The investigation of novel charge transfer systems.

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THE INVESTIGATION OF NOVEL CHARGE TRANSFER SYSTEMS

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ABSTRACT

In this project a number of synthetic procedures were investigated with a view to preparing a new type of charge transfer polymer system having a structure based on that of side chain liquid crystal polymers, in that the hoped for polymer was composed of charge transfer acceptors connected to a polymer backbone via a flexible alkyl spacer linkage. As part of this work new charge transfer complexes were prepared some of which have shown possible novel properties, such as, co-operative magnetic effects and film forming capabilities. Finally, in order to characterise materials prepared, a Faraday magnetic susceptibility balance and instrumentation for measuring electrical conductivity has been built.

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1.General Introduction.

1.1. Molecular Electronics.

Over the last few years the effects of electromagnetic radiation on matter have received considerable attention with a view to the development of new materials for devices and applications in which the properties of the electromagnetic radiation can be harnessed or modified. This is a large area of research which encompasses optics and electro-optics, computers, display devices, biological sensors, and superconductors. This area of science has become known as Molecular Electronics[1].

The work described here is associated with electrically conducting organic substances. Such materials take different forms including polymers like polyacetylene (PA), conducting crystals such as charge transfer complexes (CTCs), and novel materials that are rather like molecular wires such as the square planar organo-platinum salts.

There follows a brief review of the different types of conducting organic system, some of their applications and an outline of the aims of this project. It should be noted that this is not a comprehensive review, as at the time of writing there are approximately ten publications in the general area each week.

1.2. Electrical Conductivity.

Before discussing organic conducting systems it is necessary to describe electrical conductivity. There are many books that explain electrical conductivity in detail[2] and only a brief overview is given here.

1.2.1. Band Theory.[3]

Electrical conductivity is the result of the flow of free electrons through a material. Electrons in materials are located in what are termed bands. There are two types of band:

1. The valence band which is associated with the bonding electron orbitals of a material.

2. The conduction band which is usually associated with non-bonding or anti-bonding orbitals of a material.

In familiar conducting systems, such as copper metal, electrons in the valence band are bound to particular sites, whereas electrons in the conduction band are free to move through the material. It is these electrons that give rise to electrical conductivity. However, in certain conjugated π-systems the role of the π-bonding orbitals is not clear cut.

1.2.2. Factors Affecting Conduction.

The exact nature of electrical conductivity depends on three main factors, as follows:

1. The mean free path of the electron. This is the distance the electron travels before it is scattered by the system. Scattering can arise from interactions both with other electrons in the system, and with lattice vibrations (phonons). These are temperature dependent in that as the temperature increases so does the lattice vibration and electron momentum. This in turn increases the probability of an electron interacting with either the lattice or other electrons.

2. The concentration of defects, for example impurities, grain boundaries and twin domains. These are intrinsic for the material and in general give rise to a temperature independent resistance. Defects not only affect the mean free path, but can also change the band structure and phonon modes present.

3. The number of electrons present in the conduction band. This also affects the conductivity in that the greater the number of electrons in the conduction band the lower is the resistance of the material.

Electrons in the conduction band have gained enough energy to be promoted from the valence band. This means that the width of the energy gap and the temperature of the material will both affect the number of electrons in the conduction band. Obviously as the temperature increases a greater number of electrons can gain enough energy to be promoted to the conduction band. Also the closer the valence band is to the conduction band the less energy will be required for promotion.

1.2.3. Band Theory Controlled Conductivity.

The distance apart in energy of the two bands gives rise to three classes of materials (see Fig.1.1), as follows:

1. Metallic type conductors (Fig.1.1a). If the valence and conduction bands are very close together or overlap there are likely to be free electrons in the conduction band. Thus the electrical conductivity is high and decreases with increasing temperature due to increased scattering.

2. Semiconductors (Fig.1.1b). These are characterised by a greater energy difference between the valence and conduction bands. This means that the temperature will determine how many electrons are in the conduction band and hence the conductivity. Thus semiconductors show an increasing conductivity with respect to temperature as more electrons become available for conduction. However, at sufficiently high temperatures scattering begins to dominate and the conductivity starts to decrease with increasing temperature.

3. Insulators (Fig.1.1c). Here the conduction band is so far away (energetically) from the valence band that the majority of electrons cannot have sufficient energy to jump the energy gap. Thus such materials exhibit very low or no electrical conductivity.

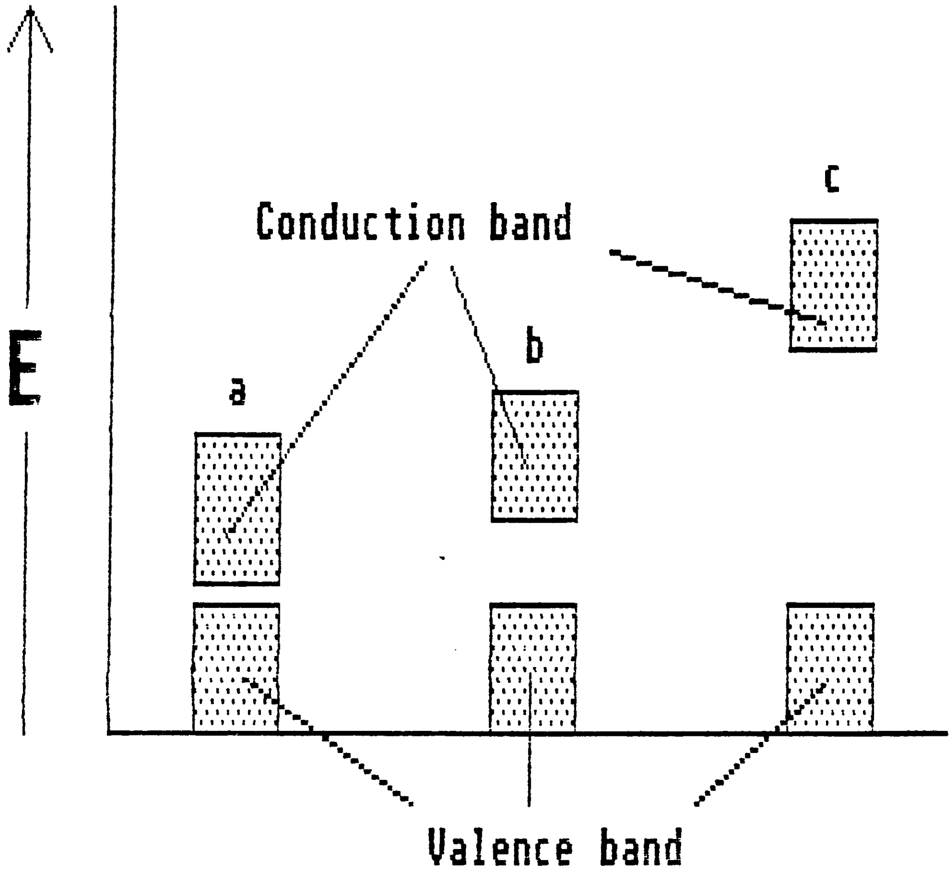


Fig.1.1.
Band Theory Schematic.

1.2.4. Other Types Of Conductivity.

There are two other major types of conductivity. These are as follows:

1. Superconduction.[4] This is a special form of conduction in that electrons move without encountering any resistance. It has received a lot of attention following the discovery of high temperature (high T_c) superconducting ceramics in 1986[5]. The theory of superconductivity is complex and not fully understood. No attempt is made to explain the theory here as it was not within the scope of the work undertaken.

However, a good explanation of high temperature superconductivity is given by J.W.Lynn[6].

2. Ionic Conduction.[7] Here ions conduct charge via the movement of charged particles through a matrix in response to a potential difference, for example in electrolytic cells or solid state batteries[8].

1.2.5. Definition of Conductivity.[9]

Electrical conductivity is defined as the reciprocal of resistivity (ρ) and is given the Greek letter sigma (σ). Its unit is (ohm-metre)$^{-1}$ ($\Omega^{-1}m^{-1}$). However, we give conductivity values in $\Omega^{-1}cm^{-1}$ as is commonplace in the literature. Equation 1.1 shows how σ is derived.

$$\rho = RA/d \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1.1.$$

$$\sigma = 1/\rho$$

Alternatively it can be defined as the ratio between current density (J), defined as I/A and the applied electrical field (E), defined as V/d.

Where:

R = Resistance in ohms.
A = Cross section in cms^2.
d = Sample length in cms.
I = Current measured in amps.
V = Voltage applied across the sample.
ρ = Resistivity.

1.3. Magnetic Susceptibility.

Magnetic susceptibility measurement is a useful technique for characterising materials, and is closely related to electrical conductivity in that transitions observed in electrical conductivity with respect to temperature change are often mirrored by the magnetic susceptibility. Also, accurate magnetic susceptibility data is more easily obtained than accurate data for electrical conductivity, despite the apparatus being more complicated. Problems associated with, for example, sample size and shape are less critical than for electrical conductivity measurement. For instance powder samples can be used as long as the sample is packed carefully.

1.3.1. Information Obtained From Magnetic Susceptibility.

Some of the physical properties that can be examined are:

1. Onset of the Peierls transition[10], where lattice constraints cause an ordered structure to become disordered with the formation of a charge density wave causing a band gap to open in the conduction band, with consequent change from conductor to insulator.

2. Evidence of solvent inclusion[11], where it has been suggested that as pockets of trapped solvent, used in the preparation of charge transfer complexes, freeze

they contract changing the ordering of the system. This possible effect can sometimes be observed as a step in the magnetic susceptibility data at approximately the freezing point of the solvent used.

3. Critical temperature for superconductivity[12].

4. Number of unpaired electrons in a sample.

1.3.2. Theory Of Magnetic Susceptibility.

Some of the relevant theory behind magnetism is laid out below and there are numerous books on the subject[13-15].

1.3.3. Unit Of Magnetic Susceptibility.[16]

It is still common to measure susceptibility in electromagnetic units (emu). Typical values are 10^{-4} emu mol^{-1} for paramagnetic materials (see section 1.3,4) and 10^{-6} emu mol^{-1} for diamagnetic materials (see section 1.3,5). The conversion to S.I. units involves multiplying the emu units by 4π, giving a dimensionless value. The symbol for magnetic susceptibility is the Greek letter chi (χ). Magnetic susceptibility is calculated from the formula given below:

$$\chi_v = \frac{M}{H} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1.2.$$

Where:

M = The magnetisation of the material.
H = The intensity of the applied magnetic field.
χ_v = The volume susceptibility.

To convert to gram susceptibility (χ_g) the volume susceptibility is divided by the density. From this the molar susceptibility (χ_m) can be calculated by multiplying the gram susceptibility by the relative molecular mass.

1.3.4. Paramagnetism.

Paramagnetism arises from electrons moving in unfilled orbitals or having unpaired electron spins, which therefore give rise to a permanent dipole. Under the influence of a magnetic field the individual dipoles experience a torque that aligns them parallel to the applied field, increasing the total field and resulting in a positive susceptibility. Furthermore paramagnetism is temperature dependent. As the temperature decreases there is less thermal energy available to disrupt the ordering effect of the applied magnetic field. This results in a temperature dependency, with susceptibility being inversely proportional to temperature. The dependence upon temperature is called the Curie-Weiss relationship (see equation. 1.3).

$$\chi_v = \frac{C}{T-\theta} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots 1.3.$$

Where:

T = Is the Temperature (Kelvin).
χ_v = Is the volume susceptibility.
θ and C = Constants for the material.

1.3.5. Diamagnetism.

Diamagnetism is a property of all matter and comes about by the change in electron orbital angular momentum under the influence of an applied magnetic field causing the material to move to an area of lower field strength. Diamagnetism is temperature independent.

1.3.6. Co-operative Magnetism.

In co-operative magnetic materials, as with paramagnetics, the magnetic dipoles line up on the application of an external field. Unlike paramagnetic materials, the alignment persists even when the applied field is removed, forming a permanent magnet. Areas of similar alignment are called domains which can possess a large magnetic moment depending upon the type of co-operative magnetism present. There are three types of co-operative magnetism which are outlined below:

1. If all the dipoles are aligned parallel the result is a permanent magnetic moment and a high positive susceptibility. This is called ferromagnetism.

2. If half the dipoles are aligned in one direction and the other half are aligned in the opposite direction (antiparallel) and are of equal magnitude, the material is antiferromagnetic. As the opposing dipoles have equal magnitude there is no net susceptibility.

3. The final type of co-operative magnetism is ferrimagnetism and results from a two component system in which the opposite facing dipoles are of different magnitudes. Here there is a small positive susceptibility, representing the difference in magnitude of the opposing dipoles.

The one factor in common with all these types of co-operative magnetic effect is that the dipoles remain aligned after the applied magnetic field has been removed. However, this is only true below a specific temperature, (the Curie temperature for a particular material). Above this temperature the energy of the system is larger than the forces keeping the dipoles aligned, and the material then behaves like a paramagnet because alignment is not preserved.

1.4. Associated Topics.

It is useful to briefly ~~look~~ at two topics that are relevant, and that feature in the planning for the preparative parts of the work to be described.

1.4.1. Liquid Crystal (Mesomorphic) Phase.[17]

Liquid crystals(LC) have attracted much attention in the last few years because their unusual properties make them useful for display devices.

The liquid crystalline state is an intermediate state between isotropic liquid and largely ordered solid. An essential property of the LC state is that the molecules are highly anisotropic in terms of their geometry.

1.4.2. Liquid Crystal Molecules.[18]

Highly anisotropic properties are found in molecules that are usually long and narrow, and often consist of two parts:

1. A head section, usually composed of an aromatic ring system.
2. A tail section, usually an aliphatic chain.

Possibly the best example is provided by alkyl cyanobiphenyls (see Fig.1.2).

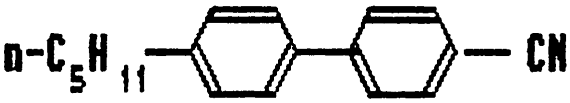
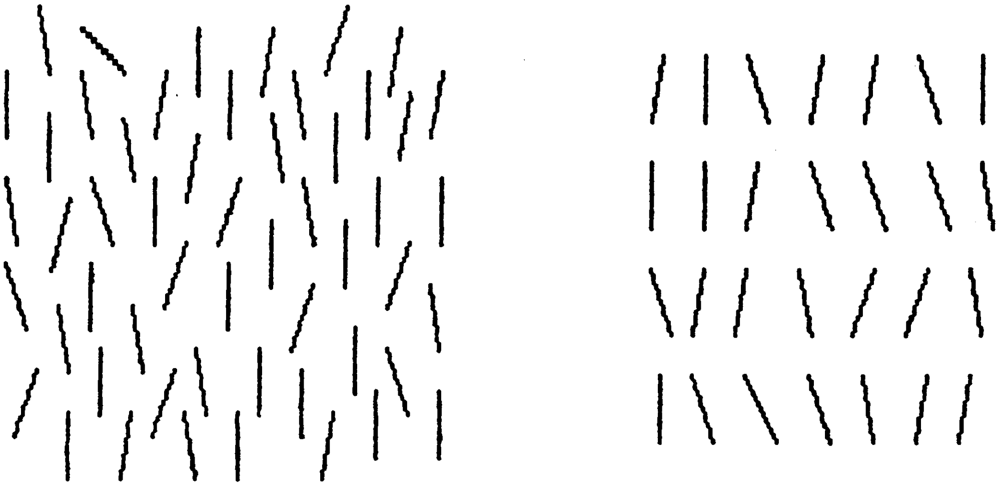


Fig.1.2.
4'-n-Pentyl-4-cyanobiphenyl Molecule.

1.4.3. Physical Properties.

LCs have proved to be interesting molecules because of their ability to form ordered phases. There are various categories of ordered phase, ranging from long range order only (nematic) to stratified layer structures (smectics). See Fig.1.3.



Nematic Phase.

Smectic Phase.

Fig.1.3.
Different Types Of LC Phases.

The alkyl cyanobiphenyls are examples of thermotropic LCs. This is because their phase is dependent on temperature, with the molecules going through different phases at different temperatures (see Fig.1.4). If the LCs' phase behaviour is solvent dependent they are called lyotropic rather than thermotropic.

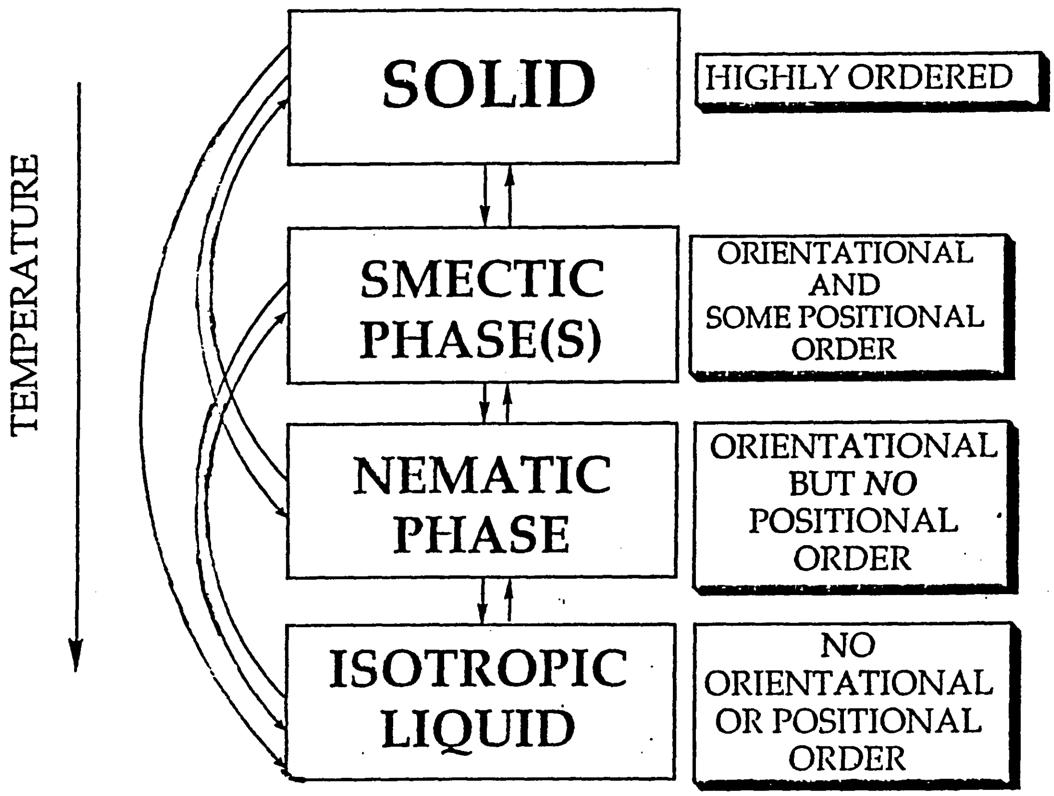


Fig.1.4.
Different Liquid Crystal Phases.

1.4.4. Liquid Crystal Polymers (LCP).

Thermotropic LCs have been polymer bound and shown to be still capable of ordered phase formation. In other words LCPs show that co-operative molecular behaviour can still occur macroscopically when the molecules are bound to a suitable polymer. It was this aspect that was of most interest in the work described here.

These types of material have become important in the last few years not only for their potential as molecular electronic materials but also for their mechanical properties[19].

We are interested in looking at LCPs because their microstructure gives some clues concerning the ordering of the side chains attached to polymers.

There are two main types of LCP as outlined below:

1.4.5. Main Chain LCP.[20]

In main chain LCPs mesogenic (LC-phase inducing) groups are located along the main chain, i.e. the polymer backbone itself (Fig.1.5).

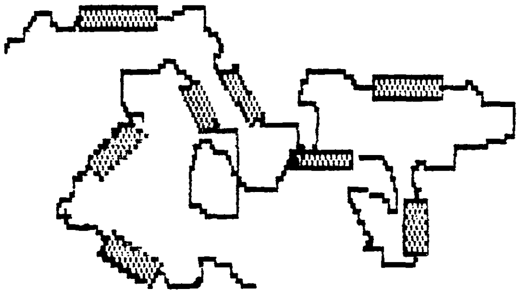


Fig.1.5.
Main Chain Liquid Crystal Polymer
(No Ordering As Shown).

1.4.6. Side Chain LCP.[21]

These differ from main chain LCPs in that the LC units are connected to the main polymer chain via a spacer group, usually an alkyl group such as $(CH_2)_n$ (see Fig.1.6). The effect of the spacer is to decouple the motions of the mesogens from those of the polymer main chain, enabling them to order. The length of the spacer groups affects the decoupling of the mesogens. Decoupling is increased as the length of the spacer increases, and the mesogens can adopt phases of higher ordering (eg. smectic rather than nematic).

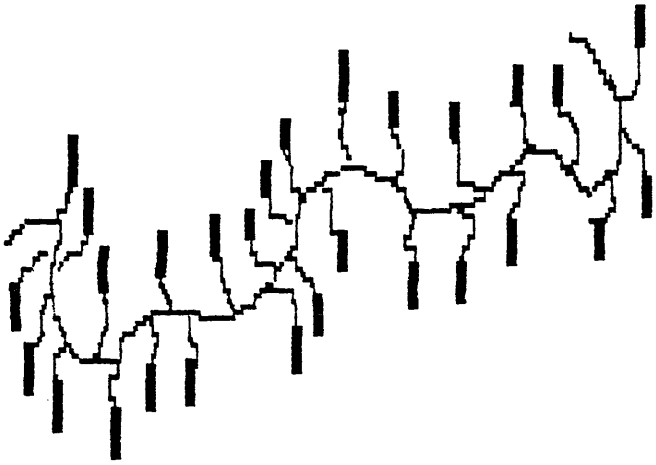


Fig.1.6.
Side Chain Liquid Crystal Polymer
(Shown With Nematic Ordering).

In common with LCs, LCPs exhibit ordered phases (smectic and/or nematic), demonstrating the effectiveness of the spacer group in decoupling the mesogens from the randomly twisted and coiled polymer backbone. This indicates that ordered phases may be possible in an analogous system where CT units are attached to a polymer backbone via a flexible spacer.

One advantage LCPs have over conventional LCs is that particular states can be "frozen in" due to the rigidity of the polymer in a glassy phase (below the glass transition temperature, T_g). This is achieved in for example data storage[22-23], where a LASER locally heats the polymer above T_g. The order of the mesogens can be modified, by for example a magnetic or electric field. The orientation is then frozen in as the LASER moves on and the polymer cools below T_g.

1.4.7. Langmuir-Blodgett Films.[24,1]

One approach to the preparation of ordered organic systems is the fabrication of Langmuir-Blodgett films. Although not part of this project it gives an insight into an alternative method of preparation of ordered structures that are required for good electrical conductivity in CT complexes. Also the approach needed in tailoring molecules for the production of successful LB films is similar to that required when forming a CT polymer of the type we propose.

1.4.8. Preparation Of Monolayers.

Monolayers on a support (substrate) are prepared by dipping the substrate (for example a glass slide) into a tank containing a monolayer of molecules on the surface of water. To keep the monolayer intact and at a constant pressure a moveable barrier is employed, compressing the monolayer at the same rate as material is deposited on the substrate. Repeated dipping of the substrate enables layered structures to be built up.

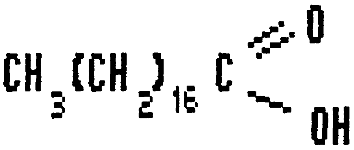
1.4.9. Molecular Structure.

Molecules have to be prepared that will form monolayers on water and can be described as "amphiphilic" in that they are composed of two parts. The two components are:

1. A hydrophobic part. This is often a long alkyl chain and is insoluble in water.

2. A hydrophilic part. This is a group that is soluble in water, such as a carboxylic acid function or carboxylate salt. A good example of an amphiphilic molecule is stearic acid (see Fig.1.7).

Monolayers are formed because the hydrophilic end dissolves in the water, whereas the hydrophobic end tries to keep as far away from the water as possible. This means that the molecules line up normal to the surface. The movable barrier ensures that there is a constant pressure applied to the system, this pressure being sufficent to maintain the monolayer.



$$CH_3(CH_2)_{16}C\begin{matrix}\nearrow O \\ \searrow OH\end{matrix}$$

Fig.1.7.
Stearic Acid Molecule.

1.4.10. Synthetic Requirements.

Although stearic acid forms good monolayers it does not possess any useful molecular electronic properties. To take advantage of LB films molecular electronic molecules need to be modified so that they can form monolayers on the surface of water. This entails putting hydrophobic groups onto electroactive hydrophilic molecules or vice versa. Work of this sort has attracted considerable attention in the last few years with groups working in areas such as modified conducting polymers [25] and charge transfer complexes[26,27]. Fig.1,8 shows a pyrrole molecule modified for incorporation into LB films.

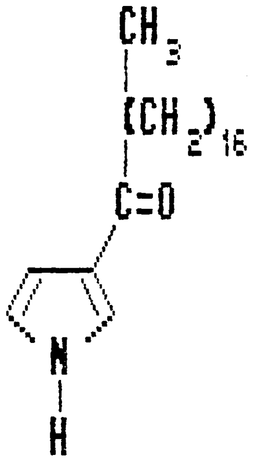


Fig.1.8.
Pyrrole Modified For LB Films
From Ref.25.

1.5. Organic Conducting Systems.

There are three main types of organic conducting systems as follows :

1. Charge transfer complexes[28].
2. Transition metal complex conductors[29].
3. Conducting polymers[30].

There follows an explanation of the conduction process in these types of materials.

1.5.1. Charge Transfer Complexes.

Interest in these compounds stems from the possibility that for organic molecular systems they can show novel properties such as superconductivity[31], semi-conductivity[32], metallic conductivity[33,34], non-linear optics[35], electrochromism and co-operative magnetism[36-38], with applications such as display devices, molecular rectifiers[39-41], frequency doublers and optical switches.

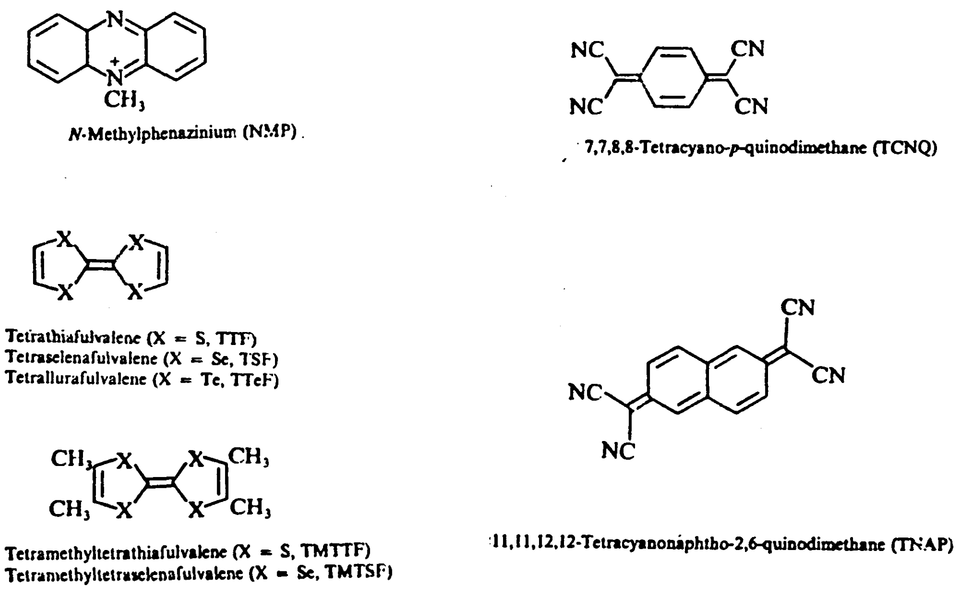
These materials consist of two components:

1. Electron Donors. These are molecules having a low ionisation energy that are able to donate electrons to other molecules. A typical example of a donor is N-methylphenazine (NMP). Its structure, with that of some other important donors, is given in Fig.1.9.

2. Electron Acceptors. These are molecules that are able to accept electrons and stabilise a resulting negative charge.

One of the best acceptors is 7,7,8,8-tetracyano-p-quinodimethane (TCNQ)[42] because it is a flat conjugated molecule composed of a quinoid ring to which are attached four cyano groups having a high electron affinity, enabling the molecule to accept an electron from almost any other species[43]. Its structure, and that of 11,11,12,12-tetracyanonaphtho-2,6-quinodimethane (TNAP), another common acceptor, is shown in Fig.1.9.

These materials are often referred to as salts. In this description in general salts are defined as materials that possess integral charge transfer, whereas complexes refer to materials that possess non-integral charge transfer.



N-Methylphenazinium (NMP)

7,7,8,8-Tetracyano-*p*-quinodimethane (TCNQ)

Tetrathiafulvalene (X = S, TTF)
Tetraselenafulvalene (X = Se, TSF)
Tetrallurafulvalene (X = Te, TTeF)

Tetramethyltetrathiafulvalene (X = S, TMTTF)
Tetramethyltetraselenafulvalene (X = Se, TMTSF)

11,11,12,12-Tetracyanonaphtho-2,6-quinodimethane (TNAP)

Donors Acceptors

Fig.1.9.
Some Examples Of CT Donor And Acceptor Molecules
Ref.44.

1.5.2. Molecular Properties Of Acceptors And Donors.

There are four major factors that make molecules suitable as CT acceptors and donors. These are:

1. They tend to be planar structures, often aromatic systems. However, constituents of the complex may be single atoms, for example electron donors such as sodium or lithium.

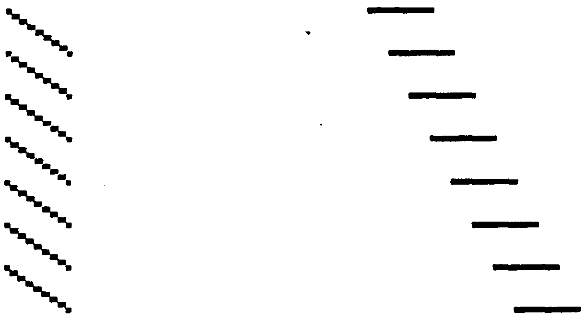
2. They are highly conjugated molecules, that is their structures contain several alternating double and single bonds, and can result in a large amount of delocalisation of electrons allowing electronic charge movement within the individual molecules, although charge tends to be localised on certain sites (near the CN groups in the case of TCNQ). Also the large amount of conjugation helps pin internal rotation by reducing the single bond nature, thus helping to keep the structure in a planer configuration.

3. They possess chemical groups that help stabilise charge, such as cyano groups in electron acceptors (eg TCNQ).

4. They should contain unpaired electrons, by this we mean that the complex formed requires unpaired electrons to allow conduction, for example TCNQ forms a radical anion in its charge transfer state.

1.5.3. Electrical Conductivity In CT Complexes.

As donor and/or acceptor molecules are planar, they can stack together rather like a pack of playing cards, giving rise to ordered columns of molecules/ions which may be tilted (Fig.1.10a) and/or be laterally displaced through the stack (Fig.1.10b).



a. Tilted stack.

b. Lateral displacement of stack.

Solid lines represent CT molecules.

Fig.1.10
Diagram Of Tilted And Laterally Displaced Stacks.

Conductivity takes place through the columns via hopping of electrons between adjacent molecules in the stacks by way of π-orbitals that project perpendicularly out of the plane of the molecules. One consequence of this is that the conductivity is highly anisotropic, with high carrier mobility only through the stacks[45].

1.5.4. Types Of Molecular Stacking.

The type of stacking has a dramatic effect on the electrical properties of the complex. There are two principal forms of stacking, these being:

1. Mixed stacking. Donor and acceptor species alternate with each other in the same column[46]. Such compounds tend to be low in conductivity because the conducting molecules are separated by non-conducting molecules/ions so that the integrity of the conducting element is broken. A good example of this is Na^+TCNQ^- [47] (see Fig.1.11).

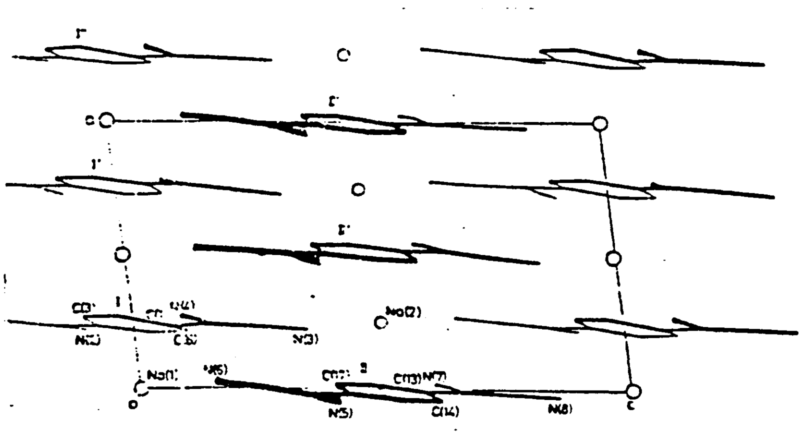
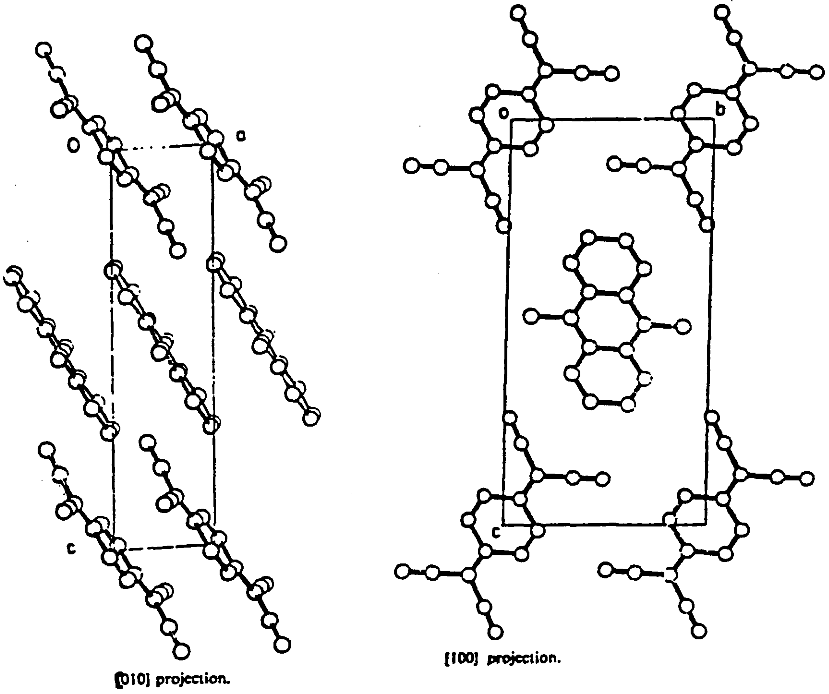


Fig.1.11.
Na^+TCNQ^- A Mixed Stacking Complex. From Ref.47.

2. Segregated stacking. Here the donor and acceptor molecules form separate columns adjacent to each other.

The complex formed between NMP and TCNQ is one of the best examples of segregated stacking complexes[43], producing needle crystals approximately 0.5mm in length with a room temperature metallic type conductivity of 200 Ω^{-1} cm^{-1} (see Fig.1.12).



[010] projection.

[100] projection.

Fig.1.12.
NMP-TCNQ An Example Of A Segregated Stacking Complex.
From Ref.43.

Segregated stacking gives rise to the highest conductivity CT complexes, as electrons are able to move through a stack unhindered[48]. It should be noted that the donor and acceptor stacks need not possess the same configuration[49]. An example of this is shown below in Fig.1.13, where the donors stack alongside the acceptor stack.

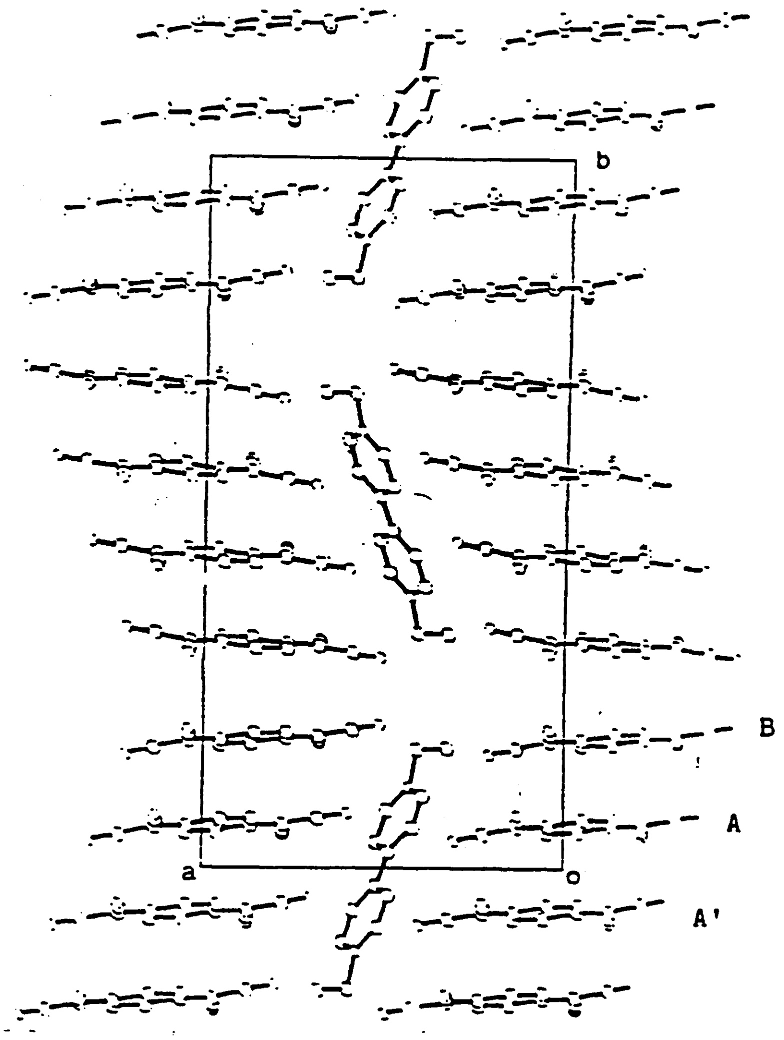


Fig. 1.13.
N,N,[diethyl-4,4'bipyridinium]$^{2+}$(TCNQ)$_4^{2-}$ From Ref.49.

1.5.5. Simple And Complex Salts/CT Complexes.

In addition to the different types of stacking the ratio of donors to acceptors can vary.

1. Simple salts/complexes are materials that possess a 1:1 ratio of cations to anions[45].

2. Complex salts/complexes are materials that contain a non-integral ratio of acceptors to donors[50].

1.5.6. Additional Considerations For High Conductivity.

1. The most conductive complexes are associated with only partial charge transfer due to the manner in which electrons move through, the acceptor stacks, (in for example the TCNQ system). In fully ionized complexes every acceptor molecule carries a negative charge and movement of electrons through the stack would involve placing two electrons on one acceptor site. The large amount of energy required to achieve this inhibits electron mobility. However, if charge transfer is only partial then there is a proportion of uncharged sites to which electrons can hop, allowing electrons to move between adjacent acceptor sites[49].

2. The shape of the constituent molecules/ions plays an important role in determining stacking characteristics of the material. For example bulky alkyl groups can hinder stacking[49], or force individual molecules further from each other demanding greater energy for site hopping of electrons. Both outcomes result in lower conductivity.

3. Defects such as trapped solvent molecules may have an effect on the conductivity[11]. It is thought that, on freezing, solvent may cause the acceptor stacks to buckle, thus disrupting electron flow. However, this effect is not universally accepted[51].

4. Metallic type conductivity requires extremely pure and highly ordered crystals to obtain a uniform conduction band structure. Disordered structures result in the opening up of band gaps resulting in semiconductive type behaviour [33].

1.6. Transition Metal Complex Conductors.

As these types of material did not form any part of our investigations only a brief mention of the different materials is given here. For a more thorough treatment see J.Ferraro and J.Williams[29].

Some of these materials were prepared as early as 1842[52] and fall into three main types which are outlined below:

1. Platinate Salts.[53] These materials have planar molecules that contain a platinum atom surrounded by ligands such as cyanide or oxalate groups in a partially oxidised form. They can form molecular stacks in a similar manner to CT complexes, but the conduction mechanism differs in that electron transport is via the overlap of the dz^2 orbitals on the central platinum atoms (see Fig.1.14).

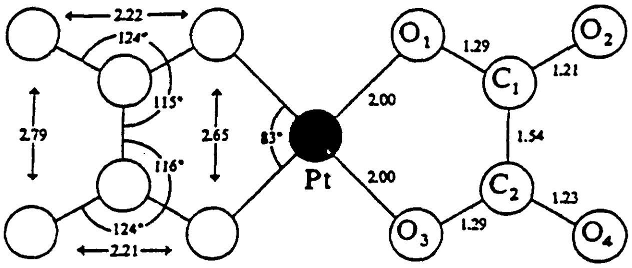


Fig.1.14.
Platinate Salts From Ref.29.

The platinates, in common with all other conducting organics, exhibit a high degree of anisotropy. For example in $Cu_{0.84}[Pt(C_2O_4)_2].7H_2O$ the conductivity along the Pt chains is 3.6-5.8 Ω^{-1} cm^{-1} with a value of 4.0-5.9x10^{-3} $\Omega^{-1}cm^{-1}$ normal to the Pt chain[54]. Conduction occurs only through the platinum dz^2 orbitals, the surrounding ligands being insulating. The unit as a whole is rather like a coated wire. Unfortunatly, like CT complexes, they form short brittle crystals which in some cases can take months to prepare[55].

<u>2. Metal Dithiolate Complexes.</u> These complexes have been known since 1962. They are composed of a metal atom bound to a dithiolate species giving a general formula $[M(S_2C_2R_2)_2]^{n-}$, where M is a transition metal atom and R may be CN,Me,H,CF_3 (see structure given in Fig.1.15).

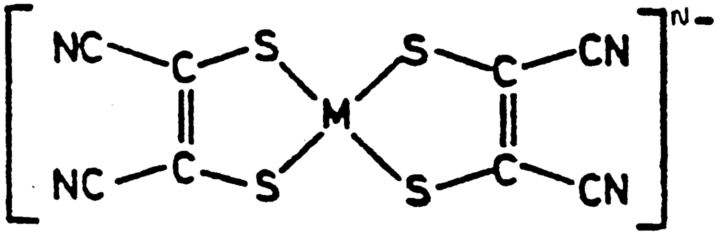


Fig.1.15.
Structure Of Metal Dithiolate Complex.

The method of conduction is similar to that of the platinate salts. As with TCNQ the cyano groups help stabilise charge and coulomb-coulomb repulsion by delocalisation, producing complexes having a range of conductivity from 1×10^{-8} to 1.1 Ω^{-1} cm^{-1} [29]. Single crystal metallic conduction of 30- 200 Ω^{-1} cm^{-1} has been reported by Underhill et.al.[56].

3. Transition Element Macrocyclic Ligand Complexes.[57]

These are composed of a central transition metal atom surrounded by macromolecular ligands, and are rendered conductive when doped by I_2 or Br_2, resulting in a stack of donors that are partially oxidised and show incomplete charge transfer. Unlike the platinate salts where the partial charge is sited on the metal atoms, in this case the partial charge is associated with the macrocycle as a whole[29]. Some structures are shown below in Fig.1.16.

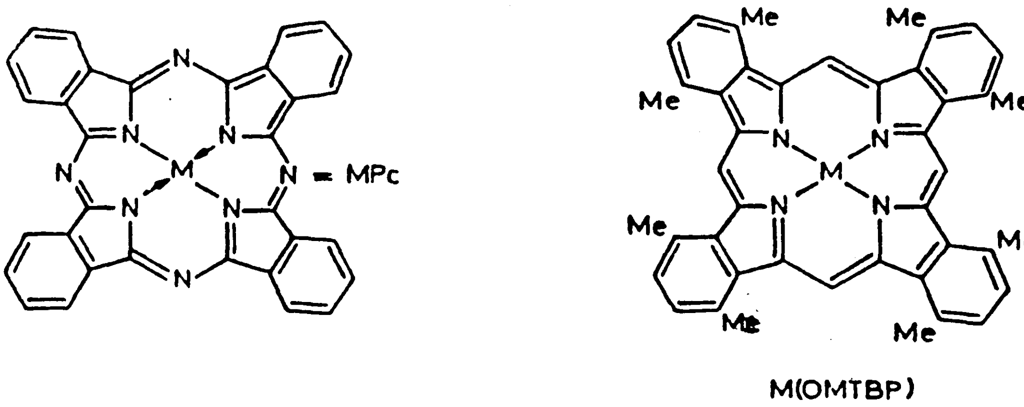


Fig.1.16.
Macrocycle Structures From Ref.29.

1.7. Polymeric Systems.

Over the last thirty years plastics have become increasingly important and there are many publications concerned with their physical and chemical properties[2a]. Traditionally they have been thought of as electrical insulators, finding widespread use in such applications as flexible insulating coatings for electrical transmission wires. However, the last few years have seen a lot of interest in the area of conducting polymers.

There are two different types of conducting polymeric systems, intrinsic and extrinsic conducting polymers.

1. Intrinsic conduction arises from the movement of electrons through the system via a conjugated π-system i.e. π-bond overlap in double bonds with resulting delocalisation of charge.

2. Extrinsic conduction arises when conducting species such as metallic flakes or CT complexes are added to a non-conducting matrix to render the polymer composite conductive. These are called filled polymers.

There is a grey area between these two extremes to which most conducting organic systems belong. Most intrinsically conducting polymers will not conduct readily unless they are doped with electrons or holes, often in high percentages, for example some workers have reported that such materials as butadiene-styrene co-polymers have been persuaded to conduct [59].

1.7.1. Intrinsic Conducting Polymers.

These polymers are composed of extensive conjugated polymer chains. The conjugated nature of the polymer system is essential for conduction. Polyacetylene(PA), the best known example, was synthesised as early as 1958 by Natta et.al.[60]. Since then there have been numerous modifications and diversifications upon the original polymers to encompass materials that contain nitrogen[61] and sulphur[62,63]. These show conductivities that range over many orders of magnitude. Fig 1.17 shows some of the different types of polymer that have been investigated.

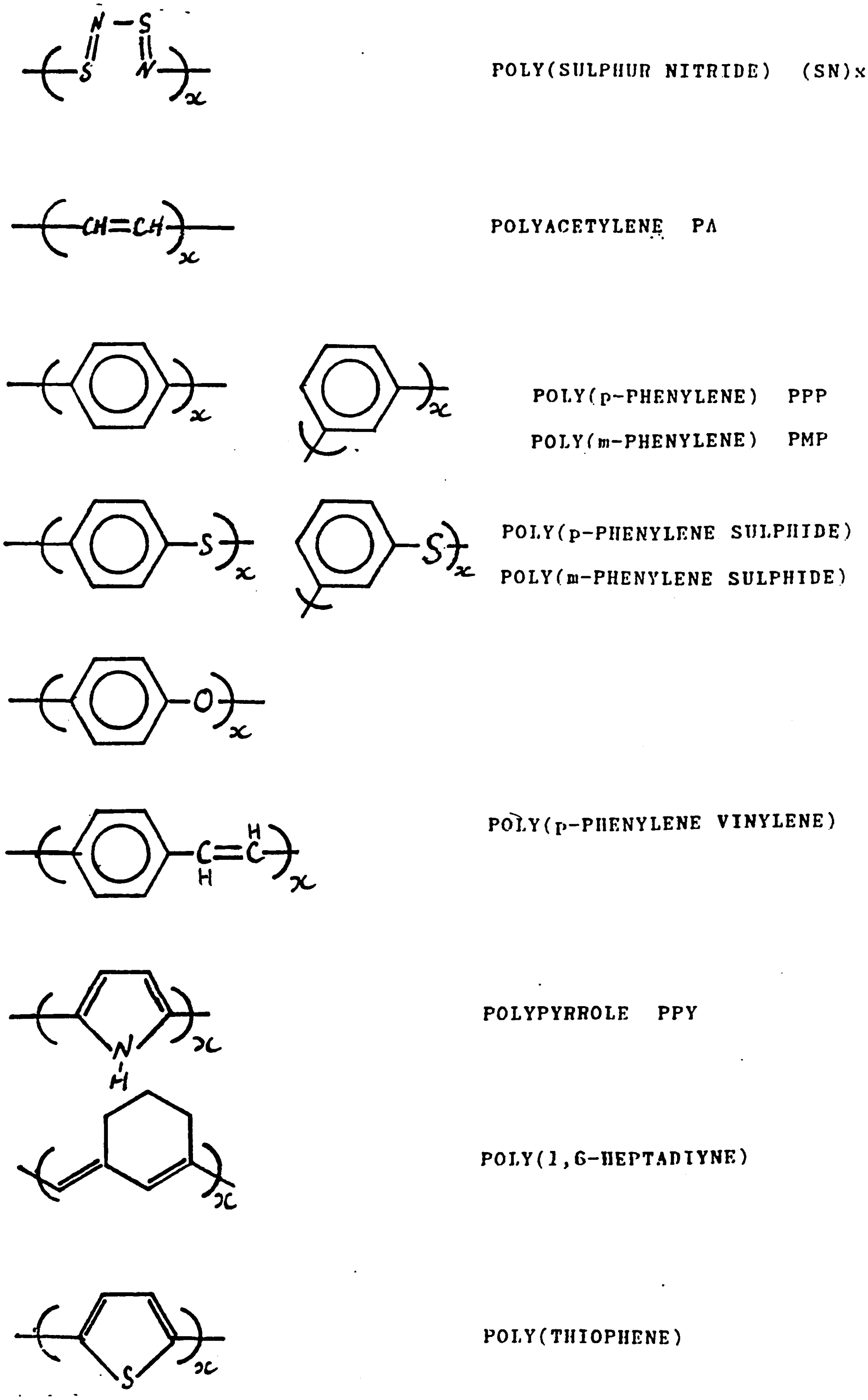


Fig.1.17.
Some Conducting Polymers.

1.7.2. Conducting Mechanism Of Intrinsic Conducting Polymers.

Only a very brief description of the conduction mechanism is given here, because it is complicated, not fully understood and it was not an important part of the work undertaken in this project. A more detailed general description is given by J.R.Reynolds et.al.[64]

Conductivity is achieved because charge is able to move through the conjugated π-system of the polymer. This leads to an anisotropic conductor[65], with the highest conductivity being along the polymer chains, and the highest resistance where charge carriers have to "jump" between polymer chains. However, the polymer on its own is not very conductive. Polyenes in their crystalline state tend to be semiconductors with conductivities that can be less than $10^{-14}\ \Omega^{-1}\ cm^{-1}$ [66]. These polymers are rendered conductive by the introduction of charge carriers (doping) which are then able to move along the conjugated polymer chains and hop between chains.

Fig.1.18 below shows an example of oxidative doping in polyacetylene (PA), where an electron has been removed from the π-system giving rise to a delocalised radical ion defect called a soliton. The charged sites generated require charge compensation. This is achieved by anions penetrating the polymer matrix during doping.

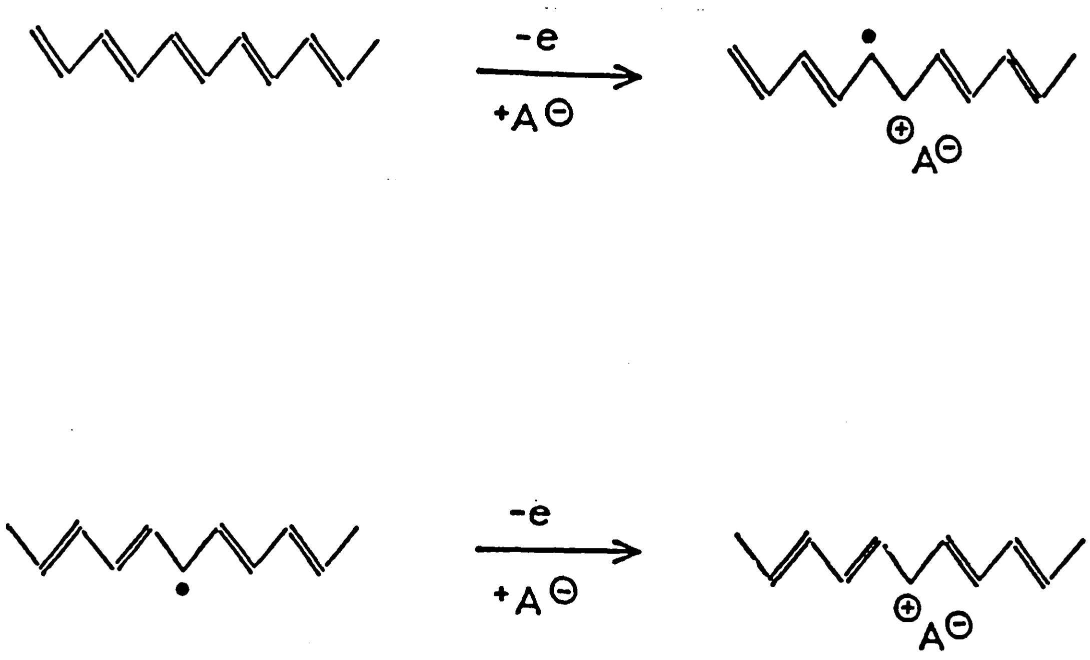


Fig.1.18.
Doping Of PA.

It should be emphasised that conductivity is by the movement of carriers along the polymer backbone and hopping between polymer chains and not by the movement of ions through the polymer matrix.

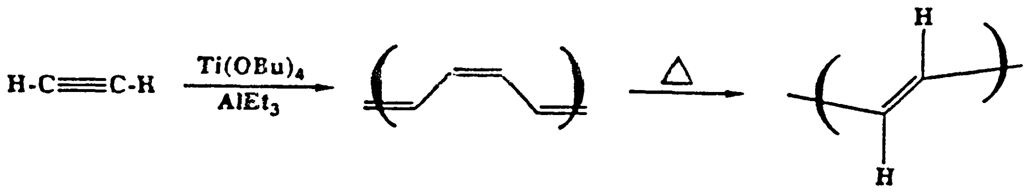
Dopants are often toxic vapours like iodine or arsenic compounds such as arsenic pentafluoride[67]. These are required in large amounts, for example 10% per carbon atom[68], compared to fractions of a percent for dopants in conventional semiconductors[69].

1.7.3. Modifications To And Diversifications From The Archetype Intrinsic Conducting Polymer (PA).

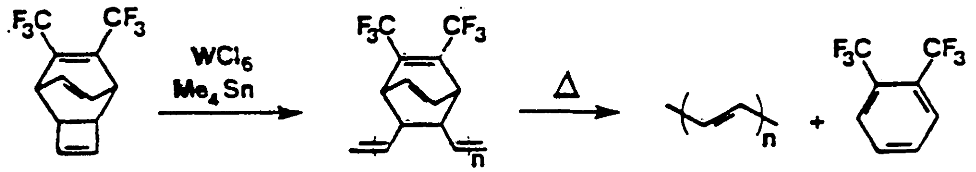
PA is the archetype intrinsically conducting polymer, the simplest and the first to be prepared. One of the original problems encountered with polyenes, was the large number of double bonds which restrict bond rotation leading to intractable materials.

Since these early discoveries there have been numerous modifications to produce polyenes of many different types. Some examples of these modifications are outlined below:

1. Different synthetic pathways. For example most research has been done on the "Shirakawa" route (Fig.1.19a). Here PA is prepared from the polymerisation of acetylene using a Ziegler-Natta catalyst[70], giving an insoluble polymer of highly crystalline fibrils which form a mat, whereas the so called "Durham route" (Fig.1.19b) uses soluble precursors that on the elimination of some small molecules give rise to fully conjugated $(CH)_x$ chains. One advantage of this route is that the morphology can be more easily controlled than with other routes[71].



a. Shirakawa Route For The Preparation of PA
From Ref.64.



b. Durham Route For The Preparation Of PA From Ref.64.

Fig.1.19.
Two Different Routes For The Preparation Of PA.

2. Different doping techniques. Three other methods are useful. Firstly, in ion bombardment[72], a polymer can be irradiated with a beam of eg. Xe^+ ions. Secondly, in electrochemical doping[73], a polymer can be used as a cell electrode (eg. polycyanoacetylene which takes up Li^+ when a current is passed through the cell). Finally, appropriate polymers can be self-doped[74], eg. a derivative of polyaniline, with SO_3^- groups on the aryl rings, such that SO_3^- removes a proton from the imine nitrogen, and thus dopes the polymer chain.

3. Other types of intrinsically conducting polymer.

Polypyrrole is one of the most common intrinsically conducting polymers. It is composed of chains of pyrrole rings, and still incorporates the basic conjugated double bond system essential for electrical conductivity (see Fig.1.20a). This material is not only more stable than PA but is also far easier to prepare[75], since it can be prepared from an aqueous solution using electrolytic techniques. The resulting polymer is in the form of a stable thin film.

Sulphur containing conducting polymers are also becoming important. Poly(2,5-thienylenevinylene) (see Fig.1.20b), has been shown to exhibit good conductivity and high reflectivity[76]. It can be prepared as films from precursors that are soluble in organic solvents[77].

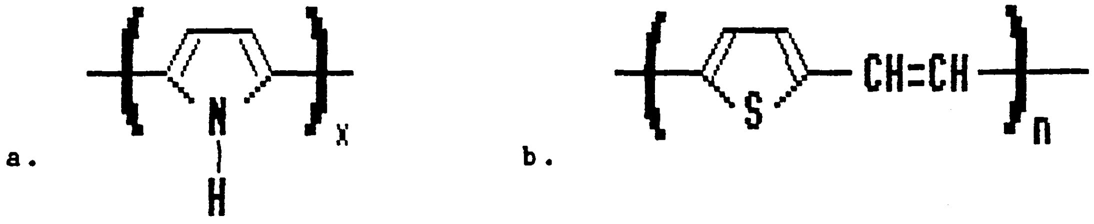


Fig.1.20.
a. Polypyrrole. b. Poly(2,5-thienylenevinylene).

4. Preparation of co-polymers or polymer blends. For example C.Armengaurd et.al.[78] have investigated the electrochemisty of polypyrrole films modified by the addition of cobalt porphyrins. However this has not shown any enhanced properties.

1.7.4. Extrinsic Conducting Polymers.

The most common types of conducting polymer in use are filled polymers[79], comprising a non-conductive polymer matrix containing a conducting filler.

1.7.5. Types Of Filler.

A variety of conducting fillers is used. The most common to date being:

1. Carbon black. This is particularly useful as it is often used as a general filler in polymers.

2. Metals. These can be in the form of metal flakes or spheres but it is preferable to use long thin fibres as this keeps the percolation threshold low (see section 1.7.7). They can also be incorporated in an ionic form, for example mercuric chloride and sodium iodide[80], or as part of the polymer in for example organometallic polymers[81].

3. CT complexes.[82,83] In this approach polymers such as polycarbonate have been filled with CT complexes such as tetrathiotetracene-TCNQ, by dissolving the CT complex and polymer in an appropriate solvent (in the above example o-dichlorobenzene). The solution was then cast onto a glass slide. As the solvent evaporated not only did the polymer come out of solution, but the CT complex precipitated forming dendritic structures within the polymer matrix. The graph below (Fig.1.21) shows how the conductivity varies with CT fill percentage[84].

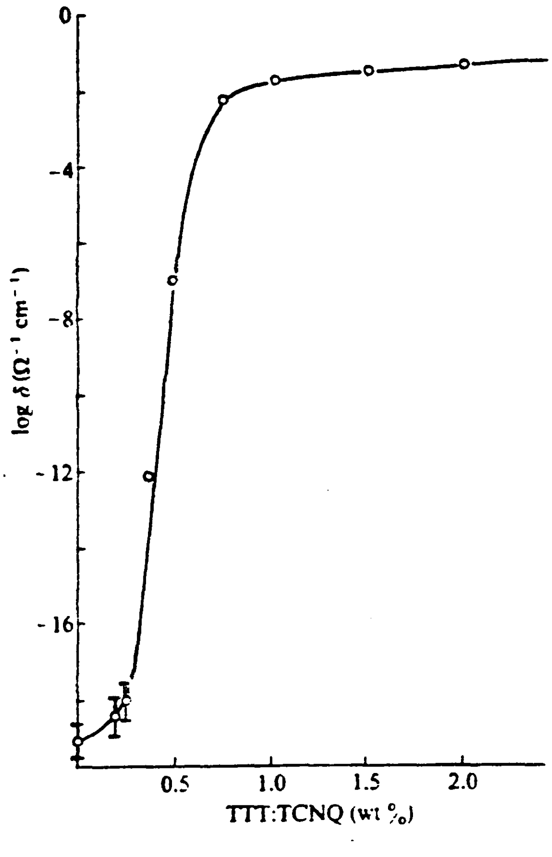


Fig.1.21.
Graph Of Fill % vs Conductivty
From Ref.84.

1.7.6. Modification Of Mechanical Properties.

A problem with using fillers is that as the percentage of filler is increased, there is also an increased effect upon the mechanical properties of the host polymer.

The effect upon the polymer is usually undesirable, in that such fillers can act as stress raisers[85] and therefore may promote cracking. Thus it is desirable to use the lowest possible fill percentage. One theory that addresses the problem of filler % is "percolation theory".

1.7.7. Percolation Theory.[86]

Percolation theory assumes that the important prerequisite for good conduction is a conductive path through the material. It has been shown that needle shaped particles give the highest conduction at the lowest fill percentages, whereas spherical particles require the highest fill percentages. For particles of similar volume the sphere has a conducting path equal to the diameter of the sphere, whereas the major axis is the longest conducting path in a needle particle. If we assume that the lowest required fill volume is obtained when each conducting element is just touching its neighbour, then it can be seen that using long thin fibres or needles of conducting material oriented so that they are just touching along their long axes, will require less volume in order to achieve conductivity than would be the case for spherical particles.

1.7.8. Reticulate Doped Polymers.[87]

Reticulate doping involves the formation of CTC networks within an insulating polymer matrix. The CTC networks grow during precipitation of the polymer as the solvent used for the preparation is driven off.

The crystals grow out in the form of dendrites from a nucleation site until there is overlap between dendrites from neighbouring sites. One advantage of this is that the mechanical properties of the polymer are unchanged, as only small amounts (0.3% by wt) of CTC additives are needed.

1.7.9. CT Polymers.

CT polymers, also known as electron donor acceptor (EDA) polymers, have been prepared. Until recently the main interest in them was not their molecular electronic properties but their ability to assist polymerisation[88] and polymer-polymer miscibility[89].

Here Electron donor acceptor (EDA) polymers such as poly[N-(ω-2-hydroxyethyl)carbazolyl methacrylate] and poly(hydroxyalkyl-3,5-dinitrobenzoyl methacrylate)s[90] have been investigated for polymer-polymer miscibility. It may be that the polymer types proposed here will also exhibit this property due to donor acceptor interaction.

1.7.10. Electro-active CT Polymers.

CT polymers are starting to receive more attention as electro-active materials. There are a variety of different types and some examples are outlined below:

1. Polycarbazole has been investigated for its electrical conductivity properties[91]. Conductivities of $1\ \Omega^{-1}\ cm^{-1}$ have been achieved. However, this type of polymer is similar to other conducting polymers in that it relies on doping, for its activity.

2. Modified poly(N-vinylcarbazole) (PVK)[92] has been investigated as a conducting material and is known to be a photoconductor. Here CT units have been attached to a polymer backbone using a spacer group. It shows some similarity to the structural units we have tried to

prepare in this project, but there is no attempt to produce ordered structures of the type under investigation in this work.

1.7.11. CT Polymers Containing TCNQ.

There have been attempts to produce polymers which contain TCNQ such as:

1. Poly(ethylene oxide)-sodium iodide (PEO-NaI) in close association with TCNQ· [PEO-NaTCNQ-I_2][93]. Here the TCNQ species form a stack with the ions and polymer bound along the edges of the TCNQ stack (see Fig.1.22). As Na(TCNQ) forms a mixed stack complex[47], then it seems that the polymeric system is modifying the CT stacking properties to give an improvement in conductivity of nearly two orders of magnitude above that for a single crystal (10 Ω^{-1} cm^{-1}) [94].

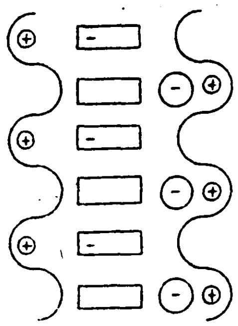


Fig.1.22.
Diagram Of PEO-NaTCNQ-I_2 From Ref.93. Small circles (+) are sodium ions, larger circles (-) are polyiodide ions, rectangles are TCNQ anions or neutral molecules and the solid wavy line represents the PEO helix.

2. Poly[-2-vinylpyridinium TCNQ][95,96]. The electrical conductivity of a powder sample of this polymer was of the order of $10^{-3}\ \Omega^{-1}\ cm^{-1}$.

1.8.Applications For Conducting Polymers.

Over the last few years conducting polymers have started to find applications[97].

1.8.1. Criteria For Using Conducting Polymers.

The type of application envisaged determines the type of conducting polymer that should be used. For example there is little point in using an expensive, highly sophisticated polymer where a relatively cheap, filled polymer will suffice.

A typical application may be in the paint industry where static electricity is a problem when spraying. Although carbon black may be one of the components of the paint it does not render the paint conductive enough to leak any charge to earth. In this case a more conductive filler is needed that will not adversely modify the properties of the paint[98].

For conducting polymers to be commercially viable they must provide superior properties over the materials they replace. Taking the example of electromagnetic shielding, the advantages of a conducting polymer over traditional materials such as steel, copper or aluminium are:

1. The processability of the polymer.
2. Lower density.
3. Corrosion resistance.
4. Possible lower production cost.
5. Dwindling resources of high quality metals.

However, it is unlikely that conducting polymers will replace traditional materials in applications that require harsh working environments, for example power transformers where conductive wire is required to withstand high current densities and high temperatures. This is because the working range for conducting polymers is very much smaller than for copper or aluminium. However, modified conducting polymers capable of fulfilling these requirements might be developed in the future. Indeed, there is on-going research designed to make molecular wires. One of the lastest developments is a molecular junction box that can provide a conducting cross link between different chains of polythiophene[99] (see Fig.1.23).

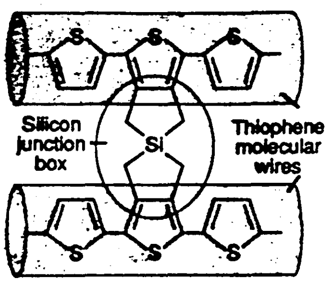


Fig.1.23.
Molecular Junction Box From Ref.99.

Conductive polymers will really come into their own in the area of molecular electronics. Here the opportunity is available to tailor devices to the application required by chemically modifiying molecular architectures. The work involved in this project is itself an example of the chemical modification of a conducting material in order to investigate the possibility of producing a more useful material. There follows some examples of applications for conducting polymers.

1.8.2. Conducting Polymers For Electromagnetic Shielding.

One of the most widespread uses is in the area of electromagnetic shielding where conductive moulded components (e.g. computer monitor cases) are required to meet low electromagnetic emission standards while keeping the units as light as possible.

One application is a product called "Shieldseal", a conductive elastomer designed to seal the joints of electromagnetic shielding boxes. It is composed of silver plated particles in a silicone rubber matrix[100]. Another product called "Cabelec 3320" is a polypropylene co-polymer that is conductive and also strong enough to provide anti-static containers[101].

1.8.3. Conductive Paints And Adhesives.

These have been used for some time. Examples such as a form of "Araldite", in which the adhesive is filled with silver particles, and "Electrodag", a conductive paint, are available from suppliers of electronic components.

1.8.4. Conducting Polymers in Batteries.

Conducting polymers are becoming increasingly important as components of batteries, for example as electrodes[102,103]. One futuristic suggested use is a battery that is part of the moulded component of a car[104]. It remains to be seen whether this type of application will become a reality.

1.8.5. Sensors.[105]

There are a number of devices in which conducting organic molecules are being used as sensor components. Conducting polymers have a great advantage over conventional materials in that they can be tailored to exhibit the properties most suitable for the particular application envisaged.

1. Biosensors.[106,107] As conducting polymers are organic based compounds they are more easily interfaced with biological systems such as the electron transfer cytochrome system[108]. One area of research is aimed at the entrapment of active species such as enzymes in a conducting polymer matrix[109,110]. An example is a

glucose oxidase electrode where polypyrrole is used as the conducting polymer. Polyacetylene is also being developed for use in a sensor for glucose detection[111] (see Fig.1.24).

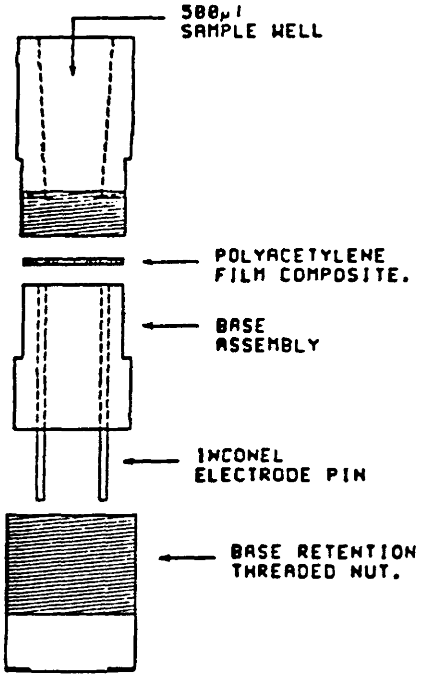


Fig.1.24.
Glucose Sensor Electrode Cell From Ref.111.

<u>2. Non Biological.</u> Conducting polymers are often incorporated as parts of solid state devices such as Schottky diodes[112] and field effect transistors (FET). In the metal insulator semi-conductor FET (MIS FET), (see Fig.1.25), polyacetylene is used for the gate of the FET. This device uses polyacetylene prepared by the so called Durham route[71]. Devices utilising such polymers can have an on/off ratio of 100,000[113] compared with greater than 10E^{100} for metal oxide semiconductor FET (MOSFET) silicon devices[114]. Another example is a device for the measurement of conductivity[115].

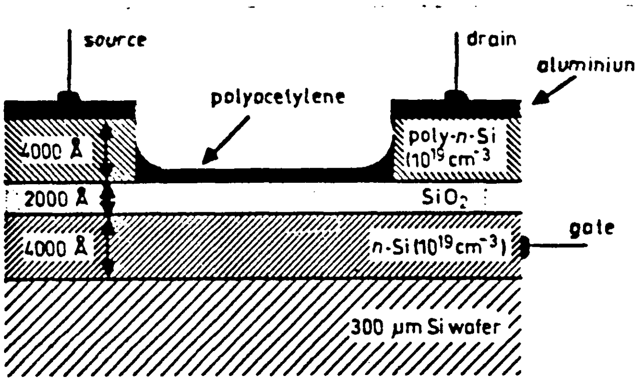


Fig.1.25.
Diagram of a MISFET From Ref.113.

A further line of research entails the preparation of water soluble materials such as a form of poly(aniline)[116]. It is interesting to note that polyaniline is unique in being the only conducting polymer where a nitrogen atom is used as the bridging atom between phenyl rings. The nitrogen atom can act as a protonation site. This means that polyaniline has the potential to exhibit many modified electrical properties[117] and has led to investigations of its potential for devices such as electrochromic displays and batteries[118].

1.9. A Proposed Novel CT Polymer Based Upon Liquid Crystal Polymer Architecture.

Although electrical conductivity is high in individual CTC crystals they have one very important drawback. At best, single crystals are only a few millimetres long and brittle. At worst, they are almost impossible to obtain in crystalline form. This means that the macroscopic order is only short range. "Real world" application of these materials will most likely involve materials that possess long range order.

1.9.1. Improvement To Long Range Order.

A variety of strategies that could possibly extend the long range order, and thus improve the conductivity, has been investigated. Two strategies are as follows:

1. Reticulate doping of polymers (see section 1.7.8).

There has been much work done in this area. Unfortunately the longest conduction path is only the length of individual crystals in the network. Electron flow is still disrupted if electrons have to jump between different crystals.

2. Orientated CTCs.[87] CTC dendrites can be orientated in the polymer by evaporating the solvent along a moving solvent front, thus initiating dendrite growth normal to, and just behind the moving solvent front. Again, the limiting factor for conduction is the energy required by the electron to "jump" between adjacent crystals.

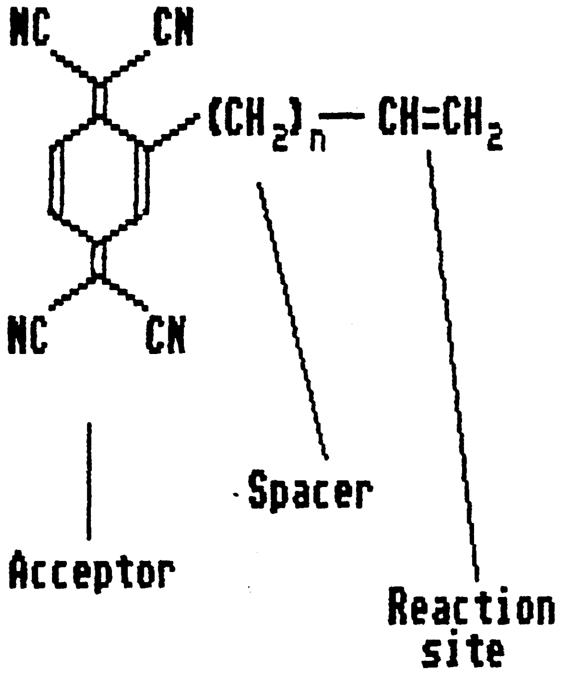
These methods, although improving electrical conductivity somewhat, are unlikely to give the optimum conductivity.

1.9.2. Proposed Structure Of CT Polymer.

One approach to the potential improvement of long range order is to synthesise a charge transfer polymer. As CTCs, like LCs, require long range stacking of the active units, it was proposed that the spacer concept of LCPs be applied to the molecular architecture of a CT-donor or CT-acceptor polymer, where CTC molecules are attached to a polymer backbone via a flexible alkyl spacer group (see Figs.1.26 - 1.28). It was hoped that the advantage of this type of system would be the ability to "marry" the electrical and stacking properties of the charge transfer complexes with the long range order that LCP architecture offers.

We must, however, be careful about drawing a direct comparison between LCPs and our proposed CT-acceptor polymer. Whereas LCPs only require neighbouring LC substituents to adopt smectic or nematic ordering, electrical conductivity in our system is dependent upon good stacking integrity allowing interaction of the π-system on the acceptor units and hence allowing the movement of electrons. This implies that a crystalline phase is required rather than a liquid crystal phase (where intermolecular spacing tends to be greater). This emphasises the importance of flexible spacer linkages between the acceptor moeities and the polymer main chain. D.Simmonds[119] has shown that, for some LCP systems, crystalline as well as liquid-crystalline phases are most likely to be observed when long flexible spacers are incorporated. It is probable, therefore, that once the synthetic procedures have been optimised, the best electrical conductivity will be achieved by polymers containing relatively long spacers, eg $(CH_2)_{11}$.

Possible precursors for attachment of a CT-acceptor derivative to a polymer backbone (where TCNQ is the acceptor) are shown below in Fig.1.26.



Or
Perhaps

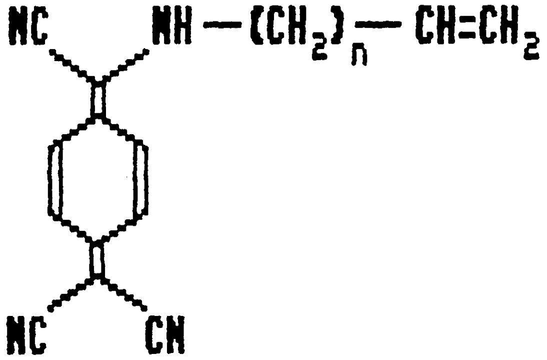
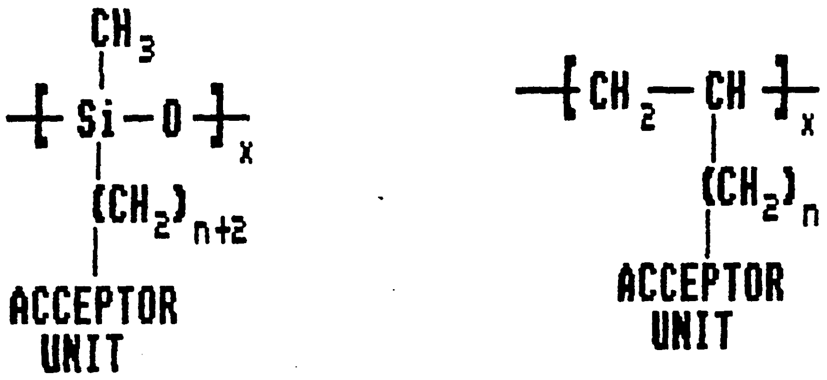


Fig.1.26.
CT-Acceptor Derivative Required For Attachment To A Polymer Backbone.

The derivative may then be attached to a polymer backbone, for example siloxane (Fig.1.27a) or vinyl (Fig.1.27b).



a. Siloxane Polymer. b. Vinyl Polymer.

Fig.1.27.
Different Types Of Polymer Backbone.

The results from Fig.1.27 may lead to the macro-structure shown in Fig.1.28 where the acceptor stack is shown to be comprised of several polymer chains.

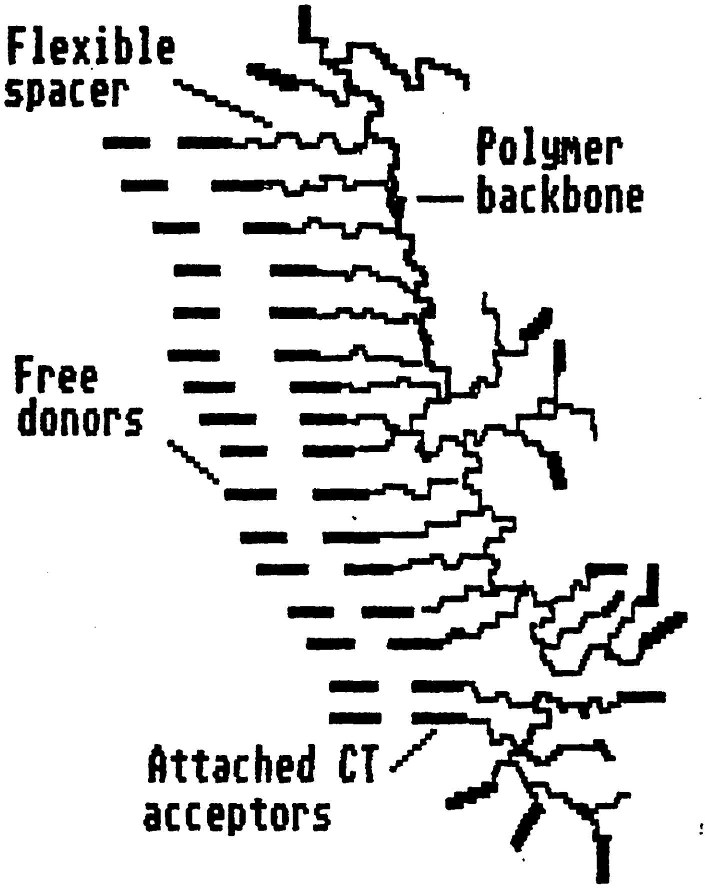


Fig.1.28.
Possible Architecture Of CT-Acceptor Polymer
As A Blend With An Appropriate Donor.

1.9.3. Assumptions For A CT Poymer.

The assumptions made are as follows:

1. The greatest barrier to electron movement in polycrystalline CT complexes is the energy required for hopping between adjacent crystals. A long continuous structure would help overcome this problem, and may be achieved if the CT units are attached to a polymer backbone.

2. It may be expected that the polymer will to some extent act as a template when the CT molecules stack thus inducing large areas of stacked acceptors. This would mean that there were no individual crystals but a continuous loose stack following the backbone polymer contour. An underlying assumption is that intermolecular attractive forces would favour an ordered rather than a random configuration of the polymer composite (cf LCPs).

3. Obviously it would be naive to expect large areas of perfectly stacked complex. What may be expected is a change in direction of the stack, controlled by the contour of the polymer. The change might be gradual enough to permit overlap between adjacent CT units over a long range and hence allow electron transport through the system, rather than the sharp discontinuity at the end of one crystal as in a conventional CT complex. Whilst ideal stacking conditions are unlikely to be dominant, enough overlap may still remain to enable electron mobility at relatively low energies.

4. At best a semi-conductor type conductivity might be expected since the proposed structure is unlikely, by its nature, to possess the highly ordered structure required for metallic type conduction.

5. It may also be possible to orientate the polymer by such processes as stretching or melting and slow-cooling, so favouring an ordering of the previously coiled polymer chains with resultant improved acceptor stacking.

There are two main ways in which these types of polymer could be built up. These are outlined below.

1.9.4. CT Acceptor And Donor Polymer Blends.

Firstly, both a CT-acceptor and a CT-donor polymer are synthesised. They are then blended together in a molten or solution phase with the expectation that the active CT groups may interact to some extent, i.e. a polymer bound analogy ~~to~~ normal CT complex formation. We feel that this is not a good strategy as the entropy involved in blending the polymers and achieving the desired stacking integrity might be unfavourable.

1.9.5. Partial Polymer Blends.

The other alternative is to blend free donors with a CT-acceptor polymer or vice versa, once again starting from a fluid phase. It seems logical to blend free donors with a CT-acceptor polymer for two reasons.

1. A continuous stack of acceptor units is required.
This is vital where the conduction mechanism in CT complexes (based on TCNQ as the charge carrier), requires continuous stacks of acceptors.

2. Donors may not always pack in stacks.[120-122] In our proposed system, where TCNQ acceptors are the charge carriers, attachment of donors to the polymer backbone may disrupt the stacking properties of the acceptors, thus polymer bound acceptors may overcome any imposed

orientation that could result from a polymer where the donors are the bound moeities.

1.9.6. Building Blocks.

It was decided to try to prepare a CT-acceptor polymer and blend it with free donors. The constituents of the proposed material are outlined below:

1. TCNQ as the acceptor. This was chosen as it is one of the best known electron acceptors. Over the years there have been more than 6000 papers published on its properties.

TCNQ is composed of a quinodimethane system to which are attached four cyano groups that have a high electron affinity. The result is a molecule that is able to delocalise and stabilise a negative charge via a resonance-stabilised radical-anion structure with the charge being centred near the cyano groups[42] (see Fig.1.29).

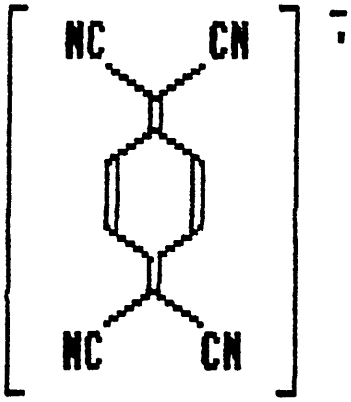


Fig.1.29.
The TCNQ Radical Anion.

2. Alkyl spacer groups of various lengths. The spacers chosen were oligomethylene groups of various lengths containing functional groups at each end. One function being a double bond, useful for incorporation into a polymer such as siloxane, or for direct polymerisation giving a vinyl polymer. The other terminal group has to be appropriate for attachment to the TCNQ molecule.

It is felt that short spacers i.e. three or four carbon units would not allow sufficient decoupling of the CT units from the polymer backbone, thus causing the backbone to exert an adverse affect on stacking. However, if the spacer group is too long then decoupling may be so great that the polymer backbone may no longer act like a template. The result may be numerous small areas of ordered CT units disconnected from their neighbours. There is likely to be an optimum chain length, but this is yet to be determined.

3. Siloxane or vinyl polymer backbone. The advantage of a vinyl polymer is that the terminal double bonds on the spacer group are used for direct polymerisation to produce a polyvinyl structure, whereas the siloxane polymer requires the attachment of the spacer to a siloxane backbone.

The approach chosen was to attach a TCNQ derivative containing the appropriate functionality to a siloxane backbone. This was preferred for several reasons:

1. We did not have sufficient TCNQ derivative to investigate all the possible procedures.

2. The chemistry used for attaching alkene species to the siloxane polymer is well known, and the techniques are already widely practised at Sheffield City Polytechnic.

3. The siloxane backbone is flexible offering considerable conformational freedom in that the polymer chains are free to move giving rise to materials that are viscous liquids or solids at room temperature. Conversely vinyl polymers have stiffer backbones resulting in glassy or plastic solids at room temperature. Consequently, when the siloxane CT-polymer is prepared, order is solely due to formation of acceptor stacks, whereas in the vinyl CT-polymer there will also be a contribution from the ordering of the polymer backbone and this may inhibit optimum stacking of the substituents.

1.9.7 Problems.

There are a variety of problems as outlined below:

1. CTC oxidation.[123] Here one of the TCNQ cyano groups is replaced by oxygen (Fig.1.30), thus removing a cyano group, which may reduce the charge stabilising properties of the molecule and possibly affect the stacking properties of the complex.

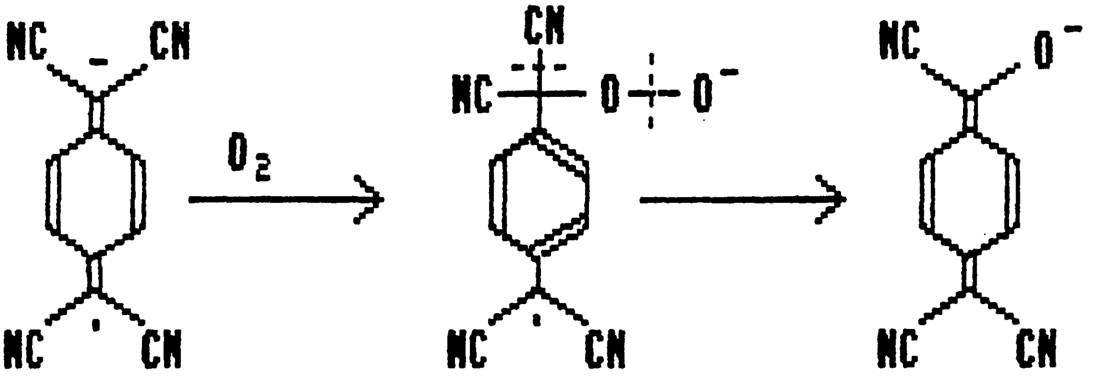


Fig.1.30.
Oxidation Pathway For The TCNQ Molecule
From Ref.123.

This problem arises especially when samples are exposed aerobically to UV radiation. The effect on stabilisation due to replacement of a cyano group by oxygen may not be as important as has been stated, since CT complexes with acceptors that only contain two cyano groups have been reported[124].

<u>2. Blending of the donors with attached acceptors.</u> This may prove difficult in that the mobility of the donors through the polymer matrix will be reduced even though they will be in solution.

<u>3. Orientation effect on the stacking of the acceptors.</u> This is due to the polymer matrix and the spacer groups, and will obviously have an effect on the electrical properties of the system.

1.10. Conclusions.

Conducting polymeric systems have a lot to offer in terms of new devices. It is unlikely that they will, in the foreseeable future, replace dwindling resources such as copper, rather they will augment the many novel materials that are at present being developed. This project attempts to investigate one small area that may lead to significant improvements in the material properties of CTCs. There follows a detailed description of the work undertaken.

2.Instrumentation.

Two major pieces of equipment have been designed and constructed during the last three years. These were a Faraday magnetic susceptibility balance and an electrical conductivity rig.

Both are able to take data with respect to temperature in the region 300 to 70 Kelvin. In order to achieve this, skills had to be acquired in the areas of cryogenics, vacuum systems, electronics and magnetism, (see for example G.W.White's book on low temperature physics[125]).

There follows a description of the equipment and relevant details of its design and construction.

2.1.Construction Of The Electrical Conductivity Apparatus.

No suitable apparatus was available for measuring electrical conductivity so an experimental rig was constructed.

2.1.1. Electrical Conductivity Measurement.

Before details of the instrumentation are given there follows an explanation of how electrical conductivity is measured.

2.1.2. Conductivity Calculations.

The measurement of electrical conductivity is achieved by the use of Ohms law (eq.2.1) and its modifications[126].

$$V = I.R \quad ....2.1.$$

Where:

V = Voltage drop in volts.
I = Current flowing in amps.
R = Resistance in ohms.

Hence from this resistivity (ρ) can be calculated from eq.2.2. (also see eq.1.1 and appendix 2).

$$\rho = \frac{V}{I}.\frac{A}{d} \quad ....2.2.$$

Where:

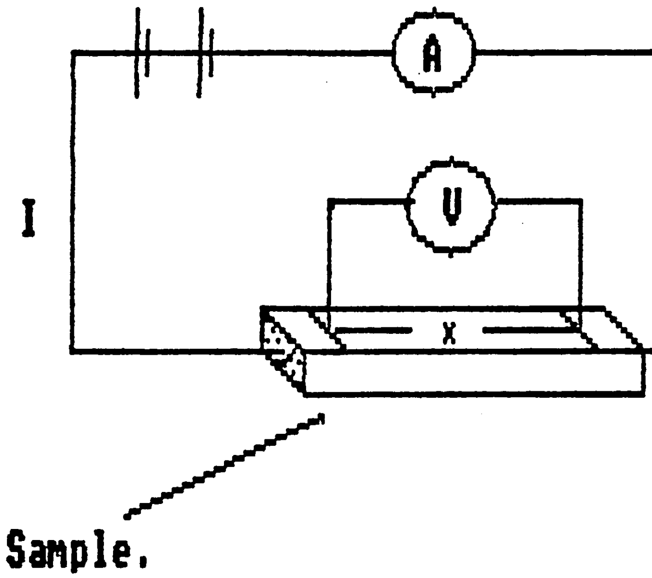
d = Sample length in cms.
A = Area in cms^2.
ρ = Resistivity.

From this conductivity (σ) is obtained as the inverse of ρ. The exact calculation used at Sheffield City Polytechnic is given in Appendix 2.

Some of the more common methods used to measure electrical conductivity are outlined below:

2.1.3. Four Point Probe.

Here a line of four contacts are placed on the sample at known distances apart. A constant or known current is passed between the outer electrodes and a voltage drop is measured across the two inner electrodes (Fig.2.1). This configuration is often used as resistance, due to connecting leads etc., does not contribute to the resistivity.



I= Current.

x= Sample length.

Fig.2.1.
Four Point Probe Conductivity Measurement.

2.1.4. Two Point Probe.

Here two electrodes of known area are attached to a disc of the sample under test and the voltage drop and current flow are measured (Fig.2.2).

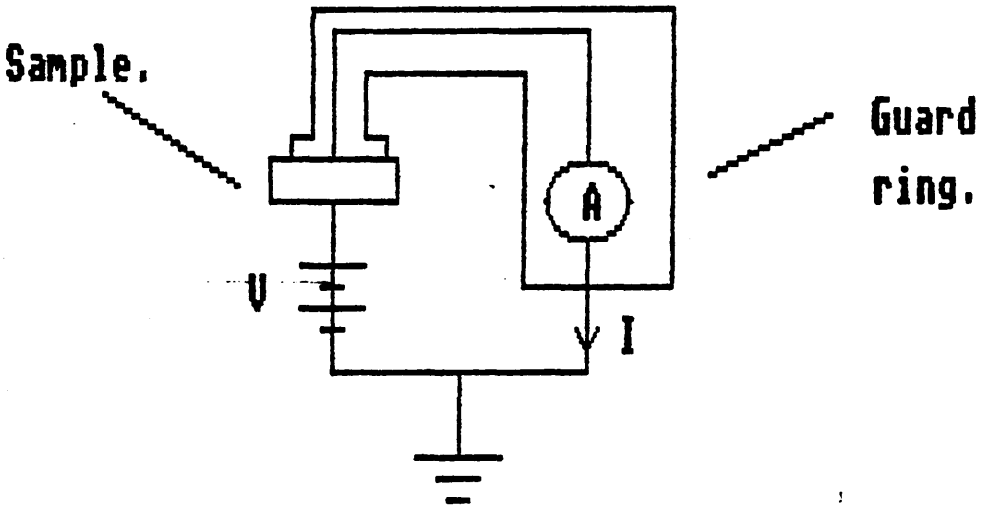


Fig.2.2.
Two Point Probe.

2.1.5. Phase Sensitive Detectors.[127]

A phase sensitive detector is a very sensitive method for measuring AC resistance of samples. It is often used for precise measurement of low resistances in materials such as superconductors.

We briefly considered the possibility of using such a technique, but dismissed the idea on two grounds. Firstly, the time required to get the system working satisfactorily was too great. Secondly, during initial testing of the available equipment, it was found that the electrical noise was too high to enable satisfactory use without the expenditure ~~of~~ considerable time and money.

2.1.6. Problems Associated With Conductivity Measurements.

At first sight it may appear easy to measure electrical conductivity. However, there are many factors requiring modifications to the basic equation for determining electrical conductivity. These are outlined below:

1. Sample shape and thickness. This has an effect that is corrected for by modifying the conductivity equation.

2. Resistivity of the sample. This will determine the method of measurement. Four point probe measurements are only applicable to samples with low resistivities, as very little current will flow through a sample of high resistivity. For high resistivities the two point probe method is more useful.

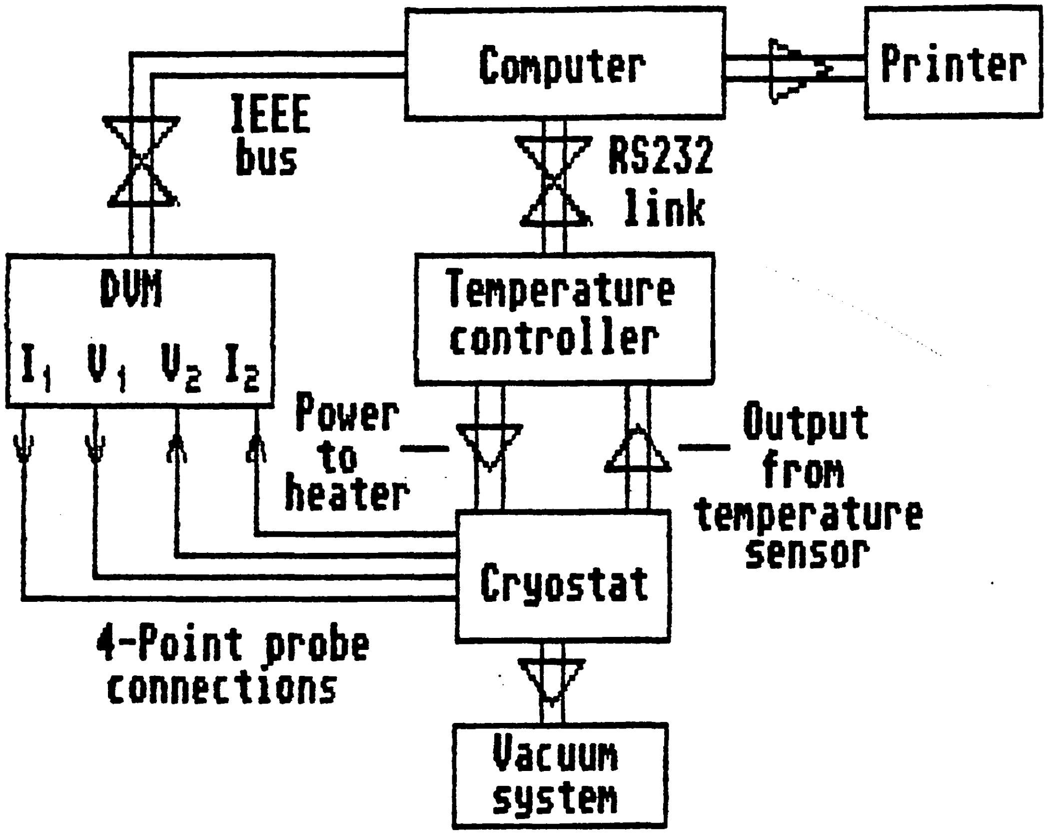
3. Surface conductivity. Surface conductivity must be taken into account, especially with samples having high resistivities. The problem can be overcome by employing a guard electrode around the sample to earth out any current flowing across the surface. This aspect of conductivity measurement is complex and many factors, such as prevention of earth loops, have to be taken into account before one can trust the accuracy of data[128].

2.1.7. Conductivity Rig Specification.

The rig had to be able to measure electrical conductivity via two and four point probe methods over the approximate temperature range 300 to 15 Kelvin, with data collection and temperature control being under computer control. A picture of the instrument is given in Fig.2.3 and a block diagram in Fig.2.4.

Overall there appear to be numerous factors affecting the electrical conductivity and it is important to realise that within the bounds of this project it is impossible to correct for every factor, so we are not looking at absolute conductivity. As we are looking at the change in electrical conductivity with respect to temperature, we are really concerned with any possible transitions over the temperature range. This was well within the limits of the instrument constructed.

Fig.2.3.
Picture Of The Electrical Conductivity Rig.



General Block Diagram.

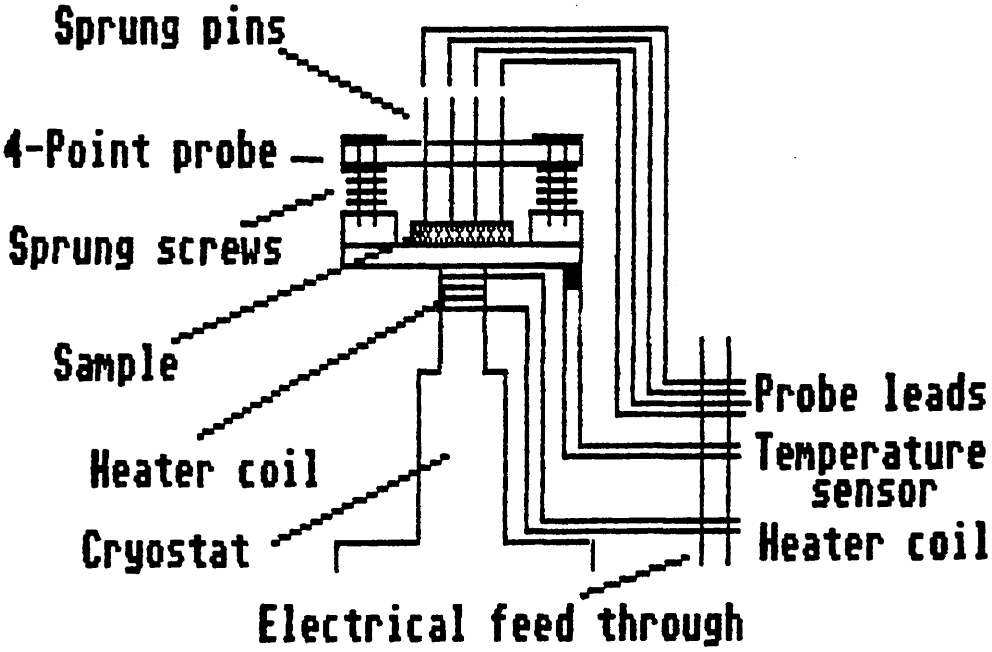


Diagram of the cryostat.

Fig.2.4.
Block Diagram Of Conductivity Apparatus.

2.1.8. Cryogenics For Conductivity Apparatus.

Cooling was provided by a Cti Cryogenics Model 20 Stirling engine able to work within the temperature range 500 to 15 Kelvin. The sample was placed on the cold tip of the engine. Minimum temperature was reached by evacuating the space around the cold tip.

2.1.9. Vacuum System For Conductivity Apparatus.

The vacuum system used to evacuate the space around the cold tip was constructed in the Sheffield City Polytechnic workshops.

The vacuum was provided by a Speedyvac pumping system consisting of a single stage rotary pump and a diffusion pump. This gave a vacuum of better than 1 x 10^{-4} torr.

The vacuum shroud was constructed to the author's design, with the following points in mind (see Fig.2.5):

1. Sample changing should be as easy as possible.
2. The shroud was provided with windows so that photo-conductivity and photovoltaic measurements could be made.
3. The shroud should support the cryostat.

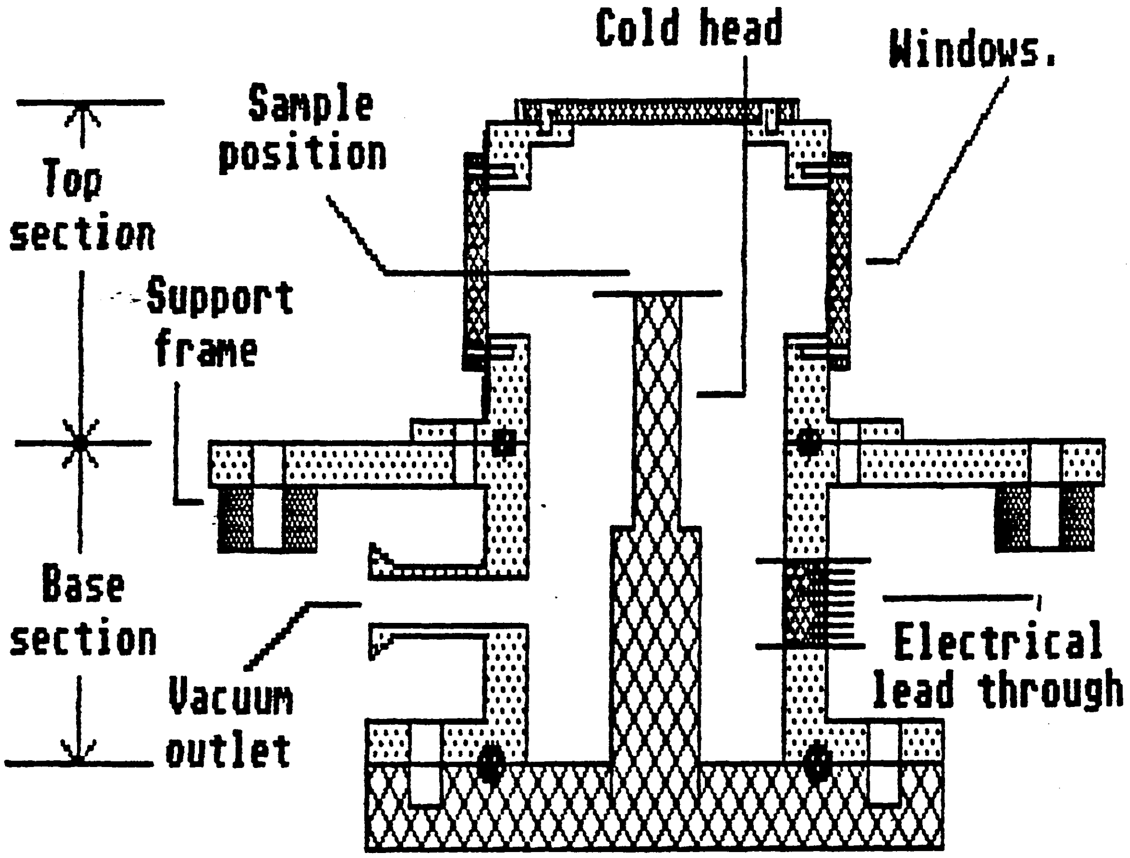


Fig.2.5.
Diagram Of Conductivity Rig Vacuum Shroud.

2.1.10. Temperature Control For Conductivity Apparatus.

Temperature control was achieved using a Scientific Instruments Inc 9600-1 temperature controller which used a silicon diode as the temperature sensor. The diode was calibrated by the manufacturer, using 13 calibration points.

The temperature controller maintained a set temperature by adjusting the power to a heating coil after comparing the temperature set by the computer with the actual temperature of the cryostat. The controller communicated with the computer using an RS232 interface, which was fast and enabled simple programming techniques to be used.

2.1.11. Method Of Conductivity Measurement Used At Sheffield City Polytechnic.

Measurement was via a four point or two point probe method using a Solatron digital voltmeter (DVM) with its own constant current source for four point probe measurement.

Communication with the computer was via an IEEE-488 link. This was more flexible than RS232 communication, but was slower and required more complicated programming.

2.1.12. Computer Control.

The data acquisition was under control of an Amstrad 1512PC computer which had an IBM IEEE-488 interface in order to communicate with the DVM. Data transfer between the computer and the temperature controller was through the computer's built in RS232 port.

Resistance measurement was completely under the control of the DVM, so that the computer only had to request a reading and the value received was then used to calculate the conductivity (see Appendix 2).

Temperature control was achieved by the Scientific Instruments Inc temperature controller. This meant that the computer only needed to:

1. Receive data from the controller.

2. Send the appropriate set temperatures.

The program was written in GW-BASIC and compiled into machine code. A listing of the program is given in Appendix 1.

2.1.13. Modifications And Development.

The conductivity rig has undergone extensive development in the period since it was first built, including:

1. Replacement of the APPLE computer with an Amstrad 1512, IBM PC compatible, machine.

2. The measurement of electrical resistance by a commercially available DVM with built-in 4-point probe capability and IEEE computer interface.

The voltage drop across a sample was originally measured using an interface built at Sheffield City Polytechnic. The output voltage was converted to a digital signal in the computer using an analog to digital converter.

3. Replacement of the platinum resistance thermometer temperature sensor, (whose resistance was measured using a similar interface to that for measuring the conductivity), with a commercially available temperature controller.

2.1.14. Effect Of Modifications.

The use of the new equipment, costing approximately £2500, has meant the accuracy of our readings has vastly improved. This is due to:

1. The elimination of errors caused by noise in analog to digital conversion.

2. Reliability of temperature sensor calibration.

3. As most of the data sampling is done by the temperature controller and DVM, the computer program is considerably simplified compared with the original version and is therefore faster in execution, more responsive and less prone to errors, (it is almost impossible to eliminate all the errors from a computer program).

2.2. Construction Of The Faraday Magnetic Susceptibility Balance.

There were several good reasons for obtaining the magnetic susceptibility of the materials under investigation:

1. Trends in electrical conductivity with respect to temperature are often mirrored in the magnetic properties.

2. Although the acquisition of accurate magnetic data with respect to temperature requires more sophisticated equipment than for measurement of electrical conductivity, there is less uncertainty in the results.

3. Magnetic data can give extra information not available from conductivity data, eg. the number of unpaired electrons.

2.2.1. Faraday Balance Specifications.

The magnetic balance at Sheffield City Polytechnic had to be capable of measuring magnetic susceptibility over the temperature range 300 to 76 Kelvin.

Computer control was desirable as a run from 300 to 76 Kelvin took four or more hours, with readings being taken every five minutes and was very time consuming if undertaken manually. Additionally, consistency of such parameters as the magnetic field strength was better than would be possible with a manual system.

2.2.2. Details Of Design.

A picture of the Faraday Balance is shown in Fig.2.6 and a block diagram is given in Fig.2.7.

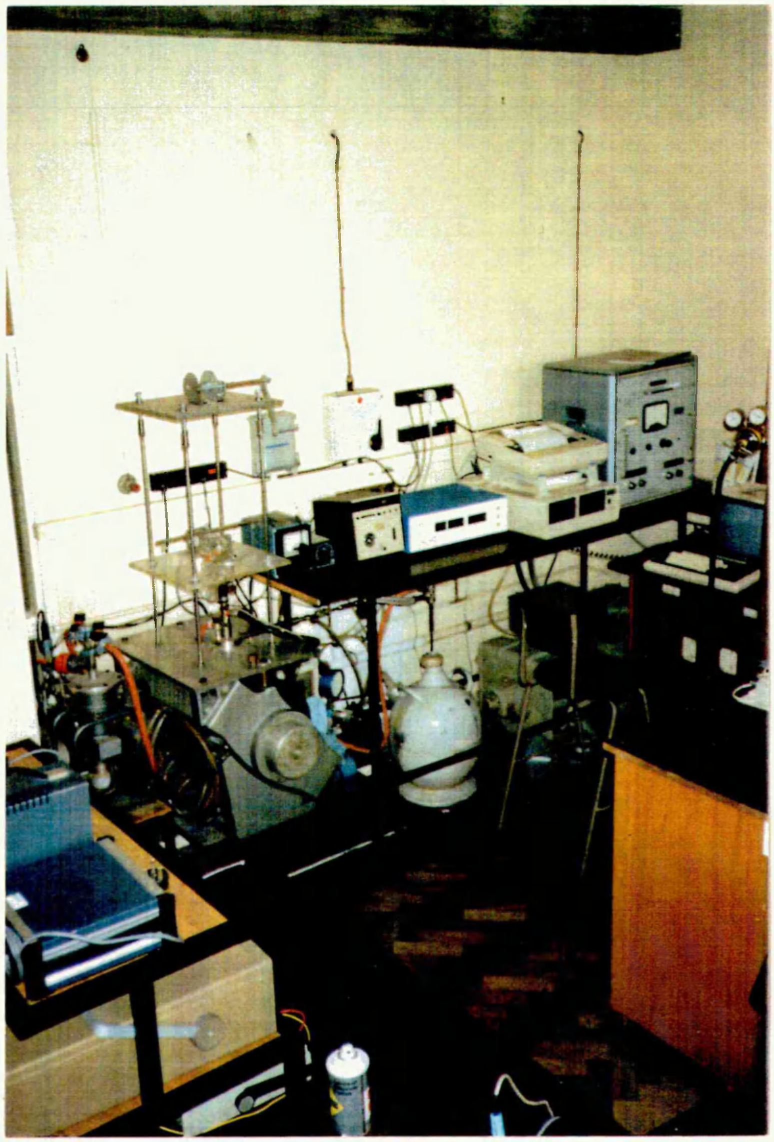
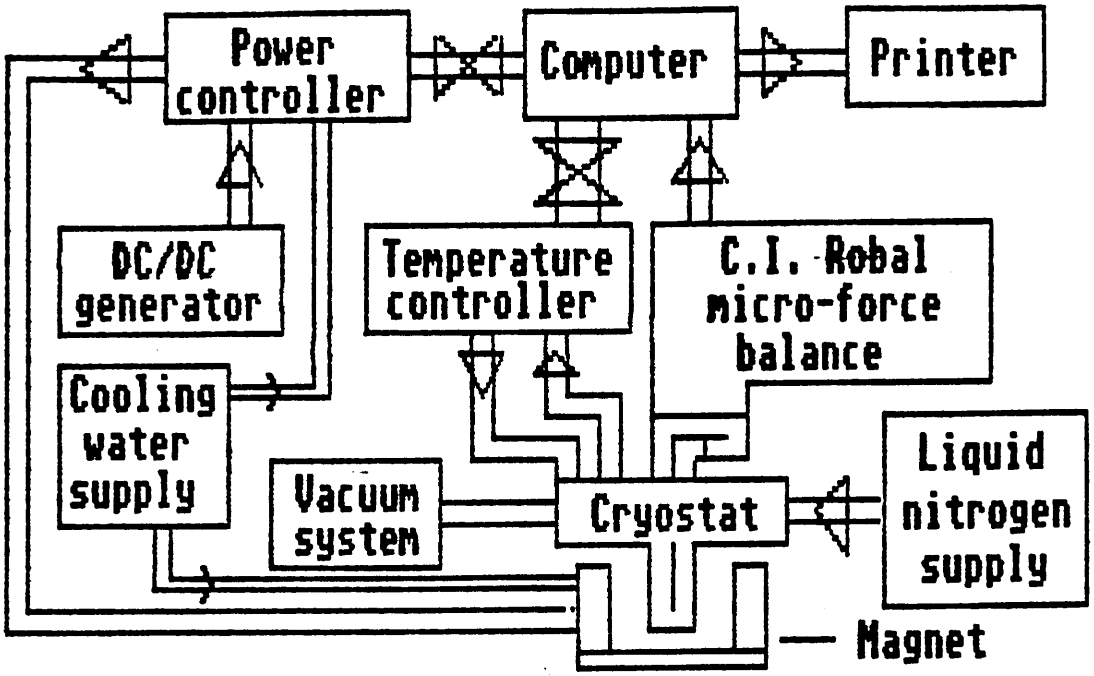


Fig.2.6.
Picture Of The Faraday Magnetic Susceptibility Balance.



General Block Diagram.

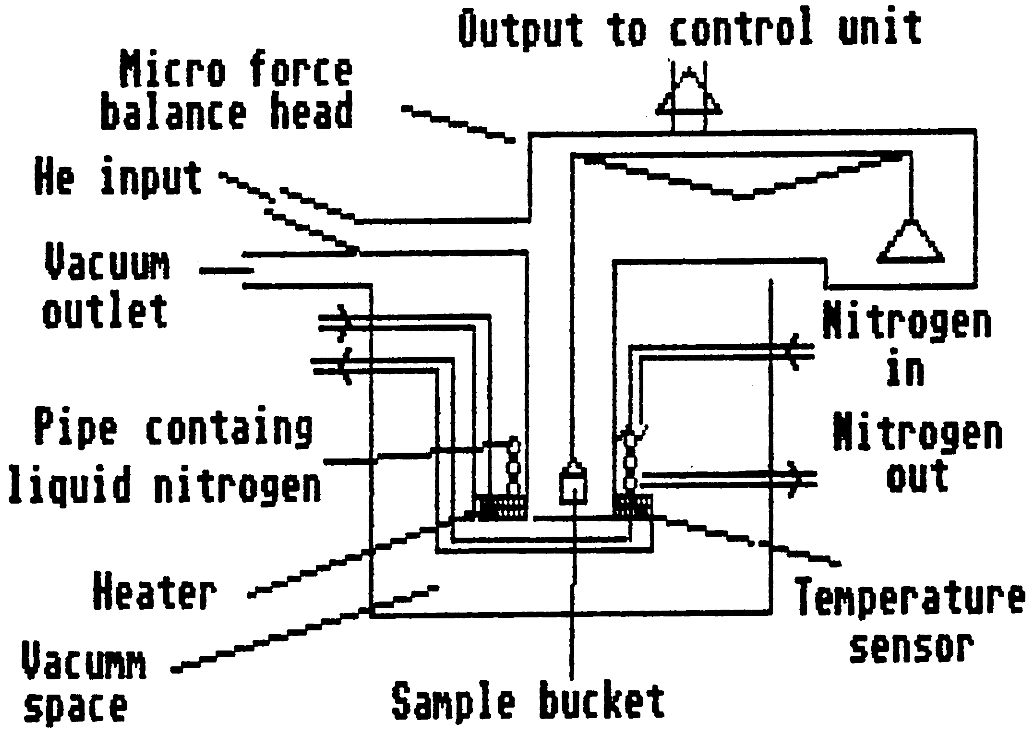


Diagram of the cryostat.

Fig.2.7.
Block Diagram Of The Faraday Magnetic Susceptibility Balance.

1. Electromagnet. The electromagnet used was a Newport Instruments magnet. It provided a magnetic field of approximately 0.4 Tesla at the sample with a current of 12A at 100V.

To improve the performance of the magnet, specially shaped pole tips were made to give a constant field gradient over a relatively large vertical distance. The shape of the pole tips had to satisfy the following equation[129].

$r^{3/2}$COS(3/2) = Constant ....2.3.

Equation in polar co-ordinates.

A diagram of the pole tips is shown below in Fig.2.8.

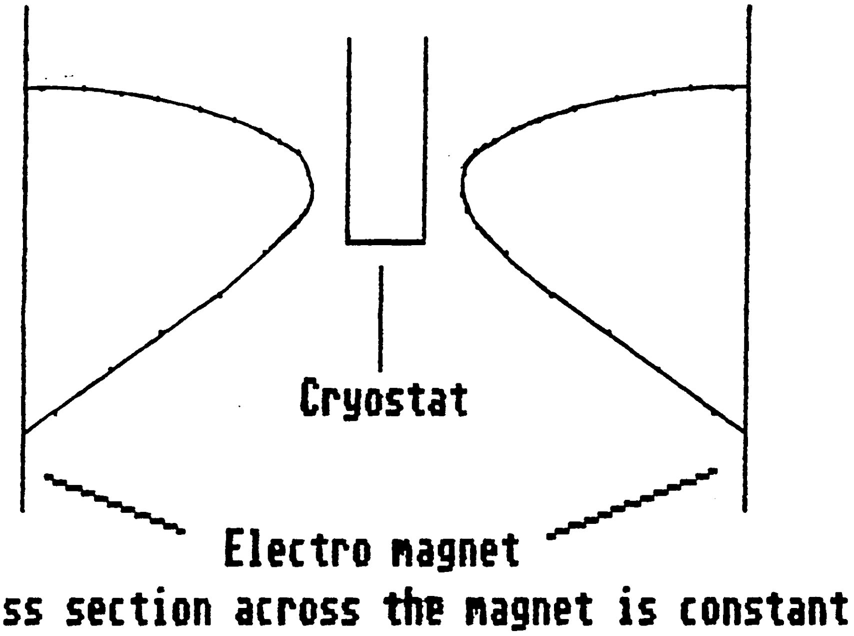


Fig.2.8.
Diagram Of Faraday Pole Tips.

2. Power supply for Faraday balance. The power for the magnet was provided by a DC/DC generator, with power control via a Newport Instruments controller.

3. Micro balance head. Sample weight change was detected using a C.I. Robal Microforce balance able to resolve changes in weight of ± 0.02 milligrams.

4. Temperature control for Faraday balance. This was achieved using an Oxford Instruments CD200 continuous flow cryostat and an Oxford Instruments DTC2 temperature controller.

2.2.3. Computer For Faraday Balance.

The computer was a Analog Devices' Macsym 150. These computers have been developed specifically for sensing and control purposes, for which they are excellent. The major drawback is that the BASIC language used is both non-standard and, at times, cumbersome.

There follows details of the control system. A computer program listing is given in Appendix 1.

1. Control of magnetic field. This was via analog to digital (A/D) and digital to analog (D/A) converters receiving or supplying control voltages.

The power for the magnet was provided by a Newport Instruments power supply, with a stabilised power source coming from a DC/DC generator. The power output was determined via a control voltage from the computer.

A feedback voltage connected to the power supply voltmeter was fed to the computer via a potential divider. This stopped the computer sweeping the power when the detected voltage was above a set value, giving better than 1% reproduceability.

<u>2. Control of the cryostat.</u> The operation of the Oxford Instruments continuous flow cryostat was quite simple. The sample chamber, filled with helium gas, was surrounded by a tube through which liquid nitrogen or helium was drawn and this, in turn, was enclosed by an evacuated space.

The temperature controller maintained a set temperature by adjusting the power to a heating coil after comparison of the set and actual temperature of the cryostat.

All functions of the temperature controller are under the command of the computer in the form of a voltage sent to or from the computer via D/A and A/D interfaces. These controls are given below:

	Temperature controller.	Computer.
Set temperature.	<-------------------------	
Set temperature echo.	------------------------->	
Actual temperature.	------------------------->	

The control signals were in the form of an analog voltage between 0 and 5 volts. The computer read the signals via a 12 bit analog to digital converter. When averaging 1000 samples an accuracy of 0.1K was approached.

3. Control of the balance head. The Balance used was a C.I. Robal microforce balance able to measure the force exerted on it to ± 0.02 milligrams. This provided an output derived from measuring the amount of current required by a solenoid on the balance arm to keep it balanced.

The position of the balance arm was detected by an electro-optical system, where a light chopper attached to the balance arm altered the amount of light a photo detector received from a light source as the arm moved (see Fig.2.9).

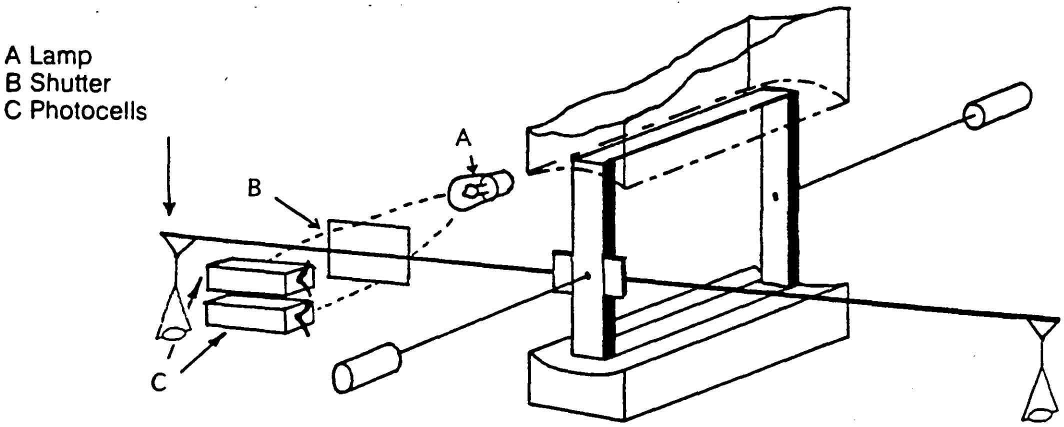


Fig.2.9.
Diagram Of C.I.Robal Microbalance Mechanism.

The C.I.Robal was connected to the computer via an RS232 link. This provided a quick and accurate method of communication, much preferred to either a proportional voltage or IEEE communication. The computer converted the "string values" sent via RS232 to real numbers for conversion from weight change to magnetic susceptibility.

2.2.4. Control And Software Detail.

The Macsym microcomputer controlled all parameters of the balance except nitrogen flow rate.

There follows a detailed description of how the computer controlled the balance. This has been included to give the reader an insight into the work required to set up such a piece of equipment and falls into two main areas.

1. User ports. The computer used was designed specifically for control and data acquisition purposes and to this end there were many extra key words in the language enabling communication with the various user ports. The balance used three different types of port:

a. Three 12 bit analog input ports;

  1. Temperature input.
  2. Set temperature monitor.
  3. Magnet power supply voltage sense.

b. Two 12 bit analog output ports;

  1. Set temperature output.
  2. Magnet power supply control voltage.

c. Two RS232 ports;

  1. C.I.Robal microforce balance.
  2. Printer.

2. Software. A two tier computer program was required to control the various peripherals.

Level 1. The individual blocks of code needed to access the various peripherals and the calculations required to obtain or provide the correct voltage input/output.

Level 2. The main code for correctly sequencing the running of the balance, and enabling the different parameters to be set up.

2.2.5 Modifications To Faraday Balance.

No matter how well programs are thought out, problems arise requiring modification to achieve the optimum performance of the instrument. An example of this is outlined below and relates to the problems encountered when reliably sweeping the magnet to a preset field strength.

Originally the computer swept the control voltage up to a preset value giving only 95% reproducibilty. To improve this a positive feedback loop was incorporated to inform the computer of the voltage being supplied to the magnet. This required modification of the software with a resultant reproducibility in the order of 99%.

The final modification was to slow down the magnet sweep speed as it came close to the required voltage. This was done for two reasons:

1. Abruptly stopping the magnet sweep when running at full speed caused a time lag, whilst the voltage applied to the magnet was matched with the control voltage, resulting in variable overshoot of the set level.

2. As the field on the sample was increased this increased the force applied to the sample and balance mechanism. When the magnet stopped sweeping dH suddenly became zero, but the inertia of the sample and mechanical parts took a few seconds to damp down.

These problems have been overcome by allowing the power to be swept to approximately three quarters of the set value, then retarded by approximately 90%, in three steps, up to the set level. This gave reproducibility better than 99% and was probably the best that could be achieved with the available power supply. Fig.2.10 shows a graph of the magnet sweep cycle as provided by the computer.

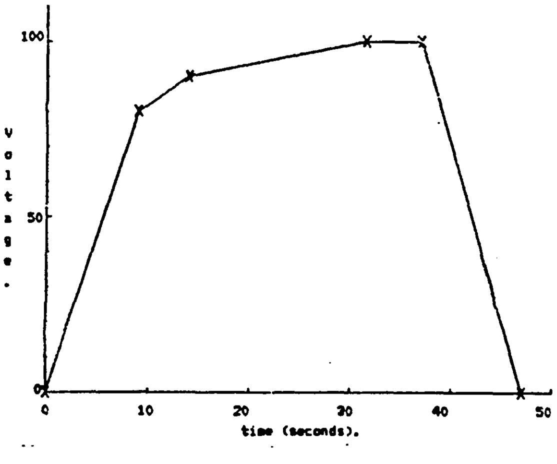


Fig.2.10.
Diagram Of The Sweep Cycle For The Magnet.

3. Chemical Methods.

The following chapter lays out the methods used for the preparation of charge transfer complexes, charge transfer polymers and precursors.

3.1. Characterisation Techniques.

All products were characterised using a variety of techniques. These were:

1. Spectra: Infra-red (I.R.)[Perkin Elmer 783], ^{13}C and ^{1}H-nuclear magnetic resonance (N.M.R.) [Bruker 80MHz], mass spectrometry [VG Mass Lab Micro Mass 30F] and ultra violet/visible (UV/Vis.) spectra [Perkin Elmer PU 8700].

2. Other techniques: Melting point, C,H,N,S micro-analysis (MEDAC Ltd), electrical conductivity, magnetic susceptibility, thin layer chromatography and column chromatography.

Not all the techniques were applied to every material as some of them were either irrelevant or impossible to undertake.

3. Chemicals: Most of the starting materials and solvents were obtained from Aldrich. These were as follows:

CT acceptors and donors; TCNQ, 9-dicyanomethylene-2,4,7,trinitrofluorene, phenazine methosulphate, toluidine blue chloride, rosaniline chloride, neutral red chloride, malachite green oxalate, methyl green zinc chloride salt and Lithium TCNQ (Li(TCNQ)).

CT polymer starting materials; 1,4-dimethoxyphenol, allyl bromide, 3-amino-1-propene, 4-amino-1-butene, 5-amino-1-pentene, 8-amino-1-octene, pyrrolidine, 1,4-cyclohexanedione mono-ethylene ketal, phthalimide and 1,3,5,7-tetramethylcyclotetrasiloxane.

Reagents and catalysts; Zinc chloride, potassium hydrogen carbonate, bis(trifluoroacetoxy)iodobenzene, magnesium sulphate, sodium hydroxide, potassium hydroxide (KOH), hydrochloric acid (HCl), 12-crown-6, hydrazine and hexachloroplatinic acid.

Solvents; The major solvent used for CT complex formation was acetonitrile. Other solvents were; Deioniosed water, dichloromethane, ethanol, toluene, methanol, diethylether, tetrahydrofuran (THF) and chloroform.

Reagents, catalysts and solvents were generally used as purchased without further purification.

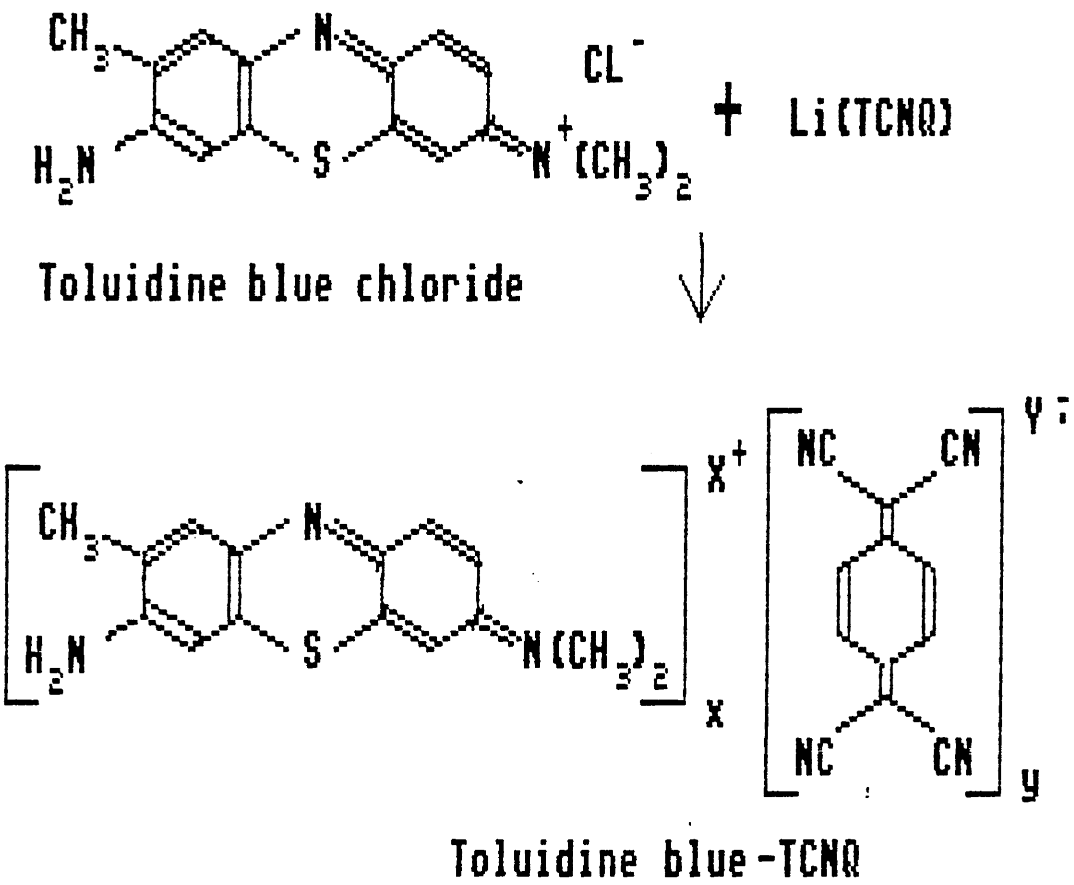
3.2. Preparation Of New Charge Transfer Complexes.

As part of the investigation of the proposed CT polymer a variety of CTCs with potentially interesting properties that may be suitable for the preparation of a CT polymer of the type proposed were investigated. The donors were organic dyestuffs and the acceptors were variations on the TCNQ molecule. The reasons for investigating these molecules were as follows:

1. Effect of side groups on the macro structure.
2. Preparation of CTCs containing useful functions for preparation of a CT polymer.
3. Preparation of potentially novel CTCs.

Several different candidates were investigated. The majority of products obtained were ill-defined but in some cases interesting properties were observed and these materials have been included despite the lack of structural and stoichiometric characterisation.

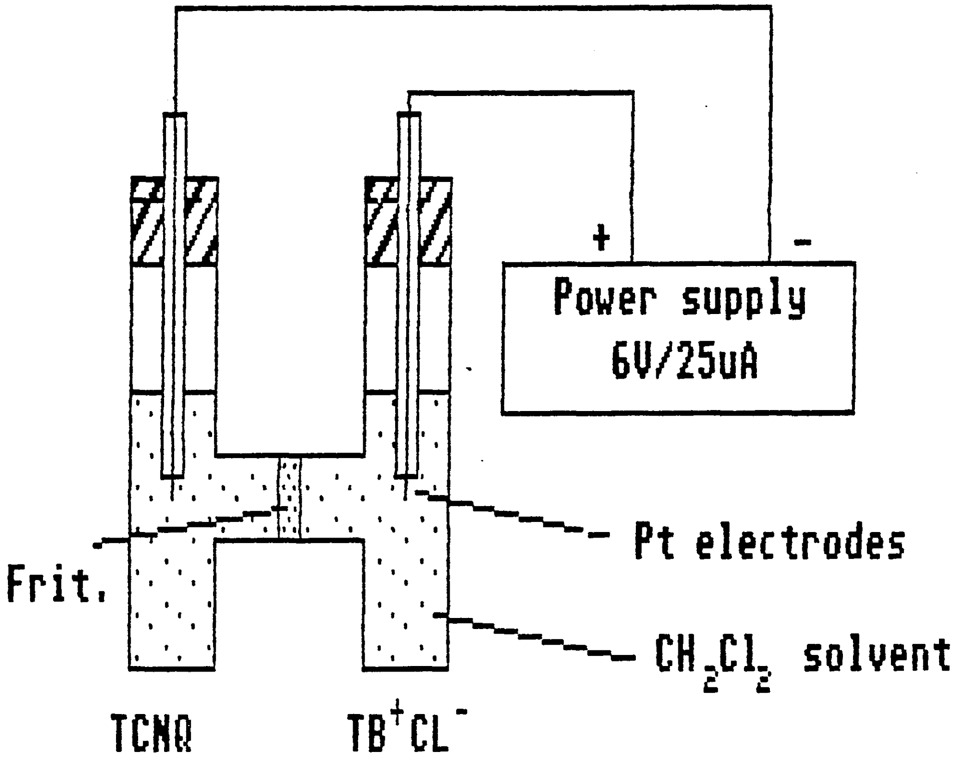
3.2.1. Preparation Of Toluidine Blue-TCNQ (TB-TCNQ).



Li(TCNQ) was prepared using a published method[42]. Li(TCNQ) (0.5g) was dissolved in acetonitrile or methanol (100ml), and to the solution was added an equimolar quantity of toluidine blue (TB) chloride. The mixture was allowed to reflux for 5 minutes, then hot filtered. The filtrate was allowed to cool to room temperature and the resulting precipitate was filtered off and washed with toluene (3x50ml), then water (3x50ml) and finally with ether (100ml) followed by oven drying at 80 °C. This gave a brown amorphous powder which decomposed above 214.2°C. Spectra: I.R.(cm^{-1}) 2350, 2200, 1110;

UV/Vis.(nm) (absorption in arbitrary units) 214.1(0.569), 289.4(1.031), 395.5(0.783), 420.9(0.673), 630.4(1.940), 744.0(0.587), 761.2(0.502), 824.9(1.084). Anal. for TB-TCNQ:0.7H_2O; Calculated C.66.57, H.4.43, N.20.12, S.6.58; Found C.66.75, H.4.15, N.19.86, S.6.46. Room temperature conductivity: 1.18E-6 $\Omega^{-1}cm^{-1}$. Room Temperature magnetic susceptibility (Sheffield City Polytechnic data): 3.69E^{-4} emu mol^{-1}.

3.2.2. Preparation Of TB-TCNQ By Electrocrystallisation.[130,131]



Electrocrystallisation cell

Saturated solutions of the acceptor and donor in dichloromethane (0.5g in 50ml) were, respectively, put in the cathode and anode sides of an electrocrystallisation cell. Electrolysis, using platinum electrodes and a current of 25 microamps at 6 volts, was continued for two days. The product (8.0mg) deposited in the cathode half cell was filtered and then washed with deionised water until the washings were colourless. The material obtained was dried with ether followed by oven drying (80°C for a week). The resulting material was a conglomerate of small shiny brown particles in the form of fine filaments. Spectra: UV/Vis.(nm) (absorption in arbitrary units)

196.5(0.115), 216.8(0.122), 289.9(0.085), 395.1(1.016), 627.4(0.103), 743.2(0.034), 843.2(0.051). Anal. for TB-TCNQ:0.09CH_2Cl_2; Calculated C.67.43, H.4.21, N.20.33, S.6.65; Found 67.47, H.3.91, N.20.35, S.6.07.

3.2.3.Preparation of Rosaniline-TCNQ (R-TCNQ).

See reaction scheme shown in Fig.3.1.

Li(TCNQ) (20mg) was dissolved completely in hot acetonitrile (100ml) and to this was added rosaniline chloride (32mg). The solution was refluxed for five minutes followed by hot filtration. Most of the solvent was removed from the filtrate using a rotary evaporator. The remaining concentrated solution was allowed to cool to room temperature and the resulting precipitate was filtered and washed with toluene (3x50ml), water (50ml) and finally ether (50ml), giving a red powder. Spectra: UV/Vis.(nm) (absorption in arbitrary units) 480.0(0.680), 742(0.005), 842.0(0.950).

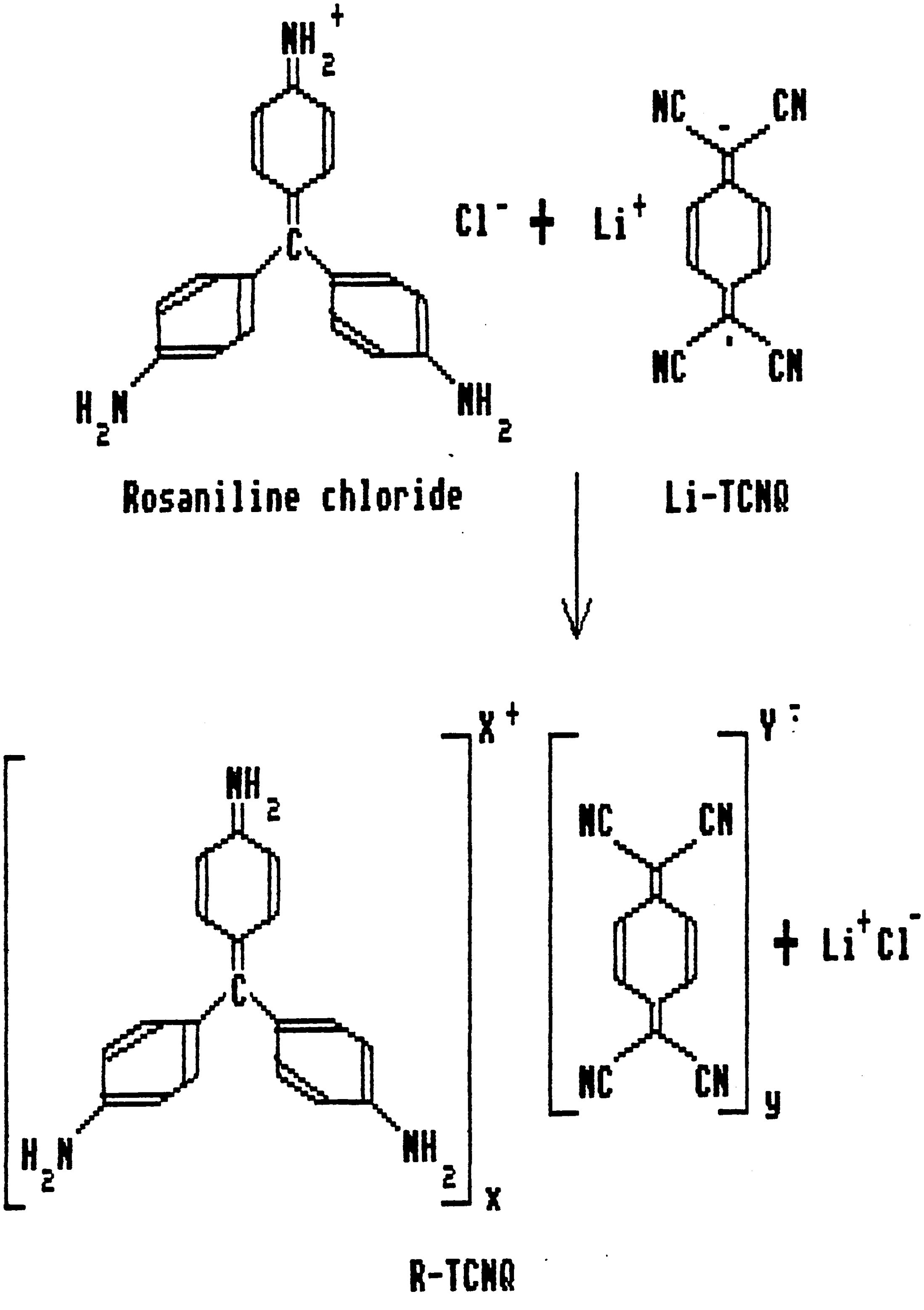
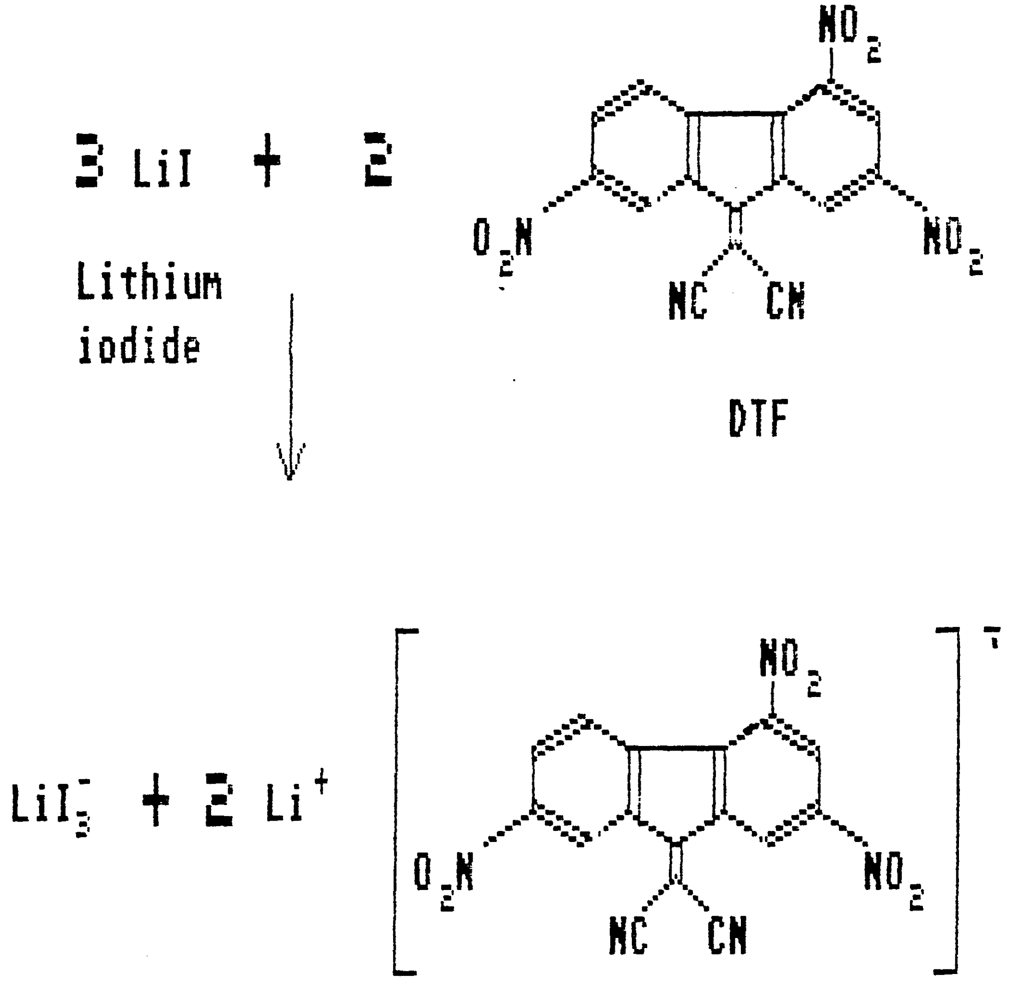


Fig.3.1.
Possible Reaction Scheme For R-TCNQ.

3.2.4. Preparation of Li-(9-dicyanomethylene-2,4,7,trinitrofluorene) (Li-DTF).

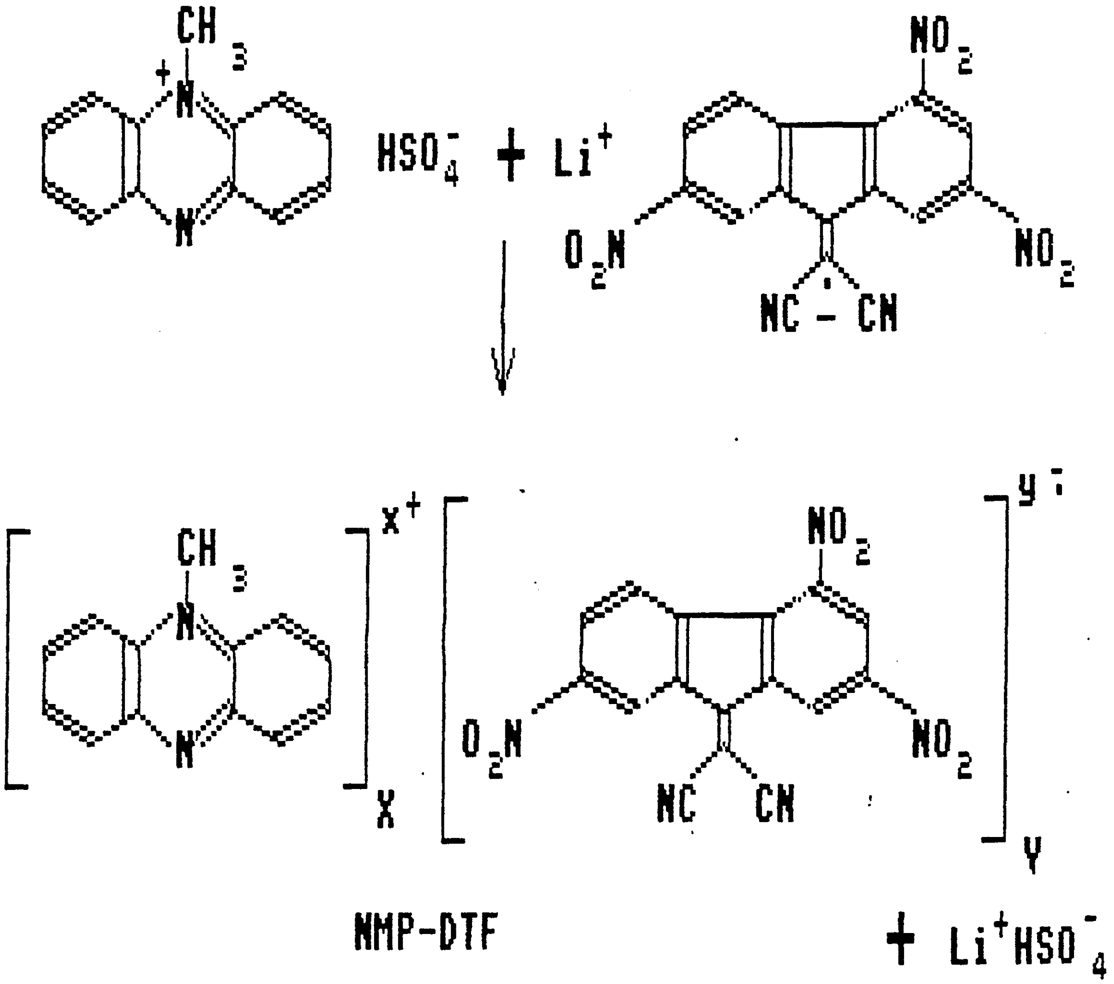
This complex had previously been investigated[132].



Li-DTF

DTF (50mg) was dissolved in acetonitrile (15ml). Lithium iodide (20mg) was added to the solution. The mixture was refluxed for five minutes and allowed to cool to room temperature. The resulting solid (40mg) was filtered, then washed with toluene (50ml), water (5ml) and finally dried after washing with ether (25ml).

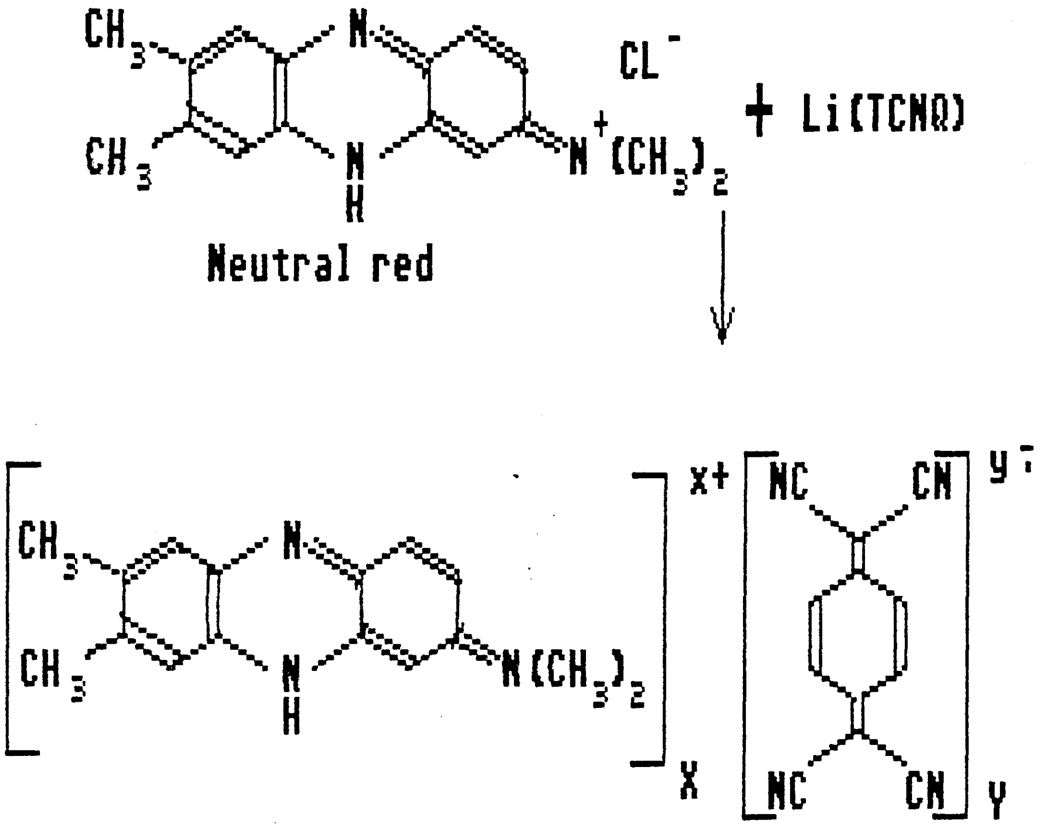
3.2.5. Preparation Of N-methylphenazinium-DTF (NMP-DTF).



NMP-DTF

Li-DTF (20mg) was dissolved in acetonitrile (15ml) and to this was added phenazine methosulphate (20mg). The solution was refluxed for one minute, allowed to cool, and the resulting precipitate was filtered and washed with toluene (50ml), water (50ml) and finally with ether (50ml). The resulting complex (6.4mg) was in the form of small black crystals. Spectra: I.R.(cm^{-1}) 2200, 1500, 1460, 1430, 830, 765; UV/Vis.(nm) (absorption in arbitrary units) 204.9(1.618), 254.1(2.187), 258.9(2.159), 272.3(1.138), 304.8(1.075), 367.5(1.023).

3.2.6. Preparation Of Neutral Red-TCNQ (NR-TCNQ).



Neutral red-TCNQ

Li(TCNQ) (0.54g) was dissolved in hot acetonitrile (100ml). To this was added neutral red chloride (0.738g). The procedure then followed that described for TB-TCNQ and gave a dark product that was insoluble in water and sublimed above 350°C. Spectra: I.R.(cm^{-1}) 2200, 1540, 1500, 1320, 1070, 820; UV/Vis.(nm) (absorption in arbitrary units) 214.0(1.075), 275.0(1.075), 395.2(1.273), 729.0(0.590), 842.4(1.034). Anal. for NR-TCNQ; Calculated C.73.67, H.4.86, N.21.48; Found C.66.46, H.3.08, N.23.80. Room temperature conductivity: $1.35E^{-5}\ \Omega^{-1}cm^{-1}$. Room temperature magnetic susceptibility: $2.3048E^{-4}$ emu mol^{-1}.

3.2.7. Preparation Of Malachite Green-TCNQ (MLG-TCNQ).

See scheme shown in Fig.3.2.

Li(TCNQ) (0.1g) was dissolved in hot acetonitrile (100ml). To this was added malachite green oxalate (0.439g) and the solution was refluxed for five minutes. After filtration half the solvent was removed from the filtrate using a rotary evaporator. The solution was then cooled in a freezer and the product isolated from the solution, using the same procedure as that for TB-TCNQ, giving a dark amorphous powder that decomposed above 200°C. Spectra: I.R.(cm^{-1}) 3400, 2920, 2100, 1590, 1480, 1170, 1050, 830, 730; UV/Vis.(nm) (absorption in arbitrary units), 396.3(0.761), 620.0(1.071), 740.0(0.190), 842.9(0.338). Anal. for MLG-TCNQ:$CH_3CN.0.25H_2O$; Calculated C.76.72, H.5.56, N.16.92; Found C.76.64, H.4.96, N.16.95. Room temperature conductivity: $3.40E^{-3}$ $\Omega^{-1}cm^{-1}$. Room temperature magnetic susceptibility: $2.128E^{-3}$ $emu.mol^{-1}$.

3.2.8. Preparation Of Methyl Green-TCNQ (MG-TCNQ)

See scheme in Fig.3.3.

Li(TCNQ) (0.89g) was dissolved in acetonitrile (100ml). To this was added methyl green (0.1g) and the mixture was refluxed for five minutes and allowed to cool. The complex was isolated from the solution following the same procedure as that for TB-TCNQ giving a black amorphous powder (0.060g) which decomposed above 182°C. Spectra: UV/Vis.(nm) (absorption in arbitrary units)

395.2(0.828), 633.6(0.331), 743.5(0.237), 761.7(0.202), 843.2(0.442). Anal. for MG-$TCNQ_2$; Calculated C.75.62, H.5.35, N.19.02; Found C.68.13, H.4.17, 18.91. Room temperature magnetic susceptibility: $1.246E^{-3}$ emu mol^{-1}.

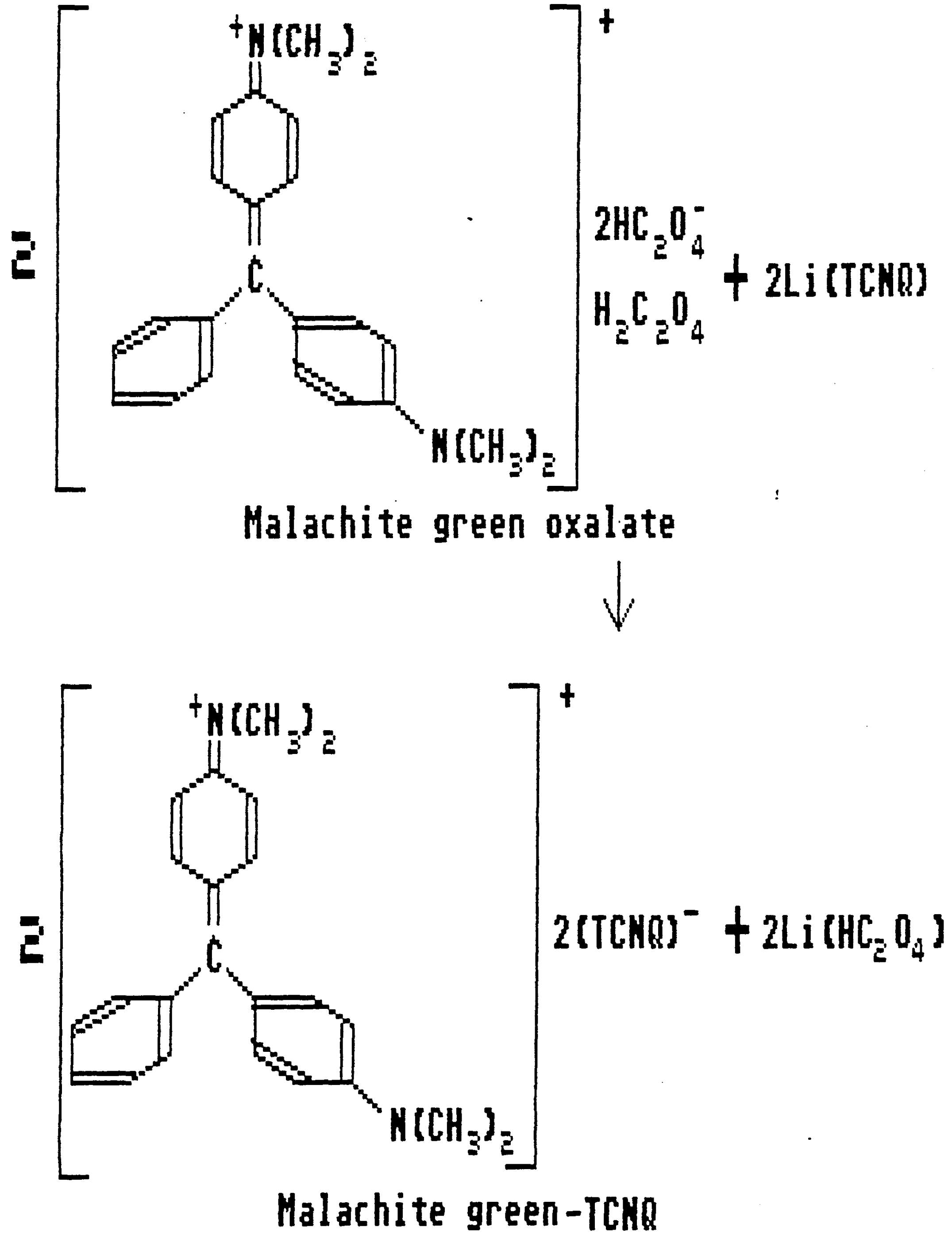


Fig.3.2.
Possible Reaction Scheme For MLG-TCNQ.

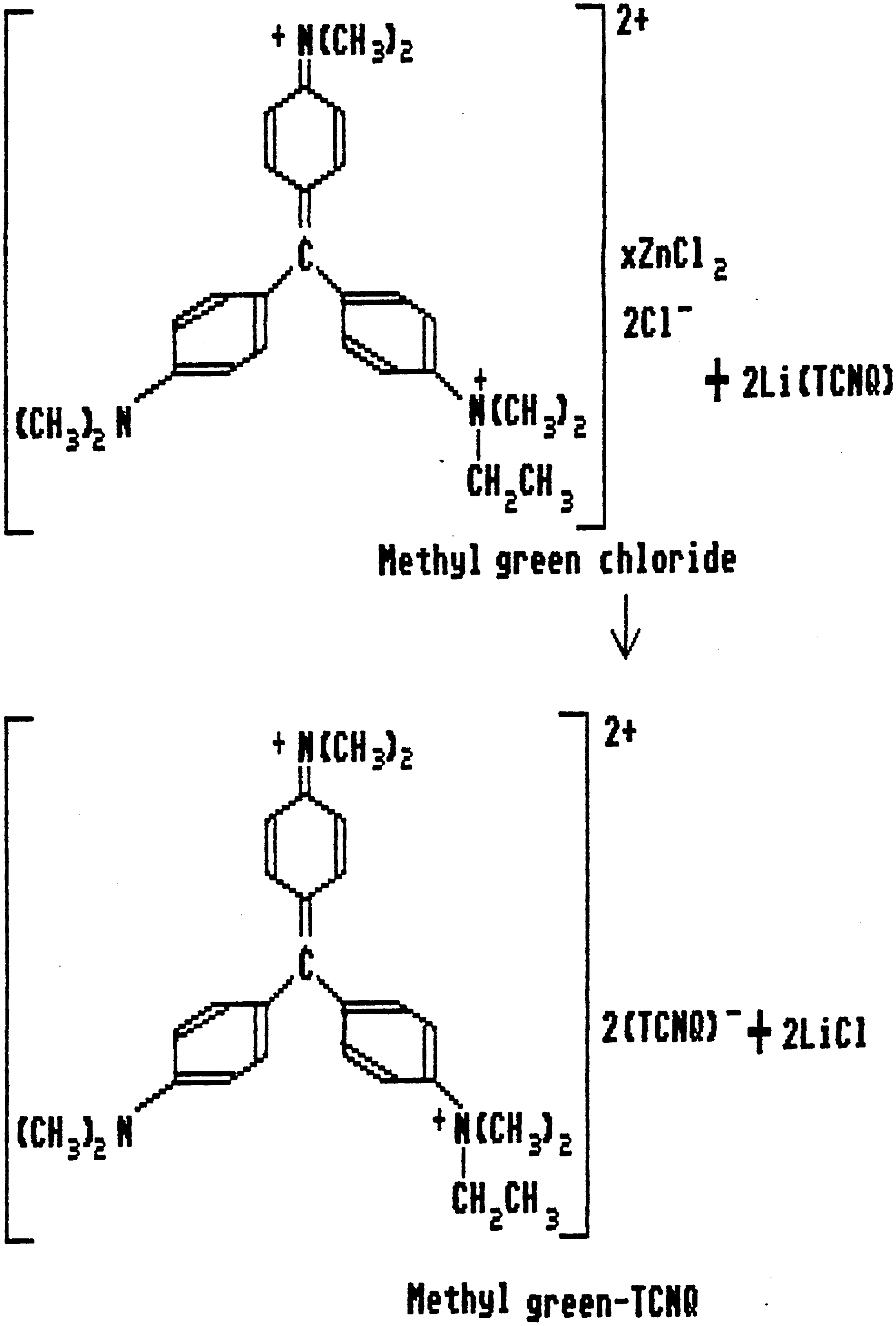


Fig.3.3.
Possible Reaction Scheme For MG-TCNQ.

3.3. Preparation of CT Polymer.

An outline and discussion of the following synthetic pathways is given in chapter 7.

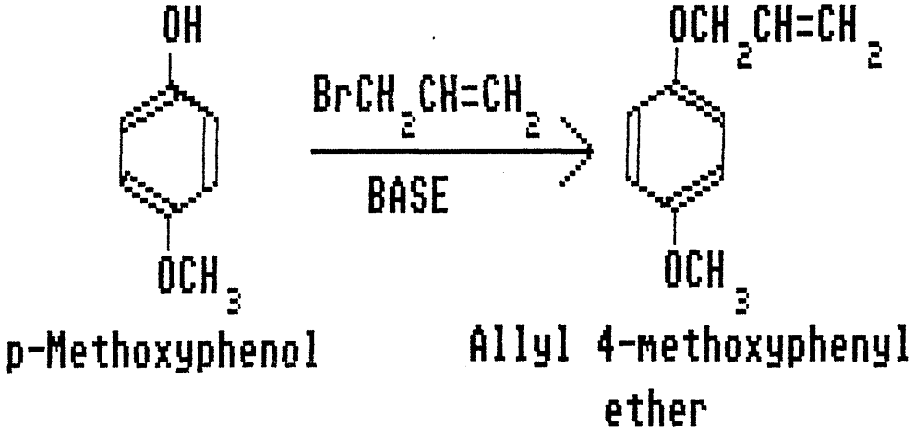
3.3.1. Friedel-Crafts Alkylation.

The first attempt at preparing a CT acceptor with attached carbon spacer involved a Friedel-Crafts alkylation reaction[133] where allyl bromide was to be attached to a precursor of TCNQ. The preparation was as follows:

1,4-dimethoxyphenol (3.85g) was dissolved in chloroform (25ml) in a carefully dried round bottomed flask which had been flushed with nitrogen. To this allyl bromide (2.03g) and zinc chloride (0.5g) were added. The mixture, under nitrogen, was carefully heated for 1 hour using a sand bath. The reaction was followed using thin layer chromatography (TLC). The product was not worked up as TLC indicated the presence of substantial impurities.

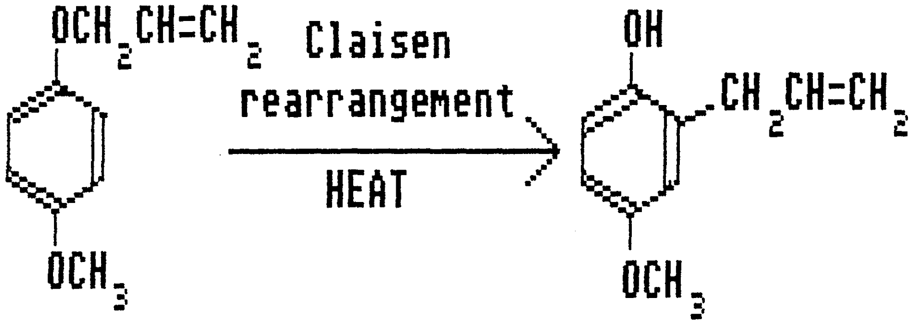
3.3.2. Attachment Of A Three Carbon Spacer Via A Claisen Rearrangement Reaction.[134,135]

1. Preparation of allyl 4-methoxyphenyl ether.



A mixture of p-methoxyphenol (63g), allyl bromide (66g) and anhydrous potassium carbonate in dry acetone (100ml) was refluxed for eight hours, then allowed to cool. To this mixture was added water (200ml) and the solution was extracted with ether (2x100ml). The extracts were combined and washed with 10% aqueous sodium hydroxide (2x100ml), then dried over anhydrous potassium carbonate. After the drying agent had been filtered off the ether was removed by rotary evaporation. The crude product was distilled (80°C/2mmHg) providing a pale yellow liquid (70.82g, 85%). Spectra: I.R.(cm^{-1}) 3080-2820, 1640, 1580, 1500, 1220, 1030, 990, 920, 820, 750; ^{1}H-N.M.R.(δ) 3.63, 4.33, 6.61.

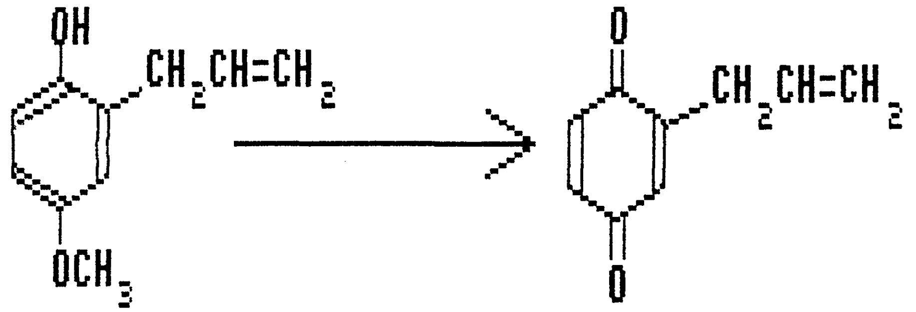
2. Preparation of 2-allyl-4-methoxyphenol.



Allyl 4-methoxyphenyl ether **2-Allyl-4-methoxyphenol**

Allyl-4-methoxyphenyl ether (5g) was added to freshly distilled N,N-dimethylaniline (5g). The solution was refluxed for three hours under an anhydrous nitrogen atmosphere. The resulting solution was extracted with dilute HCl (2M,6x50ml) followed by 10% aqueous sodium hydroxide (3x50ml). The aqueous alkaline extracts were combined and acidified by continuous addition of conc. HCl,(the pH was checked using litmus paper). The aqueous layer was extracted with ether (3x50ml), and the extracts dried with magnesium sulphate. The ether was then removed by rotary evaporation. The crude product was distilled (88°C/2mmHg) to give a pale yellow liquid (4.07g/81.5%). Spectra: I.R.(cm^{-1}) 3400, 3090, 2820, 1000, 830; ^{1}H-N.M.R.(δ) 4.7, 6.61, 4.8-6.2.

3. Preparation of 2-allylquinone.[136]

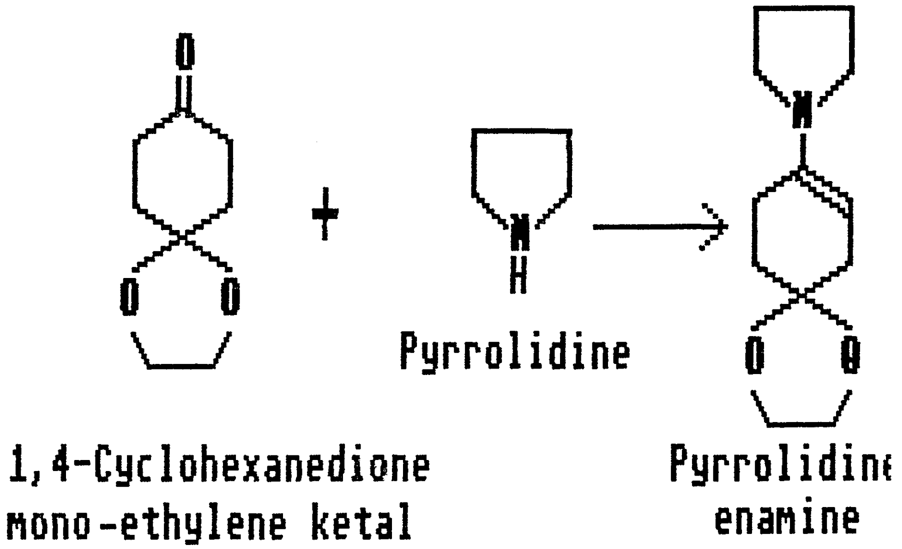


2-Allyl-4-methoxyphenol 2-Allylquinone

Bis(trifluoroacetoxy)iodobenzene (5.1g) and potassium hydrogen carbonate (1.2g) in a mixture of acetonitrile and water (2:1/36ml) was added to 2-allyl-4-methoxyphenol (2g) and the mixture refluxed for one hour. This mixture was then added to dichloromethane followed by washing successively with sodium hydrogen carbonate, sodium hydroxide and brine. The outcome was a mixture of compounds. Purification was attempted using both vacuum distillation and column chromatography, but there was only sufficient crude product to obtain spectra, some of which suggested that the desired product was present in the mixture. Spectra: I.R.(cm^{-1}) 2800-3100, 1655, 1300, 1065, 1000,840-950, 830, 730; ^{1}H-N.M.R.(δ) 2.9-3.2, 3.65, 4.8-5.3, 5.5-6.0, 6.4-7.8; ^{13}C-N.M.R.(δ) 32.46, 94.33, 118.97, 127-137.

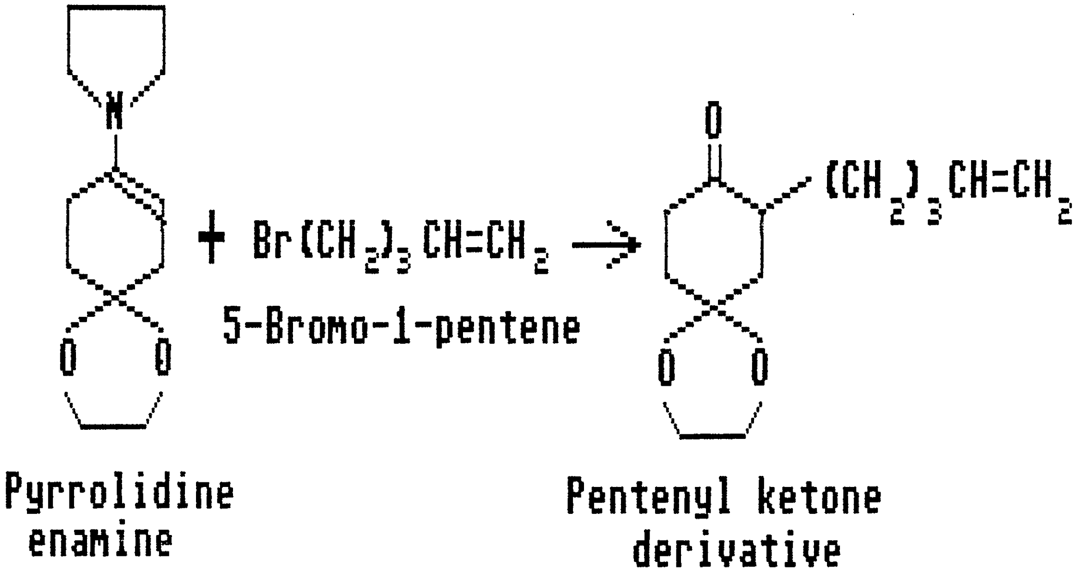
3.3.3. Stork Enamine Synthesis.[137]

1. Preparation of pyrrolidine enamine.



Pyrrolidine (5g) and 1,4-cyclohexanedione mono-ethylene ketal (10g) were refluxed together in toluene (100ml), which had previously been dried overnight, using a Dean Stark trap. The toluene was removed using a rotary evaporator and the enamine was vacuum distilled (120-130°C at 0.4mm Hg) to give a colourless liquid (11.02g/81%). As this was light sensitive and darkened quickly it was stored, in the dark, in a fridge. Spectra: I.R.(cm^{-1}) 2800-3000, 1660, 1400, 1200, 1060, 1020, 950, 850; ^{1}H-N.M.R.(δ) 1.3-1.9, 2.0-2.5, 2.7-3.0.

2. Alkylation of the enamine.

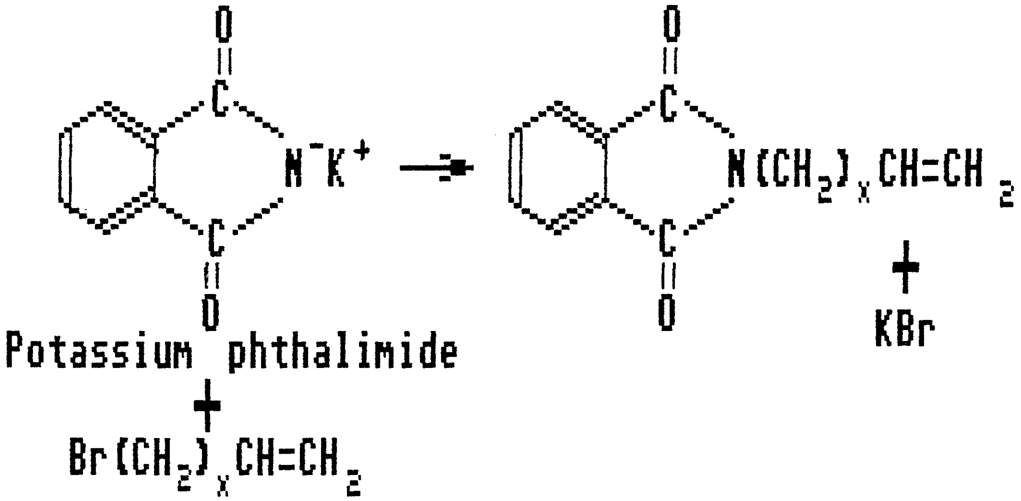


The pyrrolidine enamine from 1 above was directly reacted, without purification, with 5-bromo-1-pentene (0.067mols) in acetonitrile (100ml). The mixture was refluxed for 16 hours under a nitrogen atmosphere when TLC showed the reaction had finished. (TLC solvent was 20:1 petrol/ethyl acetate). Most of the acetonitrile was removed and the residue stirred with potassium hydroxide (100ml 10%) for 24 hours at room temperature. The resulting pentenyl ketone derivative was extracted with ether. The crude product (14g) was a solid (mp.64-72°C). As it seemed light sensitive it was stored, in the dark, in a fridge. Spectra. I.R.(cm^{-1}) 2800-3000, 1740, 1660, 910, 850, 820, 750; ^{1}H-N.M.R.(δ) 1.2-2.0, 2.2-2.7, 4.6-5.1, 5.4-6.0; ^{13}C-N.M.R.(δ) 20-40, 45, 65, 75-80, 116, 136.

3.3.4. Preparation Of N-ω-Alkenyl-tricyano Compound Derived From TCNQ.[138]

The only aminoalkene commercially available was allyl amine (from Aldrich). Longer spacers had to be prepared from the corresponding bromoalkene using a Gabriel synthesis as outlined below in 1 and 2.

1. Preparation of the phthalimidoalkenes.[139,140]



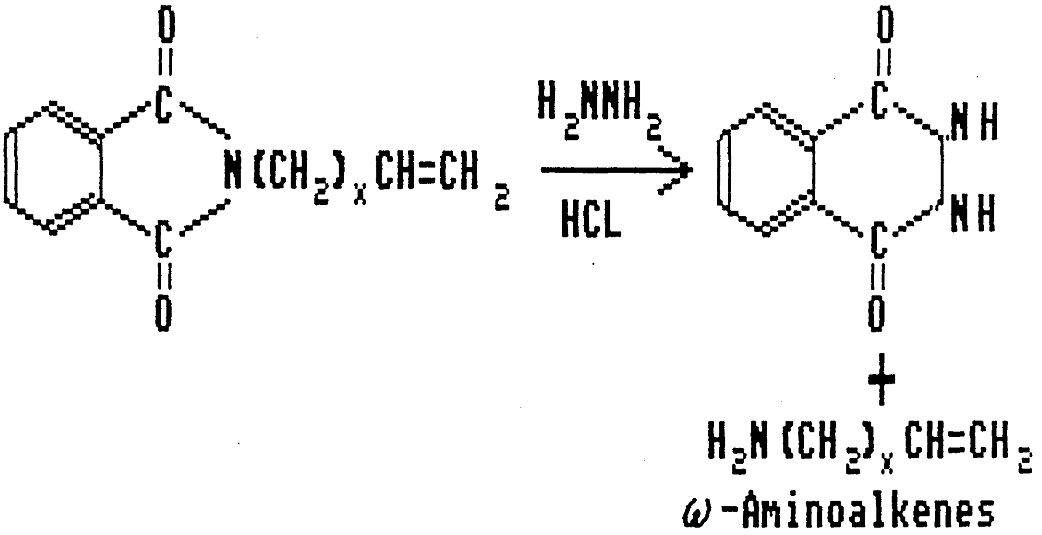
The appropriate ω-bromoalkene (0.01M) was dissolved in toluene (13ml) and to this was added potassium phthalimide* (0.012M) and catalytic 12-crown-6 (0.002M). The mixture was refluxed for six hours. After the mixture had cooled it was added to water (50ml). The aqueous layer was extracted with dichloromethane (3 x 20 ml), the organic layers were combined and the dichloromethane and toluene were removed using a rotary evaporator. The resulting

---

* Potassium phthalimide was prepared by a standard procedure[141].

product was a liquid or white solid depending upon the number of carbon atoms in the bromo alkene precursor. Spectra: I.R.(cm^{-1}) 3400-3700, 2700-3100, 2200-2500, 1600-1800, 1300-1500, 1070-1100, 880-1090, 800, 730.

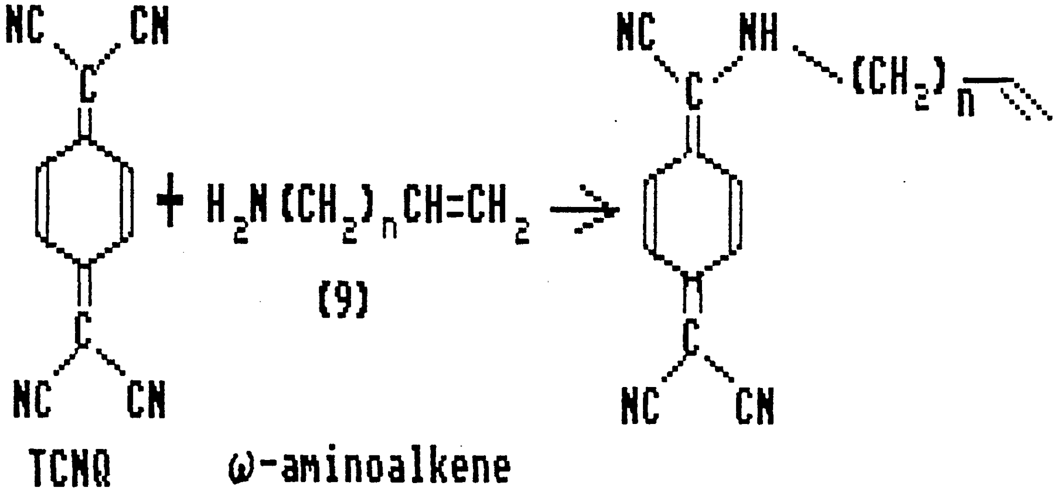
2. Formation of the ω-aminoalkenes.



To the crude product of the phthalimidoalkene, methanol (50ml) and hydrazine (2ml) were added. The mixture was refluxed for one hour. After cooling, water (25ml) was added and the methanol removed on a rotary evaporator. The remaining mixture was cooled to 0°C and concentrated hydrochloric acid (25ml) was carefully added. The white suspension formed was refluxed for one hour then cooled to 0°C in a fridge. The precipitate of phthalhydrazide was removed by filtration and the filtrate neutralised with sodium hydroxide (2M). The amine was extracted from the aqueous layer with chloroform (3x30ml). The extract was dried over magnesium sulphate and the chloroform removed on a rotary evaporator, giving a 15% yield (for the 8-amino-1-octene).

3. Reaction of ω-aminoalkene with TCNQ.

This reaction was based on a literature reaction of TCNQ with n-butylamine[138]. The procedure outlined below is for the addition of the 3-amino-1-propene, but is common for attachment of all the ω-aminoalkenes.

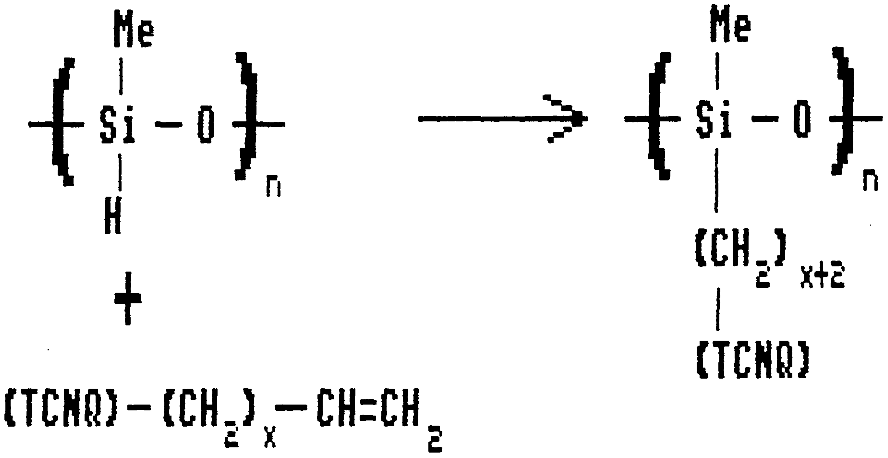


(8) (10)

TCNQ (2g/0.0092mol) was dissolved in warm THF (250ml) and allylamine (0.69g/0.0121mol) was added. The solution was left at room temperature for two days, after which time approximately half the solvent was removed on a rotary evaporator. The remaining mixture was dissolved in sodium hydroxide (100ml/2m), filtered, and the filtrate was then acidified with HCl at 0°C, acidification was monitored using litmus paper. The resulting purple precipitate (1.27g) was filtered off and dissolved in warm THF. The solution was filtered and hexane added to the filtrate to precipitate a small quantiy of a purple amorphous powder. Spectra: I.R.(cm^{-1}) 3000-3700, 2700-3000, 2110-2220, 1650, 1510, 1410, 1020, 930, 840; UV/Vis(nm) (absoption in arbitrary units) 222.9(0.768), 365.9(1.056), 422.9(0.629), 842.8(0.014); ^{1}H-N.M.R.(δ) 0.5-2.3, 2.4-3.0, 3.0-4.0, 4.9, 5.2-5.8, 7.2-8.6.

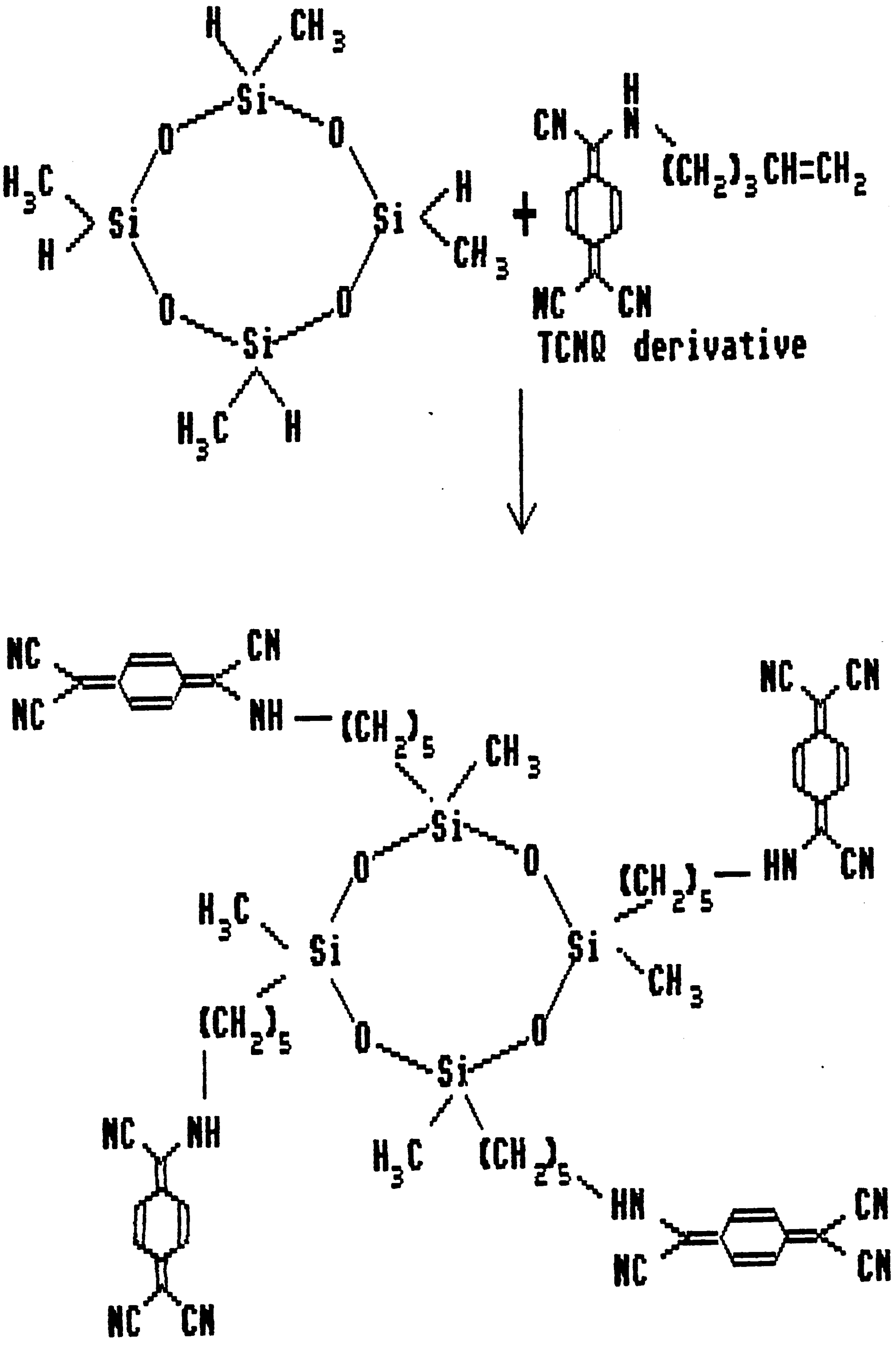
3.3.5. Attachment Of TCNQ Derivative To Siloxane Backbone.

The basic reaction scheme is shown below[142].



(TCNQ) = Modified TCNQ as specified elsewhere.

The preparation was as follows:



Note: Moisture and light were excluded from the reactions. To this end all glassware was cleaned with acetone and dried overnight in an oven (80°C). All flasks were purged with dry nitrogen. The reaction vessel was covered with aluminium foil to exclude any light.

The Five Carbon spacer TCNQ derivative (0.35g), 1,3,5,7-tetramethylcyclotetrasiloxane (0.07g) and a small quantity of hexachloroplatinic acid catalyst (1.14E^{-7} mol/ >99.5% purity) were refluxed with stirring for two days in dry THF (100ml), after which the catalyst was removed by passing the mixture through a chromatography column. The solvent was removed from the remaining solution to leave a purple glassy solid (0.021g). Spectra: I.R.(cm^{-1}) 3400, 2900-3000, 2200-2220, 1710-1780, 1650, 1600, 1510, 1150-1300, 1000, 930, 830-870, 770; ^{1}H-N.M.R.(δ) 0.5-1.4, 2.0-2.3, 6.5-8.0.

CHAPTER 4

RESULTS, DISCUSSION OF ERRORS AND INSTRUMENTATION EVALUATION

4. Results, Discussion Of Errors And Instrumentation Evaluation.

It is important to take account of and analyse the various errors associated with this work and their effect on the validity of the results. The errors are broken down into two areas; those due to the equipment used to characterise the materials, and those due to the preparation of these materials. Details are given below.

4.1. Instrumentation Errors.

The two major instruments were the conductivity rig and the Faraday balance.

4.1.1. Errors Associated With The Conductivity Rig.

The rig was designed to be computer controlled. This aim was achieved as far as possible. It should, however, be realised that the measurement of absolute conductivity is very difficult to achieve for a number of reasons which are discussed below:

Large errors can arise in the measurement of absolute conductivity due to the size and shape of the samples used.

Calibrations were made using standard resistances (see Fig.4.1), where 1% tolerance resistors of various values in the DVM's operating range were connected to the four point probe. Results showed that the instrument accuracy was good.

Standard resistance 1% tolerance resistors. in Ω	Some typical observed resistances in Ω
10	9.98
100	99.93
1000	1001.2
10000	9971.7
100000	100981.0

Fig.4.1.
Compararison Of Standard Resistances With Results Obtained From The Conductivity Rig. Results Are In Ohms (Ω).

It was, however, difficult to assess what effects changing the size of the sample had. Two possible ways of correcting and evaluating these errors are outlined below:

1. Some workers have cited corrections for sample shapes[126]. Here the apparent resistivity is divided by a correction factor that has been worked out for various geometries.

2. Comparison of the conductivity from samples of different shapes. This would at least give an insight into the magnitude of the variability of resistivity with sample shape for our equipment. To date this has not been done as a suitable sample has yet to be found. Unfortunately, the conductivity of pure silicon was too low and pure copper was too high to obtain good data with the DVM used with the rig.

It had to be asked how relevant error evaluation and corrections were to our work where absolute values are often of less interest than the reliable observation of trends. If time had allowed and a high performance four-point probe had been available the above investigation would have been a useful step towards absolute measurement.

The probe design was crucial in obtaining accurate measurements. Various approaches using sprung pins, in order to obtain an even pressure on the sample, were looked at. Some of the major factors we tried to solve were:

1. Pin spacing. It was important to ensure the pin spacing was equal. This was achieved by accurate drilling of the supporting frame, followed by measurement of the spacing using a micrometer.

2. Minimising thermal load. Using the minimum viable amounts of material with relatively low thermal conductivity meant that less time was taken for the system to reach thermal equilibrium. Therefore, when readings were taken, the probability that the sample was at the same temperature as the cold head and temperature sensor was greater. In addition, low thermal loads enable the instrument to achieve lower temperatures.

3. Minimisation of sample damage. Sharp pins tended to crack brittle samples. The problem was tackled by using pins with different point pitches, so spreading the force being applied to the sample. Unfortunately, this could create a problem in that a wider pitch point also

means that a larger area of the sample is in contact with the pin complicating conductivity measurement.

Any design used would be a compromise. The only way to get consistent results would be to follow exactly a set procedure for sample loading. A big problem would be ensuring that the same pressure was applied to each sample, bearing in mind that differences in sample hardness would affect the applied pressure.

A major factor encountered was that the DVM used was only able to work within a limited range of conductivities. One way to improve this would be to obtain a DVM with a much greater range or, for high conductivities, use a phase sensitive detector. Such equipment, however, requires financial outlay not presently available.

The final instrumentation error associated with the conductivity rig concerned temperature sensing. The purchase of commercially available equipment in 1989 has meant that far more accurate readings could be taken than were possible when the rig was first constructed, enabling the measurement and control of temperature to be better than ± 1 degree Kelvin.

The main problem with temperature sensing was the difference between the sensor and the sample temperatures. The reasons for this were:

1. The distance of the sensor from the sample. This was kept as short a possible, the sensor being thermally anchored to the cold head and separated from the sample by approximately 2mm of copper, which was part of the "cold tip" of the cryostat.

2. Heat capacity of the sample. This determined the time required for the sample to reach thermal equilibrium. Some of our data does indicate that thermal equilibrium may be a problem. One way to reduce this would be to use thinner samples. These, however, would crack very easily.

3. Thermal flow across the sample. Conductivity was measured from the top of the sample, thus thermal conduction was important. It was likely that some of the changes in conductivity seen at the lower end of the temperature range were a result of the thermal lag in the sample. As in 2 (above) thinner samples would help overcome this problem, but this creates a problem with sample damage.

To counter these problems the temperature sensor was firmly anchored to the cold head as close to the sample as possible, and sufficient time (often several minutes) was allowed for the sample to reach thermal equilibrium before readings were taken. It was found that the most accurate method of taking readings was to cool the sample to the base temperature, allow 30 minutes for the sample to reach thermal equilibrium, then let the sample heat up slowly whilst taking readings.

4.1.2. Overall Performance Of The Conductivity Rig.

In the light of the above limitations and the inherent difficulties in measuring absolute conductivity, the rig at Sheffield City Polytechnic can only be of use, at present, for the investigation of transition temperatures, obtaining "ball park" values for conductivity and establishing relative trends in a series of similar materials. As a result of the knowledge gained in constructing this instrument, it is not unreasonable to question the accuracy of some of the data published without a detailed appraisal of the equipment.

4.2 Errors Associated With The Faraday Balance.

As the Faraday Balance was a complex piece of equipment potential errors were numerous. These are outlined below:

The first possible source of error is associated with the magnet power supply. The Sheffield City Polytechnic balance had some advantages over other systems, the major one being that the power supply for the magnet was a DC/DC generator, providing a very stable output isolated from the mains which was prone to frequent voltage fluctuation. This meant that the magnet could be repeatedly swept to a predetermined point with a precision better than 1%. A/D and D/A conversion was a possible source of error. It was not good enough to take a single reading as the result from one A/D conversion was often far from the true value. Many readings were necessary and the average value was taken. The system used required the averageing of 1000 samples to achieve a precision better than 0.5k (for the exchange of temperature data). The values obtained were a trade-off between precision and the time required to take the readings. Taking more samples would give better precision, but the extra time involved would affect accuracy as the temperature changed with time.

Other sources of error associated with A/D and D/A conversion were noise and temperature dependent resistance in electrical cables and associated circuitry. Future plans to overcome these problems would include replacing voltage control lines by transmitting control information optically or as a frequency modulated signal[143].

There were two errors associated with sample weight change measurement. Firstly, C.I.Robal specify an accuracy of ± 0.02mg for their microforce balance head, which can be a disadvantage for some materials, as their change of susceptibility with respect to temperature can be within this range, thus placing a fundamental limit on the sensitivity of the balance. Secondly, static electricity on the quartz hangers resulted in false readings. This problem was solved by replacing the quartz hangers with ones made of copper. The susceptibility of the copper was corrected for by the computer.

The main error was the drift due to the correction for the sample bucket and associated hangers. Extensive studies showed that the correction was affected by such factors as how long the bucket was dried prior to the sample being loaded. It was hoped to track down all the factors contributing to this drift as the balance became fully commissioned.

4.2.1. Overall Performance Of The Faraday Balance.

Susceptibilities of NMP-TCNQ as measured on the balance match published data[42] to within the ± 0.04mg error for the microforce balance head (see Fig.4.2 and Fig.4.3). Also work with high temperature ceramic superconductors has shown temperature measurement of proven accuracy at the lower end of the temperature range (see Fig.4.4).

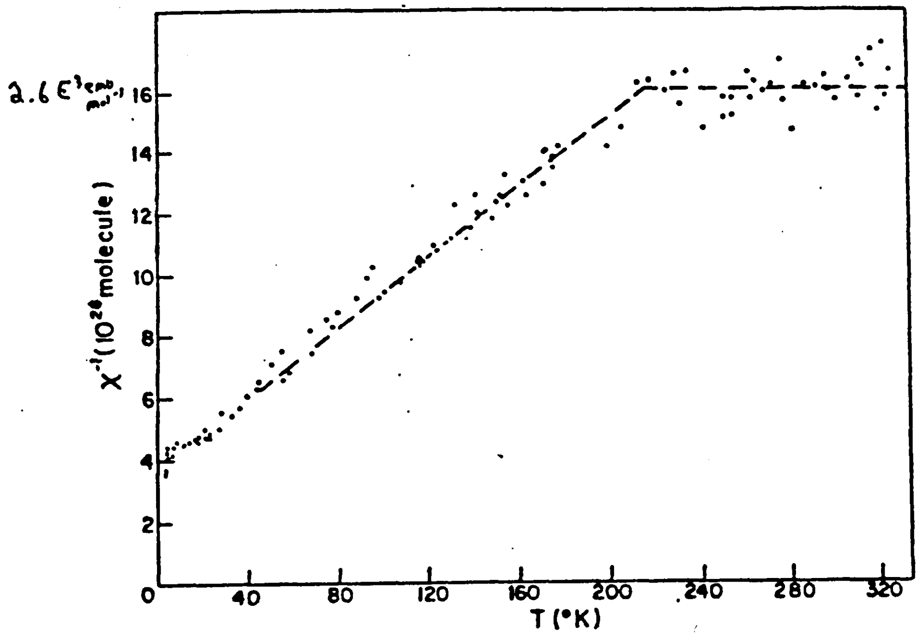


Fig.4.2.
Magnetic Susceptibility Of NMP-TCNQ From Published Data (Ref.43).

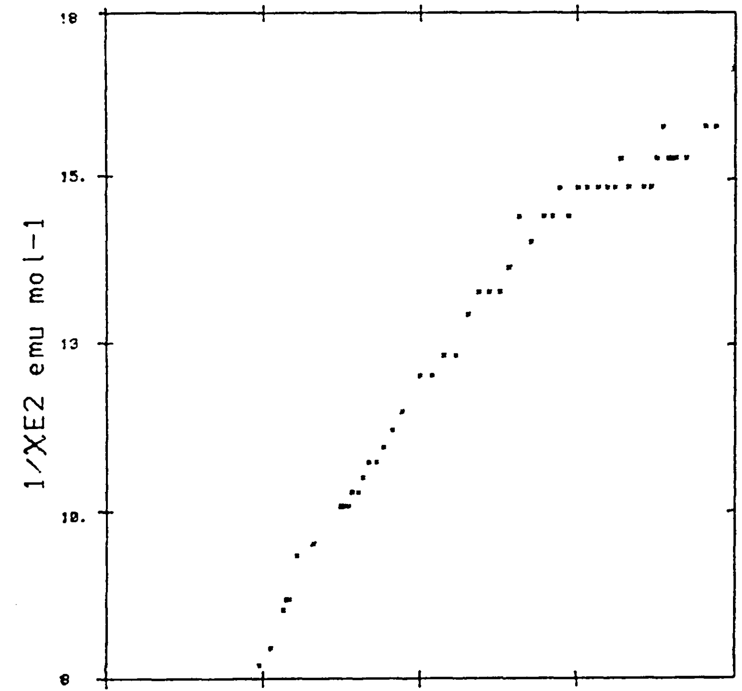
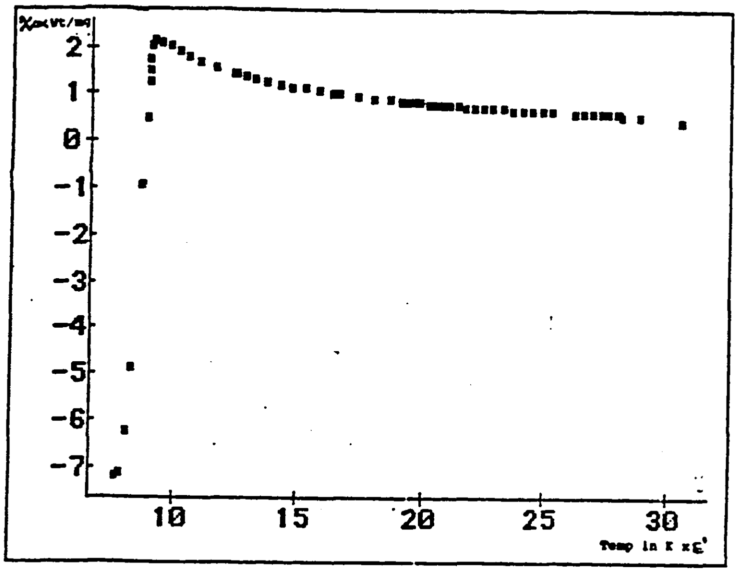


Fig.4.3.
Magnetic Susceptibility Of NMP-TCNQ From Sheffield City Polytechnic Magnetic Balance.



χ in mg vs Temp in K x E' for $YBa_2Cu_3O_{7-x}$

Fig.4.4.
Magnetic Susceptibility Of $YBa_2Cu_3O_{7-x}$ Showing The Onset Of The Superconducting Transition At Approximately 93K.

There are some minor anomalies with respect to published data. One likely cause is the method of calculating the diamagnetic correction. For example the CN^- ion has a correction of $200E^{-6}$ emu mol^{-1}. The TCNQ molecule contains four CN groups, only one of which may carry a negative charge. This is only one example of this type of problem. Also the transition shown at approximately 229K in the susceptibility of NMP-TCNQ was not precise. However, the literature suggests[11] that this is a common trait for this material (see Fig.4.5).

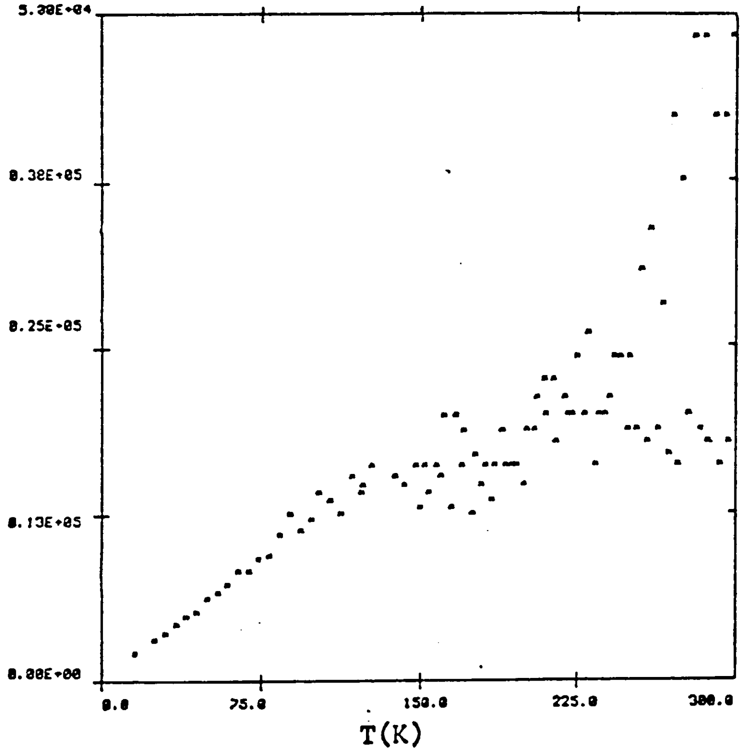


Fig.4.5.
Magnetic Susceptibility Of NMP-TCNQ From Ref.11.

Overall the Sheffield City Polytechnic balance has performed extraordinarily well considering the short development time for such a project. Data obtained has already contributed to a publication[144].

4.3. Evaluation Of Other Types Of Error.

Errors other than those concerned with the measurement of electrical conductivity and magnetic susceptibility are outlined in this section.

One problem with CT complexes is that the I.R. and N.M.R. spectra can often be unclear as the conjugated π-system tends to broaden the peaks resulting in a loss of resolution. An example of this is the I.R. spectrum of TB-TCNQ shown in Fig.4.6.

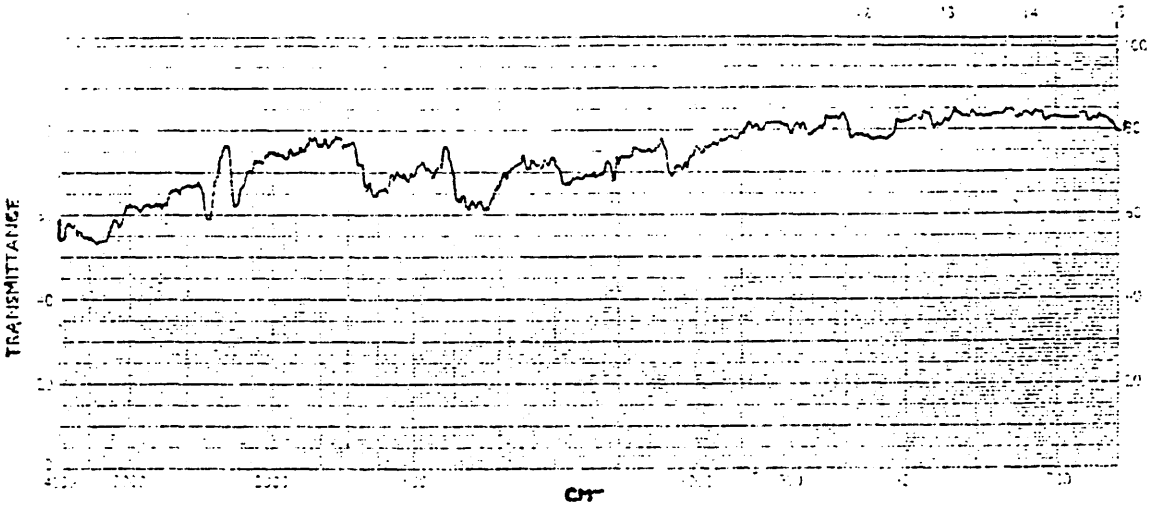


Fig.4.6.
I.R. Spectrum Of TB-TCNQ.

One attempt to improve the N.M.R. spectra was to change the solvents, but this was not very successful. Deuterated dimethyl sulphoxide appeared to give the best results for the TCNQ derivative, but even then spectra were not consistent and often gave poor ill-defined peaks (see Fig.4.7).

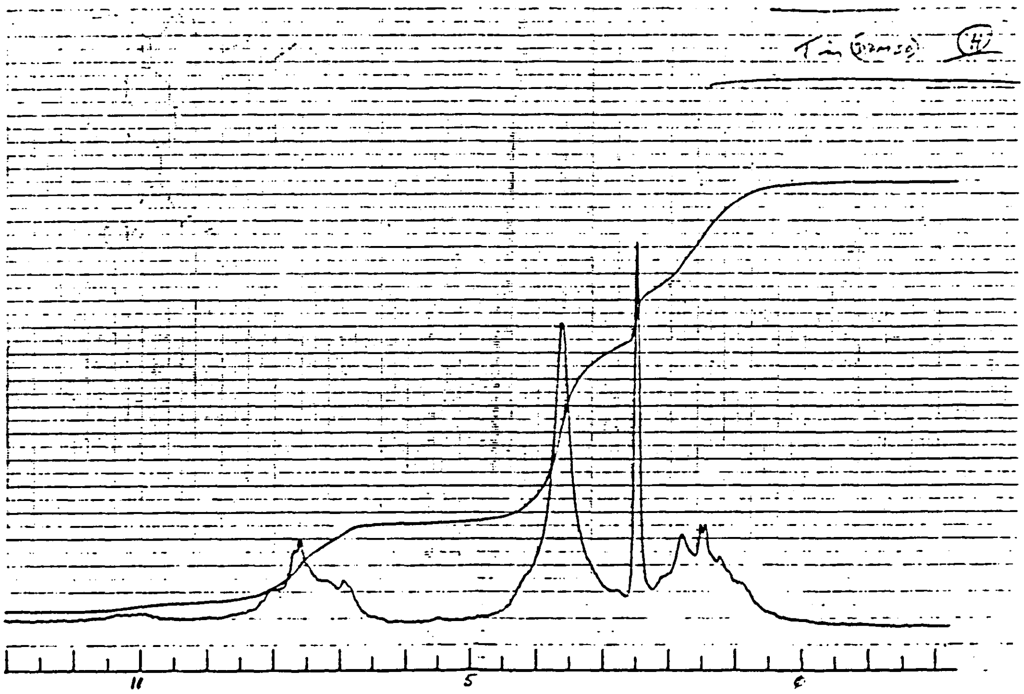


Fig.4.7.
^{1}H-N.M.R. Spectrum Of 5-Carbon Spacer TCNQ Derivative Taken Using Deuterated Dimethyl Sulphoxide.

The preparation of KBr discs for I.R. is rarely consistent and could have been a reason for poor spectra. However, good enough results have been obtained to help identify some groups such as CN (stretching frequency at 2200cm^{-1}). I.R. spectroscopy is often the best indicator of the presence of a chemical group in CT complexes.

TCNQ species are often identified using U.V./Vis spectra, which provide useful information, for example, the absorption peaks of the TCNQ radical anion (approximately 342 and 842nm) and the uncharged TCNQ molecule (approximately 395nm) have been used to estimate the amount of charge transfer (by measuring the ratios of the peaks)[11,145]. The author has not used this method for two reasons. Firstly, the complicated spectrum; often it is not possible to clearly distinguish between the peaks at 395nm and 342nm thus complicating calculations. Secondly, charge transfer can itself be affected by taking the spectrum since these compounds can be sensitive to UV radiation.

CHAPTER 5

RESULTS, DISCUSSION FOR CT COMPLEXES

5.Results, Discussion For CT Complex.

5.1. Strategy Adopted For Selecting New CT Comlexes.

A number of different complexes were investigated. Those showing some potential were then characterised using a variety of methods such as electrical conductivity and magnetic susceptibility. The amount of information obtained often depended on how much sample was available. There follows a discussion of the work undertaken.

There were a number of reasons for the speculative preparation of the CT complexes investigated. These are outlined below.

5.1.1. Potentially Useful Properties.

1. Potentially useful functional groups. CT complexes that contained functional groups of potential use in attachment of a spacer group were essential for the preparation of our proposed CT polymer. Model complexes were looked at as possible candidates for incorporation into polymer composites.

2. Molecular electronic properties. The strategy in this case was to investigate complexes, comprising donor dyestuffs and TCNQ, possessing characteristics which could result in useful molecular electronic properties. One major factor looked for was asymmetry. This is an important feature for such effects as non-linear optics

and piezoelectricity. It must be born in mind that using asymmetrical donors does not ensure an asymmetric macro structure and therefore no attempt was made to predict the outcome of these reactions. This strategy has, however, proved effective as one complex, TB-TCNQ, appeared to exhibit unusual magnetic properties.

5.1.2. Approach To Preparation.

CTCs can be prepared in a short time using only simple equipment. This made speculative preparations attractive, as complexes that showed little promise did not require a lot of valuable time and money in their preparation.

Well documented preparative methods[42] were modified for the complexes. Donor and acceptor salts were refluxed together in an appropriate solvent, usually acetonitrile, resulting in an ion exchange reaction which allowed the formation of the CT complex. For example;

$$\mathrm{Li(TCNQ)} + \mathrm{NMP(HSO_4)} \text{------>} \mathrm{NMP(TCNQ)_{(s)}} + \mathrm{Li(HSO_4)}$$

$Li(HSO_4)$ is removable by washing with water whereas the CT complex tends to be insoluble in water.

Single crystal preparation by traditional methods proved ineffective. In an attempt to overcome this two different approaches were also investigated. These are outlined below:

1. Electrocrystallisation.[130,131] This involved placing a donor salt in one side (anode) of an electrolytic cell and TCNQ in the other half (cathode) of the cell. This technique was investigated because it was not possible to prepare crystalline samples of TB-TCNQ from solution. It was also hoped that electrocrystallisation would solve some of the purity problems encountered.

2. Slow cooling of a saturated solution. Here crude samples were redissolved, filtered and allowed to cool slowly by placing a sealed flask containing the hot solution in a large vacuum flask filled with hot water. The water in the flask took approximately three days to cool.

5.2. Discussion For Toluidine Blue-TCNQ (TB-TCNQ).

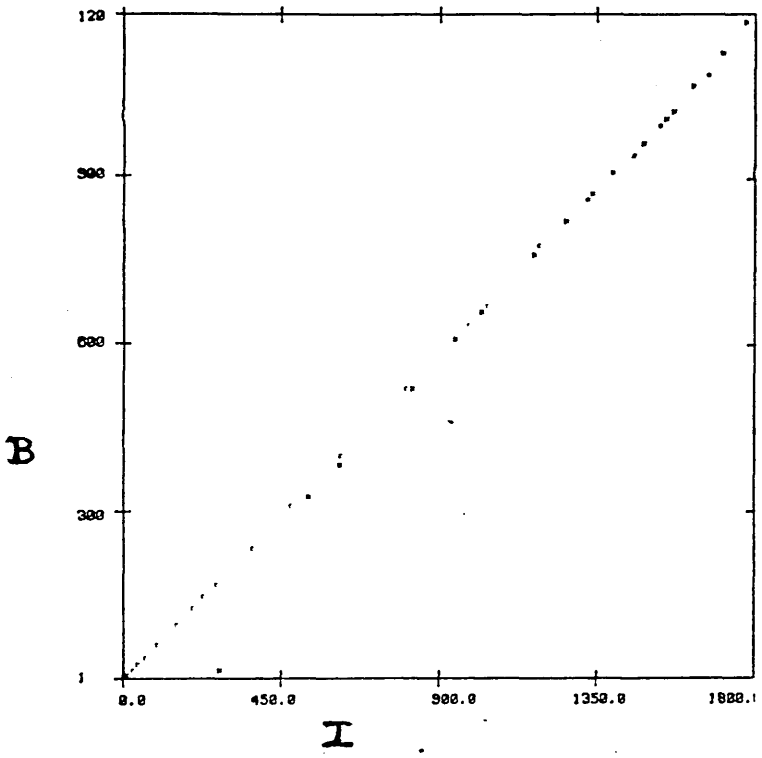
(See section 3.2,1 for preparation and structure).

This was the most interesting and intensively investigated new complex. Its properties are discussed below:

5.2.1. Magnetic Properties.

TB-TCNQ appeared to exhibit co-operative magnetism, as shown by its ability to demonstrate remanence (residual magnetism). However, this must be a qualified statement since remanence was only crudely demonstrated by observing the rotation of a pressed sample floating on water as the different poles of a magnet were brought close. In some samples the rotation direction depended upon the direction of the pole. If the sample had been paramagnetic one may have expected the direction of rotation to be unaffected by the direction of the pole.

These observations are not very scientific and did not provide any quantitative data. The standard method for demonstrating ferromagnetism involves obtaining a hysteresis loop for the magnetisation; we used a method based on a procedure outlined by Starling[146] that involves measuring the magnetisation of a solenoid whose core was a sample of TB-TCNQ. However, the apparatus constructed was not sensitive enough to enable us to draw any conclusions. A graph of the magnetisaton curve is shown in Fig.5.1.



B = Magnetic flux density I = Current passed though the
solenoid which is
proportional to H

x = Magnetisation o = Demagnetisation

Fig.5.1.
Graph Of The Magnetisation Of TB-TCNQ.

One logical explanation for the unusual magnetic observation could have been contamination by ferromagnetic impurities, but analysis for metals (eg atomic spectroscopy) revealed no sign of contamination (see Fig.5.2).

Table of results for the amounts of various elements found in TB-TCNQ compared with water and ethanol ✳			
Element	TB-TCNQ	Deionised water	Ethanol
Al Fe Ni	1444 1647 629	2275 2049 405	1406 1784 667

Fig.5.2.
A Table Of The Levels Of Some Metallic Contaminants In TB-TCNQ.

TB-TCNQ was unusual in that work carried out at Nottingham University[147] showed the susceptibility to be diamagnetic down to approximately 40K and below this it became paramagnetic (Fig.5.3). However, at Sheffield City Polytechnic, only largely temperature-independent paramagnetic susceptibility of approximately 3.125E^{-4} emu mol^{-1} (0.22 unpaired electrons) over most of the temperature range (300 to 75K) has been observed. See Fig.5.4. This discrepancy must be resolved before any conclusions can be drawn.

* Values for deionised water are taken to be zero.

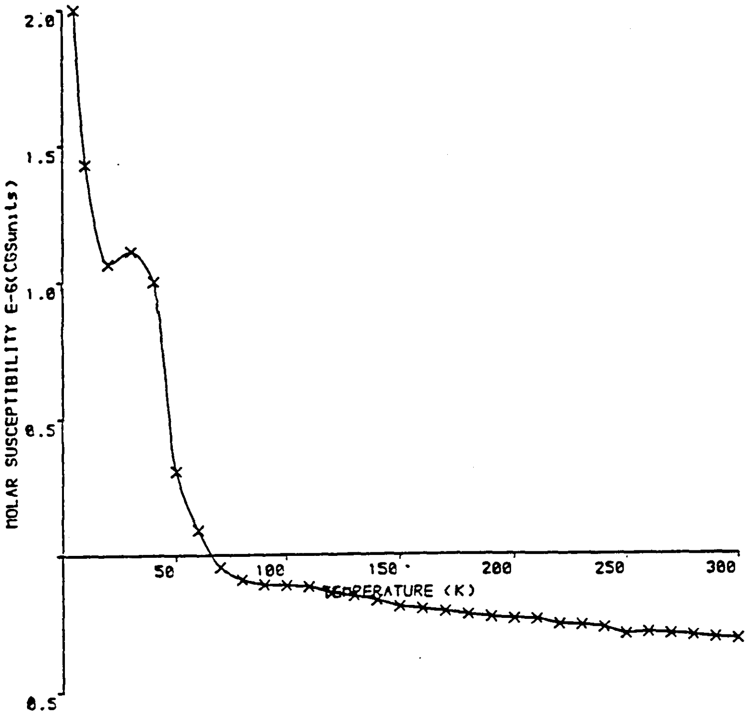


Fig.5.3.
Magnetic Susceptibility vs Temperature For TB-TCNQ. Data Taken At The University Of Nottingham.

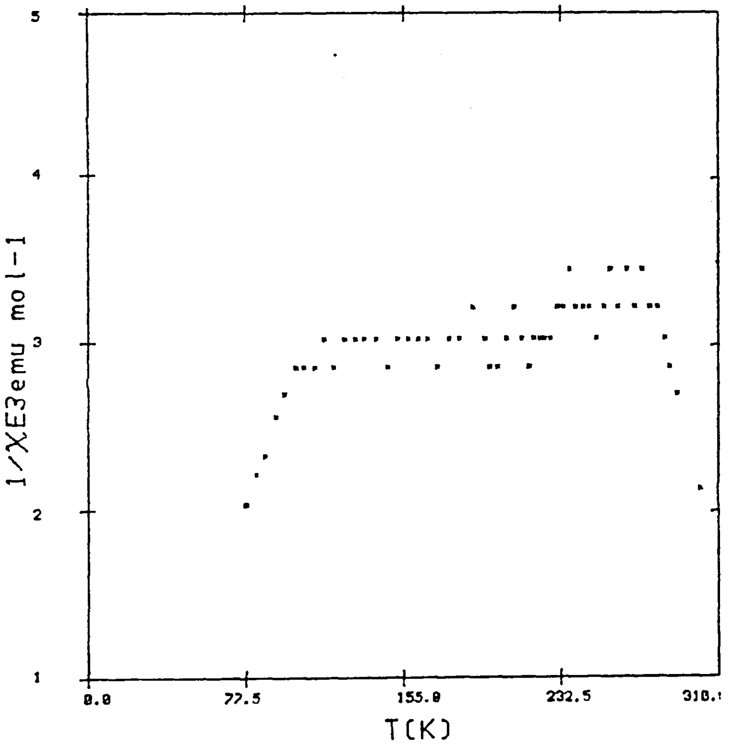


Fig.5.4.
Magnetic Susceptibility vs Temperature For TB-TCNQ. Data Taken At Sheffield City Polytechnic.

5.2.2. Electrical Properties Of TB-TCNQ.

The electrical conductivity of a pressed pellet of TB-TCNQ showed it to be a semi-conductor with a room temperature conductivity of approximately $4.0E^{-4}\ \Omega^{-1}\ cm^{-1}$. A graph of conductivity versus temperature is given in Fig.5.5. It should, however, be noted that the absolute values of these results are rarely consistent for reasons already discussed in Chapter four.

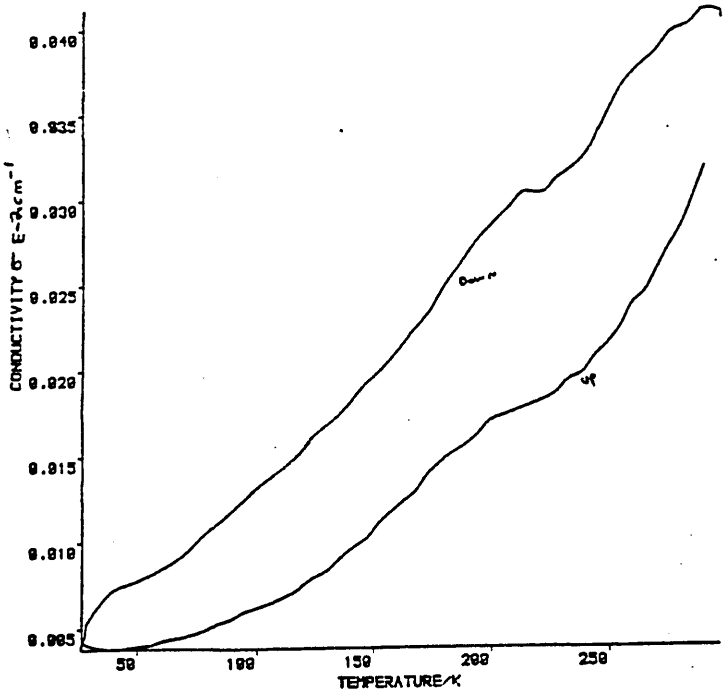


Fig.5.5.
Electrical Conductivity vs Temperature For TB-TCNQ.

5.2.3. Analytical Data For TB-TCNQ.

The greatest difficulty encountered with this complex has been the failure to prepare pure reproducible crystalline samples for use in structural determination.

Attempts to obtain single crystals included:

1. Changing the reaction conditions by:

   a. The use of different solvents, notably methanol.

   b. Altering the reaction times.

   c. Varying the donor/acceptor ratio.

   d. Using TCNQ in the form of $TCNQ^{o}$ and $TCNQ^{\cdot-}$. For example using TB, $TCNQ^{o}$, $TCNQ^{\cdot-}$ in the ratios of 1:0.5:0.5 respectively.

Despite these modifications consistent data has not yet been produced.

2. Using electrocrystallisation for the preparation.

This produced long fibrous structures that grew out from the cathode. These structures did appear to contain some extremely small crystals. Unfortunately, they were too small and rare to enable x-ray studies to be undertaken.

It has been very difficult to obtain consistent micro-analytical data from the above preparations. Fig.5.6 shows some of the data. Recent results have started to show some consistency, enabling a formula to be calculated as long as account is taken of a small amount of trapped solvent. A formula of TB_1 $TCNQ_1$:x Solvent is indicated. Differential scanning calorimetry (DSC) shown in Fig.5.7 does not, however, give any indication of the presence of trapped solvent as might be seen from peaks at the melting and boiling points of acetonitrile (-48 and 82 °C respectively).

I.R. and N.M.R. spectra were not easy to obtain due to the difficulty in preparing samples for analysis. Fig.5.8 shows a typical I.R. spectrum.

Micro-analysis data for TB-TCNQ.			
Preparation method.	Theoretical %	Found %	Formula
Electrocrystallisation.	C. 67.45 N. 20.33 H. 4.21 S. 4.58	C. 67.47 N. 20.35 H. 3.91 S. 6.46	TB-TCNQ: $0.09CH_2Cl_2$
Aqueous	C. 66.57 N. 20.12 H. 4.43 S. 6.58	C. 66.75 N. 19.86 H. 4.15 S. 6.45	TB-TCNQ: $0.7H_2O$

Fig.5.6.
Micro-Analytical Data For TB-TCNQ.

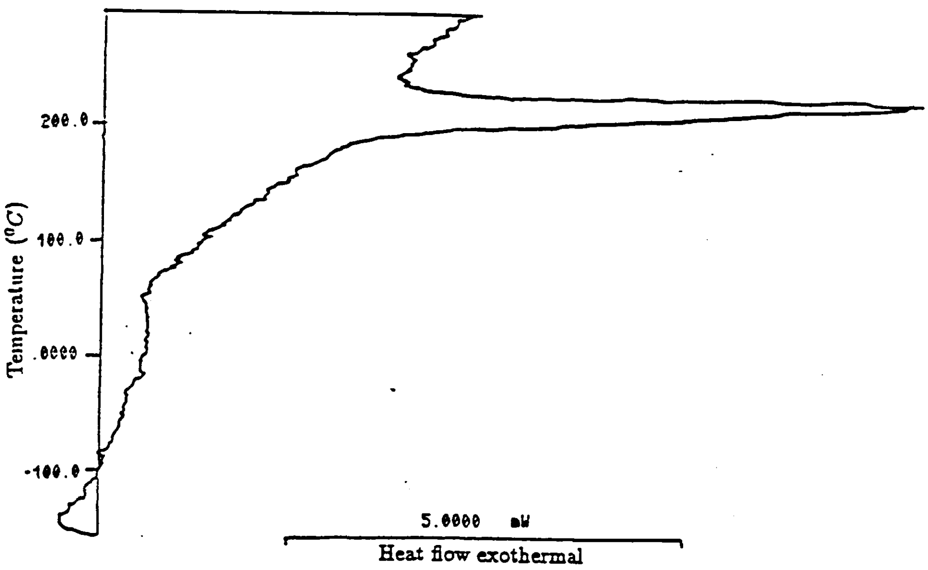


Fig.5.7.
DSC For TB-TCNQ.

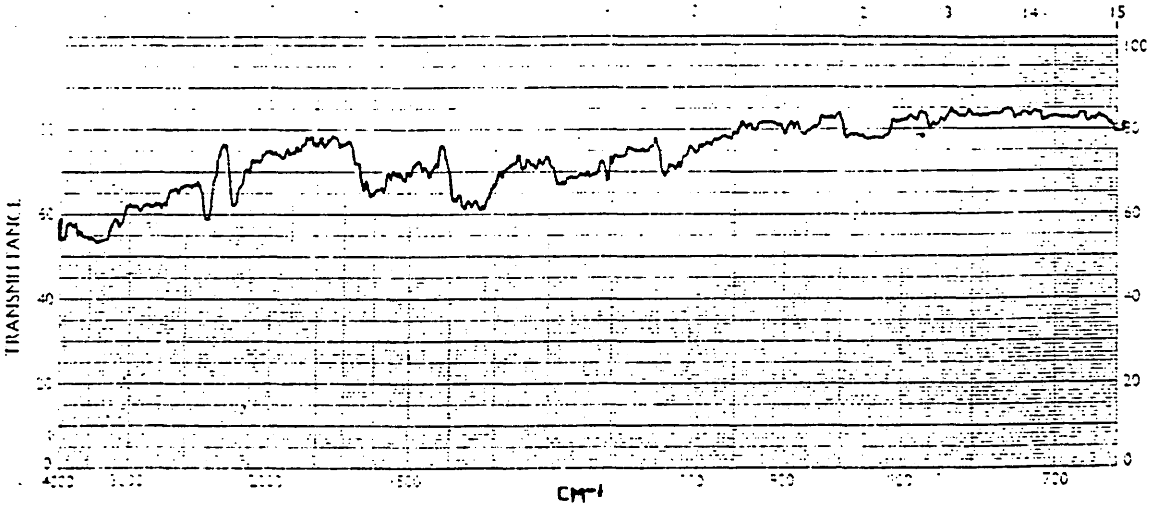


Fig.5.8.
I.R. Spectrum For TB-TCNQ.

UV/Vis spectra were more informative indicating that in aqueous preparations TCNQ$^{\cdot-}$ species were present (as shown by the TCNQ radical anion peak at approximately 842nm). However, preparations using electrocrystallisation seemed to contain mainly uncharged TCNQ as indicated from the small absorption peaks for TB (630nm obtained from studies with the starting material) and TCNQ$^{\cdot-}$ (at approximately 842nm). However, there was a strong absorption peak at approximately 395nm (arising from neutral TCNQ). The ratios of the various peaks were rarely consistent and further investigation will be required in an attempt to resolve these problems. Fig.5.9 shows the UV/Vis spectraum for an aqueous preparation of TB-TCNQ and Fig.5.10 shows the UV/Vis spectrum for TB-TCNQ prepared using electocrystllisation.

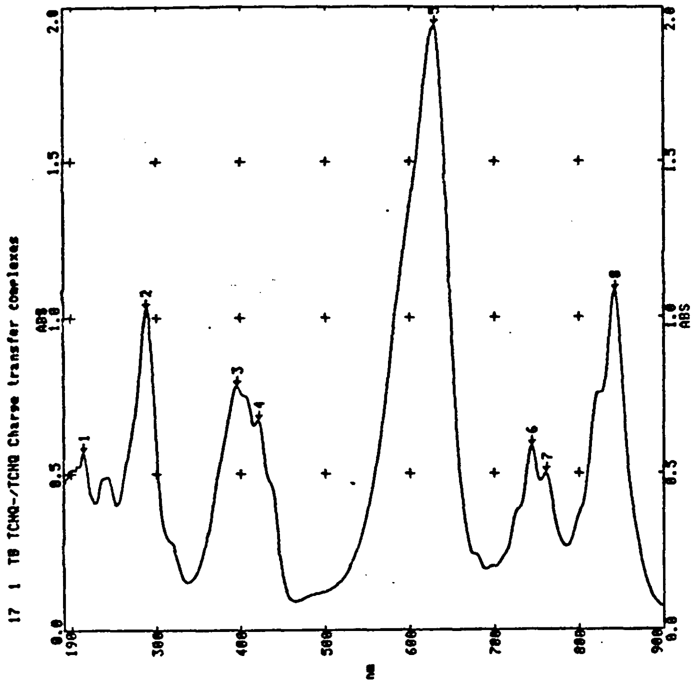


Fig.5.9.
UV/Vis Spectra For TB-TCNQ From Aqueous Preparation.

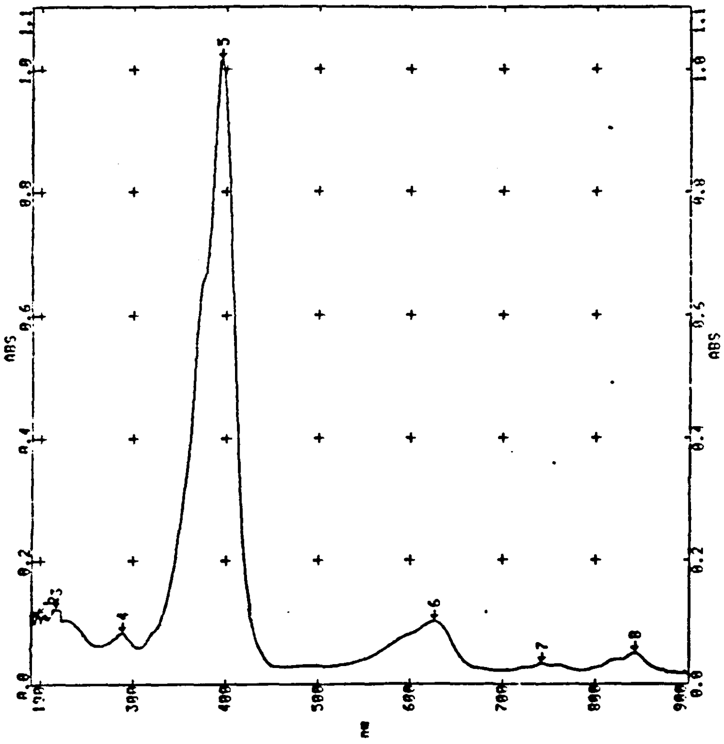


Fig.5.10.
UV/Vis Spectra For TB-TCNQ Prepared By Electrocrytallisation.

5.2.4. Conclusions For TB-TCNQ.

1. The difficulty in producing single crystals indicates that good stacking integrity over relatively large distances (eg 0.5cm as in NMP-TCNQ) is not present. This would explain the low conductivity.

2. The magnetic properties may be useful in orientating a potential CT polymer in a magnetic field. Until the effect of polymer backbone upon long-range stacking has been investigated we are unable to predict the usefulness of this complex as part of a conductor CT polymer composite.

3. From the magnetic data it may be that this material could be ferrimagnetic. Confirmatory evidence, however, is required to clarify a number of points. Firstly, quantitative data on magnetisation is required and could possibly be gained from studies of the change of susceptibility with respect to field strength. This work could be carried out on the Sheffield City Polytechnic magnetic balance with some softwear modification. Secondly, the anomalies in the magnetic susceptibility measurements between different samples require explanation.

4. The difficulty in obtaining good single crystals will make structural identification very difficult. Further work is required in order to obtain single crystal samples for X-ray crystallographic studies.

5.3. Discussion For N-methylphenazinium-(9-dicyanomethylene-2,4,7-trinitrofluorene) (NMP-DTF).

(See section 3.2,5 for a preparation and structure).

A literature search revealed that derivatives of DTF such as Li-DTF have been previously prepared[132]. Li-DTF was used as a starting material for the preparation of NMP-DTF.

Fig.5.11 tabulates some of the relevant I.R. absorption peaks of NMP-DTF. The spectrum is shown in Fig.5.12.

Table of the relevant I.R. absorption peaks for NMP-DTF.	
Absorption frequency cm^{-1}.	Associated chemical groups
2200 1350 870	CN- strech NO_2 =C-H

Fig.5.11.
Relevant Absorption Peaks In The I.R. Spectrum Of NMP-DTF.

The UV/Vis spectrum (Fig.5.13) revealed little information and requires more detailed investigation. No magnetic or conductivity data were obtained for NMP-DTF because these techniques were not available when it was investigated, and only a small amount of sample was available.

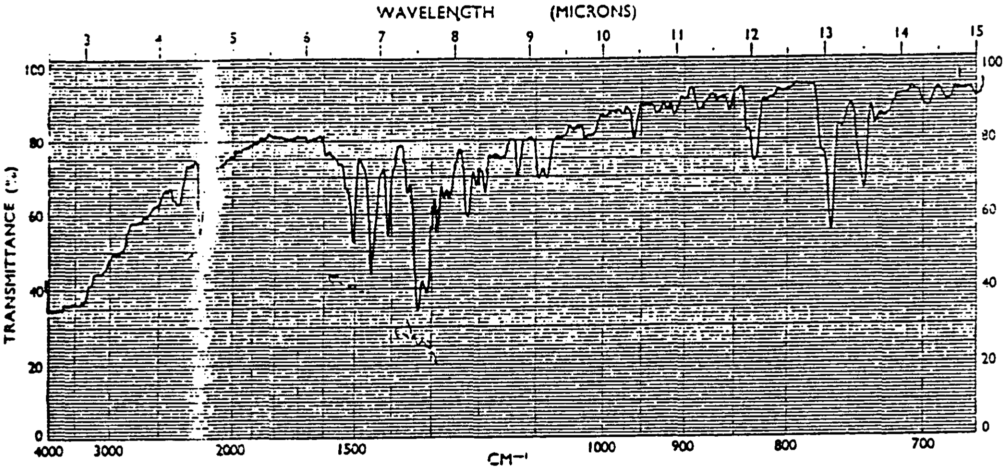


Fig.5.12.
I.R. Spectrum Of NMP-DTF.

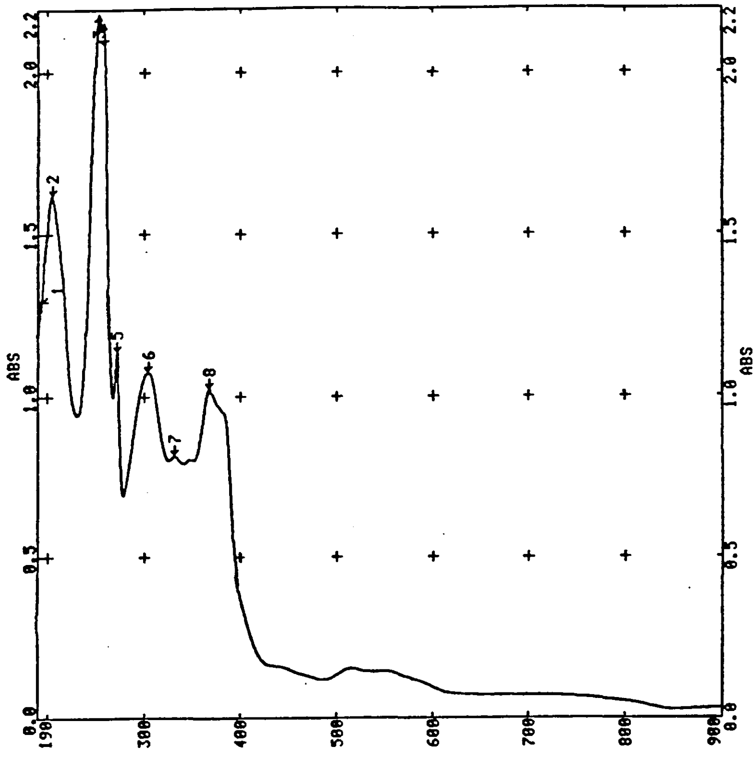


Fig.5.13.
UV/Vis Spectrum Of NMP-DTF.

The important property found was that NMP-DTF can be prepared using less than a tenth of the solvent (often acetonitrile) normally used to prepare CT complexes. If the conductivity of NMP-DTF should prove to be as high as its analog NMP-TCNQ, (200 $\Omega^{-1}cm^{-1}$ for a single crystal), then commercial preparation of this compound would be much more attractive. In addition, it may be a good candidate for preparation of the proposed CT polymer, in that it may possess suitable sites for the attachment of an alkyl spacer.

5.4. Discussion For Neutral Red-TCNQ (NR-TCNQ).

(See section 3.2,6 for preparation and structure).

NR-TCNQ was investigated partly because it has a similar structure to NMP-TCNQ. One striking difference between the two was the inability to obtain single crystals of NR-TCNQ, whereas NMP-TCNQ readily forms needle crystals. A possible reason for this is that the side groups on NR disrupt stacking.

5.4.1. Magnetic And Electrical Properties Of NR-TCNQ.

Fig.5.14 shows the electrical and magnetic data for NR-TCNQ compared with that of NMP-TCNQ.

Magnetic and electrical data for NMP-TCNQ and NR-TCNQ.

Property	NMP-TCNQ	NR-TCNQ.
Conductivity at approximately 295K for pressed pellet.	-	$1.72E^{-6}$ Ω^{-1} cm^{-1}
Conductivity at approximately 295K for a single crystal[43]	200 Ω^{-1} cm^{-1}	-
Magnetic susceptibility at approximately 295K	$6.14E^{-4}$emu mol^{-1}	$3.36.0E^{-4}$emu mol^{-1}
No of unpaired electrons at approximately 296K	0.58	0.34

Fig.5.14.
Comparative Data Of NR-TCNQ and NMP-TCNQ.

The magnetic susceptibility of NR-TCNQ (Fig.5.15) was $2.87E^{-4}$ lower than that for NMP-TCNQ. There was little evidence of a temperature independent region above 230K similar to that often observed for NMP-TCNQ (Fig.5.16), but the data was not very clear, making any assessment difficult. A pressed pellet sample of NR-TCNQ exhibited semiconductor-type electrical conductivity (Fig.5.17), with a room temperature conductivity of $1.72E^{-6}$ Ω^{-1} cm^{-1}. Unfortunately, a room temperature conductivity for NMP-TCNQ was not available.

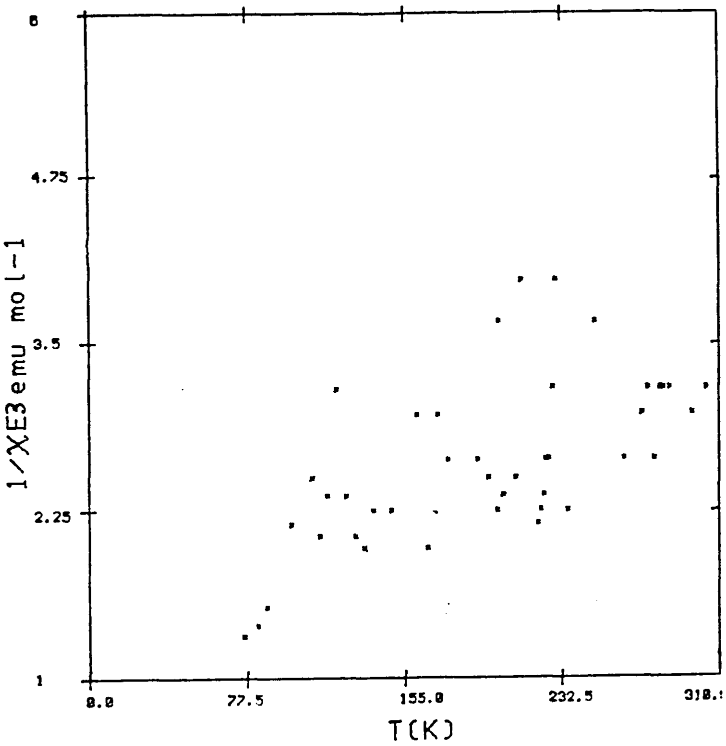


Fig.5.15.
Magnetic Susceptibility vs Temperature For NR-TCNQ.

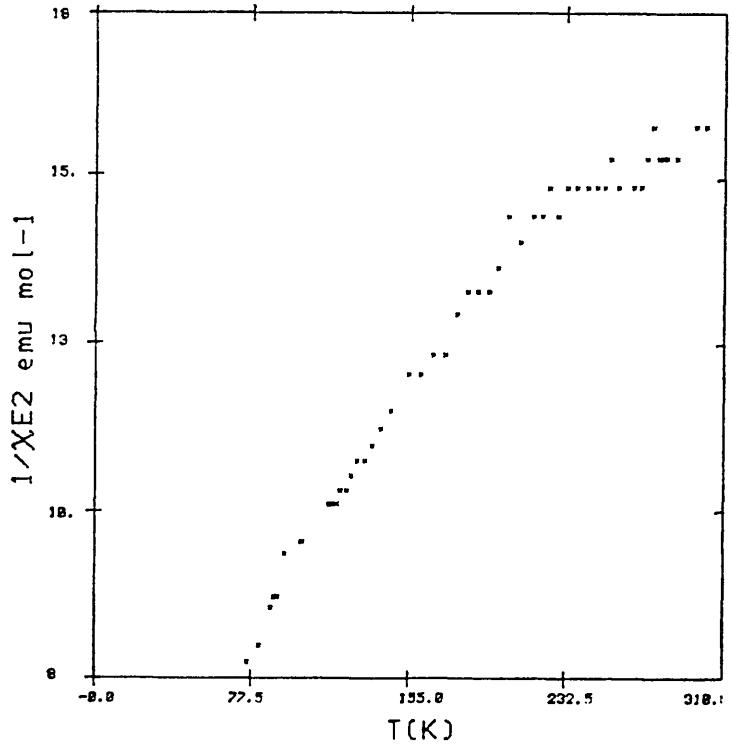


Fig.5.16.
Magnetic Susceptibility vs Temperature For NMP-TCNQ.

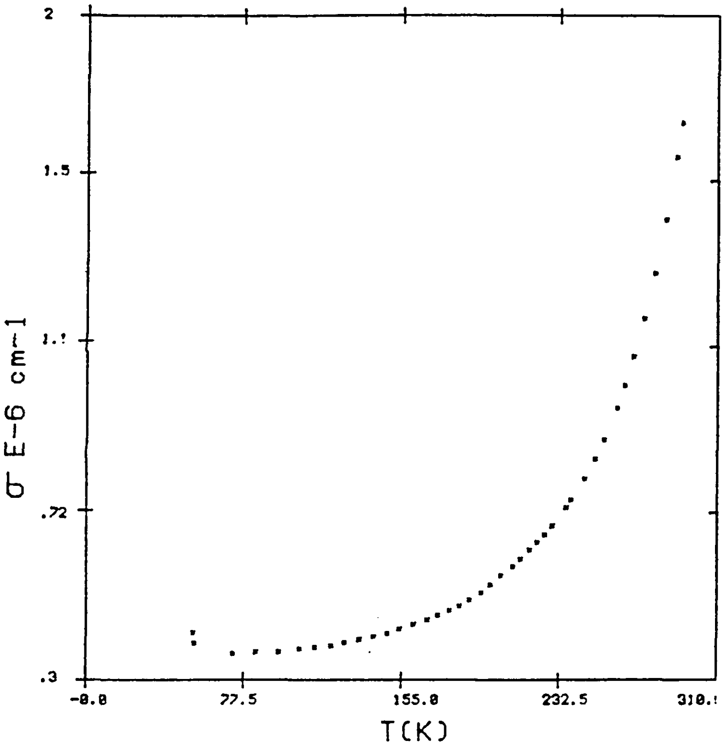


Fig.5.17.
Electrical Conductivity vs Temperature For NR-TCNQ.

Magnetic data obtained using the Sheffield City Polytechnic balance indicated a lower level of charge transfer for NR-TCNQ (0.34) compared to that for NMP-TCNQ (0.56). This may be due to differences in the ionisation energies of NR and NMP.

5.4.2. Spectra For NR-TCNQ.

The I.R. spectrum did not contain much detail. However, it was clear enough to identify some of the groups present (the data is tabulated in Fig.5.18). The 842nm absorption peak in the UV/Vis spectrum indicated that there were $\text{TCNQ}^{\cdot -}$ species present, as confirmed by the magnetic data (ie unpaired electrons). The UV/Vis data is tabulated in Fig.5.19.

<table>
<tr><th colspan="2">Table of the relevant I.R. absorption peaks for NR-TCNQ</th></tr>
<tr><td>Absorption frequency cm^{-1}</td><td>Associated chemical group.</td></tr>
<tr><td>3330-3370</td><td></td></tr>
<tr><td>2200</td><td>CN- strech</td></tr>
<tr><td>1400</td><td>NO_2</td></tr>
<tr><td>820</td><td>=C-H</td></tr>
</table>

Fig.5.18.
Relevant I.R. Absorption Peaks For NR-TCNQ.

<table>
<tr><th colspan="2">Table of the relevant UV/VIS absorption peaks for NR-TCNQ</th></tr>
<tr><td>Absorption frequency in nm</td><td>Associated chemical species</td></tr>
<tr><td>325-475</td><td>Combined TCNQ^{o}/TCNQ$^{\cdot-}$ and NR.</td></tr>
<tr><td>532</td><td>NR (from studies with the starting material)</td></tr>
<tr><td>842</td><td>TCNQ$^{\cdot-}$</td></tr>
</table>

Fig.5.19.
Relevant UV/Vis Absorption Peaks For NR-TCNQ.

5.4.3. Conclusion For NR-TCNQ.

The data obtained for NR-TCNQ when compared to NMP-TCNQ seemed to indicate that the addition of even relatively small side groups can affect the ability to form single crystals. One can suggest two reasons for this. Firstly, side groups may reduce the planar nature of the molecule hindering the stacking required for good crystal formation. Consequently π-overlap could be severely hindered giving rise to the semiconductor conductivity profile observed. Secondly, varying the side groups on the donors will alter the ionisation energy and thus affect the lattice energy.

These conclusions have implications for our proposed CT-acceptor polymer composite. Whilst the work here was centred around the effects on a donor, it is reasonable to assume that similar effects would be observed for acceptors. "Stacking" properties in a CT-donor polymer composite will most likely be due to a combination of two factors. Firstly, the lattice energy of the donors and acceptors and secondly, the orientating properties of the polymer backbone. Close stacking of the donors and therefore high conductivity will still, in part, be dependant on the lattice energy of the complex. Thus it is important to try to obtain CTCs with acceptors that are suitable for incorporation into a CT polymer and that will provide good stacking integrity.

5.5. Discussion For The Discotic Donors.

The following three materials were complexes containing TCNQ and donor molecules that can be described as "discotic". By this we mean that in contrast to the more usual donors which are often comprised of linear ring systems, they are planar dyestuffs possessing conjugated π-systems where a central carbon atom is surrounded by three Phenyl groups, the Phenyl groups possessing a variety of functionality (for example nitro, amino and alkyl groups).

These materials were investigated because the side groups could have been useful for attachment to a spacer group, as would be required in the preparation of a CT-donor polymer, and also to investigate any novel magnetic or electrical properties. These materials are discussed below.

5.6. Discussion For Rosaniline-TCNQ (R-TCNQ).

(See section 3.2,3 for a preparation and structure).

Although this complex was only briefly looked at, it was interesting in that when acetone was added to an aqueous solution of the complex, a golden coloured film was formed on the surface of the water. However, single crystals were never obtained, only an amorphous red powder.

5.6.1. Electrical And Magnetic Properties For R-TCNQ.

Initial conductivity measurements indicated that conductivity was low $<2E^{-6}\ \Omega^{-1}\ cm^{-1}$, whilst the magnetic susceptibility appeared to be temperature independent and quite large $7.16E^{-3}$ emu mol^{-1} at 295K (see Fig.5.20). We were not able to repeat the experiment due to the small amount of sample available (10mg). Conclusions cannot be drawn until further preparations and susceptibility measurements have been undertaken.

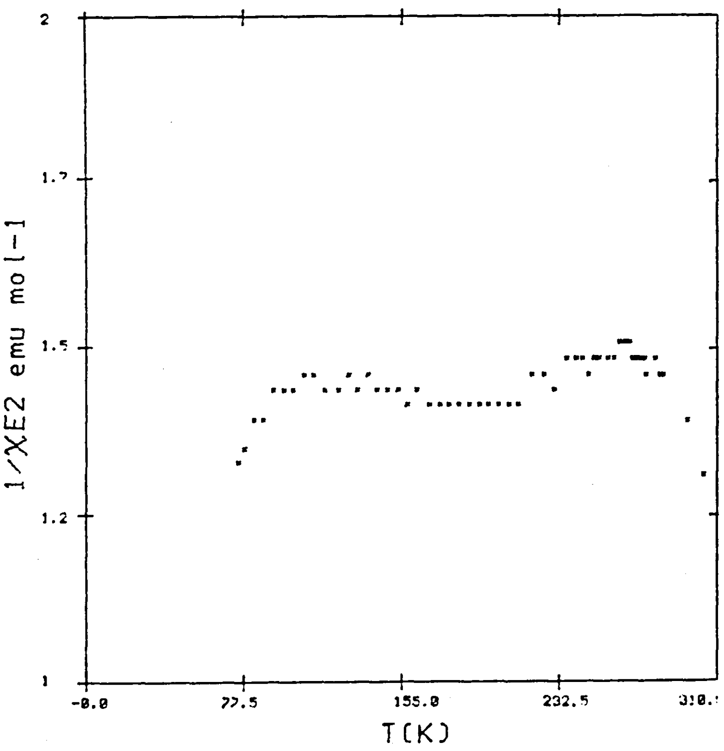


Fig.5.20.
Magnetic Susceptibility vs Temperature For R-TCNQ.

5.6.2. Discussion Of Spectra For R-TCNQ.

As is common for CT complexes the spectra were very uninformative, although the UV/Vis spectrum (Fig.5.21) showed an absorption peak at approximately 842nm indicating the presence of $\text{TCNQ}^{\cdot -}$.

Table of the relevant UV/VIS absorption peaks for R-TCNQ

Absorption frequency in nm	Associated chemical species
400-600	Combination of TCNQ° and R (from Studies with the starting material).
840	$\text{TCNQ}^{\cdot -}$

Fig.5.21.
Relevant UV/Vis Absorption Peaks For R-TCNQ.

5.6.3. Conclusion For R-TCNQ.

The only interesting property found was the ability of R-TCNQ to form films. As the electrical conductivity appeared to be so low, this material is unlikely to attract any attention for applications such as transparent electrodes. It may be, however, that the complex could possess useful optical properties and it is to this area that further studies should be directed.

5.7. Discussion For Malachite Green-TCNQ (MLG-TCNQ).

(See section 3.2,7 for a preparation and structure).

The complex was a dark amorphous powder. In common with the other complexes investigated we were unable to obtain single crystals.

5.7.1. Magnetic And Electrical Properties Of MLG-TCNQ.

The electrical conductivity with respect to temperature for a pressed pellet (Fig.5.22) indicated that this material was semi-conductive. Conductivity appeared to increase below about 100K. This was possibly due to thermal lag in the sample. However, there does appear to be a small reproducible step in the conductivity at approximately 155K. This was of interest as there is also a marked upturn in the magnetic susceptibility at about this temperature (see Fig.5.23). It would be reasonable to assume that there was a real transition at this point. The complex needs further investigation to assess the nature of the transition. However, it is possible that the anomaly in the data is due to the onset of the Peierls transition. There is also some evidence for the presence of a transition at approximately 230K, that may be due to trapped solvent (see section 5.10).

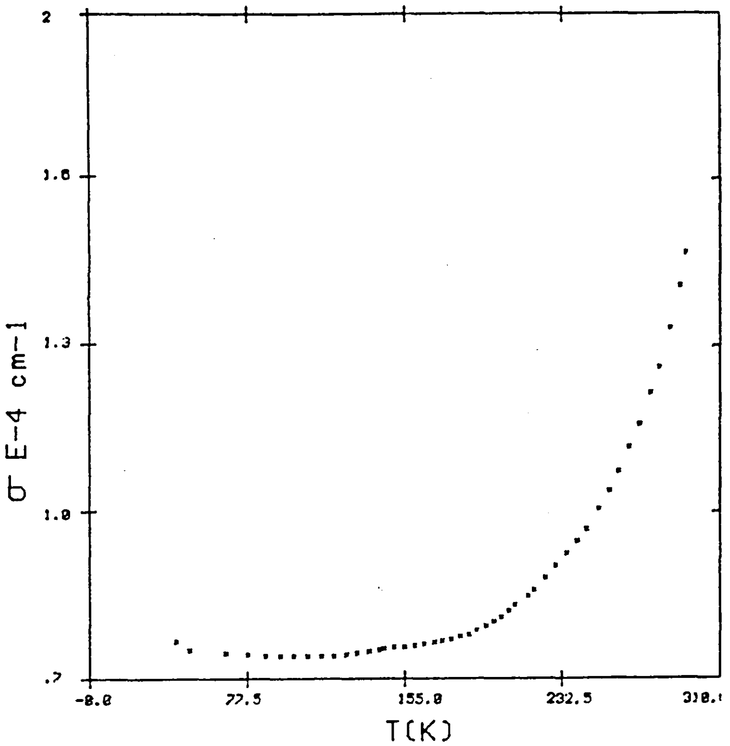


Fig.5.22.
Electrical Conductivity vs Temperature For MLG-TCNQ.

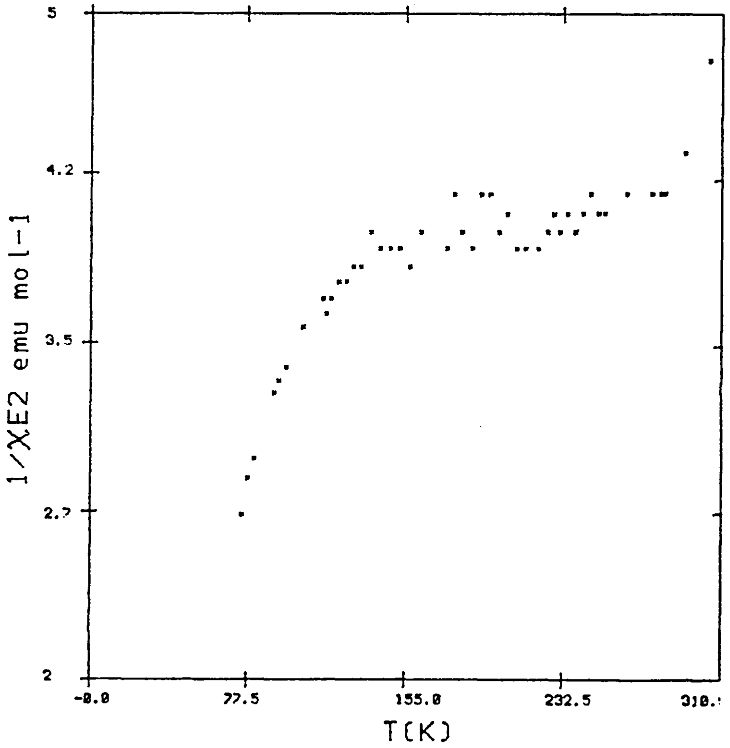


Fig.5.23.
Magnetic Susceptibility vs Temperature For MLG-TCNQ.

5.7.2. Discussion Of Spectra For MLG-TCNQ.

The I.R. spectrum was poor, producing only broad peaks, but some information was obtained and is tabulated in Fig.5.24. The UV/Vis spectral data is tabulated in Fig.5.25 and indicates charge transfer from the absorption peak at 843nm due to the presence of the $TCNQ^{\cdot-}$ species.

Table of the relevant I.R. absorption peaks for MLG-TCNQ	
Absorption frequency cm^{-1}	Associated chemical group
3500-2200	H_2O
3400	CH3 strech
1600	
1350	
830	=CHR
720	=C-H

Fig.5.24.
Relevant I.R. Absorption Peaks For MLG-TCNQ.

Table of the relevant UV/VIS absorption peaks for MLG-TCNQ	
Absorption frequency in nm	Associated chemical species
396.1	$TCNQ^{\circ}$/$TCNQ^{\cdot -}$
620.0	MLG (from studies with the starting material).
843.0	$TCNQ^{\cdot -}$

Fig.5.25.
Relevant UV/Vis Absorption Peaks For MLG-TCNQ.

5.7.3. Conclusions For MLG-TCNQ.

This complex had one of the highest room temperature electrical conductivities of all the complexes that were investigated (1.53E^{-4} Ω^{-1} cm^{-1}). Future work on this complex should be concentrated upon the preparation of single crystals, which may prove to have some useful conductivity.

5.8. Discussion For Methyl Green-TCNQ (MG-TCNQ).

(See section 3.2,8 for a preparation and structure).

This complex was difficult to prepare and was only obtained in low yields, as a black amorphous powder.

5.8.1. Electrical And Magnetic Properties Of MG-TCNQ.

Electrical conductivity data was not obtained due to the lack of sample for preparation of a pressed pellet. The magnetic susceptibility (see Fig.5.26) was of a similar order of magnitude to that of R-TCNQ and MLG-TCNQ.

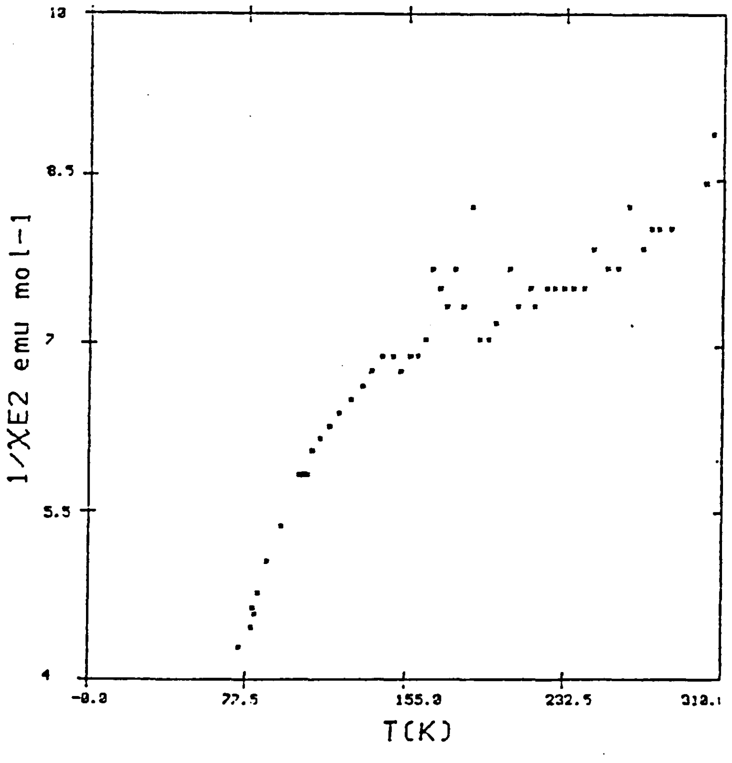


Fig.5.26.
Magnetic Susceptibility vs Temperature For MG-TCNQ.

5.8.2. Discussion Of Spectra For MG-TCNQ.

The absorption peak at 843.2nm in the UV/Vis spectrum indicated the presence of the $TCNQ^{\cdot-}$ species. This information is tabulated in Fig.5.27. Unfortunately other spectra were not available.

Table of the relevant UV/VIS absorption peaks for MG-TCNQ	
Absorption frequency in nm	Associated chemical species
395.2	$TCNQ^{o}/TCNQ^{\cdot-}$
633.6	MG (from studies with the starting material)
843.2	$TCNQ^{\cdot-}$

Fig.5.27.
Relevant UV/Vis Absorption Peaks For MG-TCNQ.

5.8.3. Conclusion For MG-TCNQ.

This complex received very little attention, partly due to shortage of time and also because of the very low yields obtained. The low yield is one factor making it unattractive for further investigation, unless a better preparative method can be devised.

5.9. Conclusions For Discotic Donors.

Initial investigations gave no indication that these complexes would be useful as highly conductive materials. All gave problems regarding single crystal formation which is essential for high conductivity. It is perhaps not surprising that these materials do not possess good stacking properties, since they contain bulky side groups and structures that, although conjugated, are probably susceptible to a certain amount of conformational flexibility.

One interesting property was that the magnetic susceptibilities tended to be rather larger than those observed for other complexes. Fig.5.28 tabulates the magnetic data at approximately 295K for these and other complexes. Originally it was thought that the results were due to impurities in the samples and arose because the preparations required washing with large quantities of water to remove the water soluble starting materials, (donor salts and Li(TCNQ)). It was impractical to use vast quanties of deionised water and so it was only used for the final few washings. If the samples were insufficiently washed with deionised water they could contain contaminants that may account for the larger susceptibility observed for the discotic donors. Whilst this has not been ruled out it should, however, be noted that both NR-TCNQ and TB-TCNQ exhibited a much smaller susceptibility and were prepared in an identical manner to the discotic donor materials. Furthermore, analysis of TB-TCNQ did not reveal any significant levels of ferromagnetic impurities. We would have liked to repeat these experiments with freshly prepared samples, but shortage of time did not allow this.

Magnetic susceptibility at 295K for the prepared CT complexes		
Complex	emu mol^{-1}	Comments
R-TCNQ	7.16E^{-3}	Discotic (temperature independent)
MLG-TCNQ	2.38E^{-3}	Discotic
MG-TCNQ	1.17E^{-3}	Discotic
NR-TCNQ	3.36E^{-4}	
NMP-TCNQ	6.14E^{-4}	Sheffield City Polytechnic result.
NMP-TCNQ	4.80E^{-4}	From ref.11.
TB-TCNQ	3.12E^{-4}	Sheffield City Polytechnic result.
TB-TCNQ	-2.5E^{-7}	University Of Nottingham result[147].
Trimethyl sulphonium iodide-TCNQ.	3.17E^{-4}	Sheffield City Polytechnic result.

Fig.5.28.
Magnetic Susceptibility Data For Discotic Donor Complexes Compared To Complexes Involving Other Donor Types.

Despite the apparent low electrical conductivity of these materials they may find applications in other areas of molecular electronics. Indeed R-TCNQ was interesting in itself for its film forming ability.

5.10. Comments On The Possible Solvent Effect.

It has been suggested that there is a possible effect due to trapped solvent[11], producing a step in the magnetic and conductivity data for complexes such as NMP-TCNQ. Work carried out by the author at Cranfield Institute of Technology showed that when acetonitrile was the solvent in the preparations there was a transition at approximately its freezing point (229K). When using other solvents the results were inconclusive.

It was possible that transitions observed at Cranfield Institute of Technology could have been attributed to errors in the magnetic balance used. However, similar results have been observed in some of the magnetic (Fig.5.29) and electrical conductivity (Fig.30) data obtained at Sheffield City Polytechnic.

The only commom piece of equipment at Sheffield City Polytechnic and Cranfield Istitute of Technology was the C.I.Robal microbalance. It is, therefore, the view of the author that instrumental error in this matter has been eliminated, and this possible effect (the focus of debate) warrants further investigation.

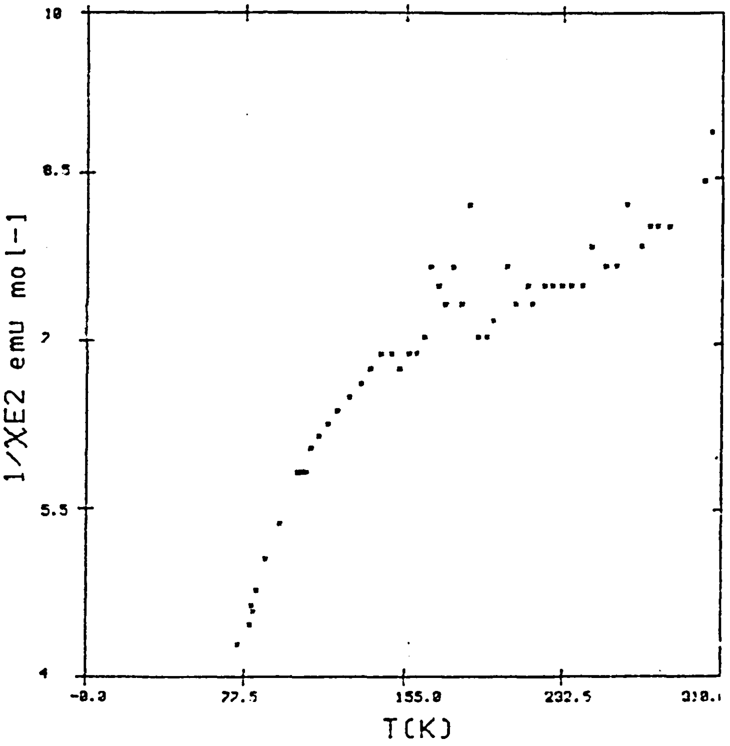


Fig.5.29.
Magnetic Susceptibility Of MG-TCNQ Showing An Anomaly At Approximately 229K Possibly Due To Trapped Solvent.

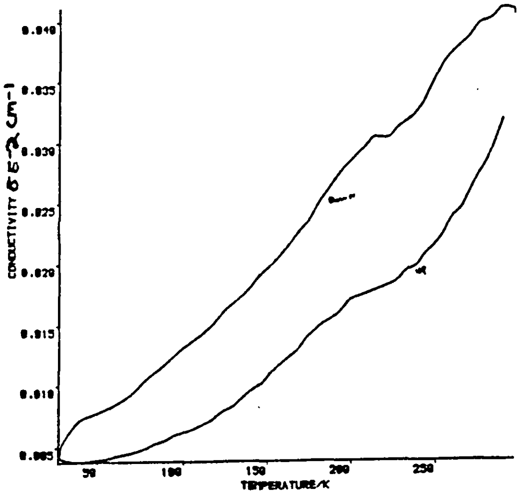


Fig.5.30.
Electrical Conductivity Data For TB-TCNQ Showing An Anomaly At Approximately 229K Possibly Due To Trapped Solvent.

CHAPTER 6

RESULTS, DISCUSSION FOR CT POLYMER SYNTHESIS

6.Results, Discussion For CT Polymer Synthesis.

The aim of this part of the project was to investigate the possibility of preparing a CT polymer composite with a structure somewhat similar to a side chain liquid crystal polymer blended with a complementary, small molecular species (see sections 6.1 and 6.2).

It was not intended to take one synthetic pathway and persuade it to work, as this could have taken the whole three years and not produced a result, but rather to look at a number of possible synthetic routes to assess their viability.

Over the course of this project a number of pathways and options were investigated. These are outlined below:

6.1. Types Of CT Polymer Considered.

Three types of constitution were envisaged:

6.1.1. Polymer Bound Donors And Acceptors.

This was not considered viable as the entropy of the system in the necessary configuration, (i.e. segregated and long range stacking), would be very unfavourable in the context of normal polymer conformational behaviour.

6.1.2. Polymer Bound Donors Blended With Monomeric Acceptors.

Again this was not investigated because the important criteria for conduction in many CT systems is a continuous stack of CT electron acceptor molecules. Blending free acceptors with a CT donor polymer would not guarantee the correct stacking of the acceptors.

The only advantages in this strategy were, firstly, that it may have been simpler to attach the spacer groups to the type of chemical species found on donor molecules and secondly, that in some systems donors are associated with conduction (eg via holes). This approach was rejected on the grounds of both cost (many donors and their precursors are very expensive) and of the need to adopt a target and concentrate upon it.

6.1.3. Polymer Bound Acceptors Blended With Monomeric Donors.

This was the strategy eventually adopted in the hope of producing a TCNQ derivative chemically bound to a suitable polymer. It was envisaged that the polymer backbone would influence the long range ordering of the CT units, whilst short range CT stacking may be expected to be influenced by both spacer design, and factors that would effect unbound crystal formation, such as lattice energy. At this stage we do not know what effect the combination of these factors will have on the overall ordering of the system. Conductive (probably semi-conductive) polymer blends might be obtained if the polymer could be made to produce appropriate ordered phases and the TCNQ moeities could be doped by blending with appropriate donor species.

The sought for ordered phase would be encouraged by slow cooling of the composite material from the molten or solution state. Using this approach side chain crystallisation, (eg by stacking of acceptors), should be optimised, as in the case of analogous LC systems possessing long spacer linkages.

The aim was to look at poly(alkylmethylsiloxane) or monosubstituted polyethylene as selected polymer candidates with siloxane the first choice since it is a particularly flexible polymer, and should allow the TCNQ moeities greater freedom to form ordered stacks than would be the case for monosubstituted polyethylene. In both cases the TCNQ derivative is attached to the polymer via an alkyl spacer group as shown below in Fig.6.1.

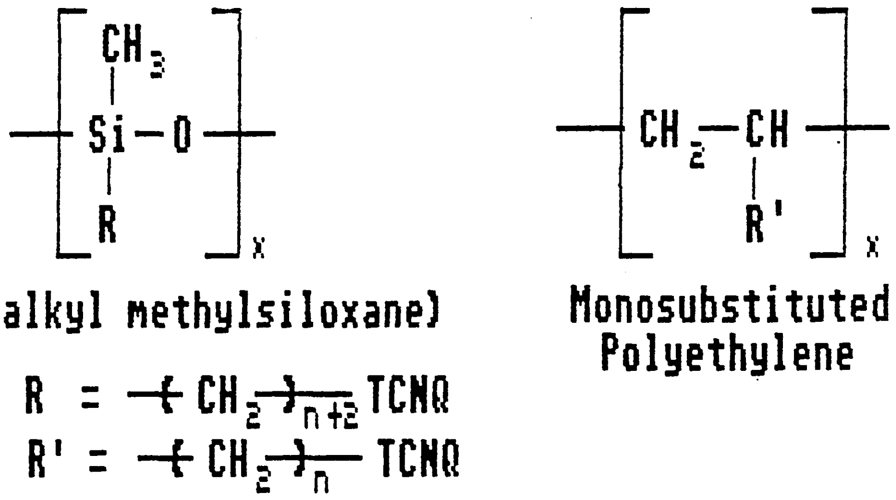


Fig.6.1.
Diagram Of The Different Polymer Types Proposed.

The synthesis of such a system required TCNQ units to be attached to a siloxane polymer backbone via a flexible alkyl spacer. The initial step in this process was to synthesise a TCNQ derivative in which an oligoalkyl spacer containing a terminal alkene suitable for reaction onto the siloxane polymer, was attached to TCNQ.

6.2. Synthetic Pathways Attempted.

Outlined below are three reaction schemes that were investigated in order to find a viable synthesis for the TCNQ derivative.

1. Claisen rearrangement reaction on a precursor of TCNQ, followed by conversion to the TCNQ derivative (scheme 1A).
2. Friedel-Crafts reactions on precursors of TCNQ, followed by conversion to the TCNQ derivatives (scheme 1B).
3. Similar to 1 except a Stork enamine synthesis was to be used (scheme 2).
4. Replacement of a cyano group in TCNQ with an amino-alkyl spacer (scheme 3).

The details of the reaction schemes are outlined below:

6.3. Reaction Scheme 1 (P169).

There were two approaches to producing the alkenylmethoxyphenol(1). Firstly, a pathway involving a Claisen rearrangement, but this was only suitable for a three carbon spacer (scheme 1A), and secondly, by Friedel-Crafts chemistry (scheme 1B).

6.3.1. Claisen Rearrangement (Reaction Pathway 1A).

In scheme 1A p-methoxyphenol was converted to the allyl ether and subjected to a Claisen rearrangement to give an alkenylmonomethylhydroquinone(1)[134-136].

The experimental work has shown 1A to be simple and effective, but the preparation of the quinone derivative(2) resulted in complex mixtures and low yields.

6.3.2. Friedel-Crafts Synthesis (Reaction Pathway 1B).

Scheme 1B was seen as a useful approach since the spacer chain length, (defined by x in the scheme), can be varied whereas 1A is specific to x=1. However, our initial results were not promising and it will be necessary to tackle the considerable amount of literature covering the numerous variants on Friedel-Crafts methodology before a serious attempt at the required organic synthesis can be undertaken.

6.3.3. Outcome Of Scheme 1.

There are numerous problems associated with this scheme as outlined below:

1. Oxidation of hydroquinone to quinone(2) by the method investigated would prove difficult, although given time these problems should be solved since similar oxidations have been previously reported[138].

2. Double condensation with malonitrile leading to the TCNQ derivative(3). There is literature precedent for this stage[148]. However, low yields due to steric hindrance could be expected; hence, either the TCNQ derivative would only have been obtained in small yields or very long reaction times would be required.

In order to optimise these reactions further work will be required but, at least, their feasibility has been demonstrated to some extent.

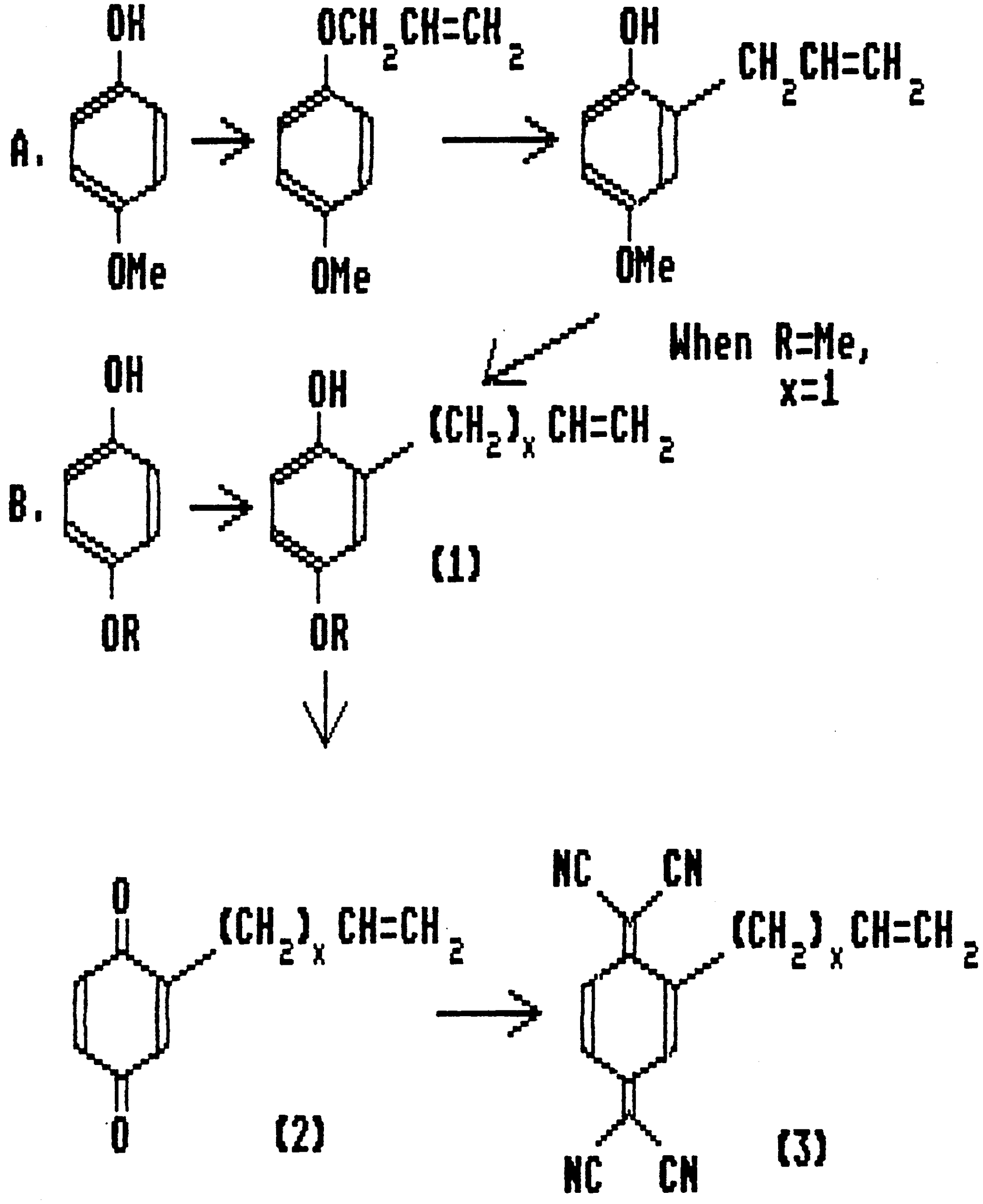


Fig.6.2.
Reaction Scheme 1.

6.4. Stork Synthesis (Reaction Scheme 2) (P171).

Scheme 2 shows an alternative procedure where steric hindrance is minimised by the use of a cyclohexanedione substrate in place of the quinone(2). The commercially available monoacetal(4) yields the alkenyldiketone(5) via Stork enamine chemistry[137] and hydolysis.

Scheme 2 has an advantage over scheme 1 in that double condensation should provide (6), with far less steric hindrance than in scheme 1. (6) would yield (3) after dehydrogenation. Although this pathway looked hopeful there were problems to be overcome. Firstly, the percentage conversion appeared to be low for the overall process (4) to (5) since such conversions can be rather complex and may require in-depth synthetic development for optimisation. Secondly, it was likely that dehydrogenation of (6) to yield (3) would create significant problems, although there is some precedent for a similar reaction for the preparation of TCNQ[14a].

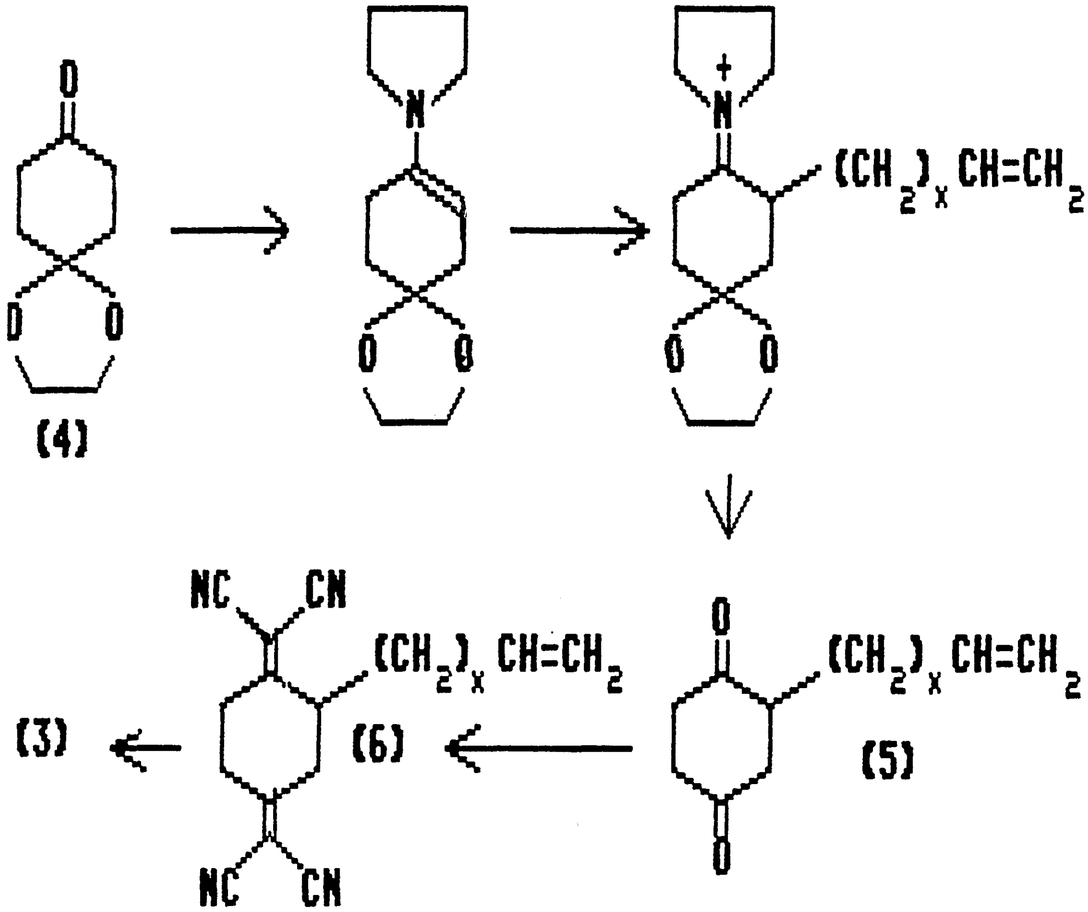


Fig.6.3.
Reaction Scheme 2.

6.5. Cyano Substitution (Reaction Scheme 3) (P173).

This pathway provided a different approach to the problem, circumventing the difficulties encountered in the other schemes. Instead of attempting to attach a spacer group in the quinoid ring, one of the cyano groups was sacrificed and replaced with an amino alkyl spacer containing a terminal double bond, modifying the basic TCNQ structure to give (10).

6.5.1. Analogous Synthesis.

There is literature precedent for the type of reaction proposed[138]. There is also precedent to indicate that the loss of one of the cyano groups would not stop the formation of complexes[124,132], so it was felt that the sacrifice of one group would not unduly affect the properties of the molecule. If anything, the attachment of the spacer group might hinder the stacking properties essential for electrical conductivity.

Reactions unearthed from the literature involved the direct attachment of aminobutane to TCNQ in a straightforward reaction, producing high yields. The only modification to these reactions was to use an aminoalkene, thus providing the terminal double bond for connection to the host polymer.

6.5.2. Variable Spacer Length.

Attachment of spacer groups of different lengths was attempted. The three carbon amine was freely available, however longer amino-alkene spacers (9) had to be prepared from the corresponding halo-alkenes(7) by Gabriel synthesis[139,140].

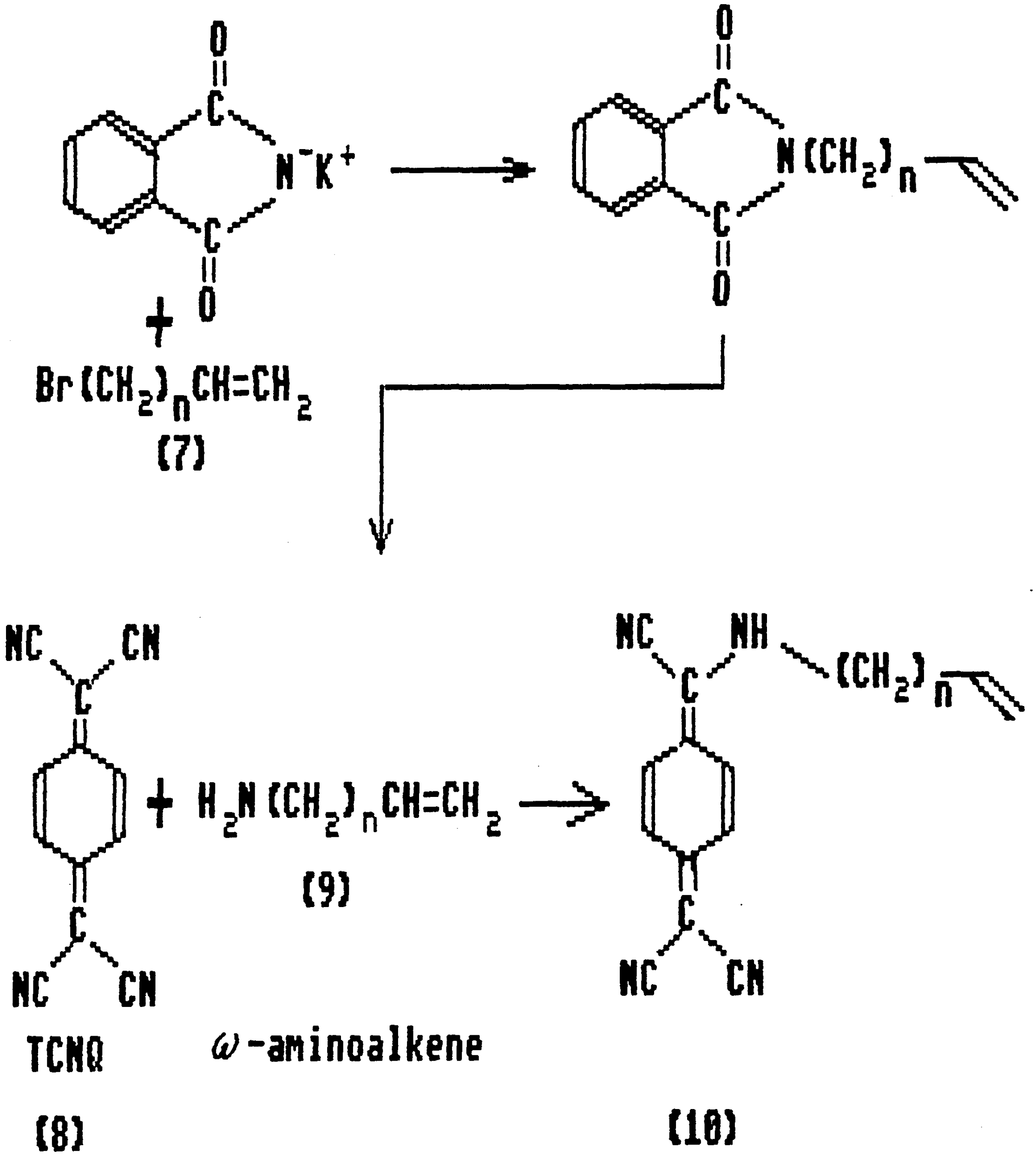


Fig.6.4.
Reaction Scheme 3.

6.6. Synthesis Of CT Polymer (Reaction Scheme 4) (P175).

6.6.1. Suitable TCNQ Derivative.

Low yields from both the Gabriel synthesis and the attachment of the allylamine to TCNQ left the five carbon spacer derivative(10) as the only suitable TCNQ derivative available for further development.

6.6.2. Suitable Polymer.

A linear siloxane chain would have been preferred for the attachment of the TCNQ derivative, but this was very expensive and not immediately available. A four unit siloxane ring system(11) was substituted as a model compound, giving a molecule containing a four ring siloxane with a TCNQ derivative attached at each silicon site (12), thus demonstrating the feasibility of the procedure.

Although this did not produce the desired polymer it did at least give some insight into the problems encountered in attaching the TCNQ derivative to the polymer. Also the cyclic tetramer(11) or (12) can be converted to a linear polymer by cationic ring-opening polymerisation[149].

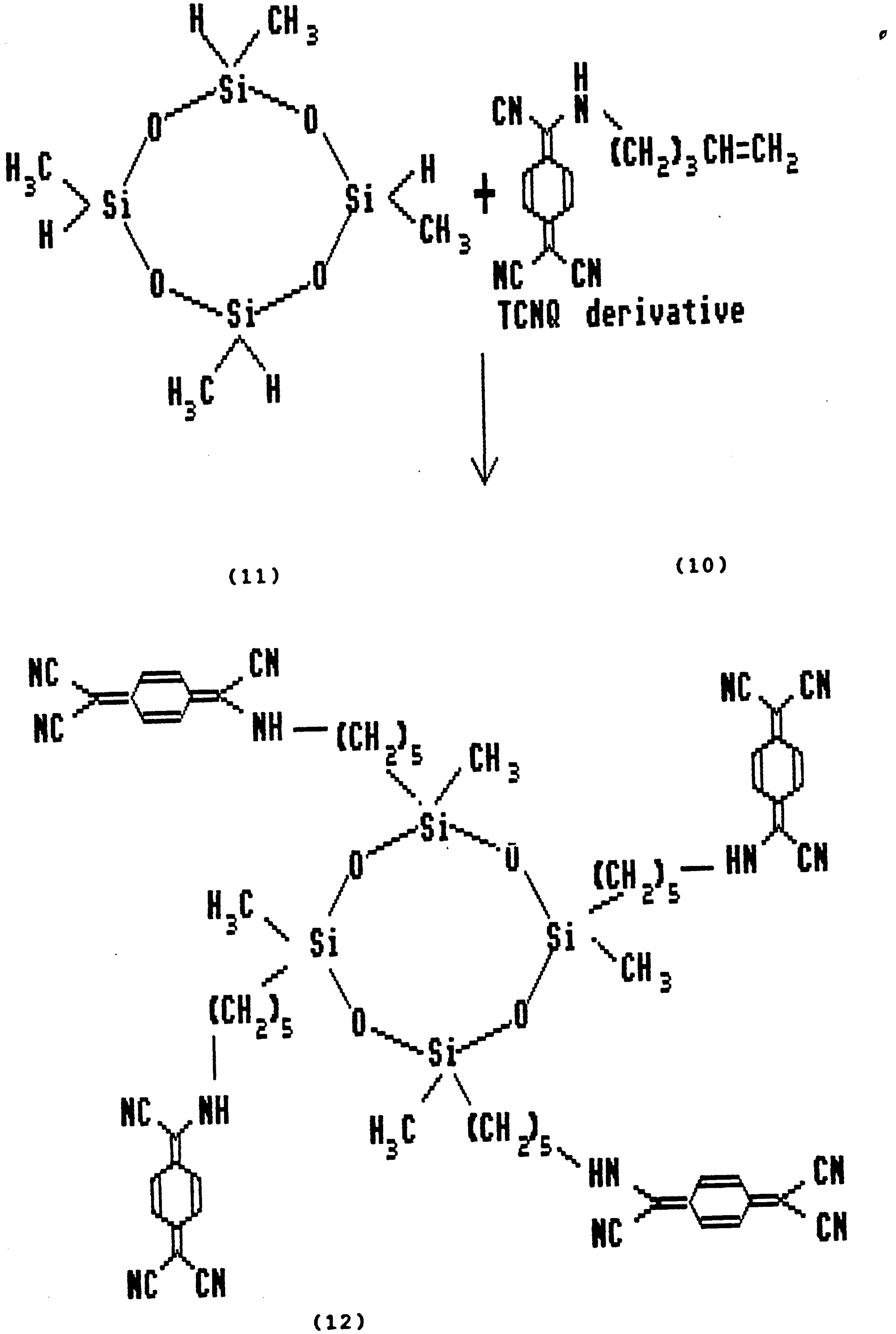


Fig.6.5.
Reaction Scheme 4.

6.7. Discussion Of The Preparation Of The CT Polymer.

The first step in the synthesis was the preparation of a CT acceptor/donor with a spacer group that had a functional group (ie a double bond) to allow attachment onto the polymer backbone.

6.7.1. Friedel-Crafts Synthesis Of The TCNQ Derivative.

The first step of the reaction was followed using TLC and proved to be unproductive with low yields as well as complex mixtures being encountered. In an attempt to overcome these problems the reaction conditions were modified by varying the reaction temperature, the solvent used and the reaction time. The first two modifications had little or no effect on the process and changing the reaction times only increased the amount of by-products.

A modification not attempted was to change the catalyst. It was felt that the considerable time and effort required to find a suitable candidate from the large variety available was not within the scope of this project, especially as there was no guarantee it would work and alternative approaches may give a better result more quickly. It is, however, likely that the problem with this reaction is due to not using the appropriate catalyst for our particular starting material (p-methoxyphenol).

In common with some of the other methods investigated, this approach clearly requires a significant project (synthetic organic chemistry) involving model compounds and detailed optimisation. The present work has demonstrated that reactions do indeed occur under Friedel-Crafts conditions, but optimisation must await longer term commitment by a synthetic specialist.

6.7.2. Claisen Rearrangement (Scheme 1A).

A Claisen rearrangement reaction was considered as an alternative to the Friedel-Crafts synthesis, but it had the inherent disadvantage of being appropriate only for a three carbon spacer. Whilst the three carbon spacer TCNQ derivative would have made a useful model compound, it was felt that a longer spacer would be required for the proposed polymer, in order to provide sufficient decoupling of the CT units from the polymer backbone and allow the desired stacking of the CT units essential for electrical conductivity.

6.7.3. Problems Associated With Scheme 1B.

This route was taken to the penultimate stage where purification problems hindered further progress. Both distillation and column chromatography have disadvantages in that recoveries were poor and, from TLC and spectra (see Figs.6.6 and 6.7), the product still contained a lot of the unreacted methoxyphenol. As we anticipate only small yields of the TCNQ derivative (3) from the allylquinone (see section 6.3.9), we require a reliable high yielding synthesis of the allylquinone. If this cannot be achieved the cost of using many low yielding reactions will become prohibitive. Should these problems be satisfactorily resolved in the future, there will only be one step remaining before it will be possible to prepare a TCNQ molecule with a three carbon spacer containing a terminal double bond which would be suitable for hydrosilylation onto a siloxane polymer or prepolymer.

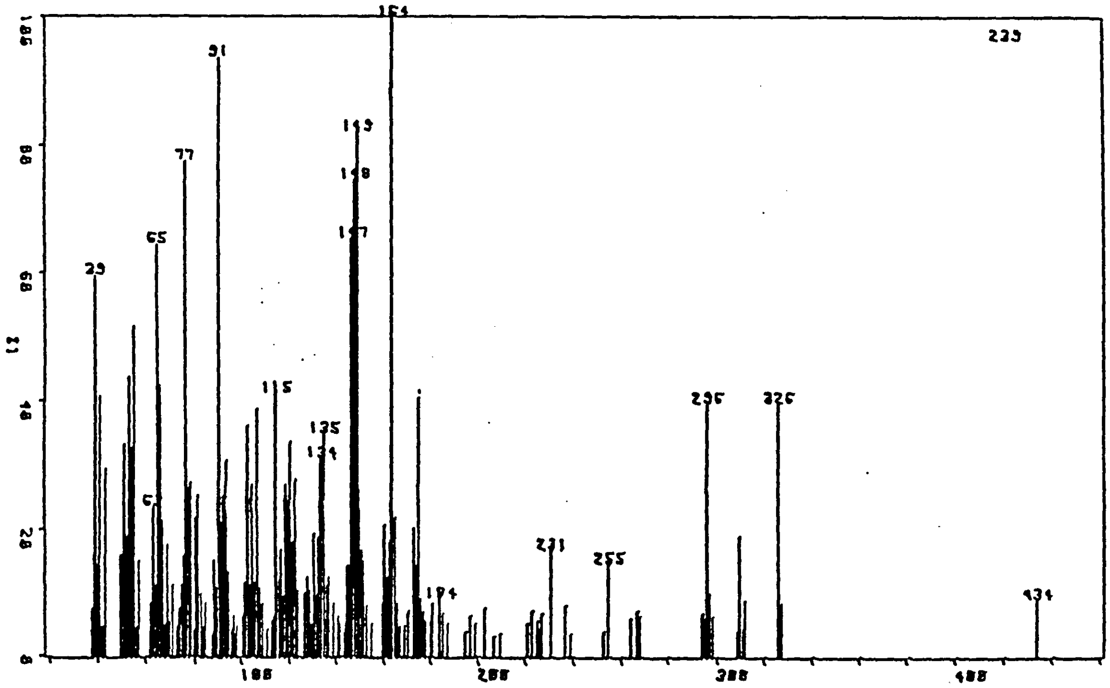


Fig.6.6.
Mass Spectrum Of The Product From The Attempted Preparation Of Allylquinone.

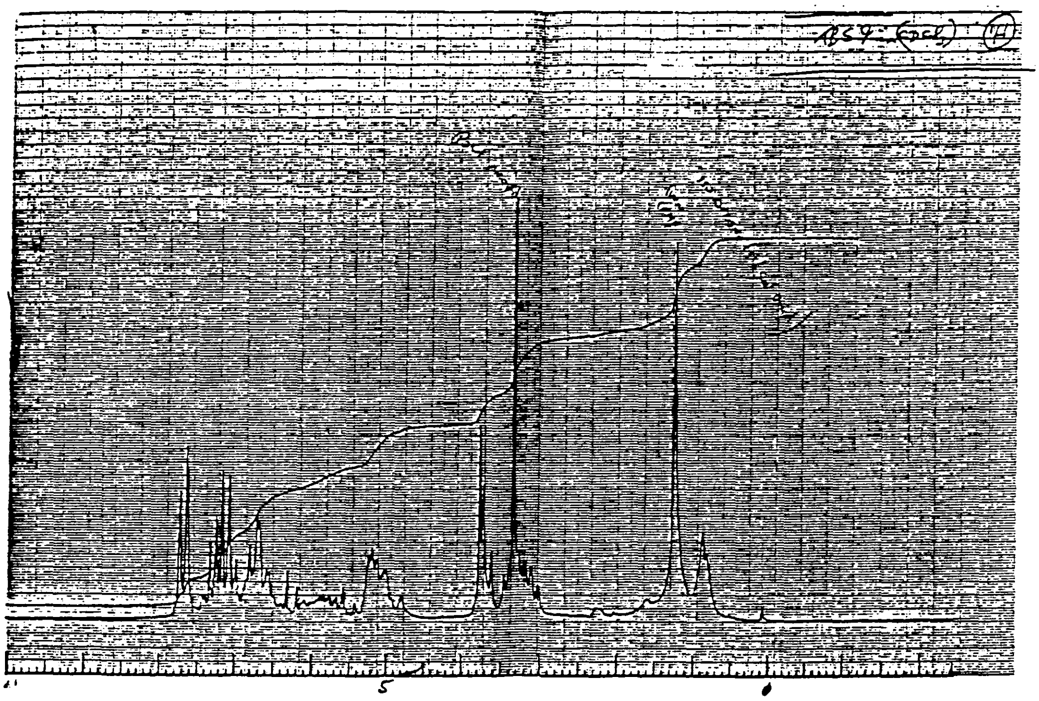


Fig.6.7.
^{1}H-N.M.R. Spectrum Of Product From The Attempted Preparation Of Allylquinone.

6.7.4. Discussion For Stork Synthesis (Reaction Scheme 2).

The procedure worked reasonably well for all but the penultimate step, i.e. the formation of the 2-allyl-1,4-cyclohexanedione(5). This approach is worthy of future work to optimise the formation of (5) as there is literature precedent for the preparation of TCNQ from 1,4-cyclohexanedione[14a].

6.7.5. Conversion To TCNQ Derivative.

For reaction schemes 1 and 2 one of the most difficult steps would have been the conversion of the precursor to the TCNQ derivative, because of:

1. Side Reactions. Preparations of TCNQ use bromine in the synthesis. This might, unfortunately, add across the terminal double bond thus removing the active group required for attachment to the polymer backbone. Since dehydrobromination is also involved, the unsaturation might be recovered at that step. However, alternative procedures demand consideration.

2. Steric Hindrance. It is likely that the preparation of the TCNQ derivative could be affected by hindrance from the attached spacer group resulting in the inability of malonitrile to approach the quinone in the correct orientation for reaction to take place. It was envisaged that this would drastically reduce the reaction rate. There is, however, literature precedent for a similar reaction[150], as shown below in Fig.6.8.

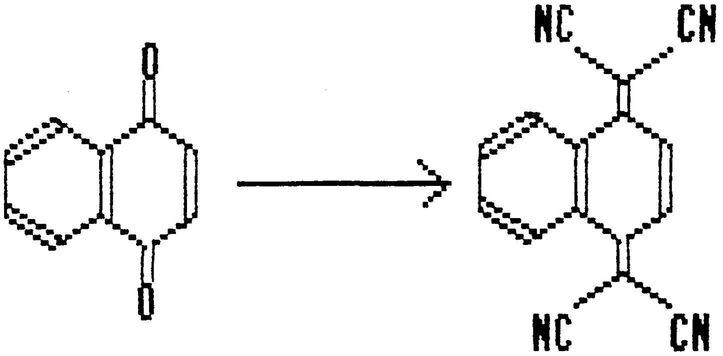


Fig.6.8.
A Sterically Hindered Molecule That Reacts With Malonitrile.

6.7.6. Conclusion For Reaction Schemes 1 And 2.

The idea of trying to insert a spacer group into the ring system of the TCNQ molecule was deferred mainly because:

1. Yields of the quinone with the attached spacer, (this being the precursor to TCNQ), were low and the products were impure.

2. The problems envisaged in the final step of the reaction.

It was concluded that scheme 3 provided a better chance of working in the short term. The reasons for this are outlined below.

6.7.7. Discussion Of Reaction Between TCNQ And ω-Aminoalkenes (Reaction Scheme 3).

This pathway was considered worth pursuing for three main reasons:

1. There was literature precedent for similar reactions to the one investigated[13a], where aminobutane replaced one of the cyano groups on the TCNQ molecule.

2. The synthetic methods were relatively simple.

3. The reaction involved attachment of the spacer directly onto the TCNQ molecule, thus avoiding the problems associated with incorporation of the cyano groups required in the other schemes.

6.7.8. Assessment Of The Effect Of Losing A Cyano Group.

Before attempting to prepare any systems, the effect of losing a cyano group on the charge-stabilising properties of the modified molecule had to be assessed. It was felt that, at worst, there would be a 25% loss in stabilisation. This did not take into account any undetermined stabilisation resulting from the secondary amine which replaced the lost cyano group.

An attempted preparation of a CT complex using the three carbon spacer TCNQ derivative with lithium iodide, (utilising identical procedures to those for the preparation of Li(TCNQ)[11]), did not provide any product. This indicated that there may be a problem forming CT complexes using our materials. Further work is required when enough product of high purity is available, as the literature cites CT complexes involving acceptors that contain only two cyano groups[124,132].

6.7.9. Different Spacer Lengths.

The preparation of a modified TCNQ molecule containing a three carbon spacer was first attempted. This was relatively easy as allylamine was readily available. However, high yields of the TCNQ derivative were not obtained, as might have been expected from the literature preparation using aminobutane.

Longer aminoalkene spacers had to be synthesised from the bromoalkenes. To date aminoalkenes via Gabriel synthesis have given rise to four, five and eight carbon spacers, but the yields have been very low (in the order of 15%). Until optimum conditions for the conversion have been found only small quantities of the bromoalkene can be used, due to their high cost.

6.7.10. Purification Of The Modified TCNQ Derivative.

To date the correct reaction conditions for the reliable preparation of pure products have not been found. It was hoped that on attachment of the derivative to the siloxane backbone the reaction would be selective and it would be possible to remove impurities i.e. purify at that stage. One problem, however, is that unreacted aminoalkene may become attached to the siloxane backbone as an impurity (see Fig.6.9).

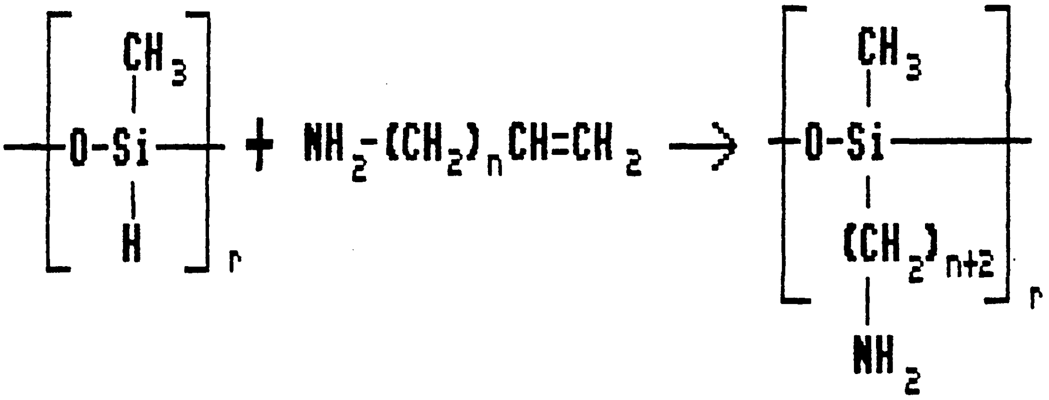


Fig.6.9.
Possible Unwanted Reaction Between ω-Aminoalkene And The Polymer.

6.7.11. Discussion For Gabriel Synthesis.

The problems were as follows:

1. The low yields. This was the biggest problem encountered. Whilst we were able to repeat literature synthesis[139] of n-aminooctane and obtain reasonable yields, the preparation of 8-bromo-1-octene by the same method provided very little product. This indicated that the alkene function may in some way be responsible for the low yields obtained for preparation of the aminoalkene from the bromoalkene. Further work is required to find the optimum reaction conditions.

2. The cost of the bromoalkenes. These were prohibitively expensive (5g of 8-bromo-1-octene is £35.90). For this reason only small quantities were used in this project.

Future work will have to be directed to either finding an alternative synthetic pathway for the preparation of ω-aminoalkenes or making the Gabriel synthesis more efficient by modification of the reaction conditions.

6.7.12. Effects Of Different Length Of Spacer.

Despite the problems involved we have been able to obtain preliminary results for TCNQ molecules using 3, 4, 5 and 8 carbon spacers. One significant difference observed for the reaction between TCNQ and the different length spacers was that the time required to obtain the product, (conveniently estimated from the length of time required for the green solution to turn red), increased as the length of chain being attached was increased. These results are tabulated in Fig.6.10 below.

Reaction times of different aminoalkenes with TCNQ		
Amine	Reaction time	Comment
3-Amino-propene	Two hours	
4-Amino-butane	Two Days	Time from published data[138].
4-Amino-butene	> Two days	Had darkened considerably. Did not turn red.
5-Amino-pentene	Two weeks	Solution turned burgundy
8-Amino-octene	> Two weeks	Took many weeks to show any colour change.

Fig.6.10.
Reaction Times For The Different Lengths Of Amine Spacer With TCNQ.

There are two possible reasons for the decrease in reaction rate as the the alkyl spacer becomes longer, these being:

1. The reaction involves nucleophilic attack by -NH2.

This means that the more nucleophilic the attacking species is the faster the reaction will proceed. The terminal alkene may contribute to the nucleophilicity of the amine, with the amount of contribution depending upon its proximity to the alkene function. Whilst this may be expected with allylamine, as the distance of the two terminal groups increases any such effect will be drastically reduced.

2. An entropy effect. The proposed mechanism (Fig.6.11) requires that the molecules are in the correct orientation to react. This will be easier for shorter, less bulky, molecules and implies that the attainment of the correct, unhindered, geometry would become less probable as the chain length increases.

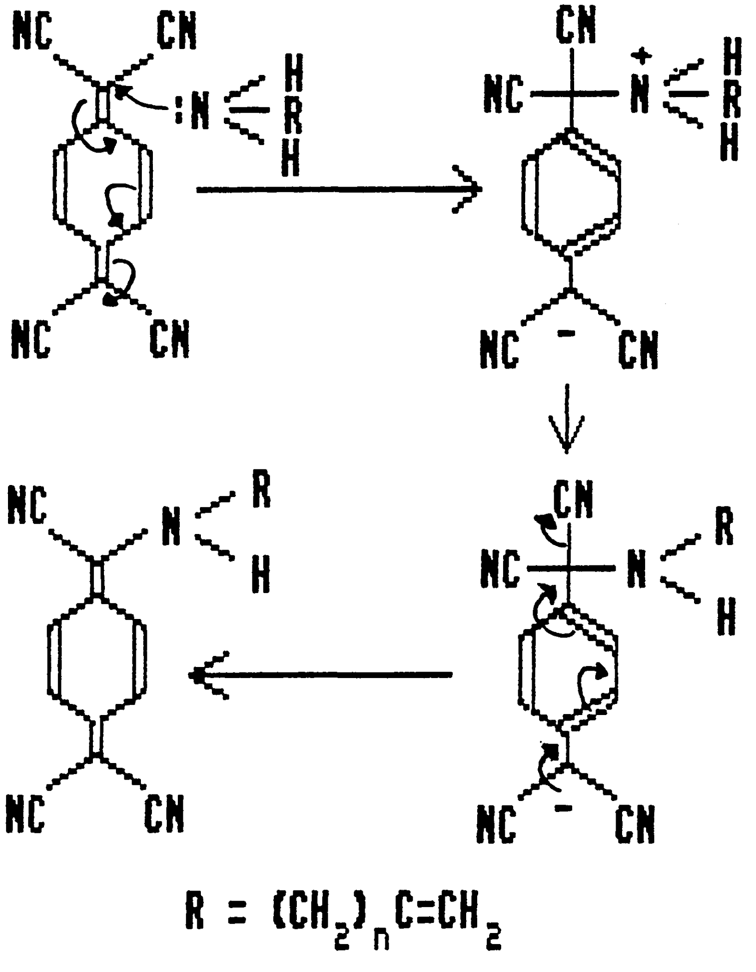


Fig.6.11.
Proposed Mechanism For The Substitution Reaction Of ω-Aminoalkene With TCNQ.

6.7.13. Purification Of ω-Aminoalkenes.

Purification of the prepared aminoalkenes was not extensively undertaken, due to the small amounts of products. One solution to the extraction and purification problem was to react the TCNQ with the crude aminoalkene when in the final solvent used for its preparation. This did appear to be successful. Despite giving some hopeful spectral data, further work will be required to quantify this procedure and identify an effective purification technique.

6.7.14. Conclusions For The ω-Aminoalkene Substitution (Reaction Scheme 3).

Despite the setbacks, scheme 3 does appear to provide a viable pathway for the preparation of a TCNQ derivative possessing an alkyl spacer group that includes a terminal alkene function suitable for incorporation into a polymer. Such derivatives of TCNQ containing 3, 4, 5 and 8 carbon spacers have been examined to date. A comparison of the I.R. spectra for the three carbon spacer TCNQ derivative (Fig.6.12) and the five carbon spacer TCNQ derivative (Fig.6.13) show that they are very similar (as were the I.R. spectra for all spacer length TCNQ derivatives), suggesting that the products are all very similar. This is a good indicator that our reactions have been profitable, especially considering that the three carbon spacer reaction uses pure aminoalkene and, presumably gives a relatively high quality product (therefore useful for comparison with the other TCNQ derivatives). Another good indicator that the reaction has been successful was that the CN stretching frequency at approximately 2200 cm^{-1} was split into two peaks, indicating the presence of two different environments for CN groups. This is as expected with one peak being attributed to the two CN groups at one end of the molecule, whilst the other peak is due to the single CN group on the side of the molecule where cyano substitution has taken place.

This work, however, has two drawbacks which are outlined below:

1. Expense of starting materials. Because the aminoalkenes are expensive, an alternative pathway using cheaper starting materials would seem desirable. This would be vital for these materials if any useful resulting polymers are to find a niche in the commercial market, although the price of the aminoalkenes could be expected to drop if the materials produced find commerical applications.

2. CTC preparation. Preparation of CT complexes from the three and five carbon spacer TCNQ derivatives was not successful. Whilst there is little doubt that purity was a major contributing factor, it would be logical to suggest that the modified molecule containing only three cyano groups could be the cause. This is unlikely as CT complexes, where the acceptor possesses only two cyano groups, have been successfully prepared[124,132].

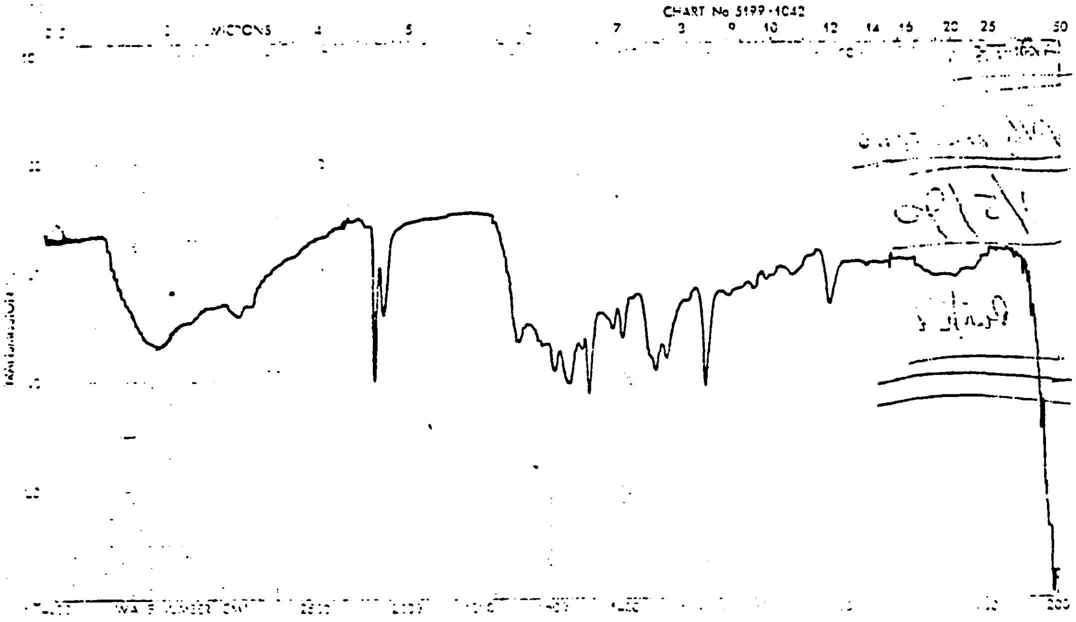


Fig.6.12.
I.R. Spectrum For The Three Carbon Spacer TCNQ Derivative.

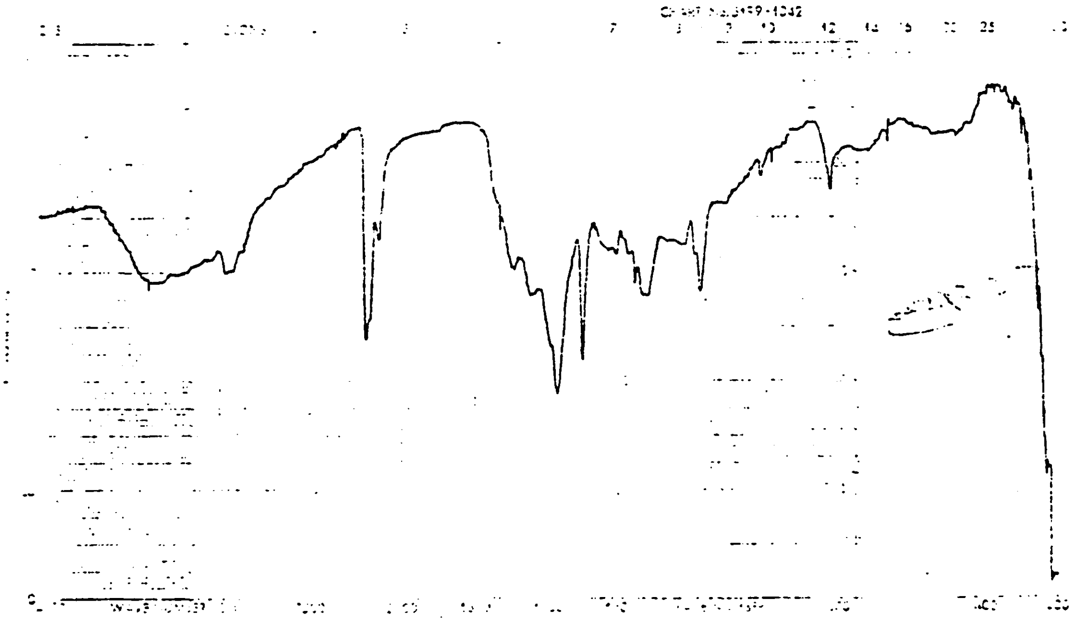


Fig.6.13.
I.R. Spectrum For The Five Carbon Spacer TCNQ Derivative.

6.8. Discussion Of The Prepared CT Polymer Model.

Only preliminary results were obtained for the siloxane ring system containing the TCNQ side groups. As yet no confirmatory evidence has been obtained to show that the TCNQ derivative has attached to the siloxane. The I.R. spectra (see Fig.6.14) suggested that the Si-H group (absorption peak at 2100cm^{-1}) was no longer present. It also indicated that there may have been some free alkene, (arising from unreacted TCNQ derivative), still present.

Table of the relevant I.R. absorption peak for CT-acceptor polymer	
Absorption frequency cm^{-1}	Associated chemical group
3400	>NH stretch (broad)
2950	C-H stretch
2200	CN stretch
1650	$R_2C=CH_2$ stretch
1170	Si-CH_x(weak) or Si-O-Si
830	$R_2C=CH_2$ (C-H deformation)

Fig.6.14.
Some Of The Relevant I.R. Absorption Peaks For The CT-Acceptor Polymer.

DSC analysis showed the presence of a crystalline phase which became liquid at 50°C and decomposed above 200°C (see Fig.6.15). Procedures to remove the unreacted derivative will have to be undertaken before a realistic assessment of the reaction can be determined.

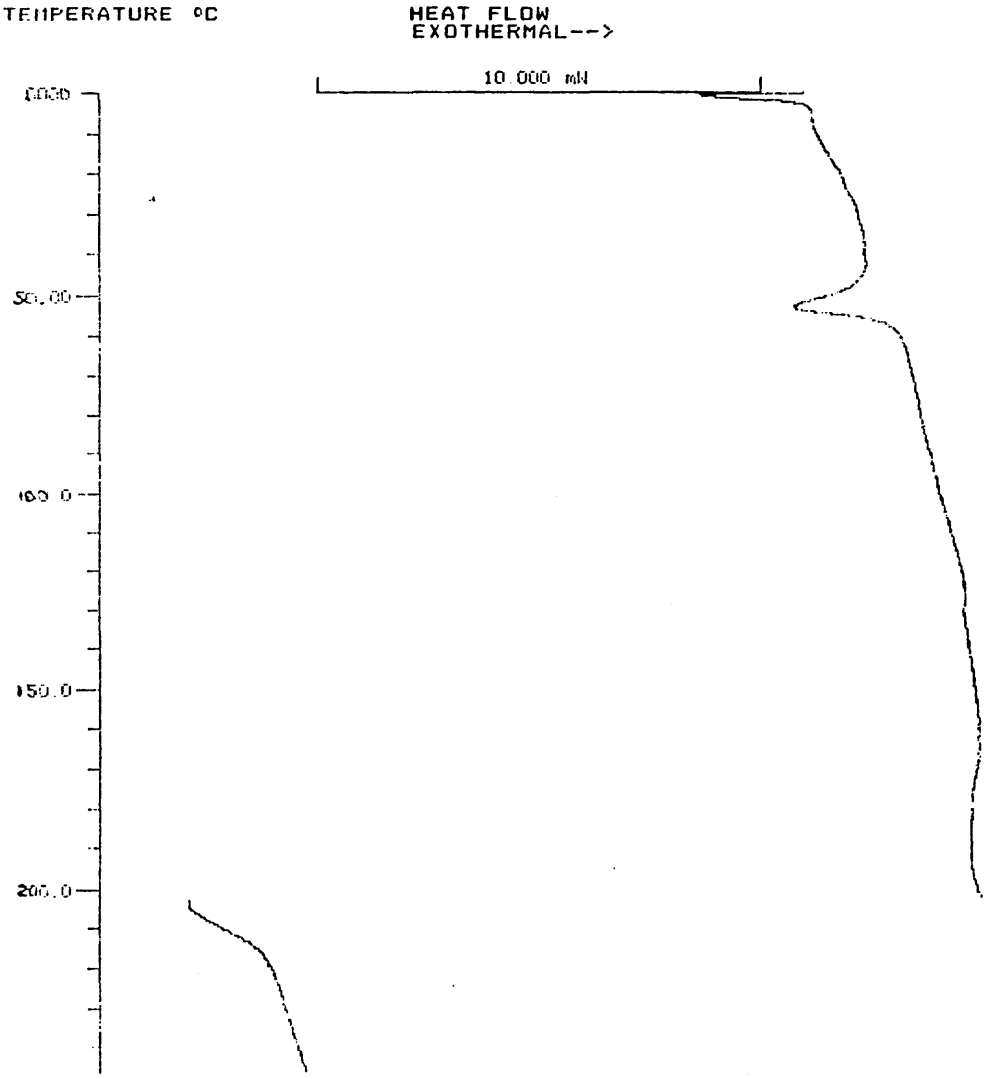


Fig.6.15.
Data From DSC Analysis For CT-Acceptor Polymer.

7.Conclusions.

7.1. Electrical conductivity Rig.

The electrical conductivity rig has, unfortunately, not performed as well as we would have liked, and has not attained the anticipated level of usefulness. This was due to two major factors. Firstly, inherent difficulty associated with obtaining accurate data. Secondly, we did not have a DVM that could measure resistance over a large enough range.

Future work on the conductivity rig would have to include the development of a reliable four point probe, (possibly discarding the pins and placing electrodes on samples by vacuum coating techniques). In addition, a DVM that can measure a far greater range of conductivities is required before the full potential of the rig can be realised.

7.2. Faraday Magnetic Susceptibility Balance.

The Faraday balance has proved very useful, although there are still some minor problems to be solved. One of these is the ability to computer control the nitrogen flow in the cryostat. This facility would automate the balance as fully as possible and also give better control of temperature changes. Another problem is concerned with tracing the cause of bucket calibration drift. Future work must address these problems. In addition, it would be useful to be able to obtain susceptibility not only with respect to temperature but also to field strength. This would require some modification to the software, enabling the detection of co-operative magnetic properties.

7.3. Conclusions For New CT Complexes.

A number of new CT complexes were prepared but none of them provided crystals suitable for X-ray studies, thus hindering structural analysis. A lot more work is required to obtain unambiguous structures and formulae for most of these materials.

The most promising new CT complex prepared was TB-TCNQ. The unusual magnetic properties it appears to exhibit will require much investigation on both practical and theoretical fronts. The biggest problem to be overcome is the preparation of single crystals. The other complex of some interest was R-TCNQ because of its ability to form films. Further work will be required to establish whether it possesses other molecular electronic properties.

Overall the work on CT complexes has lead to two major conclusions.

1. Discotic type donors do not easily give crystalline complexes with TCNQ as the acceptor.

2. The attachment of bulky side groups such as the spacers required for the preparation of the CT polymer are likely to hinder the production of the highly ordered systems we had hoped to prepare. This does not mean that

the polymer will not find applications. The conductivity may well be high enough for use as a material for electromagnetic shielding containers, or more interestingly, as a substrate for molecular electronic devices, especially if the TCNQ moieties can be ordered by an external magnetic field. The latter may be possible by blending in toluidine blue as a donor.

7.4. Conclusions For CT-Acceptor Polymer.

The attachment of the alkyl spacer to the TCNQ molecule via one of the cyano groups appears, at this time, to be the most viable route to preparing the TCNQ derivative quickly, efficiently at minimum cost. Further work will be required in order to attach the spacer to the quinone ring by such methods as hydroboration[151,152]. Although TCNQ containing a methyl group has already been prepared[153], the addition of longer spacers may prove more difficult because of entropy considerations.

Whilst we seemed able to attach the TCNQ derivative to a siloxane polymer precursor, unfortunately, not enough material was available for full analysis, in particular for the investigation of the electrical conductivity. Once the optimum reaction conditions have been achieved, the form of the polymer will make measurement of electrical conductivity relatively easy.

On the whole the project achieved most of its aims, in that the viability of such a system has been investigated, at least from a synthesic point of view and, to a certain extent, deductions can be made about the likely physical structure with regards to the effect of attached alkyl groups. Also, a novel new CT complex (TB-TCNQ) has been prepared. Finally, over the last three years approximately £80,000 of equipment has been built for a capital outlay of around £5000. The construction of this equipment has given the author an invaluable insight into the validity of magnetic and electrical conductivity measurements.

7.5. Recommendations For Future Work.

These fall into a number of categories.

1.Instrumentation. The conductivity rig would benefit from the purchase of a DVM that is able to measure resistivity over a large range. Also, a reliable four point probe needs to be developed. The manufacturers of the Cti cryostat can supply a four point probe for about £200, but it is unlikely to be suitable for all situations. Sheffield City Polytechnic has coating facilities so a project should be undertaken to investigate coating gold electrodes onto samples. Possible the most important work for the future must be to find an accurate calibration method.

Future work on the Faraday balance should be aimed at three areas.

1. Eliminating any remaining anomalies with published data.

2. Development of the facility to enable the measurement of susceptibility with respect to field strength.

3. Computerising the control of the nitrogen flow, thus enabling better temperature control.

4. Replacement of the computer by a PC compatible machine. This would make data formats between the Faraday balance and the conductivity rig compatible.

Modifications of both instruments will result in a powerful characterisation tool incorporating softwear capable of analysing and comparing conductive, photoconductive, photovoltaic and magnetic data with respect to temperature.

<u>2. CT Complexes.</u> Future work in this area should involve continued investigation to find preparative methods that will provide samples suitable for structural analysis. Once this has been achieved, the materials require investigations to determine if they possess any useful molecular electronic properties.

<u>3. CT Polymer.</u> In this area major work must be to optimise the yields from the reaction pathways investigated in this project and to pursue new pathways. This will require a major project by a synthetic organic chemist. Once sufficient polymer has been obtained, it will require full characterisation, not only for electrical conductivity but also for its magnetic and optical properties.

```
1 CLS PNT 183
2
5 PRINT"                          Faraday balance driver."
6 PRINT"                                       by"
7 print"                          S.Batty.  (1990) V 1.2"
8 REM SET UP CONSTANTS --------------
10 OFF$=" "
20 MI$=" "
26 MI$=" "
30 EI$="<OFF>"
31 SWT=0 EWT=0
40 DF$="<OFF>"
45 FOR J = 1 TO 1500 NEXT J
50 TU=295 tl=76 tmi = 5 ti=5
55 F=P-1
60 ST$="<OFF>"
65 PRND=0
70 TF$="<ON> "
72 R=666.1997 M=63.0 C=4291.845 D=152E-6
76 MAG= -.9000
80 TU$=STR$(TU)
82 TL$=STR$(TL)
84 TMI$=STR$(TMI)
85 AUT$="A"
86 TI$=STR(TI)
88 TEMP$="          "
89 STEMP$="       "
90 WT$="     " STM=0
91 CHI$="   "
92 OPENW:10"$GTD:0" PRINT:10 CHR$(15) CLOSE
93 ATTN=1 SE$=" "
94 DIM A(10),TP(100),WT(100,10),CHI(100,10),BK(100,10),TPE(100),W(11)
95 DIM E(10)
96 FLAG=0 CT=0 KB$="A" stp= 298  CUT=0
97 AOT:0(2,2)=4.8 TCT=0
98 SWV=0.01 AOT:0(2,3)=0.02 EU=50 GPVA=0 SWST=0.001
99 GOSUB 8400 GOSUB 4700 REM SET TEMP AND GET CONSTANTS
100 REM  ---END---
101
150
190 REM MAIN MENU---------------------------
200 PNT 174
205 STEMP=300
210 PRINT "--------------------------------------MAIN MENU-------------------------------"
220 PRINT PRINT "1. Set Parameters ."
230 PRINT PRINT "2. Magnet Calibration.
240 PRINT PRINT "3. Bucket Calibration
250 print PRINT "4. Balance Calibration."
260 PRINT PRINT "5. start 224 run.
300 PRINT PRINT "6. Data on request"
302 PRINT PRINT "7. Start field Sweep wt run."
303 PRINT PRINT "8. Sample bucket calibration."
310 pnt 180 PRINT
320 INPUT"ENTER CHOICE>",B1
325 B2=B1
330 PNT 183
350 ON B1 GOSUB 1000,3000,1600,4000,5000,2000,5000,500
400 GOTO 200
410 REM  ---END---
415
500 REM SAMPLE BUCKET CALIBRATION SET UP-----------
510 CLS
520 PRINT "Sample bucket calibration"
```

```
530 BULL=1
540 GOTO 5000
550 BUCL=0
560 RETURN
570 REM  ---END---
580
686
990 REM SET UP PARAMETERS--------------------------
1000 PNT 174
1010 PRINT "--------------------------------------PARAMETERS---------------------------------"
1020 PRINT PRINT "1. Bucket constant.           > ";B
1030 PRINT       "2. Diamagnetic constant.      > ";D
1040   PRINT       "3. Calibration constant.      > ";C
1050  PRINT        "4. Rel Mol Mass.              > ";R
1060  PRINT        "5. Sample mass.               > ";M
1070  PRINT        "6. Sample name: "
1080  PRINT S$
1090 PRINT
1092 PRINT "7. Max temperature.           >";TU$;"K.     Min temperature.       >";TL$;"K.
1094 PRINT "8. Time interval.             >";TI$;" Mins.    Temperature interval.  >";TMI$;"K."
1096 PRINT           "9. TO MAIN MENU."
1100  PRINT PRINT PRINT PRINT
1120 PNT 180 PRINT "Enter choise >"; INPUT A2
1130 PNT 183 ON A2 GOSUB 1300,1320,1340,1360,1380,1400,1450,1500
1140 IF A2=9 THEN RETURN
1190 GOTO 1000
1300 PRINT  PRINT "Enter Bucket Constant."; INPUT B
1310 RETURN
1320 PRINT PRINT  "Enter Diamagnetic correction."; INPUT D
1330 RETURN
1340 PRINT PRINT "Enter Calibration Constant. "; INPUT C
1350 RETURN
1360 PRINT PRINT "Enter Rel atomic mass. "; INPUT R
1370 RETURN
1380 PRINT PRINT "Enter Sample mass in milligrams! "; INPUT M
1390 RETURN
1400 PRINT PRINT "Enter sample name. ";         INPUT S$
1410 RETURN
1450 REM TEMP UPPER/LOWER SET
1460 INPUT "Enter Upper temperature limit. >",TU
1465 INPUT "Enter Lower temperature limit. >",TL
1470 TU$=STR$(TU)
1475 TL$=STR$(TL)
1480 STP=TU GOSUB 8400
1490 RETURN
1499 REM TEM/TIME INTERVAL
1500 INPUT "Enter time interval in minites. >",TI$
1510 INPUT "Enter temperature interval in Kelvin. >",TMI
1520 TMI$=STR$(TMI)
1530 TI=VAL(TI$)
1540 RETURN
1550 REM  ---REM---
1560
1600 CLS PNT 174
1610 REM ENTER BUCKET CONSTANTS-----------------------------
1620 PRINT "DATA ENTRY FOR BUCKET CONSTANTS"
1630 PRINT PRINT PRINT"The balance should first be run with no sample using option 8."
1640 input "Enter C to continue or any other key to main menu.  ",btc$
1650 IF BTC$="C" THEN GOTO 1700
1660 IF BTC$="c" THEN GOTO 1700
1670 RETURN
1680
1700 cls pnt 174
1705 print print"This will give data values of bucket weight change with respect to temperature.
"
1710 print print"These values are plotted on a computer package such as CURFIT."
```

```
1720 PRINT PRINT "A best fit is obtained from a polynomial to the power 6 shown below;"
1730 print print"Bucket constant = E1 + (E2*Temp) + (E3*(Temp^2)) + (E4*(Temp^3))        + (E5*(
emp^4) + (E6*(Temp^5)) + (E7*(Temp^6))"
1750 print print print "Enter the constants as prompted below."
1760 PRINT PRINT
1770 PRINT "Enter E1, present is :",E(1)
1775 INPUT E(1) PRINT
1780 PRINT "Enter E2, present is :",E(2)
1785 INPUT E(2) PRINT
1790 PRINT "Enter E3, present is :",E(3)
1795 INPUT E(3) PRINT
1800 PRINT "Enter E4, present is :",E(4)
1805 INPUT E(4) PRINT
1810 PRINT "Enter E5, present is :",E(5)
1815 INPUT E(5) PRINT
1820 PRINT "Enter E6, present is :",E(6)
1825 INPUT E(6) PRINT
1830 PRINT "Enter E7, present is :",E(7)
1835 INPUT E(7) PRINT
1850 GOSUB 4400
1860 RETURN
1870 REM --END--
1880
1900 stop
2000 REM DATA ON DEMAND
2003
2004
2005 PNT 174
2010 PRINT "-----------------------------------DATA ON REQUEST------------------------------"
2015 PRINT PRINT PRINT "D to get and print data to printer"
2017 gosub 8000 gosub 8100
2020 PRINT PRINT"T to set temperature         present set temp     >";STEMP$
2030 PRINT PRINT"                              present sample temp >";TEMP$
2032 PRINT PRINT"E to main menue."
2035 PRINT PRINT PRINT INPUT "ENTER CHOISE >",DT$
2040 IF DT$="E" THEN RETURN
2045 IF DT$="T" THEN GOSUB 7000
2047 IF DT$="T" THEN GOTO 2005
2050 IF FLAG=0 THEN GOSUB 8800
2060 FLAG = 1
2070 GOSUB 8500
2080 GOSUB 8000
2090 GOSUB 8900
2100 GOTO 2005
2970 INPUT; 5 WT(T2,CURR)
3000 REM SWEEP UP/DOWN TEST PROG
3010 PNT 174
3015 PRINT "THE MAGNET SHOULD SWEEP TO 12 AMPS (see display on power supply).
3020 print PRINT "Enter value to go to. or E to exit to main menu."
3025 print PRINT "PRESENT VALUE IS >";MAG MAG=MAG/10
3030 print input MAG$
3040 IF MAG$="E" THEN RETURN
3041 IF MAG$="e" THEN RETURN
[illegible]


[illegible]
3105 SU=SWV ACT:O(2,3)=SWV
3110 FOR Z = 1 TO 10
3115 SPVA = SPVA + MAG
3120 GOSUB 6200
3130 NEXT Z  SPVA = 0
3131 MVAL=50
3132 GOSUB 9900
3133 PMVAL=MVAL
3136 PRINT SU
3140 INPUT"PRESS ANY KEY TO SWEEP DOWN",Q$
[illegible]
```

```
3150 SD=SU print "magnet sweeping down"
3160 FOR Z=1 TO 10
3170 GOSUB 8300
3180 NEXT Z
3190 GOTO 3010
3500 PRINT "********* ENTER A VALUE BETWEEN 0 AND 0.-9999 ********"
3510 FOR QW=1 TO 1000 NEXT QW
3520 GOTO 3030
4000 REM BALANCE CALIBRATION--------------------------------
4010 CLS PNT 183
4020 PRINT "Before the Calibration constant for the balance is found"
4030 print "please ensure the following have been done:"
4040 print
4050 print "1. The magnet power supply has been aloud to warm up for at least two hours." pri
4060 print "2. A known weight of HgCo(SCN)4 calibrant has been put in the balance." print
4070 print "3. The magnet has been calibrated to sweep to 12 amps." PRINT PRINT
4100 input "If you are ready to proceed press C, any other key to main menu.",Cbnt$
4110 if CBNT$="C" THEN GOTO 4200
4120 IF CBNT$="c" THEN GOTO 4200
4130 RETURN
4200 cls pnt 183
4210 input "Enter the weight in milligrams of the sample of HgCo(SCN)4.  :",CALMS print
4220 print " The magnet will now sweep five times please wait. "
4250  FOR IJ = 1 TO 5 PRINT"SWEEP NO", IJ
4255 GOSUB 8000 T2=TEMP
4260  GOSUB 8500 W1=WT WAIT 2 GOSUB 8500 W1=W1+WT WS=W1/2
4270  FOR Z=1 TO 10 SPVA=SPVA+MAS GOSUB 8200 NEXT Z
4280  WAIT 6 GOSUB 8500 W2=WT WAIT 3 GOSUB 8500 W2=W2+WT WM=W2/2
4290  SD=SU GOSUB 8300 WAIT 6
4300  GOSUB 8500 W3=WT WAIT 2 GOSUB 8500 W3=W3+WT WE=W3/2
4310  CALWT=CALWT + WM-((WS+WE)/2)
4315 W1=0 W2=0 W3=0 WS=0 WM=0 WE=0 SPVA=0 ACT:O(2,3)=0.01 MV6=0 MV7=0
4317 GOSUB 8000 T3=T2+TEMP T4=T3/2 T2=0 TEMP=0 T3=0
4318 T5=T5+T4 T4=0
4320 NEXT IJ
4330 CALMB=CALWT/5 CALWT=0
4332 TEMP=T5/5 T5=0
4333
4335 GOSUB 6800
4340 CALCON= CALMB-B
4342
4350 CACHI=((4981/(283+(TEMP-273))) *1E-6)*CALMS
4352 PRINT CACHI
4360 C= CALCON/CACHI
4370 PRINT C
4400 REM STORE CONSTANTS----------------------------
4410 INPUT "DO YOU WANT TO STORE THIS VALUE Y/N. ",YN$
4420 IF YN$="N" THEN RETURN
4430 IF YN$="n" THEN RETURN
4440 DK$="CAL"
4450 OPENW: 5 DK$
4460 PRINT PRINT PRINT "SAVING CALIBRATION CONSTANT AND BUCKET CONSTANTS"
4470 PRINT:5 C
[illegible]
[illegible]
[illegible]
4500 CLOSE
4600 RETURN
4610  REM --END--
4620
4700 REM LOAD CONSTANTS----------------------------
4710 DK$="CAL"
4720 OPENR:5 DK$
4730 INPUT:5 C
4740 FOR WW= 1 TO 7
4750 INPUT:5 E(WW)
```

```
4760 NEXT ww
4770 CLOSE
4780 RETURN
5000 CLS PNT 183
5002 IF SU=50 THEN GOTO 10200
5005 INPUT "Enter file name :",F$
5006 INPUT "Enter operator name :",OP$
5007 print "Enter the date " input "Day :",dy input "Month :",MY  input"Year :",YR
5008 SDATE MY,DY,YR
5010 GRAPHICS 4
5020 DISPLAY 4
5030 COLOR 7,0
5040 PAGE 4
5050 FONT 0
5060 VIEW 9
5070 VIEW 5 WINDOW -40,40,-20,20
6000 CLS 4
6001 GOSUB 8000
6002 STP=TU GOSUB 8400 GOSUB 6100
6003 IF TEMP<3 THEN GOTO 10000
6004 GOSUB 8000
6005 VIEW 5 window -40,40,-10,10
6010 HPRINT -40,8,"---------------------------------------DATA COLLECTION-----------------------
-"
6020 HPRINT -35,4,"UPPER TEMP    >    K               LOWER TEMP    >    K"
6022 HPRINT -19,4,TU$
6024 HPRINT 15,4,TL$
6030 HPRINT -35, 2,"TIME INTERVAL >                    TEMP INTERVAL >     "
6032 HPRINT -19, 2,TI$
6034 HPRINT 15, 2,TMI$
6040 HPRINT -35,-2,"ENTER: CONTROL-B TO ESCAPE.  "
6045 HPRINT -35,-5,"        RUN 100 <CR> TO RE RUN THE PROGRAM"
6047 HPRINT -35,-7,"        WITHOUT CLEARING THE VARIABLES."
6050 HPRINT -40,-9,"---------------------------------------------------------------------------
--"
6055 VIEW 3 WINDOW -20,20,-10,10
6057 HPRINT -5,6,"        TIME          : "
6060 HPRINT -5,4,"ON LINE TEMP          >"
6070 HPRINT -5,2,"SET TEMP              >"
6075 HPRINT -5,0,"ERROR                 >"
6080 HPRINT -5,-4,"WT IN MG              >"
6090 HPRINT -5,-6,"SUSCEPTIBILITY        >"
6100 REM SCREEN PRINT
6105 VIEW 4 WINDOW -20,20,-10,10
6107  CLS,4,4,1
6110 HPRINT -20,6, HR$
6111 HPRINT -17,6,":"
6112 HPRINT -15,6,MI$
6113 HPRINT -12,6,":"
6114 HPRINT -10,6,SE$
6119 HPRINT -20,4,TEMP$
6120 HPRINT -20,2,STEMP$
6130 HPRINT -20,-4,WT$
6140 HPRINT -20,-6,CHI$
6155 REM TEMP DATA COLLECT
6200 GOSUB 8000
6210 GOSUB 6100
6230 GOSUB 8500
6235 GTIME HR,MZ,SE
6240 HR$=STR(HR)
6244 MI$=STR(MZ)
6245
6246 SE$=STR(SE)
6260 IF MZ>=STM THEN GOSUB 6500
6270 IF TEMP<TL THEN GOTO 10100
6280 TCT=TCT+1
```

```
6290 IF TCT> (30*TI) THEN GOSUB 6500
6490 CLS,4,4,1
6495 GOTO  6110
6500 REM MAIN PROGRAM DRIVER-------
6505 CT=CT+1
6510 HPRINT -20,8, "**********READING DATA**********"
6515 IF B2= 5 THEN GOSUB 8600
6520 IF B2= 7 THEN GOSUB 6530
6522 IF B2=8 THEN GOSUB 8600
6525 GOSUB 6900
6527 RETURN
6528
6530 REM FIELD SWEEP -------------------
6540 IF PRHD=0 THEN GOSUB 7700 PRHD=1
6545 GOSUB 8000  STEMP=TEM
6550 GOSUB 8500
6555 SU=SKV  STPZ=STP
6560 MSS=WT
6570 WAIT 2
6580 GOSUB 8500  MSS=MSS+WT
6590 MSS=MSS/2
6600 FOR J=1 TO 10
6602 STP=STP-0.2 GOSUB 8400
6605 SPVA = SPVA + MAG
6610 GOSUB 8200 WAIT 3
6620 GOSUB 8500  MDT=WT
6630 WAIT 2 GOSUB 8500
6640 MDT=MDT+WT W(J)=MDT/2
6645 MDT=0
6650 NEXT J
6652 SPVA=0
6655 SD=SU
6660 GOSUB 8300 STP=STPZ GOSUB 8400
6670 WAIT 3 GOSUB 8500
6680 MES=WT WAIT 2
6690 GOSUB 8500 MES=MES+WT
6700 MES=MES/2
6705 GOSUB 8000 FTEMP = TEM
6707 TEMP= (STEMP+FTEMP)/2
6710 FOR I = 1 TO 10
6720 A(I)=W(I)-((MES+MSS)/2)
6730 NEXT I
6731 A(9)=A(10)
6732 GOSUB 6800 A(10)=A(10)-B
6735 MES=0 MSS=0
6736 GOSUB 7810
6790 RETURN
6792 REM END ---END---
6794
6800 REM BUCKET CORRECTION-------------------------------------
6810 B3=E(1)+(E(2)*TEMP)+(E(3)*(TEMP^2))+(E(4)*(TEMP^3))
6820 B=B3+(E(5)*(TEMP^4))+(E(6)*(TEMP^5))+(E(7)*(TEMP^6))
6830 RETURN
6850 REM ---END---
6852
6900 REM TIMING [illegible] -------------------------
6905 STP=STP-TMI
6910 GOSUB 8400
6915 GTIME HR,MI,SE
6920 STM=MI+TI
6940 TCT=0
6990 RETURN
6992 REM ---END---
6995
7700 REM FIELD STRENTH DATA SWEEP-------
7704 OPENW:10"$DTO:0" PRINT:10 CHR$(15) CLOSE
[illegible]
```

```
7705 OPENW:10"$0T0:0"
7706 PTIME: 10 PRINT:10 CHR$(13) PRINT:10 "File name :",F$; PRINT:10 "                    Operator :'
OP$
7707 PRINT:10 "TEMP  >AMPS";
7708 FOR I = 1 TO 10 STEP AITN
7709 PRINT:10 "          ";I;
7710 NEXT I
7711 PRINT:10 CHR$(13)
7720 CLOSE
7725 RETURN
7730 INPUT "INPUT SET TEMP >",STP
7735 GOSUB 8400
7740 INPUT "TAKE TEMP >"
7742
7744 REM MAIN DATA INPUT ---------
7745 CUT=CUT+1
7750 GOSUB 8000
7760 FOR I = 1 TO 10 STEP AITN
7770 PRINT "TAKE VALUE FOR ";I
7780 INPUT A  GOSUB 8500
7790 A(I)=WT
7795 WT(CUT,I)=WT TP(CUT)=TEMP
7800 NEXT I
7810 OPENW:10 "$0T0:0"
7820 PRINT USING:10 "-£££.££      " TEMP;
7830 FOR I = 1 TO 10 STEP AITN
7840 PRINT USING :10 "       +££.££",A(I);
7850 NEXT I
7860 PRINT:10 CHR$(13)
7865 CLOSE
7866 IF AUT$="A" THEN RETURN
7870 GOTO 7730
7920 REM ---END---
7930
8000 REM TEMP INPUT----------------------
8010 FOR I = 1 TO 1000
8020 RE=AIN:0(1,0)
8030 A=A+RE
8040 NEXT I
8050 A1=A/1000
8060 A=0 RE=0
8070 TEMP=(A1*59.35)+.415
8080 A1=0  TEM=TEMP
8090 TEMP$=STR$(TEMP)
8095 RETURN
8097 REM ---END---
8098
8100 REM SET TEMP -----------------------
8110 FOR I =1 TO 1000
8120 SRE=AIN :0(1,1)
8130 SUM=SUM+SRE
8140 NEXT I
8150 A2=SUM/1000
8160 SRE=0 SUM=0
8170 STEMP=(A2*58.5000)+5
8180 A2 =0
[illegible]
8195 RETURN
8197 REM ---END---
8198
8200 REM MAGNET UP SWEEP------------------
8201 IF Z<6 THEN NLEV = 15
8202 IF Z>6 THEN NLEV = 25
8203 IF Z> 7 THEN NLEV=30
8204 IF Z >8 THEN NLEV=50
8205 IF Z>9  THEN SWST=0.0005
```

```
8206 IF Z>9 THEN NLEV = 100
8209 GOSUB 9900
8210 IF MVAL < SPVA     THEN GOTO 8270
8220 SU=SU+SWST
8230 ACT:0(2,3)=SU
8235 IF SU > 1.6  THEN GOTO 11000
8240 GOTO 8200
8260 GOSUB 8400
8270 SD=SU SWST=0.001
8280 NLEV=20
8290 RETURN
8295 REM ---END---
8297
8300 REM MAGNET SWEEP DOWN-----------------
8310 NLEV = 15
8320 SD=SD-0.001
8325 IF SD < 0.01 THEN GOTO 8350
8330 ADT:0(2,3)=SD
8335 GOSUB 9900
8340 GOTO 8300
8350 SU=SD
8390 RETURN
8395 REM ---END---
8397
8400 REM SET TEMP-------------------------
8410 IF STP > 400 THEN STP = 300
8420 IF STP < 2 THEN STP = 2
8430 ADT:0(2,2)=((0.014*STP)*1.2045)-0.019
8450 RETURN
8460 REM ---END---
8495
8500 REM WT INPUT---------------------------
8505 OPENW:10 "$QTD:1"
8510 PRINT:10 CHR$(13)
8520 CLOSE
8530 OPENR:20 "$QTI:1"
8540 INPUT:20 WT$
8550 WT=VAL(WT$)
8560 CLOSE
8570 RETURN
8580 REM ---END---
8595
8600 REM DATA INPUT FOR 12A READINGS--------------------------
8602 IF PRHD=0 THEN GOSUB 8800 PRHD=1
8605 SU=SWV
8607 GOSUB 8000 T1=TEMP
8610 GOSUB 8500 W1=WT WAIT 2 GOSUB 8500 W1=W1+WT W5=W1/2
8620 FOR Z=1 TO 10 SPVA=SPVA+MAG GOSUB 8200 STP=STP-0.2 GOSUB 8400 NEXT Z
8622 GOSUB 9900 MV6=MVAL
8625 WAIT 6 GOSUB 8500 W2=WT WAIT 3 GOSUB 8500 W2=W2+WT WM=W2/2
8627 GOSUB 9900 MV6=MV6+MVAL MV7=MV6/2
8630 SD=SU GOSUB 8300:STP=STP+2 GOSUB 8400 WAIT 6
8640 GOSUB 8500 W3=WT WAIT 2 GOSUB 8500 W3=W3+WT WE=W3/2
8650 DWT=WM-((W5+WE)/2)
8655 MPER=(MV7/PMVAL)*100
8657 GOSUB 8000 T2=TEMP+T1
8658 TEMP = T2/2
8660 W1=0 W2=0 W3=0 W5=0 WM=0 WE=0 SPVA=0:ADT:0(2,3)=0.01 MV6=0 MV7=0
8665 T1=0 T2=0
8670 GOSUB 6800
8680
8700 REM CALCULATION OF SUSCEPTIBILITY.-----------
8710 DELWT= DWT-B
8720 MOLAR= R/M
8730 CHI=((DELWT/C)*(R/M))+D
8780 CHI$=STR$(CHI)
```

```
8785 GOSUB 8900
8790 RETURN
8792 REM    ---END---
8794 REM  ---END---
8796
8800 REM PRINTER DRIVER-----------------------------
8805
8810 REM PRINTER HEADINGS------------------
8815 IF BUCL= 1 THEN GOTO 9000
8820 OPENW:10 "$GTD:0"
8825 PRINT:10 CHR$(15)
8827 PTIME:10
8830 PRINT:10 TAB(32); "Sample :";F$;tab(72);"Operator :";OP$
8850 print:10 "Sample mass  mg:";M;Tab(50);"Rel mol mass :";R
8860 print:10 "Diamag corrct. :";D;Tab(50);"Cal Const.   :";C
8870 print:10 chr$(13)
8880 print:10 " no";tab(8);"Temp(K)";tab(21);"dwt(mg)";tab(34);"  Xmole ";Tab(49);"  1/X";Tab(68
);"1000/T";tab(83);"log(XT)";tab(97);"Ueff";tab(106);"unpaired e-"; TAB(122);"mag%"
8885 CLOSE
8890 RETURN
8892 REM ---END---
8895
8900 REM DATA PRINTING---------------------
8905 IF BUCL=1 THEN GOTO 9100
8910 OPENW:10 "$GTD:0"
8970 PRINT USING:10 "-£££    -£££.££",CT,TEMP;
8972 PRINT USING:10"      +£££.££",DELWT;
8974 PRINT USING:10 "     +£.££££^^^^",CHI;
8976 PRINT USING:10 "     +£.£££££^^^^"1/CHI;
8978 PRINT USING:10 "     +£.£££££^^^^",1000/TEMP;
8979 IF CHI<0 THEN CHI=ABS(CHI)
8980 PRINT USING:10  "     +£££.££££",(LOG(TEMP*CHI)/LOG(10));
8983 UEFF=2.828*SQR(CHI*TEMP)
8984 PRINT USING:10 "   -£££.£££",UEFF;
8986 PRINT USING:10"      +££.££",-.5733637+(.8903523*UEFF)+(8.49811E-3*(UEFF^2));
8988 PRINT USING:10"       +£££.£",MPER
8989 CLOSE
8990 RETURN
8992 REM  ---END---
8994
9000 REM BUCKET CALIBRATION PRINTER--------
9010
9020 REM PRINTER HEADER------------
9030 OPENW:10 "$GTD:0"
9040 PRINT:10 CHR$(15)
9050 PTIME:10
9060 PRINT:10 TAB(20);"Bucket Calibration"; Tab(60);"Operator :";OP$
9070 PRINT:10 CHR$(13)
9080 PRINT:10 TAB(10);" NO."; TAB(22);"Temp in K";Tab(39);"Total wt.Change.";Tab(63);"Bucket wt.
";tab(83);"Correction Error"; tab(109);"Mag%"
9090 close
9095 RETURN
9096 REM  ---END---
9097
9100 REM DATA IN----------------------
9110 OPENW:10 "$GTD:0"
9120 PRINT USING:10"         -£££         -£££.££",CT,TEMP;
9130 PRINT USING:10"            -£££.££",DWT;
9135 PRINT USING:10"              -£££.£££",B;
9140 PRINT USING:10"               -££££.£££",DELWT;
9150 PRINT USING:10"             -£££.£££",MPER
9160 CLOSE
9170 RETURN
9175 REM  ---END---
9180
9655
```

```
9895 REM -----SWEEP SENCE-----
9900 FOR AZ = 1 TO NLEV
9920 AX=AX+AIN:0(1,2)
9930 NEXT AZ
9940 MVAL=AX/NLEV
9950 AX=0
9960 RETURN
9970 REM  --END--
9980
10000 REM ERROR TRAPS
10010 HPRINT -20,8,"*****IS THE TEMPERATURE CONTROLLER SWICHED ON******"
10020
10030 INPUT J1
10035 PAGE 1 VIEW 9 PNT 183
10040 RETURN
10042 REM  ---END---
10044
10100 HPRINT -20,8,"END OF RUN RETURNING TO TEMPERATURE TO 300 K"
10110 STP=300 GOSUB 8400
10120 GOTO 100
10200 REM MAGNET NOT CALIBRATED-----------------
10210 CLS PNT 174
10230 PRINT "**********THE MAGNET HAS NOT BEEN CALIBRATED ********"
10240 PRINT PRINT INPUT "PRESS CARRAGE RETURN TO GOTO THE MAIN MENU",EOR$
10250 GOTO 100
10252 REM  ---END---
10254
11000 PRINT "MAGNET ERROR"
11010 GOSUB 8300
11020 GOTO 100
11030 REM  ---END---
11040
```

```
2 REM ELECTRICAL CONDUCTIVITY RIG.
5 COMMON IBSTA%, IBERR%, IBCNT%
10 GOTO 10000' GET IEEE KEY WORDS.
15 CLS
20 LOCATE 5,20: PRINT "Conductivity Rig driver (1990) V2.1."
22 LOCATE 7,20: PRINT "                by"
24 LOCATE 9,20: PRINT "            S.Batty."
25 KEY OFF
40 ED$="<OFF>":HC$="<OFF>":MODE$="<Sigma vs Temp>"
   :IFO$="<IEEE>":RU$="<OFF>"
50 D1=.2:D2=.2:D3=.2:COND$="Sigma /cm"
60 DIM TC(15), TC$(15)
62 TC(1)=450:TC(2)=270:TC(3)=80:TC(4)=60:TC(5)=50:TC(6)=40:
   TC(7)=30:TC(8)=20:TC(9)=10:TC(10)=8:TC(11)=6:TC(12)=4:
   TC(13)=2
64 TC$(1)="a":TC$(2)="b":TC$(3)="c":TC$(4)="d":TC$(5)="e":
   TC$(6)="f":TC$(7)="g":TC$(8)="h":TC$(9)="i":TC$(10)="j":
   TC$(11)="k":TC$(12)="l":TC$(13)="m"
65 DIM XG(500),YG(500):DS$="<GRAPHIC>":GR=1:SG$="<OFF>"
70 DR$="C:": DIM C(500), T(500)
80 KEY 1,"M":KEY 2, "Z"
85 TU=300:TL=15:TI=-5:TMI=1  :TC$="<OFF>":C1$="Y":T1$="Y":
   TEMP$="Temp in K."
87 LOCATE 11,1: PRINT "<SYSTEM CHECK>"
90 GOTO 6100'INITALISE DVM:
91 COMFIL$="COM1:"+"1200"+",N,8,1"
92 GOSUB 8000:GOSUB 300: LOCATE 13,1: PRINT "<RS232 ON LINE>"
93 STEMP=300 : GOSUB 8100 ' SET TEMP TO 300k
94 LOCATE 14,1: PRINT "<PARAMETERS SET>"
95 FOR E = 1 TO 5000 : NEXT E
100 CLS : SCREEN 0
110 PRINT "-------------------------------------MAIN MENU
    ---------------------------------"
115 LOCATE 2,1 : PRINT "E to END and exit to DOS"
120 LOCATE 3,1:PRINT "1. To change parameters.  <OFF>"
130 LOCATE 4,1:PRINT "2. Load/Save data.        <OFF>"
140 LOCATE 5,1:PRINT"3. Start run.             ";RU$
145 LOCATE 6,1:PRINT"4. Show graph.            ";SG$
150 LOCATE 2,40: PRINT "Set temp is :";STEMP;" Kelvin."
160 LOCATE 4,40:PRINT "6. Hard copy.          ";HC$
170 LOCATE 5,40:PRINT "7. Mode of operation. ";MODE$
175 LOCATE 6,40:PRINT "8. Display.            ";DS$
180 LOCATE 7,40:PRINT "File name :            ";F$
190 LOCATE 7,1 :PRINT "5.Temperature control :   <OFF>"
195 IF TC$="O" THEN COLOR 0,3:LOCATE 7,27 :PRINT "<ON>":
    COLOR 3,0:LOCATE 7,31:PRINT" "
197 LOCATE 9,4: PRINT "Press E Before You end. This will
    exit and Park the hard disc."
200 LOCATE 13,1:PRINT "__________________________________
    _____________________________________________"
210 LOCATE 11,1: GOSUB 500
215 COLOR 3,0
220 ON A GOSUB 1000,2000,2000,600,300,400,800,450
230 IF A=0 THEN END
290 GOTO 100
300 REM -- TEM ON/OFF-
310 GOSUB 8300
340  IF TC$="O" THEN GOTO 360
```

```
350  TC$="O":RETURN
360  TC$="I"
370  RETURN
400 REM
418 GOTO 4005
435 LOCATE 23,1:PRINT SPC(60)
450 IF DS$="<NUMERIC>" THEN GOTO 470
460 DS$="<NUMERIC>":GR=0:RETURN
470 DS$="<GRAPHIC>":GR=1:RETURN
500 PRINT "Enter option >"
502 A$=INKEY$:IF A$="" THEN GOTO 502
503 IF A$= "E" THEN SYSTEM
504 IF A$="e" THEN SYSTEM
505 A=VAL(A$)
510 RETURN
600 LOCATE 12,1:PRINT "1. Show Temp vs Conductivity. "
610 LOCATE 13,1: PRINT "2. Show 1/Temp vs Log
    Conductivity."
620 LOCATE 14,1:PRINT "3. To main menu. "
640 LOCATE 6,27: COLOR 0,3: PRINT "<ON> ":COLOR 3,0
650 LOCATE 18,1 : INPUT "Enter option >";SP
660 ON SP GOSUB 700,750
670 IF SP = 3 THEN RETURN
680 GOTO 600
700 L5= 0
710 GOSUB 7000
720 GOSUB 7200
740 B$= INKEY$ : IF B$<> "" THEN GOSUB 9000
745 GOTO 740
750 L5 = 1
760 GOSUB 7000
770 GOSUB 7200
780 GOTO 740
800  REM MODE CHANGE
810 IF MODE$="<Sigma vs Temp>" THEN GOTO 830
820 MODE$ ="<Sigma vs Temp>": RETURN
830 MODE$="<Lg sigma vs 1/t>" :RETURN
850 RETURN
1000 CLS:REM PARAMETER SET UP ---------------------------
     ------------------
1005 PRINT"--------------------------------CHANGE
     PARAMETERS------------------------------"
1020 LOCATE 3,1:PRINT"1. temperature sensor calibration."
1030 LOCATE 5,1:PRINT"2. Set maximum and minimun
     temperatures."
1055 LOCATE 8,1:PRINT "3. Set temperature and time
     intervals."
1060  LOCATE 6,5:PRINT "Upper Temp    >";TU;"K":
      LOCATE 6,40: PRINT "Lower temp        >";TL;"K":
      STEMP=TU
1070  LOCATE 9,5:PRINT "Temp interval >";TI;"K":
      LOCATE 9,40: PRINT "Time interval >";TMI;"Minutes."
1080 LOCATE 12,1:PRINT "5. Main menu."
1200 LOCATE 19,1: GOSUB 500
1210 IF A = 5 THEN RETURN
1220 ON A GOSUB 1300,1900,1920,100
1290 GOTO 1000
```

```
1300 CLS: LOCATE 1,1: PRINT "Temperature controller
     calibration"
1302 LOCATE 3,1:PRINT "1. To enter new calibration values."
1304 LOCATE 4,1:PRINT "2. To view calibration values form
     controller."
1305 LOCATE 5,1:PRINT "3. To set heater control
     parameters."
1306 LOCATE 6,1:PRINT "4. To view heater control
     parameters."
1307 LOCATE 7,1:PRINT "5. To menu."
1308 LOCATE 9,1:INPUT"Enter number <CR> >";CA
1309 ON CA GOSUB 1320,1400,1500,1600
1310 LOCATE 3,1: PRINT "Enter 13 sensor calibration data
     points below "
1312 IF CA=5 THEN RETURN
1314 GOTO 1300
1320 OPEN COMFIL$ AS 1
1330 FOR A4= 1 TO 13
1340 PRINT "Enter the value for ";TC(A4);"K";:INPUT A5$
1350 A6$=TC$(A4)+A5$
1370 PRINT£1,A6$+CHR$(13)
1380 A6$=""
1390 NEXT A4
1392 PRINT:INPUT"Enter Reference voltage ";REF$
1394 REFS$="R"+REF$ + CHR$(13):PRINT£1,REFS$: REFS$=""
1396 CLOSE £1 : RETURN
1400 OPEN COMFIL$ AS 1
1410 LOCATE 8,1
1430 FOR I =1 TO 13
1440 PRINT£1, TC$(I)+CHR$(13)
1450 LINE INPUT£1, TCAL$ : PRINT "Temp> ";TC(I);"
     calibration >";TCAL$
1455 NEXT I
1460 PRINT£1,"R"+CHR$(13):LINE INPUT£1,REF$:
     PRINT "Reference voltage > ";REF$
1480 CLOSE£1
1485 PRINT:PRINT"ANY KEY TO MENU"
1490 Q$= INKEY$:IF Q$="" THEN GOTO 1490
1495 RETURN
1497 REM --END--
1500 LOCATE 10,1
1510 INPUT "Enter Proportional term. ";PRO$
1520 INPUT "Enter Integral term.     ";INTG$
1530 INPUT "Enter Derivative term.   ";DER$
1540 OPEN COMFIL$ AS 1
1550 PRINT£1,"P"+PRO$+CHR$(13)
1560 PRINT£1,"I"+INTG$+CHR$(13)
1570 PRINT£1,"D"+DER$+CHR$(13)
1580 CLOSE£1
1590 PRINT "DATA SENT"
1595 RETURN
1597 REM --END--
1600 LOCATE 10,1
1610 OPEN COMFIL$ AS 1
1620 PRINT£1,"P"+CHR$(13):LINE INPUT£1,PROI$
1630 PRINT£1,"I"+CHR$(13):LINE INPUT£1,INTGI$
1640 PRINT£1,"D"+CHR$(13):LINE INPUT£1,DERI$
1650 CLOSE£1
```

```
1660 PRINT "Proportional term is. ";PROI$
1670 PRINT "intergral term is.    ";INTGI$"
1680 PRINT"Derivative term is.   ";DERI$
1690 PRINT:PRINT "ANY KEY TO MENU"
1695 Q$=INKEY$:IF Q$="" THEN GOTO 1695
1697 RETURN
1698 REM --END--
1800 INPUT "CONDUTIVITY Y/N";C1$
1810 RETURN
1900 LOCATE 19,1: INPUT "Enter new upper temperature :";TU
1910 INPUT "Enter new lower temperature :";TL
1915 RETURN
1920 INPUT "Enter new temperature interval :";TI
1930 INPUT "Enter new time interval  :";TMI
1940 FOR T=19 TO 22:LOCATE T,1:PRINT SPC(60):NEXT T
1960 RETURN
2000 REM MAIN PROGRAM----------
2010 LOCATE 5,27: COLOR 0,3:PRINT"<RUNNING>":CT=0:
     COLOR 3,0
2020 IF TI<0 THEN STEMP=TU
2030 IF TI>0 THEN STEMP=TL
2050 LOCATE 15,1:PRINT "Make sure you have a formatted
     disc in drive A:"
2060 LOCATE 17,1:INPUT "Enter file name.";F$
2070 LOCATE 17,1:PRINT SPC(60)
2080 LOCATE 7,53:PRINT F$
2090 LOCATE 17,1: INPUT "ON LINE PRINT OUT Y/N ";P$
2190 REM
2195 CLS
2245 CLOSE
2250 GOSUB 6600' SET DVM RANGE
2260 GOSUB 7000' DRAW GRAPHIC HEADER
2300 REM START MAIN LOOP
2310 LOCATE 1,1:PRINT TIME$
2340 B$=INKEY$:IF INKEY$<>"" THEN GOTO 9000
2350 LOCATE 11,1: PRINT CT
2360 GOSUB 8000 :LOCATE 13,1:PRINT TEMP'GET ON LINE TEMP.
2380 LOCATE 15,2:PRINT STEMP'GET SETTEMP STATUS.
2390 GOSUB 8400 :LOCATE 17,2:PRINT HT$'GET HEATER STATUS
2400 L1=LEN(TIME$) : TIME=VAL(MID$(TIME$,4,2))
2405 IF SMJ>54 THEN GOSUB 2420
2410 IF TIME>SMI THEN GOSUB 3000 'GET DATA
2420 TMTS=TMTS+1
2430 IF TMTS> ((TMI*30)+10) THEN GOSUB 3000' TIME FALURE
     TRAP
2500 GOTO 2300
3000 REM -MAIN ROUTIENE----
3002  CT=CT+1
3005 GOSUB 8000: T4=TEMP : TEMP=0
3010 GOSUB 6700 'GET SIGMA
3020 GOSUB 8000 :T(CT)=(T4+TEMP)/2
3030 GOSUB 7200' PLOT POINT
3040 L1=LEN(TIME$) : TIME=VAL(MID$(TIME$,4,2))
3050 SMJ=TIME+TMI:SMI=SMJ
3055 IF SMJ>59 THEN SMI=SMJ-60
3060 STEMP=STEMP+TI
3065 GOSUB 8100' set new temperature.
3070 T1=0:TEMP=0:TMTS=0
```

```
3080 IF P$="Y" THEN GOSUB 6800
3085 IF P$="y" THEN GOSUB 6800
3090 DKS=DKS+1
3095 IF DKS>5 THEN GOSUB 5000
3100 RETURN
3110 '  --END--
3120 '
3990 STOP
4005 LOCATE 3,62:PRINT "<ON> ":CO=0
4010 G=0:IF CO<0 THEN CO=0
4020 CO=CO+1:G=G+1
4030 IF CO > N  THEN GOTO 4200
4050 LOCATE 9 +G ,1: PRINT SPC(60)
4055 LOCATE 9 +G ,1
4060 PRINT TAB(1);CO; TAB(25);T(CO);" K";TAB(50);C(CO);"s"
4070 IF G= 10 THEN GOTO 4100
4090 GOTO 4020
4100 LOCATE 21,1: PRINT "Scroll U or D , E to Edit ,
     M to main menue."
4110 A$=INKEY$:IF A$="" THEN GOTO 4110
4120 IF A$="U" THEN CO=CO-20
4130 IF A$="D" THEN GOTO 4010
4140 IF A$="M" THEN RETURN
4150 IF A$="E" THEN GOSUB 4300
4180 CO=CO-10
4190 GOTO 4010
4200 LOCATE G+9,1:PRINT SPC(60)
4210 G=G+1
4220 IF G=11 THEN GOTO 4100
4230 GOTO 4200
4300 LOCATE 23,1:INPUT "Enter no to EDIT ";N
4310 LOCATE 23,1:PRINT SPC(60)
4320 LOCATE 23,1:INPUT "Enter new temp in K   >";T(N)
4325 LOCATE 23,1:PRINT SPC(60)
4330 LOCATE 23,1: INPUT "Enter new conductivity value >"
     ;C(N)
4335 LOCATE 23,1:PRINT SPC(60)
4340 RETURN
4500 REM HARD COPY
4510 LOCATE 11,1:PRINT "D  to print data."
4520 LOCATE 12,1:PRINT "P  to plot data ."
4525 LOCATE 13,1:PRINT "M to main menue."
4530 LOCATE 15,1:PRINT "For dot matrix plot please use
     sciplot."
4550 LOCATE 20,1:GOSUB 500
4560 IF A$="D" THEN GOSUB 4600
4570 IF A$="P" THEN STOP
4580 IF A$="M" THEN RETURN
4590 LOCATE 20,1:PRINT SPC(60):GOTO 4550
4600 LOCATE 3,62:PRINT "<DATA PRINT>"
4610 LPRINT "File name :";F$:LPRINT
4700 LPRINT TAB(1) ;"No"; TAB(17);"Temp in K";TAB(45);
     "Conductiviy in siemens"
4710 LPRINT
4720 FOR I = 1 TO CT
4730 LPRINT TAB(1);I;TAB(25);T(I);TAB(60);C(I)
4740 NEXT I
4750 A$="M"
```

```
4990 RETURN
4995 REM-------------------------------------------------
5000 REM DISC STORAGE ROTINE-------------------
5001 IF F$="" THEN F$="EMPTY"
5005 LOCATE 21,1:PRINT "<DISC UPDATE>"
5006 DK$="A:"+F$+".DAT"
5010 OPEN DK$ FOR OUTPUT AS £1
5020 PRINT £1,CT
5030 FOR DS=1 TO CT
5040 PRINT £1,T(DS) : PRINT £1, C(DS)
5060 NEXT DS
5070 CLOSE £1
5080 DKS=0
5090 LOCATE 21,1:PRINT "             "
5095 RETURN
5097 '---------END---------
5098 '
6100 '   DIGITAL VOLT METER IEEE DRIVER INITALISE
6110 VM$="DVM"
6120 CALL IBFIND(VM$,DVM%)
6140 IF DVM% <0 THEN GOTO 6160
6145 CALL IBCLR(DVM%)
6150  LOCATE 12,1:PRINT "<DVM GPIB ON LINE>"
6155 GOTO 91
6160 IF GR = 0 THEN PRINT "<DVM GPIB NOT BOOTED>"
6170 CALL IBCLR(DVM%)
6175 LOCATE 14,60
6176 IF IBSTA% <0 THEN PRINT "<DVM DEVICE ERROR>"
6180 GOTO 91
6185 ' --END--
6190 '
6600 '   DVM SET UP -----------------------
6610 RT$="C0D0I3J0K0M2N0Q0R0T1U0Y0Z0"
6620 RA$=" ]":CALL IBCMD(DVM%,RA$)
6630 CALL IBWRT(DVM%,RT$)
6640 RA$="?":CALL IBCMD(DVM%,RA$)
6650 PRINT "range set "
6660 RETURN
6670 '  --END--
6680 '
6700 '   DATA AUIQITION--------------------
6705 LOCATE 4,1 :PRINT "<DVM ON LINE>": LOCATE 5,1 : PRINT
     SPC(25)
6720 RES$=SPACE$(255)
6730 RA$=" ]":CALL IBCMD (DVM%,RA$)
6740 CALL IBRD(DVM%,RES$)
6745 RA$="?":CALL IBCMD(DVM%,RA$)
6750 CON = VAL(RES$)
6752 LOCATE 4,1:PRINT "F1 to MENU" :LOCATE 5,1:PRINT"F2
      then Shift * to print"
6755 C(CT)=1/(1000*((0.2/Iog(2))*CON))
6756 IF C(CT)>YU THEN YU = C(CT)
6758 IF CT < 3 THEN GOSUB 6765
6759 IF YU=YL THEN GOSUB 6787
6762 RETURN
6765 IF CT=1 THEN YL=0
6770 IF CT=2 THEN YL= C(1)
6775 IF CT=2 THEN YU= C(2)
```

```
6780 IF YU < YL THEN SWAP YU,YL
6785 RETURN
6787 H5=((YU-YL)/100)*5
6790 YU= YU-H5
6792 IF YL< 0 THEN YL =0
6795 IF YL< 0 THEN YL =0
6796 RETURN
6797 '  --END--
6798 '
6800 REM ON LINE PRINTING------------------------------------
6820 IF CT > 1 THEN GOTO 6900
6830 LPRINT "4-Point probe mode using Solatron 7150 under
     IEE GPIB control."
6835 LPRINT: LPRINT "Sample name  :";F$
6837 LPRINT TAB(1);"NO." ;TAB(8);"Temp in K";TAB(25);
    "1/Temp"; TAB(40);"conductivity (sigma/cm).";
     TAB(70);"Log sigma"
6900 LPRINT TAB(1);CT;:LPRINT TAB(9) USING"£££.££";T(CT);:
     LPRINT TAB(23) USING"££.£££^^^^";1/(T(CT));:LPRINT
     TAB(44) USING"££.£££^^^^";C(CT);: LPRINT TAB(67)
     USING„£££.££^^^^";(LOG(C(CT)/LOG(10))
6920 RETURN
7000 REM GRAPH ROUTIENE-------------------------------
7010 REM AXIS DRAW
7020 CLS :SCREEN 2:YT=8
7027 LOCATE 1,30:PRINT F$
7030 PSET (200,YT)
7040 DRAW "R5L10R5D75L5R10L5D75L5R10L5D5U5"
7050 FOR DW=1 TO 4:DRAW "R50U2D4U2R50U2D8U6":NEXT DW
7060 LOCATE 22,74:PRINT TU   :LOCATE 22,48:PRINT TU/2:
     LOCATE 22,25:PRINT 0
7065 LOCATE 22,61:PRINT TU*.75:LOCATE 22,36:PRINT TU*.25
7070 LOCATE 23,45:PRINT TEMP$:YT=90
7080 PSET (100,YT) :GOSUB 7600
7090 LOCATE 10,1:PRINT "Data no."
7100 LOCATE 12,1:PRINT "Temp.    "
7110 LOCATE 14,1:PRINT "Set temp."
7120 LOCATE 16,1:PRINT "Heater %."
7130 RETURN
7200 REM DRAW ROUTINE---------------------------------
7205 IF CT = 1 THEN GOTO 7300
7210 FOR G= 1 TO CT-1
7220 PRESET (XG(G),YG(G))
7230 NEXT G
7240 IF YU=YL THEN YL=YL-((YU/100)*90)
7300 RX= 400/TU : RY= 150/(YU-YL)
7305 FOR K = 1 TO CT
7310 XG(K)=INT((RX*T(K))+200):YG(K)=INT((150-((RY*C(K))-
     (RY*YL)))+8)
7330 PSET (XG(K),YG(K))
7340 NEXT K
7350 LOCATE 2,15:PRINT USING "££.£££^^^^";YU
7355 LOCATE 10,15:PRINT USING "££.£££^^^^";((YU-YL)/2)+YL
7360 LOCATE 20,15: PRINT USING "££.£££^^^^";YL
7370 PSET(200,158):FOR DW=1 TO 4:DRAW "R50U2D4U2R50U2D8U6"
     :NEXT DW
7400 RETURN
7600 REM HEADER ROUTINE
```

```
7650 DRAW"D7R1D1R5U1R1U1R1U1L1U1L2U1L4":YT=YT-12
7660 PSET(100,YT):DRAW "D6R8U6":YT=YT-9
7680 PSET(108,YT):DRAW "L8D1R1D1R1D1R1D1L1D1L1D1L1R8":
     YT=YT-9
7690 PSET (100,YT):DRAW "D5R1U1R1U1R1U1R1U1R1UR2D5":YT=YT-5
7700 PSET (102,YT): DRAW "D2":YT=YT-2
7710 PSET (100,YT): DRAW "R4"
7750 RETURN
7790 RETURN
8000 '    ON LINE TEMPERATURE----
8010 OPEN COMFIL$ AS 1
8020 PRINT£1,"T"+CHR$(13):GOSUB 8900:LINE INPUT£1,T$
8030 CLOSE£1
8040 T1=LEN(T$)
8050 TEM$= MID$(T$,2,T1-1) :TEMP=VAL(TEM$)
8055 GOSUB 8900'WAIT
8060 RETURN
8070 '    --END--
8080 '
8100 ' SET TEMP----------------
8105 IF STEMP > 399 THEN STEMP=300
8110 T2$=STR$(INT(STEMP))
8112 MD1=LEN(T2$):T3$=MID$(T2$,2,MD1-1)
8114 TS$="S"+T3$+".0"
8120 OPEN COMFIL$ AS 1
8130 PRINT£1,TS$+CHR$(13)
8140 CLOSE£1
8145 GOSUB 8900'WAIT
8150 RETURN
8160 '    --END--
8170 '
8200 '    GET TEMP SETPOINT-----
8210 OPEN COMFIL$ AS 1
8220 PRINT£1,"S"+CHR$(13): GOSUB 8900:LINE INPUT£1,ST$
8230 CLOSE£1
8240 MS3=LEN(ST$):ST$=MID$(ST$,2,MS3-1)
8245 GOSUB 8900'WAIT
8250 RETURN
8260 '    --END--
8270 '
8300 REM HEATER ON/OFF--------
8310 OPEN COMFIL$ AS 1
8320 PRINT£1, "X"+CHR$(13)
8330 CLOSE£1
8335 GOSUB 8900'WAIT
8340 RETURN
8350 ' --END--
8360 '
8400 ' HEATER OUTPUT--------------------------------
8410 OPEN COMFIL$ AS 1
8420 PRINT£1,"H"+CHR$(13)
8430 LINE INPUT£1, HT$
8440 CLOSE£1
8450 MS4=LEN(HT$):HT$=MID$(HT$,2,MS4-1)
8455 GOSUB 8900'WAIT
8460 RETURN
8470 '  --END--
8480 '
```

```
8900 '   WAIT ROUTINE--------------------------------
8905 FOR I = 1 TO 1000:NEXT I
8910 B$=INKEY$:IF B$<>"" THEN GOTO 9000
8920 FOR I = 1 TO 1000:NEXT I
8925 B$=INKEY$:IF B$<>"" THEN GOTO 9000
8930 RETURN
8940 ' --END--
8950 '
9000 REM
9001 GOSUB 5000
9004 IF B$="M" THEN GOTO 9040
9005 IF B$="Z" THEN GOTO 9200
9006 IF LK=1 THEN GOTO 2190
9010 GOTO 2300
9040 LOCATE 20,60:PRINT "<END>"
9050 FOR I = 1 TO 1000 : NEXT I
9100 CALL IBCLR(DVM%):CALL IBCLR(CCS%)
9110 N=CT
9120 GOTO 100
9200 FOR I = 1 TO 14 : LOCATE I,1:PRINT SPC(12):NEXT I
9210 LOCATE 4,1: PRINT SPC(20)
9215 LOCATE 5,1: PRINT SPC(24)
9220 FOR S= 12 TO 18
9230 LOCATE S,1:PRINT SPC(12)
9240 NEXT S
6820 IF CT > 1 THEN GOTO 6900
9250 B$= INKEY$:IF B$ <> "" THEN GOSUB 9000
9260 GOTO 9250
9940 REM END ROUTINE---------------------------------
9950 '
10000       REM GPIB-PC Declarations for IBM Compile BASIC
10020       REM The following declarations may optionally
             be included in the user application program.
            They provide appropriate mnemonics by which
10030       REM to reference commonly used values.
            Some mnemonics have a "B" preceding them in
            order to distinguish them from Compile
            BASIC keywords.
10040       REM
10050       REM GPIB Commands
10060       REM
10070        UNL% = &H3F     ' GPIB unlisten command
10080        UNT% = &H5F     ' GPIB untalk command
10090      GTL% = &H1     ' GPIB go to local
10100      SDC% = &H4     ' GPIB selected device clear
10110      PPC% = &H5     ' GPIB parallel poll conf.
10120      BGET% = &H8    ' GPIB group execute trigger
10130      TCT% = &H9     ' GPIB take control
10140      LLO% = &H11     ' GPIB local lock out
10150      DCL% = &H14     ' GPIB device clear
10160      PPU% = &H15     ' GPIB ppoll unconfigure
10170      SPE% = &H18     ' GPIB serial poll enable
10180      SPD% = &H19     ' GPIB serial poll disable
10190      PPE% = &H60     ' GPIB parallel poll enable
10200      PPD% = &H70     ' GPIB parallel poll disable
10210      REM
10220      REM GPIB status bit vector
10230      REM global variable IBSTA% and wait mask
```

```
10240       REM
10250       BERR% = &H8000   ' Error detected
10260       TIMO% = &H4000   ' Timeout
10270       BEND% = &H2000   ' EOI or EOS detected
10280       SRQI% = &H1000   ' SRQ detected by CIC
10290       RQS% = &H800     ' Device needs service
10300       CMPL% = &H100    ' I/O completed
10310       LOK% = &H80      ' Local lockout state
10320       REM% = &H40      ' Remote state
10330       CIC% = &H20      ' Controller-In-Charge
10340       BATN% = &H10     ' Attention asserted
10350       TACS% = &H8      ' Talker active
10360       LACS% = &H4      ' Listener active
10370       DTAS% = &H2      ' Device trigger state
10380       DCAS% = &H1      ' Device clear state
10390       REM
10400       REM Error messages returned in global variable
            IBERR%
10410       REM
10420       EDVR% =  0       ' DOS error
10430       ECIC% =  1       ' Not CIC (or lost CIC during
                               command)
10440       ENOL% =  2       ' Write detected no listeners
10450       EADR% =  3       ' Board not addressed correctly
10460       EARG% =  4       ' Bad argument to function call
10470       ESAC% =  5       ' Function requires board to be
                               SAC
10480       EABO% =  6       ' Asynchronous operation was
                               aborted
10490       ENOA% =  7       ' Non-existent board
10500       ESYN% = 10       ' New I/O attempted with old
                               I/O in progress
10510       ECAP% = 11       ' No capability for intended
                               operation
10520       EFIL% = 12       ' File system operation error
10530       EBUS% = 14       ' Bus error
10540       ESTB% = 15       ' Serial poll status byte lost
10550       ESRQ% = 16       ' SRQ remains asserted
10560       REM
10570       REM EOS mode bits
10580       BIN% = &H1000    ' Eight bit compare
10590       XEOS% = &H800    ' Send EOI with EOS byte
10600       REOS% = &H400    ' Terminate read on EOS
10610       REM
10620       REM Timeout values and meanings
10630       TNONE% =   0     ' Infinite timeout (disabled)
10640       T10US% =   1     ' Timeout of 10 us (ideal)
10650       T30US% =   2     ' Timeout of 30 us (ideal)
10660       T100US% =  3     ' Timeout of 100 us (ideal)
10670       T300US% =  4     ' Timeout of 300 us (ideal)
10680       T1MS% =    5     ' Timeout of 1 ms (ideal)
10690       T3MS% =    6     ' Timeout of 3 ms (ideal)
10700       T10MS% =   7     ' Timeout of 10 ms (ideal)
10710       T30MS% =   8     ' Timeout of 30 ms (ideal)
10720       T100MS% =  9     ' Timeout of 100 ms (ideal)
10730       T300MS% = 10     ' Timeout of 300 ms (ideal)
10740       T1S% =    11     ' Timeout of 1 s (ideal)
10750       T3S% =    12     ' Timeout of 3 s (ideal)
```

```
10760        T10S% =   13     ' Timeout of 10 s (ideal)
10770        T30S% =   14     ' Timeout of 30 s (ideal)
10780        T100S% =  15     ' Timeout of 100 s (ideal)
10790        T300S% =  16     ' Timeout of 300 s (ideal)
10800        T1000S% = 17     ' Timeout of 1000 s (maximum)
10810        REM
10820        REM Miscellaneous
10830        REM
10840        S% = &H8
10850        LF% = &HA
10860        REM
10870        REM Application program variables passed to
10880        REM GPIB functions
10890        REM
10900        CMD$ = SPACE$(10)          ' command buffer
10910        RD$ = SPACE$(255)          ' read buffer
10920        WRT$ = SPACE$(255)         ' write buffer
10930        BDNAME$ = SPACE$(7)        ' board/device name
10940        FILE$ = SPACE$(50)         ' file name
10950 GOTO 15
```

CALCULATION OF MAGNETIC SUSCEPTIBILITY

1.1 Magnetic Susceptibility.

Magnetic susceptibility is given by equation 1

$$\chi_v = \frac{M}{H} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1.$$

Where:

H = Applied magnetic field.
M = Magnetisation.
χ_v = Volume susceptibility.

The Faraday method measures total susceptibility χ_T This is of the form shown in eq.2.

$$\chi_T = \chi_D + \chi_S + \chi_{VV} + \chi_L \quad \ldots\ldots\ldots\ldots\ldots 2.$$

Where:

χ_D = Core diamagnetic contribution.
χ_S = Spin-paramagnetism.
χ_{VV} = Van Vleck susceptibility.
χ_L = Orbital Landau contribution.

χ_{VV} and χ_L can be ignored for quasi-one dimensional systems[28].

As we are only concerned with the spin paramagnetic susceptibility we only have to take into account the core diamagnetic contribution. χ_S is obtained as in eq.3

$$\chi_S = \chi_T - \chi_D \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.$$

χ_D is obtained by summing the Pascals constants for each atom and/or species. These constants are available from the literature[154].

1.2. Calibration of Balance.

Before we could get any useful data from the balance it had to be calibrated (a procedure that should be repeated on a regular basis). This was achieved by measuring the weight change for a sample of known susceptibility such as mercury colbalt thiocyanate ($HgCo(SCN)_4$). Its gram susceptibility is given in eq.4.

$$\chi_g = \frac{4981}{290 + T} \ E^{-6} \ emu \ \ldots\ldots\ldots\ldots\ldots 4.$$

T = temperature in °C.
χ_g = Gram susceptibility.

To obtain a calibration constant for the balance eq.1 is rearranged to give the form in eq.5.

$$H = \frac{M}{(\chi_g . Calwt)} \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots 5.$$

H = Calibration constant.
M = Wt change in a constant magnetic field.
Calwt = Mass of the calibrant.
χ_g = Gram susceptibility of the calibrant.

The value for H can then be substituted back into eq.1 to obtain the susceptibility value for an unknown.

Note: that H in this case is NOT the magnetic field because we are measuring the magnetisation in the form of a weight change in milligrams.

The susceptibility of the calibrant is obtained by multiplying the gram susceptibility by the sample weight.

1.3. Calculation of Molar Susceptibility.

Eq.1 will give the total volume susceptibility of the sample in the balance and the sample bucket. To standardise the results they are converted to molar susceptibilities. This is achieved by:

1. Making an assumption that volumes of the calibrant and sample are comparable, thus we do not need to correct for volume.

2. Subtracting the value for the bucket from the weight change obtained.

3. Multiplying the value obtained from 2 by the relative molecular mass divided by the sample mass. This gives the total molar susceptibility.

4. The diamagnetic correction is then added to the result of 2. This is laid out in eq.6.

$$\chi_m = (((Delwt-B)/C)*(RMM/SM))+D \quad .....6.$$

Delwt = Total weight change.
B = Weight change due to sample holder.
C = Calibration constant.
RMM = Relative molecular mass.
SM = Sample mass.
D = Diamagnetic correction.
χ_m = Molar susceptibility.

The resulting values are in emu mol^{-1}.

1.4. Calculation Of The Number Of Unpaired Electrons.

This can be calculated from eq.7 and 8 as shown below.

$$u_{eff} = 2.828.\sqrt{\chi_m.T} \quad ....7.$$

Where:

u_{eff} = Is the effective magnetic moment in Bohr Magnetons (BM).

χ_m = Paramagnetic χ_m.

T = Temperature in Kelvin.

$$u_{eff} = [n(n+2)]^{0.5} \text{ BM.} \quad ....8.$$

Where:

n = No of unpaired electrons.

1.5. Calculations For Electrical Conductivity.

The calculations used were based on those outlined by Blyth[126].

The four point probe used was in the form of four pins in a line each being 0.2cm apart. Eq.9 has been used to calculate the conductivity for this type of probe.

$$V = \frac{I.\rho.In\ 2}{d.\pi} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 9.$$

Where:

V = Voltage drop (in volts).
I = Current supplied to probe (in amps).
d = Pin spacing (0.2cm).
ρ = Resistivity ($\Omega\ cm^{-1}$).

This can be rearranged to give resistivity (eq.10).

$$\rho = \frac{d.\pi}{In(2)}.R \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 10.$$

where;

R=Resistance in Ω.

From this the conductivity is obtained as the inverse of the resistivity. The DVM sends resistance values to the computer which is then converted to conductivity values using an equation based on eq.10.

1.6.Micro Analysis Calculations.

Using equation 11 shown below:

$$\text{Theoretical percentage} = \frac{E_i \,.\, M_i}{\Sigma\, E_i \,.\, M_i} \quad ..11.$$

Where:

E_i = The number of atoms of the element i.
M_i = The mass number of element i.
i = Carbon, nitrogen, hydrogen and sulphur.
E = The number of atoms of the element that the percentage is being calculated for.
M = The mass number of the element the percentage is being calcuated for.

Sample Calculation For TB(TCNQ)

Proposed formula for TB(TCNQ).0.5 H_2O.

No. of C atoms = 27	RAM = 12.011	E.M = 324.297
No. of N atoms = 7	RAM = 14.0067	E.M = 98.047
No. of H atoms = 22	RAM = 1.0079	E.M = 22.174
No. of S atoms = 1	RAM = 32.06	E.M = 32.06
No. of O atoms = 1	RAM = 15.999	E.M = 15.999
		Total = 492.577

RAM = Relative atom mass.

From this:

$$C\% = \frac{324.297}{492.577} \,.\, 100 \qquad N\% = \frac{98.047}{492.577} \,.\, 100 \qquad H\% = \frac{22.174}{492.577} \,.\, 100$$

$$S\% = \frac{32.06}{492.577} \,.\, 100 \qquad O\% = \frac{15.999}{492.577} \,.\, 100$$

Thus

C% = 65.83
N% = 19.9
H% = 04.5
S% = 06.5
O% = 03.25

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The Optimum Production of Superconducting Oxide Ceramics

ABSTRACT

A simplified procedure is described for the production of $YBa_2Cu_3O_7$ with a much shorter elevated sintering temperature and a shorter and more convenient annealing process.

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The Production of Quaternary Copper Oxides[1]

The discovery that Tc for $(La, Ba)_2 Cu O_4$ is > 30 K by BEDNORZ AND MULLER [2] immediately touched off a world-wide search for related oxides with higher critical temperatures. The most important observation was made by CHU and WU[3] after they found that dTc/dP was positive and very large in $(La, Ba)_2 Cu O_4$. This suggested to them the possibility of greatly increasing Tc through an internal pressure generated by a large A-B size difference in an A B Cu O compound, with possibly a new crystal structure.

Their hopes were confirmed with the discovery of $Y Ba_2 Cu_2 O_7$ (Tc ~ 93 K) in a large open layered structure with some similarity to perovskite in the sense that Cu could be octahedrally coordinated i.e. in a formally filled structure $Y Ba_2 Cu_3 O_9$. If no oxygen were removed the formal valence of Cu^{+n} would be n = 3.

In $Y Ba_2 Cu_3 O_{7-x}$ n = 2.33. No stable copper compounds are known with n = 3 which suggests that $Y Ba_2 Cu_3 O_{7-x}$ should not be stable at all. In practice annealing in oxygen is needed to reduce x to zero and produce high critical temperatures.

Optimum Sintering Time for the Production of $Y Ba_2 Cu_3 O_{7-x}$

Many workers have reported different sample preparation procedures for the production of superconducting $Y Ba_2 Cu_3 O_7$. In most of these a barium salt, usually $Ba CO_3$, is made to decompose by heating in the presence of Cu O and $Y_2 O_3$ to form the defective perovskite according to the equation:

$$Y_2O_3 + 4 Ba CO_3 + 6 Cu O = 2 Y Ba_2 Cu_3 O_{6.5} + 4 CO_2$$

This reaction is usually carried out in an atmosphere of O_2 or air and the sample is allowed to cool in the gas stream during which the superconducting phase is formed by the addition of oxygen.

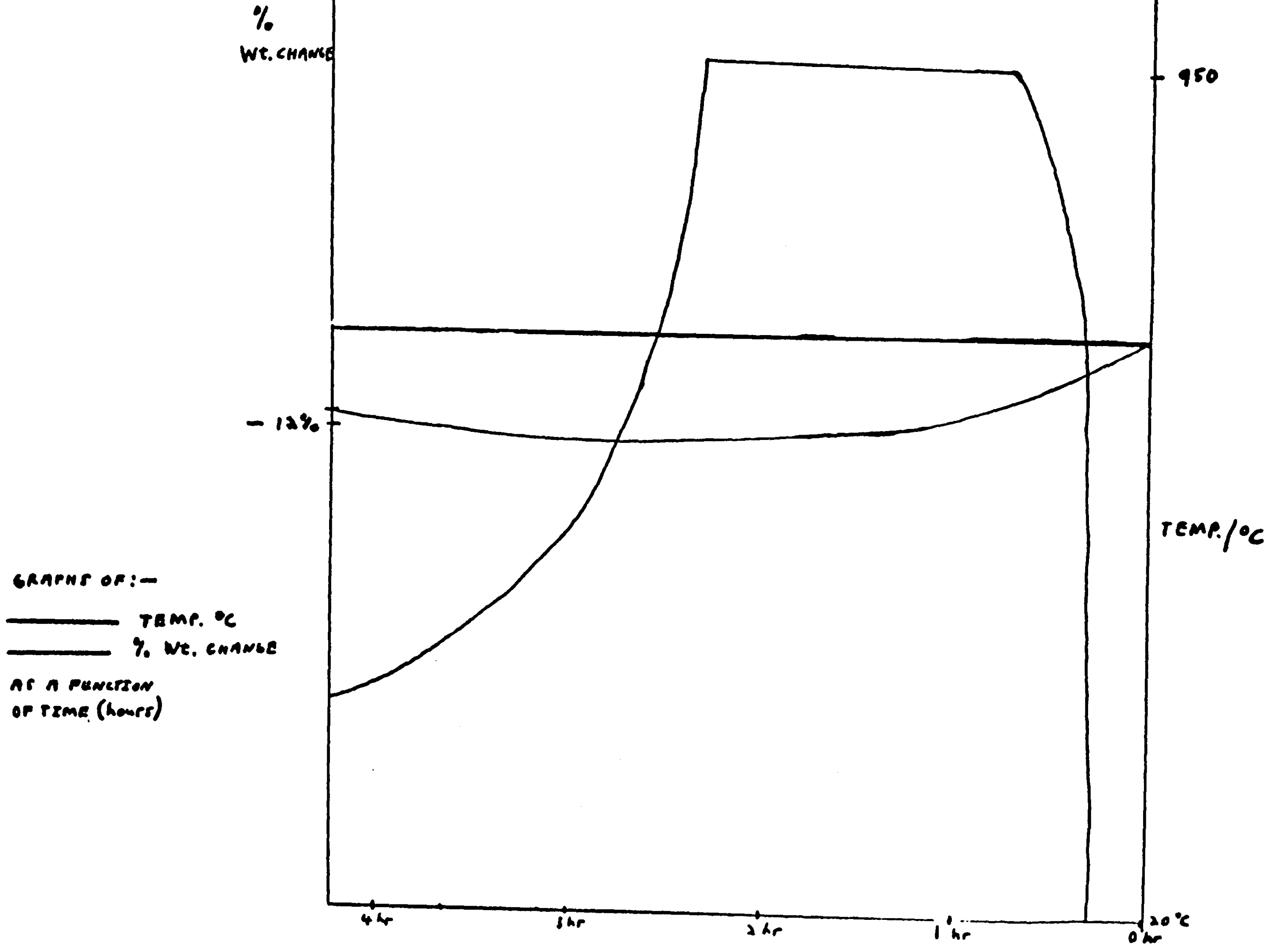
$$4 Y Ba_2 Cu_3 O_{6.5} + O_2 = 4 Y Ba_2 Cu_3 O_7$$

X ray analysis shows that by adding Oxygen the structure of the sample changes from the tetragonal at $x = 6.2$ which is a semiconductor to orthorhombic at $x = 7.0$ which is metallic.

We report here a more rapid formation of the superconductor than has been observed previously. Using a thermogravimetric technique we have monitored weight changes over a period of only eight hours of which only approximately two hours has been spent at an elevated temperature. FIG 1.

FIG 1.

REDUCED SINTERING TIME FOR FORMATION OF $YBa_2Cu_3O_{7-x}$



In the process 0.5g of Y_2O_3, 1.75 g of Ba CO_3 and 1.055g of CuO were ground in an agate mortar for one hour, sintered in a stream of O_2 at 950°C for approximately two hours and then allowed to cool still in a stream of O_2 for a further six hours.

The resulting ceramic was ground into a powder and superconductivity was demonstrated by measuring magnetic susceptibility using a Faraday balance. FIG 2 shows the superconducting transition to diamagnetism occurring at 91.5 K.

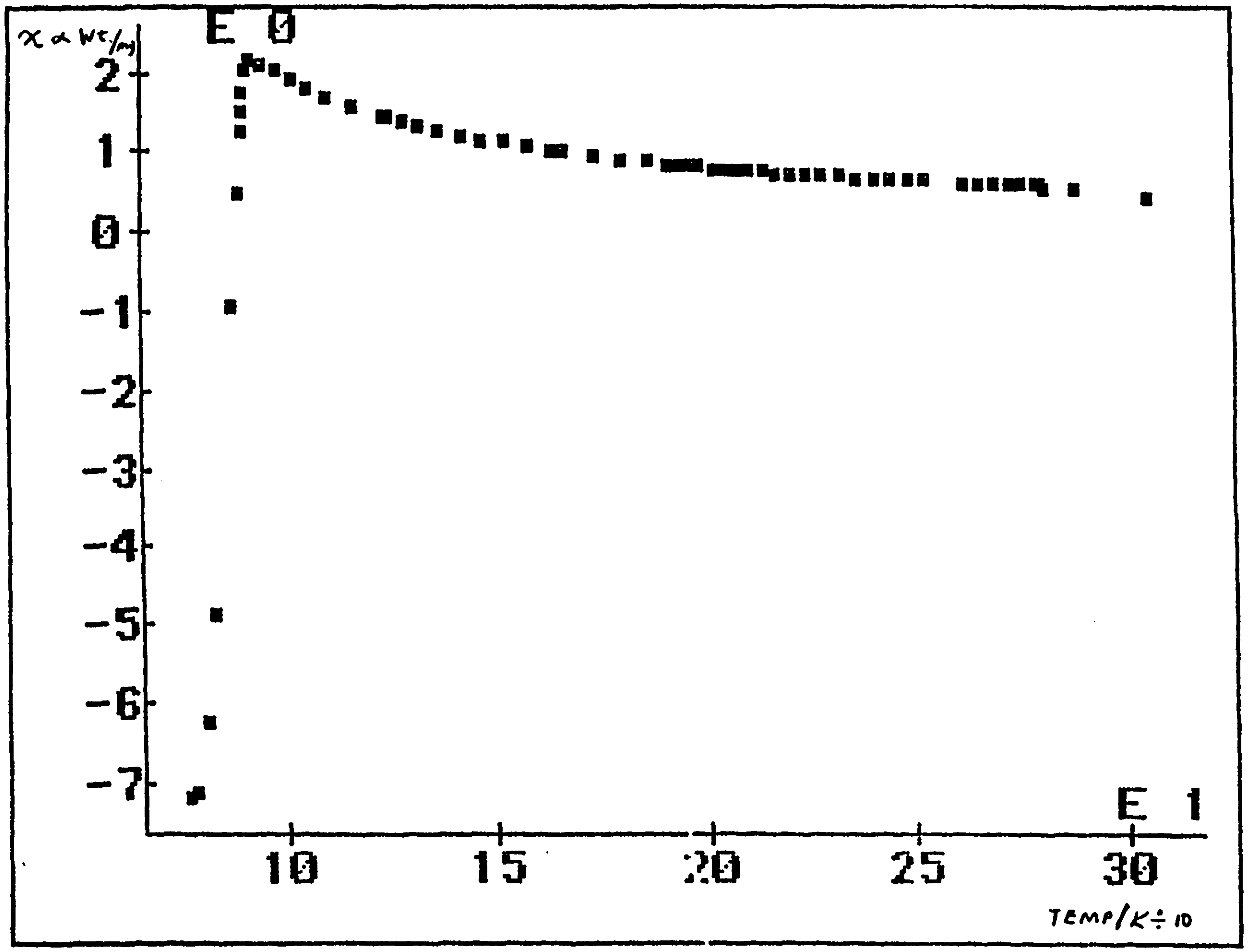
From FIG 1 it is seen that the first reaction involving the loss of the CO_2 occurs during the first hour of heating and that O_2 absorption is almost complete after two hours heating at 950°K followed by two hours cooling. This is a far simpler and quicker procedure than has been previously reported.

A Simple Valence Theory of the Phases of Y Ba_2 Cu_3 O_{7-x}

Y Ba_2 Cu_3 O_{7-x} is both structurally and chemically complex. The formal ionic valencies of the constituents are Y(3+) , Ba(2+), Cu(+1) as in Cu_2 O and Cu(+2) as in CuO. Even a small fraction of Cu(+3) would be surprising. It seems more reasonable to suppose that oxygen is in a $O[(2-\delta)-]$ state.

For Y Ba_2 Cu_3 O_7 with x = O the formal valence of Cu is 2.33 if O is 2-. However, it is more probable that Oxygen is in a valence state of $(2-\delta)-$.

FIG.2



χ IN mg VS TEMP./K ÷ 10 FOR $YBa_2Cu_3O_7$

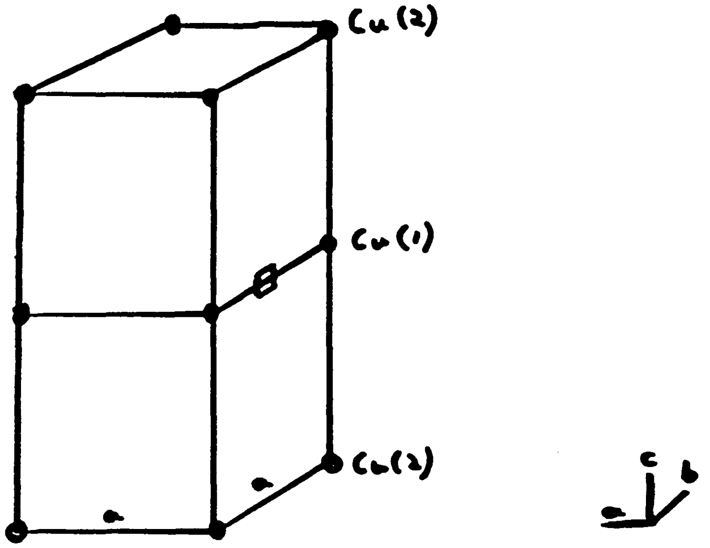
There are two inequivalent copper sites and for x = 0 the material is metallic and superconducting below ~93K. The coordination numbers are N_c [Cu(1)] = 4 and N_c [Cu(2)] = 5.

For x = 1 oxygen vacancies are created in the Cu(1) chains and the presence of these vacancies creates localized energy levels which may act as acceptors to dope the Cu(2) planes. The sample is therefore in a semiconductive state. It is also antiferromagnetic. The phase change from semiconductive to metallic state may occur when these holes are filled by the oxygen annealing process.

Even in the metallic $Y Ba_2 Cu_3 O_7$ state there will still be non-stoichiometry with vacancies in the $Cu O_2$ layers which may allow pairing of migratory holes below the critical temperature i.e it is a p-type superconductor.

These changes are illustrated by the primitive crystal structures shown. FIGS 3,4.

FIG 3.
$YBa_2Cu_3O_6$ ANTIFERROMAGNETIC SEMICONDUCTOR.



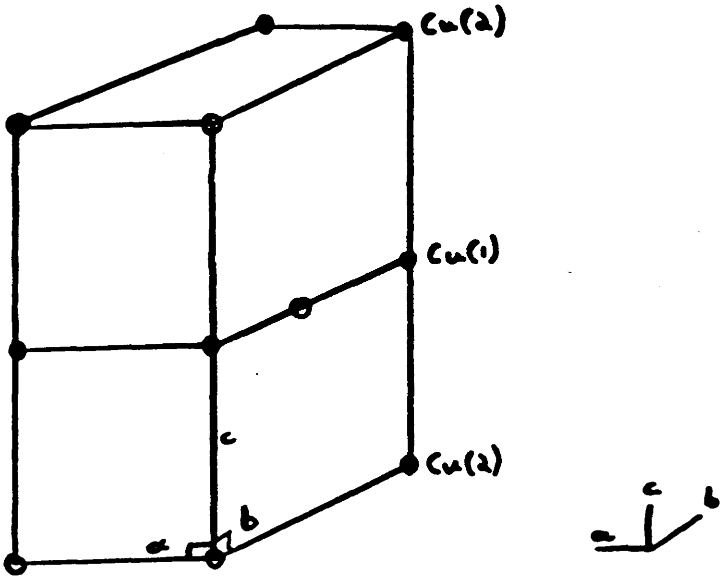
○ Cu ATOMS

□ O VANCANCIES

TETRAGONAL O VACANCIES ON b axis.

FIG 4.

$YBa_2Cu_3O_7$ SUPERCONDUCTING METAL.



○ Cu ATOMS

○ O ATOMS

ORTHORHOMBIC OXYGEN VACANCIES ON b AXIS FILLED

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