)
C12 = 0.013(10)
C13 = 0.004(9)
C14 = -0.016(10)
P = -0.060(2)
C8 = -0.010(9)

Plane C: C15, C16, C17, C18, C19, C20

$-0.2925\,x - 0.3061\,y - 0.9059\,z + 5.7427 = 0.$ $\chi^2 = 8.3762$

C15 = -0.012(5)
C16 = 0.006(7)
C17 = 0.000(8)
C18 = -0.001(8)
C19 = -0.004(7)
C20 = 0.011(7)
P = 0.165(2)

Angles between the planes:

A	B	56.8°
A	C	74.9°
B	C	80.2°

Appendix 3

A3.1 Torsion angles with estimated standard deviations of error in parentheses for 1-(4-chloro-phenoxy)-3,3-dimethyl-1-(1,2,4-triazole-1-yl)-2-butanone.

C5-02-C71-C72 = -176.6(10)

C5-02-C71-C76 = 163.4(7)

C71-02-C5-N1 = 86.0(8)

C71 -02-C5-C4 = -155.4(6)

02-C5-N1-N2 = -136.4(7)

02-C5-N1-C1 = 47.1(10)

C4-C5-N1-N2 = 110.6(7)

C4-C5-N1-C1 = -66.0(10)

02-C5-C4-01 = -80.9(8)

02-C5-C4-C31 = 100.1(7)

N1-C5-C4-01 = 37.3(9)

N1-C5-C4-C31 = -141.6(6)

01-C4-C31-C32 = 136.3(8)

01-C4-C31-C33 = 13.3(10)

01-C4-C31-C34 = -104.3(8)

C5-C4-C31-C32 = -44.8(8)

C5-C4-C31-C33 = -167.8(6)

C5-C4-C31-C34 = 74.6(8)

A3.2 Torsion angles, with estimated standard deviation of errors in parentheses, for 1-(4-nitrophenyl)-4,4-dimethyl-2-(1,2,4-triazol-1-yl)-pentan-3-one

Angles in degrees

N2 - N1 - C5 - C4 = -53.6(7)

N2 - N1 - C5 - C6 = 65.7(7)

C1 - N1 - C5 - C4 = 129.5(7)

C1 - N1 - C5 - C6 =-111.1(8)

N1 - C5 - C4 - C31 = -76.2(7)

C6 - C5 - C4 - O1 = -19.4(8)

C6 - C5 - C4 - C31 = 163.8(6)

C71 - C6 - C5 - N1 = 57.9(7)

C71 - C6 - C5 - C4 = 176.3(5)

C72 - C71 - C6 - C5 = 76.9(8)

C76 - C71 - C6 - C5 =-103.2(7)

C5 - C4 - C31 - C32 = -140.7(7)

C5 - C4 - C31 - C33 = -20.5(9)

C5 - C4 - C31 - C34 = 102.3(7)

O1 - C4 - C31 - C32 = 42.5(9)

O1 - C4 - C31 - C33 = 162.7(7)

O1 - C4 - C31 - C34 = -74.5(8)

O41 - N4 - C74 - C75 = 2.4(13)

O41 - N4 - C74 - C73 = -178.4(8)

O42 - N4 - C74 - C75 = -176.5(9)

O42 - N4 - C74 - C73 = 2.7(13)

N1 - C5 - C4 - O1 = 100.6(7)

A3.3

Torsion angles, with estimated standard deviations of error in parentheses, for 1-(4-chlorophenyl)-3-(2-fluorophenyl) - 2 - (1,2,4-triazol-1-yl)-propan-1-one.

Angles in degrees

N2 - N1 - C5 - C4 = -51.7(8)
N2 - N1 - C5 - C6 = 70.9(8)
C1 - N1 - C5 - C4 = 139.6(7)
C1 - N1 - C5 - C6 = -97.9(8)
N1 - C5 - C4 - O1 = 116.4(7)
N1 - C5 - C4 - C31 = -64.8(7)
C6 - C5 - C4 - O1 = -123.0(8)
C6 - C5 - C4 - C31 = 173.0(6)

C71 - C6 - C5 - N1 = 52.7(8)
C71 - C6 - C5 - C4 = 172.7(6)
C72 - C71 - C6 - C5 = 80.2(9)
C76 - C71 - C6 - C5 = -96.1(9)
C5 - C4 - C31 - C32 = -20.8(10)
C5 - C4 - C31 - C36 = 163.1(6)
O1 - C4 - C31 - C32 = 156.0(7)
O1 - C4 - C31 - C36 = -18.2(10)

A3.4 Torsion angles with standard deviations of error in parentheses for Z-3-(4-nitrophenyl)-1-phenyl-2-(imidazol-1-yl)-prop-2-en -1-one

O1 - N3 - C1 - C2	167.1(5)
O1 - N3 - C1 - C6	-13.4(7)
O2 - N3 - C1 - C2	-11.2(7)
O2 - N1 - C1 - C6	168.3(5)
C3 - C4 - C7 - C8	-157.8(4)
C5 - C4 - C7 - C8	25.6(7)
C4 - C7 - C8 - N2	7.4(7)
C4 - C7 - C8 - C12	179.8(4)
C7 - C8 - N1 - C9	63.5(6)
C7 - C8 - N1 - C11	-119.6(5)
C12 - C8 - N1 - C9	-109.6(5)
C12 - C8 - N1 - C11	67.3(6)
C7 - C8 - C12 - O3	-152.0(4)
C7 - C8 - C12 - C13	29.1(6)
N1 - C8 - C12 - O3	21.0(6)
N1 - C8 - C12 - C13	-157.9(4)
C8 - C12 - C13 - C14	34.9(6)
C8 - C12 - C13 - C18	-153.3(4)
O3 - C12 - C13 - C14	-144.0(5)
O3 - C12 - C13 - C18	27.9(6)

A3.5 Torsion angles with standard deviations of error in parentheses for E-3-(4-nitrophenyl)-1-phenyl-2-(imidazol-1-yl)-prop-2-en -1-one

	Molecule 1	Molecule 2
O1 - N3 - C1 - C6	-9.4(14)	5.3(12)
O1 - N3 - C1 - C2	167.3(9)	-179.4(8)
O2 - N3 - C1 - C2	-11.8(13)	-2.6(13)
O2 - N3 - C1 - C6	171.6(9)	-177.9(8)
C8 - C7 - C4 - C3	152.0(9)	176.8(7)
C8 - C7 - C4 - C5	-31.8(14)	-33.6(12)
N2 - C8 - C7 - C4	172.5(8)	171.4(7)
C4 - C7 - C8 - C12	7.2(14)	-8.3(13)
C7 - C8 - N1 - C9	-41.5(12)	-40.5(12)
C7 - C8 - N1 - C11	134.6(9)	141.8(8)
C12 - C8 - N1 - C11	-45.7(10)	-38.5(10)
C12 - C8 - N1 - C9	138.2(8)	139.2(8)
O3 - C12 - C8 - C7	-69.3(11)	-64.7(11)
C13 - C12 - C8 - C7	108.1(10)	113.8(9)
O3 - C12 - C8 - N1	111.0(8)	115.6(8)
C13 - C12 - C8 - N1	-71.6(9)	-65.8(9)
C18 - C13 - C12 - C8	170.3(7)	165.5(7)
C18 - C13 - C12 - O3	-12.5(11)	-15.9(12)
C14 - C13 - C12 - C8	-11.8(10)	-20.0(11)
C14 - C13 - C12 - O3	165.4(7)	158.6(8)

Torsion angles, with estimated standard deviation of errors in parentheses, for 4'-aceto-2,3-benzo-1,4,7,10,13,16-hexaoxacyclooctadec-2-ene, strontium perchlorate.

Angles in degrees.

	Molecule 1.	Molecule 2.
C18 - C1 - O2 - C3	178	175
C1 - O2 - C3 - C4	-179	-178
O2 - C3 - C4 - O5	58	61
C3 - C4 - O5 - C6	151	149
C4 - O5 - C6 - C7	-178	-173
O5 - C6 - C7 - O8	-55	-58
C6 - C7 - O8 - C9	179	-177
C7 - O8 - C9 - C10	170	160
O8 - C9 - C10- O11	67	60
C9 - C10- O11- C12	179	167
C10 - O11- C12- C13	171	164
O11 - C12- C13- O14	-59	36
C12 - C13- O14- C15	-166	-174
C13 - O14- C15- C16	-97	-168
O14 - C15- C16- O17	-60	-74
C15 - C16- O17- C18	-175	-167
C16 - O17- C18- C1	-179	176
O17 - C18- C1 - O2	11	-3

A3.7 Torsion angles with estimated standard deviations of error in parentheses for di-isocyanato (3,15,21-triaza-6,9,12-trioxabicyclo (15.3.1) heneicosa-1(21), 2,15,17,19-pentaene) calcium(II)

N1 - C5 - C6 - N2 = -2.9(0.7)

C5 - C6 - N2 - C7 = 178.8(0.5)

N2 - C7 - C8 - O1 = -55.3(0.6)

C6 - N2 - C7 - C8 = -148.6(0.5)

C7 - C8 - O1 - C9 = -169.2(0.5)

C8 - O1 - C9 - C10 = 168.9(0.5)

O1 - C9 - C10 - O2 = 61.3(0.6)

C9 - C10 - O2 - C11 = 174.9(0.5)

C10 - O2 - C11 - C12 = -169.4(0.6)

O2 - C11 - C12 - O3 = -43.9(0.8)

C11 - C12 - O3 - C13 = -170.6(0.6)

C12 - O3 - C13 - C14 = -132.8(0.6)

O3 - C13 - C14 - N3 = -51.7(0.7)

C13 - C14 - N3 - C15 = -125.0(0.6)

C14 - N3 - C15 - C1 = -177.2(0.5)

N3 - C15 - C1 - N1 = 1.1(0.7)

C15 - C1 - N1 - C5 = 176.1(0.4)

C1 - N1 - C5 - C6 = -177.4(0.4)

N2 - C6 - C5 - C4 = 178.4(0.5)

C6 - C5 - C4 - C3 = 179.4(0.5)

N3 - C15 - C1 - C2 = 179.6(0.5)

C15 - C1 - C2 - C3 = -176.9(0.5)

A3.8 Torsion angles, with standard deviation of errors in parentheses, for aqua-di-isothiocyanato(3,15,21-triaza-6,9,12-trioxabicyclo(15.3.1) heneicosa-1(21),2,15,17,19-pentaene) strontium (II).

Angles in degrees.

C4 - C5 - C6 - N2 = -179.9(12)
N1 - C5 - C6 - N2 = -2.1(15)
C5 - C6 - N2 - C7 = -179.7(10)
C6 - N2 - C7 - C8 = 137.1(12)
N2 - C7 - C8 - O1 = 57.2(14)
C7 - C8 - O1 - C9 = 174.1(11)
C8 - O1 - C9 - C10 = 175.8(11)
O1 - C9 - C10 - O2 = -62.0(13)
C9 - C10 - O2 - C11 = -164.4(10)
C10 - O2 - C11 - C12 = 179.2(10)
O2 - C11 - C12 - O3 = 61.9(12)
C11 - C12 - O3 - C13 = 175.3(9)
C12 - O3 - C13 - C14 = -177.3(9)
C13 - C14 - N3 - C15 = -115.8(11)
C14 - N3 - C15 - C1 = 175.0(10)
N3 - C15 - C1 - N1 = -5.8(15)
N3 - C15 - C1 - C2 = 173.5(10)
C15 - C1 - N1 - C5 = 178.2(9)
C1 - N1 - C5 - C6 = 180.0(9)

A3.9 Torsion angles, with estimated standard deviations of error in parentheses, for aqua-di-isothiocyanato(3,15,21-triaza-6,9,12-trioxa bicyclo (15.3.1) heneicosa-1(21),2,15,17,19-pentaene) barium(II)

N1 - C5 - C6 - N2 = -3.2(7)
C5 - C6 - N2 - C7 = -178.2(4)
C6 - N2 - C7 - C8 = 136.4(5)
N2 - C7 - C8 - O1 = 60.3(6)
C7 - C8 - O1 - C9 = 174.4(5)
C8 - O1 - C9 - C10 = 173.4(5)
O1 - C9 - C10 - O2 = -65.0(6)
C9 - C10 - O2 - C11 = -166.3(5)
C10 - O2 - C11 - C12 = 179.3(4)
O2 - C11 - C12 - O3 = 66.2(5)
C11 - C12 - O3 - C13 = 179.2(4)
C12 - O3 - C13 - C14 = -178.9(4)
O3 - C13 - C14 - N3 = -61.2(5)
C13 - C14 - N3 - C15 = -118.1(5)
C14 - N3 - C15 - C1 = 175.7(4)
N3 - C15 - C1 - N1 = -5.9(7)
C15 - C1 - N1 - C5 = 179.1(4)
C1 - N1 - C5 - C6 = 178.3(4)
N2 - C6 - C5 - C4 = 176.4(5)
C6 - C5 - C4 - C3 = -177.0(5)
N3 - C15 - C1 - C2 = 174.2(5)
C15 - C1 - C2 - C3 = -178.2(5)

A3.10 Torsion angles for aqua-(3,15,diazo-6,9,12,20-tetraoxabicyclo (15.2.1) eicosa-2,15,17,19-tetraene) di-isothiocyanato strontium (II)

C1 - O1 - C4 - C5	-179.4 (1.4)
C3 - C4 - C5 - N1	175.1 (1.6)
O1 - C4 - C5 - N1	179.9 (1.4)
C4 - C5 - N1 - C6	179.8 (1.2)
C5 - N1 - C6 - C7	137.7 (1.3)
N1 - C6 - C7 - O2	57.5 (1.5)
C6 - C7 - O2 - C8	175.2 (1.2)
C7 - O2 - C8 - C9	177.9 (1.2)
O2 - C8 - C9 - O3	-62.7 (1.5)
C8 - C9 - O3 - C10	-165.9 (1.3)
C9 - O3 - C10 - C11	179.3 (1.3)
O3 - C10 - C11 - O4	62.5 (1.6)
C10 - C11 - O4 - C12	175.8 (1.3)
C11 - O4 - C12 - C13	-179.3 (1.2)
O4 - C12 - C13 - N2	-58.5 (1.5)
C12 - C13 - N2 - C14	-122.7 (1.4)
C13 - N2 - C14 - C1	175.9 (1.5)
N2 - C14 - C1 - O1	-1.6 (1.5)
N2 - C14 - C1 - C2	176.0 (1.6)
C4 - O1 - C1 - C14	177.1 (1.4)
C14 - C1 - C2 - C3	179.9 (1.7)
C2 - C3 - C4 - C5	179.9 (1.6)

A4.1

[illegible]

A4.2

[illegible]

4.3

<u>A4.4</u>

14.5

A4.6

H	K	L	FO	FC
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

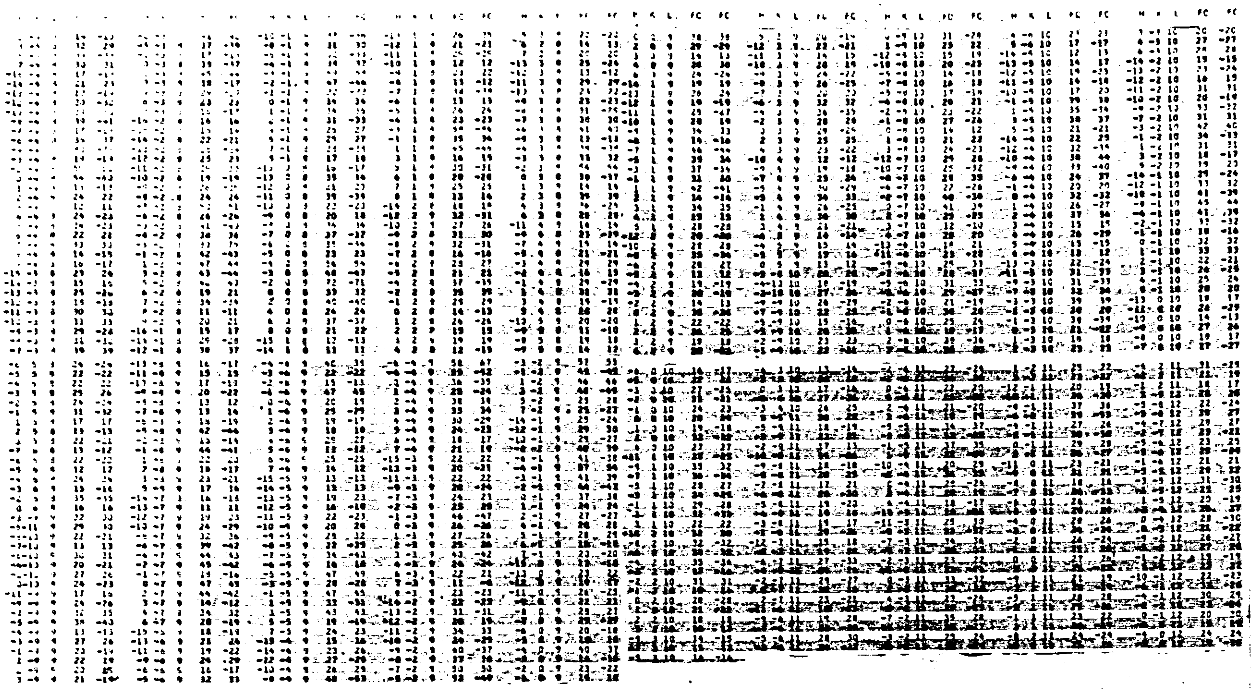
4.7

A4.8

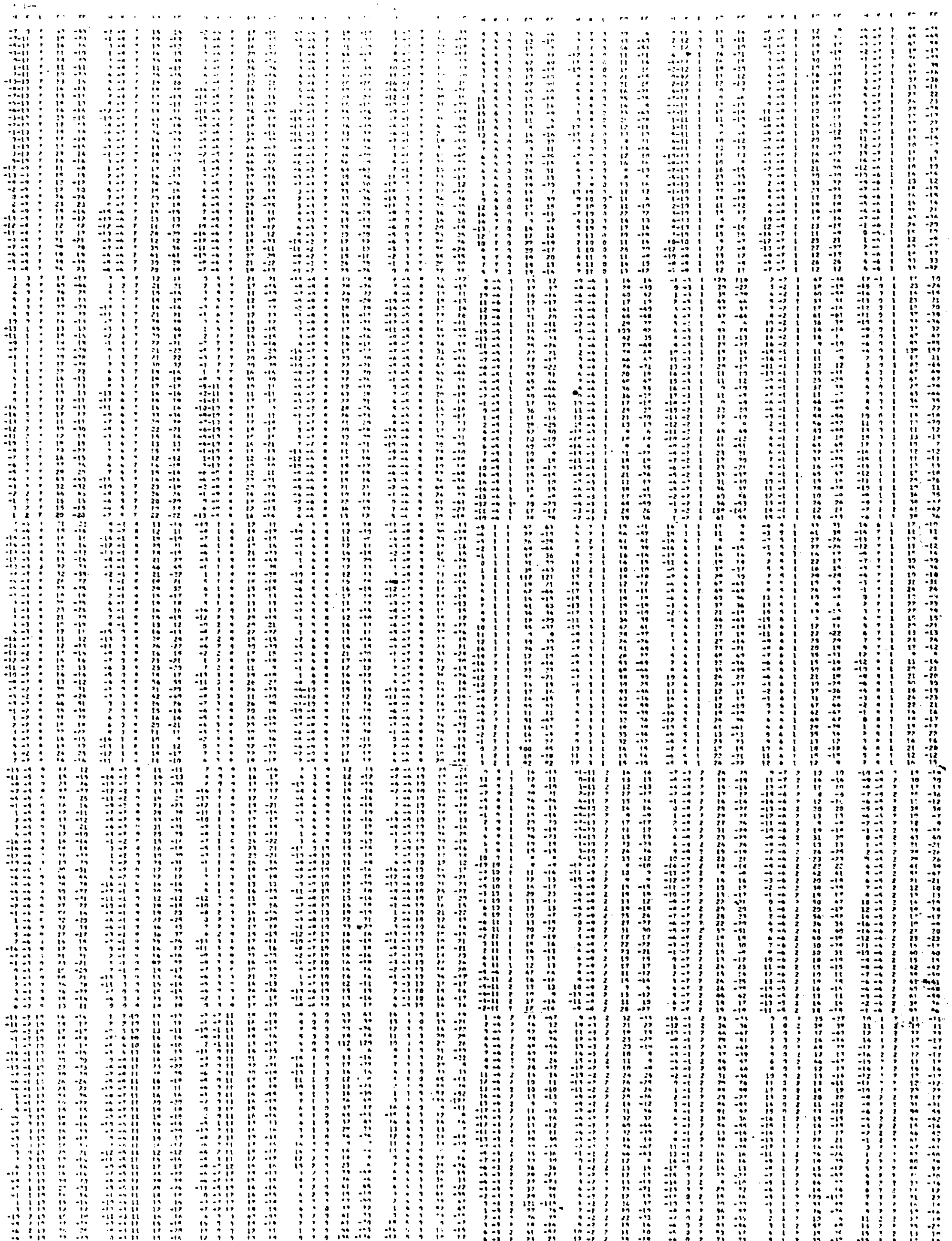
[illegible]

<u>A4.9</u>

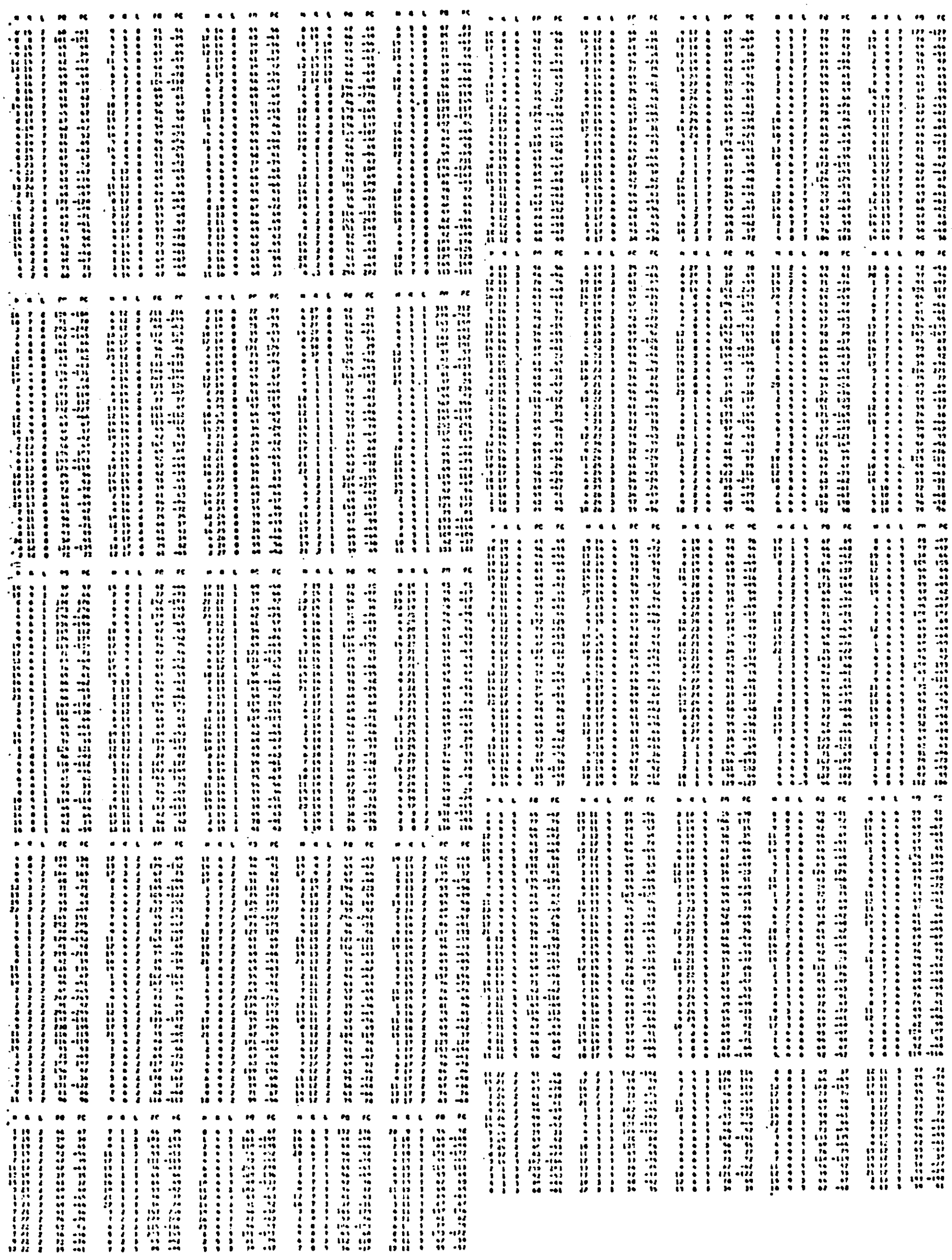
4.9 continued



A4.10



A4.12



A4.13

[illegible]

Details of post graduate study.

1. Attendance at a series of lectures at Sheffield University and Sheffield City Polytechnic on the coordination chemistry of macrocyclic compounds.

2. Attendance at a course of lectures at Leeds University on the mathematical techniques utilised in X-ray crystallography and an Open University course on the numerical solution of equations.

3. A study course in computing including the use of FORTRAN and the use of graphics facilities.

4. Four one-week work periods at the I.C.I. Plant Protection Division, Jealott's Hill.

5. A reading programme was followed which included:

   a) "Direct Methods in Crystallography", M.M.Woolfson, Clarendon Press, 1961.

   b) "X-ray Structure Determination, a Practical Guide", G.H.Stout and L.H.Jensen, Macmillan, 1968.

   c) "Fortran Programming", J.Watters, Heinemann, 1969.

   d) "Coordination Chemistry of Macrocyclic Compounds", Ed. G.A.Melson, Plenum Press, 1979.

   e) "Elements of X-ray Diffraction", B.D.Cullity, Addison-Wesley, 1956.

   f) "Crystallography and its Applications", L.S.Dent Glasser, van Nostrand, Reinhold, 1977.

   g) "Membrane Active Complexones", Yu.A.Ovchinnikov, V.T.Ivanov and A.M.Shkrob, Elsevier, Amsterdam, 1974.

   h) "Systemic Fungicides", Ed. R.W.Marsh, Longman, 1972.

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Structure of 1-(4-Chlorophenoxy)-3,3-dimethyl-1-(1,2,4-triazol-1-yl)-2-butanone

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Abstract. $C_{14}H_{16}ClN_3O_2$, $M_r = 293{\cdot}8$, $P2_1/n$, $a = 8{\cdot}076\,(3)$, $b = 20{\cdot}317\,(8)$, $c = 9{\cdot}307\,(3)$ Å, $\beta = 97{\cdot}43\,(5)°$, $U = 1514{\cdot}2$ Å^3, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $Z = 4$, $D_m = 1{\cdot}31\,(2)$, $D_c = 1{\cdot}29$ Mg m^{-3}, $\mu = 0{\cdot}21$ mm^{-1}, $F(000) = 616$. The structure was solved by direct methods and refined to $R = 0{\cdot}058$ for 1023 counter reflections classed as observed. The triazolyl ring, which shows significant delocalization, is planar and inclined at angles of 73·1 (9) and 61·8 (9)° to the *p*-chlorophenyl ring and to the C—C(O)—C grouping respectively. The exocyclic angles at N(1) of the triazolyl ring are very asymmetric with C—N—N 119·5 (6) and C—N—C 130·7 (6)°.

Introduction. 1-(4-Chlorophenoxy)-3,3-dimethyl-1-(1,2,4-triazol-1-yl)-2-butanone, triadimefon, is well established as an effective systemic fungicide (Martin & Morris, 1979). While the exact mode of action of the fungicide has not been established, treatment of fungi with the compound results in the inhibition of ergosterol biosynthesis (Buchenauer, 1976). From the study of structure–activity relationships in related compounds, it was believed that the triazolyl group and the overall conformation of the molecule played important roles. It is to establish the conformation, albeit in the solid state, that we have determined the crystal structure of the title compound.

A crystal 0·20 × 0·24 × 0·35 mm was mounted about the crystallographic *a* axis and data were collected on a Stoe Stadi-2 two-circle diffractometer in layers of constant *h* up to *h* = 9. The data were

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Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($\times 10^3$) *calculated by reference to Willis & Pryor* (1975); *e.s.d.'s are in parentheses*

	x	y	z	U_{eq} (Å^2)
Cl	−2894 (4)	9666 (2)	5907 (3)	10 (3)
O(1)	1799 (8)	8481 (3)	−1736 (5)	76 (5)
O(2)	186 (7)	8950 (2)	718 (5)	45 (4)
N(1)	−52 (9)	7815 (3)	150 (6)	39 (4)
N(2)	107 (11)	7226 (3)	818 (7)	71 (6)
N(3)	−1929 (10)	7193 (4)	−1075 (7)	62 (5)
C(1)	−1261 (12)	7787 (4)	−966 (7)	52 (6)
C(2)	−1047 (16)	6880 (4)	33 (10)	76 (7)
C(31)	4079 (11)	8674 (3)	147 (7)	46 (5)
C(32)	4097 (14)	9155 (4)	1423 (9)	65 (6)
C(33)	5000 (13)	8961 (4)	−1056 (9)	66 (6)
C(34)	4908 (12)	8017 (4)	670 (8)	60 (6)
C(4)	2292 (10)	8505 (3)	−468 (7)	43 (5)
C(5)	1076 (10)	8345 (3)	654 (7)	40 (5)
C(71)	−525 (11)	9081 (4)	1989 (7)	45 (5)
C(72)	−802 (12)	8613 (4)	2992 (8)	54 (6)
C(73)	−1521 (13)	8797 (4)	4222 (8)	63 (7)
C(74)	−1963 (12)	9438 (5)	4370 (8)	61 (6)
C(75)	−1677 (12)	9909 (4)	3367 (10)	61 (6)
C(76)	−964 (12)	9727 (4)	2160 (8)	52 (5)

processed to give 2773 planes of which 1023 had $I \geq 2{\cdot}5\sigma(I)$ and were classed as observed. Systematic absences were $h0l$, $h + l = 2n + 1$, and $0k0$, $k = 2n + 1$, corresponding to space group $P2_1/n$. The structure was solved by multisolution direct methods (Sheldrick, 1976). The H atoms were included in positions calculated from the geometry of the molecule (C—H = 1·08 Å). A final isotropic $U = 0{\cdot}049\,(20)$ Å^2 was refined for H(5) while the common isotropic temperature factors applied to the methyl and to the remaining H atoms refined to $U = 0{\cdot}081\,(7)$ and 0·082 (10) Å^2 respectively. Scattering factors were calculated using an analytical approximation (*International Tables for X-ray Crystallography*, 1974) and the weighting scheme adopted was $w = 0{\cdot}8614/[\sigma^2(F_o) + 0{\cdot}0016(F_o)^2]$. Full-matrix least-squares refinement with anisotropic temperature factors for all non-H atoms gave the final $R = 0{\cdot}058$ and $R' = 0{\cdot}063$. The final atomic coordinates and equivalent isotropic thermal parameters are given in Table 1.*

Discussion. Bond lengths and angles are given in Table 2, torsion angles in Table 3, and mean planes in Table 4. The molecule is found to adopt a conformation such that the triazolyl ring is inclined at an angle of 73·1 (9)° to the aromatic ring and at an angle of

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

N(1)—N(2)	1·348 (8)	C(31)—C(33)	1·537 (12)
N(1)—C(1)	1·332 (10)	C(31)—C(34)	1·544 (10)
N(2)—C(2)	1·311 (13)	O(2)—C(71)	1·406 (9)
C(2)—N(3)	1·336 (12)	C(71)—C(72)	1·371 (11)
N(3)—C(1)	1·319 (11)	C(71)—C(76)	1·374 (11)
N(1)—C(5)	1·449 (9)	C(72)—C(73)	1·399 (12)
C(5)—C(4)	1·558 (11)	C(73)—C(74)	1·363 (14)
C(5)—O(2)	1·429 (9)	C(74)—C(75)	1·377 (13)
C(4)—O(1)	1·196 (8)	C(75)—C(76)	1·378 (13)
C(4)—C(31)	1·521 (11)	C(74)—Cl	1·761 (9)
C(31)—C(32)	1·537 (10)		

C(5)—N(1)—N(2)	119·5 (6)	C(4)—C(31)—C(34)	105·9 (6)
C(5)—N(1)—C(1)	130·7 (6)	C(32)—C(31)—C(33)	111·4 (6)
C(1)—N(1)—N(2)	109·7 (6)	C(32)—C(31)—C(34)	110·2 (6)
N(1)—N(2)—C(2)	101·6 (6)	C(33)—C(31)—C(34)	109·1 (7)
N(2)—C(2)—N(3)	116·3 (8)	C(5)—O(2)—C(71)	117·4 (5)
C(1)—N(3)—C(2)	101·8 (7)	O(2)—C(71)—C(72)	124·2 (7)
N(1)—C(1)—N(3)	110·5 (7)	O(2)—C(71)—C(76)	114·7 (6)
N(1)—C(5)—C(4)	111·3 (5)	C(72)—C(71)—C(76)	121·1 (7)
N(1)—C(5)—O(2)	110·7 (6)	C(71)—C(72)—C(73)	119·5 (8)
C(4)—C(5)—O(2)	102·3 (5)	C(72)—C(73)—C(74)	118·7 (8)
C(5)—C(4)—O(1)	119·6 (7)	C(73)—C(74)—C(75)	121·8 (8)
C(5)—C(4)—C(31)	116·4 (6)	C(73)—C(74)—Cl	118·5 (7)
O(1)—C(4)—C(31)	124·0 (7)	Cl—C(74)—C(75)	119·6 (7)
C(4)—C(31)—C(32)	110·4 (7)	C(74)—C(75)—C(76)	119·3 (8)
C(4)—C(31)—C(33)	109·7 (6)	C(75)—C(76)—C(71)	119·5 (7)

Table 3. *Torsion angles* (°) *with e.s.d.'s in parentheses*

C(5)—O(2)—C(71)—C(72)	−17·6 (10)	O(2)—C(5)—C(4)—C(31)	100·1 (7)
C(5)—O(2)—C(71)—C(76)	163·4 (7)	N(1)—C(5)—C(4)—O(1)	37·3 (9)
C(71)—O(2)—C(5)—N(1)	86·0 (7)	N(1)—C(5)—C(4)—C(31)	−141·6 (6)
C(71)—O(2)—C(5)—C(4)	−155·4 (6)	O(1)—C(4)—C(31)—C(32)	136·3 (8)
O(2)—C(5)—N(1)—N(2)	−136·4 (7)	O(1)—C(4)—C(31)—C(33)	13·3 (10)
O(2)—C(5)—N(1)—C(1)	47·1 (10)	O(1)—C(4)—C(31)—C(34)	−104·3 (8)
C(4)—C(5)—N(1)—N(2)	110·6 (7)	C(5)—C(4)—C(31)—C(32)	−44·8 (8)
C(4)—C(5)—N(1)—C(1)	−66·0 (10)	C(5)—C(4)—C(31)—C(33)	−167·8 (6)
O(2)—C(5)—C(4)—O(1)	−80·9 (8)	C(5)—C(4)—C(31)—C(34)	74·6 (8)

Table 4. *Equations of least-squares planes referred to orthogonal axes with distances* (Å) *of atoms from the planes in square brackets*

Plane A: N(1), N(2), N(3), C(1), C(2)

$$0{\cdot}7512X - 0{\cdot}2781Y - 0{\cdot}5986Z + 4{\cdot}5433 = 0{\cdot}0000$$

[N(1), 0·0001 (66); N(2), −0·0000 (79); N(3), 0·0002 (76); C(1), −0·0002 (86); C(2), −0·0001 (114); C(5), 0·061 (7)]

Plane B: C(71)–C(76)

$$-0{\cdot}8494X - 0{\cdot}1808Y - 0{\cdot}4958Z + 3{\cdot}6807 = 0{\cdot}0000$$

[C(71), −0·001 (8); C(72), 0·004 (9); C(73), −0·007 (10); C(74), 0·008 (9); C(75), −0·005 (10); C(76), 0·002 (9); Cl, 0·017 (3); O(2), 0·011 (5)]

Plane C: C(5), C(4), O(1), C(31)

$$0{\cdot}2561X - 0{\cdot}9664Y - 0{\cdot}0202Z + 16{\cdot}1969 = 0{\cdot}0000$$

[C(5), 0·002 (6); C(4), −0·006 (6); O(1), 0·002 (6), C(31), 0·002 (6)]

Angles between planes (°), e.s.d.'s 0·9–1·5°

A–B	73·1	A–C	61·8	B–C	88·1

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* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36692 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

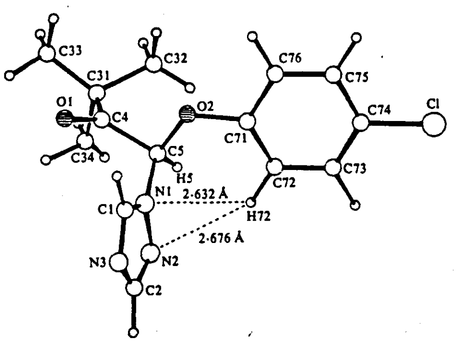

Fig. 1. The conformation of 1-(4-chlorophenoxy)-3,3-dimethyl-1-(1,2,4-triazol-1-yl)-2-butanone.

61·8 (9)° to the C(31), C(4), O(1), C(5) grouping (Fig. 1). The resulting arrangement leads to the close approach of the *ortho*-H, H(72), to the triazolyl atoms N(1) and N(2), such that both N···H distances lie within the sum of the van der Waals radii of N and H (Fig. 1). There is an accompanying distortion of the exocyclic angles at C(71), with the O(2)—C(71)—C(72) bond angle of 124·2 (7)° being considerably larger than the value found for O(2)—C(71)—C(76) [114·7 (6)°].

The triazolyl ring is planar, with C(5) lying only 0·061 (7) Å from the mean plane (Table 4). Although the C(1)—N(1) and C(2)—N(3) distances are somewhat larger than those found for C(1)—N(3) and C(2)—N(2), in keeping with the uncharged canonical valence form, all four C—N distances are shorter than a normal single bond (1·47 Å). The N(1)—N(2) bond is also shorter than a normal single bond (1·45 Å) and the three atoms bonded to N(1) are almost coplanar with it. Taken together these data indicate extensive delocalization within the heterocyclic ring. The most noteworthy feature of the heterocyclic ring is the asymmetry of the exocyclic angles at N(1) [119·5, 130·7 (6)°]. We have observed a similar pattern in related triazole systems (Anderson, Branch, Mann, Nowell & Walker, 1971, unpublished results) and it appears to be a function of the triazolyl ring itself rather than the influence of any inter- or intramolecular interactions.

The C(31), C(4), C(5), O(2), C(71) backbone is rather compressed resulting in the main from the orientation of the *tert*-butyl group, the C(31)—C(4)—C(5)—O(2) torsion angle being only 100·1 (7)°.

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Alkaline Earth Metal Complexes of Furanyl-containing Schiff Base Macrocycles; *X*-Ray Crystal and Molecular Structure of the Strontium Complex

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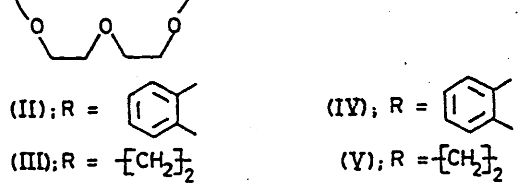
Summary Novel alkaline earth metal thiocyanate complexes are formed by the template condensation of furan-2,5-dicarbaldehyde with 1,11-diamino-3,6,9-trioxaundecane and 1,5-bis(2-aminophenoxy)-3-oxapentane; the *X*-ray structure of aqua-(3,15-diaza-6,9,12,20-tetraoxabicyclo[15,2,1]eicosa-2,15,17,19-tetraene)-di-isothiocyanatostrontium(II) has been determined.



Reaction conditions: (II), EtOH or BuOH; (III), BuOH, N_2, triethyl orthoformate. M = Ca, Sr, or Ba.

The observation that many of the neutral and monocarboxylic acid antibiotics capable of complexing the alkali and alkaline earth metal cations and effecting their transfer across natural or synthetic membranes contain the 2,5-dimethyltetrahydrofuranyl group has stimulated interest in the synthesis of macrocyclic ligands containing furanyl groups.[1] Macrocyclic polyethers of this type have been reported recently, together with brief comment on their metal complexing ability.[2,3]

We have investigated the synthesis of macrocycles derived from furan-2,5-dicarbaldehyde (I) and α,ω-amino-ethers in the presence of alkaline earth metal cations. The reactions of (I) with 1,8-diamino-3,6-dioxaoctane, 1,2-bis-(2-aminophenoxy)ethane, 1,3-bis(2-aminophenoxy)propane, 1,5-bis(2-aminophenoxy)-3-oxapentane (II), and 1,11-diamino-3,6,9-trioxaundecane (III) in alcoholic media, in the absence of metal ions, gave no recognisable macrocyclic products. When Ca, Sr, and Ba thiocyanates were used as templating cations in these reactions, macrocyclic complexes were isolated with the diamines (II) and (III) only. The use of Mg^{2+} as the potential templating cation gave no recognisable macrocyclic products, and this is a further illustration of the cation size control factor previously noted in the synthesis of the comparable pyridine-containing macrocycles.[4] Only the higher alkaline earth metals form products with the macrocycles derived from the three oxygen-containing amino-ethers. The complexes (IV) and (V) were characterised by chemical analysis and i.r. and mass spectrometry, and represent the first example of such macrocyclic Schiff bases derived from furanyl-containing precursors.

The i.r. spectra show no carbonyl stretching frequencies [$1675\ cm^{-1}$ in (I)] and the presence of bands in the 1610—$1620\ cm^{-1}$ region is indicative of $\nu(C{=}N)$. All but one of the complexes (IV; M = Ca) show a splitting of the thiocyanate CN stretching frequency,[5] though the CS stretch and NCS bending modes are obscured by ligand bands. It not possible to deduce the mode of thiocyanate bonding, or to advance a reason for the nonequivalence as evidenced by the splitting of ν(C=N) solely from the spectral information.

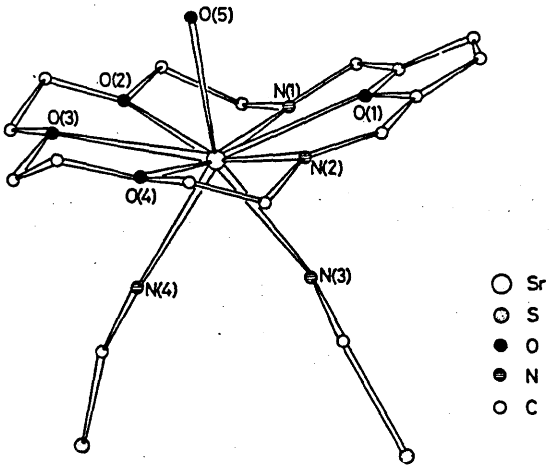


FIGURE. Molecular structure of $Sr(L)(NCS)_2.H_2O$ (V).

The complex $Sr(L)(NCS)_2.H_2O$ (L = ligand) (V), $M = 502{\cdot}1$, forms triclinic crystals from aqueous ethanol; $a = 13{\cdot}556(4)$, $b = 9{\cdot}130(2)$, $c = 9{\cdot}895(2)$ Å, $\alpha = 107{\cdot}81(4)$, $\beta = 109{\cdot}10(4)$, $\gamma = 84{\cdot}01(3)°$, space group $P\bar{1}$, $Z = 2$. Intensity data were collected using Mo-K_α radiation on a Stöe-Stadi 2 diffractometer. For 3221 independent reflections having $I/\sigma(I) \geqslant 4$, R is currently 0·060.†

The nitrogen and oxygen atoms of the macrocycle lie at distances 2·69—2·80 Å from the strontium ion. Interaction of these six atoms with strontium together with the bonding of a water molecule from one side of the ring and two N-bonded thiocyanate groups from the other side give an effective nine-co-ordination of the strontium. The cation lies below the mean plane of the macrocycle donor atoms and towards the thiocyanate anions such that the O(5)–Sr–N,O(macrocycle) angles lie in the range 68·7—84·3°.

The Sr–O(5) distance of 2·582(8) Å shows the water molecule to be strongly co-ordinated to strontium and the two Sr–N(thiocyanate) distances (mean, 2·633 Å) are, as expected, significantly shorter than the Sr–N(macrocycle) values of 2·799(10) and 2·785(8) Å. The plane through O(5),N(3),N(4) is inclined at 85° to that associated with the furanyl ring, with the strontium effectively co-planar with both planes. The O(5),N(3),N(4) plane is orientated such that one thiocyanate anion is beneath the furanyl species and the other beneath the ethylene-oxy chain. The unsymmetrical disposition of these groups with respect to the macrocycle, along with a small difference in the Sr–N–CS bond angles (164 and 168°) would account for the splitting of ν(C≡N) observed for the complex [2085 and 2070 (shoulder) cm^{-1}]. Furthermore, the water molecule is hydrogen-bonded to one thiocyanate anion from an adjacent molecule.

The bonding and spatial arrangement of the anions in the analogous calcium and barium complexes is not necessarily similar to that in the strontium complex as relationships between ion size and ligand cavity diameter must be considered, as with the complexes of the alkali and alkaline earth metals with cyclic polyethers.[6]

We thank the S.R.C. for a studentship to D.H.C.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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Alkaline Earth Metal Complexes of Pyridinyl Containing Schiff Base Macrocycles: *X*-Ray Crystal and Molecular Structures of the Calcium and Strontium Complexes

By David E. Fenton* and Diana H. Cook
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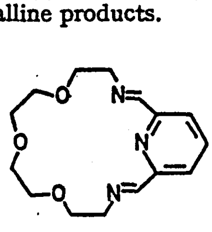
Summary Novel alkaline earth metal thiocyanate complexes are formed by the template condensation of 1,11-diamino-3,6,9-trioxaundecane with pyridine-2,6-dicarbaldehyde; the X-ray structures of (3,15,21-triaza-6,9,12-trioxabicyclo[15.3.1]heneicosa-1(21),2,15,17,19-pentaene)di-isothiocyanatocalcium(II) and aqua-(3,15,21-triaza-6,9,12-trioxabicyclo[15.3.1]heneicosa-1(21),2,15,17,19-pentaene)di-isothiocyanatostrontium(II) have been determined and the ready exchange of alkaline earth cations for lead(II) in these complexes is reported.

Calcium, strontium, and barium complexes of the macrocyclic Schiff base, 3,15,21-triaza-6,9,12-trioxabicyclo[15.3.1]-heneicosa-1(21),2,15,17,19-pentaene, (L), may be prepared by application of the metal ion template effect. The condensation of pyridine-2,6-dicarbaldehyde with 1,11-diamino-3,6,9-trioxaundecane in 1:1 molar ratio in butan-1-ol in the presence of the alkaline earth metal thiocyanate yields $Ca(L)(NCS)_2$, (I), $Sr(L)(NCS)_2.H_2O$, (II), or $Ba(L)(NCS)_2.H_2O$, (III), as crystalline products.



(L)

Crystal data. (I): $M = 447·6$, monoclinic with $a = 9·624(2)$, $b = 26·103(7)$, $c = 8·636(2)$ Å, $\beta = 90·25(3)°$, space group $P2_1/c$, $Z = 4$. $R = 0·040$ for 2084 independent reflections. (II): $M = 513·2$, triclinic with $a = 13·660(4)$, $b = 9·124(2)$, $c = 10·070(2)$ Å, $\alpha = 108·50(4)$, $\beta = 108·42(4)$ $\gamma = 83·11(3)°$, space group $P\bar{1}$, $Z = 2$. $R = 0·047$ for 1999 independent reflections.† (III): Preliminary *X*-ray photographic work indicates this barium complex to be isostructural with the strontium complex (II).

While the metal ions in both (I) and (II) are found to be co-ordinated to the macrocyclic ligand, the smaller calcium is located much more within the cavity of the macrocycle compared to strontium. Thus the calcium ion lies in the mean plane of the macrocycle oxygen and nitrogen atoms whereas the strontium ion is displaced by 0·53 Å from this plane. The relative location of the metals with respect to the macrocycle is also reflected by the value of the N(1)–M–O(2) bond angle, which is 146·0 and 175·6° for the strontium and calcium complexes, respectively. Both metals appear to be equally disposed towards the nitrogen and oxygen atoms of the macrocycle and the mean metal–N(macrocycle) and metal–O(macrocycle) distances do not differ significantly for either strontium (2·78 Å) or calcium (2·64 Å). The difference between these mean metal–donor distances, 0·14 Å, reflects the different cation radii (Sr^{2+} 1·25, Ca^{2+} 1·12 Å), and it would seem that it is to attain suitable Ca–donor distances that the smaller metal ion is drawn into the macrocyclic cavity. In so doing the conformation adopted by the macrocycle in (I) appears to be more strained than that in (II), as is indicated by torsion angle calculations. The torsion angle for one of the C–O bonds, for example, is only 133° in (I) compared to an expected value of *ca.* 180° [the corresponding angle in (II) is 177°].

The presence of six donor atoms in the macrocyclic ligand along with two N-bonded thiocyanate groups gives calcium a co-ordination number of 8 in (I), while the co-ordination of strontium in (II) is increased to 9 by a water molecule. The

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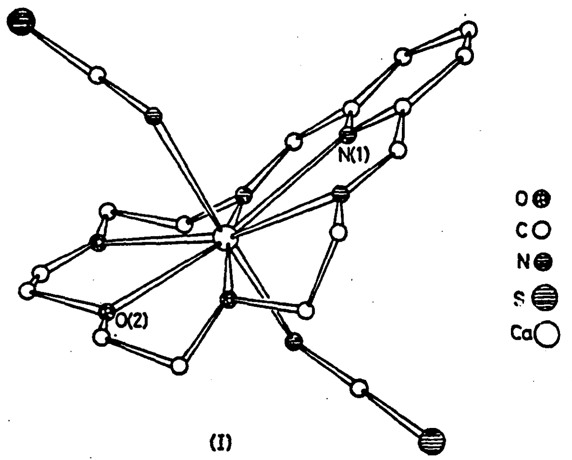
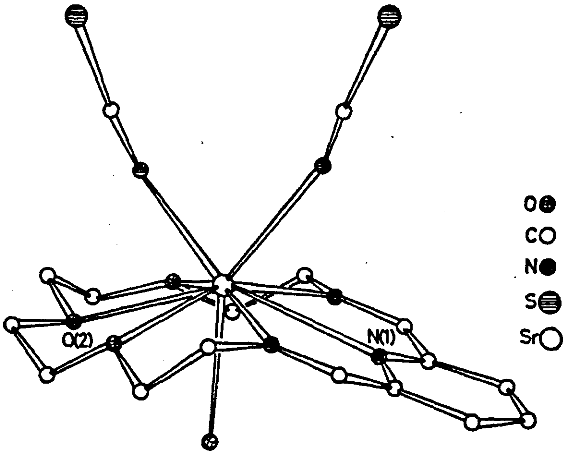
† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for the communication.



(I)



(II)

FIGURE. Molecular structures of Ca(L)(NCS)$_2$ (I) and Sr(L)(NCS)$_2$.H$_2$O (II).

latter co-ordinates strongly, the Sr–O distance being 2·59 Å, and also gives rise to hydrogen bonding involving a thiocyanate anion from an adjacent molecule. No significant intermolecular interactions are found in the calcium complex.

When the alkaline earth metal complexes are refluxed in aqueous ethanol over lead thiocyanate for *ca.* 10 min a cation exchange process occurs readily to give the previously reported[1] lead complex, Pb(L)(NCS)(SCN), (IV). The reverse reactions do not appear to proceed. In contrast to the metal in (I) and (II), the lead in complex (IV) interacts preferentially with the nitrogen atoms of the macrocycle. Not only is the mean Pb–N(macrocycle) distance of 2·60 Å far smaller than the mean Pb–O(macrocycle) distance of 3·07 Å but it is also significantly shorter than that found for the metal–donor atom distance in (I) or (II). We suggest therefore that this relatively strong affinity of the 'softer' lead for nitrogen atoms of the macrocyclic ligand is the driving force of the observed exchange reactions.

The i.r. spectra of the complexes show different patterns for the thiocyanate CN stretching frequencies: (I), 2065; (II), 2081 and 2073; and (III), 2070 cm^{-1} (broad). Although retrospectively these values may be related to the structural type we have noted that it is not possible to use the i.r. data to predict with certainty the mode of thiocyanate bonding in this general class of complexes. This is in contrast to transition metal thiocyanate derivatives where a defined relationship between $\nu_{C=N}$ and the SCN bonding mode has been established.[2] Further evidence for this difference is exhibited in the i.r. spectrum of (IV) where $\nu_{C=N}$ occurs at 2085 and 2065 cm^{-1}, *i.e.* at comparable values to those found for (II) despite the fact that in (IV) linkage isomerism occurs.[1] The CS stretching and NCS bending modes are obscured by ligand bands.

We thank the S.R.C. for a studentship to D.H.C.

(*Received*, 20*th December* 1977; *Com.* 1293.)

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[1] D. E. Fenton, D. H. Cook, and I. W. Nowell, *J.C.S. Chem. Comm.*, 1977, 274.

[2] A. H. Norbury and A. I. P. Sinha, *Quart. Rev.*, 1970, 24, 69; the ranges quoted for $\nu_{C=N}$ are: 'free' NCS, 2100; S-bonded, 2120—2080, and N-bonded, 2080—2040 cm^{-1}.

Alkali and Alkaline-earth Metal Complexes of 4′-Acetobenzo-crown Ethers. Crystal and Molecular Structure of (18-Acetyl-2,3,5,6,8,9,11,12,-14,15-decahydro-1,4,7,10,13,16-benzohexaoxacyclo-octadecin)diperchloratostrontium

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Alkali and alkaline-earth metal complexes of 4′-acetobenzo-15-crown-5 and 4′-acetobenzo-18-crown-6 have been prepared and characterised by i.r. and n.m.r. spectroscopy. The crystal and molecular structure of 4′-acetobenzo-18-crown-6·Sr[ClO$_4$]$_2$ (the title complex) has been determined. No intermolecular interaction between the metal ion and the aceto-group has been observed. The reaction of several metal salts with 4′-(bromoaceto)benzo-15-crown-5 gives rise to internal nucleophilic displacement of the bromine by the anion to yield novel crown ethers.

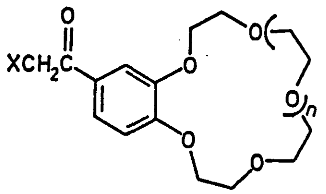
THE co-ordination chemistry of the alkali and alkaline-earth metal cations has been extensively studied [1] since the initial discovery [2] of the cyclic polyethers. The nature and stability of the complexes formed in the crystalline state and in solution has been shown to be dependent upon such factors as the size of the cation and polyether ring cavity, the nature of the anion of the solvent, and the type of substituent present on the polyether ring. Crown polyethers have been used to activate anions through complexation reactions with a metal salt. The co-ordination of the ligand to the metal cation generates the so called ' naked ' anions [3] with accompanying enhancement of nucleophilic reactivity, and a wide range of anions, *e.g.* Br$^-$, F$^-$, CN$^-$, O$_2^-$, and CH$_3$COO$^-$, has been used in substitution reactions.[4]

In this paper we report the complexing properties of aceto-substituted benzo-crown ethers towards alkali and alkaline-earth metal perchlorates and thiocyanates, together with the crystal structure of 4′-acetobenzo-18-crown-6·Sr[ClO$_4$]$_2$. We also show that alkali and alkaline-earth metal complexes of 4′-(bromoaceto)benzo-15-crown-5 can act as ' self-reagents ' by their ability to liberate reactive nucleophiles which will replace bromine and so generate bifunctional crown ethers of further synthetic value. The nomenclature used throughout this work for cyclic polyethers is based on that originally defined by Pedersen.[2]

EXPERIMENTAL

The polyethers, 4′-acetobenzo-15-crown-5 (L^1), 4′-acetobenzo-18-crown-6 (L^2), and 4′-(bromoaceto)benzo-15-crown-5 (L^3), were prepared according to literature procedures.[5,6] Calcium thiocyanate was used as a 78% solution in water (K and K Ltd.), and strontium thiocyanate was prepared by mixing aqueous solutions of strontium hydroxide and ammonium thiocyanate in stoicheiometric amounts and evaporating to dryness. The product was washed with ice-cold ethanol and dried over silica gel *in vacuo*.

Infrared spectra were recorded as KBr discs using a Perkin-Elmer 297 spectrometer. Hydrogen-1 n.m.r. spectra were obtained at 100 MHz (Varian HA100) or at 220 MHz (Perkin-Elmer R34). Carbon-13 n.m.r. spectra were recorded at 25.15 MHz (JEOL PFT-100 FT), with ^{1}H noise decoupled. Elemental analyses were carried out by the University of Sheffield Microanalytical Service.



L^1 $n = 1$, X = H
L^2 $n = 2$, X = H
L^3 $n = 1$, X = Br

Complexation Reactions of 4′-Acetobenzo-crown Ethers.—The following procedures were adopted to obtain crystalline complexes. The metal salt (0.001 mol) in hot ethanol (20 cm^3) was added to the crown ether (0.001 mol) in hot ethanol (20 cm^3) with stirring. In the reaction with Ba[ClO$_4$]$_2$ with L^2 a white precipitate formed immediately and was filtered off; in the other cases the mixture was filtered hot and left to cool whereupon the complex crystallised out. The crystals were collected, washed with diethyl ether to remove unreacted crown ether, and dried over silica gel *in vacuo*. If no complex crystallised out the solution was reduced in volume and ethyl acetate added to precipitate crystalline solids which were dried *in vacuo*. The analytical data are given in Table 1. **CAUTION:** It must be emphasised that, although we have experienced no problems of detonation, perchlorate complexes should be handled with care.

Reaction of 4′-(Bromoaceto)benzo-15-crown-5.—NaBr *and* KBr *Complexes.* Alkali-metal halide (0.001 mol) was added to a solution of 4′-(bromoaceto)benzo-15-crown-5 (0.001 mol) in ethanol (40 cm^3), and the mixture stirred for 18 h. After filtering, the ethanol was removed under reduced pressure and chloroform (20 cm^3) added to the residual oil. The solution was added dropwise to diethyl ether (100 cm^3) to give a precipitate which was collected. Yields: NaBr complex, 16%; KBr complex, 32% (Found: C, 35.9; H, 4.1; Br, 27.8. Calc. for C$_{16}$H$_{21}$Br$_2$NaO$_6$·2H$_2$O: C, 36.4; H, 4.8; Br, 30.3%. Found: C, 41.5; H, 4.4; Br, 25.6. Calc. for C$_{32}$H$_{42}$Br$_3$KO$_{12}$: C, 42.2; H, 4.7; Br, 26.7%).

Reaction with Ca[NCS]$_2$. Calcium thiocyanate (0.32 g, 78% solution) was added to a solution of 4′-(bromoaceto)benzo-15-crown-5 (0.62 g) in ethyl acetate (20 cm^3) to give a brown precipitate which was filtered off. Evaporation of

TABLE 1

Analytical data

	Found (%)					Calc. (%)				
	C	H	N	S	Cl	C	H	N	S	Cl
(*a*) Complexes of 4′-acetobenzo-15-crown-5 (L^1)										
$L^1 \cdot Li[NCS]$	53.7	6.1	4.2	9.9		54.4	5.9	3.7	8.8	
$L^1 \cdot Na[NCS]$	52.5	5.5	3.4	8.5		52.2	5.6	3.5	8.2	
$2L^1 \cdot K[NCS]$	55.3	6.1	1.9	4.6		55.2	6.2	1.5	4.5	
$L^1 \cdot Mg[NCS]_2$	48.1	5.3	6.2	14.4		47.9	4.4	6.2	14.2	
$L^1 \cdot Ca[NCS]_2$	46.5	4.6	5.7	13.6		46.3	4.7	6.0	13.7	
$L^1 \cdot Sr[NCS]_2$	42.2	4.3	5.3	8.9 *		42.1	4.3	5.8	12.5	
$L^1 \cdot Ba[NCS]_2$	38.0	4.2	4.8	9.9 *		38.3	3.9	4.9	11.4	
$L^1 \cdot [NH_4][NCS]$	52.5	6.8	7.1	8.6		52.8	6.8	7.2	8.3	
$L^1 \cdot Li[ClO_4]$	46.4	5.3			8.5	46.1	5.3			8.5
$L^1 \cdot Na[ClO_4]$	44.6	5.2			8.0	44.4	5.1			8.1
$2L^1 \cdot K[ClO_4]$	50.6	5.7			4.7	50.6	5.8			4.7
$L^1 \cdot Mg[ClO_4]_2 \cdot 2H_2O$	33.7	4.6			12.7	33.7	4.6			12.4
$L^1 \cdot Ca[ClO_4]_2$	34.8	4.3			13.0	34.9	4.0			12.9
$2L^1 \cdot Sr[ClO_4]_2$	41.6	5.1			7.8	41.9	4.8			7.7
$2L^1 \cdot Ba[ClO_4]_2$	40.3	4.3			7.4	40.2	4.6			7.4
(*b*) Complexes of 4′-acetobenzo-18-crown-6 (L^2)										
$L^2 \cdot Li[NCS] \cdot H_2O$	51.9	6.6	3.1	7.6		52.2	6.5	3.2	7.3	
$L^2 \cdot Na[NCS] \cdot H_2O$	50.2	6.0	3.1	7.5		50.3	6.2	3.1	7.1	
$L^2 \cdot K[NCS]$	50.8	5.7	3.1	7.6		50.5	5.8	3.1	7.1	
$L^2 \cdot Mg[NCS]_2 \cdot H_2O$	46.7	5.8	5.6	12.0		46.8	5.5	5.5	12.5	
$L^2 \cdot Ca[NCS]_2$	47.3	5.0	5.2	12.3		47.0	5.1	5.4	12.6	
$L^2 \cdot Ba[NCS]_2$	39.3	4.4	4.5	8.1 *		39.5	4.3	4.6	10.6	
$L^2 \cdot Li[ClO_4] \cdot H_2O$	45.0	6.3			6.7	45.2	5.9			7.4
$L^2 \cdot Na[ClO_4]$	45.1	5.4			6.3	45.3	5.5			7.4
$L^2 \cdot K[ClO_4]$	43.7	5.2			7.5	43.9	5.3			7.2
$L^2 \cdot Mg[ClO_4]_2 \cdot 4H_2O$	33.2	5.2			10.5	33.3	5.3			10.9
$L^2 \cdot Ca[ClO_4]_2$	36.5	4.4			11.7	36.4	4.4			11.9
$L^2 \cdot Sr[ClO_4]_2$	33.9	4.2			11.1	33.7	4.1			11.1
$L^2 \cdot Ba[ClO_4]_2$	31.2	3.5			10.5	31.3	3.8			10.3

* S values are low due to interference of insoluble sulphates.

the filtrate gave an off-white solid. The solid materials were combined, dissolved in distilled water (20 cm^3), and extracted with chloroform. After drying over Mg[SO$_4$], the chloroform was removed under reduced pressure to give a pale yellow solid. Crystallisation from n-heptane gave 0.30 g (51%) of 4′-(thiocyanatoaceto)benzo-15-crown-5 as a pale yellow solid (m.p. 109—110 °C) (Found: C, 55.8; H, 5.6; N, 3.7; S, 8.9%; $M^{\cdot +}$ 367. Calc. for $C_{17}H_{21}NO_6S$: C, 55.6; H, 5.8; N, 3.8; S, 8.7%; *M* 367). I.r.: 2 170 cm^{-1} (SCN stretch), 1 680 cm^{-1} (CO stretch).

Reaction of potassium thiocyanate with 4′-(bromoaceto)benzo-15-crown-5 in aqueous ethyl acetate gave an 85% yield of 4′-(thiocyanatoaceto)benzo-15-crown-5.

Reaction with potassium phthalimide. Potassium phthalimide (0.15 g) was added to a solution of 4′-(bromoaceto)benzo-15-crown-5 (0.3 g) in ethyl methyl ketone (20 cm^3). After 24 h stirring, the mixture was filtered and the filtrate evaporated to give a yellow oil. Extraction with ethyl acetate followed by solvent evaporation gave yellow crystals of 4′-(phthalimidoaceto)benzo-15-crown-5 (0.21 g, 58%), m.p. 144—146 °C (Found: C, 63.4; H, 5.7; N, 3.0%; $M^{\cdot +}$ 455. Calc. for $C_{24}H_{25}NO_8$: C, 63.3; H, 5.5; N, 3.1%; *M* 455. I.r.: 1 760, 1 710, and 1 670 cm^{-1} (C=O stretches).

Reaction with potassium kojate (5-hydroxy-2-hydroxymethyl-4H-pyran-4-onate). Potassium hydroxide (0.15 g) in distilled water (2 cm^3) was added to a solution of kojic acid (0.37 g) in warm ethanol (20 cm^3) followed by 4′-(bromoaceto)benzo-15-crown-5 (1.0 g) in warm ethanol (10 cm^3). After refluxing for 4 h the mixture was cooled to give a yellow precipitate. Recrystallisation from ethanol gave off-white microcrystals of 2(phenacyl-15-crown-5 koiate)·KBr·2H$_2$O (1.0 g, 87%), m.p. 156—158 °C (Found: C, 47.9; H, 5.2; Br, 7.1%; $M^{\cdot +}$ 450. Calc. for $C_{44}H_{52}BrKO_{20} \cdot 2H_2O$: C, 48.4; H, 5.4; Br, 7.3%; *M*(*P* — KBr·2H$_2$O) 450). I.r.: 1 680, 1 640, 1 615, and 1 600 cm^{-1} (C=C, C=O stretches).

Crystal Data.—$C_{18}H_{26}Cl_2O_{15}Sr$, $M_r = 640.91$, Triclinic, space group $P\bar{1}$, $a = 17.174(15)$, $b = 9.036(9)$, $c = 19.959(16)$ Å, $\alpha = 87.42(5)$, $\beta = 124.82(7)$, $\gamma = 96.07(5)°$, $U = 2\,528.19$ Å^3, Mo-K_α, $\lambda = 0.710\,69$ Å, $D_m = 1.77$, $Z = 4$, $D_c = 1.75$ Mg m^{-3}, μ(Mo-K_α) = 2.34 mm^{-1}, $F(000) = 1\,304$.

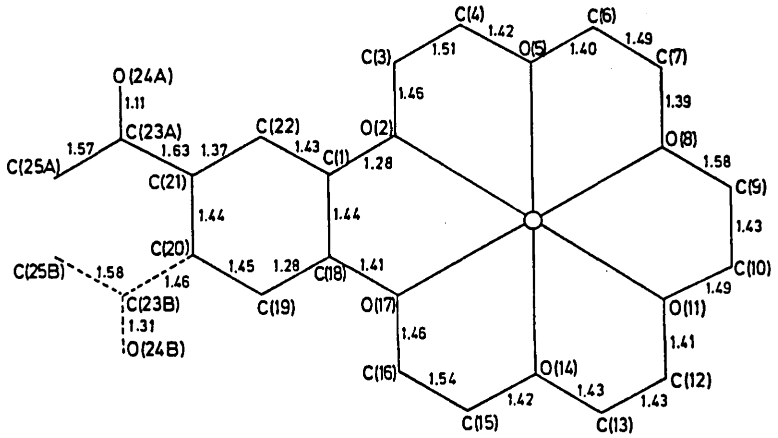
X-*Ray Intensity Measurements.*—Crystal quality was poor and great difficulty was found in selecting a crystal suitable for data collection. Eventually a crystal of approximate dimensions 0.16 × 0.22 × 0.31 mm was mounted with the *a* axis coincident with the ω axis of a Stöe Stadi 2 two-circle diffractometer. Data were collected using monochromated Mo-K_α radiation and the background-ω scan-background technique. Corrections for Lorentz and polarisation effects were applied but no corrections for absorption were made. 2 054 Observed reflections having $I \geqslant 3\sigma(I)$ were used in the subsequent structure analysis.

Structure Determination and Refinement.—Interpretation of a three-dimensional Patterson map on the basis of two independent molecules in the asymmetric unit (*i.e.* space group $P\bar{1}$) readily afforded the positions of the two independent strontium atoms. The perchlorate groups and the non-hydrogen atoms of the macrocyclic ligands were located from successive electron-density maps. High correlation was observed between the refined parameters of the two independent molecules which appeared to be related by a translation of $a/2$. However, the failure to find a higher-symmetry space group and the observation of small yet significant differences in the conformations of the molecules to continuation of the refinement in $P\bar{1}$. Within each e macrocyclic ligands, two sets of positions were found he acetyl group [being attached to C(20) or C(21)] and ement of a disordered model with 50% occupancy for acetyl group gave satisfactory thermal parameters. ever, geometry calculations showed unrealistically intermolecular contacts between acetyl oxygen atoms 1.5 Å) and refinement was attempted in $P1$. The extent of correlations between all four of the independent molecules was such as to prevent a more satisfactory refinement. In view of the extreme length of computations in $P1$ and the apparent correctness of the centrosymmetric space group for all but the acetyl groups, the final stages of refinement were conducted in $P\bar{1}$ with the acetyl groups being statistically disordered. Scattering factors were calculated using an analytical approxim-

TABLE 2

Final fractional co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses

	Molecule I			Molecule II		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Sr	7 156(2)	7 992(4)	7 115(2)	2 016(2)	7 889(4)	6 838(2)
C(1)	9 501(20)	9 249(32)	8 801(16)	4 167(17)	9 262(29)	8 634(13)
O(2)	9 025(13)	8 032(26)	8 427(12)	3 801(12)	7 978(22)	8 275(10)
C(3)	9 579(19)	6 815(32)	8 402(16)	4 405(18)	7 008(30)	8 333(16)
C(4)	8 916(19)	5 525(33)	7 938(17)	3 796(21)	5 562(33)	7 833(19)
O(5)	8 204(16)	6 005(29)	7 131(14)	3 158(14)	5 934(26)	7 018(13)
C(6)	7 811(19)	4 972(32)	6 519(16)	2 875(17)	4 853(29)	6 384(15)
C(7)	7 141(18)	5 671(31)	5 762(16)	2 301(23)	5 756(35)	5 612(20)
O(8)	6 473(13)	6 320(24)	5 813(11)	1 553(14)	6 314(26)	5 562(12)
C(9)	5 689(20)	7 181(32)	5 007(17)	888(20)	7 188(32)	4 787(17)
C(10)	4 965(19)	7 529(32)	5 125(16)	32(20)	7 182(32)	4 728(16)
O(11)	5 458(13)	8 675(25)	5 819(11)	322(14)	7 924(26)	5 480(12)
C(12)	4 830(18)	9 131(32)	5 987(16)	−464(18)	8 328(32)	5 457(17)
C(13)	5 401(18)	10 020(31)	6 737(15)	−232(20)	8 667(33)	6 240(19)
O(14)	6 099(12)	9 316(24)	7 421(11)	728(13)	9 417(26)	6 784(12)
C(15)	6 517(19)	10 019(32)	8 190(16)	1 000(19)	9 611(32)	7 601(17)
C(16)	7 391(19)	10 869(32)	8 446(16)	1 980(21)	10 773(33)	7 997(18)
O(17)	8 038(13)	9 812(25)	8 500(11)	2 652(12)	9 827(23)	8 091(11)
C(18)	8 984(19)	10 501(32)	8 817(16)	3 613(18)	10 322(30)	8 555(15)
C(19)	9 359(20)	11 729(33)	9 141(17)	3 929(19)	11 708(32)	8 865(16)
C(20)	10 322(20)	12 166(33)	9 440(17)	4 959(20)	12 195(32)	9 334(17)
C(21)	10 843(19)	11 139(32)	9 401(16)	5 490(18)	10 912(31)	9 411(16)
C(22)	10 444(19)	9 645(32)	9 101(16)	5 219(21)	9 550(33)	9 120(17)
C(23A)	11 898(29)	11 556(39)	9 807(25)	6 730(29)	11 275(38)	9 984(25)
C(23B)	10 803(29)	13 666(39)	9 882(26)	5 445(29)	13 516(39)	9 768(25)
O(24A)	12 258(23)	10 570(36)	9 896(20)	7 137(24)	10 311(36)	10 061(21)
O(24B)	10 283(23)	14 434(36)	9 994(21)	4 890(25)	14 413(36)	9 766(21)
C(25A)	12 302(30)	13 318(39)	10 077(27)	6 927(29)	12 893(38)	10 183(26)
C(25B)	11 770(29)	14 244(39)	9 985(26)	6 541(30)	13 900(39)	10 167(27)
Cl(1)	7 928(5)	10 861(12)	6 476(5)	2 986(5)	10 793(13)	6 375(5)
Cl(2)	6 115(7)	5 023(15)	7 587(6)	1 134(6)	5 071(13)	7 527(6)
O(31)	7 928(15)	9 371(27)	6 374(12)	3 200(15)	9 325(27)	6 473(13)
O(32)	7 344(15)	11 542(27)	5 673(12)	2 739(16)	11 285(28)	5 628(13)
O(33)	7 478(13)	11 058(26)	6 895(12)	2 202(14)	10 812(26)	6 435(12)
O(34)	8 838(15)	11 638(28)	6 953(13)	3 818(15)	11 587(27)	7 019(13)
O(41)	7 014(15)	5 988(27)	7 987(13)	1 662(20)	6 618(32)	7 861(17)
O(42)	5 810(15)	5 186(28)	8 088(13)	136(18)	5 094(31)	7 173(17)
O(43)	6 111(17)	3 799(30)	7 237(15)	1 576(22)	3 949(33)	8 064(19)
O(44)	5 448(18)	5 643(30)	6 829(15)	1 123(21)	5 147(33)	6 847(18)



E 1 Average bond distances (Å) for the two independent macrocyclic ligands in $L^2 \cdot Sr[ClO_4]_2$. Estimated standard deviations *ca.* 0.04 Å

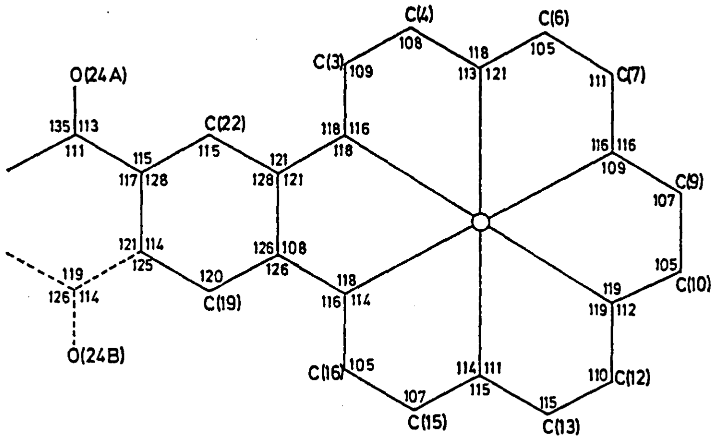


FIGURE 2 Average bond angles (°) for the two independent macrocyclic ligands in $L^2 \cdot Sr[ClO_4]_2$. Numbering of atoms is as in Figure 1. Estimated standard deviations *ca.* 2°

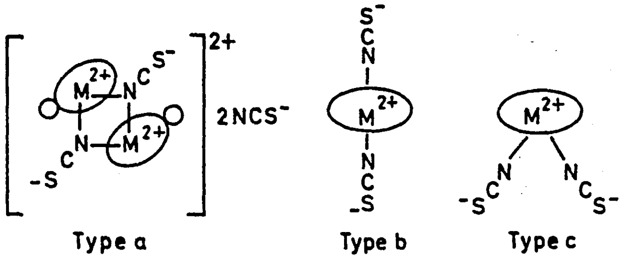
ation[7] and the weighting scheme adopted was $w = 4.1767/[\sigma^2(F_o) + 0.0034(F_o)^2]$. Full-matrix refinement with anisotropic thermal parameters applied to all atoms gave the final $R = 0.103$ and $R' = 0.103$. Final atomic parameters are listed in Table 2; average bond distances and angles for the two independent macrocyclic ligands are given in Figures 1 and 2. Observed and calculated structure factors and thermal parameters have been deposited as Supplementary Publication No. SUP 23174 (13 pp.).*

Structure Calculations.—All calculations, apart from preliminary data processing, were carried out on an IBM 370/165 computer using the SHELX computing package.[8]

RESULTS AND DISCUSSION

In general the stoicheiometries for the alkali and alkaline-earth metal complexes of L^1 and L^2 follow the trends reviewed in the literature.[1] 1 : 1 Complexes are formed between L^2 and all of the cations used, and it is probable that the ligand circumscribes the metal for the smaller cations, and is disposed to one side of the metal as the cation size increases as has been observed for the corresponding complexes of 18-crown-6 and dibenzo-18-crown-6.[9] The complexes of the smaller cations, Li^+ ($r = 0.60$ Å), Na^+ (0.95 Å), and Mg^{2+} (0.65 Å), show retention of water molecules whereas the remaining complexes are dehydrated.

Compound L^1 gives two classes of compounds; 1 : 1 species with Li^+, Na^+, Mg^{2+}, and Ca^{2+} as the cation, and with the thiocyanates of Sr^{2+} and Ba^{2+}, and 2 : 1 complexes with K^+ as the cation, and with the perchlorates of Sr^{2+} and Ba^{2+}. Ionic size and ring-cavity compatibility are of importance in determining the nature of complexes formed with polyethers. With benzo-15-crown-5 it was shown that Mg^{2+} forms only a 1 : 1 complex, whereas only 2 : 1 complexes are isolated for K^+ (1.33 Å), Sr^{2+} (1.13 Å), and Ba^{2+} (1.35 Å). The cations Na^+ and Ca^{2+} were shown to be able to form either 1 : 1 or 2 : 1 complexes.[2,10,11] Calcium forms 1 : 1 complexes when a co-ordinating anion such as thiocyanate is used but a 2 : 1 complex with tetraphenylborate present. Perchlorate complexes of Ca^{2+} have been prepared but not well characterised. These appear to be 2 : 1 with some degree of hydration.[10] The Na^+ ion generally forms 1 : 1 complexes, but from concentrated solution a 2 : 1 perchlorate complex has been recovered.[11] The 1 : 1 complexes formed between L^1 and the thiocyanates of Sr^{2+} and Ba^{2+} would appear to have anomalous stoicheiometry. However, by analogy with the caesium (1.69 Å) complexes of 18-crown-6[12] and tetramethyldibenzo-18-crown-6[13] it is possible to postulate that a dimeric species is formed in which the cation sits to one side of the heteroatom ring and two such units are bridged by thiocyanate anions (type a). The i.r. spectrum (see later) does not differentiate between a tetrabridged species, or a dibridged species with two free anions. No crystals suitable for *X*-ray analysis could be grown for these compounds.



Infrared Spectra.—Relevant i.r. stretching and bending modes for the aceto-group and the thiocyanate and perchlorate anions are listed in Table 3. The CN and CS stretching frequencies have been used to diagnose the mode of thiocyanate bonding[14] in metal complexes, as have the asymmetric Cl–O stretching and bonding frequencies.[15] In the complexes of L^1 and L^2, ligand absorptions obscure the CS stretch and Cl–O stretch; it is however possible to detect the CN stretch and Cl–O bonding frequency.

Much of the evidence for assignment of the bonding modes for thiocyanates has been obtained from transi-

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

n-metal complexes,[14] *e.g.* CN stretch: *N*-bonded, 40—2 080 cm^{-1}; *S*-bonded, 2 080—2 120 cm^{-1}; and ic NCS$^-$, *ca.* 2 100 cm^{-1}. It has been shown that a ple translation of these assignments to alkaline-earth tal and main-group species can present problems of ambiguous assignment as there is no longer a clear elation between wavenumber and bonding mode.[16] vertheless, certain features emerge from the i.r.

TABLE 3

Infrared spectra (cm^{-1})

Metal salt	C=O stretch	CN stretch	Cl–O asym. bend
a) Complexes of 4′-acetobenzo-15-crown-5			
complexed	1 660		
CS]	1 670	2 080	
[NCS]	1 670	2 060	
CS]	1 675	2 055	
[NCS]$_2$	1 680	2 080	
CS]$_2$	1 675	2 100, 2 070	
NCS]$_2$	1 670	2 090, 2 060	
[NCS]$_2$	1 660	2 090, 2 050	
ClO$_4$]	1 675		625
[ClO$_4$]	1 675		625
lO$_4$]	1 680		625
[ClO$_4$]$_2$·2H$_2$O	1 670		625
ClO$_4$]$_2$	1 670		630
ClO$_4$]$_2$	1 670		625
[ClO$_4$]$_2$	1 675		625
b) Complexes of 4′-acetobenzo-18-crown-6			
complexed	1 660		
NCS]·H$_2$O	1 665	2 075	
[NCS]·H$_2$O	1 675	2 100	
CS]	1 680	2 060	
[NCS]$_2$·H$_2$O	1 670	2 095, 2 090	
CS]$_2$	1 665	2 050	
CS]$_2$	1 665	2 050	
ICS]$_2$	1 670	2 080, 2 065	
lO$_4$]·H$_2$O	1 665		625
ClO$_4$]	1 665		620
lO$_4$]	1 670		620
[ClO$_4$]$_2$·4H$_2$O	1 665		630
ClO$_4$]$_2$	1 665		625
lO$_4$]$_2$	1 665		625
ClO$_4$]$_2$	1 665		630

tra. The alkali-metal complexes of L^1 and L^2 show ingle CN band at wavenumber varying between 2 055 2 100 cm^{-1}; L^1·Mg[NCS]$_2$ has a single band at 2 080 $^{-1}$. As these compounds are expected to be 'ionic' *N*-bonded by analogy with known structures,[9] *e.g.* zo-15-crown-5·Mg[NCS]$_2$ has structure type b,[17] the blem of assignment within the literature range is ıediately apparent. The remaining alkaline-earth tal complexes show two bands in their complexes h L^1. The crystal structure of benzo-15-crown-5· NCS]$_2$·ROH is of structure type c;[17] the i.r. spec- m shows two bands at 2 080 and 2 100 cm^{-1} attri- able to an asymmetry in the co-ordination geometry. ıcture type c is therefore proposed, by analogy, for Ca[NCS]$_2$. As has been noted earlier, the i.r. evidence ot incompatible with the proposal of structure type a L^1·Sr[NCS]$_2$ and L^1·Ba[NCS]$_2$ as two bands are erned for the CN stretch. The alkaline-earth metal cyanate complexes with the larger macrocycle, show single bands for the CN stretch, with the eption of Ba^{2+}, and so are designated as structure type b. The complex L^1·Ba[NCS]$_2$ has two bands and so is proposed as having structure type c.

The perchlorate complexes show a strong sharp band at *ca.* 625 cm^{-1} in all of the complexes and this is indicative of 'ionic' perchlorate. Certainly in the 2 : 1 complexes this assignment is substantiated as the anion would be separated from the metal. It is conceivable that some unidentation could occur, but that any splitting of the band would be masked by the proximal ligand bands. In order to solve this problem, and to determine the potential involvement of the aceto-side chain in complex formation, the *X*-ray crystal structure of L^2·Sr[ClO$_4$]$_2$ was determined.

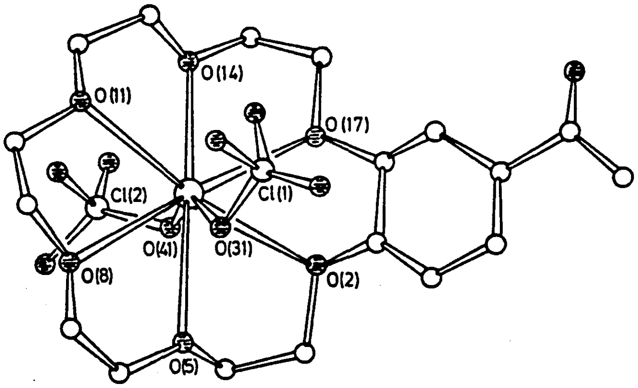


FIGURE 3 Molecule I of L^2·Sr[ClO$_4$]$_2$

The Structure of L^2·Sr[ClO$_4$]$_2$.—While the combination of poor crystal quality and crystallographic difficulties preclude a detailed discussion of the structure, the following features may nevertheless be noted. The overall arrangement about the strontium ion is the same in each independent molecule, with the metal ion interacting with both perchlorate groups and with all six macrocyclic oxygen atoms (Figures 3 and 4). The resulting eight-co-ordination may be contrasted with the nine-co-ordination found in the complex benzo-18-crown-6·Sr[ClO$_4$]$_2$·3H$_2$O.[18] In this species the perchlorates are not co-ordinated to the metal which is surrounded by the six ether oxygen atoms and three oxygens from the water molecules. There is no evidence that the acetyl group is involved in bonding to a neighbouring

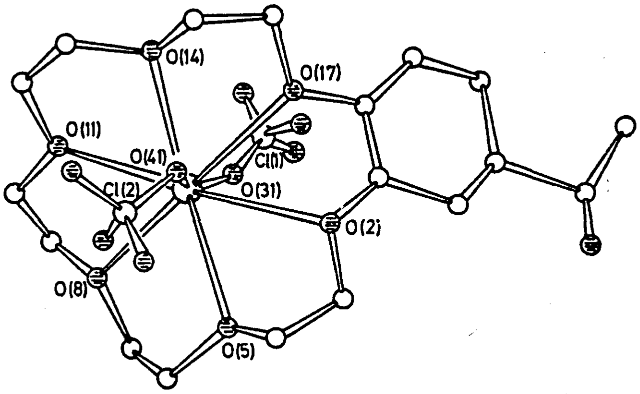


FIGURE 4 Molecule II of L^2·Sr[ClO$_4$]$_2$

TABLE 4

Complex	Range of M–O (macrocycle) distances/Å	Mean M–O (macrocycle) distance/Å	Distance of M from weighted mean plane through six macrocyclic oxygen atoms/Å	Sum of van der Waals radius of oxygen and ionic radius of M/Å [a]	Ref.
4′-Acetobenzo-18-crown-6·$Sr[ClO_4]_2$	2.624—2.782 Molecule I	2.688	0.01	Sr^{2+}, O 2.65	This work
	2.611—2.749 Molecule II	2.671	0.01		
4′-Nitrobenzo-18-crown-6·Rb[NCS]	2.964—3.082	3.008	1.17	Rb^+, O 3.00	19
18-Crown-6·Rb[NCS]	2.929—3.146	3.024	1.19	Rb^+, O 3.00	*b*, *c*
4′-Nitrobenzo-18-crown-6·Cs[NCS]	3.040—3.248	3.146	1.46	Cs^+, O 3.18	20
18-Crown-6·Cs[NCS]	3.035—3.274	3.146	1.44	Cs^+, O 3.18	12, *c*

[a] Van der Waals radius of oxygen taken as 1.40 Å (L. Pauling, ' The Nature of the Chemical Bond,' 2nd edn., Cornell University Press, Ithaca, 1960). Ionic radii taken from ref. 22. [b] M. Dobler and R. P. Phizackerley, *Acta Crystallogr., Sect. B*, 1974, **30**, 2746. [c] J. D. Dunitz, M. Dobler, P. Seiler, and R. P. Phizackerley, *Acta Crystallogr., Sect. B*, 1974, **30**, 2733.

TABLE 5

Selected bond distances and angles for L^2·$Sr[ClO_4]_2$

	Molecule I	Molecule II
(*a*) Strontium ion environment		
(*i*) Distances (Å)		
Sr–O(2)	2.75(2)	2.75(1)
Sr–O(5)	2.66(3)	2.64(3)
Sr–O(8)	2.63(2)	2.63(2)
Sr–O(11)	2.68(2)	2.61(2)
Sr–O(14)	2.62(3)	2.68(3)
Sr–O(17)	2.78(2)	2.72(2)
Sr–O(31)	2.69(3)	2.72(3)
Sr–O(41)	2.55(3)	2.63(4)
(*ii*) Angles		
O(2)–Sr–O(5)	61.9(7)	62.1(6)
O(5)–Sr–O(8)	60.1(6)	60.9(6)
O(8)–Sr–O(11)	66.0(7)	59.9(8)
O(11)–Sr–O(14)	63.4(7)	60.6(7)
O(14)–Sr–O(17)	60.8(6)	62.6(6)
O(31)–Sr–O(2)	83.2(7)	75.1(6)
O(31)–Sr–O(5)	76.0(9)	79.2(8)
O(31)–Sr–O(8)	76.0(7)	73.6(8)
O(31)–Sr–O(11)	87.3(7)	104.1(7)
O(31)–Sr–O(14)	122.5(7)	118.4(8)
O(31)–Sr–O(17)	99.5(7)	91.7(7)
O(41)–Sr–O(2)	79.4(7)	77.6(7)
O(41)–Sr–O(5)	79.4(9)	117.8(8)
O(41)–Sr–O(8)	97.5(7)	95.3(10)
O(41)–Sr–O(11)	112.9(7)	103.1(8)
O(41)–Sr–O(14)	81.8(8)	73.2(9)
O(41)–Sr–O(17)	85.3(7)	71.2(8)
O(41)–Sr–O(31)	154.5(8)	152.6(6)
(*b*) Perchlorate groups		
(*i*) Distances (Å)		
Cl(1)–O(31)	1.37(3)	1.39(3)
Cl(1)–O(32)	1.47(2)	1.36(3)
Cl(1)–O(33)	1.45(3)	1.42(3)
Cl(1)–O(34)	1.40(2)	1.41(2)
Cl(2)–O(41)	1.47(2)	1.53(3)
Cl(2)–O(42)	1.39(4)	1.44(3)
Cl(2)–O(43)	1.33(3)	1.37(3)
Cl(2)–O(44)	1.41(3)	1.34(4)
(*ii*) Angles (°)		
O(31)–Cl(1)–O(32)	110(1)	110(2)
O(31)–Cl(1)–O(33)	109(2)	107(2)
O(31)–Cl(1)–O(34)	115(2)	105(1)
O(32)–Cl(1)–O(33)	106(2)	110(2)
O(32)–Cl(1)–O(34)	111(2)	112(2)
O(33)–Cl(1)–O(34)	106(2)	113(2)
O(41)–Cl(2)–O(42)	103(2)	111(2)
O(41)–Cl(2)–O(43)	114(2)	113(2)
O(41)–Cl(2)–O(44)	109(2)	96(2)
O(42)–Cl(2)–O(43)	130(2)	116(2)
O(42)–Cl(2)–O(44)	107(2)	100(2)
O(43)–Cl(2)–O(44)	93(2)	119(3)

metal ion. This is in contrast to the rubidium and caesium thiocyanate complexes of 4′-nitrobenzo-18-crown-6, where intermolecular alkali-metal–nitro-oxygen interactions are observed.[19,20] The estimated radius of the macrocyclic cavity for 18-crown-6 (1.3—1.6 Å)[21] is such that the strontium ion (ionic radius 1.25 Å)[22] would be expected to fit readily into the cavity of L^2. This would appear to be the case, for in both independent molecules the metal ion is found to be essentially coplanar with the weighted mean plane through the six macrocyclic oxygen atoms. This may be contrasted with related rubidium and caesium complexes where the metal ions lie out of the macrocyclic cavity, the extent of displacement reflecting the size of the metal ion (Table 4). The Sr–O (macrocycle) distances vary from 2.611(16) to 2.782(21) Å (Table 5), with the Sr–O(2),O(17) values being substantially greater than the remaining values. The mean Sr–O (macrocycle) distance of 2.679 Å lies close to the sum of the van der Waals radius of oxygen and the ionic radius of strontium (2.65 Å), and fits into the pattern of mean values given in Table 4. While the conformations of the major portion of the macrocycle are similar in the two independent molecules, there are differences in the O(14) portion of the ring and the torsion angles about C(12)–C(13), O(14)–C(15) are strikingly different (Table 6).

TABLE 6

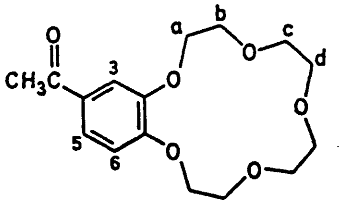
Torsion angles (°) in the macrocyclic rings. Estimated standard deviations are ≈2.5°

	Molecule I	Molecule II
C(18)–C(1)–O(2)–C(3)	178	175
C(1)–O(2)–C(3)–C(4)	−179	−178
O(2)–C(3)–C(4)–O(5)	58	61
C(3)–C(4)–C(5)–C(6)	151	149
C(4)–O(5)–C(6)–C(7)	−178	−173
O(5)–C(6)–C(7)–O(8)	−55	−58
C(6)–C(7)–O(8)–C(9)	179	−177
C(7)–O(8)–C(9)–C(10)	170	160
O(8)–C(9)–C(10)–O(11)	67	60
C(9)–C(10)–O(11)–C(12)	179	167
C(10)–O(11)–C(12)–C(13)	171	164
O(11)–C(12)–C(13)–O(14)	−59	36
C(12)–C(13)–O(14)–C(15)	−166	−174
C(13)–O(14)–C(15)–C(16)	−97	−168
O(14)–C(15)–C(16)–O(17)	−60	−74
C(15)–C(16)–O(17)–C(18)	−175	−167
C(16)–O(17)–C(18)–C(1)	−179	176
O(17)–C(18)–C(1)–O(2)	11	−3

.M.R. *Spectra.*—The ^{1}H n.m.r. spectra of the comxes were recorded in [^{2}H$_6$]acetone thus allowing parison with studies on non-substituted crown ers.[23] The unsymmetrical nature of the acetozo-crown ethers has made exact assignments of the protons complicated, but tentative assignments are en in Table 7. It has been noted that the shifts are 'lar for both acetobenzo- and benzo-crown ethers 'cating that the conformations in solution are similar. 'ay studies have shown that in the solid state benzown ethers and their complexes can have similar formations, and that small changes can occur on plexation.[24-26] In general all the resonances in the .r. spectra are shifted to lower field on complexn; the exceptions are the potassium complexes of where several upfield shifts are detected. These can attributed to 2 : 1 complex formation by analogy with the work of Lockhart *et al.*[27] in which the direction of the shift has been empirically related to the stoicheiometry of the complex formed. A 1 : 1 complex gives a downfield shift and a 2 : 1 complex gives an upfield shift, relative to the free ligand.

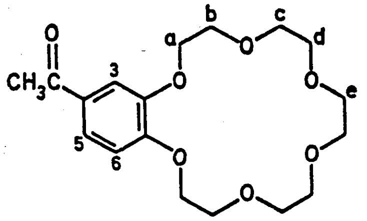
TABLE 7

Proton n.m.r. spectra (in [^{2}H$_6$]acetone)



) Complexes of 4′-acetobenzo-15-crown-5

Metal salt	Chemical Shift (τ) H^5	H^3	H^6	aa′	bb′	cc′, dd′
ncomplexed	2.40	2.51	3.02	5.85	6.15	6.33
i[NCS]	2.31	2.43	2.88	5.71	6.04	6.25
i[ClO$_4$]	2.26	2.38	2.79	5.61	5.98	6.18
a[NCS]	2.26	2.34	2.77	5.60	5.96	6.18
a[ClO$_4$]	2.26	2.35	2.78	5.61	5.99	6.18
[NCS]	2.38	2.80	3.12	5.98	6.27	6.18
[ClO$_4$]	2.36	2.76	3.12	5.95	6.26	6.16
g[NCS]$_2$	2.18	2.29	2.68	5.40	5.74	5.99
g[ClO$_4$]$_2$	2.15	2.25	2.60	5.30	5.68	5.86
a[ClO$_4$]$_2$	2.19	2.20	2.63	5.40	5.80	5.92
a[ClO$_4$]$_2$	2.25	2.42	2.78	5.50	5.91	5.91



) Complexes of 4′-acetobenzo-18-crown-6

	H^5	H^3	H^6	aa′	bb′	c—e
ncomplexed	2.38	2.49	2.99	5.80	6.12	6.30—6.42
i[NCS]	2.35	2.46	2.93	5.74	6.07	6.28—6.36
i[ClO$_4$]	2.35	2.49	2.91	5.72	6.07	6.30—6.34
a[NCS]	2.32	2.48	2.88	5.69	6.01	6.25—6.34
a[ClO$_4$]	2.32	2.48	2.88	5.70	6.05	6.30—6.32
[NCS]	2.31	2.42	2.83	5.61	6.00	6.22—6.29
ClO$_4$]	2.31	2.42	2.83	5.62	6.02	6.24—6.31
g[ClO$_4$]$_2$	2.36	2.48	2.94	5.71	6.05	6.26—6.30
a[ClO$_4$]$_2$	2.24	2.37	2.76	5.48	5.88	6.09—6.13
r[ClO$_4$]$_2$	2.24	2.34	2.74	5.48	5.85	6.02—6.10
[ClO$_4$]$_2$	2.24	2.34	2.72	5.46	5.85	6.04—6.08

Comparison of the spectra for 1 : 1 thiocyanate and perchlorate complexes of L^1 and L^2 show that δ is relatively independent of the anion; this suggests that ion pairing is not important in [^{2}H$_6$]acetone. For sodium complexes of dibenzo-18-crown-6 a significant difference in shift was detected for similar complexes and attributed to ion pairing.[23] A less pronounced effect was noted for sodium complexes of benzo-18-crown-6 and it was suggested that extra flexibility in the benzo-18-crown-6 was responsible for the effect.[23]

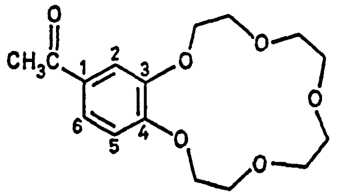
The low solubility of the complexes made it difficult to obtain ^{13}C n.m.r. spectra. The results for complexes of L^1 are shown in Table 8, and indicate small changes in chemical shift which may be related to changes in conformation on complexation. The asymmetry of the crown has led to an assignment problem for the carbons in the heteroatom ring, and so only the values of the shifts are given. Carbon-13 n.m.r. spectroscopy has also been used to observe the thiocyanate anion and to determine its mode of bonding.[28] *S*-Bonded species lie in the range 112—118 p.p.m., *N*-bonded in the range 134—141 p.p.m., and ionic thiocyanates in the range 133—134 p.p.m. The resonance for L^1·Na[NCS] is at 132.7 p.p.m., and for 2L^1·K[NCS] is *ca.* 131.5 p.p.m. where it is somewhat masked by the aromatic resonances. These values lie closest to the range for ionic species further indicating the absence of ion pairing.

Reactions of 4′-(*Bromoaceto*)*benzo*-15-*crown*-5, L^3.—Monobromination of L^1 by bromine in chloroform yields L^3.[5] Compound L^3 readily forms a 1 : 1 monohydrated complex with NaBr, and a 2 : 1 sandwich complex with KBr. However, when the complexation reaction was attempted with Ca[SCN]$_2$ in ethyl acetate the product recovered analysed as L^3·Ca[SCN]$_2$ but showed i.r. peaks at 2 170, 2 100, and 2 070 cm^{-1} indicating that as well as metal co-ordination an internal nucleophilic displacement has occurred to give 4′-(thiocyanatoaceto)benzo-15-crown-5 (L^4), as its complex, L^4·Ca[SCN]Br. Treatment of the complex with water, followed by chloroform extraction, yielded pure L^4, with a single peak at 2 170 cm^{-1} attributable to *S*-bonded thiocyanate. Compound L^4 is also prepared by reaction of aqueous K[NCS] with L^3 in ethyl acetate.

The reaction, which proceeds in good yield, is believed to proceed *via* initial complexation of the metal thiocyanate to release the activated nucleophile, followed by the substitution reaction at the side chain. Compound L^4 has been characterised by i.r. and mass spectroscopy, in which a parent peak is seen at $M^{\cdot +}$ 367, followed by a characteristic polyether breakdown pattern.[29] The ^{13}C-{^{1}H} n.m.r. spectrum shows a peak at 112.1 p.p.m. assignable to the SCN carbon atom (C$_2$H$_5$SCN, 112.1 p.p.m.).[28] Compound L^4 can act as an intermediate in the preparation of bifunctional polyethers.[30] For

TABLE 8

^{13}C-{^1H} n.m.r. spectra of 4′-acetobenzo-15-crown-5 complexes in [$^2H_6$]acetone

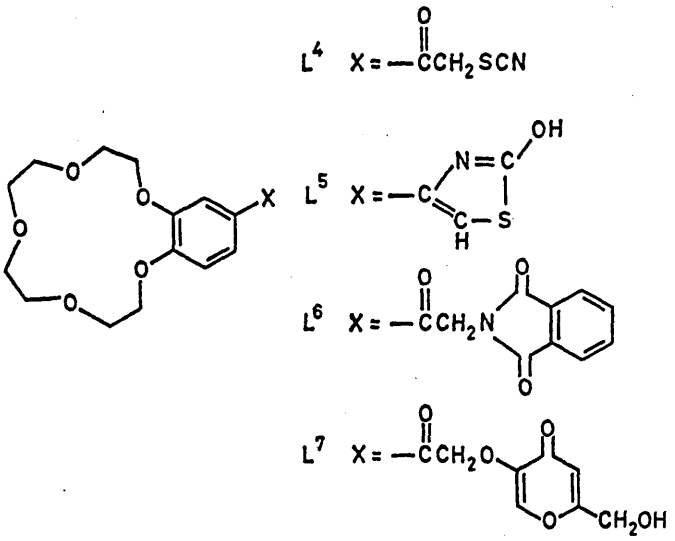


	Chemical shift/p.p.m.													
									Ether carbons *					
Metal salt	CH_3	C=O (NCS)	C^1	C^2	C^3	C^4	C^5	C^6						
Uncomplexed	26.3	196.2	131.4	113.4	149.6	154.2	112.7	123.9	72.0	71.2	71.0	70.1	69.9	69.5
Li[ClO$_4$]	26.4	196.4	132.1	112.5	147.7	151.8	112.1	124.5	69.6	69.4	68.5	69.4	67.9	67.7
Na[NCS]	26.5	196.5 (132.7)	132.3	113.3	148.2	152.5	113.2	124.7	69.9	69.3	68.7	68.6	68.3	
K[NCS]	26.5	196.3 (131.5)	131.5	112.5	148.0	152.5	112.5	124.3	69.5	68.6	68.5	67.9	67.7	

* Specific assignments for the ring ether carbon atoms have not been made.

example, the thiazole derivative L^5 is prepared by reaction of L^4 with aqueous HCl.

The role of alkali-metal complexes as 'self-reagents' has been extended to include other anions. Potassium phthalimide reacted readily to give L^6, and sodium iodide gave 4′-(iodoaceto)benzo-15-crown-5. However, no reaction was found for KF or KCl and this is a reflection of the poor complexation of these salts by the more rigid polyethers. Compound L^4 was also used to prepare an analogue of phenacyl kojate, itself a good complexor of alkali-metal cations.[31] The addition of L^4 to an aqueous ethanol solution of K[OH] and kojic acid gave a yellow precipitate which on recrystallisation from ethanol gave white crystals of 2L^7·KBr. Similar reactions using Li[OH] and Na[OH] gave hydrated complexes of formula L^7·1.2 MBr. The stoicheiometries observed suggest that the metal ions are preferentially complexed by the crown ether ring. A higher alkali-metal load per molecule of L^7 would be expected if the kojate chains were also participating in complexation.



Attempts to obtain free L^7 from the complexes using aqueous extraction techniques were unsuccessful in contrast to the easy removal of alkali-metal halide from phenacyl kojate.[32]

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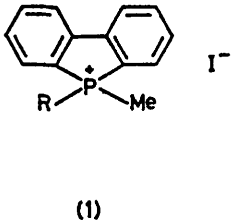
Ring Strain and the Reactivity of Dibenzophospholes and their Quaternary Salts: Crystal and Molecular Structure of 5-(*p*-Bromobenzyl)-5-phenyldibenzophospholium Bromide

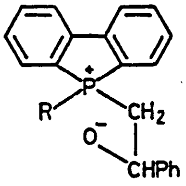
By **David W. Allen,*** **Ian W. Nowell, A. Christopher Oades,** and **Philip E. Walker,** Department of Chemistry, Sheffield City Polytechnic, Pond Street, Sheffield S1 1WB

Crystals of the title compound are monoclinic, $a = 25.685(15)$, $b = 10.444(6)$, $c = 18.818(11)$, $\beta = 119.18(5)°$, $Z = 8$ in space group $C2/c$, with the oxygens of water molecules present in the crystals lying along two-fold axes. The structure was determined by Patterson and electron-density methods and refined by least-squares techniques to $R = 0.066$ for 992 independent reflections. The fused ring system of the dibenzophospholium cation is almost planar and while the exocyclic C–P–C angles lie in the range 110—117°, the endocyclic angle is 93.9°. It is suggested that this low value is consistent with the presence of considerable ring strain, which is relieved either on phosphorane formation following nucleophilic attack at phosphorus, or on dealkylation of dibenzophospholium salts. The implications of ring strain in dibenzophospholium salts are discussed in connection with the possible aromaticity of the dibenzophospholes.

WE have shown previously that dibenzophospholium salts (1; R = Me or Ph) undergo alkaline hydrolysis (with ring-opening) extremely rapidly in comparison with their acyclic analogues.[1,2] Similarly dibenzophospholium betaines (*e.g.* 2; R = Ph or Bu^t) collapse rapidly in protic media to the expected Wittig reaction products whereas under the same conditions, the analogous acyclic phosphonium betaines decompose to give a range of abnormal products which arise via the intermediacy of vinylphosphonium salts derived from the betaines.[3,4] Furthermore, certain dibenzophospholium salts undergo alkaline hydrolysis with ring expansion to form derivatives of the dibenzo[*b,d*] phosphorin system.[2,5,6]

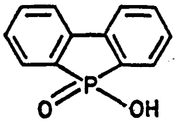


(1)

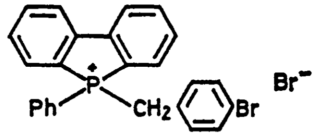


(2)

It has been suggested that the foregoing reactions occur as a consequence of ring strain in the dibenzophospholium salts which is relieved on formation of a trigonal bipyramidal phosphorane in which the ring system spans an apical-equatorial position; nucleophilic attack at the phosphonium centre is therefore facilitated. However, there is very little structural information on dibenzophosphole derivatives to support this argument. A number of metal complexes of 5-alkyldibenzophospholes have been studied by *X*-ray techniques[7] as has also the phosphinic acid (3),[8] but the structures of simple quaternary salts of the dibenzophosphole system have not been reported. Accordingly we have carried out and now report a single-crystal *X*-ray study of the salt (4).



(3)



(4)

EXPERIMENTAL

5-p-*Bromobenzyl-5-phenyldibenzophospholium Bromide* (4).—5-Phenyldibenzophosphole (0.13 g, 0.5 mmol) and *p*-bromobenzyl bromide (0.2 g, excess) were heated under reflux in benzene (5 cm³) for 2 h, during which time the salt separated from the solution. After filtration and washing with benzene, the salt was recrystallised from absolute ethanol to give *crystals*, m.p. 306—307 °C [Found: C, 58.25; H, 3.8. $C_{25}H_{19}Br_2P(0.5H_2O)$ requires C, 57.85; H, 3.75%]; $\bar{\nu}_{max}$(mull): 3 460 and 3 410 cm^{-1} (O–H).

Crystal Data.—$[C_{25}H_{19}PBr]^+Br^-\cdot\frac{1}{2}H_2O$, $M = 519.2$. Monoclinic, $a = 25.685(15)$, $b = 10.444(6)$, $c = 18.818(11)$, $\beta = 119.18(5)°$, $U = 4\,407.32$ Å^3, $D_m = 1.56$, $Z = 8$, $D_c = 1.57$ g cm^{-3}, $F(000) = 2\,080$. Mo-K_α radiation, $\lambda = 0.710\,69$ Å; μ(Mo-K_α) = 36.6 cm^{-1}. Space group $C2/c$ (C^6_{2h}, No. 15) from systematic absences.

Intensities were measured on a Stöe–Stadi 2 diffractometer by the background–ω scan–background technique, to give 992 independent reflections, having $I/\sigma(I) \geqslant 2.5$. Lorentz and polarization factors were applied, but no absorption correction was made.

Structure Solution and Refinement.—The positions of the bromine atoms were determined from a Patterson synthesis, and the remaining non-hydrogen atoms were located from successive electron-density difference syntheses. The four oxygen atoms per unit cell lie along two-fold axes at the special positions $0,y,\frac{1}{4}$; $0,-y,\frac{3}{4}$; $\frac{1}{2},\frac{1}{2}+y,\frac{1}{4}$; $\frac{1}{2},\frac{1}{2}-y,\frac{3}{4}$. The structure was refined by full-matrix least-squares methods, finally with all atoms given anisotropic thermal

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parameters and using the weighting scheme $w = 0.1277/[\sigma^2(F) + 0.046F^2]$. The scattering factors of ref. 9 were used and the refinement converged at R 0.066 for the 992 observed reflections. Final observed and calculated structure factors and thermal parameters are listed in Supplementary Publication No. 22130 (8 pp.).[*] Positional parameters are given in Table 1, bond lengths and valency angles in Table 2, and the equations of some least-square planes in Table 3.

TABLE 1

Final positional parameters with standard deviations in parentheses

	x	*y*	*z*
Br^-	0.062 3(1)	0.329 8(3)	0.661 7(2)
Br	0.187 2(1)	0.222 0(3)	0.332 8(2)
P	0.116 5(2)	0.669 0(6)	0.560 8(3)
O	0.000 0	0.156 1(20)	0.750 0
C(1)	0.071 9(9)	0.757 8(23)	0.593 9(12)
C(2)	0.042 6(8)	0.685 9(24)	0.629 5(10)
C(3)	0.008 4(9)	0.759 8(27)	0.654 0(10)
C(4)	0.007 7(10)	0.890 0(27)	0.652 0(17)
C(5)	0.036 9(10)	0.955 8(26)	0.618 9(15)
C(6)	0.070 2(8)	0.889 9(23)	0.589 3(12)
C(7)	0.074 9(8)	0.536 0(21)	0.500 9(12)
C(8)	0.105 5(9)	0.459 6(23)	0.461 5(11)
C(9)	0.096 7(10)	0.501 9(23)	0.385 1(14)
C(10)	0.120 9(9)	0.431 4(21)	0.347 1(12)
C(11)	0.155 0(9)	0.328 7(25)	0.386 2(12)
C(12)	0.165 0(9)	0.284 8(24)	0.461 9(14)
C(13)	0.141 6(8)	0.357 0(24)	0.500 8(11)
C(14)	0.145 9(8)	0.772 7(23)	0.516 6(10)
C(15)	0.206 6(9)	0.787 1(23)	0.565 6(12)
C(16)	0.240 1(9)	0.875 1(24)	0.546 7(13)
C(17)	0.209 2(10)	0.940 0(21)	0.473 4(13)
C(18)	0.148 4(11)	0.920 1(28)	0.421 2(12)
C(19)	0.116 4(8)	0.839 5(22)	0.441 6(12)
C(20)	0.190 0(8)	0.624 9(22)	0.645 5(12)
C(21)	0.203 1(7)	0.535 7(23)	0.707 3(11)
C(22)	0.261 4(10)	0.528 5(28)	0.765 2(12)
C(23)	0.306 2(9)	0.605 2(26)	0.761 5(13)
C(24)	0.291 7(9)	0.695 9(25)	0.700 8(11)
C(25)	0.231 1(7)	0.703 1(18)	0.641 6(10)

DISCUSSION

The fused ring system of the dibenzophospholium cation (Figure 1) is almost planar. The four carbons of the five-membered ring are effectively co-planar [Table 3, plane (*a*)] and the attached six-membered rings are inclined at angles of 2.60 and 2.84° to this plane while the phosphorus lies 0.159 Å out of it. The planes associated with the C(8)—(13) *p*-bromobenzyl and C(1)—(6) phenyl rings, make angles of 73.0 and 72.8° with plane (*a*) and 44.4° with each other, and presumably reflect packing requirements rather than stereochemical interactions within the cation itself. The C–P–C exocyclic bond angles lie in the range 110—117°, but the endocyclic C(14)–P–C(20) angle is only 93.9(9)°, and close to the value (93.4°) found for the phosphinic acid (3). This small value for the endocyclic angle would seem to

TABLE 2

Bond distances (Å) and angles (°), with standard deviations in parentheses

(*a*) Distances

P–C(1)	1.80(2)	C(11)–C(12)	1.40(3)
P–C(7)	1.78(2)	C(12)–C(13)	1.38(3)
P–C(14)	1.75(2)	C(14)–C(15)	1.38(2)
P–C(20)	1.84(2)	C(14)–C(19)	1.42(2)
C(1)–C(2)	1.44(3)	C(15)–C(16)	1.42(3)
C(1)–C(6)	1.38(3)	C(15)–C(25)	1.53(2)
C(2)–C(3)	1.41(3)	C(16)–C(17)	1.39(3)
C(3)–C(4)	1.36(3)	C(17)–C(18)	1.40(3)
C(4)–C(5)	1.37(4)	C(18)–C(19)	1.36(3)
C(5)–C(6)	1.41(3)	C(20)–C(21)	1.40(3)
C(7)–C(8)	1.54(3)	C(20)–C(25)	1.37(3)
C(8)–C(9)	1.41(3)	C(21)–C(22)	1.36(2)
C(8)–C(13)	1.37(3)	C(22)–C(23)	1.43(3)
C(9)–C(10)	1.37(3)	C(23)–C(24)	1.39(3)
C(10)–C(11)	1.35(3)	C(24)–C(25)	1.41(2)
C(11)–Br	1.94(2)		
$Br^- \cdots O$	3.35(2)		

(*b*) Angles

C(1)–P–C(7)	109.5(11)	C(11)–C(12)–C(13)	117(2)
C(1)–P–C(14)	109.9(12)	C(8)–C(13)–C(12)	120(2)
C(1)–P–C(20)	112.8(10)	P–C(14)–C(15)	111(1)
C(7)–P–C(14)	116.6(11)	P–C(14)–C(19)	129(1)
C(7)–P–C(20)	113.5(10)	C(15)–C(14)–C(19)	120(2)
C(14)–P–C(20)	93.9(9)	C(14)–C(15)–C(16)	122(2)
P–C(1)–C(2)	117(2)	C(14)–C(15)–C(25)	112(2)
P–C(1)–C(6)	120(2)	C(16)–C(15)–C(25)	126(1)
C(2)–C(1)–C(6)	123(2)	C(15)–C(16)–C(17)	116(2)
C(1)–C(2)–C(3)	115(2)	C(16)–C(17)–C(18)	122(2)
C(2)–C(3)–C(4)	123(3)	C(17)–C(18)–C(19)	121(2)
C(3)–C(4)–C(5)	121(3)	C(14)–C(19)–C(18)	119(2)
C(4)–C(5)–C(6)	121(2)	P–C(20)–C(21)	128(2)
C(1)–C(6)–C(5)	118(2)	P–C(20)–C(25)	107(1)
P–C(7)–C(8)	115(1)	C(21)–C(20)–C(25)	124(1)
C(7)–C(8)–C(9)	118(2)	C(20)–C(21)–C(22)	115(2)
C(7)–C(8)–C(13)	121(2)	C(21)–C(22)–C(23)	122(2)
C(9)–C(8)–C(13)	122(2)	C(22)–C(23)–C(24)	122(2)
C(8)–C(9)–C(10)	118(2)	C(23)–C(24)–C(25)	116(2)
C(9)–C(10)–C(11)	119(2)	C(15)–C(25)–C(20)	115(1)
Br–C(11)–C(10)	120(2)	C(15)–C(25)–C(24)	124(2)
Br–C(11)–C(12)	115(2)	C(20)–C(25)–C(24)	121(2)
C(10)–C(11)–C(12)	124(2)		

TABLE 3

Equations of least-squares planes referred to orthogonal axes with distances (Å) of relevant atoms from the planes in square brackets

Plane (*a*): C(14), C(15), C(20), C(25)

$$0.4835X - 0.7168Y - 0.5025Z + 10.5202 = 0$$

[C(14) −0.009, C(15) 0.016, C(20) 0.009, C(25) −0.016, P −0.159]

Plane (*b*): C(14)—(19)

$$0.4833X - 0.7419Y - 0.4647Z + 10.3886 = 0$$

[C(14) −0.023, C(15) 0.028, C(16) −0.010, C(17) −0.012, C(18) 0.018, C(19) −0.000]

Plane (*c*): C(20)—(25)

$$0.4701X - 0.6945Y - 0.5447Z + 10.8114 = 0$$

[C(20) 0.012, C(21) −0.002, C(22) −0.014, C(23) 0.019, C(24) −0.009, C(25) −0.007]

Plane (*d*): C(8)—(13)

$$-0.6930X - 0.5769Y - 0.4324Z + 5.0170 = 0$$

[C(8) 0.026, C(9) −0.015, C(10) 0.008, C(11) −0.010, C(12) 0.020, C(13) −0.028, Br 0.100, C(7) 0.081]

Plane (*e*): C(1)—(6)

$$-0.4193X - 0.0547Y - 0.9062Z + 7.7753 = 0$$

[C(1) 0.011, C(2) −0.027, C(3) 0.030, C(4) −0.015, C(5) −0.002, C(6) 0.003]

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[*] See Notice to Authors No. 7, in *J.C.S. Perkin II*, 1976, Index issue.

[9] 'International Tables for *X*-Ray Crystallography,' vol. IV, Kynoch Press, Birmingham, 1974.

indicate considerable deformation of bond angles for a quaternary phosphonium centre compared with an acyclic phosphonium salt. For example,[10] for the cation $Ph_3\overset{+}{P}Me$, the smallest angle about phosphorus is 105°. It is therefore reasonable to suppose that as a result of the deformation of bond angles at phosphorus there is appreciable ring strain in the dibenzophospholium salt which would be relieved on formation of a quinquecovalent trigonal bipyramidal phosphorane, in which the endocyclic C–P–C angle would be 90°, assuming that the five-membered ring occupies apical-equatorial positions as is generally found.[11] Apical bond-cleavage or migration of the apical substituent to an equatorially disposed site then leads to either ring opening or ring expansion respectively with the formation of a relatively strain-free structure. The increased rate of nucleophilic attack at phosphorus in dibenzophospholium salts and the subsequent reactions undergone can therefore be accommodated in this framework.

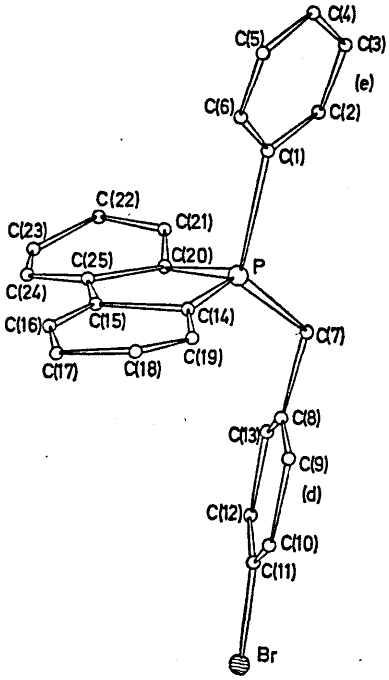
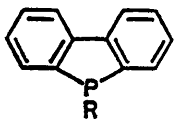


FIGURE 1 The structure of the cation

If it is accepted that the small endocyclic angle at phosphorus in dibenzophospholium salts is indicative of ring strain, then much of the data obtained in experiments aimed at assessing the degree of delocalisation of the lone pair at phosphorus in the parent dibenzophosphole system (5; R = alkyl or aryl) and subsequently cited as evidence of phosphole aromaticity is in need of reconsideration and reinterpretation.

It is generally accepted that in its tervalent compounds, phosphorus uses mainly *p* orbitals in σ-bonding, with only a small amount of *s* character mixed in. Thus in the parent dibenzophosphole system, one would expect an endocyclic C–P–C angle of *ca.* 90° (by analogy with that found in 1-benzylphosphole [12]) which would not involve undue deformation of bond angles for a tertiary phosphine. Bond-angle strain at phosphorus would however be introduced on quaternisation, and this factor may well be responsible for the reduced rate of quaternisation of 5-phenyldibenzophosphole relative to triphenylphosphine [13] and also for the reduction in the P=O bond energy of 5-phenyldibenzophosphole oxide [14] compared with Ph_3PO, rather than effects based



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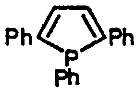

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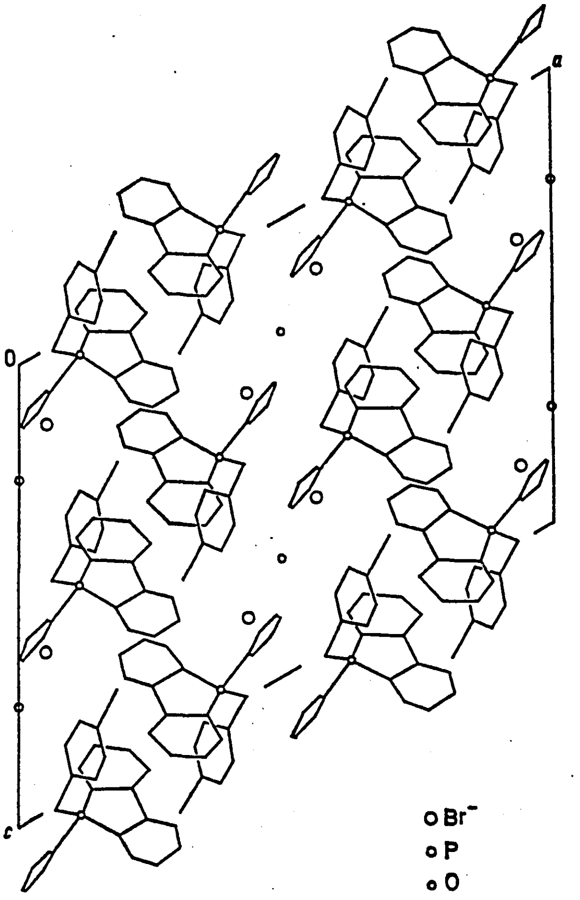

FIGURE 2 The (010) projection of the unit cell

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on the ' aromatic ' stabilisation of the dibenzophosphole system by delocalisation of the lone pair at phosphorus. Similarly, the increased rate of retrocyanoethylation of cyanoethyldibenzophospholium salts[15] and the ease of electrochemical reduction of dibenzophospholium salts,[13] compared to corresponding acyclic systems, can be explained on the basis of relief of ring strain attending conversion of the quaternary derivative to the parent phosphole.

These arguments can be similarly applied to a discussion of the chemistry of non-annelated phospholes, *e.g.* 1,2,5-triphenylphosphole (6), and our results support the suggestion[16] that one of the likely causes of the reduced nucleophilicity of 1,2,5-triphenylphosphole compared to triphenylphosphine is the increase in ring strain in the five-membered phosphole ring on conversion from the tervalent into an intermediate quaternary state.

Figure 2 shows the packing of the ions and water molecules in the unit cell. Pairs of bromide ions, related by two-fold axes, are separated along the (010) direction by water molecules. The shortness of the $Br^- \cdots O$ contacts, 3.35(2) Å, points to significant interactions. The final electron-density difference map lends support to this view, as it indicates the presence of hydrogen atoms at positions suitable for attachment to the oxygen atoms and for interactions with the bromide ions.

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FURTHER STUDIES IN THE CHEMISTRY OF 10-PHENYLPHENOXAPHOSPHINE

Rate of Quaternization, and an X-ray Structural Study of a Related Phosphonium Salt, 10(-4-Bromobenzyl)-10-Phenylphenoxaphosphonium Bromide

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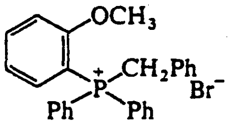
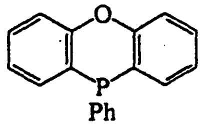
10-Phenylphenoxaphosphine (2) undergoes quaternization with phenacyl bromide in nitromethane five times more slowly than triphenylphosphine and almost twenty times more slowly than *o*-methoxyphenyldiphenylphosphine. It is argued that stabilization of the developing phosphonium centre by interaction with the ortho-oxygen atom, previously suggested as being involved in the quaternization of the latter (McEwen *et al.*[1]), is not significant for the quaternization of the phenoxaphosphine (2), and that the predominant role of the ether oxygen is electron-withdrawal from phosphorus. This conclusion is supported by an X-ray structural study of the title compound (3). Crystals of (3) are orthorhombic, $a = 18.954\,(11)$, $b = 25.715\,(14)$, $c = 9.322\,(5)$ Å, $Z = 8$, in space group $P\,b\,c\,a$ (D_{2h}^{15}, No. 61). The structure was determined by Patterson and electrondensity methods, and refined by least squares techniques to $R = 0.045$ for 1505 independent reflections. The fused ring system of the phenoxaphosphonium cation is not planar, the central ring having a boat-like conformation with the phosphorus and oxygen atoms displaced from the four effectively coplanar carbon atoms by 0.14 and 0.07 Å respectively. The average exocyclic angles at phosphorus are 110.7°; the endocyclic angle is 103.1°. The transannular $P^+ \ldots O$ distance is 3.11 Å, indicating little interaction.

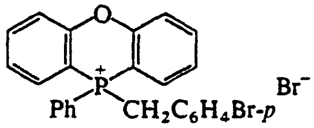
It has been shown that the presence of an *o*-methoxy substituent in an aryl phosphine causes a significant acceleration of the rate of quaternization with alkyl halides. Thus e.g. *o*-methoxyphenyldiphenylphosphine undergoes quaternization with benzyl chloride some four times faster than the corresponding *para*-isomer, and seven times faster than triphenylphosphine. It has been suggested that these effects are due to the overlap of a pair of 2p electrons of the *o*-methoxy group with a 3*d* (or hybrid orbital) of phosphorus in the transition state of the reaction, such that the developing phosphonium centre is stabilised. Evidence in support of this type of interaction has been adduced from spectroscopic studies of the parent phosphines and related phosphonium salts,[1,2] and also from the results of an X-ray diffraction study of the salt (1) in which the observed $P^+ \ldots O$ distance of 2.88 Å suggests a weak bonding interaction,[3] the sum of the accepted Van der Waals radii being 3.30 Å.[4] In related studies, the reduction in the rate of alkaline hydrolysis of salts of type (1) compared to the corresponding *para*-isomers has also been attributed to the stabilisation of the phosphonium cation by such an interaction.[5]



(1)



(2)



(3)

In extension of our earlier studies on the chemistry of phenoxaphosphines e.g. (2) and related phosphonium salts,[6,7] we wished to investigate whether a similar $P^+ \ldots O$ interaction was significant between the *o*-ether oxygen and phosphorus in a heterocyclic system in which the oxygen was perhaps not as free to move towards phosphorus as in the above example (1). Accordingly, we now report rate data for the quaternization of 10-phenylphenoxaphosphine (2), together with comparable data for triphenylphosphine and *o*-methoxyphenyldiphenylphosphine, and also the results of an X-ray structural study of the salt (3).

QUATERNIZATION STUDIES

Rate and activation data for the quaternization of 10-phenylphenoxaphosphine (2) and related acyclic phosphines with phenacyl bromide are presented in Table I. It is seen that the phenoxaphosphine (2) undergoes quaternization some five times more slowly than triphenylphosphine. In contrast *o*-methoxyphenyldiphenylphosphine quaternizes almost four times faster than triphenylphosphine, in keeping with earlier studies with other alkyl halides.[1,2] There is thus almost a twentyfold difference in the rate of quaternization of the phenoxaphosphine (2) and *o*-methoxyphenyldiphenylphosphine, which is due to the significantly lower activation energy for quaternization of the latter, in keeping with the earlier suggestion of the stabilisation of the forming phosphonium centre in the transition state of the reaction by oxygen (2p)-phosphorus (3d) interaction.[1,2] Clearly, this is not significant for the phenoxaphosphine system, and the predominant effect of the oxygen atom here would seem to be an electron withdrawal from phosphorus, thereby causing a reduction in the rate of quaternization. It is of interest that while the enthalpy of activation for the quaternization of the *o*-methoxyphenyldiphenylphosphine with phenacyl bromide is the lowest of the series, the entropy of activation for this reaction is the most negative of the series, perhaps supporting the suggestion of a specific orientation of oxygen and phosphorus in the transition state of the reaction. In contrast, in the systems studied by McEwen *et al.*,[1,2] the entropy of activation rather than E_a has been the dominant term, being much less negative for *o*-methoxyphenyldiphenylphosphine than e.g. for the *p*-methoxy analogue, suggesting solvation effects to be of importance.

The Structure of 10-(4-bromobenzyl)-10-phenylphenoxaphosphonium Bromide (3)

Crystal data $[C_{25}H_{19}OPBr]^+ Br^-$, $M = 526.2$. Orthorhombic, $a = 18.954\ (11)$, $b = 25.715\ (14)$, $c = 9.322\ (5)$ Å, $U = 4{,}543.38$ Å^3, $D_m = 1.55$, $Z = 8$, $D_c = 1.54\,\mathrm{g\,cm^{-3}}$, $F(000) = 2{,}104$. Mo $- K_\alpha$ radiation, $\lambda = 0.710\ 69$ Å; μ (Mo $- K_\alpha$) = 35.5 cm^{-1}. Space group $Pbca$ (D_{2h}^{15}, No. 61) from systematic absences.

Intensity data were measured on a Stöe-Stadi 2 diffractometer; the crystal was mounted with the *c*-axis coincident with the rotation (ω) axis. The background—ω scan—background technique was used to collect 4,171 reflections of which 1,505 had $I \geqslant 2.5\ \sigma\ (I)$ and were classed as observed. Lorentz and polarization factors were applied but no absorption correction was made.

Structure solution and refinement The positions of the bromines were determined from a Patterson synthesis, and the remaining atoms (including hydrogens) located from successive electron-density difference syntheses. The structure was refined by full-matrix least-squares methods with all non-hydrogen atoms given anisotropic thermal parameters for the final stages of refinement. Once located from difference maps, hydrogen atoms were included in positions calculated from the geometry of the molecule (C—H bond length 1.08 Å) and a common isotropic temperature factor applied. Scattering factors were calculated using an analytical approximation[9] and the weighting scheme $w = 0.523\ 9/[\sigma^2(F) + 0.0025\ F^2]$ used. Refinement converged at $R = 0.045$ and the final difference map showed no peaks greater than 0.47 e. Å^{-3}. Final observed and calculated structure factors, thermal parameters and least-square planes equations are available on request from the authors (IWN). Positional parameters are given in Table II, bond lengths and valency angles in Table III.

TABLE I

Second order rate data and activation parameters for quaternization of phosphines with phenacyl bromide in nitromethane

Phosphine	k(l mol^{-1} sec^{-1}) 30°C	40°C	Relative rate at 30°C	E_a (kJmol^{-1})	$\Delta S^\ddagger$(JK^{-1} mol^{-1})
10-phenylphenoxaphosphine (2)	0.012	0.023	0.18	48.0	−131.4
triphenylphosphine[8]	0.064	0.115	1.00	45.2	−126.7
o-methoxyphenyldiphenylphosphine	0.228	0.370	3.56	38.1	−139.8

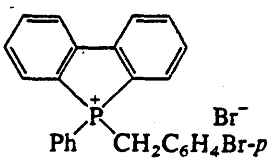
TABLE II

Final positional parameters with standard deviations in parentheses

	x	y	z
Br^-	0.352 6(1)	0.543 0(1)	0.604 0(1)
Br	0.079 6(1)	0.181 0(1)	−0.130 5(2)
P	0.341 7(1)	0.107 9(1)	0.371 4(3)
O	0.393 5(4)	0.219 8(3)	0.300 5(9)
C(1)	0.387 5(5)	0.072 2(4)	0.509 1(12)
C(2)	0.349 2(6)	0.044 4(5)	0.611 0(14)
C(3)	0.384 5(7)	0.020 5(5)	0.723 8(16)
C(4)	0.455 4(7)	0.024 1(5)	0.731 4(18)
C(5)	0.493 5(6)	0.050 7(6)	0.630 3(16)
C(6)	0.460 3(6)	0.074 6(5)	0.517 2(15)
C(7)	0.270 3(5)	0.067 9(4)	0.305 6(12)
C(8)	0.224 6(5)	0.095 4(4)	0.198 6(12)
C(9)	0.166 4(5)	0.123 4(4)	0.244 8(14)
C(10)	0.122 3(6)	0.148 9(5)	0.146 8(14)
C(11)	0.137 1(6)	0.143 3(4)	0.001 3(15)
C(12)	0.192 9(6)	0.114 8(5)	−0.050 3(15)
C(13)	0.235 6(6)	0.091 0(5)	0.051 3(13)
C(14)	0.310 6(5)	0.167 7(4)	0.442 6(12)
C(15)	0.340 1(6)	0.215 1(4)	0.397 7(14)
C(16)	0.315 8(8)	0.261 2(5)	0.457 6(17)
C(17)	0.265 6(8)	0.261 2(6)	0.558 0(17)
C(18)	0.234 5(7)	0.215 1(5)	0.603 4(16)
C(19)	0.257 7(6)	0.168 2(5)	0.543 8(13)
C(20)	0.401 0(5)	0.128 1(4)	0.233 2(13)
C(21)	0.431 9(6)	0.089 9(5)	0.146 7(14)
C(22)	0.481 9(7)	0.106 3(7)	0.046 3(16)
C(23)	0.500 1(7)	0.157 9(7)	0.032 8(17)
C(24)	0.467 5(6)	0.194 5(5)	0.119 7(16)
C(25)	0.419 3(5)	0.179 8(4)	0.220 1(12)
H(2)	0.292 5	0.041 4	0.602 5
H(3)	0.355 1	−0.000 4	0.804 7
H(4)	0.482 7	0.005 2	0.818 8
H(5)	0.550 2	0.053 0	0.639 4
H(6)	0.490 7	0.095 0	0.436 9
H(71)	0.238 2	0.055 8	0.394 8
H(72)	0.292 7	0.034 0	0.253 8
H(9)	0.154 7	0.125 4	0.358 0
H(10)	0.078 6	0.172 4	0.183 0
H(12)	0.202 9	0.111 1	−0.163 9
H(13)	0.279 6	0.067 9	0.014 5
H(16)	0.338 0	0.297 6	0.422 1
H(17)	0.249 2	0.297 8	0.604 5
H(18)	0.193 1	0.215 4	0.683 1
H(19)	0.234 2	0.131 9	0.577 1
H(21)	0.417 8	0.049 3	0.157 5
H(22)	0.506 4	0.077 9	−0.022 9
H(23)	0.539 4	0.169 6	−0.044 6
H(24)	0.480 7	0.235 1	0.108 1

DISCUSSION

As with the parent phosphine[10] (2), the fused ring system of the phosphonium cation is not planar (Figure). In particular, the central ring has a boat-like conformation with the phosphorus and oxygen atoms displaced from the four effectively co-planar carbon atoms by 0.14 and 0.07 Å respectively. These displacements are less than those found in 10-phenylphenoxaphosphine (2) (0.22 and 0.17 Å for phosphorus and oxygen) and the overall displacement from planarity is less for the phosphonium cation with the dihedral angle between the outer rings being considerably smaller (4.1° compared to 15° in (2)). Quaternization produces significant changes in the bond angles about phosphorus, with the endocyclic and average exocyclic C–P–C angles increasing from 98.0 and 101.0° in (2) to 103.1 and 110.7° in (3). Accompanying quaternization, there is also a change from 87 to 76.7° in the dihedral angle between the C(1)–(6) phenyl ring (plane B) and the plane containing C(14), C(15), C(20) and C(25) (plane A). The plane associated with the C(8)–(13) of the p-bromobenzyl phenyl ring makes angles of 69.7 and 49.2° with planes A and B respectively, which are similar to the values of 73.0 and 44.4° found in the dibenzophospholium salt (4).[11]



(4)

While the P . . . O distances in both (2) and (3), (3.20 and 3.11 Å respectively) lie within the sum of the Van der Waals radii (3.30 Å), they are very significantly larger than the value of 2.88 Å found in (1). It thus seems unlikely that the weak phosphorus - oxygen interactions suggested for the acyclic salt (1) are significant in either (2) or (3).

The endocyclic C–P–C angles in (2) and (3), 98.0 and 103.1° respectively are equally distorted from the ideal strain-free values of *ca* 90 and 109.5° for the phosphine and phosphonium salt respectively. However, the endocyclic angle at phosphorus in the phosphonium salt (3) is very close to the smallest angle at phosphorus (105°) in the cation $Ph_3\overset{+}{P}Me$[12] (which may be considered as an acyclic analogue of (3)), implying that there is little significant deformation of bond angle at phosphorus in (3), and that the reduction in rate of quaternization of the phenoxaphosphine (2) cannot be attributed to an increase in angle strain at phosphorus. The structural data therefore lends support to the above suggestion that in the phenoxaphosphonium system the predominant

TABLE III

Bond distances (Å) and angles (°), with standard deviations in parentheses

(a) *Distances*

P—C(1)	1.80 (1)	C(11)—C(12)	1.37 (2)
P—C(7)	1.81 (1)	C(12)—C(13)	1.39 (2)
P—C(14)	1.78 (1)	C(14)—C(15)	1.40 (2)
P—C(20)	1.79 (1)	C(14)—C(19)	1.38 (2)
C(1)—C(2)	1.39 (2)	C(15)—O	1.36 (2)
C(1)—C(6)	1.38 (2)	C(15)—C(16)	1.39 (2)
C(2)—C(3)	1.39 (2)	C(16)—C(17)	1.33 (2)
C(3)—C(4)	1.35 (2)	C(17)—C(18)	1.39 (2)
C(4)—C(5)	1.37 (2)	C(18)—C(19)	1.40 (2)
C(5)—C(6)	1.37 (2)	C(20)—C(21)	1.40 (2)
C(7)—C(8)	1.50 (1)	C(20)—C(25)	1.38 (1)
C(8)—C(9)	1.39 (1)	C(21)—C(22)	1.40 (2)
C(8)—C(13)	1.39 (2)	C(22)—C(23)	1.38 (3)
C(9)—C(10)	1.40 (2)	C(23)—C(24)	1.39 (2)
C(10)—C(11)	1.39 (2)	C(24)—C(25)	1.36 (2)
C(11)—Br	1.91 (1)	C(25)—O	1.37 (1)

(b) *Angles*

C(1)—P—C(7)	108.3 (5)	C(11)—C(12)—C(13)	116 (1)
C(1)—P—C(14)	109.6 (5)	C(8)—C(13)—C(12)	123 (1)
C(1)—P—C(20)	111.0 (5)	P—C(14)—C(15)	121 (1)
C(7)—P—C(14)	111.8 (5)	P—C(14)—C(19)	120 (1)
C(7)—P—C(20)	113.0 (5)	C(15)—C(14)—C(19)	119 (1)
C(14)—P—C(20)	103.1 (5)	O—C(15)—C(14)	125 (1)
P—C(1)—C(2)	120 (1)	O—C(15)—C(16)	116 (1)
P—C(1)—C(6)	120 (1)	C(14)—C(15)—C(16)	119 (1)
C(2)—C(1)—C(16)	120 (1)	C(15)—C(16)—C(17)	121 (1)
C(1)—C(2)—C(3)	120 (1)	C(16)—C(17)—C(18)	121 (1)
C(2)—C(3)—C(4)	119 (1)	C(17)—C(18)—C(19)	119 (1)
C(3)—C(4)—C(5)	122 (1)	C(14)—C(19)—C(18)	121 (1)
C(4)—C(5)—C(6)	121 (1)	P—C(20)—C(21)	118 (1)
C(1)—C(16)—C(5)	119 (1)	P—C(20)—C(25)	120 (1)
P—C(7)—C(8)	113 (1)	C(21)—C(20)—C(25)	121 (1)
C(7)—C(8)—C(9)	120 (1)	C(20)—C(21)—C(22)	117 (1)
C(7)—C(8)—C(13)	122 (1)	C(21)—C(22)—C(23)	122 (1)
C(9)—C(8)—C(13)	118 (1)	C(22)—C(23)—C(24)	119 (1)
C(8)—C(9)—C(10)	121 (1)	C(23)—C(24)—C(25)	121 (1)
C(9)—C(10)—C(11)	118 (1)	O—C(25)—C(20)	126 (1)
Br—C(11)—C(10)	117 (1)	O—C(25)—C(24)	114 (1)
Br—C(11)—C(12)	120 (1)	C(20)—C(25)—C(24)	120 (1)
C(10)—C(11)—C(12)	123 (1)	C(15)—O—C(25)	124 (1)

effect of the oxygen atom is electron-withdrawal from phosphorus. This effect is without doubt also responsible for the greatly increased rate of alkaline hydrolysis of phenoxaphosphonium salts compared to related acyclic salts.[7,15]

EXPERIMENTAL

^{1}H nmr spectra were recorded at 60 MHz on a JEOL spectrometer, using tetramethylsilane as internal standard. Operations involving tertiary phosphines were conducted under nitrogen.

10 - Phenylphenoxaphosphine[13] and o - methoxyphenyldiphenylphosphine[1] were prepared as described previously.

KINETIC STUDIES

The rates of quaternization of the above phosphines with α-bromoacetophenone in nitromethane solution were determined using the conductance procedure described by Borowitz *et al.*[14] A Wayne-Kerr conductance bridge was employed. The quaternization reactions followed a second order rate law. Rate constants and activation parameters were calculated as described by Borowitz *et al.*[14] and are presented in Table I. Evaporation of the solution obtained at the conclusion of each kinetic run gave the appropriate phenacylphosphonium salt, whose structure was confirmed by microanalysis and ^{1}H nmr spectroscopy. The following salts were characterised:

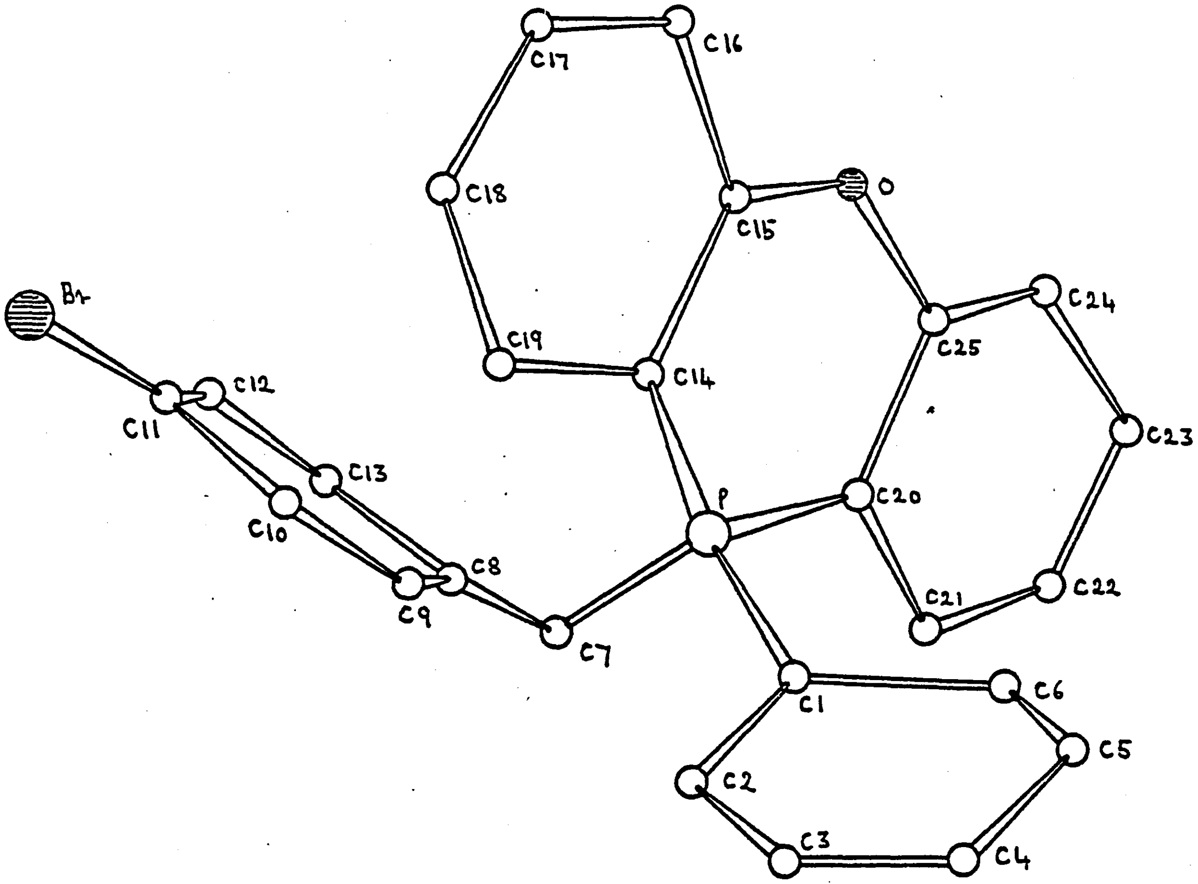


FIGURE 1 The structure of the 10-(4-bromobenzyl)-10-phenylphenoxaphosphonium cation.

o - Methoxyphenyl(phenacyl)diphenylphosphonium Bromide, m.p. 195–196° (ex EtOAc-EtOH). Found: C, 65.95; H, 5.05. $C_{27}H_{24}BrO_2P$ requires C, 65.95; H, 4.95%). $\delta(CDCl_3)$: 8.6–7.0 (m, 19 ArH); 6.09 (d, $^2J_{PCH}$ 13.5 Hz, $\dot{P}CH_2$) and 3.58 (s, 3H, OCH_3) ppm.

10 - Phenacyl - 10 - phenylphenoxaphosphonium Bromide (as the mono hydrate), m.p. 220° (ex EtOAc-EtOH). (Found: C, 63.7; H, 4.65; $C_{26}H_{20}BrO_2P.H_2O$ requires C, 63.3; H, 4.5%). $\delta(CDCl_3)$: 8.7–7.1 (m, 18 ArH) and 6.4 (d, $^2J_{PCH}$ 12.75 Hz, $\dot{P}CH_2$).

Preparation of 10 - (4 - bromobenzyl) - 10 - phenylphenoxaphosphonium Bromide(3)-10-Phenylphenoxaphosphine (0.138 g, 0.5 mmol), and 4-bromobenzyl bromide (0.15 g, excess) were heated together under reflux in toluene (3 cm³) for 2 hr. After filtration and washing with ether, the salt was recrystallised from ethyl acetate-ethanol to give *crystals*, m.p. > 250° d. (Found: C, 56.5; H, 4.05; $C_{25}H_{19}BrO_2P$ requires C, 57.0; H, 3.65%).

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X-ray Structural Study of 5-Phenyl-10,11-dihydrodibenzo[b,f]phosphepin-5-oxide

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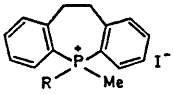
Phosphorus Heterocycles Reactivity, Phosphepin Oxide Structure

Crystals of the title compound are triclinic, $a = 8.533(5)$, $b = 11.106(6)$, $c = 8.815(5)$ Å, $\alpha = 107.83(6)$, $\beta = 104.99(6)$, $\gamma = 81.30(5)°$, $Z = 2$, space group P$\bar{1}$. The structure was determined by multisolution direct methods and electron density methods. Refinement by least-squares techniques gave a final $R = 0.081$ for the 1753 independent reflections. The molecule adopts a *butterfly-type* conformation such that the fused phenyl rings are inclined to each other at an angle of 56.8°. The P–O bond distance is 1.506(4) Å; the endocyclic angle at phosphorus is 107.2(3)° and the exocyclic angles vary from 106.5 to 111.9(3)°.

Compared with four-, five- and six-membered ring phosphorus heterocycles, little has been reported on the chemistry and structure of compounds in which the phosphorus atom forms part of a seven-membered ring system. We have recently described [1] some reactions of quaternary derivatives (**1**, R = Me or Ph) of the 10,11-dihydrodibenzo[b,f]-phosphepin system together with a comparison with those of related acyclic and five-membered ring systems (2).



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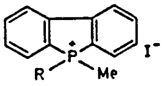

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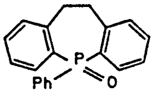

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It was shown that the salt (**1**, R = Me) undergoes alkaline hydrolysis with ring-opening at a rate comparable with the acyclic salt dimethyldiphenylphosphonium iodide but much more slowly than the five-membered ring salt (2, R = Me). It was suggested that the much faster rate of hydrolysis of the latter (in which the exocyclic angle at phosphorus is close to 90°) is presumably due to relief of bond angle strain attending the formation of the intermediate hydroxyphosphorane, where the ring system spans apical-equatorial positions [2, 3]. The reduced rate of hydrolysis of the seven-membered ring salt was attributed in part to the likelihood of there being little comparable bond angle strain involved in the seven-membered ring phosphonium cation, since the endocyclic angle at phosphorus was expected to be much larger than in the five-membered ring salts (2). In order to gain support for this suggestion, we have undertaken structural studies of some seven-membered ring compounds in the above series. Our attempts to carry out single crystal X-ray studies on the phosphonium salts (**1**, R = Me or Ph), and a related *p*-bromobenzyl salt of 5-phenyl-10,11-dihydrodibenzo[b,f]phosphepin, were frustrated by the poor quality of the crystals obtained. However, we were successful in obtaining suitable crystals of the cyclic oxide (3), in which the geometry at phosphorus would be expected to be very similar to the above phosphonium salts, and a crystallographic study of this compound is now reported:

Crystal data – $C_{20}H_{17}PO$, $M_r = 304.33$.

Triclinic, $a = 8.533(5)$, $b = 11.106(2)$, $c = 8.815(5)$ Å, $\alpha = 107.83(6)$, $\beta = 104.99(6)$, $\gamma = 81.30(5)°$, $U = 765.74$ Å^3, $D_m = 1.33$, $Z = 2$, $D_c = 1.32$ g cm^{-3}, $F(000) = 320$. Mo–K$_\alpha$ radiation, $\lambda = 0.7107$ Å; μ(Mo–K$_\alpha$) $\doteqdot$ 1.36 cm^{-1}. Space group P$\bar{1}$.

Intensity data were measured on a Stöe-Stadi 2 two-circle diffractometer; the crystal of dimensions 0.24 × 0.31 × 0.45 mm being mounted with its *a*-axis coincident with the rotation (ω) axis. The background-ω scan-background technique was used to collect 3110 independent reflections of which 1753 had $I > 4.0\ \sigma(I)$ and were classed as observed. Lorentz and polarization factors were applied, but no absorption correction was made.

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Structure Solution and Refinement

The structure was solved by multisolution direct methods [4] and refined by full-matrix least-squares methods with all non-hydrogen atoms given anisotropic thermal parameters for the final stages of refinement. Once located from difference maps, hydrogen atoms were included in positions calculated from the geometry of the molecule (C–H bond length 1.08 Å). A common isotropic temperature factor was applied to all hydrogens and refined to a final value of $U = 0.082(7)$ Å^2. Scattering factors were calculated using an analytical approximation [5] and the weighting scheme $w = 2.0396/[\sigma^2(F_o) + 0.0037\,(F_o)^2]$ adopted. Refinement converged at $R = 0.081$ and $R' = 0.090$ and the final difference-Fourier map showed no peaks greater than 0.63 e. Å^{-3}. Final observed and calculated structure factors, thermal parameters and least-square planes equations are available on request from the authors (IWN). Positional parameters are given in Table I, bond lengths and valency angles in Table II.

Table I. Final positional parameters (× 10^4) with estimated standard deviations for non-hydrogen atoms in parentheses.

	x	*y*	*z*
P	2234(2)	2469(1)	6771(2)
O	953(6)	2070(4)	5217(5)
C1	2368(8)	1482(5)	8079(7)
C2	1385(9)	480(5)	7511(8)
C3	1365(10)	−291(6)	8481(9)
C4	2308(11)	−39(6)	10040(9)
C5	3320(11)	955(7)	10613(9)
C6	3387(9)	1728(5)	9670(7)
C7	4497(9)	2805(6)	10289(8)
C8	3652(11)	4108(6)	10838(8)
C9	2427(10)	4682(5)	9594(8)
C10	1805(9)	4092(5)	7932(7)
C11	640(11)	4784(6)	7012(8)
C12	137(12)	6034(7)	7679(11)
C13	739(11)	6615(6)	9330(10)
C14	1834(12)	5940(6)	10248(9)
C15	4174(9)	2410(5)	6296(6)
C16	5359(9)	1400(6)	6422(8)
C17	6787(11)	1303(7)	5901(9)
C18	7042(11)	2208(8)	5217(9)
C19	5874(11)	3209(7)	5066(9)
C20	4448(10)	3284(6)	5585(8)
H2	618	296	6292
H3	615	−1084	8012
H4	2268	−610	10823
H5	4076	1129	11837
H71	5062	2792	9319
H72	5423	2642	11319
H81	3014	4069	11730
H82	4595	4757	11420
H11	120	4327	5745
H12	−716	6557	6925
H13	343	7588	9873
H14	2267	6392	11535
H16	5159	686	6938
H17	7693	526	6024
H18	8148	2135	4803
H19	6071	3923	4549
H20	3528	4046	5429

Table II. Bond distances (Å) and angles (°) with estimated standard deviations in parentheses.

a) Distances

P–O	1.506(4)	C8–C9	1.528(10)
P–C1	1.793(7)	C9–C10	1.404(8)
P–C10	1.815(5)	C9–C14	1.408(8)
P–C15	1.797(8)	C10–C11	1.403(10)
C1–C2	1.384(9)	C11–C12	1.382(9)
C1–C6	1.416(8)	C12–C13	1.392(11)
C2–C3	1.388(11)	C13–C14	1.363(11)
C3–C4	1.369(10)	C15–C16	1.403(9)
C4–C5	1.393(12)	C15–C20	1.381(11)
C5–C6	1.381(12)	C16–C17	1.388(13)
C6–C7	1.517(10)	C17–C18	1.387(14)
C7–C8	1.512(9)	C18–C19	1.391(11)
		C19–C20	1.390(14)

b) Angles

O–P–C1	111.3(3)	C8–C9–C10	127.8(5)
O–P–C10	111.9(3)	C8–C9–C14	114.3(6)
O–P–C15	109.9(3)	C10–C9–C14	117.8(6)
C1–P–C10	107.2(3)	P–C10–C9	128.3(5)
C1–P–C15	109.9(3)	P–C10–C11	113.1(4)
C10–P–C15	106.5(3)	C9–C10–C11	118.6(5)
P–C1–C2	117.7(4)	C10–C11–C12	121.9(6)
P–C1–C6	122.2(5)	C11–C12–C13	119.5(7)
C2–C1–C6	120.0(6)	C12–C13–C14	119.1(6)
C1–C2–C3	121.1(6)	C13–C14–C9	123.0(6)
C2–C3–C4	119.3(7)	P–C15–C16	121.9(6)
C3–C4–C5	119.9(8)	P–C15–C20	119.8(5)
C4–C5–C6	122.2(7)	C16–C15–C20	117.8(7)
C1–C6–C5	117.4(6)	C15–C16–C17	121.2(7)
C1–C6–C7	120.4(6)	C16–C17–C18	119.7(7)
C5–C6–C7	122.2(6)	C17–C18–C19	120.0(9)
C6–C7–C8	114.6(7)	C18–C19–C20	119.5(9)
C7–C8–C9	120.3(5)	C15–C20–C19	121.8(7)

Discussion

The 5-phenyl-10,11-dihydrodibenzo[b,f]phosphepin oxide is found to adopt a *butterfly-type* conformation (Figure). Ring A and Ring B (Table III) are inclined at 56.8° to each other and at angles of 80.2 and 74.9° respectively to the exocyclic phenyl ring (Ring C). C7 and C8 are almost coplanar with the rings to which they are attached (Ring B, Ring A respectively), while P lies at distances of −0.060, −0.108 and 0.165 Å out of the best least-squares planes associated with Rings A, B and C.

The conformation adopted within the seven-membered ring in the present compound is strikingly different to the *boat-conformation* found [6] in the

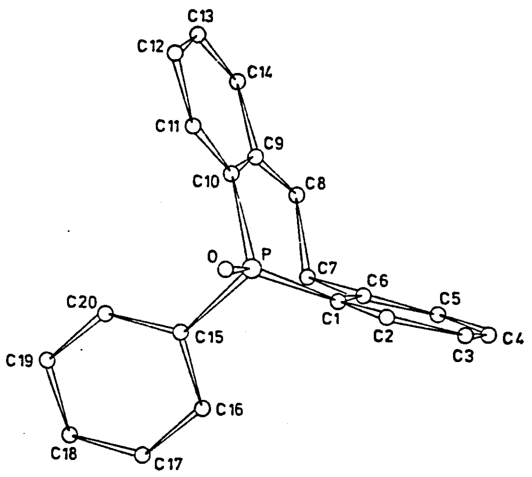


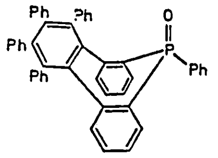
Figure. Molecular structure and atom numbering scheme for 3. Hydrogen atoms have been omitted for clarity.

Table III. Mean planes through groups of atoms and distances (Å) of relevant atoms in square brackets.

Ring A: C9–C14
[C9, 0.011; C10, 0.005; C11, —0.017; C12, 0.013; C13, 0.004; C14, —0.016; P, —0.060; C8, —0.010]

Ring B: C1–C6
[C1, 0.009; C2, —0.001; C3, 0.012; C4, —0.012; C5, 0.001; C6, 0.009; P, —0.108; C7, 0.033]

Ring C: C15–C20
[C15, —0.012; C16, 0.006; C17, 0.000; C18, —0.001; C19, —0.004; C20, 0.011; P, 0.165]



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5-phenyl-tribenzo[b,d,f]phosphepin oxide (4). The presence of such a substituted phenyl group across C7 and C8 in 4 not only introduces major conformational changes but would also appear to be responsible for considerable strain within the seven-membered ring. Thus while the C6–C7, C8–C9 bonds in 3 adopt a staggered arrangement with respect to the C7–C8 direction, such that the C9–C8–C7–C6 torsion angle is 67.4°, in 4 the equivalent bonds are effectively eclipsed with the torsion angle being 3.3°. In contrast to the unexpectedly low endocyclic angle at phosphorus in 4, 99.0(5)°, the corresponding angle of 107.2(3)° found in 3 lies much closer to the regular tetrahedral value. The exocyclic angles at phosphorus in the present compound vary from 106.5–111.9(3)°, while the P–O bond distance of 1.506(4) Å is similar to the value of 1.49 Å found in 4.

That the endocyclic angle at P in 3 is very close to the ideal tetrahedral angle indicates the absence of significant bond angle strain, thereby supporting our earlier suggestions in connection with the chemistry of the related phosphonium salts. The study also lends some support to our suggestion [1] that the above seven-membered ring system may prefer to occupy diequatorial positions in intermediate phosphoranes (with an ideal endocyclic angle of 120°) rather than an apical-equatorial position where the ideal endocyclic angle would be only 90°. Clearly there is less bond angle deformation in passing from the quaternary derivative to the former than to the latter arrangement.

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