CHARGE TRANSFER IN
ORGANOTELLURIUM CHEMISTRY

A thesis submitted for the degree of

Doctor of Philosophy

by

Harkesh Bahadur Singh

at

The University of Aston in Birmingham

September 1983

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Summary

A range of organotellurium(II) compounds, together with some selenium compounds are used as donors to form donor-acceptor complexes with 7,7,8,8-tetracyano-p-quinodimethane(TCNQ) and chloranil. A method of assessing the degree of charge transfer for donor-acceptor complexes of organotellurium compounds using Mössbauer spectroscopy is described. The crystal and molecular structure of dibenzotellurophene-TCNQ has been determined and molecular parameters compared with the known structure of the component molecules. Charge transfer salts of the general formula $DX_{(1-3)}$ (D=3,4-benzo-1-telluracyclopentane, $X=PF_6^-, BF_4^-, ClO_4^-, I^-$) have been prepared electrochemically.

The reaction of 2,3-bis(bromomethyl)quinoxaline with tellurium and sodium iodide gives 3,4-quinoxalino-1-telluracyclopentane-1,1-diiodide, which may be reduced to 3,4-quinoxalino-1-telluracyclopentane. The latter compound readily forms a black 1:1 charge transfer complex with TCNQ. When 2,3-bis(bromomethyl)quinoxaline is reacted with tellurium and potassium iodide, a yellow 1:1 adduct of the above diiodide and 2,3-bis(iodomethyl)quinoxaline is isolated. The structure of the 1:1 adduct consists of discrete molecules of $C_{10}H_8N_2TeI_2$ and $C_{10}H_8N_2I_2$, two pairs of each being linked with centrosymmetric dimers by weak Te....I linkages. The crystal and molecular structure of 3,4-quinoxaline-1-telluracyclopentane has also been determined. The structure consists of discrete molecules with strong intermolecular Te....Te interactions.

The reaction of tellurium tetrachloride with m-methoxybenzylideneaniline and p-nitrophenylhydrazones results in the protonation of the Schiff bases. These bases are *ortho*-mercurated when treated with mercuric acetate. Transmetallation reactions of the *ortho*-mercurated with tellurium tetrachloride, tellurium tetrabromide, tellurium tetraiodide and p-ethoxyphenyl tellurium trichloride have been studied. The reduction of m-(methoxybenzylideneaniline-C^2,N)tellurium(IV) tribromide affords a novel organotelluenyl bromide. Spectroscopic data (I.R., ^1H and ^{13}C N.M.R., mass spectra) show unambiguously that the aryl group has become metallated in a position *ortho* to the azomethine and amino group.

Telluraxanthene does not form a charge transfer complex with TCNQ. Attempts to prepare telluraxanthylium tetrafluroborate were unsuccessful. Dichlorocarbene reacts with diorganoditellurides to give insertion derivative. However, most of the ditelluride reacts to give a tellurinic anhydride.

Key Words:

ORGANOTELLURIUM
CHARGE TRANSFER
QUINOXALINE
SCHIFF BASE
DICHLOROCARBENE

DECLARATION

The work described in this thesis was carried out between 1980 and 1983 at the University of Aston in Birmingham. It has been done independently and has not been submitted for any other degree.

H.B. Singh
H B Singh

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I would like to acknowledge with thanks, the service rendered by the members of the technical staff in the Department of Chemistry.

I am most grateful to my wife Usha who has so often provided the moral support which has lifted my flagging spirits.

Finally, I am indebted to the Government of India, for awarding me a study scholarship.

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CHAPTER ONE

GENERAL INTRODUCTION

1.0 General Introduction

Superconductivity could be extremely useful both in research and technology. But the full potential has been largely unrealised because superconductivity can only be observed at temperatures close to absolute zero. A large number of metals and alloys become superconducting when cooled below a certain critical temperature which is typically of the order of a few degrees Kelvin(1). In this state the electrical resistivity is immeasurably small and currents can be carried without loss of energy.

Physicists predicted that some materials could be superconducting at more manageable temperatures. These substances are organic: a paradox, at first sight, as organic materials have traditionally been known as insulators. The breakthrough in understanding superconductivity came in 1957 when John Bardeen, L.N.Cooper and J.R.Schrieffer in the U.S. developed a successful model(2). The essence of the BCS theory is that the conduction electrons are highly organised in the superconducting state. They form loose pairs. In 1964 W.A.Little(3) proposed using large and strongly polarisable organic molecules to provoke an attractive interaction between electrons as they move along an organic chain. Fritz London suggested that superconductivity could exist in molecular crystals(4).

Organic molecular solids and organic polymers are normally considered to be very good insulators and are frequently used as such. However, strong π-molecular donor (D) and acceptor (A) molecules often react to form ion radical salts and charge-transfer (CT) compounds:

$X^{+}A^{\underset{\cdot}{-}}$, $D^{\underset{\cdot}{+}}X^{-}$ ion radical salt

DA , $D^{\underset{\cdot}{+}}A^{\underset{\cdot}{-}}$ charge-transfer complex

These organic charge-transfer salts have received considerable attention in recent years due to their considerably high conductivities. Conducting organic solids fall into two major categories: polymers and molecular crystals. Strength, elasticity and fractional resistance are typical properties of metals but today are also characteristics of polymers. This however, is not the case with one of the most salient properties of metals: their electrical conductivity. The question of producing macromolecular materials which exhibit a conductivity similar to that of metals, has long been posed. Despite numerous and concerted attempts, it was not until very recently that the production of macromolecular materials whose conductivity characteristics were closely similar(5) to those of metals, was possible. Polymers such as polyacetylene (PA) can be transformed by oxidation (i) or reduction (ii) into conductive CT complexes. The reasons for the observed pseudo-metallic conductivity are not yet fully understood.

$$\mathrm{\{CH{=}CH\}_n + AgClO_4 \longrightarrow \{CH{=}CH\}_n^{\oplus}\,{}^{\odot} + ClO_4^- + Ag} \qquad \text{(i)}$$

In the reaction, segments of polymer chain of length n are oxidised and the structures are formed having the character of a delocalised radical cation.

$$\mathrm{\{CH{=}CH\}_n + R_4N^+X^- + e \longrightarrow [\{CH{=}CH\}^{\odot}\,{}^{\ominus}R_4N^+] + X^-} \qquad \text{(ii)}$$

The reduced polymer becomes conducting.

Polymeric sulphur nitride $(SN)_x$(6) also possess metallic properties. Polythiazyl and its bromine derivatives remain unique examples of superconducting polymers. The $(SN)_x$ chain structure and crystal structure(7) are shown in Fig. 1.1.

An important breakthrough in the manufacture of highly conducting molecular complexes was made at Dupont in 1962(8) with the synthesis of the organic molecule tetracyano-p-quinodimethane (TCNQ). According to X-ray diffraction data(9) the TCNQ unit cell has the following parameters: $a=8.906A$, $b=7.06^{0}A$ and $C=16.395A$, $\beta=98.54^{\circ}$. The bond angles and bond lengths are shown in Fig. 1.2.

The most highly conducting of these salts, N-methylquinolinium-TCNQ (iii) was at that time the best organic conductor known(10). The first of the highly conducting quasi-one dimensional organic materials to be studied in detail by solid state physicists was N-methylphenazinim(11)-(NMP)-TCNQ (iv).

$(SN)_x$

Monoclinic $P2_1/C$

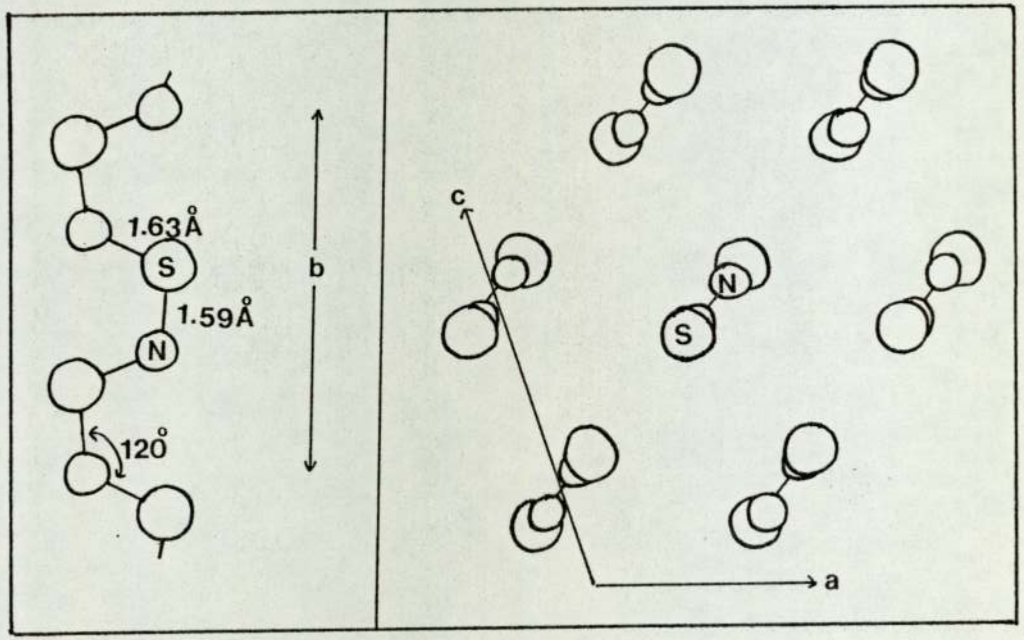
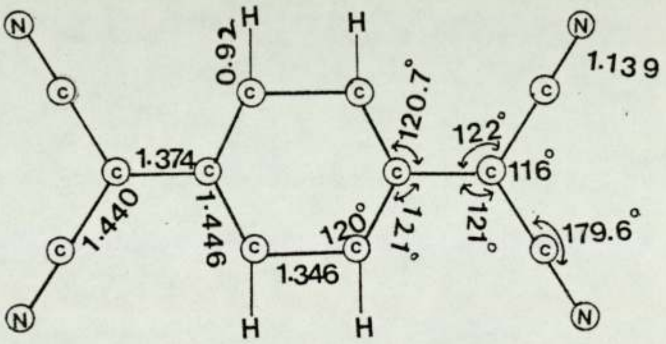
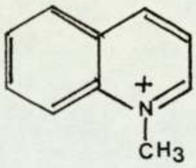
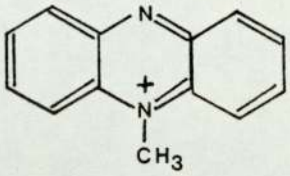


Figure 1.1 Structure of $(SN)_x$ looking down the chain axis

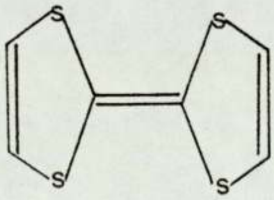


TCNQ

Figure 1.2 TCNQ

		$\sigma(\Omega^{-1}cm^{-1})$	
	TCNQ	10^{-7}	(iii)
	TCNQ	2	(iv)

In 1972 it was discovered that the chloride salt of a new organic donor, TTF (tetrathiafulvalene (v)), has a high pellet conductivity $0.2\Omega^{-1}cm^{-1}$(12). The following year the TCNQ salt was prepared and found to have a conductivity which increases dramatically below room temperature rising as high as $10^4\ \Omega^{-1}cm^{-1}$ near 60 K and was termed the first "organic metal"(13). This term indicates that materials, produced by methods of organic chemistry, can exhibit electrical properties of metals(14).

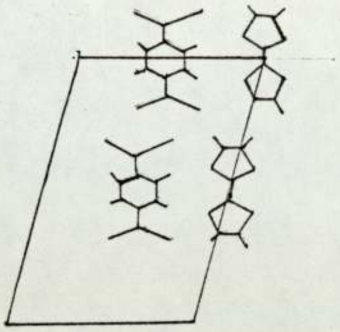


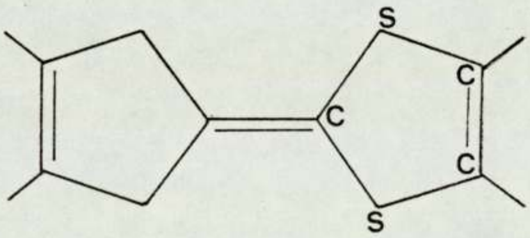
(v)

TTF

A view of the parallel chain structure of the salt is given in Fig. 1.3.

TTF-TCNQ is a simple 1:1 complex crystallising in segregated stacks of TTF and TCNQ molecules(15). The charge-transfer from donor to acceptor stack is incomplete as

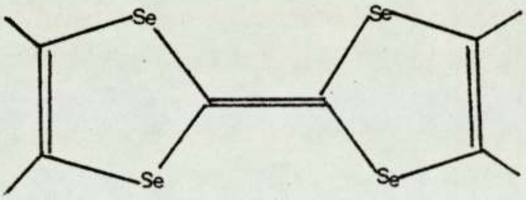




TTF

Figure 1.3 Parallel chain structure of TTF.TCNQ and molecular TTF demonstrated by diffuse X-ray scattering experiments(16). Room temperature single crystal conductivities of 500 $\Omega^{-1}cm^{-1}$ are frequently observed. At 53, 47 and 30 K three consecutive transitions occur ultimately leading to 3-D order and an insulating state. The electronic properties of TTF.TCNQ are highly anisotropic, since the solids are built of large flat molecules with extensive π interaction along the stacks and 1-D or quasi 1-D phenomena are to be expected.

The four sulphur atoms of the TTF molecule can be substituted with selenium, to create the molecule TSF (tetraselenofulvalene (vi)). Recently it has been shown that solid TMTSF-DMTCNQ(17) remains conducting down to the lowest accessible temperatures (∿1 K) by applying hydrostatic pressure.



(vi)

TMTSF

This material has an average of half an electron per molecule transferred from the 'donor' stack (TMTSF) to the 'acceptor' stack (DMTCNQ). Subsequently other materials based on TMTSF stacks were synthesised. A series of the materials of the form $(TMTSF)_2X$,(18) where X was PF_6^-, AsF_6^-, SbF_6^-, NO_3^-, ClO_4^- or BF_4^- was prepared and for the first time in 1979 superconductivity was detected in a synthetic organic conductor $(TMTSF)_2PF_6$. The structure is shown in Fig.1.4.

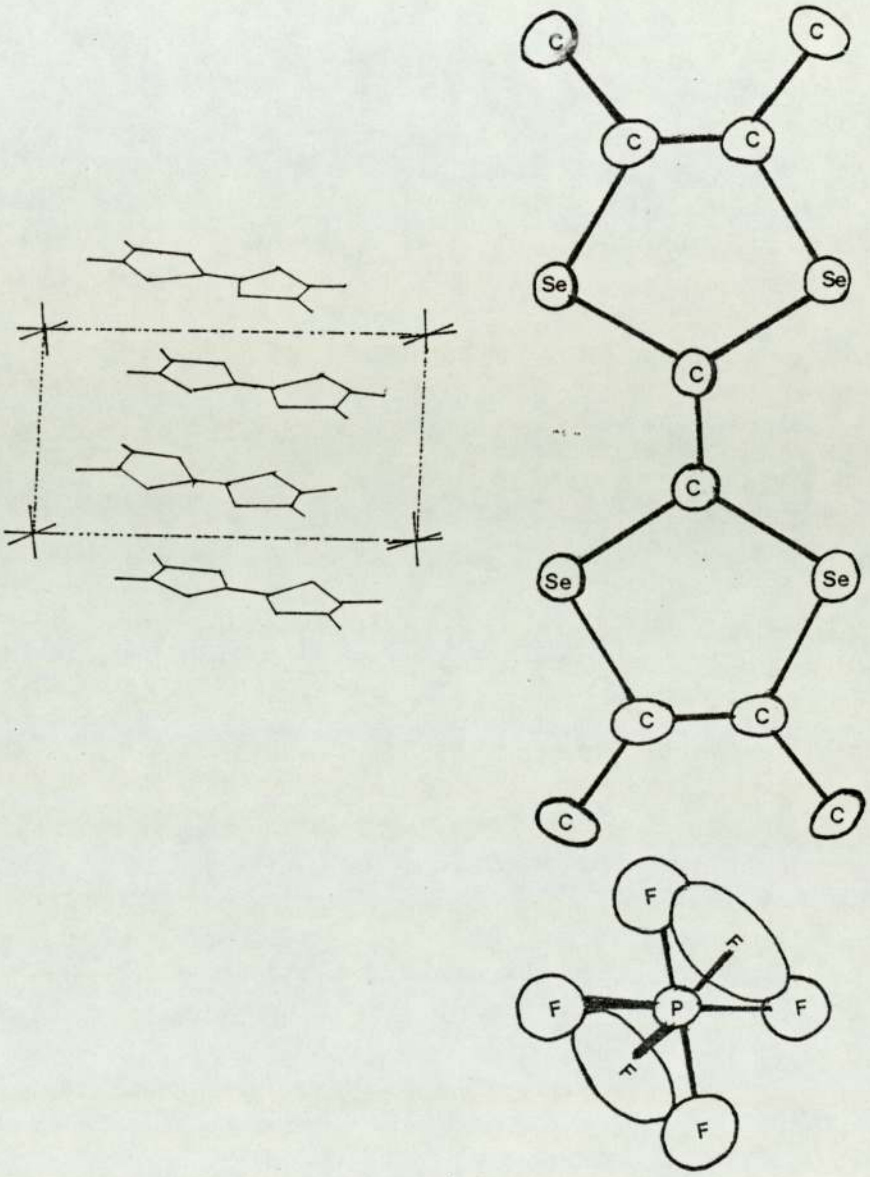


Figure 1.4 Unit cell view along b and molecular components TMTSF, PF_6

The TMTSF molecules stacked on top of each other in a zig-zag pattern(19).

There is a wealth of carefully determined experimental data on these organic conductors and a number of theories have been proposed to rationalise and explain the properties of these materials. In these materials the donors and acceptors which are large, flat molecules, stack face-to-face in segregated stacks. In this arrangement the electrons are to a great extent constrained to move along the stacks. Early conductivity measurements demonstrated the highly one-dimensional nature of TTF-TCNQ.

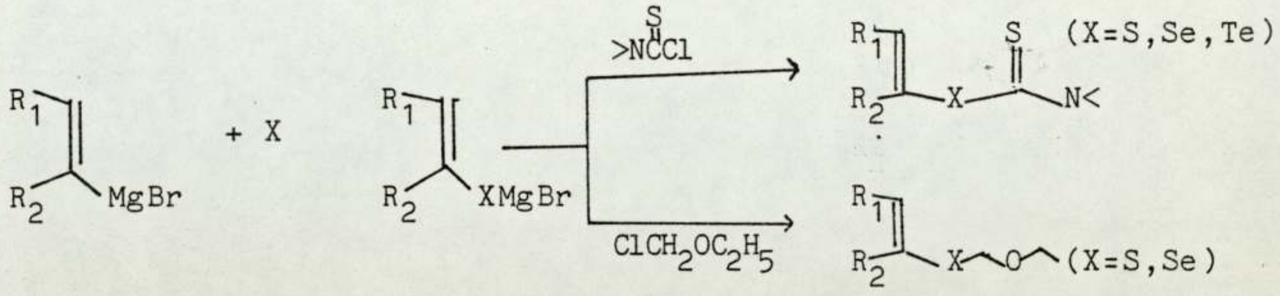
X-ray crystallographic studies pointed to the importance of the π-orbitals within the separate donor and acceptor stacks. A number of experimental results including X-ray bond lengths, electron density plots, ESCA data, optical spectra and diffuse X-ray scattering results show that there is significant electron transfer in these solids(20). ESR studies on TTF.TCNQ(21), NMR results(22) and band structure calculations(23) all indicated that the room temperature conductivity of TTF.TCNQ is dominated by the TCNQ stacks.

It is well known that the conductivity of a metal is related to the band width. It would be expected that changes which lead to wider bands on either the donor or acceptor stacks would produce materials with higher conductivities than TTF.TCNQ. The band structure calculations(23) indicate that in TTF.TCNQ the TCNQ band was significantly wider than the TTF band. On the other hand, the calculations of TTF dimers showed that the overlap of HOMO's is poor for the geometry found in TTF.TCNQ(23). One method to increase the MO overlap in the stacks and hence increase the conductivity, is to replace the elements in the donor with elements lower in the periodic table. The atomic orbitals of these elements are usually more diffuse and larger than those of the second or third period and hence can provide better intermolecular overlap.

A successful application of this occurs when the S atoms of TTF are replaced by Se atoms in TSF. A band structure calculation(24) of TSF.TCNQ indicates that the donor TSF band width is comparable to that of TCNQ band width. Since the orbitals on tellurium are even larger than those of Se, the tellurium analogue may be a superconductor at higher temperatures.

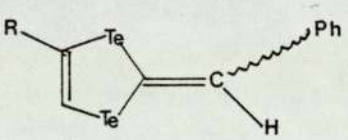
Since the discovery of the first 'organic metal' different groups have been involved in the design and synthesis of tellurium analogues of TTF and its alkylated derivatives. Substituted selenafulvalenes have been efficiently synthesised via selenacarbamates. The latter can be prepared from phosgene iminium chloride and hydrogen selenide. Parallel attempts to get substituted tellurafulvalenes by

Wudl et al(25) lead to reduction of phosgene iminim chloride by hydrogen telluride. However, telluracarbamates were synthesised by a different method shown below:



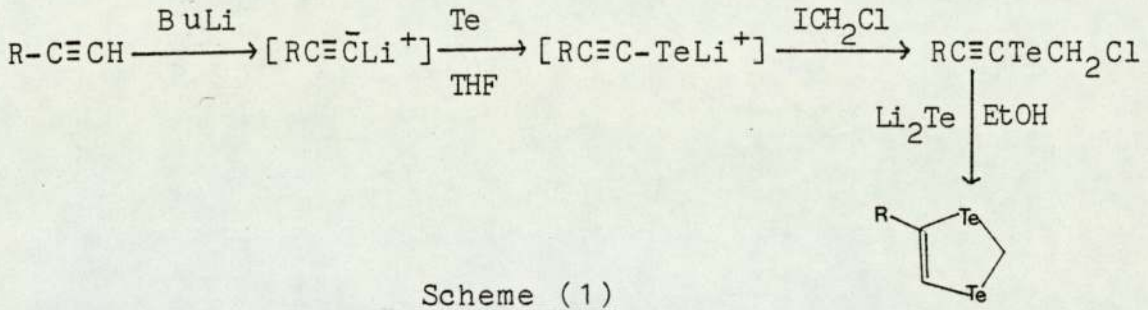
Attempted cyclisations with HBF_4/HOAc result in decomposition of the telluracarbamate.

Attempts to synthesise tellurafulvalene were pursued further after the Russian claim that 1,3 ditellurole(26)(vii) could be isolated and was stable.



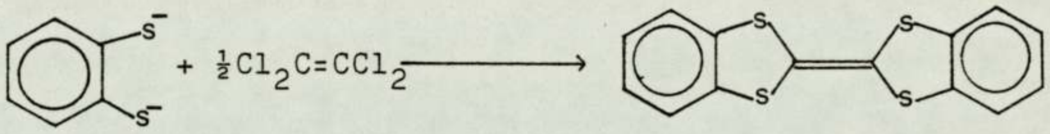
(vii)

This claim was refuted by Cava and co-workers(27). However, 1,3 ditelluroles have been reported in a modified version of the original claim. Detty et al(28) have recently reported successful preparation of 1,3 ditellurole by following scheme (1):



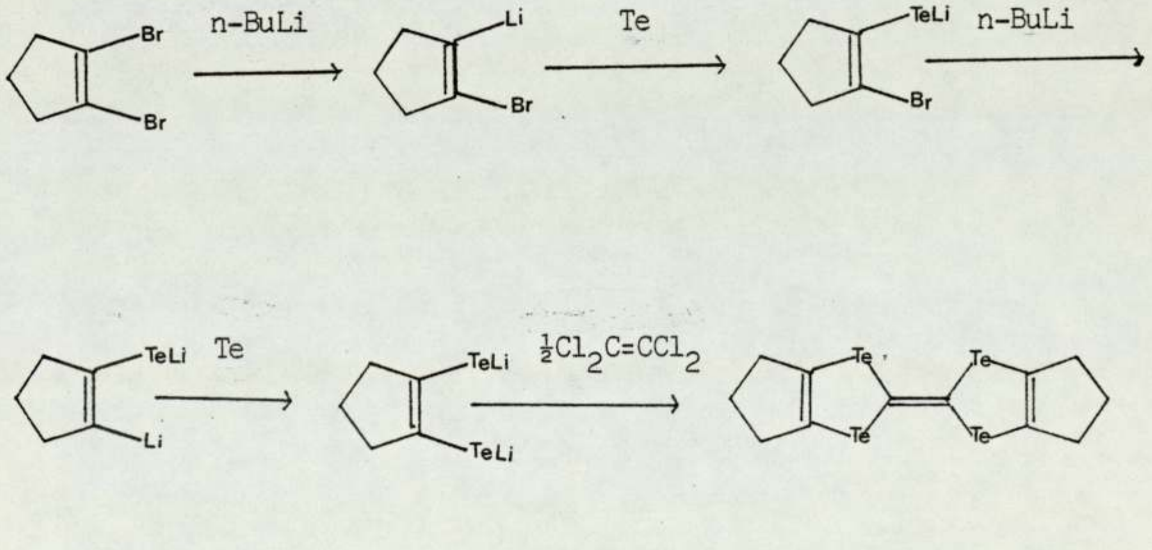
Scheme (1)

Finally the synthesis of hexymethyltetratellurafulvalene (HMTTeF) was reported by Wudl and Aharon-Shalom in 1982(29) following the preparation of benzologues of tetrathiafulvalene(30) shown in scheme (2):

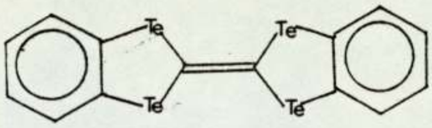


Scheme (2)

Scheme (3) depicts the synthesis of HMTTeF:



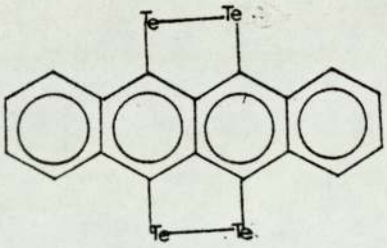
More recently Cowan(31) and co-workers have reported the tellurium homologues of TTF by the same method used by Wudl et al. The valence state ionisation potential of dibenzotetratellurafulvalene (viii) is less than S and Se analogues.



(viii)

DBTTeF

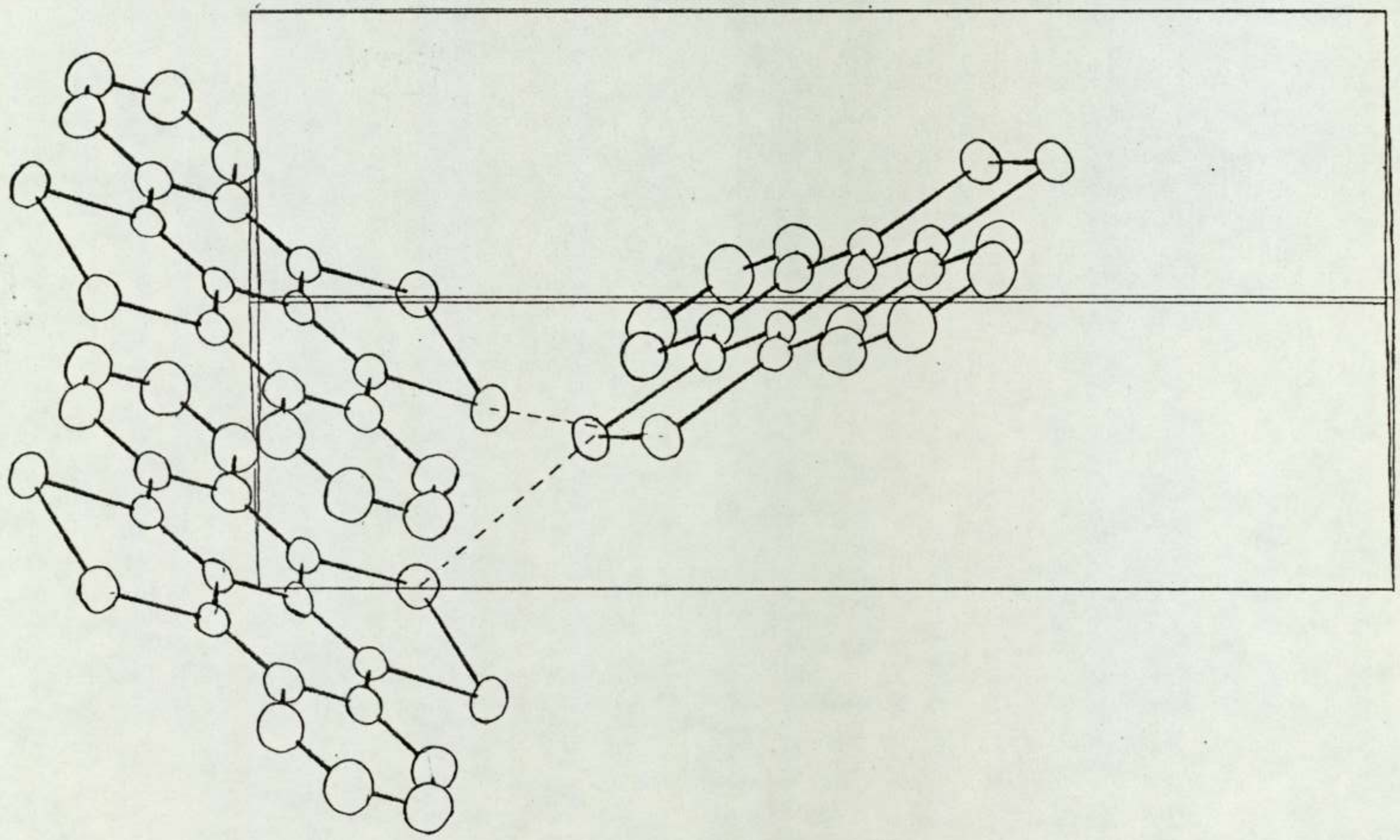
Another important development in the area of π-Te donors has been the synthesis of tetratelluratetracene (TTeT)$^{(32)}$. Crystal structure shows linear chain structure and very short Te....Te contacts$^{(33)}$. Tetratellurotetracene (ix) was obtained in low yields from tetrachlorotetracene and a new sodium ditelluride reagent. TTeT absorbs at longer wavelengths in both solution and solid state and is oxidised electrochemically at a lower potential compared to its Se analogue.



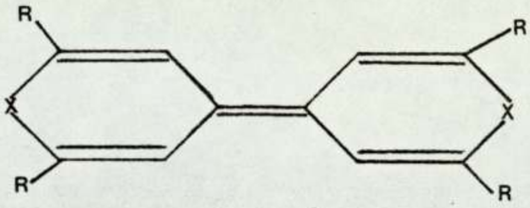
TTeT (ix)

The intermolecular Te-Te distance (3.707 Å) is the lowest observed for any organotellurium compound. The crystal structure is shown in Fig. 1.5.

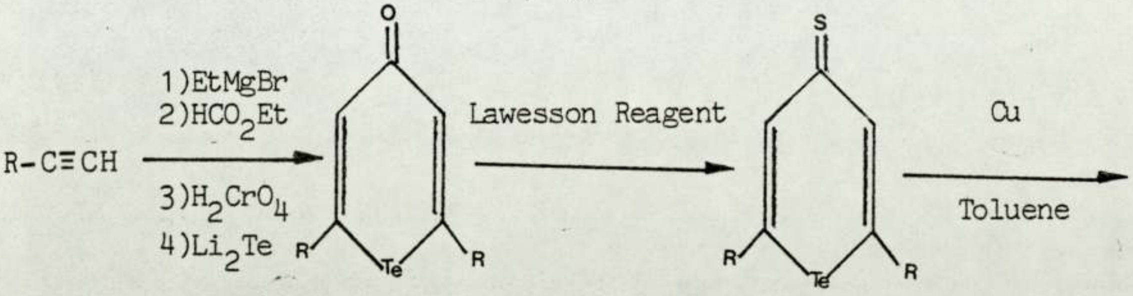
More recently, Detty et al$^{(34)}$ have reported tellurium analogues of (pyranyl)pyrans (x) which form electrically conductive complexes with electron acceptors$^{(35)}$. The preparation of (telluropyranyl)telluropyrans (xa) is shown in scheme (4).

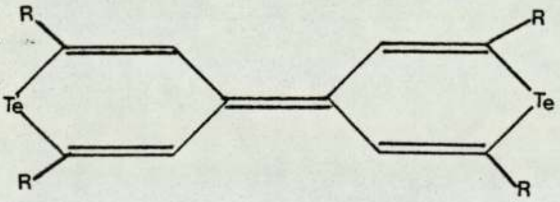


<u>Figure 1.5</u> Partial packing diagram of TTeT, showing individual molecules stacked along the b direction.



X=O, S, Se (x)





R=Ph, Me, tert-Bu (xa)

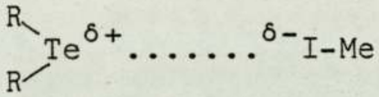
Scheme 4

(Telluropyranyl)telluropyran formed a 1:1 complex with TCNQ. Also, when donor dications were mixed with neutral donors, complex salts with closed-shell anions were isolated.

The electrical conductivity of 1:2 complex with TCNQ shows a conductivity of $4\Omega^{-1}\text{cm}^{-1}$. This conductivity is high enough to require a segregated stack structure.

The charge-transfer complexes of organosulphur and - selenium donors with different π-acceptors are well known. On the other hand there are just a few reports in literature concerning CT complexes of organotellurium donors.

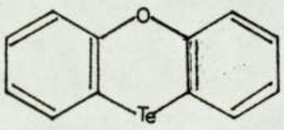
Some years back, it was suggested by McWhinnie and co-workers(36) that the oxidative addition reaction of diorganotellurides with methyliodide went through an intermediate which was a CT complex (xi).



$$R_2Te^{\delta+}\ldots\ldots\ldots{}^{\delta-}I\text{-}Me$$

(xi)

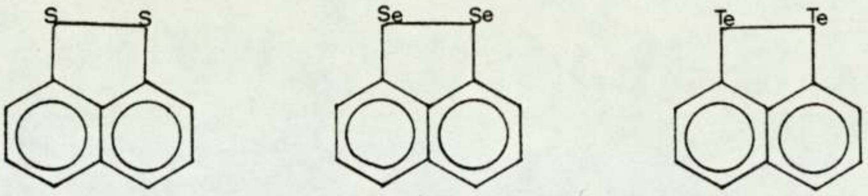
Zingaro et al(37) have studied the donor abilities of phenoxatellurine (xii) towards TCNQ, TCNE and chloranil and the interaction is interpreted in terms of π to π type bonding involving a delocalised orbital of the phenoxatellurine rather than non-bonding orbitals of the tellurium.



(xii)

Phenoxatellurine

Deeply coloured 1:1 donor-acceptor complex(38) of [1,8-c,d]-1,2 ditellurole (xiii) and TCNQ was isolated by mixing equimolar, hot solutions. The compressed pellet resistivity of the complex was found to be 50Ωcm.



(xiii)

Naphthalene Dichalcogenides (NDC)

It has also been established that in the symmetrical NDC-TCNQ series, as one goes to larger, more polarisable chalcogens, the conductivity of the TCNQ complexes increases dramatically.

The TCNQ salt of newly reported HMTTeF shows a room temperature resistivity of $\sim 1\,\Omega\,\mathrm{cm}$(29).

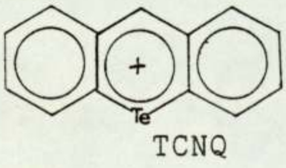
During recent years, much effort has been devoted to study the solid-state properties of 'organic metals'. The conducting materials have been subjected to a variety of sophisticated physical measurements by solid-state physicists. Of particular interest have been the conductivity measurements. The design and execution of measurement techniques of the accurate determination of the solid-state conductivity have attracted considerable attention from the workers in the area for the orderly development of organic metals. Conductivity data for CT complexes have frequently been obtained by measuring the d-c resistance of compressed powder samples(39). This procedure assumes the elimination of interparticle contact resistance due to the pressure application. However, it has been pointed out that while such measurements can yield qualitative information, they also mask important phenomenon such as crystalline anisotropy.

In an attempt to eliminate the interparticle contact resistances, a-c methods of resistance measurements have been used by many workers. The technique consists of determining the net effective resistance of a sample at audio or radio frequency using suitable bridge(40). Many organic compounds can be readily sublimed in vacuum at moderate temperatures without decomposition. The evaporated films have then been employed to ascertain electronic conductivities.

The linear chain structure of organic metals is extremely sensitive to defects and disorder. Because of high susceptibility to disruption, their intrinsic conductivity can be measured accurately only in crystals that are pure and crystallographically perfect. Many such compounds, however, have been discarded because the last step in the preparation - the growth of crystal suitable for conductivity measurement has failed. Special techniques have been devised for preparing such crystals. One of the methods employs conductivity to grow crystals(41). Specimens of the salt $K_{1.75}Pt(CN)_4 \cdot 1.5H_2O$ prepared in this way have a room temperature conductivity 10^5 times greater than crystals grown by more conventional methods. Although the art of growing crystals has been substantially advanced, most of the organic materials of interest for conductor studies are available in the form of powders comprising of minute crystals.

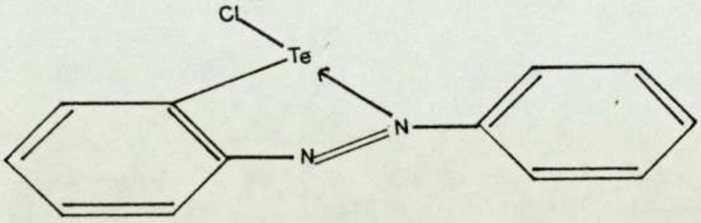
The foregoing discussion gives a concise account of the various aspects of the CT complexes of the TCNQ. The aim of one aspect of our research is to design organic conductors with high room temperature conductivities. Our synthetic studies have concentrated on organotellurium π-donors that are (a) planar, (b) have strong intermolecular contacts, (c) surrounded by cloud of π-electrons and (d) structurally related to TTF.

The tellurium analogues of the pyrilium salts afford a system where tellurium is in an aromatic ring and therefore planar. Such a compound may exhibit the donor properties of π-donors as well as the desired geometry to form a complex with TCNQ which might, in its crystal structure, possess the desired segregated donor and acceptor stacked structure. Attempts to prepare such compounds led us to the synthesis of telluraxanthylium salt (xiv).



(xiv)

Another approach to synthesise new organotellurium π-donors involves designing systems where there is delocalisation of π-electrons over a heterocyclic ring. McWhinnie et al(42) reported synthesis and crystal structure of (2-phenylazophenyl-C^2,N)-tellurium(II)chloride (xv).



(xv)

^{125}Te Mössbauer studies revealed that quadrupole splitting was less than calculated values and was interpreted in terms of delocalisation of electrons over the five-membered ring.

If the nitrogen atom of the azo group were replaced by a carbon, this would provide a similar situation as in azobenzene derivative.

Some organic derivatives of tellurium are known to have strong Te-I, Te-N, Te---Te intermolecular interactions. It was thought that a planar tellurium heterocyclic containing both tellurium and nitrogen, might have the stronger intermolecular tellurium---nitrogen contacts which might avert the conventional mixed stack structure if the Te---N contacts persisted after charge-transfer.

The synthesis and characterisation of 3,4-quinoxalino-1-telluracyclopentane was undertaken with the view that this tellurium heterocyclic might have the required properties of the donor to form CT complex.

CHAPTER TWO

EXPERIMENTAL

2.0 Experimental

2.1 Chemicals

All the known organotellurium compounds used in the present study, were prepared by literature methods starting from either $TeCl_4$(BDH) or Te(BDH). All materials had satisfactory melting points and spectra (I.R., ^{1}H NMR). 7,7,8,8-tetracyanoquinodimethane (TCNQ) was either obtained from Aldrich Chemicals or synthesised by the literature method(8). Chloranil was obtained from Koch-Light.

2.2 Solvents

All solvents were obtained from commerical sources and were purified where necessary by literature methods(43). In general, all solvents were distilled prior to use and stored over molecular sieves.

2.3 Elemental Analysis

Analysis for C, H, N was carried out by the Analytical Services Unit, University of Aston; tellurium was analysed volumetrically by the following method(44):

A known weight of the compound was oxidised with a mixture (2:1) of concentrated nitric and perchloric acid. The excess acid was removed by evaporating the mixture on a sandbath. The colourless residual solution was diluted with water. A known excess of standard 0.1N potassium dichromate solution was added and allowed to stand half an hour. Then, the solution was treated with the same volume of 0.1N ferrous ammonium sulphate solution and 20 ml of dilute sulphuric acid. Excess of ferrous ammonium sulphate was back-titrated with standard potassium dichromate solution using N-phenylanthranilic acid as indicator.

1 ml N $K_2Cr_2O_7 \equiv 0.0638$ g Te

2.4 Melting Points

The melting points are uncorrected and were determined using a Gallenkamp electrically heated Melting Point Apparatus.

2.5 Conductivity Measurements

Molar conductance of some compounds in anhydrous acetonitrile was measured at room temperature using a standard conductivity bridge, and a Mullard type E7591 B cell.

2.6 Solid State Conductivity Measurements

Samples were ground in an agate mortar and compressed into discs of diameter 13 mm and thickness 0.6-0.8 mm. Silver paste was painted on each side of the pellet to function as electrodes. Gold wires were attached by silver paste and the conductance was measured by the two pulse method or in some cases, the four probe method using a 610C Solid State Electrometer (Keithley Instruments) and Stabilised Power Supply (Kingshill) model 305. Facilities were available to monitor conductance in the range 40°C to -190°C. For the complex of dibenzotellurophene with TCNQ, one measurement was made by the four probe method on a single crystal.

2.7 Mass Spectra

Mass spectra were recorded with an AE1 MS9 spectrometer, generally at an ionisation potential of 70 eV. Appearance potentials were measured from the variation of ion current by varying the exciting voltage from 70 eV to 6 eV. Argon was incorporated with the samples as a standard of known ionisation potential. Measurements were carried out on ^{130}Te isotope which is the isotope of largest mass number and highest relative abundance.

2.8 Mössbauer Measurements

These were obtained as previously reported (45) using a ^{125}Sb/Cu source. Both source and absorber were at 4°K.

2.9 U.V. and Visible Spectra

Measurements of U.V. and visible spectra in solution (*) were performed with a Unicam SP8-100 Spectrophotometer.

(*) acetonitrile, dichloromethane

2.10 Infra-red Spectra

Spectra in the range 4000-200 cm^{-1} were recorded on a Perkin-Elmer 599B spectrophotometer. Solid state samples were examined as mulls supported between CsI plates. Nujol paraffin oil and hexachlorobutadiene were used as mulling agents.

2.11 Nuclear Magnetic Resonance Spectra

^{1}H NMR spectra were determined with a Perkin-Elmer R12B instrument (60 MHz) using tetramethylsilane as internal standard.

Proton decoupled natural abundance ^{13}C NMR were obtained on an FX 90Q (JEOL) spectrometer at 22.5 MHz.

2.12 Electrochemical Preparation

Some compounds were prepared by electrochemical oxidation of 3,4-benzo-1-telluracyclopentane in dichloromethane using platinum electrodes $\sim$1 cm apart. The appropriate tetrabutylammonium salts were used as supporting electrolyte.

2.13 Electron Spin Resonance Spectra

ESR spectra at room temperature were obtained at X-band frequency with a JEOL PE-1X spectrometer. Calibration was done with a standard manganese (II) sample diluted with magnesium oxide.

Measurement of g-values

The ESR spectrum of manganese (II) ($I = 5/2$) consists of six lines. The g-value for the fourth line is 1.981 and the third and fourth lines are 86.99 apart. Using these values, the g-value of unknown sample is calculated by the following equation:

$$g = \frac{g_1 H_1}{H + \Delta H}$$

where g is the g-value of the unknown sample,

g_1 is the g-value of the standard sample,

H is the value of the field for the unknown peak,

H_1 is the value of the field for the standard peak,

ΔH is the difference in field positions between the unknown and standard peaks.

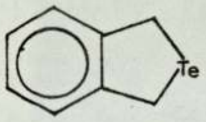
CHAPTER THREE

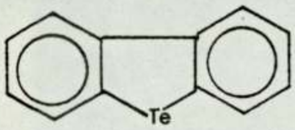
CHARGE TRANSFER COMPLEXES

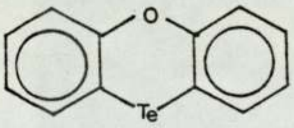
3.1 Introduction

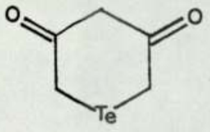
Charge-transfer complexes have played an important role in the development of molecular conductors ('organic metals') typified by the complex of tetrathiafulvalene (TTF) with 7,7,8,8-tetracyano-p-quinodimethane (TCNQ). The composition and properties of such complexes in the solid state are determined to a certain extent by the character of the interaction between the donor (D) and acceptor (A), by the geometry of the resulting complexes and by the degree of charge-transfer. It has been suggested that various molecular criteria, such as high polarisibility, symmetry and molecular orbitals perpendicular to the plane of the molecule are necessary to achieve conductivity. A major problem in the preparation of such complexes is that the characteristics such as degree of charge transfer, crystal structure and intermolecular atomic interaction, cannot be predicted.

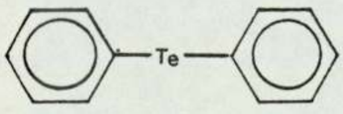
Since Te is more electropositive than S and Se and is considerably larger, incorporation into donors would tend to increase both intra- and interstack delocalisation of electrons and consequently conductivity. The literature is sparse in its reference to charge-transfer complexes of organotellurium compounds. To date, the measurement of physical properties of single crystals of a Tellurium containing D-A salt have not been reported. The following work was carried out with the main objective of understanding charge-transfer phenomena in organotellurium chemistry. A range of CT complexes of organotellurium donors with acceptors, mainly TCNQ and sometimes chloranil (2,3,5,6-tetrachloro-p-benzoquinone), were synthesised. Physical properties of the new compounds are discussed and attention is drawn, in particular to the potential use of ^{125}Te Mössbauer spectroscopy as an investigative tool for the compounds. The crystal structure of one of the complexes (dbt-TCNQ),which is the first example of the type, is also discussed. The following organotellurium donors, together with two selenium compounds were chosen:

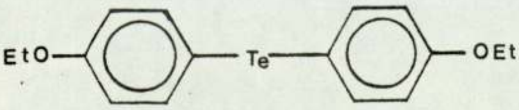


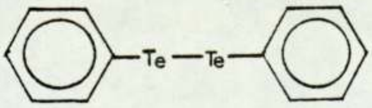


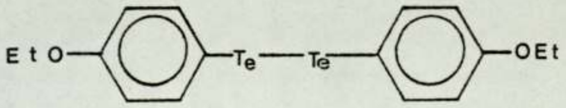


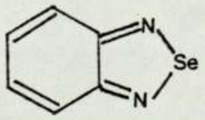


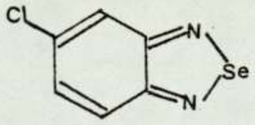












3.2 Experimental

3.2.1 Synthesis of Charge-Transfer Complexes

Organotellurium donors were synthesised following the indicated literature methods: dibenzotellurophene(46), 1-tellura-3,4-benzocyclopentane(47), phenoxatellurine(48), 1-telluracyclohexane-3,4-dione(49), diphenyltelluride(50), diphenylditelluride(51), bis(p-ethoxyphenyl)ditelluride(52), bis(p-ethoxyphenyl)telluride(53). Two organoselenium donors were also considered, namely 2,1,3-benzoselenadiazole and the 5-chloro-derivative(54).

All the complexes were synthesised by essentially similar methods and the following experiments are typical of those carried out.

3.2.1.1 Synthesis of 2,1,3-Benzoselenadiazole('Paiaselenole'). TCNQ Complex

To a solution of paiaselenole (0.37 g, 2 m mole) in boiling acetonitrile (20 cm^3) was added TCNQ (0.41 g, 2 m mole) in hot acetonitrile (20 cm^3). The mixture was stirred and refluxed for 1 hour after which the volume was reduced to 10 cm^3. On cooling to room temperature, crystals of the complex [$C_6H_4N_2Se$][TCNQ] were obtained.

3.2.1.2 Synthesis of bis(p-ethoxyphenyl)ditelluride.TCNQ Complex

In a dinitrogen filled dry box, the ditelluride (0.5 g, 1 m mole) and TCNQ (0.41 g, 2 m mole) were mixed in a flask to which acetonitrile (100 cm^3) was added. The mixture was heated to reflux for 1 hour, after which the volume was reduced to 50 cm^3. On cooling the solution to room temperature, crystals of the complex $[(p\text{-}EtOPh)_2Te]_2.[TCNQ]_2$ were obtained.

3.3 Results and Discussion

Generally, the reaction of organotellurium(II) compounds with TCNQ in acetonitrile solution afforded complexes of 1:1 stoichiometry. Exceptions were the two ditellurides considered, where the stoichiometry was $R_2Te_2.2(TCNQ)$. Table 3.1 lists the complexes isolated and their melting points, and analytical data, with some remarks. Most of the complexes were crystalline. A variety of colours were found in these CT complexes. All the complexes were found to be stable in air for several months.

3.4 Electrical Conductivities

The conductivity of compacted discs was investigated and the data (Table 3.2) fall into two categories. Some complexes are clearly insulators - of most interest in the light of further discussion is the insulating nature of the complexes

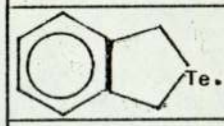
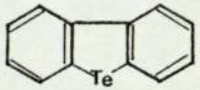
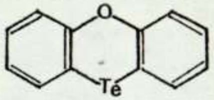
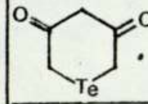
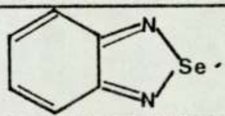
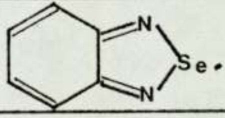
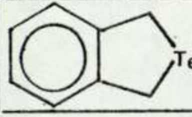
Compound	Colour	mp(^{o}C)	%Te (calc)	Compound	Colour	mp(^{o}C)	%Te (calc)	%C (calc)	%H (calc)	%N (calc)
 . TCNQ	greenish-brown	170 (dec)	29.1 (29.3)	Ph_2Te_2.2TCNQ	black	>250	31.4 (31.2)	-	-	-
 ·TCNQ	deep violet	200 (dec)	25.5 (26.4)	$(p.EtOC_6H_4)_2Te$.TCNQ	black	200 (dec)	21.8 (22.2)	-	-	-
 ·TCNQ	black	250	24.8 (25.5)	$(p.EtOC_6H_4)_2Te_2$.2TCNQ	purple	150 (dec)	28.6 (28.2)	52.6 (53.1)	2.90 (2.89)	11.9 (12.4)
 . TCNQ	greenish-brown	160 (dec)	28.8 (29.7)	 · TCNQ	violet	180	-	54.9 (55.8)	2.20 (2.08)	21.0 (21.7)
Ph_2Te.TCNQ	violet	210 (dec)	26.2 (26.3)	 · TCNQ	green	162	-	50.4 (51.3)	1.50 (1.67)	19.7 (19.9)
 .chloranil	violet	168	28.0 (26.7)							

Table 3.1 Analytical data for donor-acceptor complexes of organotellurium and organoselenium compounds

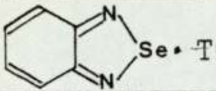
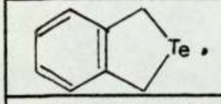
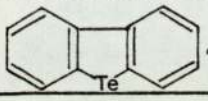
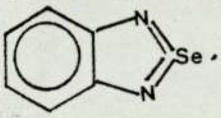
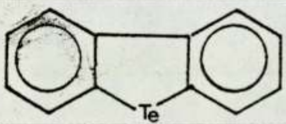
Compound	Conductivity ($\Omega^{-1}cm^{-1}$)
 ·TCNQ	$> 10^{-14}$
 · TCNQ	$> 10^{-14}$
 ·TCNQ	10^{-7} (a)
$(p.EtOC_6H_4)_2Te_2.2TCNQ$	1.8×10^{-8} (293K) 3.6×10^{-9} (77K)
$Ph_2Te_2.2TCNQ$	2.6×10^{-8} (293K) 4×10^{-9} (77K)
Compound (acetonitrile solution)	Conductivity ($\Omega^{-1}cm^2mol^{-1}$)
 · TCNQ	15
 ·TCNQ	12

Table 3.2 Compressed disc conductivity data (together with some solution data)

(a) Single crystal measurement

of TCNQ with 3,4-benzo-1-telluracyclopentane. The second group has conductivities some six or seven orders of magnitude greater. The two ditellurides give 1:2 complexes which show semiconducting behaviour (increase in resistivity on lowering the temperature). The complex of dibenzotellurophene (dbt) gives a single crystal conductivity of $10^{-7}\ \Omega^{-1}cm^{-1}$, this is significantly lower than the value of $0.8 \times 10^{-4}\ \Omega^{-1}cm^{-1}$ reported by Engler(55).

It is also of interest to note that the paiaselenole complex, $C_6H_4N_2Se$.TCNQ, initially violet, changed to green after 20 hours in vacuo prior to sputtering on silver contacts. The conductivity reported is that for the green modification. Solution conductivities were monitored for two complexes. Low conductivities in acetonitrile (Table 3.2) solution were observed which showed little concentration dependence.

3.5 Electronic Absorption Spectroscopy

Electronic absorption spectra of TCNQ complexes have been investigated for solids (single crystals and powdered samples) and for solutions by many people. Recently the study on optical spectra has become more important, since the remarkable electronic properties of high conducting TCNQ may be elucidated by analysis of their electronic spectra(56). It has been clarified that the semiconducting and metallic properties arise from the crystal structure with one dimensional TCNQ columns. The electronic spectra of such complexes showed CT absorption band between adjacent TCNQ in the I.R. region. Electronic absorption data of all the complexes are gathered in Table 3.3.

The electronic absorption spectra were measured in acetonitrile solution. Figures 3.1 and 3.2 show the electronic absorption spectra of TCNQ and its complex with bis(p-ethoxyphenyl)$_2$ telluride. The observed absorptions around 700-900 nm are attributable to the absorption of TCNQ$^{\cdot -}$ and the band at ~395 nm is a sum of TCNQ$^{\cdot -}$ and neutral TCNQ absorptions(57). It is, however, reasonable to assume that the bands in the range 606-656 nm are due to a HOMO-LUMO transition. An examination of the work of Zingaro et al(37) indicates that the type of donor interactions of the tellurides and ditellurides in CT systems involving TCNQ as an acceptor are of π-π type. This is corroborated by the observed mixed-stack arrangement of DBT.TCNQ complex (see crystal structure), which is typical for donor-acceptor π-π type complexes(58).

3.6 Infra-Red Absorption Spectroscopy

It is well established that in order for conductivity to occur in 'organic metals', the conduction band is populated through transfer of charge between the constituent donor and acceptor molecules(59). Partial transfer of charge is essential for high conductivity of these organic compounds. The degree of charge-transfer, Z, depends heavily upon the

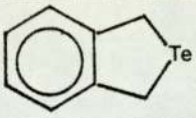
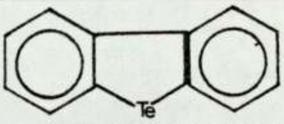
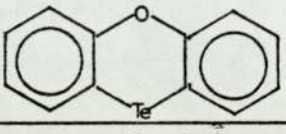
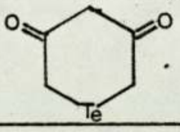
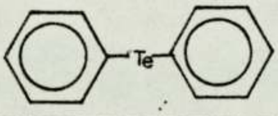
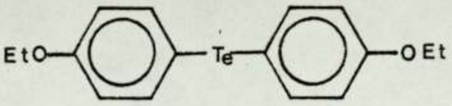
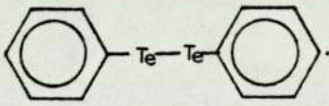
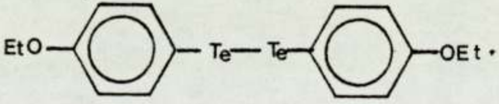
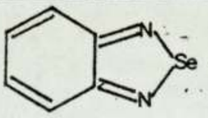
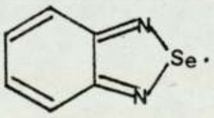
No.	Compound	E.S. $\lambda_{(max)}$ nm
1	 · TCNQ	629
2	 · TCNQ	656
3	 · TCNQ	641
4	 · TCNQ	655
5	 · TCNQ	650
6	 . TCNQ	625
7	 ·2TCNQ	606
8	 · 2TCNQ	653
9	 · TCNQ	615
10	 · TCNQ	625

Table 3.3 E.A. spectral data for the complexes

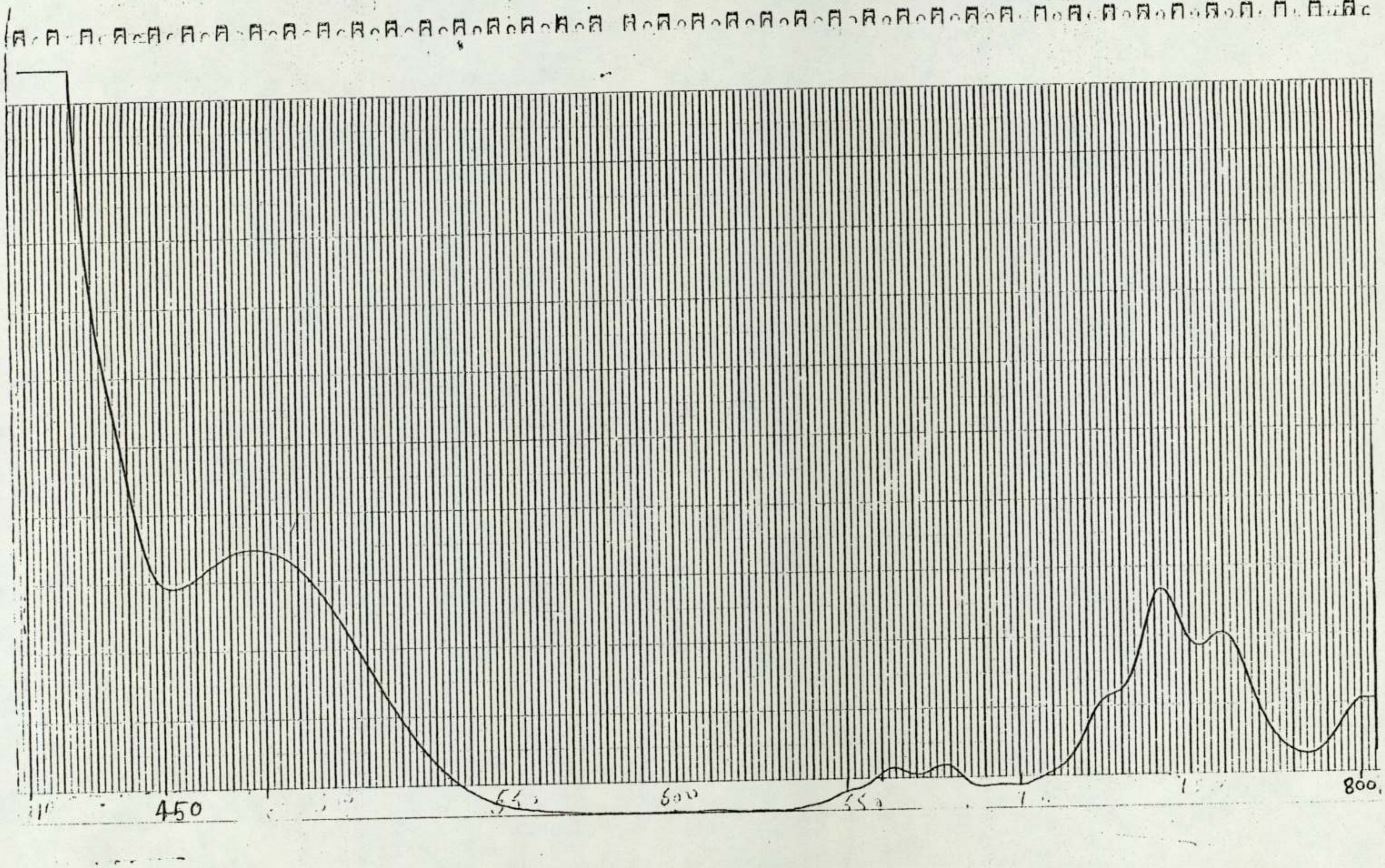


Figure 3.1 Electronic spectrum of TCNQ

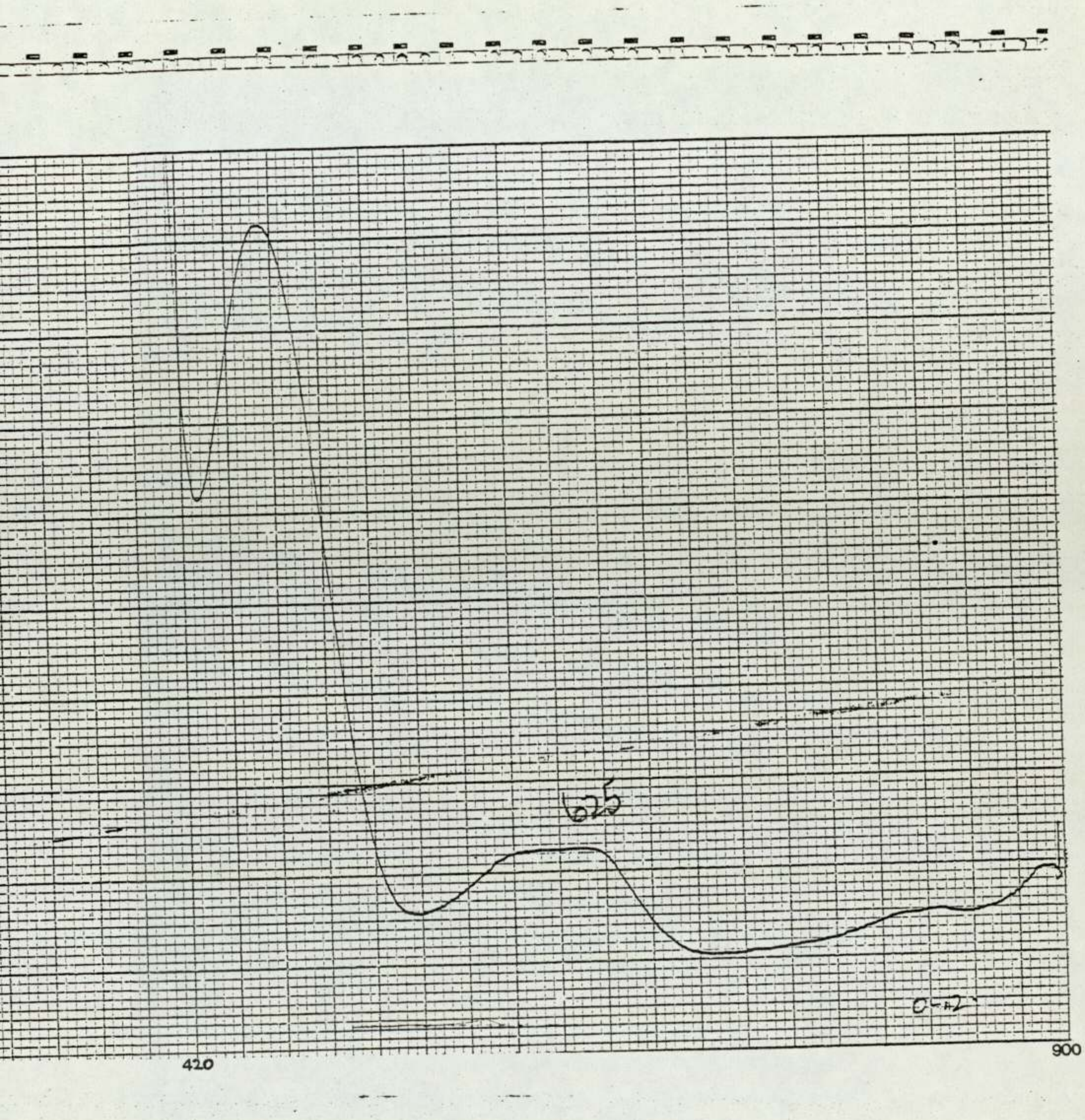


Figure 3.2 Electronic spectrum of p-$(EtOPh)_2Te.TCNQ$

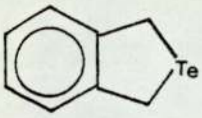
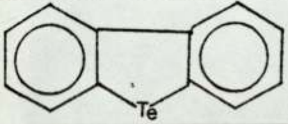
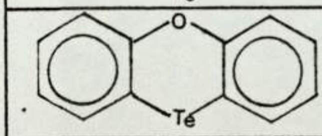
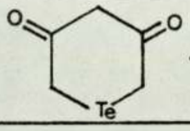
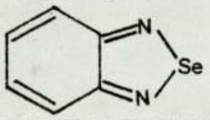
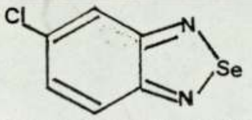
Complex	ν(CN) cm^{-1}	ESR - g factor ($\pm$0.003)
 . TCNQ	2183 2112	2.004 2.001 (CH_3CN solution)
 · TCNQ	2220	2.001
 · TCNQ	2186 2148	1.999
 · TCNQ	2208 2160	-
Ph_2Te.TCNQ	2228	2.001
(p-EtO.C_6H_4)$_2$Te.TCNQ	2236	1.996
[Ph_2Te_2]·[TCNQ]$_2$	2228	2.003
[(p-EtO.C_6H_4)$_2Te_2$]·[TCNQ]$_2$	2226	2.002
 · TCNQ	2225	2.002
 · TCNQ	2232	1.999

Table 3.4 Infra-red and ESR data for TCNQ complexes with organotellurium and organoselenium donors

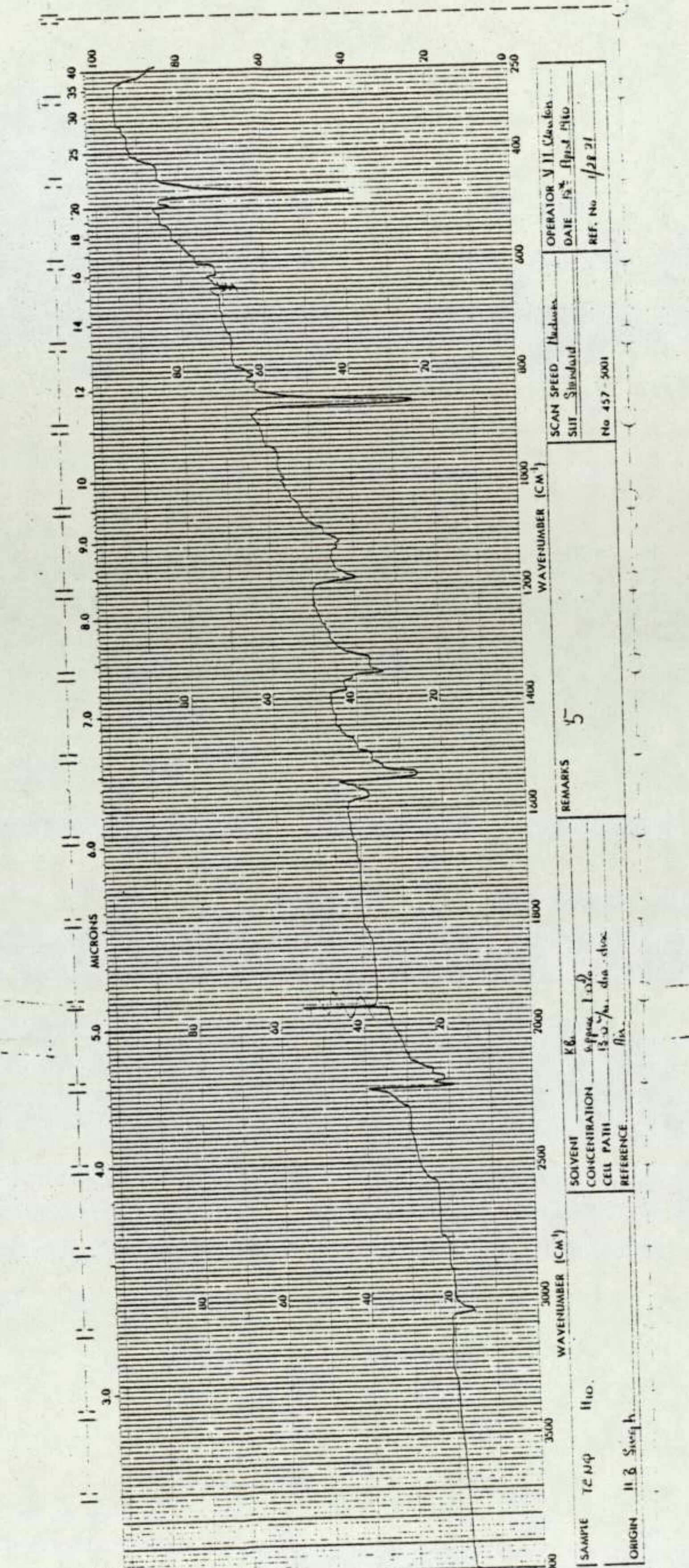


Figure 3.3 I.R. spectrum of TCNQ

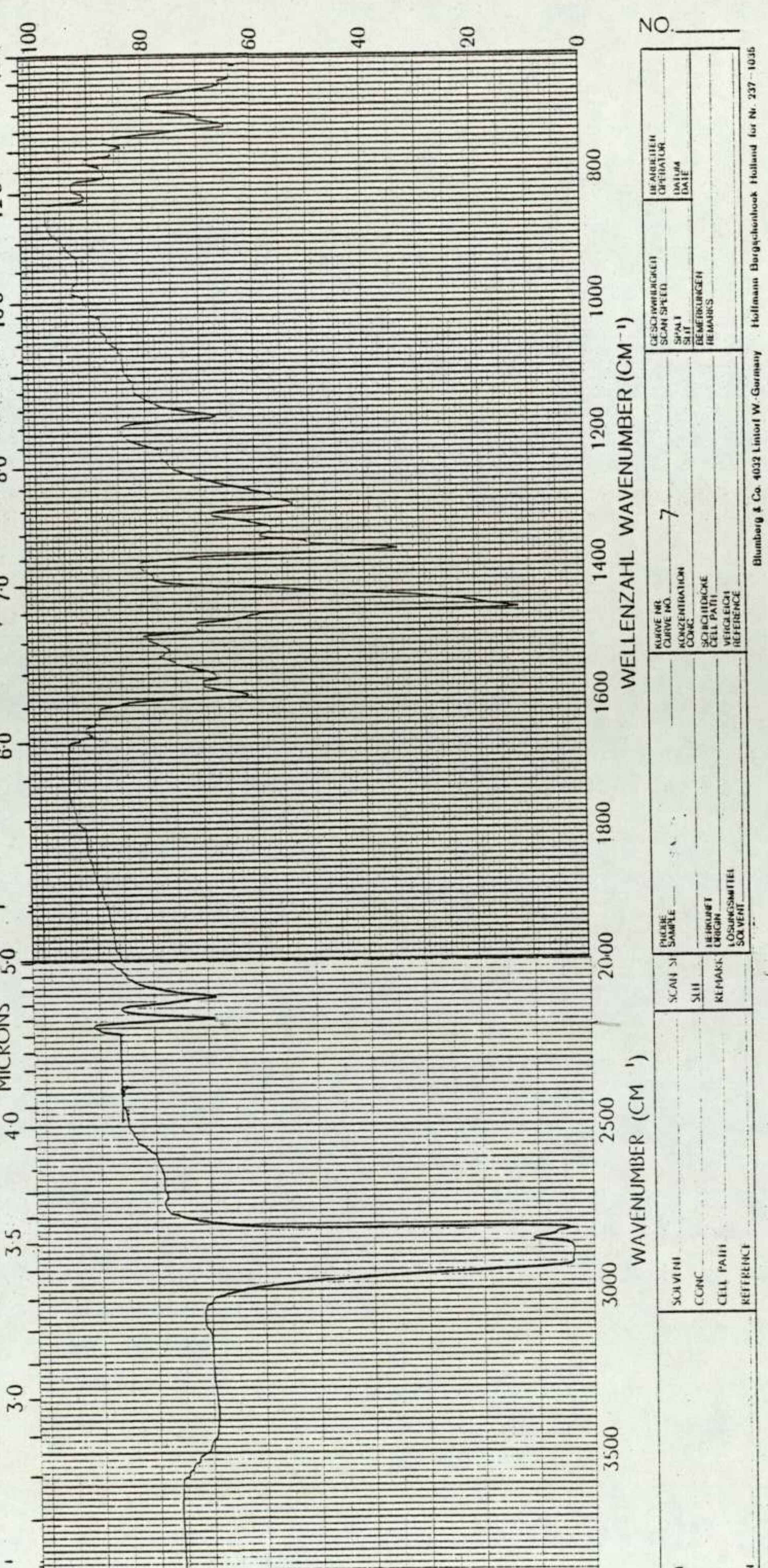


Figure 3.4 I.R. spectrum of $C_8H_8Te.TCNQ$

crystal binding energy and the character of Peierls transition to a periodically distorted semiconductor at low temperatures(60). Generally, Z has been determined by using X-ray scattering techniques(61) or from the totally symmetric intramolecular vibrations by using resonance Raman spectroscopy(62). More recently, infra-red spectroscopy has also been used for the purpose(63).

The coupling between conduction electrons and intramolecular phonons takes different forms for totally symmetric and nontotally symmetric vibration modes. It has been shown that for totally symmetric modes, the coupling is proportional to the occupancy of the conduction band and for nontotally symmetric modes, the lower order coupling term gives rise to shift in phonon frequency proportional to occupancy of conduction band.

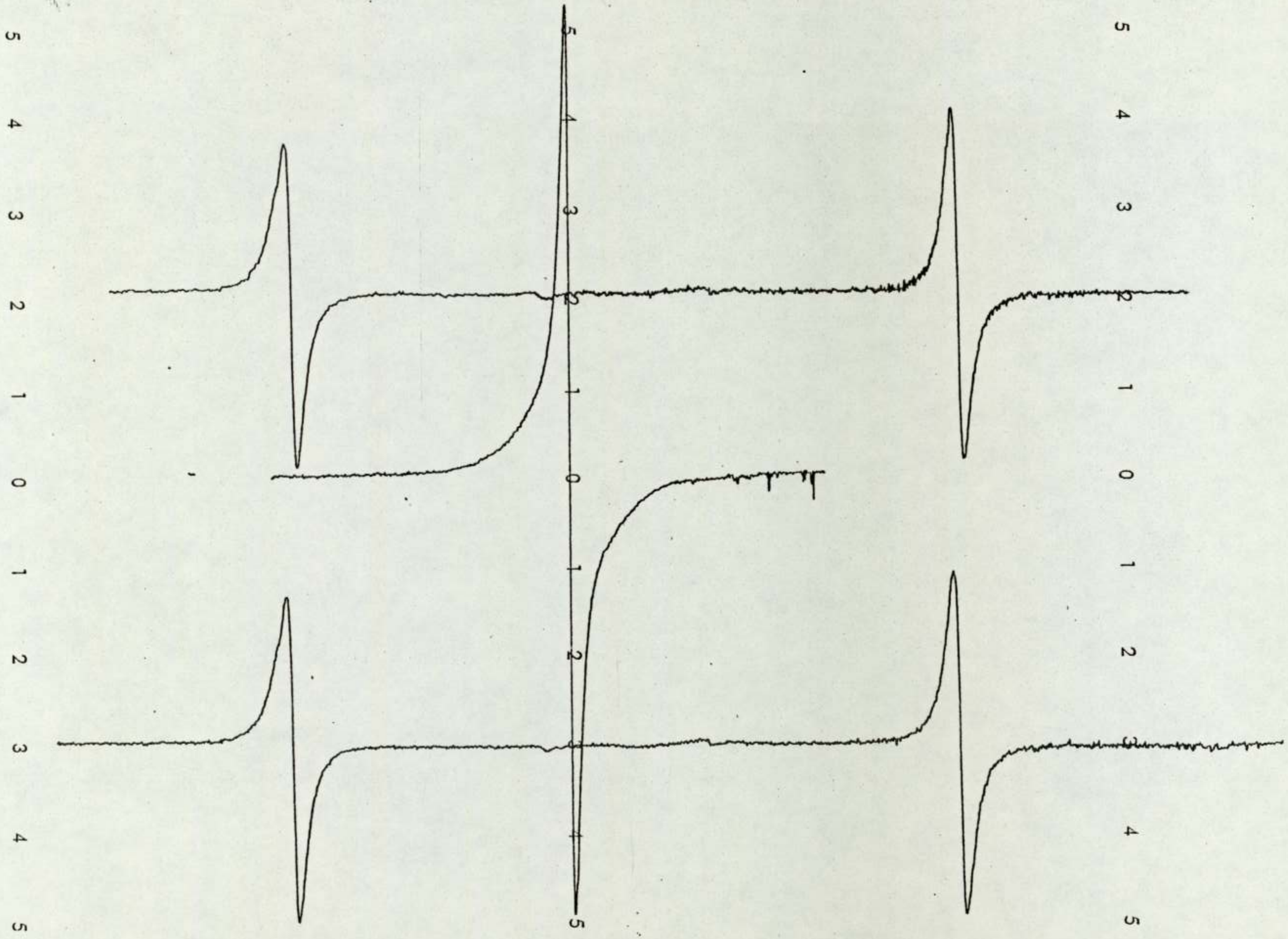
Some infra-red data are given in Table 3.4. The spectra of the TCNQ and its complex with 3,4-benzo-1-telluracyclopentane, as a representative type, are given in Figures 3.3 and 3.4. A recent report suggested that the degree of CT in organic conductors could be monitored by examination of νCN for TCNQ(63). The method is applicable to only conducting materials, however, the compounds in Table 3.4 do fall into two categories: (a) those which show νCN around 2230 cm^{-1} (the value for TCNQ) and (b) the complexes of 3,4-benzotelluracyclopentane and phenoxatellurine which show one νCN around 2180 cm^{-1}, a value similar to that observed for the salts Na^+TCNQ^- and K^+TCNQ^-. Only one compound fails to fit into these categories, namely the complex of 1-telluracyclohexane-3,5-dione. For 3,4-benzotelluracyclopentane.chloranil complex, no significant change in νCO was found. A simplistic conclusion would be that in the majority of cases, there is very little charge-transfer, but that in two cases essentially ionic compounds may have been formed.

3.7 Electron Spin Resonance Spectroscopy

The CT complexes may be written by two conventional resonance structures.

$$DA \rightleftharpoons D^{\cdot +} + A^{\cdot -}$$

For molecules with great donor and acceptor capacity, a complete electron transfer process may be assumed in the ground state. Thus the system becomes paramagnetic and is expected to show free radical behaviour. The electron spin resonance measurements were carried out on the freshly prepared CT samples at room temperature. Solid state E.S.R. data (Table 3.4) in general show a single line (line width 6-25 gauss) which cannot be annealed out of the samples by heating and cooling. A typical spectrum is reproduced in Figure 3.5. The g-factor is, within the errors, the same for each sample and is very close to the free electron value suggesting that the signal arises from



<u>Figure 3.5</u> E.S.R. spectrum of 'piaselenole'.TCNQ

unpaired electron density on TCNQ. In no case was it possible to see a resonance from a tellurium centred radical. This was not surprising since even when reasonable evidence exists for the electrochemical formation of a radical cation such as that procured from phenoxatellurine, no ESR signal was detected(64). The authors attribute the failure to observe signals to the rapid formation of a dimer which, in turn, interacts with a phenoxatellurine molecule to give a complex cation which may be isolated as the perchlorate. ESR data have been obtained for anion radicals formed by electrochemical reduction of nitro-substituted phenoxatellurines, however it is not surprising that unpaired electron density was largely associated with the nitro group(65). These remarks are of particular significance for the complex of TCNQ with 3,4-benzo-1-telluracyclopentane which other data suggest to be ionic. Even for this compound no tellurium centred resonance is observed. This may be a consequence of the increasingly large spin-orbit coupling as the series S, Se, Te is traversed(66).

Thus in a series of radicals derived from a series of naphthalene-1,8-dichalcogenides - no signal was obtained from the ditelluride. Also, despite failure to observe signals from radical cations of phenoxatellurine, the selenium analogue does give a broad ESR spectrum from which ^{77}Se hyperfine splitting is just discernable(67). An alternative explanation could be that the 3,4-benzo-1-telluracyclopentane complex contains cation dimers with a singlet ground state.

3.8 Mössbauer Spectroscopy

The Mössbauer technique provides useful information about electron distribution around the resonant nucleus. Thus, it seemed possible that ^{125}Te Mössbauer spectroscopy could be a suitable method to probe the electronic structures of the complexes more deeply. Mössbauer data for all the tellurides and ditellurides chosen in the present study have been reported and it was of interest to determine what effects charge-transfer might have on the ^{125}Te Mössbauer parameters.

A brief review of the theory used in interpreting the Mössbauer parameters is given below.

3.8.1 Isomer Shift (δ)

The value of isomer shift (mm sec^{-1}) represents the energy difference between the ground and excited energy levels in a particular electronic environment, compared with the energy difference in a different electronic environment (standard). The electron density around nucleus interacts with the nuclear charge, thus influences the energy of transition from ground to excited state.

Since s electrons have a finite probability of being found at the nucleus, the isomer shift gives the measure of the s electron density at the nucleus. The isomer shift is indirectly influenced by other electrons (p,d) as they shield the s electrons. Whether δ would increase or decrease with increase in s electron density, depends on the sign of nuclear radius term, δR/R. This term is positive for ^{125}Te and δ becomes more positive with the increase in s electron density. The ^{125}Te isomer shifts span only a small range from -1.2 to +1.8 mm sec^{-1} and as such are not a particularly useful probe to changes in chemical environment.

3.8.2 The Quadrupole Splitting (Δ)

The quadrupole splitting arises from the asymmetric electron distribution around the nucleus. The resulting electron field gradient splits the excited nuclear state (I=3/2), which is degenerate if the electron density is symmetrical. Thus, the degree of splitting is related to the dissymmetry of electron density around the tellurium nucleus. The **Townes and Dailey** model has successfully been used for interpretation of quadrupole splitting of Te(IV) and Te(II) compounds. The stereochemistry of organotellurium compounds suggests that bonding primarily involves the 5p orbitals with some s electron participation.

Table 3.5 gives ^{125}Te Mössbauer data for some typical complexes of organotellurium compounds and Figure 3.6 shows a typical Mössbauer spectrum. It will be noted that in many cases the parameters seem, within the errors, insen-

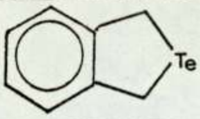
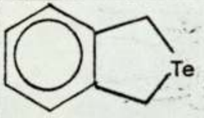
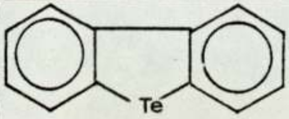
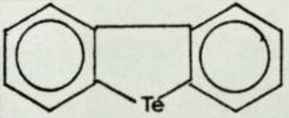
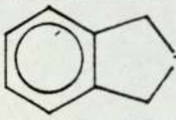
Complex	δ(Sb/Cu) (mms^{-1})	δ(I/Cu) (mms^{-1}) (δ Sb/Cu+.15)	Δ (mms^{-1})	Γ_{exp} (mms^{-1})
	0.07±.11	0.22	10.24±.24	5.8±.4
 · TCNQ	0.31±.11	0.46	8.72±.22	6.5±.3
		0.14±.08	9.3 ±.2	5.8
 ·TCNQ	0.07±.10	0.22	9.16±.21	5.4±.3
(p-EtO.C_6H_4)$_2$Te$_2$		0.28±.08	10.6±.1	6.4
[(p-EtO.C_6H_4)$_2$Te$_2$]·[TCNQ]$_2$	0.18±.12	0.33	10.5±.3	5.6±.4
Ph_2Te_2		0.37±.08	10.7±.1	6.1
[Ph_2Te_2]·[TCNQ]$_2$	0.21±.21	0.36	9.7±.3	5.9±.6
[(p-EtOC_6H_4)$_2$Te]		0.24	11.13	
(p-EtOC_6H_4)$_2$Te.TCNQ	0.04±.13	0.19	10.9±.3	5.8±.4
 ·chloranil		0.32±0.08	10.4±.1	6.3

Table 3.5 Some ^{125}Te Mössbauer data for organotellurium complexes with TCNQ

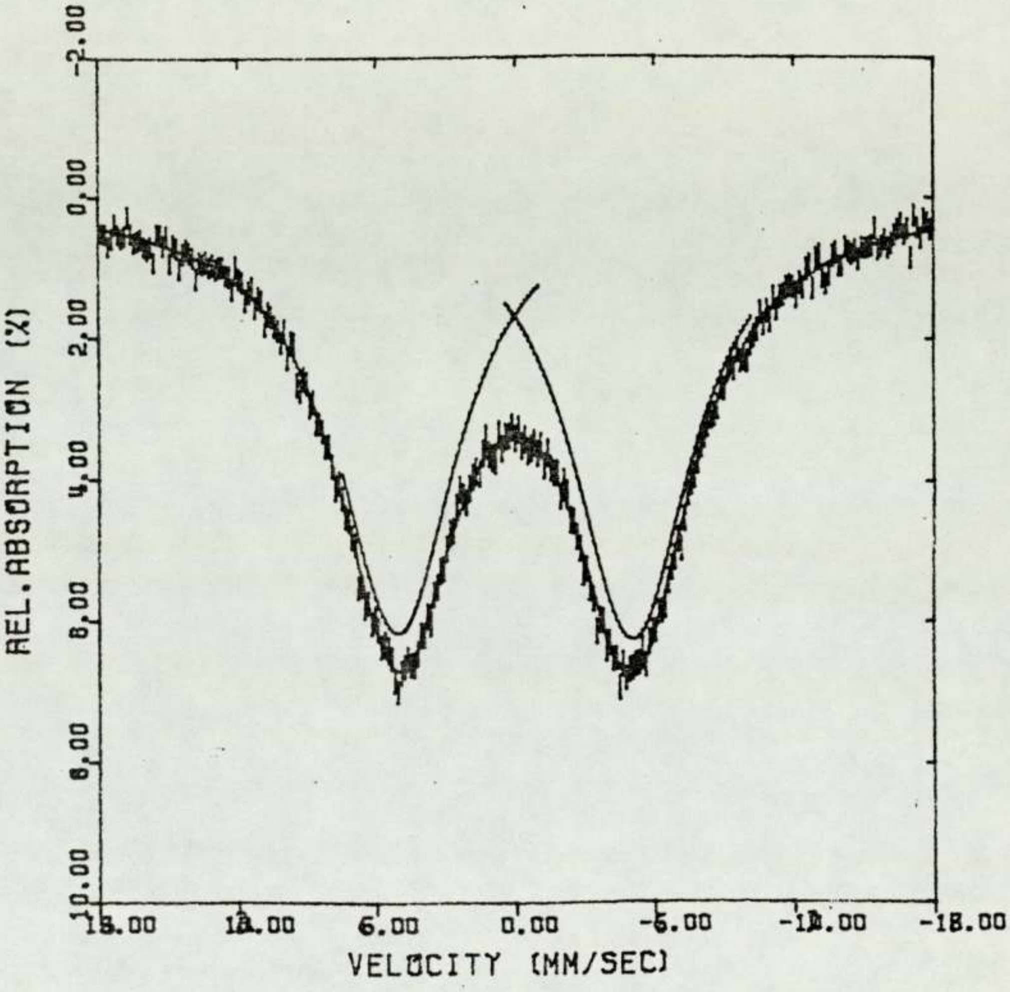
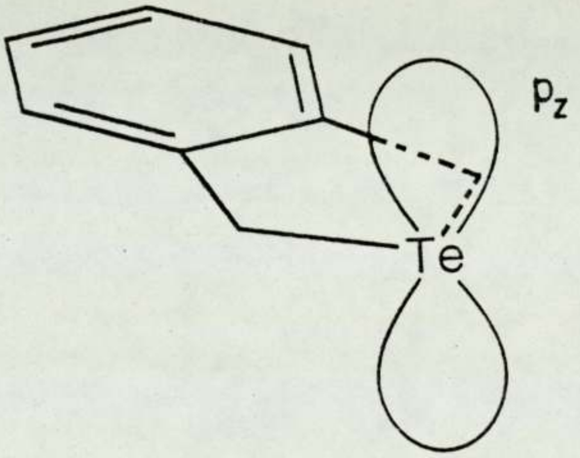


Figure 3.6 Mössbauer spectrum of C_8H_8Te.chloranil

sitive to the presence of the acceptor. Two organotellurium compounds show considerably modified Mössbauer parameters in the presence of TCNQ, namely Ph_2Te_2 and 3,4-benzo-1-telluracyclopentane(1). We synthesised a further complex of the latter donor with 2,3,5,6-tetrachloro-p-benzoquinone ('chloranil') but the material gave, within the errors, values of δ and Δ indistinguishable from those of the telluride.

McWhinnie et al have previously suggested that Mössbauer spectroscopy may be successfully used to set up a scale of Lewis acidity relative to a standard organotellurium base $[(p\text{-}EtOPh)_2Te]$(68). Withdrawl of p-electron density would lead to a reduction of Δ, hence Δ(complex) could be correlated with the coordinate bond strength. An extension of this argument is applicable here. The complex of 3,4-benzo-1-telluracyclopentane has been used to illustrate the potential value of Mössbauer measurements.

It is assumed that electron density will be removed from pz orbital in forming the complex with TCNQ and it is further assumed that Te-C bonds involve relatively pure p-orbitals. Some justification for these assumptions is available. The ionisation potential for (I) is 6.55 eV (by mass spectrometry; 1 eV = 96.5 $kJmol^{-1}$). This certainly implies ionisation from a π(p) type orbital. The assumption of relatively pure p-orbital involvement in Te-C bonds of (I) has some indirect support from the crystal structure of the



[1]

diiodide of (I)$^{(69)}$ in which at 86° the C-Te-C angle is close to the ideal 90°. Similar C-Te-C angles are observed for a series of telluronium salts derived from (I)$^{(70)}$.

Given the above assumptions, it would follow that$^{(45)}$:

$$\frac{e^2q\theta}{e^2q_o\theta} = -U_p \qquad (1)$$

where $e^2q\theta$ is quadrupole coupling constant, $e^2q_o\theta$ is the quadrupole coupling constant for one 5p electron on tellurium, and

U_p is p-orbital imbalance.

Also $\Delta = \frac{1}{2}e^2q\theta$

and $e^2q_o\theta$ has a value of 24 mmsec$^{-1(71)}$.

It leads to the second equation where

$$\frac{2\Delta}{24} = -U_p \qquad (2)$$

$$\text{or} \quad \frac{\Delta}{12} = U_z - U_c \qquad (3)$$

where Δ is the ^{125}Te Mössbauer quadrupole splitting (mmsec^{-1}), U_z the occupancy of the p_z orbital (2.00 for the free telluride), and U_c the occupancy of the p_x and p_y orbitals (calculated to be 1.14).

If electron density is withdrawn from p_z, the occupancy of p_x and p_y should change as tellurium becomes more positive, than for the complex:

$$\frac{\Delta(\text{complex})}{12} = \sigma - [a_o + A(2 - \sigma)] \qquad (4)$$

where σ is the new occupancy of p_z, $a_o = 1.14$ and A is a positive constant reflecting the increased occupancy of p_x and p_y which is assumed to be proportional to the electron withdrawl from p_z i.e., $(2-\sigma)$, thus:

$$\frac{\Delta(\text{complex})}{12} = \sigma(A + 1) - (a_o + 2A) \qquad (5)$$

Hence, for a series of complexes of (I) (or indeed for any given organotellurium donor) with a range of acceptors, Δ(complex) is linearly related to σ or $(2-\sigma)$ the quantity of charge transferred. This should then be a useful addition to other methods for the estimation of the degree of CT. There is one caveat in using the method, namely that all measurements are made at 4^oK and should strictly be compared with other physical measurements at the same temperature.

It would appear that there is a negligible transfer of charge from the tellurium p_z-orbital of (I) in the complex with chloranil, thus the variation of Δ with acceptor is illustrated. The Mössbauer data for the two complexes, and the normal value of Δ for (I) make it improbable that the interaction of (I) with the acceptor is of π-π type, a proposal that has more reasonably been made for phenoxatellurine.TCNQ(37). In an effort to produce a derivative of (I) in which $(2-\sigma)$ was unambiguously equal to unity (and hence to evaluate A), attempts have been made to electrochemically oxidise the telluride and the preliminary results are discussed in the latter part of this chapter. The only other complex in which significant charge-transfer is present is that of diphenylditelluride with TCNQ. Given that some tetratellurafulvalene compounds are now available(29,31), it will be interesting to see the variation of ^{125}Te Mössbauer parameters with acceptor as more complexes become available for study.

In the case of (I), That A is indeed positive and probably small, is supported by a more positive chemical isomer shift for (I).TCNQ indicating that withdrawl of electron density from p_z is dominant.

3.9 Ionisation Potential Measurements

Mass spectroscopy offers a means of obtaining fundamental information concerning bonding fairly readily from the study of the energetics of systems by means of ionisation and appearance potential measurements.

The first ionisation potential of a molecule may be defined as the minimum energy required to remove an electron from the highest occupied molecular orbital, both the original molecule and the resultant molecular ion being in their ground vibrational states. This energy is the difference between the $\nu=0$ and $\nu'=0$ vibrational levels and is termed as the adiabatic ionisation potential. If the electron energy is high enough, ionisation of a molecule followed by dissociation may occur. The minimum energy required to fragment ion in its ground vibrational state from the original molecule in its ground vibrational state is referred to as the appearance potential of that ion. A number of methods have previously been used for these determinations and are described here briefly.

3.9.1 Vanishing Current Method

The earliest determinations of ionisation potential were made by noting the electron energy at the onset of ionisation, or alternatively by recording electron energy at which the ion current vanishes(72).

3.9.2 Linear Extrapolation Method

Generally the ionisation efficiency curve diverges from linearity at low values of ion current, thus this method does not give accurate values for the appearance potential.

3.9.3 Semi-Logarithmic Method

Lossing et al(73) plotted the ion current expressed as a percent of its value at 50 eV on a log scale against the electron energy. It was found that the curves so obtained were very nearly parallel for sample and calibrant gas for low values of ion current.

3.9.4 Extrapolated Voltage Difference Method(74)

A calibrant gas such as argon, for which an accurate value of the appearance potential is known is incorporated in the sample and ionisation efficiency curves are plotted for the sample and calibrant ion. The curve of either the sample ion or the calibrant ion is then plotted on a suitably adjusted ion current scale so that the linear portions of the curve are parallel.

This is accomplished by multiplying the ion current values of one of the curves by the appropriate factor and then plotting on the original scale. The voltage difference ΔV between the sample and calibrant curves at a particular value of the ion current is determined and repeated for a succession of points on the initial sections of the curves. The values of ΔV so obtained are plotted against the ion current, and a linear extrapolation back to zero ion current made to obtain a value of ΔV_o, which is taken as the difference between the I.P. of the calibrant and the sample.

3.9.5 Determination of Ionisation Potential

The extrapolated voltage difference method was applied for the measurement of the appearance potentials of the molecular ions by electron bombardment of gaseous molecules. An example of this method is given on pages 63, 64 and 65.

The ionisation energies for tellurides are compiled in Table 3.6. The mass spectroscopic measurements showed considerably lowered appearance potentials for 3,4-benzotelluracyclopentane and phenoxatellurine indicating removal of an electron from a π(p) orbital(75).

The value of 6.55 eV for the A.P. of 3,4-benzo-1-telluracyclopentane is the lowest known for any organotellurium derivative. A.P. of this telluride also supports the I.R. and Mössbauer results which show easy removal of one electron compared to other tellurides and ditellurides.

The I.P. for phenoxatellurine is 8.75 eV whereas it has been found at 7.61 by P.E.S.(75) illustrating the problem of mass spectroscopically deduced values being often greater than those obtained by P.E.S.

Since the acceptor is common, the difference between incomplete CT in other complexes and almost complete CT in 3,4-benzo-1-telluracyclopentane and phenoxatellurine complexes might depend mostly on the difference in adiabatic

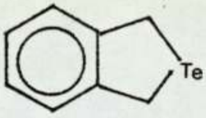
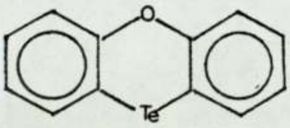
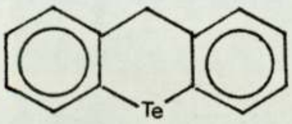
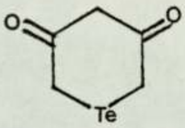
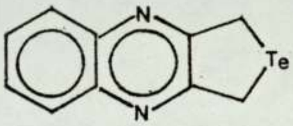
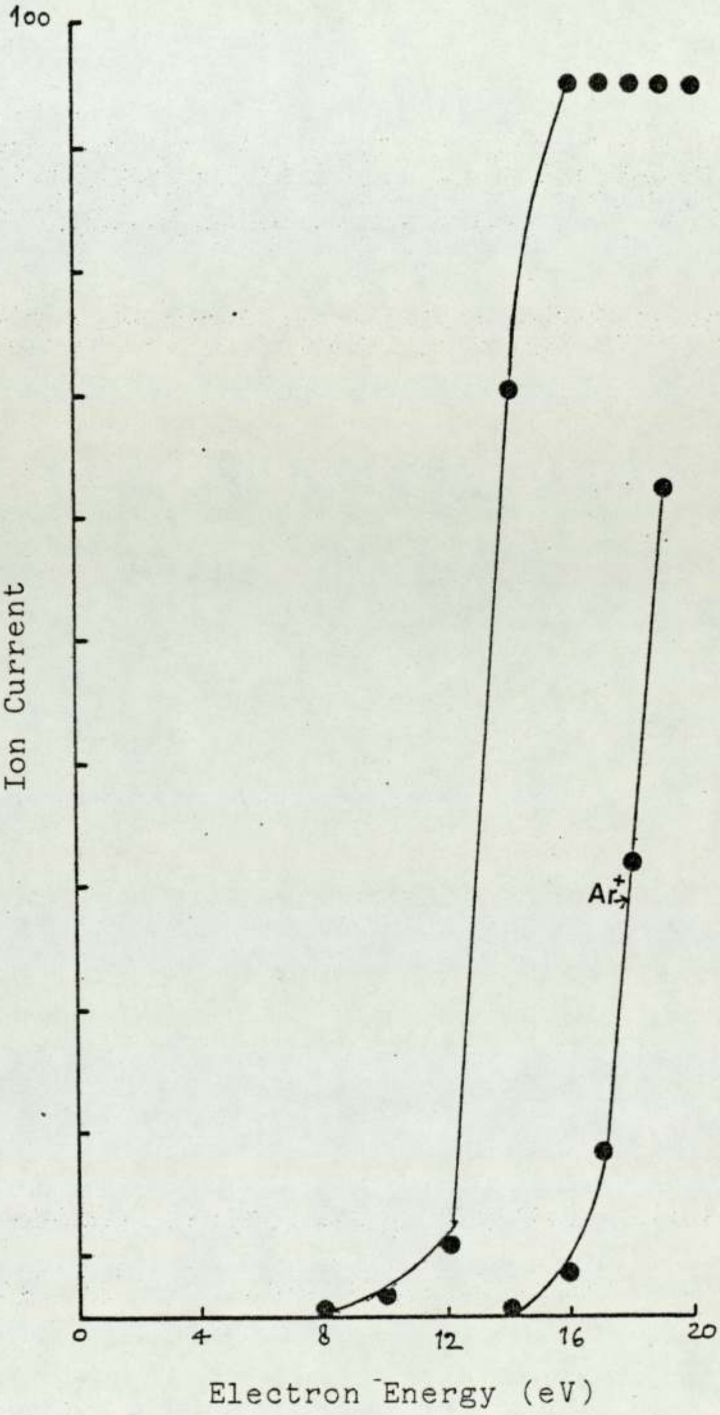
Compound	Appearance Potential (eV)
	6.55
	8.75
	10.25
	13.65
	9.65
Ph_2Te_2	8.85

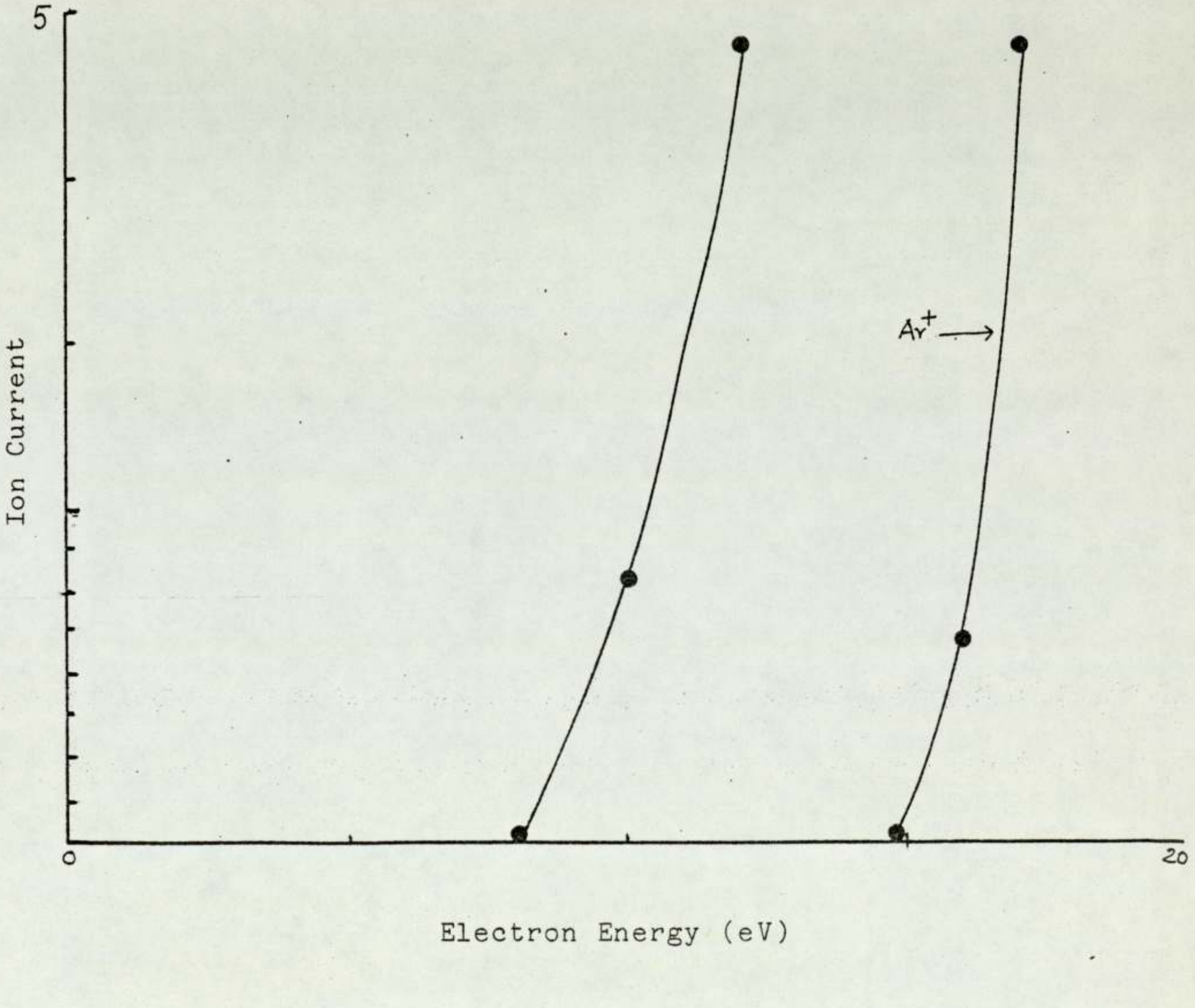
Table 3.6 Appearance potentials of organotellurium(II) donors

ionisation potentials. In view of the value of the I.P., the 3,4-benzo-1-telluracyclopentane.TCNQ might undergo ionisation more easily in the solid state than is the case for the other complexes studied. McConnell et al(76) showed that, under certain conditions, a slight change in the ionisation potential of the donor or in the electron affinity of the acceptor might sharply discriminate an ionic state from a nonionic state in solid charge transfer complexes.

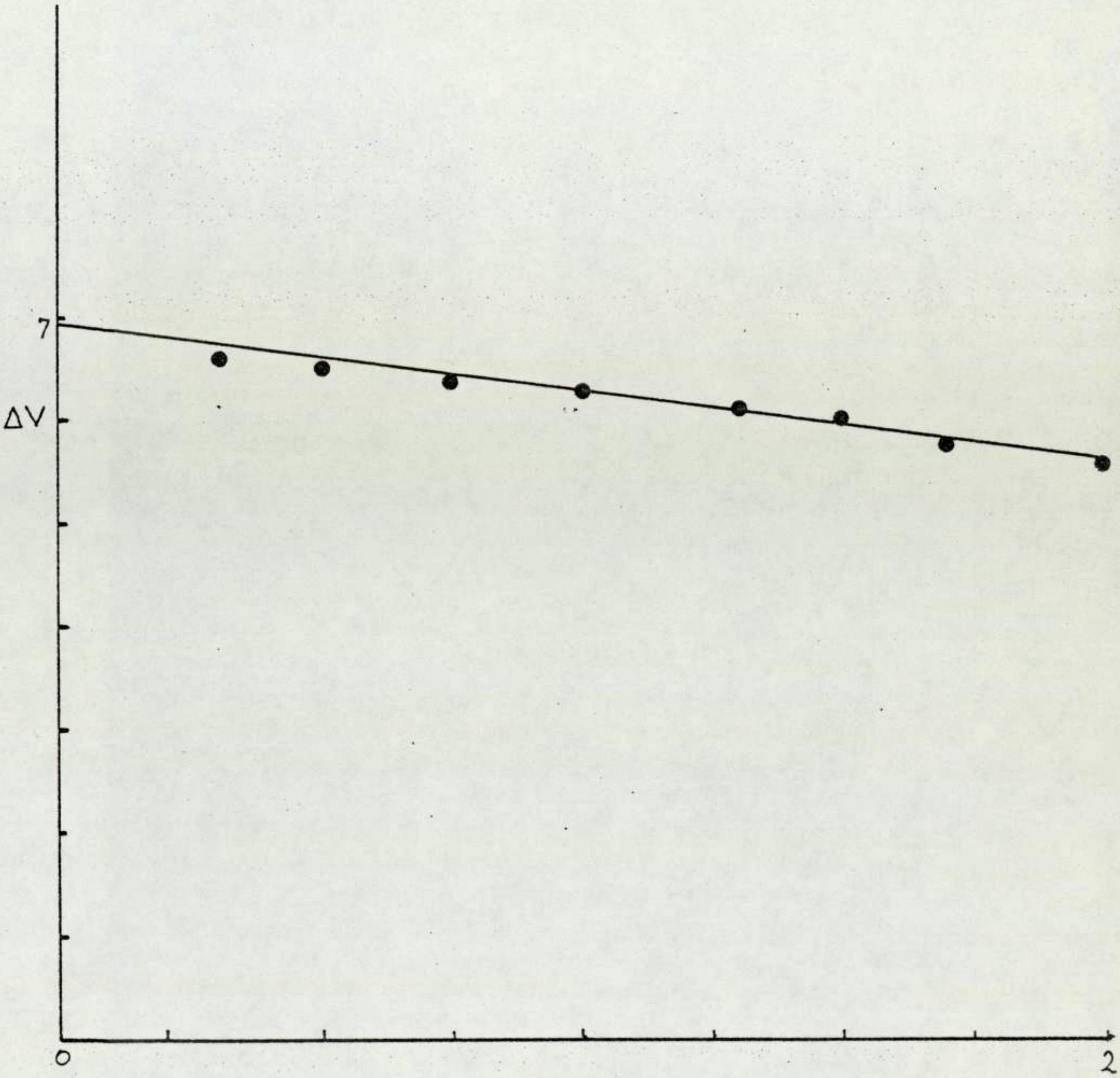
It may be safely concluded that the difference in the ionisation potentials between 3,4-benzo-1-telluracyclopentane (BTP), phenoxatellurine (PT) and other tellurides and ditellurides causes considerable difference in the degree of charge-transfer between BTP.TCNQ,PT.TCNQ and other complexes of the type R_2Te.TCNQ and R_2Te_2.2TCNQ.



Graph of ion current against electron energy for phenoxatellurine → (phenoxatellurine)$^+$



Graph of ion current against electron energy for phenoxatellurine → (phenoxatellurine)$^+$



Graph of ion current against voltage difference (ΔV) for phenoxatellurine → (phenoxatellurine)$^+$

3.10 Crystal and Molecular Structure of dbt.TCNQ Complex*

Crystals of the complex were obtained as deep violet needles by slowly cooling the hot solution of dbt and TCNQ in acetonitrile. Cell constants and an orientation for data collection were obtained from a least squares refinement, using the setting angles of 25 reflections in the range $4<\theta<11^{\circ}$. Data were collected on an Enraf-Norius CAD 4 automatic diffractometer with a crystal measuring 0.10 x 0.12 x 0.20 mm. A total of 4987 reflections were collected for $2\theta<55.0^{\circ}$ of which 4514 were unique and not systematically absent. The intensities were corrected for Lorentz and polarisation effects. Crystal data are given in Table 3.7

$TeC_{12}H_8$ TCNQ
$C_{24}H_{12}TeN_4$
F.W. 483.99 F(000) = 944
Crystal dimensions: 0.10 x 0.12 x 0.20 mm
Mo Kα radiation ($\lambda = 0.71073$ Å)
Temperature = $23 \pm 1^{\circ}$
Monoclinic space group $P2_1/n$
a = 14.849 (5) Å b = 8.172 (2) Å c = 16.275 (4) Å
$\beta = 92.05\ (3)^{\circ}$
V = 1973.8 Å^3
Z = 4 $\rho = 1.63$ g/cm^3
$\mu = 15.8$ cm^{-1}

Table 3.7 Crystal data

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*The structure determination was carried out at Molecular Structure Corporation, College Station, Texas 77840. The details are those obtained from Dr.R.F.Ziolo.

3.10.1 Structure Solution and Refinement

The structure was solved by Patterson and Fourier methods. Full matrix least squares refinement (310 variables) produced agreement factors of $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|=0.041$ and $R^1=[\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o]^{\frac{1}{2}}=0.046$ using 2295 reflections with $F_o^2>3.0\sigma(F_o^2)$. The function minimized was $\Sigma w(|F_o|-|F_c|)^2$ where $w=4F_o^2/\sigma^2(F_o)^2$. Scattering factors were taken from Cromer and Waber$^{(77)}$. Anamalous dispersion effects were included in $F_c$$^{(78)}$; the values for $\Delta f'$ and $\Delta f''$ were those of Cromer$^{(79)}$. The experimental details of the intensity measurements, the solution and the refinement are given in Table 3.8.

The final positional parameters are given in Table 3.9. The thermal parameters* (U_{ij}) for the non-hydrogen atoms are presented in Table 3.10. Figures 3.7, 3.8 and 3.9 give perspective views of dibenzotellurophene and TCNQ with atom labelling schemes and Figure 3.10 is a stereoscopic packing diagram and unit cell of dbt.TCNQ.

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* The positional and thermal parameters for hydrogen atoms, the observed and calculated structure factors, and the root-mean-square displacements along the principal axes of the temperature factor ellipsoids for the non-hydrogen atoms have been submitted to J.C.S. Dalton transaction 1983.

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Intensity Measurements

Instrument:	Enraf-Nonius CAD4 diffractometer
Monochromator:	Graphite crystal, incident beam
Attenuator:	Zr foil, factor 20.7
Take-off angle:	2.8°
Detector aperture:	2.0 to 2.5 mm horizontal 2.0 mm vertical
Crystal-detector dist:	21 cm
Scan type:	$\omega - \theta$
Scan rate:	$2 - 2\theta^{\circ}$/min (in omega)
Scan width, deg:	$0.7 + 0.350 \tan\theta$
Maximum 2θ:	55.0°
No. of refl. measured:	4987 total, 4514 unique
Corrections:	Lorentz-polarization
Peak width at half-height:	0.20°

Structure solution and Refinement

Solution:	Patterson method
Hydrogen atoms:	Located and refined isotropically
Refinement:	Full-matrix least-squares
Minimization function:	$\Sigma w(\|Fo\| - \|Fc\|)^2$
Least-squares weights:	$4Fo^2/\sigma^2(Fo^2)$
"Ignorance" factor:	0.050
Anomalous dispersion:	All non-hydrogen atoms
Reflections included:	2295 with $Fo^2 > 3.0\sigma(Fo^2)$
Parameters refined:	310
Unweighted agreement factor:	0.041
Weighted agreement factor:	0.046
Factor including unobs.data:	0.147
Esd of obs.of unit weight:	1.10
Convergence,largest shift:	0.07σ
High peak in final diff.map:	0.70(10) e/A^3
Computer hardware:	Linked PDP-11/45-11/60
Computer software:	Enfar-Nonius SDP and private programs of Molecular Structure Corporation

Table 3.8 Experimental details

Atom	x	y	z
TE	0.24254(3)	-0.17328(6)	0.09482(3)
N1	0.4205(5)	0.7219(9)	0.2448(4)
N2	0.3855(4)	1.0281(8)	0.4634(4)
N3	-0.0639(5)	0.5592(9)	0.2165(4)
N4	-0.0962(5)	0.9842(8)	0.3701(4)
C1	0.2298(4)	-0.0879(8)	-0.0257(4)
C2	0.1981(4)	-0.1786(8)	-0.0939(4)
C3	0.1948(5)	-0.1028(10)	-0.1700(4)
C4	0.2237(5)	0.0568(10)	-0.1776(4)
C5	0.2539(4)	0.1457(9)	-0.1109(4)
C6	0.2580(4)	0.0738(8)	-0.0332(4)
C7	0.2900(4)	0.1542(8)	0.0418(4)
C8	0.3191(4)	0.3164(8)	0.0459(4)
C9	0.3481(5)	0.3842(8)	0.1208(5)
C10	0.3476(5)	0.2927(9)	0.1910(4)
C11	0.3204(4)	0.1307(9)	0.1888(4)
C12	0.2895(4)	0.0626(8)	0.1142(4)
C13	0.4720(4)	0.6447(7)	0.5382(4)
C14	0.4958(4)	0.4772(8)	0.4156(4)
C15	0.4663(4)	0.6292(7)	0.4497(4)
C16	0.4340(4)	0.7538(8)	0.4016(4)
C17	0.4266(5)	0.7358(8)	0.3140(4)
C18	0.4064(4)	0.9072(8)	0.4351(4)
C19	-0.0060(4)	0.4218(9)	0.4240(4)
C20	-0.0212(4)	0.6644(8)	0.5102(4)
C21	-0.0286(4)	0.5911(8)	0.4297(4)
C22	-0.0555(4)	0.6794(9)	0.3621(4)
C23	-0.0603(5)	0.6106(10)	0.2806(4)
C24	-0.0781(5)	0.8515(9)	0.3665(4)

Table 3.9 Atomic co-ordinates with standard deviations in parentheses

Atom	U(1,1)	U (2,2)	U (3,3)	U (1,2)	U (1,3)	U (2,3)
TE	0.00373(2)	0.01296(6)	0.0038(1)	-0.00164(8)	-0.00041(3)	0.00354(8)
N1	0.0094(5)	0.025(1)	0.0050(3)	-0.002(1)	-0.0027(6)	0.008(1)
N2	0.0065(4)	0.014(1)	0.0079(4)	0.005(1)	-0.0012(6)	-0.001(1)
N3	0.0091(4)	0.030(2)	0.0044(3)	0.009(2)	-0.0007(6)	-0.002(1)
N4	0.0095(4)	0.017(1)	0.0062(3)	0.009(1)	0.0006(7)	0.000(1)
C1	0.0022(2)	0.0139(10)	0.0034(3)	0.0008(9)	0.0004(4)	0.0022(9)
C2	0.0038(3)	0.0137(10)	0.0049(3)	0.004(12)	-0.0001(5)	-0.0032(12)
C3	0.0048(4)	0.0238(15)	0.0034(3)	0.0001(13)	-0.0009(5)	-0.0041(12)
C4	0.0059(4)	0.0218(15)	0.0038(3)	-0.0012(14)	0.0008(6)	0.0014(12)
C5	0.0049(3)	0.0172(13)	0.0035(3)	-0.0019(12)	0.0005(5)	0.0026(10)
C6	0.0027(3)	0.0116(10)	0.0039(3)	0.0001(9)	0.0008(5)	0.0013(9)
C7	0.0030(2)	0.0122(10)	0.0034(2)	0.0017(10)	0.0005(4)	-0.0006(9)
C8	0.0043(3)	0.0093(9)	0.0049(3)	0.0009(11)	0.0008(5)	0.0023(10)
C9	0.0052(4)	0.0121(11)	0.0064(4)	-0.0016(11)	0.0023(6)	-0.0038(11)
C10	0.0049(4)	0.0204(15)	0.0048(3)	0.006(13)	0.0006(6)	-0.0082(11)
C11	0.0045(3)	0.0188(14)	0.0034(3)	-0.0001(11)	0.0001(5)	0.0004(10)
C12	0.0027(3)	0.0141(11)	0.0033(3)	0.0002(10)	0.0006(4)	-0.0001(9)
C13	0.0033(3)	0.0102(10)	0.0032(2)	0.0006(9)	-0.0003(4)	0.0003(8)
C14	0.0032(3)	0.0155(11)	0.0026(2)	0.0014(10)	-0.0001(4)	0.0001(9)
C15	0.0025(2)	0.0102(10)	0.0034(2)	-0.0002(8)	-0.0010(4)	0.0008(8)
C16	0.0036(3)	0.0119(9)	0.0039(3)	-0.0021(10)	-0.0013(5)	0.0023(10)
C17	0.0053(4)	0.0130(10)	0.0043(3)	-0.0015(11)	-0.0014(6)	0.0054(10)
C18	0.0042(3)	0.0126(10)	0.0046(3)	-0.0003(11)	-0.0025(5)	0.0048(10)
C19	0.0040(3)	0.0176(12)	0.0036(3)	0.0007(11)	0.0018(5)	-0.0021(10)
C20	0.0040(3)	0.0131(10)	0.0041(3)	0.0005(11)	0.0021(5)	-0.0026(11)
C21	0.0029(3)	0.0147(11)	0.0037(3)	-0.0008(10)	0.0020(5)	-0.0002(10)
C22	0.0041(3)	0.0159(11)	0.0039(3)	0.0022(12)	0.0013(5)	0.0015(11)
C23	0.0056(4)	0.0200(14)	0.0043(3)	0.0043(13)	0.0011(6)	-0.0002(12)
C24	0.0047(3)	0.0198(14)	0.0041(3)	0.0023(13)	0.0002(5)	-0.0001(12)

Table 3.10 Atomic thermal parameters and their estimated standard deviations

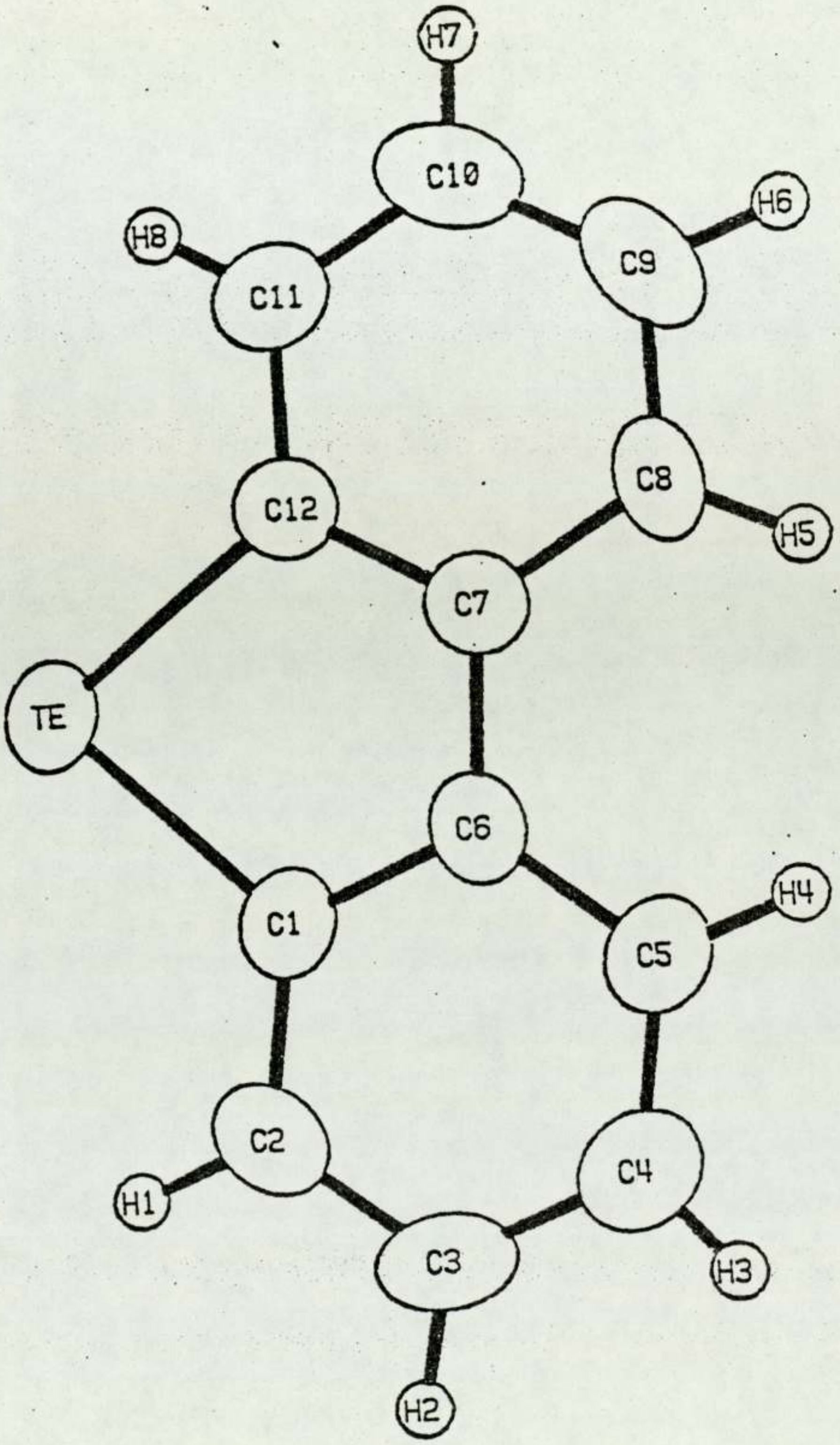

Figure 3.7 Perspective view of dibenzotellurophene

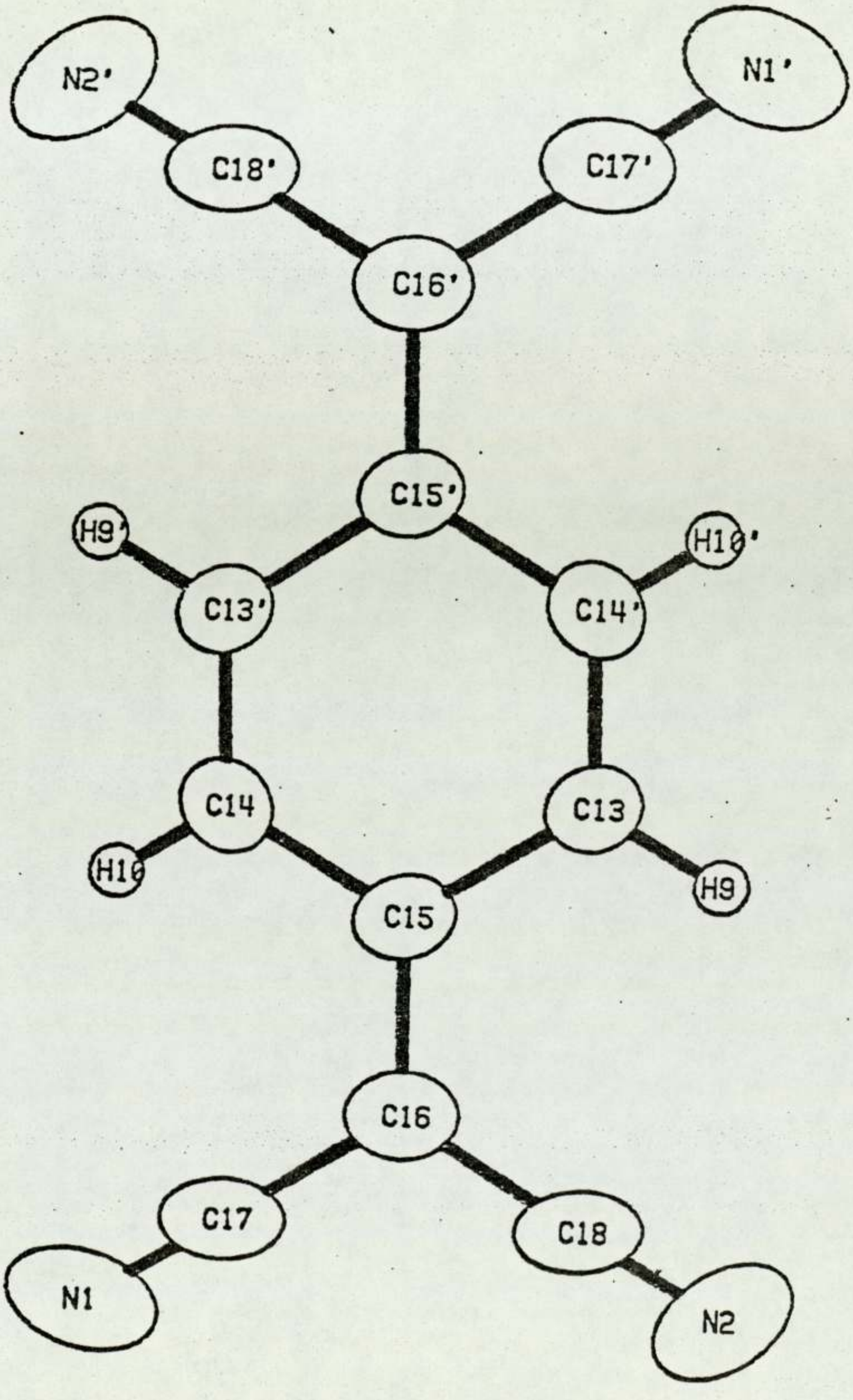

Figure 3.8 Perspective view of TCNQ

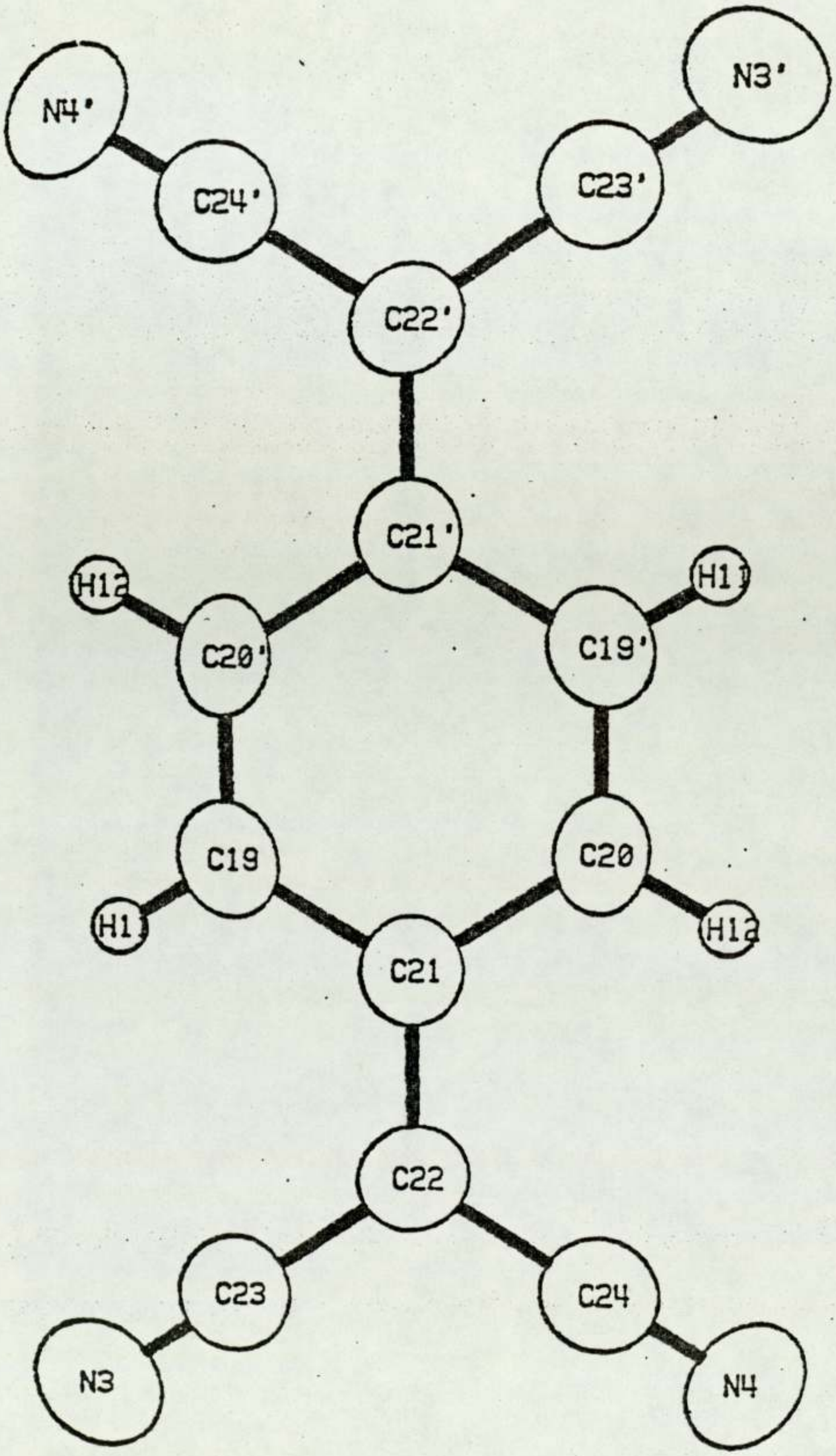

Figure 3.9 Perspective view of TCNQ

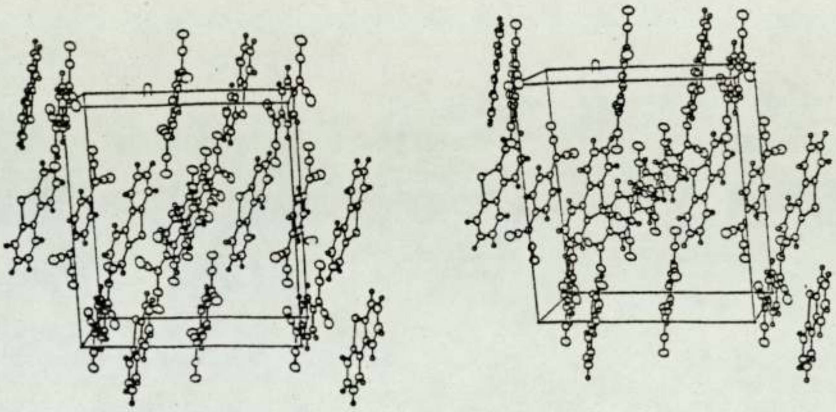

Figure 3.10 Stereoscopic packing diagram and unit cell of DBT.TCNQ

3.10.2 The Crystal and Molecular Structure of Dibenzotellurophene-TCNQ

Dibenzotellurophene.TCNQ (dbt.TCNQ) is an example of a complex for which the structure of donor (dbt) and the acceptor (TCNQ) are individually known, thus the determination of the structure of the complex afforded an opportunity to ascertain to what extent, if any, molecular dimensions would be influenced by the interaction. A perspective view of dbt.TCNQ components with the atom labelling scheme are given in Figures 3.7,3.8 and 3.9 . The bond distances and angles are given in Tables 3.11 and 3.12. The dbt and TCNQ molecules are nearly planar and are dimensionally identical to the uncomplexed dbt(80) and TCNQ(9) molecules, consistent with a found charge of zero for the TCNQ molecule in the present structure(81)*. This is also consistent with conclusions from I.R. and Mössbauer data.

It may be seen from Table 3.13 that the unit cell dimensions and space groups of dbt.TCNQ differ from those of related CT complexes that have been studied. The unit cell is much larger and has four molecules per unit cell.

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* The root mean square (r.m.s.) discrepancy between the complexed and uncomplexed molecules, in both cases is 0.01A or approximately one e.s.d. No respective bond length differs by more than 3 e.s.d. and the maximum difference in bond angles is less than 2 e.s.d., the r.m.s. being 1°. The r.m.s. derivations for the 13 and 8 non-hydrogen atoms from their respective dbt and TCNQ least square plane, is 0.014A and 0.015A, respectively. These values are close to the e.s.d. of the C atom positions.

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
TE	C1	2.084(6)	C5	H4	0.98(6)	C14	C15	1.435(8)
TE	C12	2.070(6)	C6	C7	1.451(8)	C14	H10	0.88(5)
N1	C17	1.132(9)	C7	C8	1.395(9)	C15	C16	1.361(8)
N2	C18	1.138(9)	C7	C12	1.397(8)	C16	C17	1.435(10)
N3	C23	1.124(9)	C8	C9	1.393(11)	C16	C18	1.433(10)
N4	C24	1.120(9)	C8	H5	0.97(6)	C19	C20	1.333(10)
C1	C2	1.402(9)	C9	C10	1.365(11)	C19	C21	1.427(10)
C1	C6	1.393(8)	C9	H6	0.93(7)	C19	H11	0.86(7)
C2	C3	1.385(10)	C10	C11	1.384(11)	C20	C21	1.441(9)
C2	H1	0.98(8)	C10	H7	0.91(7)	C20	H12	0.94(5)
C3	C4	1.379(11)	C11	C12	1.398(9)	C21	C22	1.363(9)
C3	H2	0.98(9)	C11	H8	0.87(8)	C22	C23	1.440(10)
C4	C5	1.370(10)	C13	C14	1.327(8)	C22	C24	1.448(10)
C4	H3	0.87(8)	C13	C15	1.446(9)			
C5	C6	1.394(9)	C13	H9	0.99(7)			

Numbers in parentheses are estimated standard deviations in the least significant digits

Table 3.11 Bond distances in Angstroms

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
C1	TE	C12	81.4(3)	C7	C8	C9	120.4(7)	C13	C15	C16	120.9(6)
TE	C1	C2	125.8(5)	C7	C8	H5	123.(4)	C14	C15	C16	122.2(6)
TE	C1	C6	112.5(5)	C9	C8	H5	116.(4)	C15	C16	C17	120.5(6)
C2	C1	C6	121.7(7)	C8	C9	C10	120.2(7)	C15	C16	C18	122.5(6)
C1	C2	C3	118.2(8)	C8	C9	H6	109.(4)	C17	C16	C18	117.1(6)
C1	C2	H1	121.(5)	C10	C9	H6	131.(4)	N1	C17	C16	179.8(7)
C3	C2	H1	120.(5)	C9	C10	C11	120.9(8)	N2	C18	C16	178.3(8)
C2	C3	C4	120.1(8)	C9	C10	H7	116.(4)	C20	C19	C21	121.7(8)
C2	C3	H2	115.(6)	C11	C10	H7	123.(4)	C20	C19	H11	120.(5)
C4	C3	H2	125.(6)	C10	C11	C12	119.3(8)	C21	C19	H11	118.(5)
C3	C4	C5	121.6(8)	C10	C11	H8	119.(6)	C19	C20	C21	121.5(7)
C3	C4	H3	109.(6)	C12	C11	H8	122.(6)	C19	C20	H12	121.(3)
C5	C4	H3	129.(6)	TE	C12	C7	112.5(4)	C21	C20	H12	117.(3)
C4	C5	C6	119.9(7)	TE	C12	C11	127.0(5)	C19	C21	C20	116.9(7)
C4	C5	H4	119.(3)	C7	C12	C11	120.6(6)	C19	C21	C22	121.6(7)
C6	C5	H4	121.(3)	C14	C13	C15	120.4(6)	C20	C21	C22	121.6(7)
C1	C6	C5	118.5(7)	C14	C13	H9	122.(4)	C21	C22	C23	122.7(7)
C1	C6	C7	116.5(6)	C15	C13	H9	118.(4)	C21	C22	C24	122.5(7)
C5	C6	C7	125.0(6)	C13	C14	C15	122.7(6)	C23	C22	C24	114.8(6)
C6	C7	C8	124.3(6)	C13	C14	H10	121.(4)	N3	C23	C22	179.0(9)
C6	C7	C12	117.1(6)	C15	C14	H10	117.(4)	N4	C24	C22	179.4(8)
C8	C7	C12	118.6(6)	C13	C15	C14	116.9(5)				

<u>Table 3.12</u> Bond Angles in Degrees　　Numbers in parentheses are estimated standard deviations in the least significant digits

Formula	Symmetry	Space Group	a(Å)	b(Å)	c(Å)	α	β	γ	V(Å)^3	Z
$C_{12}H_8O.C_{12}H_4N_4$ (Ref. 86)	Triclinic	-	8.010(2)	8.997(2)	6.780( )	97.75(2)	100.68(2)	99.58(3)	466.5	1
$C_{12}H_8S.C_{12}H_4N_4$ (Ref. 86)	Triclinic	P1	16.316(4)	8.910(2)	6.839(3)	98.35(3)	98.66(4)	100.13(2)	952.4	2
$C_{12}H_8Te.C_{12}H_4N_4$ (Ref. This work)	Monoclinic	P21/h	14.849(5)	8.172(2)	16.275(4)		92.05(3)		1974	4
$C_{12}H_8N_2.C_{12}H_4N_4$ (Ref. 87)	Monoclinic	P21/h	7.417(1)	19.904(3)	13.079(4)		92.47(5)		1929	4

Table 3.13 Comparison of the unit cell of dbt.TCNQ with those of related complexes

However, the space group and number of molecules are similar to those of o-phenanthroline complex which has mixed stack structure.

In dbt.TCNQ, the two component molecules alternate along the quasi-hexagonal packed mixed stacks parallel to the a axis (Figure 3.10). The crystal is built of stacks of alternating donor and acceptor molecules characteristic of $\pi - \pi^*$ electron donor-acceptor complexes. The crystal structure does not provide appreciable interstack donor-donor or acceptor-acceptor π-orbital overlap. There are thus no structural features facilitating separation of CT excited state ion pairs to produce charge carriers and this is consistent with our observations that this complex is a poor conductor. The most significant intermolecular interaction occurs between stacks as seen in the short Te.....N(2)[0.5-x, -1.5+y, 0.5-z] distance at 3.2126(6)Å. This value is approximately 0.4 to 0.5Å shorter than van der Waals distances(82,83) and is comparable to the short intermolecular Te.....N distances in Ph_3TeSCN(84) and Ph_3TeNCO(85). Other distances involving Te and TCNQ at or near the van der Waals distances are the interstack Te.....N(1)[x, -1+y, z] distance at 3.635(7)Å and the interstack Te-C(14) [0.5-x, -0.5+y, 0.5-z] (=[A]) distance at 3.746(6)Å. All other intermolecular distances involving Te and TCNQ (non-hydrogen atoms) are greater than 3.8Å. All intermolecular C-C distances less than 3.5Å (van der Waals distance, 3.4Å)(83) are between dbt and TCNQ in the

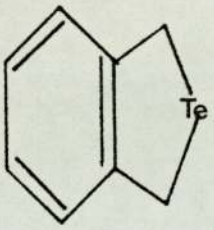
stack. These distances are:
$C_{(10)}-C_{(22)}$[A] at 3.36(1)Å, $C_{(8)}-C_{(20)}$[A] at 3.402(9)Å, $C_{(9)}-C_{(24)}$[A] at 3.43(1)Å, $C_{(2)}-C_{(14')}$[A] at 3.432(9)Å, $C_{(8)}-C_{(18)}$[A] at 3.455Å, $C_{(6)}-C_{(13)}$[A] at 3.463(8)Å, $C_{(3)}-C_{(14')}$[A] at 3.47(1)Å and $C_{(12)}-C_{(19)}$[A] at 3.492(9)Å. The only intermolecular C-N distance less than 3.4Å is $N_{(3)}-C_{(17)}$[A] at 3.39(1)Å. All of the intermolecular C-H and N-H distances are greater than 2.9Å except $N_{(1)}-H_{(11)}$ [0.5-x, 0.5+y, 0.5-z] at 2.75(7)Å, $N_{(2)}-H_{(1)}$[A] at 2.68(8)Å and $N_{(4)}-H_{(4,5)}$[-0.5+x, 1.5-y, 0.5+z] at 2.9(1) and 2.7(1)Å respectively. There are no close H-H contacts; the shortest is $H_{9''0}-H_{(3)}$[0.5-x, -0.5+y, -0.5-z] at 2.8(1)Å.

Thus interactions appear to occur between adjacent molecules within the stacks as well as between molecules in different stacks.

It is the latter feature which distinguishes the structure from those of other mixed stacks equimolar donor-acceptor complexes where the only significant intermolecular interactions occur between molecules within a stack.

3.11 Electrochemical Oxidation

On reconsidering the appearance potentials of different tellurides and 3,4-benzo-1-telluracyclopentane(I) in particular, relatively low values for (I) and phenoxatellurine suggest ionisation from π-molecular orbitals. ^{125}Te Mössbauer, I.R. and conductivity data for the TCNQ complex of (I) also imply that there is considerable charge transfer compared to other complexes of the series.



(1)

Most interesting is the rather low appearance potential of (I) which suggests that it might well be oxidised electrochemically in solution to its radical cation. Moreover, the radical cations of phenoxatellurine are known to be generated by a redox reaction between dissolved partners, followed by crystallisation$^{(64)}$. It was therefore tempting to investigate the electrochemical oxidation of 3,4-benzo-1-telluracyclopentane.

3.11.1 Sample Preparation

A typical experiment is described here: A solution of 3,4-benzo-1-telluracyclopentane (10 m mole) in dichloromethane (200 ml) was treated with tetrabutylammonium hexafluorophosphate (20 m mole). The solution was electrolysed between platinum electrodes with a spacing of ∿1cm and a constant current of 2 mA. Shiny crystals of the desired product started depositing on anode in a few minutes.

3.11.2 Discussion

Thus far three salts of the formula $[C_8H_8Te]^+[X]^-_{n(1-2)}$ have been prepared and characterised where X is PF_6^-, ClO_4^-, BF_4^-. The appropriate tetrabutylammonium salts were used as supporting electrolytes. Elemental analysis of the hexafluorophosphate derivative of (I) showed a 1:1 cation to anion ratio whereas the cation to anion ratio for the tetrafluoroborate derivative was 1:2. All the salts are brightly coloured. Analytical and I.R. data are presented in Tables 3.14 and 3.15 respectively. These salts were found to be stable over a long period. The perchlorate derivative of (I) exploded on heating. In the case of The hexafluorophosphate derivative, the formal oxidation state of tellurium is (III) which is not very common.

3.11.3 I.R. Spectra

Figures 3.11, 3.12, 3.13 and 3.14 show the infra-red spectra of 3,4-benzo-1-telluracyclopentane, $[(C_8H_8Te)^+PF_6^-]$, $[(C_8H_8Te)^+ClO_4^-]$ and $[(C_8H_8Te)^{2+}(BF_4^-)_2]$ respectively.

Compound	m.p. °C	Colour	C(calc)%	H(calc)%
$[C_8H_8Te]^+PF_6^-$	140	greenish black	25.60 (25.50)	2.18 (2.14)
$[C_8H_8Te]^{2+}[BF_4^-]_2$	150(d)	black	23.40 (23.70)	2.0 (1.99)
$[C_8H_8Te]^+ClO_4^-$	-	black	-	-
$[C_8H_8Te]^+I_3^-$	-	deep yellow	15.50 (15.68)	1.42 (1.31)

Table 3.14 Analytical data

$[C_8H_8Te]^+PF_6^-$	$[C_8H_8Te]^+ClO_4^-$	$[C_8H_8Te]^{2+}[BF_4^-]_2$
1090w	1142	1110
	1115	1075
872vw	1090	1037
844vs	1037sh	
820sh		
566s	642	542
	630s	530

Table 3.15 I.R. data/cm^{-1}

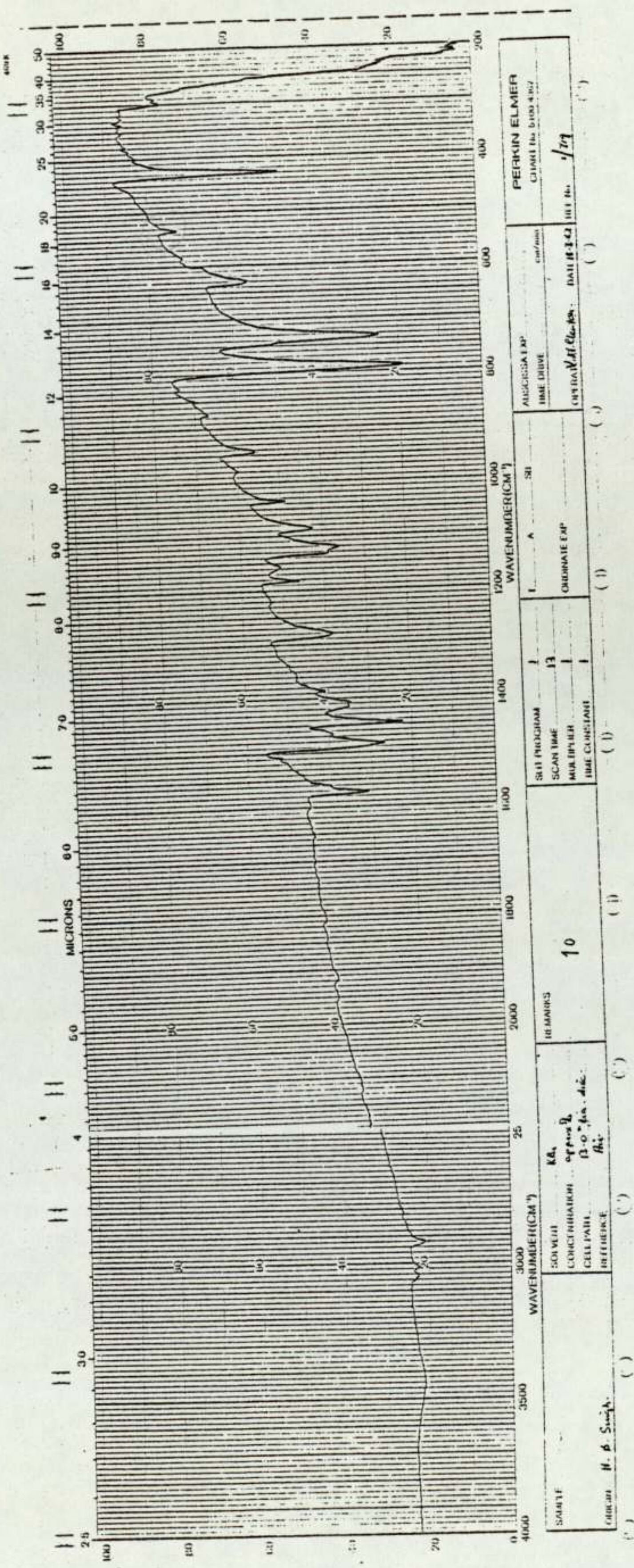


Figure 3.11 I.R. spectrum of 3,4-benzo-1-telluracyclopentane

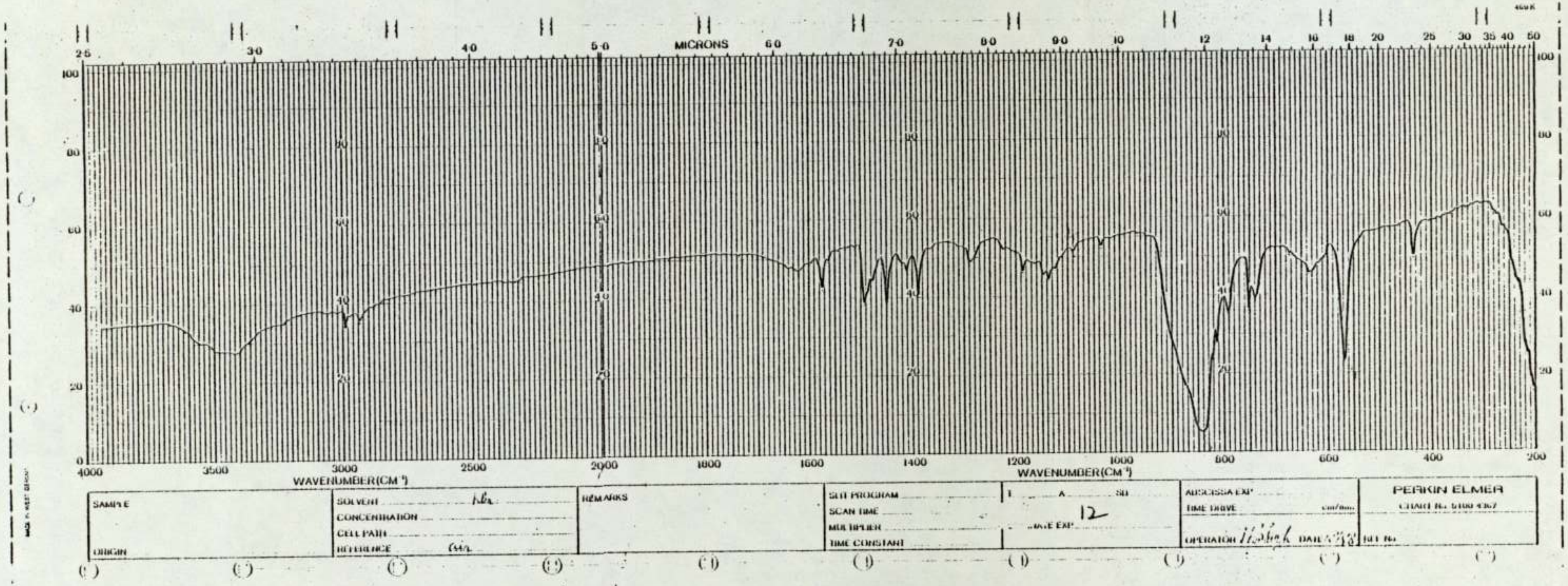


Figure 3.12 I.R. spectrum of $[(C_8H_8Te)^+PF_6^-]$

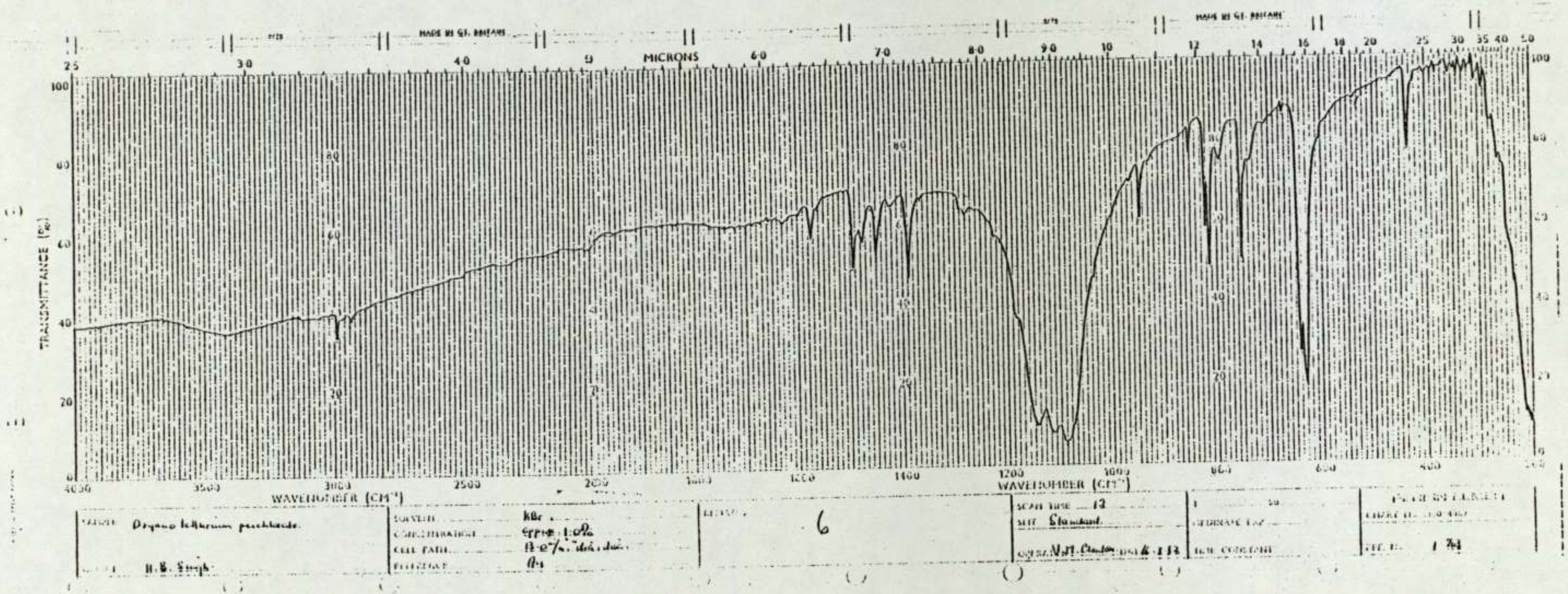


Figure 3.13 I.R. spectrum of $[(C_8H_8Te)^+ClO_4^-]$

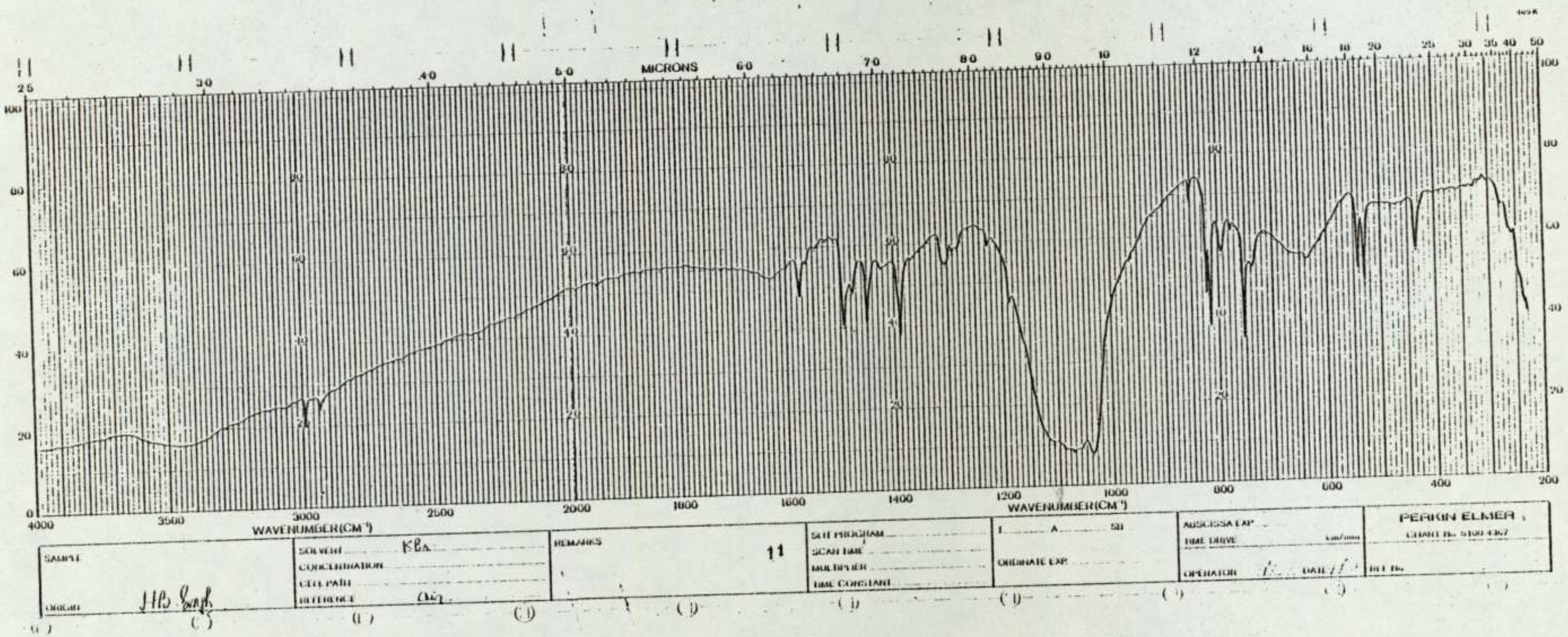
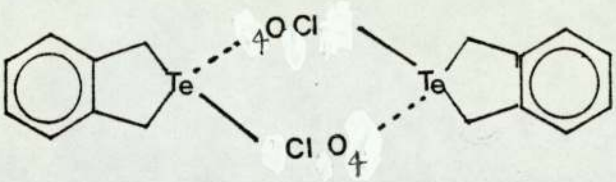


Figure 3.14 I.R. spectrum of $[(C_8H_8Te)^{2+}(BF_4^-)_2]$

The vibrational spectra of simple hexafluorophosphate salts have been examined in detail by several groups(88) and the infra-red and Raman data have satisfactorily been interpreted in terms of O_h symmetry. Perturbation of the PF_6^- ion; for example by coordination of one fluorine atom to a metal, lowers the local symmetry to C_{4v} which, in turn, leads to resolution of some degeneracies and to alteration of the selection rules. An octahedral molecule or ion MF_6^-, should have two ν_3 and ν_4 infra-red active vibrations. The higher frequency is due to the vibration ν_3 and that at the lower to the vibration ν_4(89).

Modes ν_3 and ν_4 have been assigned to 844cm^{-1} and 566cm^{-1} respectively. Since ν_4 is a sharp and single band, it is unlikely that the splitting of ν_3 implies an interaction with tellurium.

Figure 3.13 shows the infra-red spectrum of the perchlorate derivative. The observed frequencies for ν_4 and ν_3 are different from those expected for an ionic perchlorate salt. Instead, a splitting of the ν_4 and ν_3 bands is noted. The splitting is well resolved and interpreted in the terms of lower symmetry for the perchlorate group. Similar observations have been made by McWhinnie et al(90) for a telluronium salt of 3,4-benzo-1-telluracyclopentane. The lower symmetry of the perchlorate results, most probably, due to the interaction of the anion and cation via Te-O bonding, in the higher pressure modification of material possibly to give a dimer of the type:



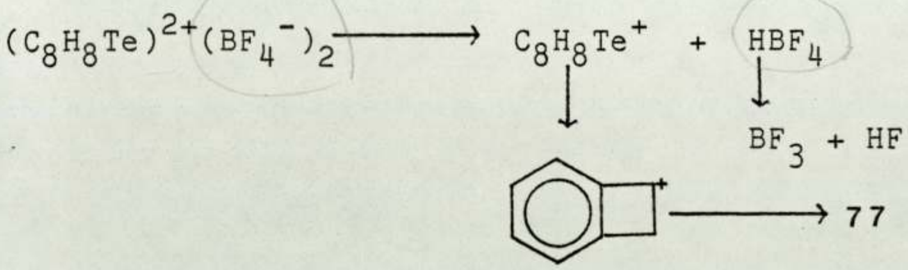
The infra-red spectrum of $[(C_8H_8Te)^{2+}(BF_4^-)_2]$ is shown in Figure 3.14. The I.R. of simple tetrafluoroborates has been investigated by Cote and Thompson$^{(91)}$ using sublimed films and paraffin mulls at room temperature and revealed that the strong broad ν_3 band had two maxima and two shoulders between 1100 and 1000 m^{-1} and a doublet at 521, 534 m^{-1} assigned as ν_4. The complex structure of the fundamental ν_3 and ν_4 was discussed in terms of the isotopic species boron 10 and 11. Clark and O'Brien reported splitting of ν_3 and ν_4 bands in the I.R. spectrum of $(CH_3)_3SnBF_4$$^{(92)}$. In the case of tetrafluoroborate derivative of 3,4-benzotelluracyclopentane, ν_3 band is observed as a broad and very strong band between 1088 and 1038 m^{-1} indicating an environment similar to the simple tetrafluoroborates.

3.11.4 E.S.R. Spectra

No E.S.R. signals could be detected for any of these salts. This observation is in agreement with the argument given previously that due to high spin orbit coupling (λ_{Te}=0.49eV), the line-width increases$^{(66)}$.

3.11.5 Mass Spectrum

The mass spectrum of $[(C_8H_8Te)^{2+}(BF_4^-)_2]$ did not show the peak for the molecular ion. The highest peak observed corresponds to $(C_8H_8Te^+)$. In addition $^{11}B^{19}F_3^+$ was identified at 68 together with an isotopic ion at m/e 67($^{10}B^{19}F_3$).



The observation of HF at m/e = 20 may be explained by an alternative formulation of the parent compound e.g., $[C_8H_8Te]^+BF_4^-.HBF_4$. However, this formulation is not supported by infra-red studies. Therefore, the observation of HF may be explained in terms of themolysis.

CHAPTER FOUR

NEW ORGANOTELLURIUM COMPOUNDS DERIVED FROM QUINOXALINE

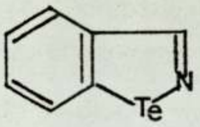
4.0 Introduction

Some of the basic features believed necessary for an organic conductor, as exemplified by TTF.TCNQ(14) family, are as follows:

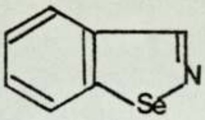
(1) Segregated stacks of uniformly spaced molecules
(2) Incomplete charge-transfer between donor and acceptor
(3) Large, planar, stable, polarisable molecules.

Wudl et al(93) in the initial structural study of TTF, observed a lattice constant of 4.023 Å indicating a uniform chain structure. This suggested that the conventional mixed stack structure of DA......DA type could be averted if the TTF chains persisted after charge-transfer. Charge-transfer salts of TTF and TSeF family have been the subject of exhaustive and meticulous experiments for the past ten years and these have revealed that conductivity in these organic metals is due to long range delocalisation among donors. For $(TMTSeF)_2X$ series of organic conductors, short intermolecular Se.....Se contacts were also observed(94). Synthesis and crystallographic studies of neutral organotellurium donors are of continuing interest with respect to their intermolecular and intramolecular interactions. Structural studies on a variety of organotellurium compounds have disclosed close intermolecular contacts of various types.

In organotellurium diiodides, strong Te....I and I....I interactions have been observed(95-100). Similar pronounced interactions between Te and chlorine have been described in p-methoxyphenyltellurium trihalides(101). Sandman et al have observed very short Te....Te contacts in TTeT(33). Apart from halogens, only N has been found to have short intermolecular contacts. Anomalous physical properties such as high melting point and low solubility of 1,2 benzoisotellurazole(I) were explained by very short Te....N intermolecular contacts (2.4 Å)(102).



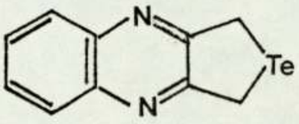
(I)



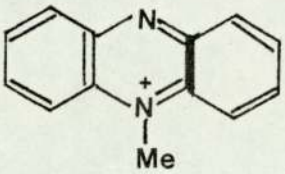
(II)

Such interactions were not observed in the crystal structure of 1,2 benzoisoselenazole(II) and properties were those expected.

In this chapter the synthesis and structure of some new heterocycles containing both Te and N atoms is reported. It is hoped that the new donor would have strong Te....N intermolecular contacts and eventually afford a CT complex with segregated stacks of donors and acceptors. In addition the new organotellurium(II) donor, namely 3,4-quinoxalino-1-telluracyclopentane(III) would also be structurally similar to N-methylphenazinium ion whose CT complex with TCNQ is known to have highest conducting for an organic compound(11).

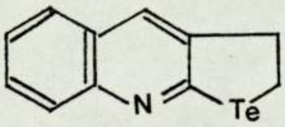


(III)

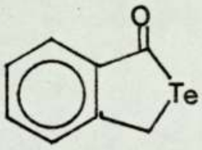


(IV)

A variety of methods have been employed to form tellurium-carbon bonds. These involve, in general, either tellurium tetrachloride or the cheaper and easily accessible elemental tellurium as starting materials(103). Most of the recent papers have described the use of Na_2Te(104), NaHTe(105) and Na_2Te_2(32) prepared in situ from elemental tellurium. For example, treatment of sodium hydrogentelluride with 2-chloro-3(2'chloroethyl)quinoline afforded 2,3-dihydrotellurolo(2,3-b)quinoline(V)(106).

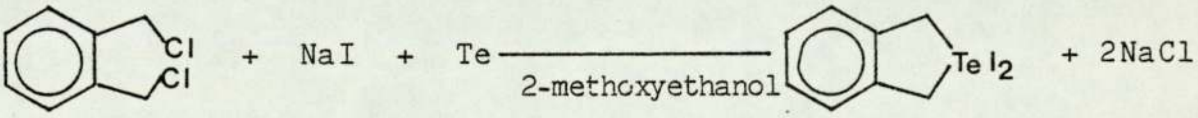


(V)



(VI)

Cava and Engman(107) found that using a phase transfer technique gave quantitative yield of tellurophthalide(VI). However, the method reported by Ziolo and Günther(108) seems to be the simplest. In the presence of NaI, α,α'-dichloro-o-xylene reacted with elemental tellurium to form 1,1-diiodo-3,4-benzotelluracyclopentane(VII).



(VII)

4.1 Experimental

1,1-Diiodo-3,4-quinoxalino-1-telluracyclopentane - A mixture of 2,3-bis(bromomethyl)quinoxaline (1.58 g, 5 m mol), sodium iodide (3.0 g, 20 m mol) and powdered tellurium (0.64 g, 5 m mol) in 2-methoxyethanol (100 cm^3) was stirred and heated to gentle reflux for 2 hours. After cooling the reaction mixture, deionized water (200 cm^3) was added to cause additional precipitation. The precipitate was filtered, washed with water and dried. The crude material was recrystallized from 2-methoxyethanol to give a deep violet crystalline solid, m.p. 148-150°C.

1,1-Diiodo-3,4-quinoxalino-1-telluracyclopentane-2,3-bis (iodomethyl)quinoxaline (1:1) complex - In a repeat experiment, 2,3-bis(bromomethyl)quinoxaline (3.16 g, 10 m mol), powdered tellurium (1.28 g, 10 m mol) and potassium iodide (6.54 g, 39 m mol) were stirred and heated gently in 2-ethoxyethanol for 1 hour. After the reaction period, deionized water (200 cm^3) was added to the mixture. The yellow precipitate formed was filtered and air dried. The crude material was dissolved in hot acetone, filtered to remove any unreacted tellurium and the filtrate was set aside to crystallize slowly. The resulting complex had m.p. 150-152°C.

3,4-Quinoxalino-1-telluracyclopentane - To a suspension of violet 1,1-diiodo-3,4-quinoxalino-1-telluracyclopentane

(1.0 g) in ethanol (75 cm^3) and water (15 cm^3) was added dropwise a solution of hydrazine hydrate (0.4 g) in alcohol (15 cm^3). The resulting solution was warmed gently until all the violet crystals of the diiodide dissolved, after which the reaction mixture was poured into water (200 cm^3) and extracted into ether. The ethereal layer was separated, dried over anhydrous Na_2SO_4 and taken to dryness on a rotatory film evaporator. The resulting yellow powder, on treatment with charcoal and ether gave yellow needles m.p. 158-160°C.

Reduction of compound (X) (Table 4.1) with hydrazine hydrate affords a pale yellow compound, m.p. 80°C (dec) which readily decomposes with the elimination of tellurium.

Attempted direct synthesis of 3,4-quinoxalino-1-telluracyclopentane - A mixture of 2,3-bis(bromomethyl)quinoxaline (1.90 g, 6 m mol), tellurium powder (0.76 g, 6 m mol) and sodium borohydride (1.2 g, 32 m mol) in ethanol was stirred and heated for 12 hours under dinitrogen. The initial green colour changed to red in 30 minutes. On completion of the reaction, the mixture was poured into water (500 cm^3) when a yellow precipitate appeared. The colourless material was extracted into ether from which solution colourless needles were obtained, m.p. 105-107°C.

Attempted synthesis of 10-ketoanthracenotritellurapentalene- A mixture of 1,8-dichloroanthroquinone (0.31 g), tellurium powder (15.24 g) and sodium borohydride (4.56 g) in ethanol, was stirred and heated for 12 hours under nitrogen. The initial green colour changed to red in half an hour. After completion of the reflux period, the reaction mixture was poured into water (500 cm^3) when a yellow precipitate separated out. It was treated with ether. The yellowish ethereal solution yielded yellow needles, m.p. 156-157°C. The insoluble portion melted with sublimation at 280°C.

Complex of 3,4-quinoxalino-1-telluracyclopentane with TCNQ (1:1) - To a solution of 3,4-quinoxalino-1-telluracyclopentane (0.28 g, 1 m mol) in acetonitrile (20 cm^3) was added a solution of TCNQ (0.21 g, 1 m mol) in acetonitrile (30 cm^3). The resulting solution was stirred under reflux for 1 hour, after which the volume of the solution was reduced to 10 cm^3 and the residue was left to crystallize. Crystals m.p. 140°C (dec) were obtained.

4.2 Results and Discussion

Tables 4.1 and 4.2 combine preparative, analytical and I.R. data. N.M.R. and U.V. data are gathered in Table 4.3.

The reaction of 2,3-bis(bromomethyl)quinoxaline with powdered tellurium and sodium iodide gives a violet coloured compound to which, on the basis of elemental analysis (Table 4.2), ^{1}H N.M.R. data (Table 4.3) structure VIII is reasonably assigned. The sequence of reactions may be

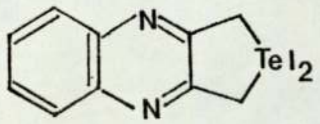
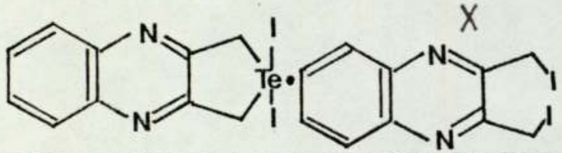
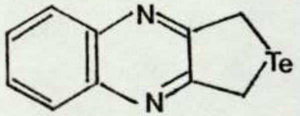
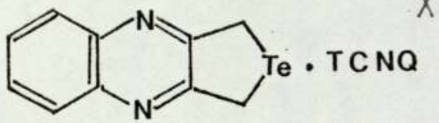
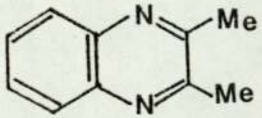
Compound	Colour	m.p. ^{o}C	Yield	I.R.cm^{-1}
 VIII	deep violet	148-150	60	ν(Te-C) 514
 X	yellow	150-152	75	ν(Te-C) 512
 IX	pale yellow	158-160	60	ν(Te-C) 500
 XVII	black	140	86	ν(C≡N) 2178 2228 ν(Te-C) 505
 XIII	colour- less	105(lit. 106-107)	82	-

Table 4.1 Yields, melting point and I.R. data

Compound No(a)	C% (calcd)	H% (calcd)	N% (calcd)	Te% (calcd)
VIII	22.5 (22.3)	1.5 (1.49)	5.00 (5.21)	23.2 (23.7)
X	25.4 (25.4)	1.70 (1.70)	5.50 (5.91)	13.4 13.5)
IX	41.6 (42.3)	2.80 (2.81)	9.50 (9.87)	44.18 (44.9)
XVII	53.8 (54.15)	2.30 (2.47)	16.4 (17.22)	27.0 (26.1)
XIII	75.8 (75.9)	6.40 (6.37)	17.5 (17.7)	-

Table 4.2 Analytical data

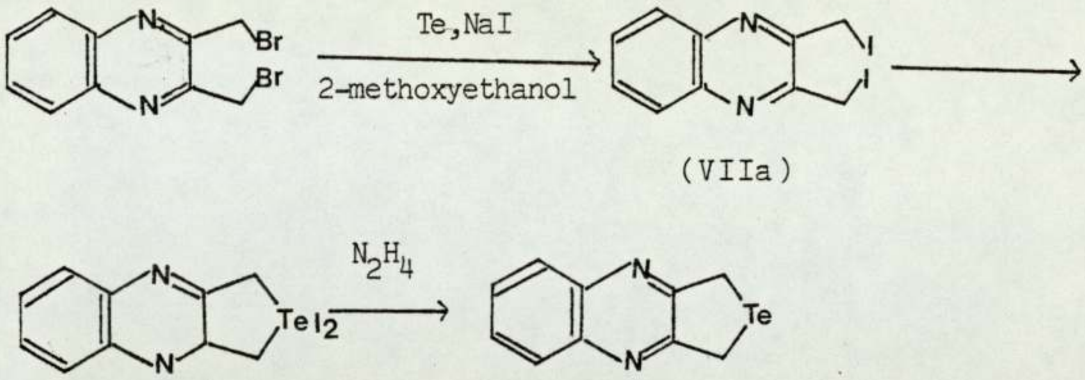
(a) see Table 4.1

Compound No[a]	U.V. maxima (CH_2Cl_2) nm	^{1}H N.M.R. (δ ppm vs TMS) J-Hz (DMSO-d_6)
VIII	242,270,328	4.74 (CH_2,s,4H,J_{Te-H}=31), 7.7-8.2 (Aromatic,m,4H)
X	245,266,335	4.74 (CH_2-Te,s,4H),4.84(CH_2-I,s,4H), 7.6-8.1 (Aromatic,m,8H)
IX	243,324	4.58 (CH_2,s,4H,J_{Te-H}=23), 7.2-8.05 (Aromatic,m,4H)
XVII	243,320, 394(TCNQ+TCNQ$^{\cdot-}$)	-
XIII	237,315	2.5 (CH_3,s,6H), 7.3-8.1 (Aromatic,m,4H)
XIII$^+$	248,337	4.92 (CH_2,s,4H) 7.5-8.0 (Aromatic,m,4H)

Table 4.3 Physico-chemical data

(a) See Table 4.1

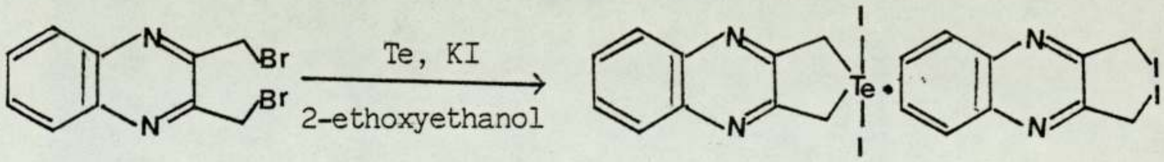
XIII$^+$ is 2,3-(bisbromomethyl)quinoxaline depicted as follows:



(VIIa)

(VIII)

(IX)



(X)

An ultraviolet spectrum of VIII shows bands at 242, 270 and 328 nm (Figure 4.1). Reduction with hydrazine hydrate in an ethanol and water mixture yielded pale yellow crystalline needles to which structure 3,4-quinoxalino-1-telluracyclopentane(IX) has been assigned on the basis of elemental analysis, mass spectral and N.M.R. evidence. The ultraviolet and visible spectrum of IX shows maxima at 243, and 324 nm (Figure 4.2). Telluroquinolines(106) and 3,4-benzotelluracyclopentane(108) which are similar to IX, are also yellow in colour. The mass spectrum of VIII shows no molecular ion at m/e 540 (^{130}Te, ^{127}I). The major fragments observed are TeI_2^+, I_2^+, $C_{10}H_8N_2Te^+$, $C_{10}H_8N_2^+$, Te^+ and I^+. Further fragmentation of $[C_{10}H_8N_2]^{\cdot +}$ proceeded

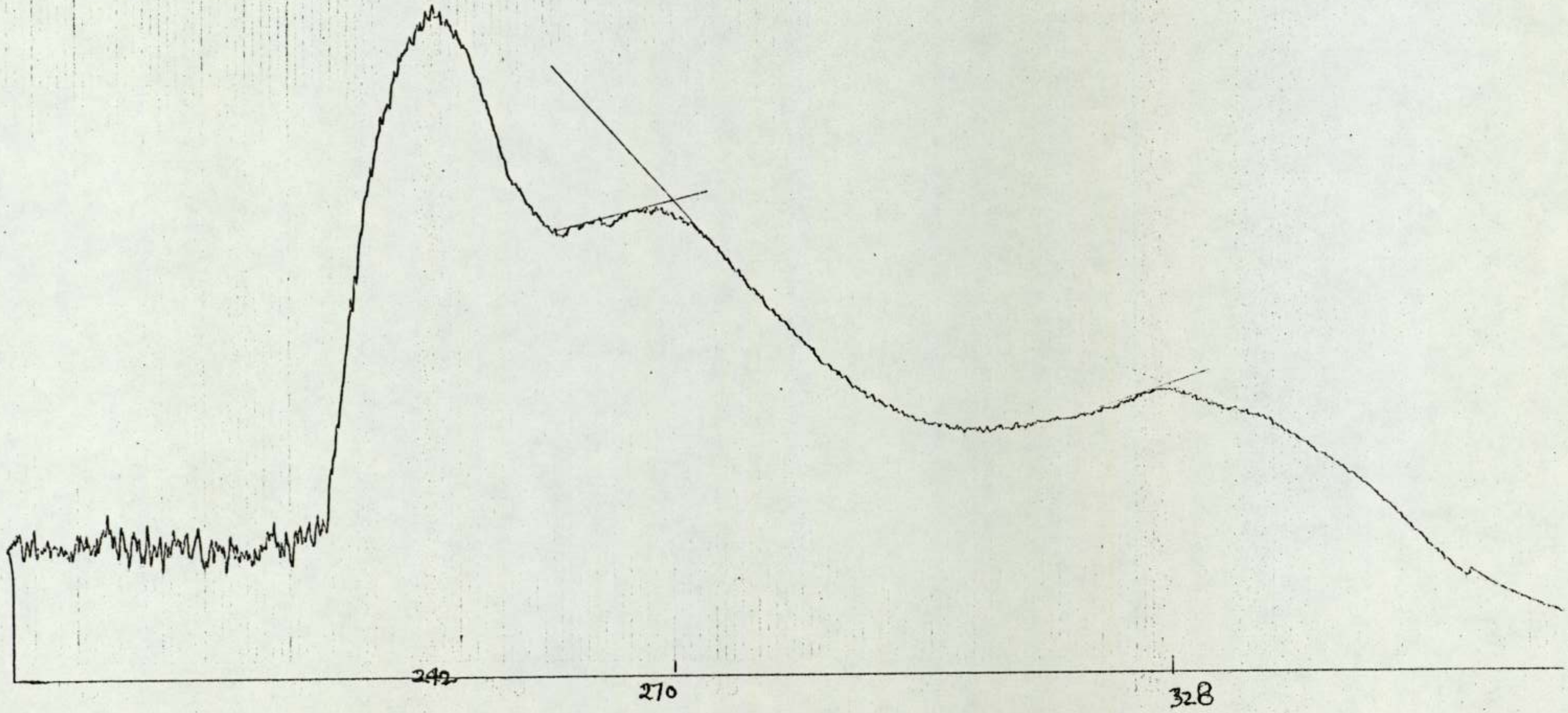
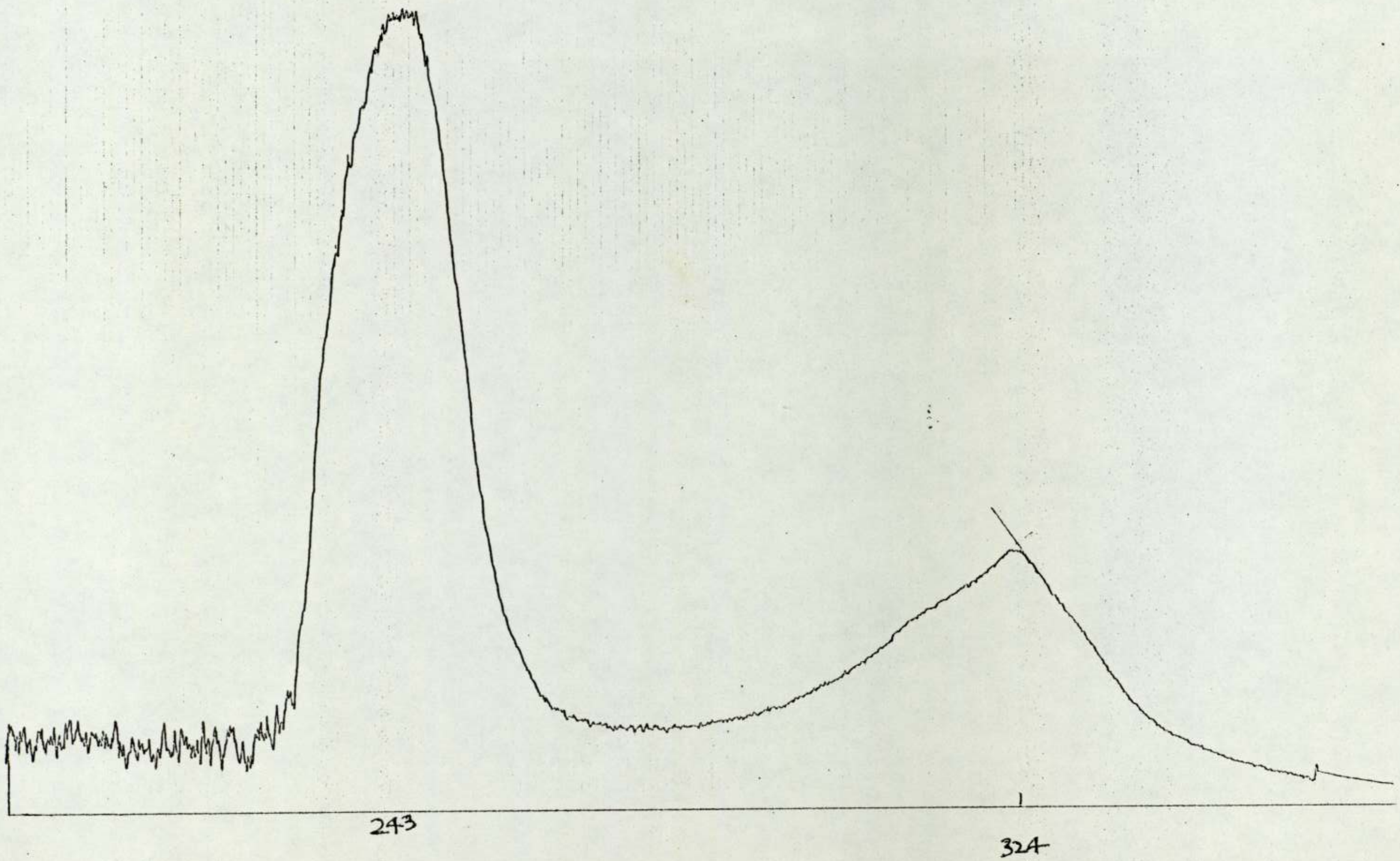


Figure 4.1 U.V. spectrum of $C_{10}H_8N_2TeI_2$

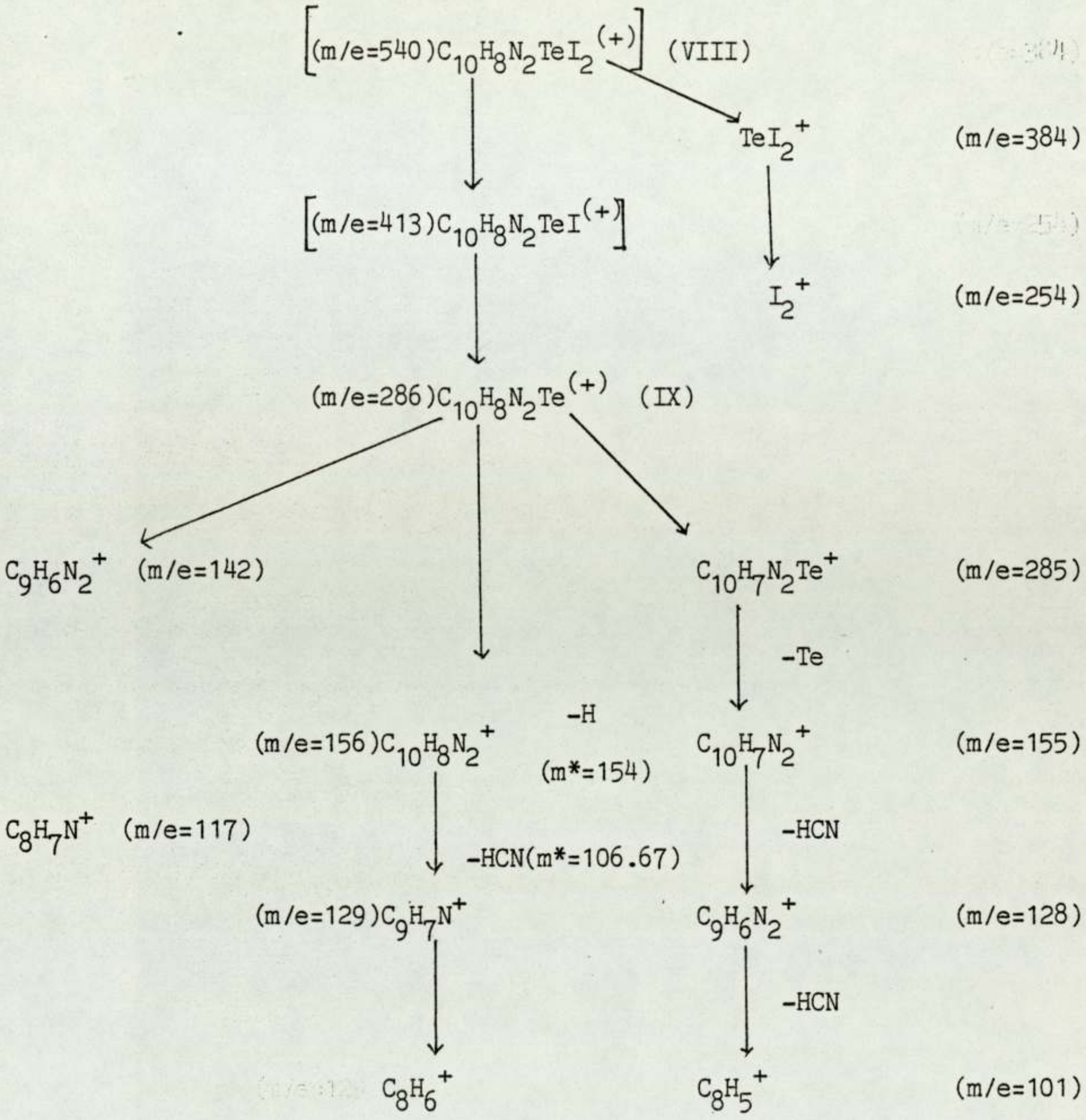


<u>Figure 4.2</u> U.V. spectrum of $C_{10}H_8N_2Te$

by the loss of HCN, to give ions $[C_9H_7N]^+$ and $[C_9H_6N]^+$ at m/e 129 and 128 (Scheme 1). The following elemental composition was found in the range: $[C_7H_5N]^+$ (m/e 103), $[C_7H_4N]^+$ (m/e 102), $[C_7H_5]$ (m/e 89), $[C_6H_4]^+$ (m/e 76), $[C_6H_3]^+$ (m/e 75), $[C_5H_3]^+$ (m/e 63) and $[C_4H_2]^+$ (m/e 50). The m/e values of the fragments are also in agreement with those described by Kovacik et al for 2,3-substituted quinoxalines(109). With the obvious exception of the iodine containing fragments, the mass spectrum of IX is superimposable on that of VIII. Many of the proposed fragmentations are supported by the observation of metastable ions at appropriate values of m/e. An interesting fragment at m/e = 144 may arise from the parent ion (m/e = 286) by loss of H_2CTe, however no metastable transition is observed to support this suggestion.

Thus the mass spectroscopic data of VIII support the formulation proposed and the observation of fragments TeI_2^+ and I_2^+ is significant and similar to 1,1-diiodo-3,4-benzo-1-telluracyclopentane(108). The violet colour of VIII implies strong intermolecular interactions in the solid state and attempts are being made to define these interactions by X-ray crystallography.

The N.M.R. spectrum of 2,3-bis(bromomethyl)quinoxaline has been studied(110) and shows resonances at $\delta = 4.92$($-CH_2$,s,4H) and at $\delta = 7.46-8.02$ (aromatic, m, 4H). The N.M.R. of VIII in DMSO-d_6 shows a multiplet at $\delta = 7.7-8.2$ (aromatic, 4H)



Scheme 1 Mass spectra of compounds (VIII) and (IX) (scheme 1) based on ^{130}Te, ^{127}I, ^{12}C, ^{14}N, ^{1}H.
(species in square bracket not observed)

and a singlet at δ=4.74 ppm ($-CH_2$, 4H). The fact that the methylene protons of VIII are more shielded than those in the starting material is in accord with simple expectation from electronegativity arguments. The methylene protons display satellites due to coupling to the ^{125}Te ($I=\frac{1}{2}$, natural abundance 7%); consistent with integrity of the heterocyclic structure in the diiodide. The coupling constant (J) for $^{125}Te-^{1}H$ was 31 Hz.

The N.M.R. spectrum of IX, the reduction derivative of VIII, displays two sets of signals at δ=7.2-8.05 (aromatic, 4H) and at δ=4.58 ($-CH_2$,4H) (Figure 4.3). In this further shielding is seen for methylene protons of IX which is in accordance with less deshielding by tellurium(II). The singlet at δ=4.58 ppm also displays two satellites due to coupling with ^{125}Te, $J(^{125}Te-^{1}H)$ was found to be 23 Hz which is in good agreement with those observed by Gysling et al(111) for tellurium(II) derivatives. The coupling constant also confirms that the Te-C linkage has remained intact.

In a separate experiment to prepare VIII, when the reaction mixture was stirred for a shorter time and potassium iodide was used instead of sodium iodide and the product was left to crystallise from acetone, a yellow compound X rather than violet product VIII was obtained. The yellow crystalline solid melted sharply at 150-152°C. The I.R. and mass spectra were nearly identical to those of those of VIII

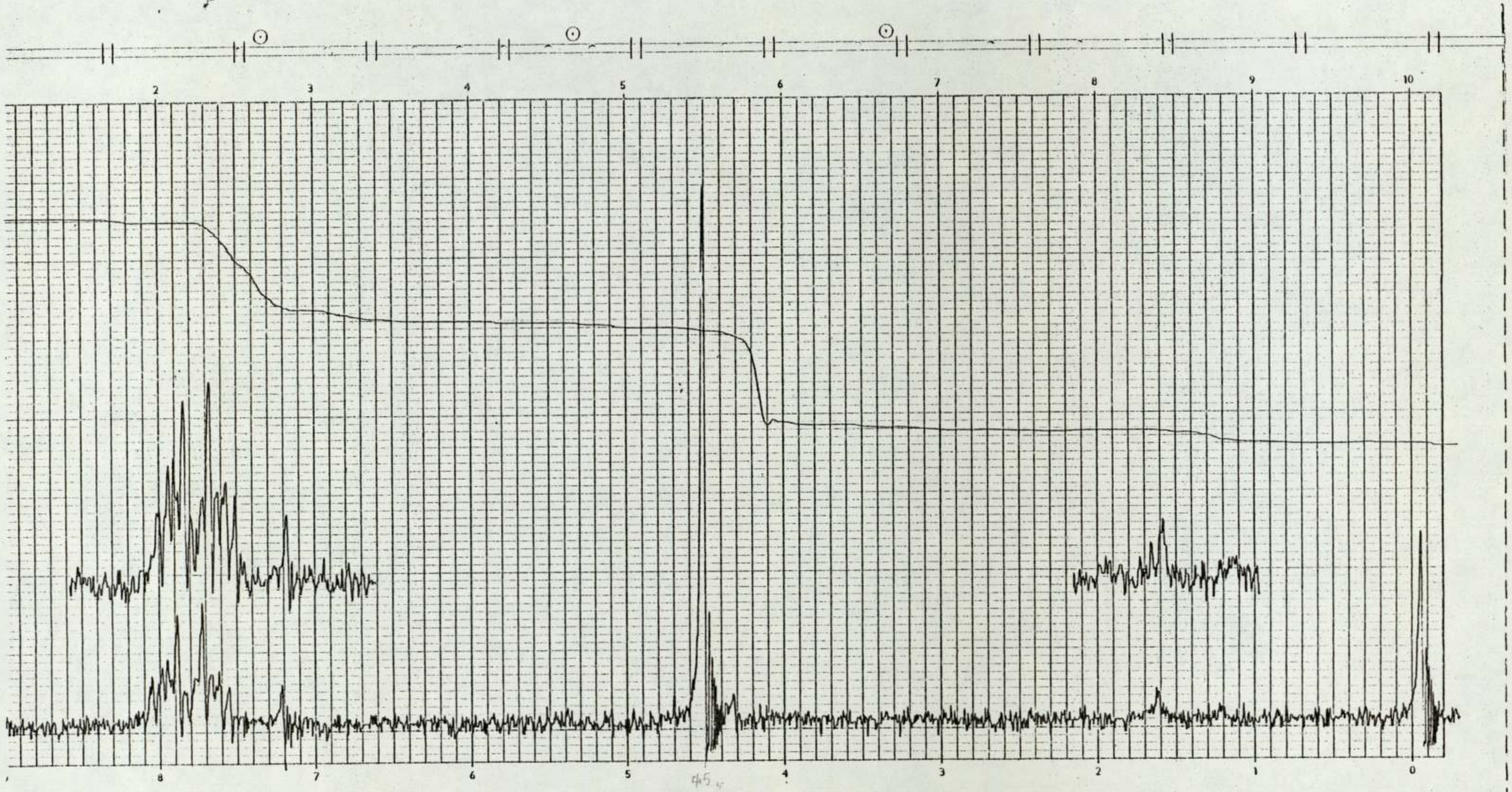
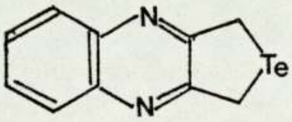


Figure 4.3 N.M.R. spectrum of $C_{10}H_8N_2Te$

except that the mass spectrum contained an ion at m/e=410 ($C_{10}H_8N_2I_2$). The N.M.R. spectrum showed two singlets at δ=4.74 and at δ=4.84 ppm due to methylene protons. The singlet at δ=4.84 ppm appears as though it is in 2,3-bis(bromomethyl)-quinoxaline (δ=4.92 ppm, $-CH_2$). In addition the results of the elemental analysis were also poor. The calculated values for the compound VIII are C=22.34%, H=1.49%, N=5.21% and Te=25.4% whereas the values obtained for compound X were C=25.4%, H=1.7%, N=5.9% and Te=13.9%. Compound X was further purified by recrystallisation and analysed but the same results for elemental analysis were found confirming that the compound was pure.

Reduction of X with hydrazine hydrate provided an unstable pale yellow compound (XI), m.p. 80°C(d) which decomposed rapidly when isolated from ethereal solution. The mass spectrum of XI shows the molecular ion peak at m/e=286. The N.M.R. spectrum is identical to IX and shows a multiplet at δ=7.3-8.12 ppm and a singlet at δ=4.53 ppm with satellites. The $J(^{125}Te-^{1}H)$ was 23 Hz. Although the compound IX seems to have formed (on the basis of N.M.R. and M.S.) on reduction of X, it decomposes to black-brown material on standing.



(XI)

A U.V. study of the compounds (Table 4.3) reveals that the bands 237-248 nm and 315-337 nm are characteristic of the quinoxaline nucleus. It would follow that the band at 270 nm (VIII) or 266 nm (X) must be due to the presence of Te-I bonds.

A slight reduction in frequency of ν(Te-C) is noted on reduction of VIII (tellurium IV), to IX (tellurium II) (Figures 4.4, 4.5).

From the above evidence it can be concluded that compound (X) is pure and compound (VIII) in its integrity (as evidenced by I.R., N.M.R., M.S. and reduction) and most probably the deep-violet coloured (VIII) and yellow coloured (X) are two different crystalline forms, namely β and α forms respectively, of the same compound. The observation of two isomeric forms was not surprising since other dialkyltellurium diiodides have been reported to exist in two isomeric forms(112). For $(CH_3)_2TeI_2$, α-form has been shown to be a compound of the type R_2TeI_2 whereas the β-form actually is a telluronium salt, by X-ray structural analysis(100).

The telluracyclopentane-1,1-diiodide and telluracyclohexane-1,1-diiodide have also been reported to exist in two forms(113,114).

McCullough and coworkers(95-98a) have demonstrated that in $RTeI_2$, R_2TeI_2 and $RTeI_3$ type compounds a variety of intermolecular Te....I and I....I contacts exists.

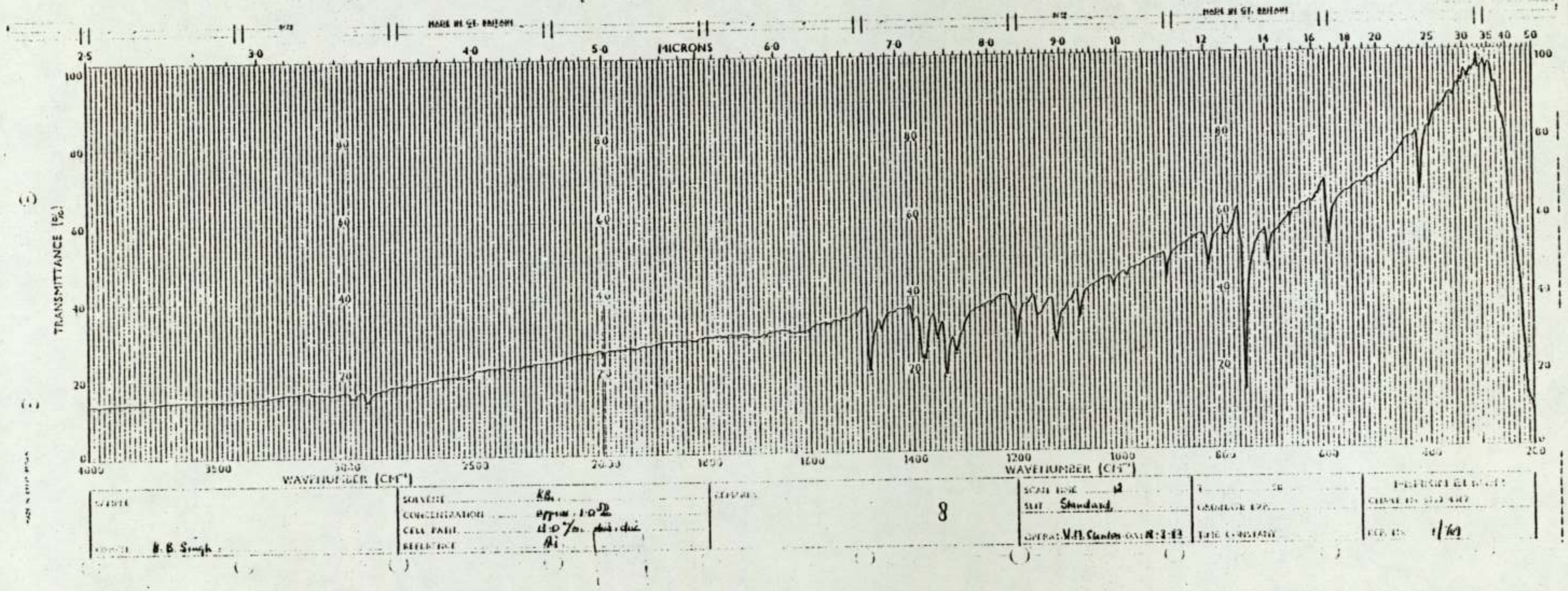


Figure 4.4 I.R. spectrum of $C_{10}H_8N_2TeI_2$

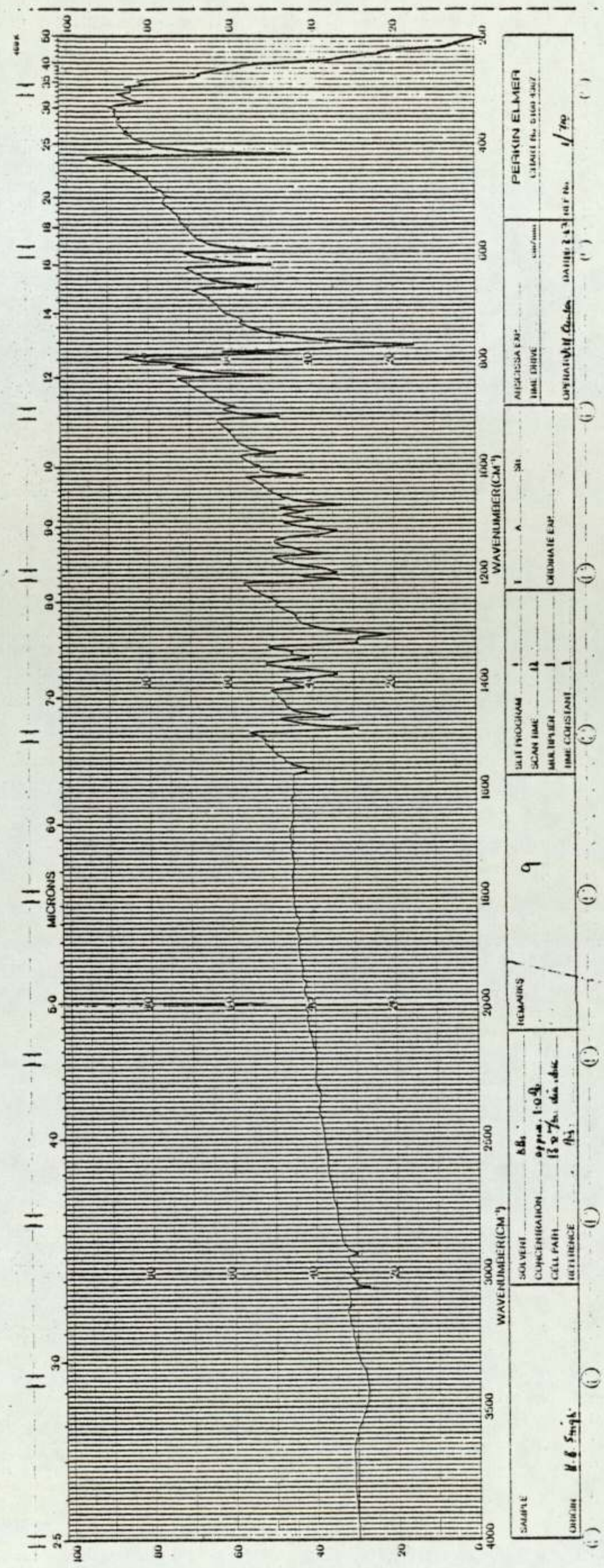


Figure 4.5 I.R. spectrum of $C_{10}H_8N_2Te$

To solve the problem of poor analytical results, X-ray diffraction analysis was performed.

4.3 X-Ray Structure Analysis of the 1,1-diiodo-3,4-quinoxalino-1-telluracyclopentane-2,3-bis(iodomethyl) quinoxaline(1:1) complex(115)*

After preliminary examination by photographic methods, a crystal with dimensions ca.0.26 x 0.18 x 0.03 mm was mounted on an Enraf-Nonius CAD-4 diffractometer, and cell dimensions and reflection intensities were measured in the $\omega/2\theta$ scan mode with graphite-monochromated M_o-K_α radiation. The scan range (ω^o) was calculated from (1.10 + 0.35 tanθ) and the scan speed varied from 1.1 to $3.5^o min^{-1}$ depending on the intensity. Backgrounds were measured at each end of the scan. 4291 reflections were scanned in the range $2<\theta<25^o$. Two standard reflections measured every 2 hours showed a slight decrease in intensity (ca.10%) and appropriate scaling factors were applied.

Lorentz, polarisation and absorption corrections were applied, and 2998 structure amplitudes [$F>7\sigma(FF)$] were considered observed and were used in the structure analysis.

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* X-ray diffraction data were obtained from Dr T A Hamor. Supplementary data: observed and calculated structure factors, anisotropic temperature factors, hydrogen atom coordinates have been deposited with J.Chem.Soc. Dalton Transactions (1983) for publication.

4.3.1 Crystal Data

$C_{20}H_{16}I_4N_4Te$

M = 947.59

Triclinic space group $P_{\bar{1}}$

$\underline{a}$ = 7.667(2), $\underline{b}$ = 11.826(4), c = 13.739(4) Å

α = 93.26(3), β = 98.37(2), γ = 83.29(2)°, $\underline{V}$ = 1223.1 Å

Dc = 2.57 gcm^{-3}, z = 2, F(000) = 856,

(Mo-Kα, λ = .71069 Å) μ = 5.88 mm^{-1}

The position of the Te and I atoms were determined by a combination of direct methods and Patterson and Fourier syntheses and those of the remaining non-hydrogen atoms from subsequent difference maps. The structure was refined by least squares using anisotropic temperature factors for the heavier atoms. Hydrogen atoms were placed in calculated positions "riding" on their respective carbon atoms. The weighing scheme used was

$$W = 1/[\sigma^2(F) + 0.001F^2]$$

and refinement converged to R = 0.059.

Complex neutral-atom scattering factors were employed(77). Computations were carried out on the University of Birmingham DEC 20 and ICL 1906A computers and on the CDC 7600 at the University of Manchester Regional Computer Centre with MULTAN(116) and SHELX(117) programs.

Fractional coordinates ($x10^4$) are given in Table 4.4 and important distances and bond angles constitute Table 4.5. Table 4.6 gives deviations of atoms (Å) from mean-planes.

4.3.2 The Crystal and Molecular Structure of (X)

The structure consists of (VIII) and free 2,3-bis(iodomethyl)quinoxaline. Two molecules of VIII and two molecules of the diiodide are however linked by relatively weak Te....I interactions into centrosymmetric dimers. These interactions are oriented trans to the Te-C bonds, Te-I(1') = 3.761(2) Å and Te-I(3) = 3.788(2) Å (see Fig. 4.6 for atom numbering). I(1') is linked to the centrosymmetrically-related Te atom by a strong bond, Te-I(1') = 2.886(2) Å, thus forming the dimer. The Te-I(3) interaction serves to link in the organic diiodide.

The coordination about tellurium is approximately octahedral with two strongly bound iodine atoms, I(1) and I(2) in the axial positions, normal to the ring system of the heterocycle and the weakly linked I(1') and I(3) in the basal plane (Table 4.6). Quite large angular deviations from ideal octahedral values, however, occur in particular in the basal plane, the angle I(1')-Te-I(3) is enlarged to 125.4(1)° with a concomitant decrease of the I(1')-Te-C(1) and I(3)-Te-C(12) angles to 71.9(4) and 76.8(4)° respectively. The Te-C bond lengths (both 2.14(1)Å) are in

Atom	x	y	z
Te	-2456(1)	5292(1)	3885(1)
I(1)	377(1)	6735(1)	4152(1)
I(2)	-5305(1)	3833(1)	3487(1)
I(3)	-5101(1)	8140(1)	4325(1)
I(4)	-9469(2)	10387(1)	3556(1)
C(1)	- 801(17)	3976(11)	3227(9)
C(2)	-1179(14)	4100(10)	2129(8)
N(3)	- 390(13)	3358(9)	1578(7)
C(4)	- 785(16)	3477(11)	567(9)
C(5)	- 16(19)	2660(12)	- 69(11)
C(6)	- 410(21)	2779(14)	-1068(11)
C(7)	-1577(20)	3714(14)	-1441(10)
C(8)	-2371(19)	4495(14)	- 824(9)
C(9)	-1963(16)	4415(11)	197(9)
N(10)	-2774(13)	5184(9)	798(7)
C(11)	-2361(15)	5037(10)	1749(8)
C(12)	-3247(17)	5898(11)	2431(9)
C(21)	-4289(21)	9381(13)	3437(11)
C(22)	-5300(16)	9377(11)	2402(10)
N(23)	-4634(15)	8626(9)	1780(8)
C(24)	-5392(17)	8606(11)	833(9)
C(25)	-4702(22)	7838(12)	142(11)
C(26)	-5455(22)	7849(13)	- 826(11)
C(27)	-6868(22)	8684(14)	-1137(11)
C(28)	-7536(19)	9456(13)	- 484(11)
C(29)	-6839(17)	9432(11)	514(10)
N(30)	-7527(14)	10177(9)	1165(9)
C(31)	-6767(18)	10165(11)	2093(11)
C(32)	-7559(20)	11066(12)	2768(11)

Table 4.4 Fractional atomic co-ordinates (x 10^4)

Te-I(1)	2.886(2)	Te-I(2")	4.245(2)
Te-I(2)	2.911(2)		
Te-I(1')	3.761(2)		
Te-I(3)	3.788(2)		
Te-C(1)	2.136(11)	I(3)-C(21)	2.161(25)
Te-C(12)	2.140(12)	I(4)-C(32)	2.190(25)
C(1)-C(2)	1.51(2)	C(21)-C(22)	1.52(2)
C(2)-N(3)	1.28(2)	C(22)-N(23)	1.31(2)
C(2)-C(11)	1.42(2)	C(22)-C(31)	1.41(2)
N(3)-C(4)	1.39(2)	N(23)-C(24)	1.35(2)
C(4)-C(5)	1.40(2)	C(24)-C(25)	1.39(2)
C(4)-C(9)	1.41(2)	C(24)-C(29)	1.43(2)
C(5)-C(6)	1.37(2)	C(25)-C(26)	1.37(2)
C(6)-C(7)	1.41(2)	C(26)-C(27)	1.41(2)
C(7)-C(8)	1.37(2)	C(27)-C(28)	1.35(2)
C(8)-C(9)	1.49(2)	C(28)-C(29)	1.40(2)
C(9)-N(10)	1.35(2)	C(29)-N(30)	1.34(2)
N(10)-C(11)	1.32(2)	N(30)-C(31)	1.32(2)
C(11)-C(12)	1.51(2)	C(31)-C(32)	1.50(2)
I(1)-Te-I(2)	176.5(1)	I(2)-Te-C(12)	87.6(4)
I(1)-Te-I(1')	95.7(1)	I(1')-Te-I(3)	125.4(1)
I(1)-Te-I(3)	80.5(1)	I(1')-Te-C(1)	71.9(4)
I(1)-Te-C(1)	90.3(4)	I(1')-Te-C(12)	157.7(4)
I(1)-Te-C(12)	89.3(4)	I(3)-Te-C(1)	160.9(4)
I(2)-Te-I(1')	86.6(1)	I(3)-Te-C(12)	76.8(4)
I(2)-Te-I(3)	100.3(1)	C(1)-Te-C(12)	86.4(4)
I(2)-Te-C(1)	87.9(4)		
Te-C(1)-C(2)	107(1)	I(3)-C(21)-C(22)	112(2)
C(1)-C(2)-N(3)	118(2)	C(21)-C(22)-N(23)	115(2)
C(1)-C(2)-C(11)	119(2)	C(21)-C(22)-C(31)	124(2)
N(3)-C(2)-C(11)	123(2)	N(23)-C(22)-C(31)	121(2)
C(2)-N(3)-C(4)	117(2)	C(22)-N(23)-C(24)	119(2)
N(3)-C(4)-C(5)	119(2)	N(23)-C(24)-C(25)	121(2)
N(3)-C(4)-C(9)	120(2)	N(23)-C(24)-C(29)	120(2)
C(5)-C(4)-C(9)	121(2)	C(25)-C(24)-C(29)	119(2)
C(4)-C(5)-C(6)	119(2)	C(24)-C(25)-C(26)	120(2)
C(5)-C(6)-C(7)	120(2)	C(25)-C(26)-C(27)	120(2)
C(6)-C(7)-C(8)	121(2)	C(26)-C(27)-C(28)	121(2)
C(7)-C(8)-C(9)	120(2)	C(27)-C(28)-C(29)	120(2)
C(8)-C(9)-N(10)	120(2)	C(28)-C(29)-N(30)	120(2)
C(8)-C(9)-C(4)	118(2)	C(28)-C(29)-C(24)	119(2)
N(10)-C(9)-C(4)	122(2)	N(30)-C(29)-C(24)	120(2)
C(9)-N(10)-C(11)	116(2)	C(29)-N(30)-C(31)	118(2)
N(10)-C(11)-C(12)	117(2)	N(30)-C(31)-C(32)	115(2)
N(10)-C(11)-C(2)	122(2)	N(30)-C(31)-C(22)	121(2)
C(12)-C(11)-C(2)	121(2)	C(32)-C(31)-C(22)	124(2)
C(11)-C(12)-Te	106(1)	C(31)-C(32)-I(4)	111(2)

Table 4.5 Distances (Å) and angles(°). (Prime and double prime refer to equivalent positions -x, 1-y, 1-z, and -1-x, 1-y, 1-z).

(a) Complexed organic residue

C(1)	-0.02	C(2)	0.00	N(3)	0.03	C(4)	0.02
C(5)	-0.01	C(6)	-0.02	C(7)	0.00	C(8)	-0.01
C(9)	0.03	N(10)	0.00	C(11)	0.01	C(12)	-0.01
Te*	-0.19	I(1)*	2.68	I(2)*	-3.06		

(b) Free organic ligand

C(21)	-0.10	C(22)	0.02	N(23)	0.02	C(24)	0.05
C(25)	0.02	C(26)	0.01	C(27)	-0.05	C(28)	-0.06
C(29)	0.01	N(30)	0.04	C(31)	0.03	C(32)	0.00
I(3)*	1.83	I(4)*	2.01				

(c) Basal plane of tellurium co-ordination octahedron

Te	-0.05	I(1')	-0.06	I(3)	0.08
C(1)	0.18	C(2)	-0.15	I(1)*	2.81
I(2)*	-2.93	I(2")*	-1.02		

Table 4.6 Deviations of atoms (Å) from mean planes. (Atoms not used in defining the planes are marked with an asterisk E.s.d.'s are ca. 0.03 Å for C and N, 0.005 Å for Te and I).

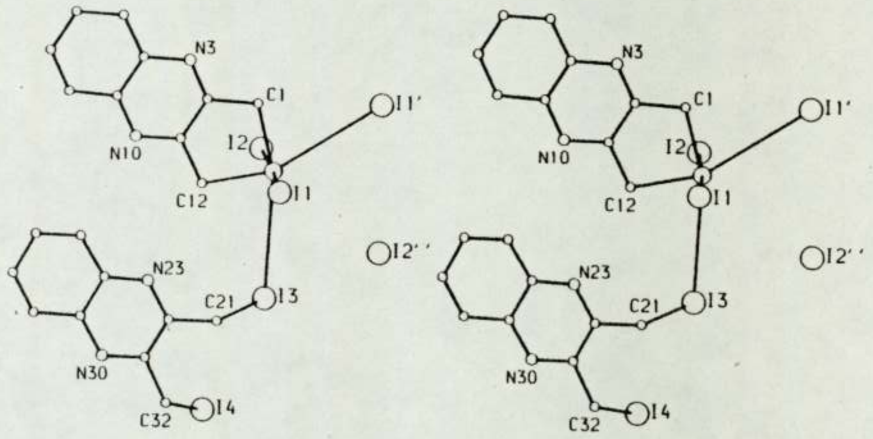


Figure 4.6 Stereoscopic pair showing atom numbering scheme of $C_{10}H_8N_2TeI_2$-$C_{10}H_8N_2I_2$

excellent agreement with previous results(69,70) and with the sum of single bond covalent radii, 2.14 Å(83). The axial Te-I bond lengths, 2.886(2) and 2.911(2) Å fall into the range ca. 2.95± 0.2 Å(70), generally considered to be characteristic of covalent bonding, although somewhat longer than the sum of the covalent radii of Te and I 2.70 Å(83). The equatorial Te-I bonds, on the other hand have lengths characteristic of secondary bonding(118), ca. 3.8±0.2 Å(70), generally trans to Te-C bonds. Similar octahedral coordination occurs in a dimethyltellurium diiodide(100), 1,1-diiodo-3,4-benzo-1-telluracyclopentane(69) and in the adduct $Me_2TeI_2.I_2$(119).

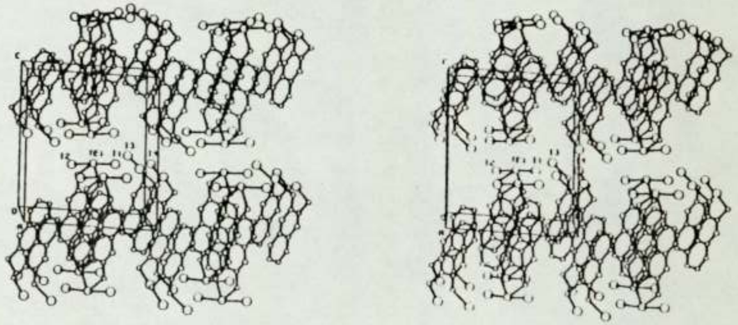
The next closest Te-I interaction involves a centrosymmetrically related iodine atom translated one cell length along x, Te....I(2")=4.245(2) Å, which is close to the van der Waals distance 4.35 Å(83). If this interaction is significant, I(2") would link the dimers into chains along x. I(2") is situated ca. 1 Å from the basal plane of the octahedron (Table 4.6) in the gap left by the large I(1')-Te-I(3) angle (Figure 4.7). The angles I(2")-Te-(1')I(3) are 70.4(1) and 57.2(1) respectively. Weak interactions clustered around the tellurium lone pair of electrons in the basal plane appear to be common in organotellurium(IV) derivatives(120).

The shortest I....I distance is 3.864(2) Å, between I(2") and I(3), which is considerably less than the sum of the van der Waals radii, 4.30 Å[(83)] but greater than distances which would be considered to indicate a bonding interaction(119,121). The packing in the crystal is characterised by parallel stacking of quinoxaline residues, as shown in Figures 4.7 and 4.8. There are however no abnormally short contact distances.

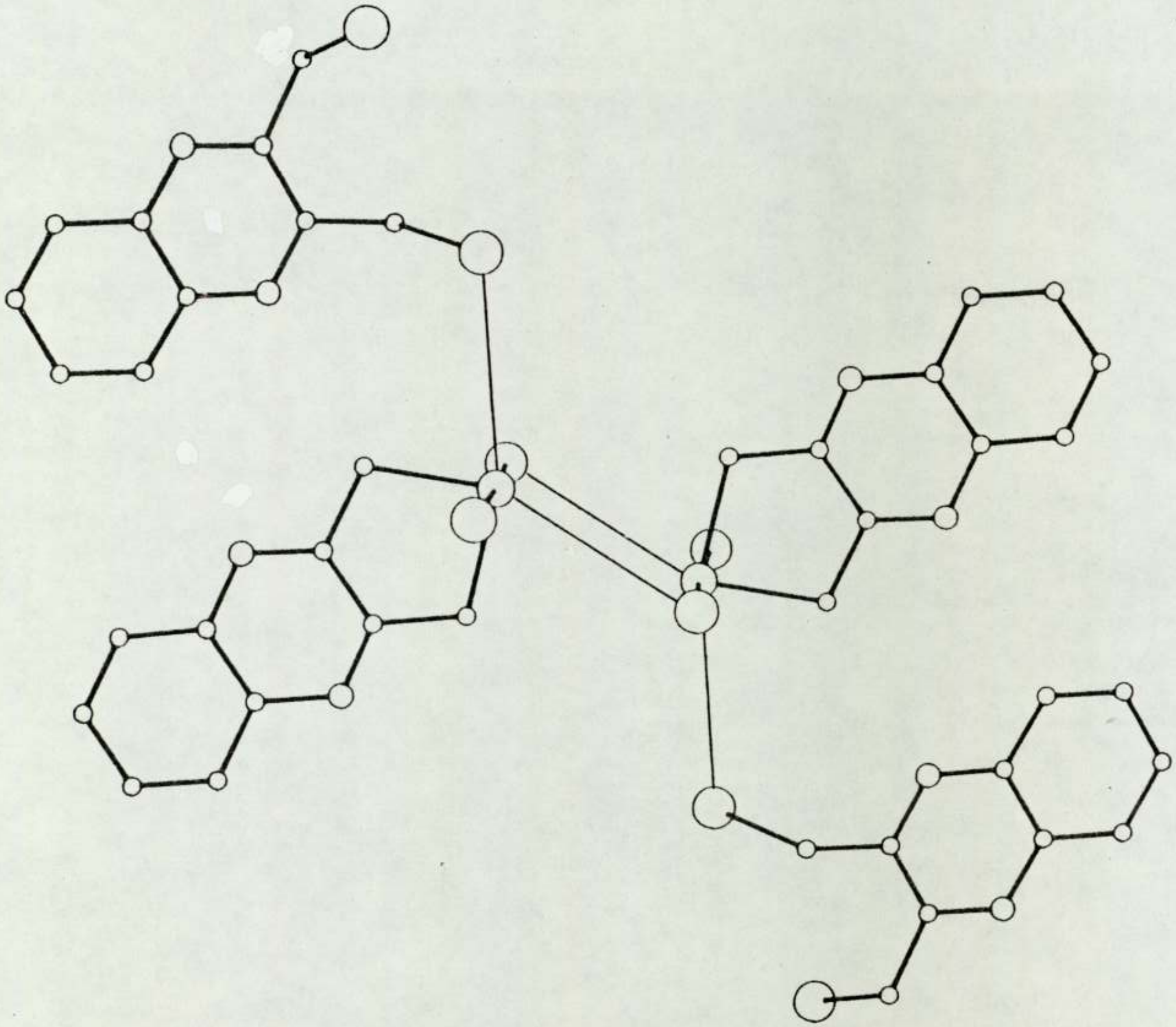
Bond lengths and angles in the organic moieties are unexceptional. The tellurium bound residue is planar to within ± 0.03 Å with the tellurium atom displaced 0.19 Å from the plane in the direction of I(2). The carbon framework of the free ligand is somewhat more distorted from planarity, with deviation of up to 0.10 Å occurring (Table 4.6). The two aromatic rings of the quinoxaline residue are each planar to within ± 0.02 Å but the two rings are twisted relative to each other making a dihedral angle of ca. $2\frac{1}{4}^{\circ}$.

McCullough and coworkers have noted correlation between colour and the type and degree of secondary bonding. The yellow colour of compound (X) supports the weak bonding found in crystal structure, whereas deep violet colour of VIII suggests strong intermolecular interactions.

Compound (X) which is a charge-transfer complex of the organotellurium (IV) iodide (VIII) and organic diiodide (V IIa) is especially important in the view of our previous suggestions regarding CT in organotellurium chemistry.

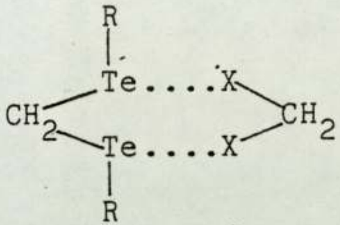


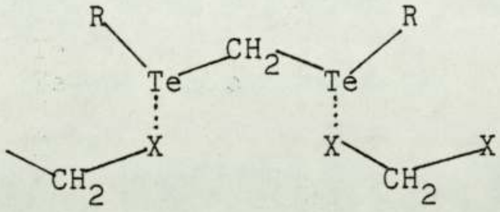
<u>Figure 4.7</u> Stereoscopic packing diagram of $C_{10}H_8N_2TeI_2$-$C_{10}H_8N_2I_2$



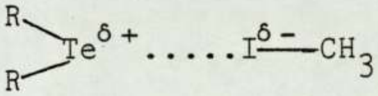
<u>Figure 4.8</u> Expanded diagram of $C_{10}H_8N_2TeI_2$-$C_{10}H_8N_2I_2$ showing intermolecular interactions

McWhinnie et al$^{(122)}$ have reported recently that the reaction of 'NaTeR' with dibromo- or diiodomethane gave a pale yellow (CH_2Br_2) or deep yellow (CH_2I_2) solids containing one mole of dihalomethane- $(RTe)_2CH_2.(CH_2X_2)$ (X=Br,I). It has been suggested that the material is a charge-transfer complex - two possible formulations are illustrated below.





It was suggested some years back$^{(31)}$ that the oxidative addition reaction of diorganotelluride with methyl iodide underwent an intermediate which was a charge-transfer complex (XII).



(XII)

It was also observed that there were two main stages in the overall reaction between I_2 and $Ar_2Te_2$$^{(123)}$. The initial reaction is fast. This is followed by a slower subsequent stage. The fast stage involves the formation of 1:1 and 1:2 donor:acceptor complexes, that is $Ar_2Te_2:I_2$ and $Ar_2Te_2:2I_2$ respectively.

The X-ray diffraction analysis of (X) confirms all these postulations.

4.4 Crystal Structure of 3,4-quinoxalino-1-telluracyclopentane

It has been pointed out earlier in the introductory section of this chapter that the compound 3,4-quinoxalino-1-telluracyclopentane, $C_{10}H_8N_2Te$, may exhibit strong intermolecular interactions such as those observed for 1,2-benzoisotellurazole(102) where the short intermolecular contacts (Te....N) of 2.4 Å explain the high melting point and low solubility of the compound. Our speculation seemed justified since newly synthesised 3,4-quinoxalino-1-telluracyclopentane has a melting point (160°C) higher than its corresponding diiodide (148-150°C) and it has relatively low solubility in ether compared to analogous tellurides indicating some kind of intermolecular interaction. The crystal and molecular structure of the above compound was studied to establish the nature and extent of these interactions.

4.4.1 Experimental

$C_{10}H_8N_2Te$ was prepared by the reduction of 1,1-diiodo-3,4-quinoxalino-1-telluracyclopentane with hydrazine hydrate and recrystallised from ether. The crystals grow as fine yellow needles which are stable in the presence of air and light. A density column was prepared from tetrabromoethane and carbontetrachloride and the density was found to be 1.91 g cm^{-3} at 20°C.

4.4.2 X-Ray Measurements*

After preliminary oscillation and equiinclination Weissenberg photographs had been taken, a crystal with dimensions 0.76 mm x 0.08 mm x 0.08 mm was mounted along the z axis of an Enraf-Nonius CAD-4 diffractometer equipped with a scintillation counter and a graphite monochrometer. The automatic centering, indexing and least-squares routines of the instrument were applied to 20 reflections to obtain lattice parameters using Mo-Kα radiation. The intensity data were collected in the $\omega/2\theta$ scan mode. The scan range (ω^{o}) was calculated from ($1.0 + 0.35 \tan\theta$) and scan speed varied from 0.5-2.5^{o}minute^{-1} depending on the intensity. 2030 reflections were scanned in the range $2<\theta<25^{o}$. Two standard reflections were monitored every two hours and the orientation of the crystal was checked every one hundred reflections. No decomposition or movement of the crystal was observed during the collection of the reflection intensities. Lorentz and polarisation corrections were applied to the data and 744 independent observed reflections with $F>7\sigma(F)$ were used in the structure analysis. The crystals were found to be tetragonal with hkl present only when h+k+l=2n, hko present only when h=2n and ool present only when l=4n consistent with the space group $I4_{1/a}$ and the number of formula weights in the unit cell is 16.

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* Supplementary data: observed and calculated structure factors have been submitted to J.Chem.Soc. Dalton Transactions (1983) for publication.

4.4.3 Crystal Data

$C_{10}H_8N_2Te$, M = 283.78, Tetragonal,

a = b = 25.315(8) Å, c = 6.010(11) Å

V = 385.38 $Å^3$, D_m = 1.91 g cm^{-3}, D_c = 1.96 g cm^{-3}

Z = 16

F(000) = 2143.14, λ(Mo-Kα) = 0.71069 Å

μ = 30.47 cm^{-1}

4.4.4 Solution and Refinement of the Structure

The atomic parameters for tellurium were found by direct methods using SHELX76(124) and confirmed by analysis of the Patterson map. The positions of the carbon and nitrogen atoms were found by using a difference map. Anisotropic temperature factors were calculated for all non-hydrogen atoms. The positional and temperature factor parameters for tellurium, carbon and nitrogen were refined by four cycles of blocked full-matrix least squares refinement with hydrogen atoms included in the calculation in their theoretical positions. The weighting scheme used was $W = 1.3438[\sigma^2(F) + 0.000F^2]$ and the refinement converged to R = 0.0408 and R_w = 0.0380.

Fractional coordinates (x 10^4) and anisotropic temperature factors (x 10^4) are given in Tables 4.7 and 4.8 respectively.

Atom	x	y	z
Te	5749(0)	2500(0)	6217(0)
C(1)	6404(5)	2759(5)	8200(25)
C(2)	6768(5)	2307(5)	8167(25)
C(3)	6754(4)	1960(5)	6344(30)
C(4)	6365(5)	2082(6)	4593(26)
N(1)	7043(4)	1535(4)	6187(25)
N(2)	7096(4)	2230(4)	9812(21)
C(5)	7418(5)	1795(5)	9734(25)
C(6)	7772(5)	1675(6)	11491(29)
C(7)	8072(5)	1242(6)	11326(36)
C(8)	8060(6)	891(6)	9639(33)
C(9)	7729(6)	994(5)	7915(28)
C(10)	7390(5)	1439(5)	7939(26)

Table 4.7 Atomic co-ordinates with standard deviations in parentheses (x 10^4)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Te	317(6)	557(7)	542(6)	161(8)	- 62(8)	2(6)
C(1)	282(70)	488(88)	308(121)	116(79)	78(71)	51(65)
C(2)	250(72)	429(85)	292(117)	- 3(75)	- 25(71)	34(65)
C(3)	223(62)	423(74)	344(93)	-129(104)	- 20(89)	58(58)
C(4)	342(77)	581(96)	492(125)	92(89)	-224(83)	6(74)
N(1)	386(64)	543(74)	322(77)	-133(90)	- 47(80)	- 2(56)
N(2)	335(61)	347(74)	278(74)	- 61(65)	119(62)	42(59)
C(5)	252(75)	437(87)	307(99)	-101(80)	65(73)	- 49(66)
C(6)	457(82)	728(104)	119(93)	- 29(99)	- 29(91)	111(82)
C(7)	363(82)	896(121)	375(103)	104(128)	88(112)	197(83)
C(8)	637(116)	466(103)	721(160)	73(102)	113(114)	326(90)
C(9)	560(97)	276(79)	523(124)	-104(80)	111(94)	156(75)
C(10)	342(83)	366(83)	424(116)	43(82)	5(79)	- 26(70)

Table 4.8 Atomic thermal parameters and their estimated standard deviations in parentheses

4.4.5 Results and Discussion

It may be seen from Table 4.9 that the unit cell dimensions and space group of 3,4-quinoxalino-1-telluracyclopentane differ from those of the related compounds that have been studied. The structure consists of one discrete repeating molecule (Figure 4.9) whose bond lengths and angles are given in Table 4.10. The intramolecualr Te-C bond lengths 2.123(14) Å and 2.145(13) Å are in good agreement with the sum of the single bond radii 2.140 Å(83) but longer than those reported for benzisotellurazole(102) [2.08(1), 2.09(1)Å] and dibenzotellurophene(80)[2.089(5), 2.084(5) Å]. The $C_{(1)}$-Te-$C_{(4)}$ angle [80.7(5)°] is smaller than those found for dibenzotellurophene[81.7(2)°] and 1,1-diiodo-3,4-benzo-1-telluracyclopentane [86.0(5)°]. The C-N bonds Av = 1.34 Å are again longer than those in benzoisotellurazole [1.27(2) and 1.28(2)°] but shorter than those found in a molecule of o-(phenylazophenyl-CN')-tellurium(II) chloride structure(42) [1.45(3), 1.43(2)°Å]. The other intramolecular distances and angles are in agreement with the reported values.

The two aromatic moieties of the quinoxaline residue are almost planar (Table 4.11). The distances of the non-hydrogen atoms from the least squares planes is small, the largest being 0.0383 Å and the angle between the planes is calculated to be 0.80°. The tellurium bonded residue is distorted from planarity and is tilted so that the tellurium

Formula	Symmetry	Space Gp	a(Å)	b(Å)	c(Å)	β	V	Z
$C_{10}H_8N_2Te$ (Ref.this work)	Tetragonal	$I4_1/a$	25.314(8)	25.314(8)	6.0098(11)		3851.38	16
C_7H_5NTe (Ref.102)	Monoclinic	$P2_1/a$	21.516(10)	13.696(6)	7.969(4)	112.71	2166.2	12
$C_{12}H_8Te$ (Ref. 80)	Orthorhombic	$P2_12_12_1$	12.621(7)	16.192(7)	4.637(2)		947.6(8)	4
$C_8H_8TeI_2$ (Ref. 69)	Monoclinic	$P2_1/c$	12.599(3)	9.899(2)	9.268(1)	104.89(1)	1117.1(4)	4
$C_{12}H_9N_2TeCl$ (Ref. 92)	Triclinic	$P\bar{1}$	9.376(6)	11.504(7)	12.616(9)	85.83(5) =105.73(4) =115.82(3)	1177.5	4

Table 4.9 Comparison of the unit cell of 3,4-quinoxalino-1-telluracyclopentane with those of related compounds

P_1 Plane defined by Te, $C_{(1)}$, $C_{(2)}$, $C_{(3)}$ and $C_{(4)}$

$0.4260x + 0.6988y - 0.5744z + 8.7094 = 0$

P_2 Plane defined by $C_{(2)}$, $C_{(3)}$, $N_{(1)}$, $N_{(2)}$, $C_{(5)}$ and $C_{(10)}$

$0.7029x + 0.5321y - 0.4720z + 12.8464 = 0$

P_3 Plane defined by $C_{(5)}$, $C_{(6)}$, $C_{(7)}$, $C_{(8)}$, $C_{(9)}$ and $C_{(10)}$

$0.7119x + 0.5253y - 0.4661z + 13.0214 = 0$

P_4 Plane defiend by Te, $C_{(1)}$, $C_{(2)}$, $C_{(3)}$, $C_{(4)}$, $N_{(1)}$, $N_{(2)}$, $C_{(5)}$, $C_{(6)}$, $C_{(7)}$, $C_{(8)}$, $C_{(9)}$ and $C_{(10)}$

$0.6590x + 0.5674y - 0.4937z + 12.0177 = 0$

P_5 Plane defined by $C_{(2)}$,$C_{(3)}$,$N_{(1)}$,$N_{(2)}$,$C_{(5)}$,$C_{(6)}$,$C_{(7)}$, $C_{(8)}$, $C_{(9)}$ and $C_{(10)}$

$0.7073x + 0.5297y - 0.4682z + 12.9305 = 0$

Atom	P_1	P_2	P_3	P_4	P_5
Te	-0.2276	-1.0124	-1.0770	-0.6801	-1.0341
$C_{(1)}$	0.2531	-0.0605	-0.1075	0.1963	-0.0720
$C_{(2)}$	-0.1422	-0.0123	-0.0433	0.1641	-0.0171
$C_{(3)}$	-0.1419	0.0125	-0.0193	0.1832	0.0054
$C_{(4)}$	0.2585	-0.0187	-0.0677	0.2290	-0.0348
$N_{(1)}$	-0.5275	-0.0012	-0.0196	0.1014	-0.0029
$N_{(2)}$	-0.4922	0.0010	-0.0153	0.1127	0.0049
$C_{(5)}$	-0.8872	0.0101	0.0085	0.0481	0.0191
$C_{(6)}$	-1.3239	-0.0200	-0.0052	-0.0549	-0.0023
$C_{(7)}$	-1.7091	-0.0226	0.0059	-0.1257	0.0006
$C_{(8)}$	-1.7606	-0.0383	-0.0099	-0.1512	-0.0170
$C_{(9)}$	-1.3406	0.0005	0.0134	-0.0439	0.0136
$C_{(10)}$	-0.9276	-0.0101	-0.0126	0.0226	-0.0034

Dihedral angles, deg

[Plane 1]-[Plane 2]	21.69
[Plane 2]-[Plane 3]	0.80
[Plane 1]-[Plane 5]	22.07

Table 4.10 Equations of least-squares planes and deviations (Å) of atoms from the planes

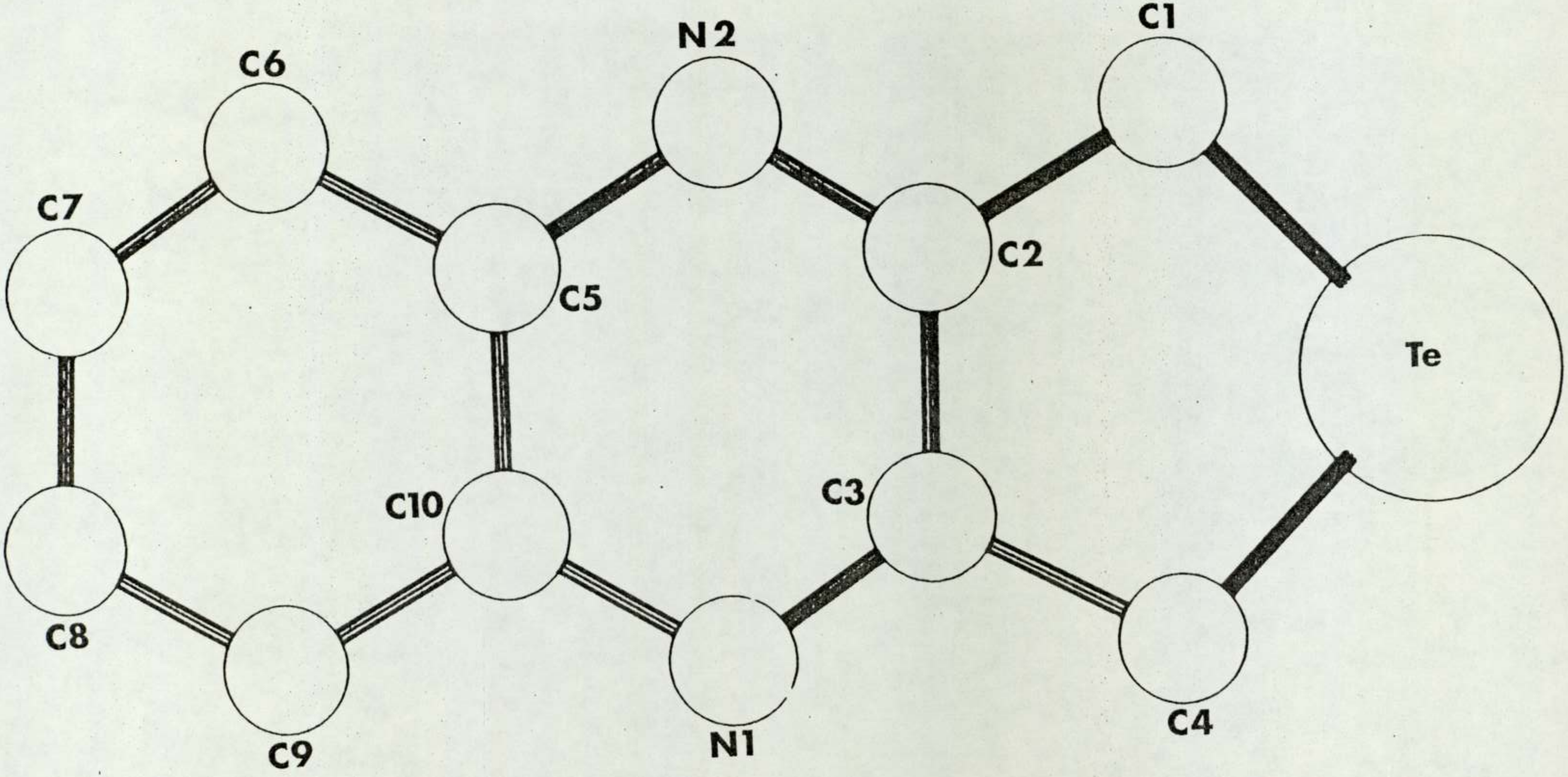


Figure 4.9 Molecular structure of $C_{10}H_8N_2Te$

$Te-C_{(1)}$	2.145(13)
$Te-C_{(4)}$	2.123(14)
$C_{(1)}-C_{(2)}$	1.469(16)
$C_{(2)}-C_{(3)}$	1.405(19)
$C_{(2)}-N_{(2)}$	1.305(16)
$C_{(3)}-C_{(4)}$	1.473(19)
$C_{(3)}-N_{(1)}$	1.304(14)
$N_{(1)}-C_{(10)}$	1.392(18)
$N_{(2)}-C_{(5)}$	1.370(15)
$C_{(5)}-C_{(6)}$	1.419(19)
$C_{(6)}-C_{(7)}$	1.337(17)
$C_{(7)}-C_{(8)}$	1.349(23)
$C_{(8)}-C_{(9)}$	1.359(20)
$C_{(9)}-C_{(10)}$	1.417(18)
$C_{(10)}-C_{(5)}$	1.407(18)

$C_{(1)}-Te-C_{(4)}$	80.7(.5)
$C_{(2)}-C_{(1)}-Te$	103.9(.9)
$C_{(3)}-C_{(2)}-C_{(1)}$	118.8(1.3)
$C_{(3)}-C_{(2)}-N_{(2)}$	120.9(1.2)
$N_{(2)}-C_{(2)}-C_{(1)}$	120.3(1.3)
$C_{(4)}-C_{(3)}-C_{(2)}$	116.3(1.1)
$C_{(4)}-C_{(3)}-N_{(1)}$	119.8(1.5)
$N_{(1)}-C_{(3)}-C_{(2)}$	123.9(1.5)
$C_{(3)}-C_{(4)}-Te$	105.5(1.0)
$C_{(3)}-N_{(1)}-C_{(10)}$	116.3(1.4)
$N_{(2)}-C_{(5)}-C_{(6)}$	121.5(1.4)
$N_{(2)}-C_{(5)}-C_{(10)}$	120.7(1.4)
$C_{(6)}-C_{(5)}-C_{(10)}$	117.7(1.3)
$C_{(5)}-N_{(2)}-C_{(2)}$	118.1(1.2)
$C_{(5)}-C_{(6)}-C_{(7)}$	118.7(1.7)
$C_{(6)}-C_{(7)}-C_{(8)}$	125.7(1.8)
$C_{(7)}-C_{(8)}-C_{(9)}$	117.4(1.4)
$C_{(8)}-C_{(9)}-C_{(10)}$	121.3(1.5)
$N_{(1)}-C_{(10)}-C_{(5)}$	120.0(1.2)
$N_{(1)}-C_{(10)}-C_{(9)}$	120.8(1.4)
$C_{(9)}-C_{(10)}-C_{(5)}$	119.1(1.4)

Table 4.11 Bond distances (Å) and angles(deg) in $C_{10}H_8N_2Te$

atom is displaced by 0.6801 Å from the least squares plane of the molecule being below $C_{(1)}$ and $C_{(5)}$. The dihedral angle between the tellurium bonded residue plane and the quinoxaline residue is 22.07°.

The packing arrangement of the molecule viewed along the z axis is shown in Figure 4.10 where the screw axis and glide plane symmetry may be observed. The tellurium atoms are arranged in layers and there are short intermolecular bonds between the tellurium atoms in the same layers, e.g., between the symmetry related positions x, y, z and 1-x, $\frac{1}{2}$+y, z(3.791 Å) and $\frac{1}{4}$+y, $\frac{3}{4}$-x, $\frac{3}{4}$-z and $\frac{1}{4}$+y, x-$\frac{1}{4}$ and $\frac{3}{4}$-z (3.998 Å). These Te....Te distances are less than the sum of the van der Waal's radii (4.40 Å) and thus indicate weak bonding. Shorter intermolecular contacts involving tellurium in relation to crystal packing and properties have been reported for some other compounds e.g., tetratelluratetracene (3.701 Å)(33), polymorph B of bis(2-naphthylditelluride) (3.707 Å)(125) and diphenyltelluroxide (3.537 Å)(126).

The intermolecular Te....N distances 4.087 and 4.090 Å provide no evidence of secondary bonding between the atoms as has been found in 1,2-benzoisotellurazole(102) where the shortest intermolecular Te....N distance is 2.46 Å and the sum of van der Waal's radii are 3.70 Å. However the short intermolecular contacts between the tellurium atoms explains the high melting point and low solubility

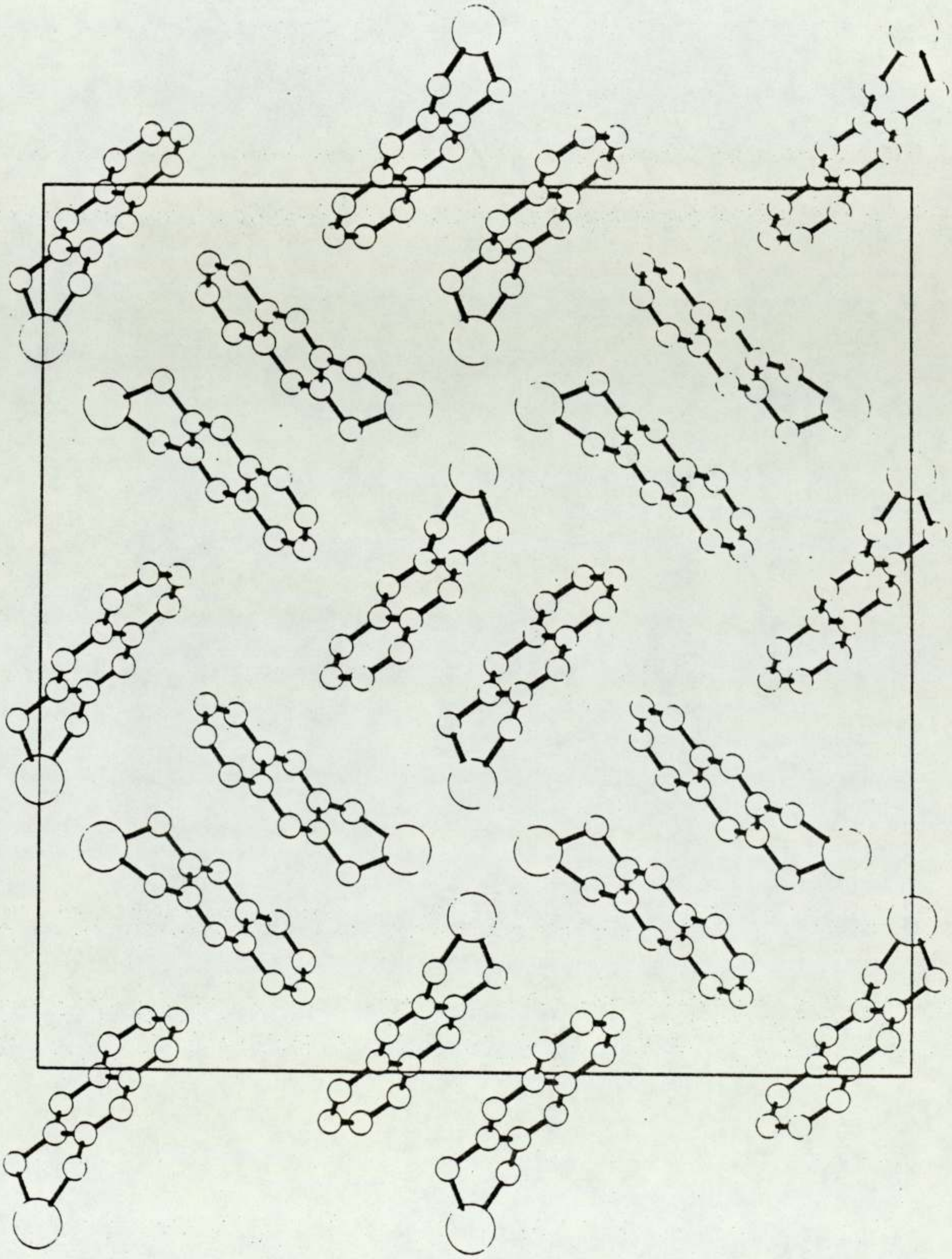
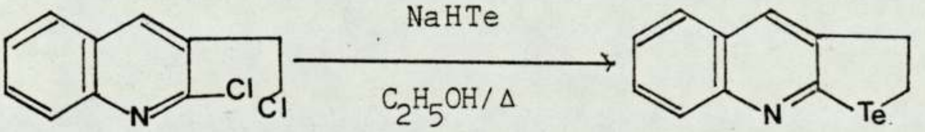


Figure 4.10 Packing diagram of $C_{10}H_8N_2Te$

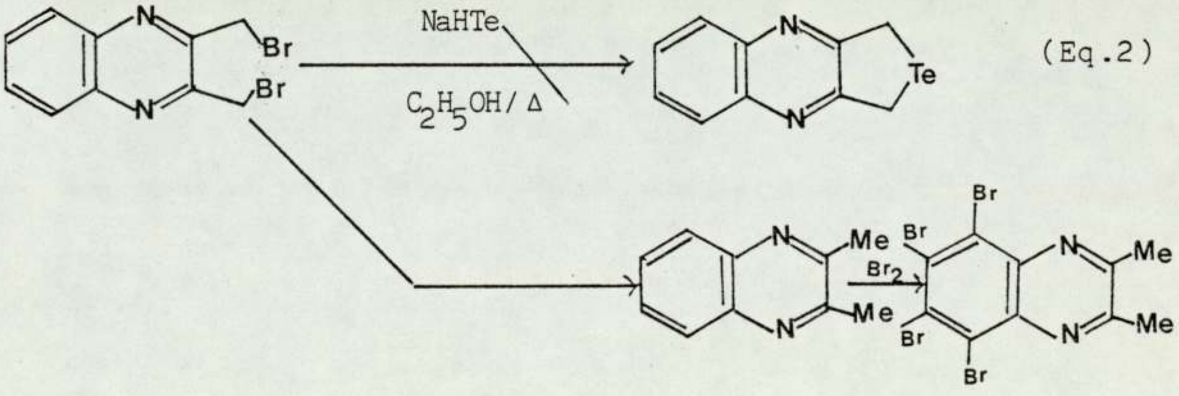
of the compound and may help in the segregation of donor and acceptor stacks when used in the preparation of charge-transfer complexes.

4.5 Attempted Direct Synthesis of 3,4-quinoxalinc-1-telluracyclopentane

In view of the reported synthesis of 2,3-dihydrotelluroquinolines$^{(106)}$ by heating 2-chloro-3-(2'-chloroethyl)-quinolines with an ethanol solution of sodium hydrogentelluride (Eq.1), it was thought that the reaction 2,3-bis(bromomethyl)quinoxaline with Na^+HTe^- might afford the desired tellurium(II) heterocycle (Eq.2).



(Eq.1)

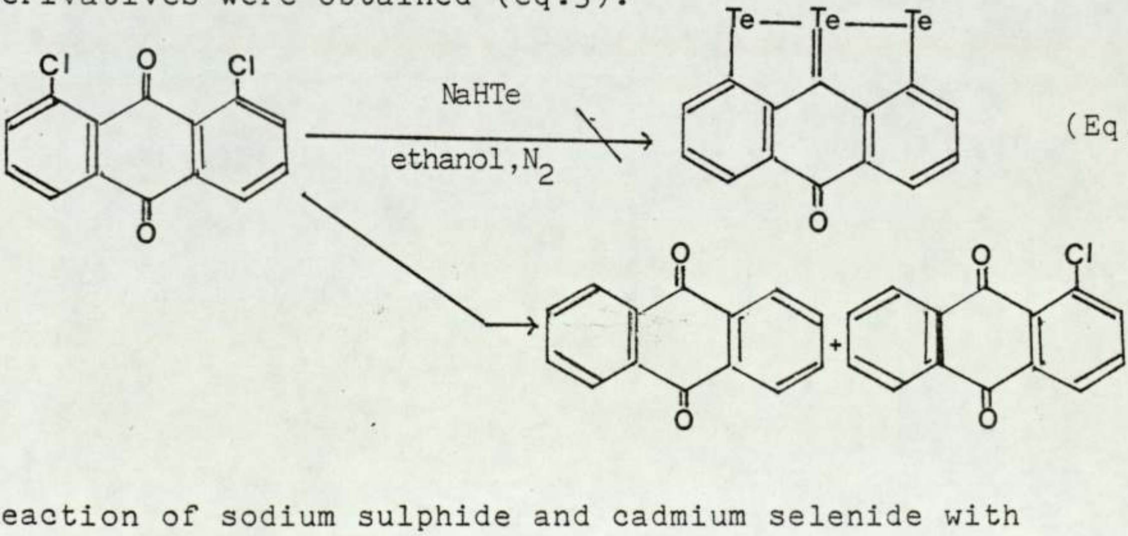


(Eq.2)

(XIII) (XIV)

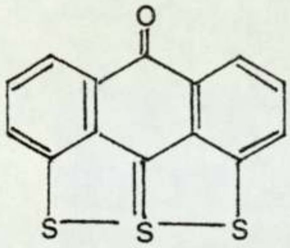
Two different methods were employed for the telluration-reaction. Firstly, the dibromide was refluxed with sodium hydrogentelluride, prepared in situ, in ethanol. The work up of the reaction provided a pure, colourless compound which contained no tellurium and was identified as 2,3-bis(methyl)quinoxaline(XIII) on the basis of melting point, elemental analyses, N.M.R. and bromination derivative. The melting point is close to the literature value(110). The N.M.R. in CCl_4 showed a multiplet at 7.03-8.05 (aromatic, 4H) , and a singlet at 2.5 ppm (6 protons). The bromination of XIII in ether yielded XIV which was identified by melting point.

It was recently shown that sodium hydrogentelluride was a useful debrominating agent(127). Even sodium hydrogenselenide caused debromination when reacted with chalkone dibromide(128). Secondly, when 2,3-bis(bromomethyl) quinoxaline was treated with NaHTe using a phase transfer technique(107), a yellow coloured ethereal extract was obtained on work up. On evaporation of the solvent, the compound starts decomposing. Similarly when 1,8-dichloroanthroquinone was refluxed with NaHTe, dehalogenated derivatives were obtained (eq.3).

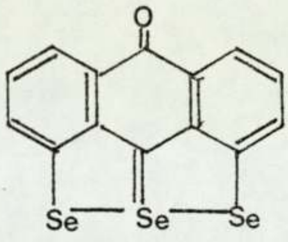


(Eq.3)

Reaction of sodium sulphide and cadmium selenide with 1,8-dichloroanthroquincne in DMF is reported to give trithiapentalene(XV)and triselenopentalene derivatives(129)(XVI).



(XV)



(XVI)

It was hoped that the tellurium isologues, if sucessfully synthesised, may act as ideal donors in the synthesis of 'organic metals'.

4.6 Charge-transfer Complex 3,4-quinoxalino-1-tellura cyclopentane(II) with TCNQ ($C_{10}H_8N_2Te:C_{12}H_4N_4$) (XVII)

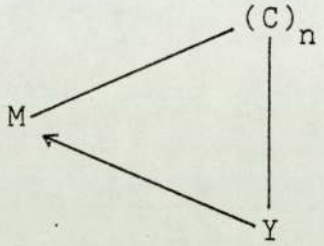
A 1:1 complex was obtained quantitatively by refluxing and evaporating an acetonitrile solution of IX and TCNQ. The complex is microcrystalline and black in colour. The solid state E.S.R. signal has a g-value of ~ 2 consistent with a free electron of a π radical. The E.S.R. signal was sharp and no hyperfine splitting was observed. It would be interesting to see whether these intermolecular interactions in IX have been strong enough to prevent the formation of mixed stack structure in the CT complex. However, the I.R. data are not very encouraging. The $\nu_{(CN)}$ stretching frequency is observed as singlet at 2178 cm^{-1} (for Li^+TCNQ^-, 2180 cm^{-1}), indicating that the complex is ionic and hence an insulator. Maybe, we have been able to synthesise a complex with segregated stacks of 3,4-quinoxalino-1-telluracyclopentane(IX) and TCNQ, however a structure in which every TCNQ carries a complete negative charge, leads one to expect an insulator, or semiconducting properties. The factors which govern the incomplete charge transfer or partial oxidation, are not yet clearly understood. Electrochemical oxidation has been used frequently to get partially oxidised products. The A.P. of the donor was measured by the extrapolated voltage difference method, and was 9.65 eV (1 eV = 96 kJ). Another way to prevent complete charge-transfer is to use a weaker acceptor than TCNQ. A donor with electron-withdrawing substituents (CO, NO_2) may also lead to incomplete charge-transfer.

CHAPTER FIVE

NEW ORGANOTELLURIUMS DERIVED FROM <u>ORTHO</u>METALLATION OF SCHIFF BASES

5.0 Introduction

Organometallic intramolecular-coordination compounds, as the term indicates, are those which have at least one metal-carbon bond and at least one ligand group forming an intramolecular coordination bond (i).

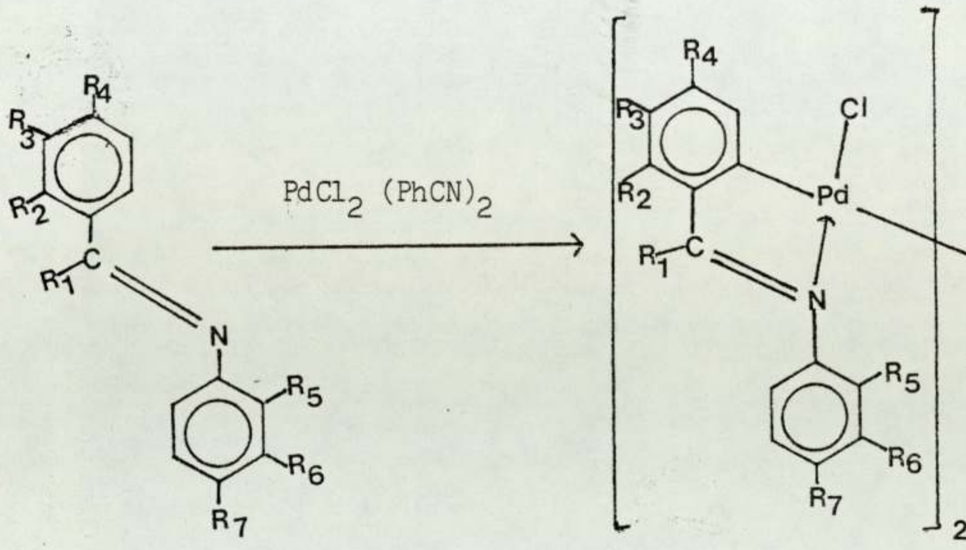


M=Metal
Y= Coordinating group

(i)

Introduction of built in donors such as oxygen, nitrogen, phosphorus and sulphur, into the ortho-position of the aryl group in organometallic compounds has been shown to be a useful method of stabilising organometallic compounds. The orthometallated complexes generally, form strain-free five-membered ring structures. Recently, a number of such complexes have been reported and the existence of ring structures has been confirmed by different physical techniques. Most of the orthometallation studies have involved transition metals and literature concerning main group metals is sparse, despite the importance of lithiation, mercuration and thallation reactions.

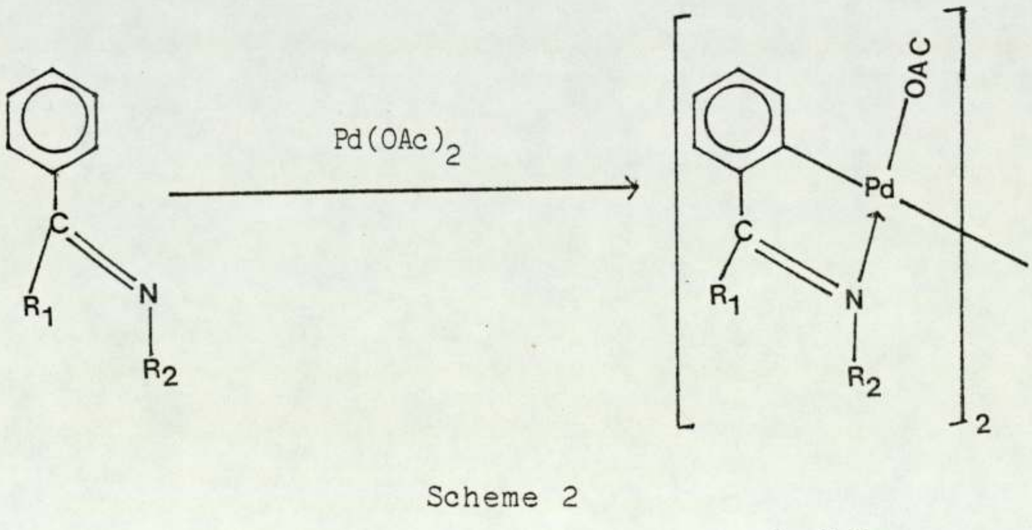
Molnar and Orchin(130) reported first in 1969 that the reaction of benzylideneaniline with bis(benzonitrile) palladium(II)chloride easily affords the five-membered ring structure (Scheme 1).



R_1-R_7:H,OMe,Cl,NO_2, Me,Ph

Scheme 1

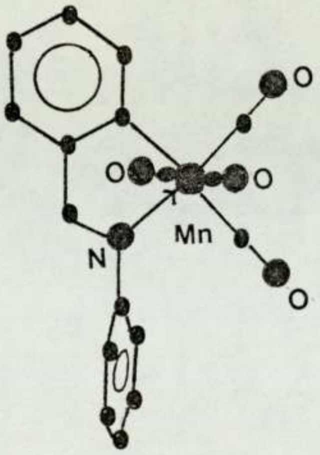
The reaction of benzylideneaniline with palladium(II) acetate affords di-μ-acetato-bis-(N-phenylbenzaldimine-C^2,N) palladium(II) (Scheme 2)(131)



Scheme 2

R_1=H,Me
R_2=Me,Ph,p-MeC_6H_4,o-MeC_6H_4

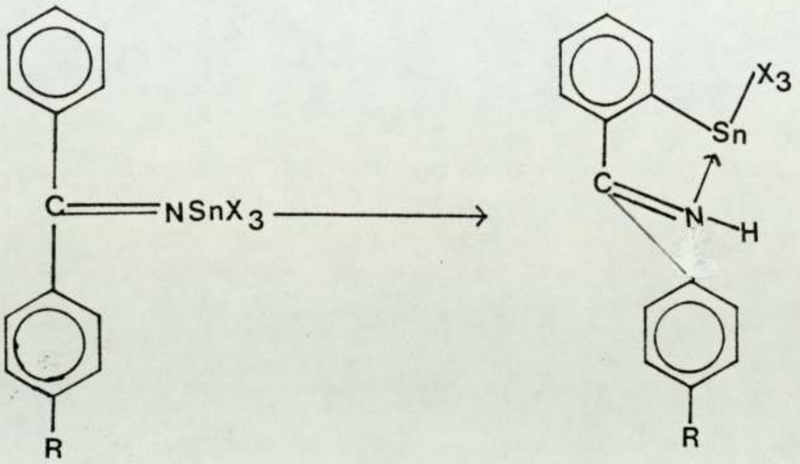
Reactions between benzylideneaniline and metal carbonyl complexes also afforded orthometallated derivatives. For example [$MeM(CO)_5$] (M=Mn,Re) gave five-membered ring structures(132). The crystal structure (ii) of tetracarbonyl[2-(N-phenyl formimidoyl-C^2,N)phenyl]manganese was determined by X-ray diffraction(133).



(ii)

A detailed review of the orthometallation reactions of transition metals(134) would be out of the scope of the present study and therefore, will not be presented here.

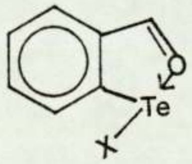
It has been pointed out that for orthometallation reactions to occur, the metal centre should be coordinatively unsaturated and highly electrophilic(135). These two properties of tin and tellurium have frequently been used to obtain the orthometallated derivatives. In 1977, Fitzsimmons and coworkers(135) reported the first example of orthometallation reactions in organotin chemistry where the ligand group was imino. The benzylideneaminotin trihalides afforded novel tin hererocycles via an easy rearrangement (Scheme 3).



X=Cl,Br
R=H,Cl or Me

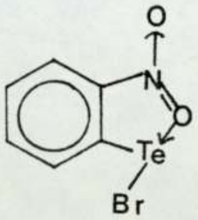
Scheme 3

The five-coordinate state of the tin atoms was confirmed by the quadrupole splitting in their Mössbauer spectra. In organotellurium chemistry, orthometallation has been successfully used to stabilise the rather unstable organotellurenyl compounds. As an example, o-carbonyl-containing groups have been shown, both in solution and in solid state, to coordinate to tellurium atom in aryltellurenyl halides (iii)(136).



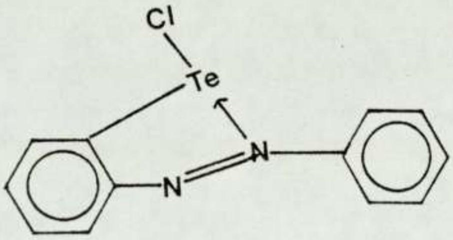
(iii)

More recently it has been shown that the o-nitro group also serves as an efficient stabilising ligand (iv)(137).



(iv)

A similar intramolecular chelation is thought to enhance the stability of a number of organosulphenyl-containing (TeII) specimens such as $\mathrm{Te[S(CH_2)_nCOOH]_2}$(138). In 1979 McWhinnie et al(42) reported first examples of compounds in which azobenzene is <u>ortho</u>metallated by tellurium (IV) and tellurium (II). The crystal and molecular structure of the latter was described(v).



(v)

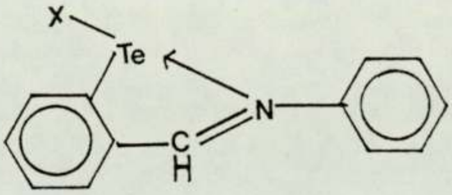
An attempt to interpret the ^{125}Te Mössbauer data was also made. It will be relevant to mention the general features of the interpretation of ^{125}Te Mössbauer parameters. The ^{125}Te quadrupole splittings are influenced mainly by the imbalance in the 5p orbital population, whereas the isomer shifts are influenced by the population of both 5s and 5p orbitals. The Mössbauer data for (v) are given below:

	Isomer Shift δmmsec^{-1}(vs Cu/Sb)	Quadrupole Splitting Δmmsec^{-1}	$\Gamma_{\frac{1}{2}}$
(v)	0.63±0.05	11.76±0.05	6.6
p-$EtOC_6H_4TeI_2^-$	0.46±0.05	13.93±0.05	7.1

The value of chemical isomer shift, for the azobenzene derivative of tellurium(II), 0.63 mmsec^{-1} is relatively large compared to other tellurium(II) compounds e.g.,Ph_2Te 0.18 mmsec^{-1}, and is also larger than the value of 0.46mmsec^{-1} obtained for the anion p-$EtOPhTeI_2^-$. The quadrupole splitting value of 11.76 mmsec^{-1} is considerably lower than the calculated value of ∿14 mmsec^{-1}. The reduction of Δ was explained in terms of removal of electrons from Te(Pz) to the π-system. It is possible that tellurium p orbital could interact with the π-orbitals associated with the chelate ring. Such delocalisation, if it did occur, would decrease the p-orbital imbalance hence Δ; also s-electrons would be less shielded hence a more positive δ.

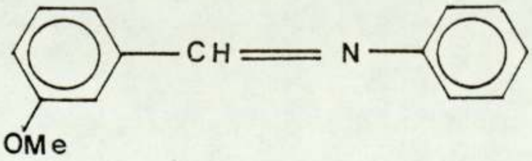
We have been interested in the design and synthesis of organotellurium heterocycles which are planar and have delocalised π-systems, to study their donor properties in CT interactions.

The similarity in the structure of azobenzene and benzylideneaniline indicated that the orthometallated derivatives of the latter may also be synthesised. The Schiff bases have a potentially planar structure, thus allowing an interaction of a tellurium p-orbital and the π-system of the chelate ring. If an interaction took place, there is the possibility of getting a planar organotellurium(II) heterocycle(vi) with delocalised π-electrons.

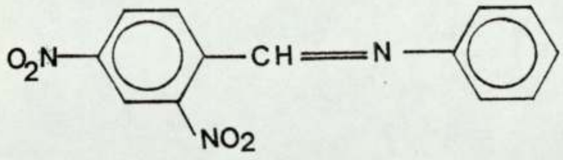


(vi)

As mentioned in Chapter One, such systems may prove to be of interest in our attempts to form "organic metals". A previous worker in the laboratory attempted the direct metallation of some typical Schiff bases by tellurium tetrachloride and tetrabromide and found that the reaction of tetrahalides gave only ionic compounds containing the protonated bases(139). Arylmetal (IB) compounds have proved valuable for their transmetallating properties and this characteristic has been used in the present study for the synthesis of desired organotellurium compounds. The two Schiff bases (vii, viii) chosen are shown below:

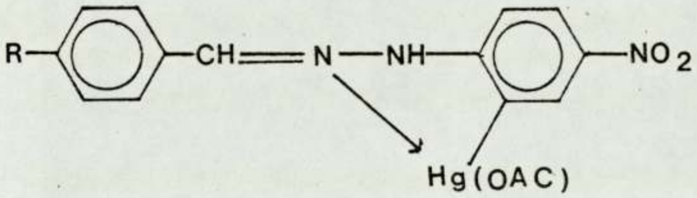


(vii)



(viii)

Phenylhydrazones have both amino and imino ligands and it has been observed by Butler et al(140) that treatment of substituted phenylhydrazones with mercuric acetate resulted in exclusive mercuration of the ortho-site of the N-phenyl ring. The ortho-mercuration occurred by an internal cyclometallation process involving the imino moiety (ix).



$R=H, CH_3, CH_3O$

(ix)

The transmetallation of such systems with tellurium tetrachloride would afford isostructural heterocycles.

5.1 Experimental

5.1.1 Preparation of m-methoxybenzylideneaniline(141)

Freshly distilled aniline (13.5 g) was added to m-methoxybenzaldehyde (12.8 g). The reaction mixture was heated to 100°C for 10 minutes and then allowed to cool to room temperature. The aqueous and organic layers were separated and the latter was extracted in benzene and dried over anyhdrous sodium sulphate. After filtration the solvent was removed on a rotary film evaporator to give the base. The purity of the liquid was checked by I.R. and N.M.R.

5.1.2 Preparation of 2,4-dinitrobenzylideneaniline

2,4-Dinitrobenzaldehyde (9.8 g) was added to freshly distilled aniline (4.7 g) in ethanol (60 ml). The reaction mixture was heated on a waterbath for 10 minutes. The red coloured reaction mixture was then filtered and the filtrate allowed to cool to room temperature. The product crystallised as orange needles.

5.1.3 Preparation of tellurium tetrabromide(142)

Tellurium tetrabromide was obtained by cautious addition of bromine to powdered tellurium. The excess of bromine was removed by passing a stream of dry nitrogen while the flask containing the substance was warmed. Crude tetrabromide was recrystallised from dry ether and dried under vacuum.

5.1.4 Preparation of tellurium tetraiodide(143)

A very concentrated telluric acid solution was mixed at room temperature and slightly more than stoichiometric quantity of fuming hydroiodic acid. A heavy grey precipitate of tellurium tetraiodide separated. After filtration, the precipitate was dried and washed with carbon tetrachloride until the wash fluid was colourless.

5.1.5 Attempted synthesis of orthometallated m-methoxybenzylideneaniline

5.1.5.1 Reaction of m-methoxybenzylideneaniline with tellurium tetrachloride

To a solution of m-methoxybenzylideneaniline (2.11 g, 10 m mole) in benzene (50 ml) was added tellurium tetrachloride (2.69 g, 10 m mole). The reaction mixture was stirred and refluxed for 5 hours. The yellow precipitate was filtered, washed with dry ether and dried in vacuo. The dried yellow product has a melting point of 180°C (d).

5.1.5.2 Synthesis of(m-methoxy benzylideneaniline-C^2,N) mercury(II)chloride

Equimolar amounts of the m-methoxybenzylideneaniline (10.55 g, 50 m mole) and mercuric acetate (15.99 g, 50 m mole) and dry methanol (250 ml) were placed in a round bottomed flask. The reaction mixture was refluxed and stirred for 24 hours. After refluxing,the reaction mixture was cooled and then lithium chloride (5 g, 120 m mole) dissolved in hot methanol, was added and the resulting precipitate was filtered, washed with ether and dried in vacuo. The solid was recrystallised from chloroform to yield a colourless product of m.p. 140-142°C. The yield of the above reaction was 40% and during recrystallisation a chloroform insoluble product was obtained m.p. 172°C(d).

5.1.5.3 Synthesis of 2,4-dinitro(benzylideneaniline-C^2,N) mercury(II)chloride

A mixture of 2,4-dinitrobenzylideneaniline (7.13 g) and mercuric acetate (10.8 g) in methanol (200 ml) was stirred and refluxed for 12 hours. After the reaction period the solution was allowed to cool to room temperature. Lithium chloride (4 g) dissolved in hot methanol (50 ml) was added to the cooled reaction mixture and stirred for 15 minutes. The resulting slurry was poured into water (500 ml); the precipitate filtered, washed with methanol and ether to give a yellow product of m.p. 172-174°C (d).

5.1.6 Preparation of benzaldehyde p-nitrophenylhydrazone(144)

A mixture of p-nitrophenylhydrazine (7.65 g) and benzaldehyde (5.30 g) and a few drops of acetic acid in ethanol (150 ml) was refluxed for 15 minutes to get a homogeneous solution. The clear solution,upon cooling, afforded crystalline benzaldehyde p-nitrophenylhydrazone. The precipitate was filtered off and recrystallised from ethanol to yield orange coloured crystalline product of m.p. 192°C.

The p-nitrophenylhydrazones from p-tolualdehyde and p-methoxybenzaldehyde were similarly prepared (Table 5.1)

5.1.7 Mercuration Reactions of p-Nitrophenylhydrazones(140)

5.1.7.1 Tolualdehyde p-nitrophenylhydrazone

To a solution of the hydrazone (2.0 g) in acetic acid (150 ml) containing acetic anhydride (3 ml) was added mercuric acetate (2.50 g) and the mixture was stirred at room temperature for 70 minutes followed by 1½ hours at 55-60°C and 15 hours at 40-45°C. The precipitated p-tolualdehyde o-acetoxymercurio-p-nitrophenylhydrazone was filtered off and recrystallised from chloroform to yield the product of m.p. 192°C. p-Tolualdehyde-o-acetoxymercurio-p-nitrophenylhydrazone (8.34 g) was stirred and refluxed in methanol (100 ml) for 30 minutes. At the completion of the reflux period, the reaction mixture was cooled to room temperature and lithium chloride (4 g) dissolved in hot methanol (50 ml) was added and the resulting thick mixture was stirred for an additional 30 minutes. Afterwards, it was poured into water (500 ml) and the precipitate was filtered, washed with a small amount of ethanol and dried. Upon recrystallisation from chloroform a deep-red p-tolualdehyde o-chloromercurio p-nitrophenylhydrazone was obtained m.p. 238-240°C.

5.1.7.2 Benzaldehyde-p-nitrophenylhydrazone and Anisaldehyde Derivatives

o-Chloromercurio-derivatives of benzaldehyde-p-nitrophenylhydrazone and anisaldehyde were prepared in a similar fashion (Table 5.2)

5.1.8 Attempted Synthesis of(m-Methoxybenzylideneaniline-C^2,N)tellurium(IV)trichloride

(m-Methoxybenzylideneaniline- C^2,N)mercury(II)chloride (0.85 g, 2 m mole) and tellurium tetrachloride were refluxed in sodium dried dioxane (20 ml) for 4 hours under dry nitrogen. After cooling, the precipitate was removed by filtration. The filtrate was concentrated on a rotary evaporator and ether was added to precipitate the compound but no solid was obtained. The precipitate melted with decomposition at 140°C.

5.1.9 Synthesis of(m-Methoxybenzylideneaniline-C^2,N)-tellurium(IV)tribromide

A solution of(m-methoxybenzylideneaniline- C^2,N)mercury(II) chloride (2.14 g, 5 m mole) and tellurium tetrabromide (2.23 g, 5 m mole) in dry chloroform (90 ml), was refluxed for 5 hours under nitrogen. After cooling the reaction mixture to room temperature, the precipitated mercuric halide was filtered off. The filtrate was concentrated to 20 ml and ether added to get the desired product m.p. 180°C.

Similar treatment of p-tolualdehyde o-chloromercurio-p-nitrophenylhydrazone and anisaldehyde o-chloromercurio-p-nitrophenylhydrazone gave the tribromide derivatives (Table 5.3).

5.1.10 Reaction of(m-Methoxybenzaldehyde- C^2,N)mercury(II) chloride with TeI_4

The reaction of tellurium tetraiodide (3.178 g, 5 m mole) and mercurated Schiff base (2.14 g, 5 m mole) was carried out in the same way as the tellurium tetrabromide reaction. After filtration, the solution was concentrated and petroleum ether (40-60°C) added. A sticky, black residue was obtained which could not be solidified and purified by treating with activated charcoal. The reaction was repeated in dioxane and the same problem was encountered. To confirm whether tellurium tetraiodide was affected, a blank experiment was done. Tellurium tetraiodide was refluxed for 5 hours and no change in tellurium tetraiodide was observed.

5.1.11 Reactions of Mercurated Schiff Bases with p-Ethoxyphenyltellurium trichloride

(m-Methoxybenzylideneaniline-C^2,N)mercury(II)chloride (1.33 g) and (4-ethoxyphenyl)tellurium(IV)trichloride (1.06 g) were mixed in 1,4-dioxane (20 ml). The mixture was stirred and refluxed for 3 hours. On cooling, crystals of $HgCl_2$.2-dioxane separated and were removed. Concentration of the solution followed by the addition of petroleum ether (40-60°C) gave the crude dichloride. The crude material was treated with activated charcoal in boiling chloroform (50 ml) to yield pale yellow product m.p. 176°C.

Reactions of p-tolualdehyde o-chloromercurio-p-nitrophenylhydrazone and anisaldehyde o-chloromercurio-p-nitrophenylhydrazone with (4-ethoxyphenyl)tellurium trichloride were performed similarly (Table 5.4).

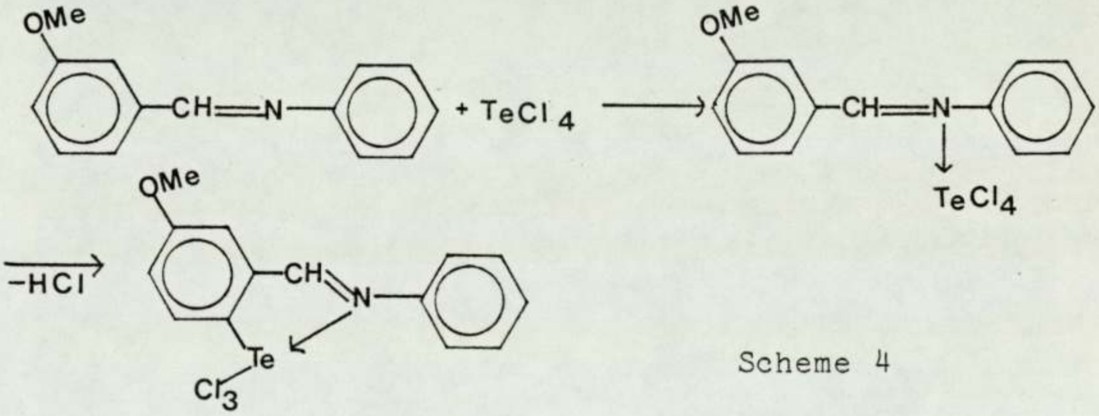
5.1.12 Reduction of (m-Methoxybenzylideneaniline-C^2,N) tellurium(IV)tribromide

(m-Methoxybenzylideneaniline-C^2,N)tellurium(IV)tribromide (0.428 g) was dissolved in warm methanol (30 ml). To the resulting yellow solution, hydrazine hydrate in methanol (10 ml) was added dropwise while the solution was stirred at room temperature. The colour changed to dark red after the addition of a few drops of the reducing agent and black precipitation was also observed. The solution was filtered to remove precipitated tellurium and a slow stream of nitrogen was passed to evaporate the solvent to yield a dark red coloured solid. The crude product was crystallised from chloroform to m.p. 110°C(d).

5.2 Results and Discussion

Tables 5.1, 5.2, 5.3 and 5.4 combine preparative and analytical data. I.R. data are gathered in Tables 5.5 and 5.6.

Orthometallation of m-methoxybenzylideneaniline was attempted by the direct reaction of the base and tellurium tetrachloride following the methods reported for transition metals. It was hoped that σ-N-coordination (Scheme 4) followed by hydrogen chloride elimination, would lead to yield the desired compound.



Scheme 4

The reaction on reflux afforded a yellow precipitate which was insoluble in common organic solvents. The microanalysis showed a great discrepancy between the observed and calculated values for the metallated derivative of the base. Analysis of the infra-red spectrum showed that no orthometallation has taken place. The out-of-plane bending modes γ(CH) have been widely used to characterise mono- and di-substituted benzenes$^{(145)}$. Orthometallation of the base would generate a 1,2-disubstituted benzene and

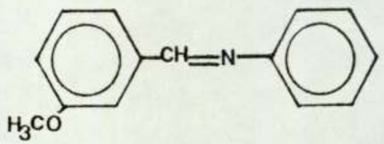
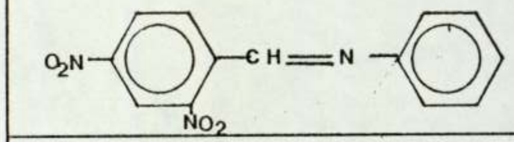
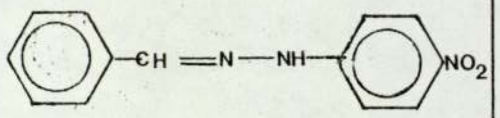
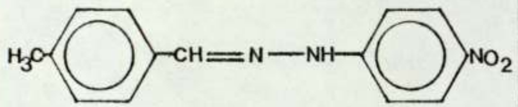
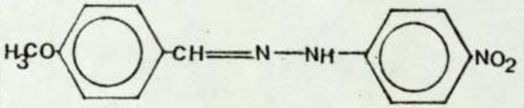
Compound	m.p. °C	Colour	C%(calc)	H%(calc)	N%(calc)
	Liquid	colourless	79.9 (79.5)	6.2 (6.2)	6.7 (6.6)
	126	orange	58.1 (57.5)	3.2 (3.3)	15.7 (15.4)
	192	brownish -red	64.8 (64.7)	4.6 (4.5)	16.9 (17.4)
	209	red	66.1 (65.8)	5.0 (5.1)	16.2 (16.4)
	161	purple	61.6 (61.9)	4.8 (4.8)	15.3 (15.4)

Table 5.1 Analytical data for substrates

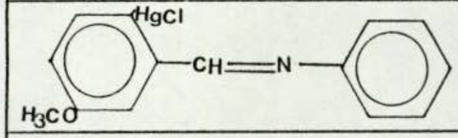
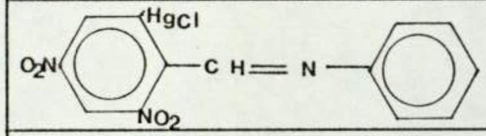
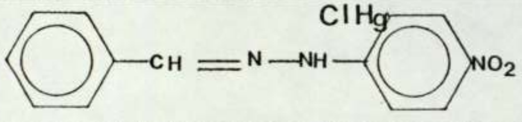
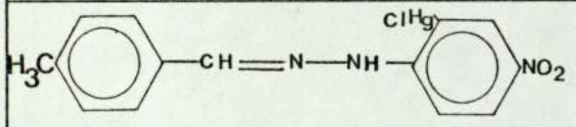
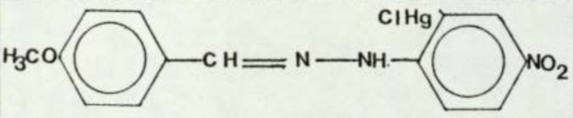
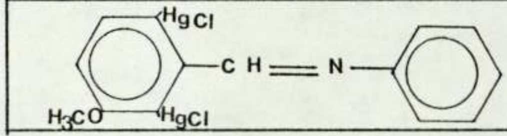
Compound	m.p. °C	Colour	Yield	C%(calc)	H%(calc)	N%(calc)
	140-142	white	40	37.5 (37.6)	3.0 (2.71)	3.8 (3.1)
	172-174 (d)	yellow	90	29.1 (30.8)	1.6 (1.59)	7.6 (8.2)
	228-230	yellow	82	32.1 (32.7)	2.14 (2.11)	8.3 (8.8)
	238-240	red	71	33.9 (34.2)	2.6 (2.46)	8.9 (8.5)
	224-225	red	75	33.2 (33.2)	2.4 (2.38)	8.6 (8.2)
	172(d)	colourless	25	24.7 (24.6)	1.9 (1.62)	2.2 (2.05)

Table 5.2 Analytical data for o-substituted aryl mercury chlorides

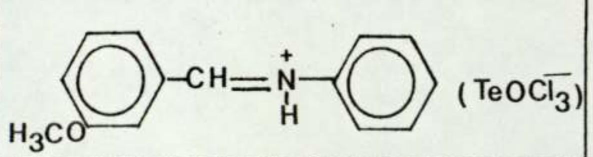
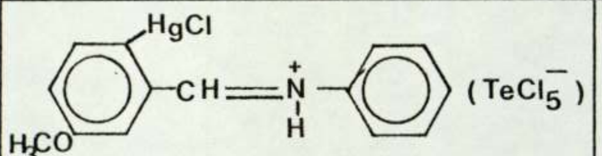
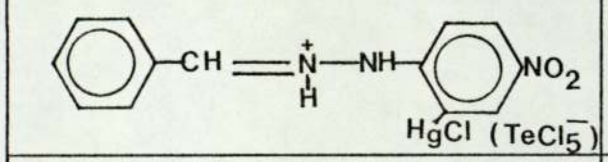
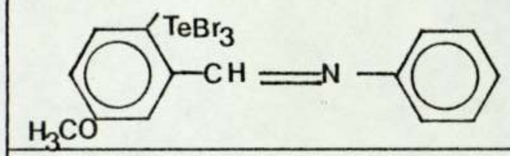
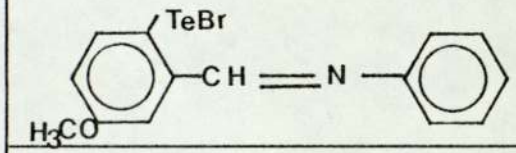
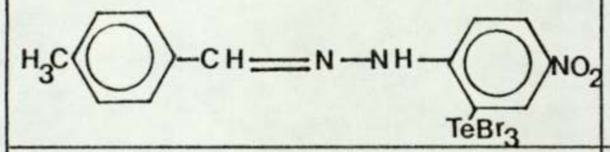
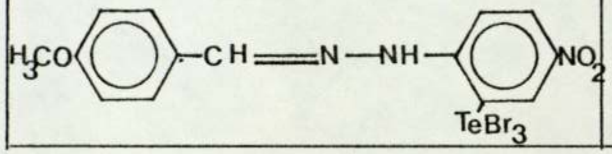
Compound	m.p. °C	Colour	Yield	C%(calc)	H%(calc)	N%(calc)	Te%(calc)
	180(d)	yellow	quantitative	-	-	-	25.3 (27.6)
	140(d)	greenish yellow	quantitative	17.4 (22.3)	2.6 (1.7)	2.6 (1.8)	- -
	165(d)	greenish yellow	quantitative	20.9 (20.4)	1.3 (1.55)	6.1 (5.5)	- -
	180	dark red	42	28.0 (29.0)	2.2 (2.08)	2.6 (2.4)	22.6 (22.9)
	110(d)	dark red	30	39.1 (40.2)	2.9 (2.89)	3.8 (3.3)	31.8 (30.5)
	170(d)	brownish red	40	26.3 (27.0)	1.8 (1.94)	5.4 (6.7)	20.2 (20.5)
	120(d)	brownish red	36	25.6 (26.3)	1.7 (1.89)	5.3 (6.5)	19.7 (20.0)

Table 5.3 Analytical data for organotellurium derivatives

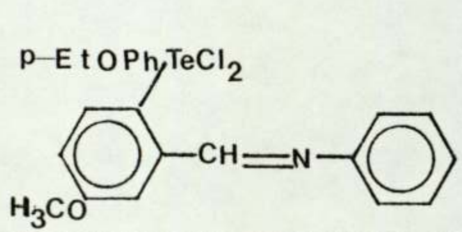
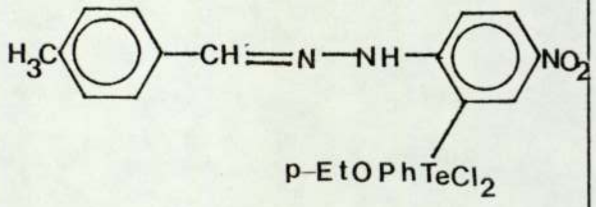
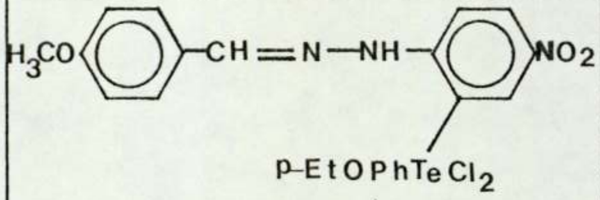
Compound	m.p. °C	Colour	Yield	C%(calc)	H%(calc)	N%(calc)	Te%(calc)
	176-177	pale yellow	70	50.6 (51.1)	4.0 (4.0)	2.2 (2.7)	23.9 (24.6)
	150-151	shiny yellow	67	45.8 (46.0)	3.6 (3.6)	7.4 (7.3)	21.8 (22.2)
	160-162	dark yellow	63	43.1 (44.7)	3.4 (3.5)	7.5 (7.1)	21.1 (21.6)

Table 5.4 Analytical data for organotellurium derivatives

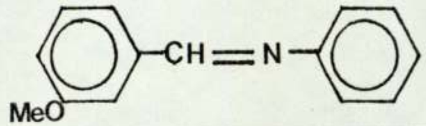
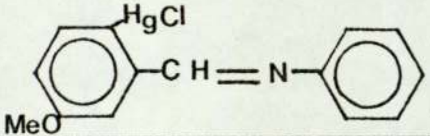
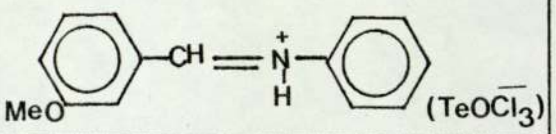
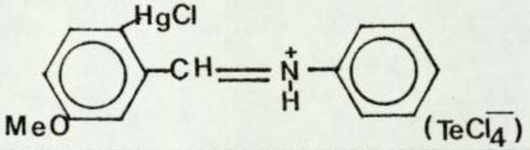
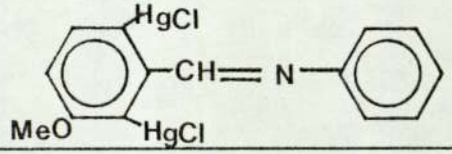
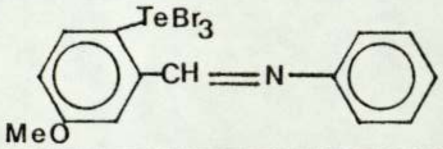
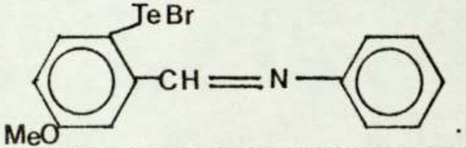
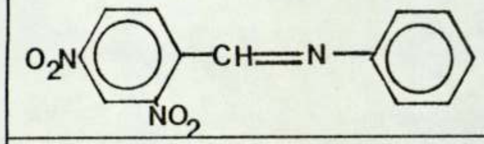
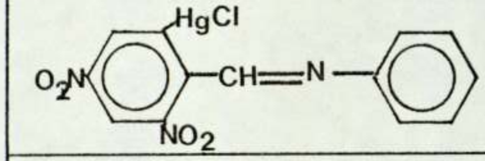
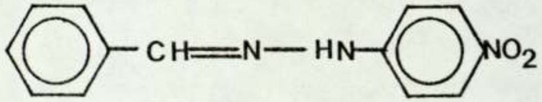
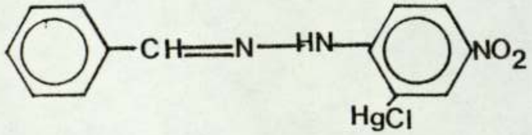
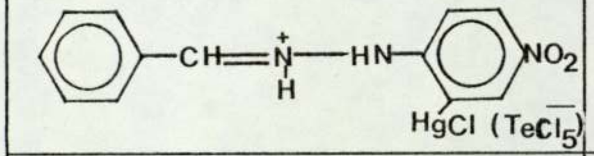
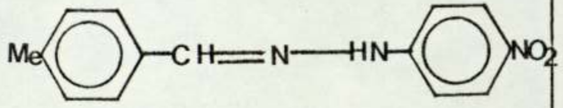
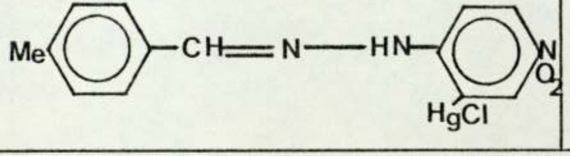
Compound	$\nu_{(C=N)}$	$\nu_{(C-H)}$	$\nu_{(Hg-Cl)}$	$\nu_{(N-H)}$	$\nu_{(Te=O)}$
	1634s, 1604w	698vs	-	-	-
	1628vs, 1600sh	718vs, 688s	326s, 305sh	-	-
	1645s, 1618vs	-	-	3590, 3530	610
	1650s, 1605w	705w	310m	3500br	-
	1626s, 1594s	808vs, 718w, 685s	330s, 306w	-	-
	1624s, 1600vw	721s	-	-	-
	1630w, 1600s	728, 700	-	-	-

Table 5.5 I.R. data/cm^{-1}

Compound	$\nu_{(C=N)}$	$\nu_{(C-H)}$	$\nu_{(Hg-Cl)}$	$\nu_{(N-H)}$	$\nu_{(Te=O)}$
	1612w, 1600s, 1584s	775s, 765, 740, 728, 698	-	-	-
	1600s	775, 765, 740w, 732s, 698	-	-	-
	1608, 1580s	748, 740w, 712s, 680vs	-	3250	-
	1600s, 1580sh, 1560s	810w, 750, 740m, 680s	332s	3280	-
	1598vs	820w, 760vs, 750s, 720w, 698vs	332s, 315w	3500m, 3230s	-
	1614s, 1598vs	820, 720w, 700s	-	3264m	
	1605s, 1585vs	830s, 820w, 722, 705s	330s, 310w	3340, 3280	

<u>Table 5.5</u> continued

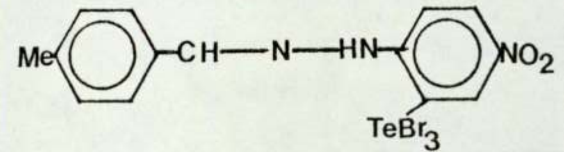
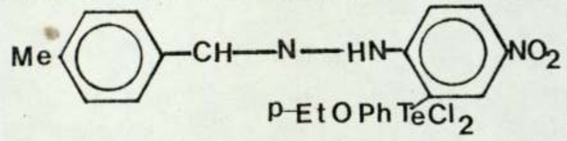
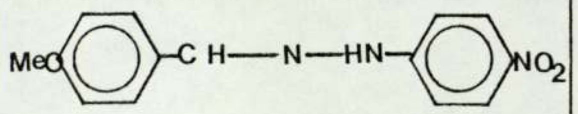
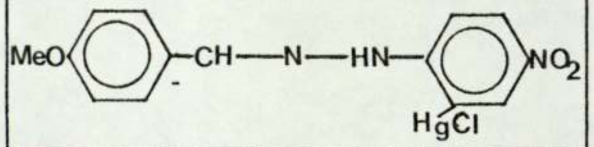
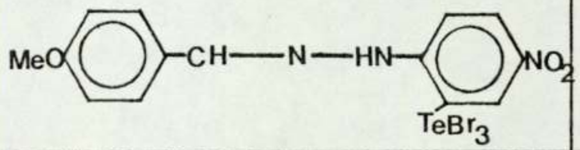
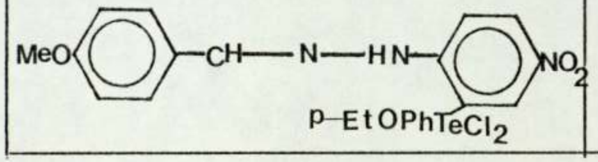
Compound	ν(C=N)	ν(C-H)	ν(Hg-Cl)	ν(N-H)	ν(Te=O)
	1605w,1588m	830,820, 720,705s	-	3400br, 3100	-
	1605,1582s	828,815, 748vs,714	-	3220	
	1620,1608	840,830vs, 800w,721w,700s	-	3280s	
	1612s,1584vs	820,714s	345vs, 300w	3340, 3285	
	1616s	835vs,705w	-	3400br	-
	1665w,1590s	810w,710s	-	3240s	-

Table 5.5 continued

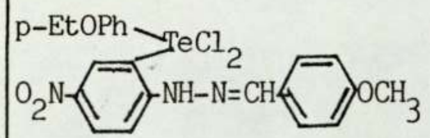
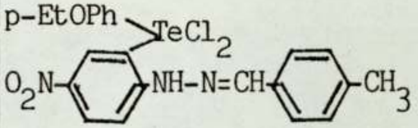
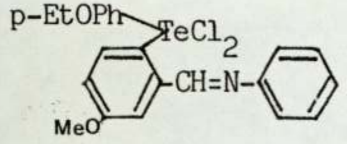
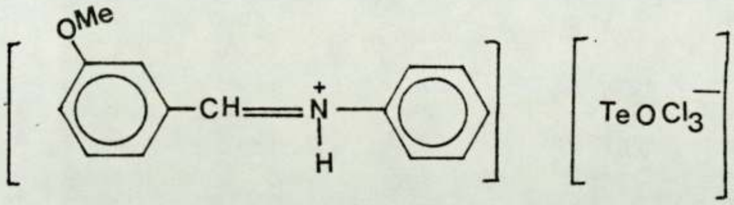
Ph_2TeCl_2 (Ref167)	$(p\text{-}EtOPh)_2TeCl_2$ (Ref168)				Assignment
285		276	271	274	ν_{sym}(Te-Cl)
265		263	260	258sh	ν_{asym}(Te-Cl)
270	298	290	293	291	ν_{sym}(Te-C)
245	238	236 244sh	232 244	232 242	ν_{asym}(Te-C)

Table 5.6 Far I.R. data for some organotellurium derivatives

changes in the 680-850 cm^{-1} region could be expected. No change in this region of the spectrum was noted. However, there were changes in the other regions of the spectrum. It was observed that there was a positive shift of $\sim$20 m^{-1} in the ν(C=N) stretching frequency which is not characteristic of coordination through azomethine group. The coordination of benzylideneamines to palladium(146) results in a shift of the ν(C=N) stretching mode to a lower frequency while the stretching frequency of olefins coordinated to Pt or Pd are reduced about 150 cm^{-1}(147-149). The small negative shift of 26 cm^{-1} was interpreted in terms of coordination through nitrogen and not through the azomethine π system.

In addition the observation of ν(N-H) in the region $\sim$3500 m^{-1} of the yellow substance leads one to conclude that Schiff base has been protonated and the protonation of the imine prevents delocalisation of the azomethine π-system leading consequently to the positive shift of the ν(C=N). Sadekov(150) et al report a positive shift of the ν(C=N) band in the complexes of N-benzylideneanilines with tellurium tetrachloride. This report seems ambiguous in view of the fact that the hydrochloride derivatives of different Schiff bases(139) show a positive shift in the vibrational frequency of ν(C=N). A strong, broad band at $\sim$600 m^{-1} was observed and has been assigned to ν(Te=O). The ν(Te=O) band could only result from the hydrolysis of the tellurium tetrachloride. The reaction of tellurium tetrachloride with the base in absence of any solvent and anhydrous conditions yielded similar product except the fact that no ν(Te=O) was observed.

From the above discussion, it is clear that the Schiff base has been protonated and the following structure(x) is suggested:

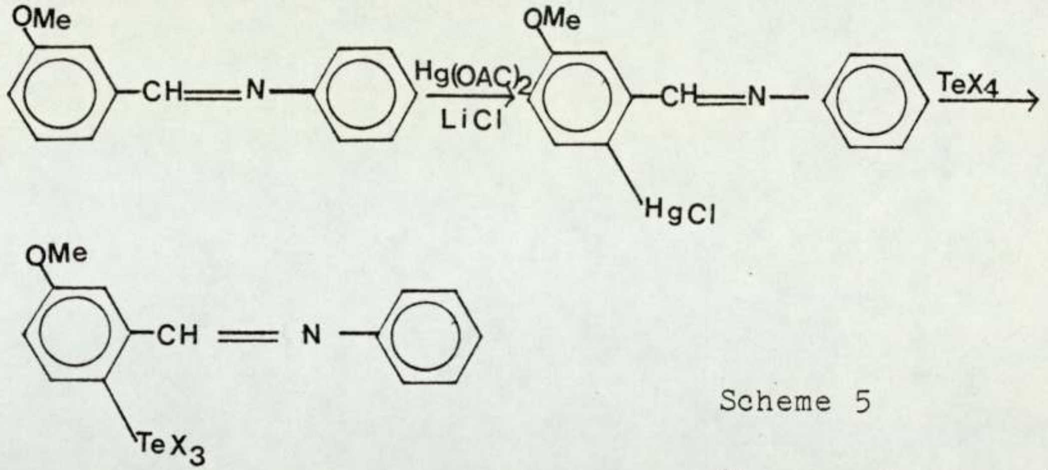


(x)

These results are identical to those observed by Brown(139).

Then the orthometallation was attempted using aluminium trichloride as catalyst but no evolution of hydrogen chloride gas was observed proving no reaction took place. Therefore, an alternative method for the synthesis of the compound was attempted by treating tellurium tetrachloride with m-methoxybenzaldehyde followed by reaction with aniline. The reaction of tellurium tetrachloride with aldehyde yielded a black residue which when subjected to E.S.R. showed a signal for the presence of free radicals.

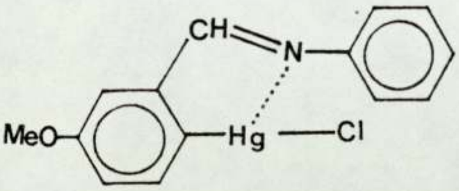
In order to obtain the orthometallated product as originally desired an attempt was made to mercurate the Schiff base. If successful, this could then be converted to the tellurium compound (Scheme 5) by transmetallation.



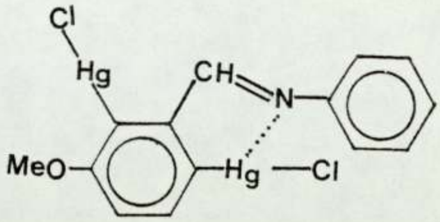
Scheme 5

Weaker electrophile mercuric acetate ($Hg^{2+}+2e \longrightarrow Hg^{o}$, $E^{o}=0.85$)(151) was used since, in its reactions, the metal often remains in the Hg(II) state giving substituents which afford stable mercurated products whereas covalent mercuric chloride is reported to be a poor electrophile(152). The difficulty in the formation of <u>ortho</u>metallated complexes by tellurium tetrachloride can also be explained by the low polarity of the Te-Cl bond, which follows from the closeness in value of the electronegativities of the Te and Cl atoms and from the relatively low values of dipole moment of tellurium tetrachloride in benzene and chlorobenzene (2.29, 2.88)(153). Attempts to prepare more ionic tellurium tetraacetate were not successful. The reaction of tellurium tetraiodide with excess of silver acetate in acetone afforded acetic acid and TeO_2.

When m-methoxybenzylideneaniline was treated with mercuric (II) acetate followed by addition of lithium chloride in methanol, compounds xi and xia were obtained resulting from the attack at 2-positions. This position is apparently activated to strong electrophiles by the methoxy group in the para position. On the basis of elemental analysis, I.R., N.M.R., mass spectrometry and ^{13}C N.M.R. data, structure XI has been assigned.

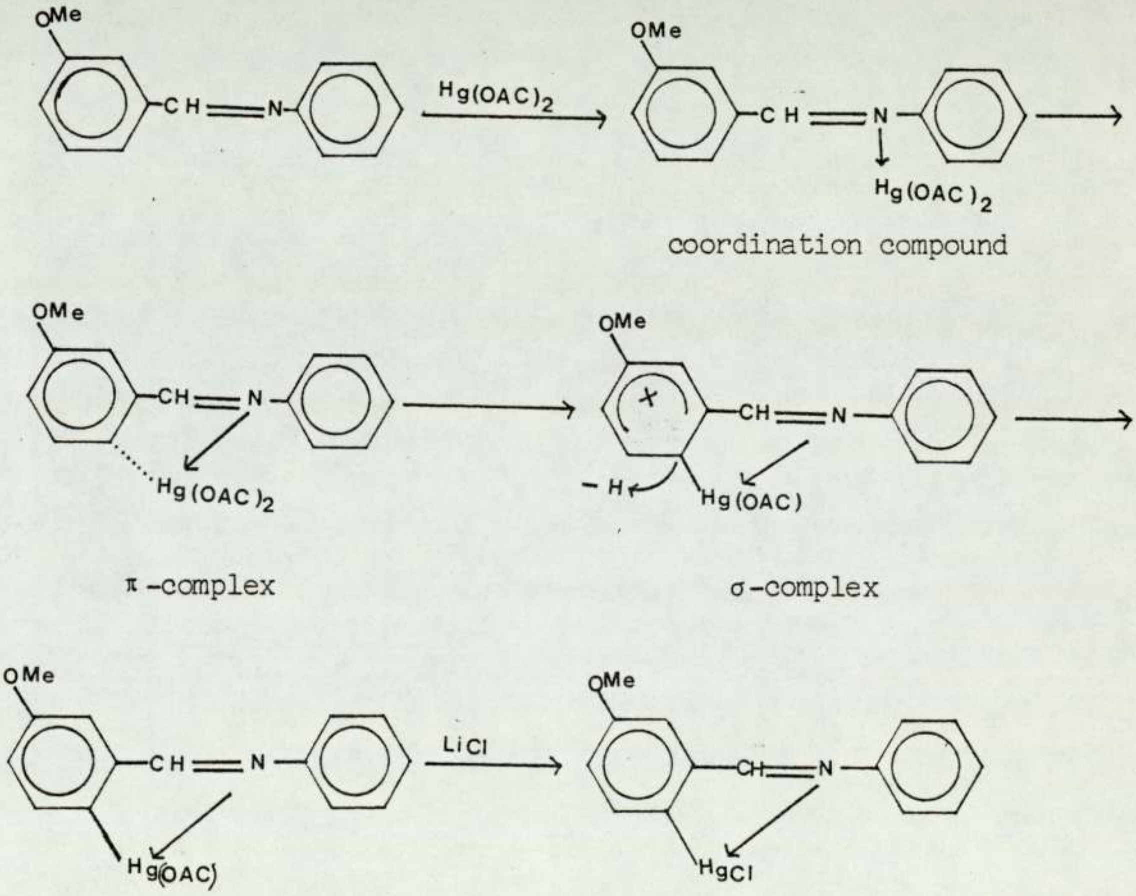


(xi)



(xia)

The possible mechanism for the mercuration of the Schiff base is given below.



5.2.1 Vibrational Spectroscopy

The ν(C=N) of the free benzylideneanilines is associated with two bands in the region 1650-1600 m^{-1}(154). Co-ordination of the base to metals would result in the negative shift of the ν(C=N). Now, in the case of mercurated derivatives of the base, there is only a small shift (∿5 cm^{-1}) which indicates that coordination of the base to mercury is almost certainly through lone pair on nitrogen and not through the azomethine π-system.

Although the coordination through nitrogen is also expected to result in negative shift ca∿20 cm^{-1} in ν(C=N), in the case of the above compounds the shift is smaller. This small shift can be interpreted in terms of weak interaction of nitrogen lone pair with mercury.

By comparing I.R. spectra of the starting Schiff base and xi, the new strong band at 720 cm^{-1} was assigned to γ(C-H) (Figures 5.1 and 5.2). In the case of mercurated p-nitrophenylhydrazones, this band was observed at ∿810 cm^{-1} (Table 5.5). This was not surprising as the nitro group is known to shift γ(C-H) to higher frequencies(155). Whereas for mercurated 2,4-dinitrobenzylideneaniline, no significant changes were noted in this region of the spectrum. This, probably, is due to heavy nitration of phenyl ring(156).

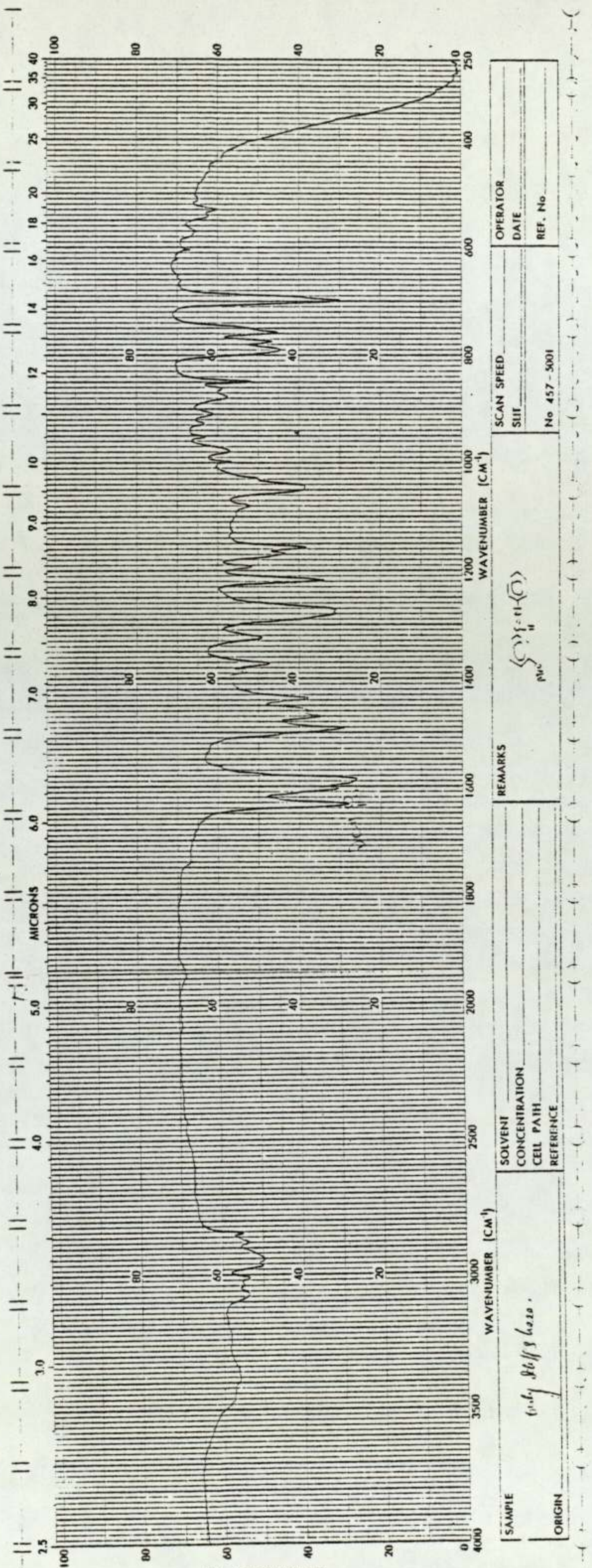


Figure 5.1 I.R. spectrum of m-methoxybenzylideneaniline

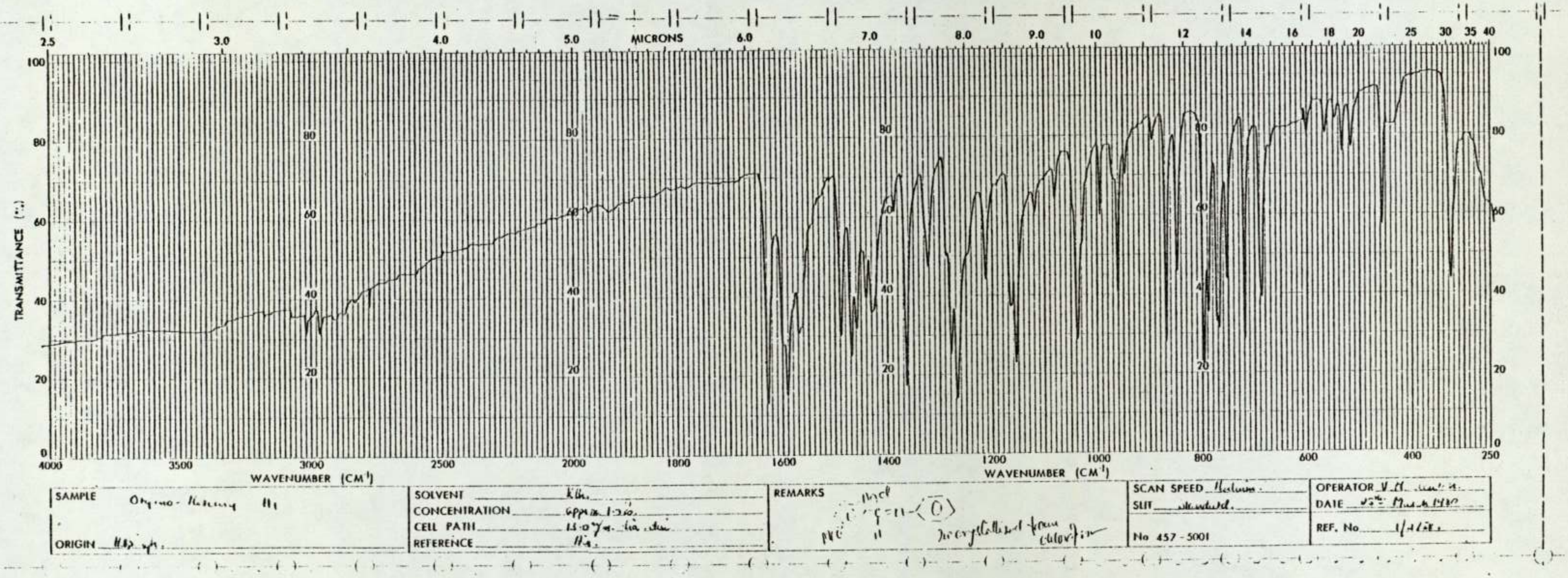
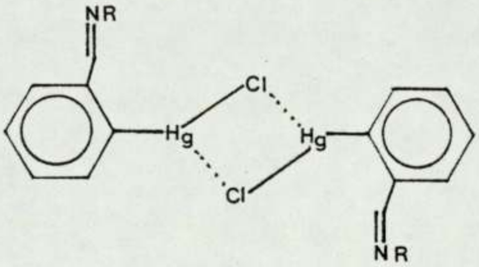


Figure 5.2 I.R. spectrum of (m-methoxybenzylideneaniline-C^2,N)mercury(II) chloride

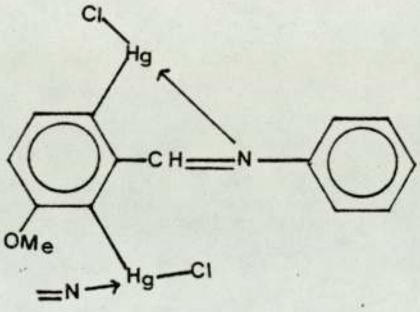
The mercury atom in these monomeric compounds (see mass spectral data) is at least two coordinate, as it is bonded to chlorine and to the aryl group. In principle, the mercury atom is three coordinate by additional interaction of the in-built ligand -CH=N-. There are no definite complexes of effective three-coordination among natural mercuric halide adducts. For neutral chloro complexes, $HgCl_2.D$, where D is a non-halogen atom, the location of ν(HgCl) may prove a desirable piece of information in predicting the structure of these complexes. For solid mercuric chloride ν_s(Hg-Cl) has been assigned at 330, 310 cm^{-1} by Mikava et al$^{(157)}$. In the case of mercurated Schiff base derivatives, two ν(Hg-Cl) absorptions were found in the region 330-300 cm^{-1}. The location of the second weak peak at ~310 or a shoulder in some cases, may be due to factor group splitting. A structure with bridging chlorines (xii) should lead to a lowering of ν(Hg-Cl).



(xii)

Therefore the structure (xi) where R-Hg-X is linear and where azomethine nitrogen is weakly interacting, seems more probable.

Also from this mercuration reaction there remained a chloroform insoluble solid (xia). The elemental analysis data agree well with the dimercurial formula. The compound is insoluble in common organic solvents suggesting the polymeric nature of the material. I.R. and N.M.R. data indicate that no protonation of the Schiff base has taken place. On the basis of elemental analyses, I.R. and N.M.R. data, following structure is suggested:



(xia)

Similar dimercurated derivatives have been obtained for azobenzene by Rolling et al$^{(158)}$.

5.2.2 Nuclear Magnetic Resonance Spectra

The ^{1}H N.M.R. data of the free ligands, mercurated derivatives and tellurium derivatives are listed in Table 5.7. Assignments were reached by comparing with model compounds and by adding the effects of substituents to monosubstituted benzene$^{(159)}$. No ^{199}Hg-^{1}H coupling could be observed under normal conditions of the experiments.

The ^{1}H N.M.R. of m-methoxybenzylideneaniline displays two singlets at δ3.6 ppm and δ 8.22 ppm, the intensity ratio being 3/1, these have been assigned to the methoxy and to

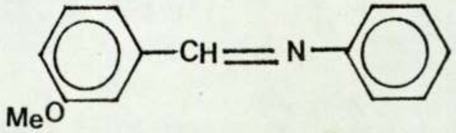
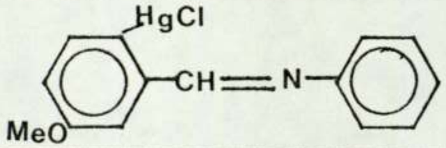
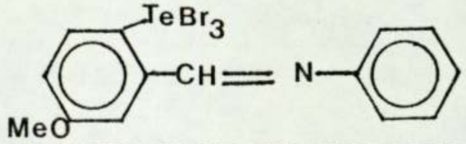
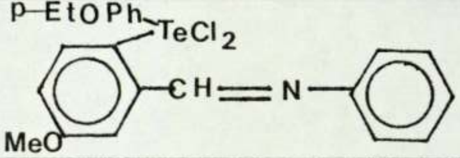
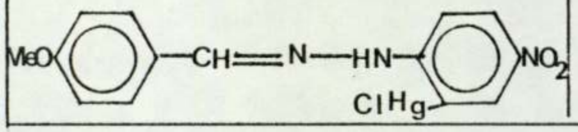
Compound	-CH=N	Ar-OCH$_3$	Ar-OCH$_2$CH$_3$	Ar-CH$_3$	Aryl protons
	8.2	3.6			7.2(m)
	8.65	3.9			7.4(m)
	9.28	3.9			7.5(m)
	8.8	3.95	O-CH$_2$, 1.45 masked		7.0-7.7(m)
	8.3	3.8			6.9-8.0(m)

Table 5.7 ^{1}H N.M.R. data for <u>ortho</u>-substituted Arylmercury, -tellurium compounds and the free ligands, δ(ppm)*

* ppm from internal TMS

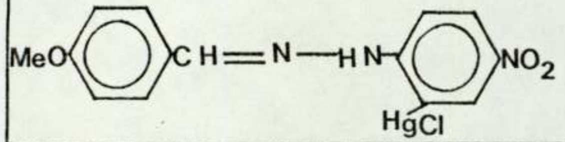
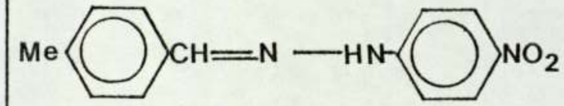
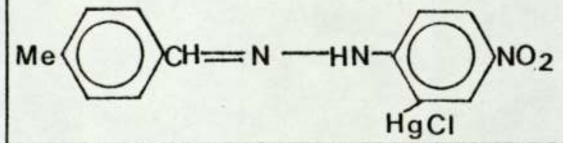
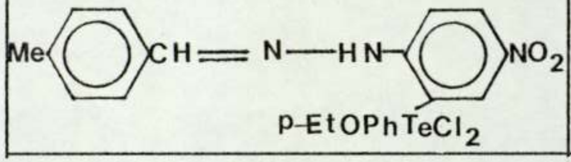
Compound	-CH=N	Ar-OCH$_3$	Ar-OCH$_2$CH$_3$	Ar-CH$_3$	Aryl protons
	8.1	3.8			6.9-8.4(m)
	8.14			2.35	7.0-8.4(m)
	8.08			2.3	6.85-8.35(m)
	8.15		3.85, 1.3	2.3	7.0-8.15(m)

Table 5.7 continued

the azomethine proton respectively. The aromatic protons give a multiplet centered at δ7.2 ppm, the integral ratio indicating the participation of nine protons (Figure 5.5).

The signal of azomethine proton (8.65) in the mercurated base is close to the free ligand (8.22), thus providing strong evidence in favour of the coordination of azomethine to mercury atom through the nitrogen lone pair. If the π-electrons of azomethine had been involved in the coordination process, the azomethine proton would have shifted by ca. 2 ppm upfield(160) (Figure 5.6).

^{1}H N.M.R. studies of p-nitrophenylhydrazones and their o-acetoxymercurio derivatives have been reported(161). ^{1}H N.M.R. spectra of the o-chloromercurio derivative showed the expected signals including the characteristic splitting pattern HO, HM, HP (Figure 5.7).

5.2.3 ^{13}C N.M.R. Spectra

^{13}C chemical shifts and ^{199}Hg-^{13}C coupling constants were measured on a JEOL FX-90Q Fourier transform multi-nuclear magnetic resonance spectrometer operating on 22.5 MHz. Solvent was used as internal standard. The normal operating temperature was ca. 290 K and pulse width of 15 μsec and repetition rate of 1.5 seconds were used. The spectral width was approximately 6 KHz.

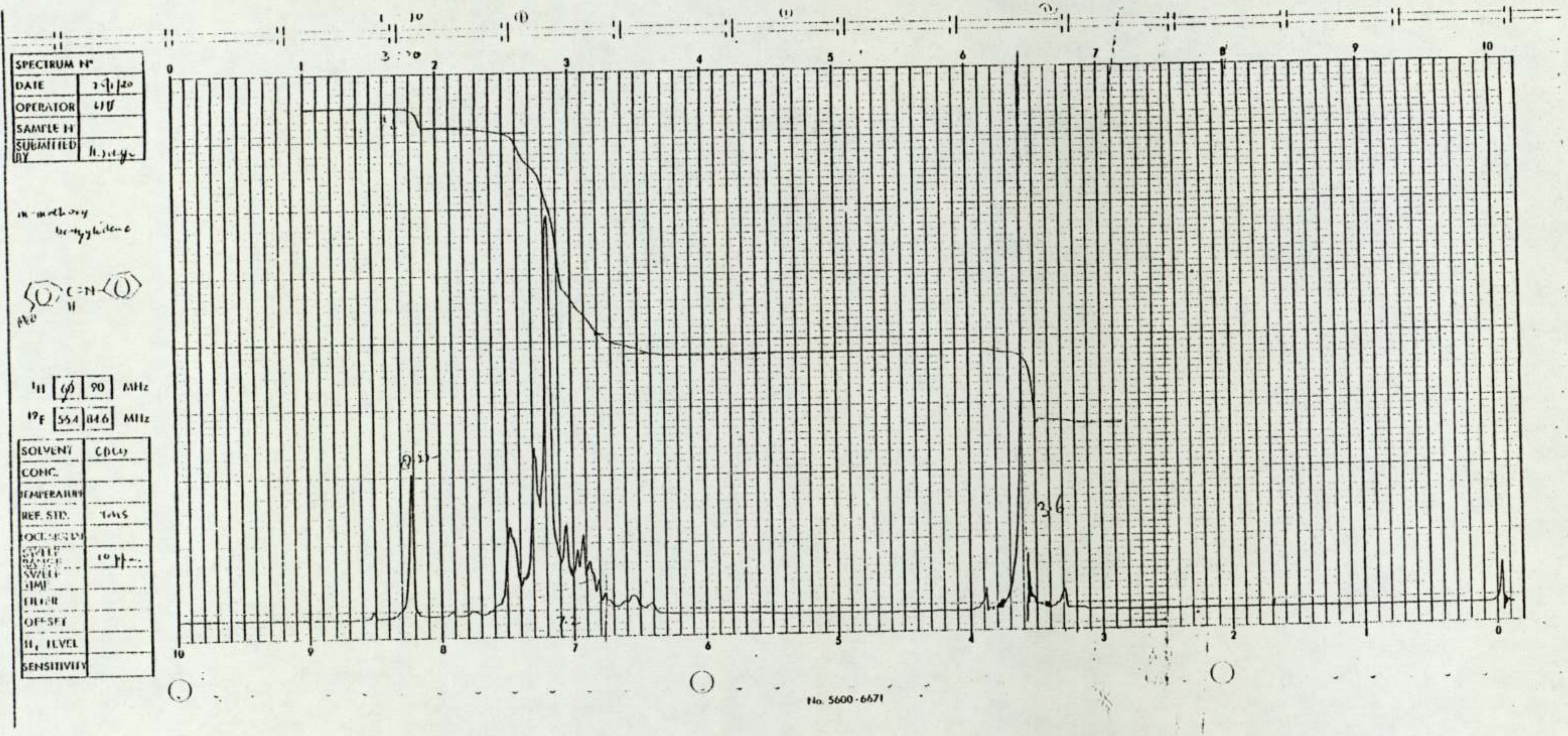


Figure 5.5 ^{1}H N.M.R. spectrum of m-methoxybenzylideneaniline

Figure 5.6 ^{1}H N.M.R. spectrum of (m-methoxybenzylideneaniline-C^{2},N)mercury(II) chloride

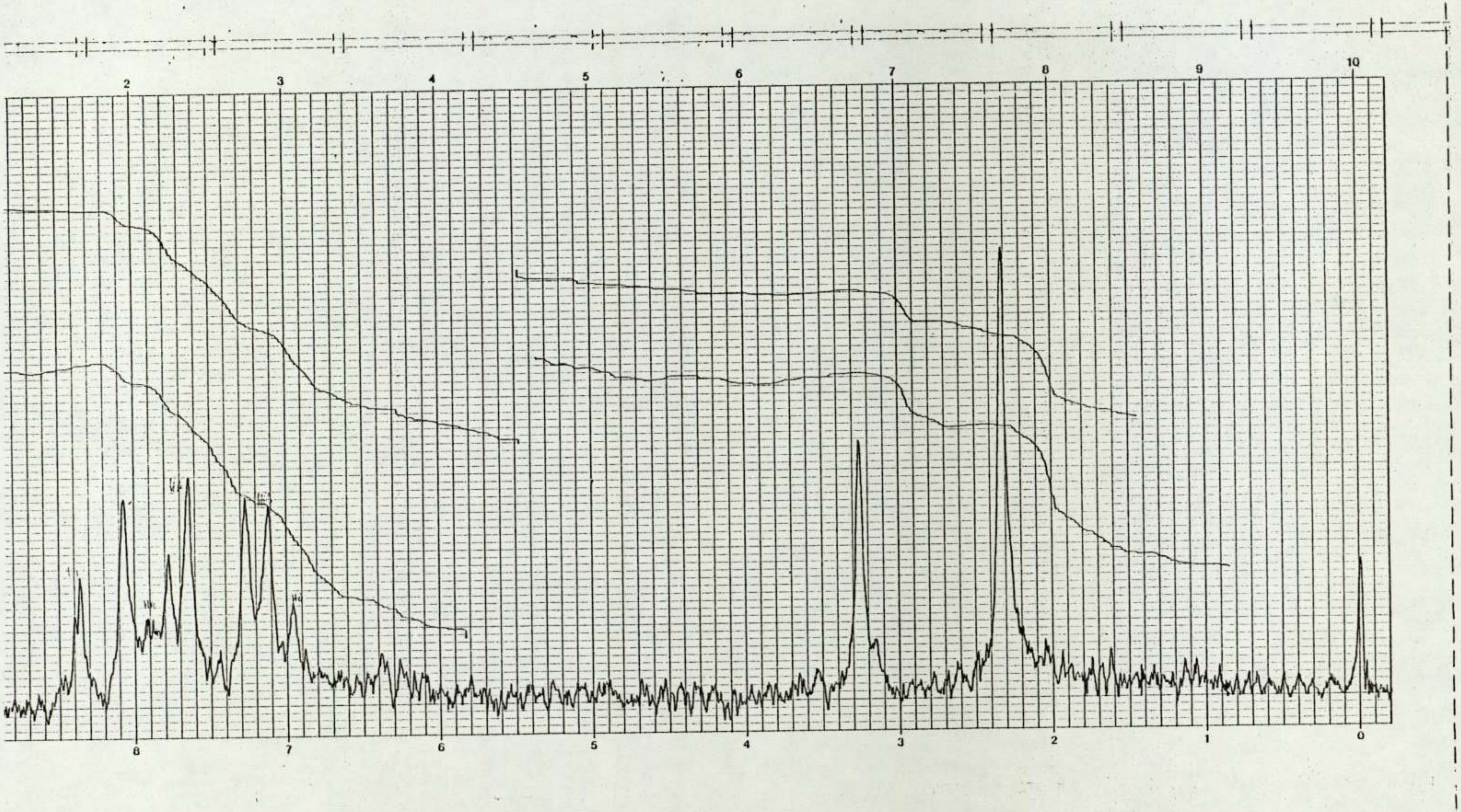


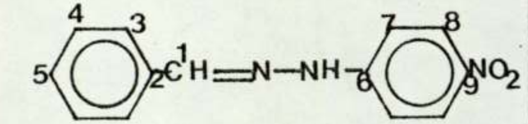
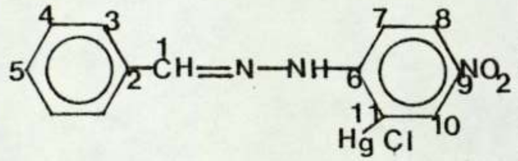
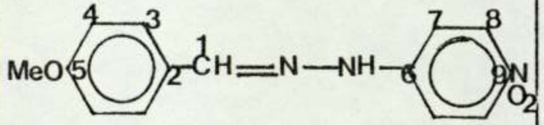
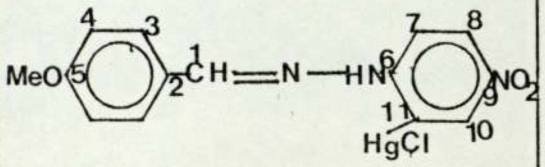
Figure 5.7 ^{1}H N.M.R. spectrum of p-tolualdehyde o-chloro-mercurio p-nitrophenylhydrazone

The chemical shifts are presented in Table 5.8. Some of the actual spectra observed, are reproduced in Figures 5.8 and 5.9. ^{13}C chemical shift assignments were based on comparisons with suitable model compounds as well as estimates of the effects of substituents on the aryl moiety, and on consideration of peak intensity. To assign substituted phenyl carbons by simple additivity relationships, the values of ^{13}C chemical shifts of unsubstituted benzene (128.5 ppm) and monosubstituted benzenes were taken from reference$^{(162)}$. Coupling constants between ^{199}Hg-^{13}C atoms were measured using ^{13}C resonances and observing the ^{199}Hg satellites.

The assignment of carbons bearing mercury was confirmed on the basis of the large one-bond coupling. Regarding coupling constants, the one-bond coupling is noteworthy and probably due to increased nuclear charge at the metal in these mercury(II) derivatives. The sequence $J(Hg\text{-}C_{meta}) > J(Hg\text{-}C_{ortho}) > J(Hg\text{-}C_{para})$ concurs with data for phenyl derivatives of other heavy atoms$^{(163)}$. To compare the ^{199}Hg-^{13}C coupling constants, the ^{13}C N.M.R. spectra of azobenzene and monomercurated azobenzene were obtained, but satellite for ^{199}Hg-^{13}C coupling could not be observed due to low solubility (Figures 5.10 and 5.11).

The carbon atoms bonded to mercury in these compounds show chemical shifts within the range $\delta = 132-142$ ppm. Signal intensities are low because of the long relaxation times.

Table 5.8 ^{13}C N.M.R. data in DMSO(d_6) δ(ppm)

Compound	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	
	141.6	134.6	125.9	128.6	129	150.4	111.1	126.3	138.3				
	142.6	133.9	127	128.5	129.3	152.8 J= 74.20 Hz	112.4 J= 148.4 Hz	125.1	138.4	134.8	132.7 J= 1874 Hz		
	141.8	127.2	127.9	114.2	160.2	150.6	110.9	126.1	137.9				55.2 (OCH_3)
	143	126.4	128.7	114.0	160.5	153.1 J= 42.8 Hz	112.3 J= 146.5 Hz	125.3 J= 21.5 Hz	138.2	134.9	132.3 J= 2742 Hz		55.3 (OCH_3)

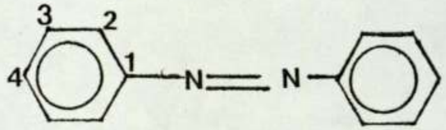
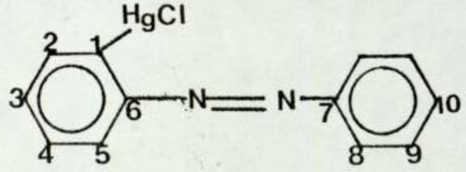
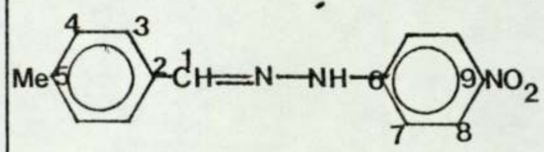
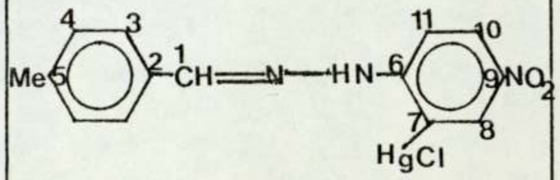
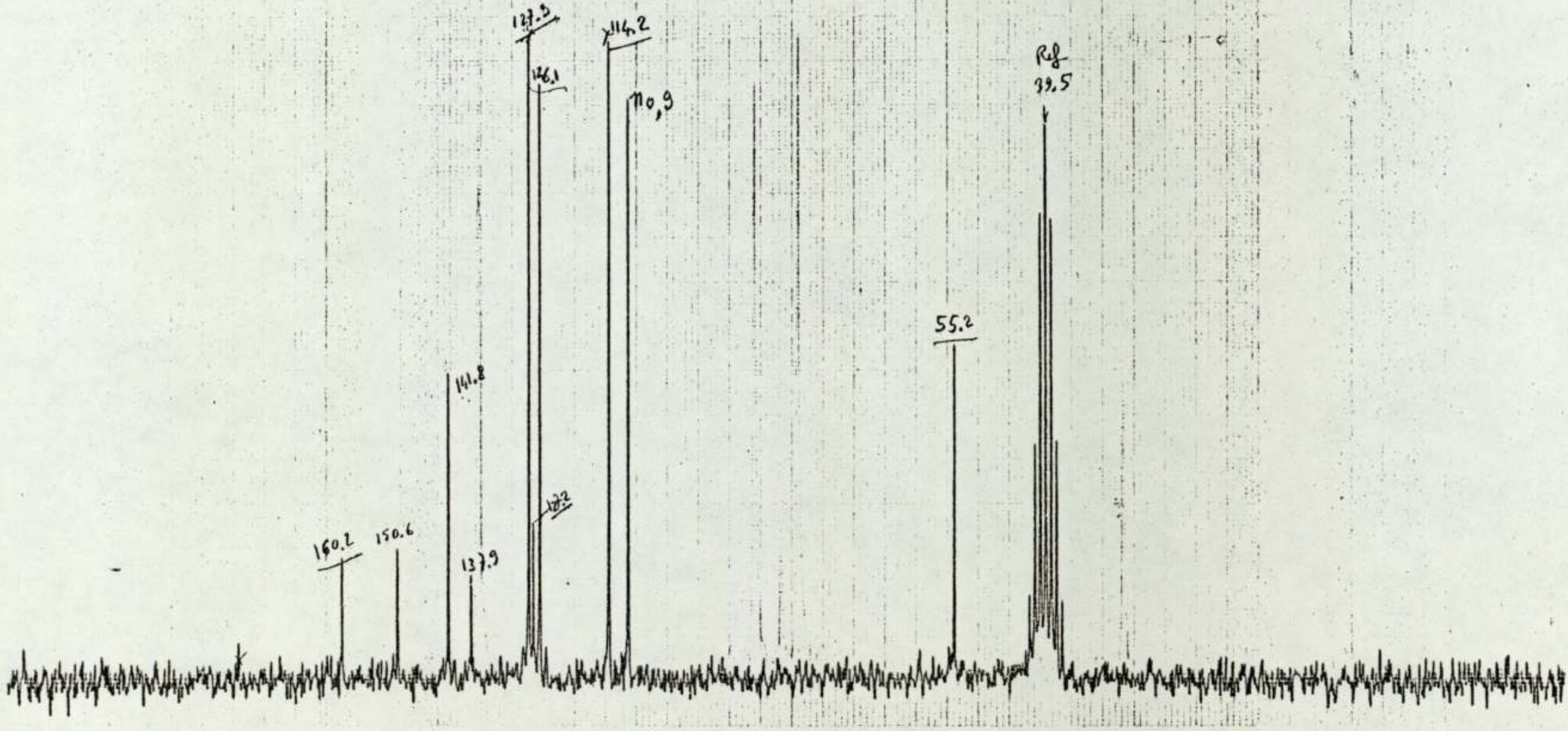
Compound	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	
	152.4	122.7	128.9	130.7									
	143.2	137.7	130.1	128.9	122.5	n.o.	150.9	122.5	129.5	131.7			
	141.9	131.7	126	129.6	138.9	150.6	111	126.3	138.5				20.9 $(-CH_3)$
	142.8	131.4	127	129.2	138.4	153.3	132.6	134.8	138.4	125.1	112.3		21.0 $(-CH_3)$

Table 5.8 continued



<u>Figure 5.8</u> ^{13}C N.M.R. spectrum of p-methoxybenzaldehyde p-nitrophenylhydrazone

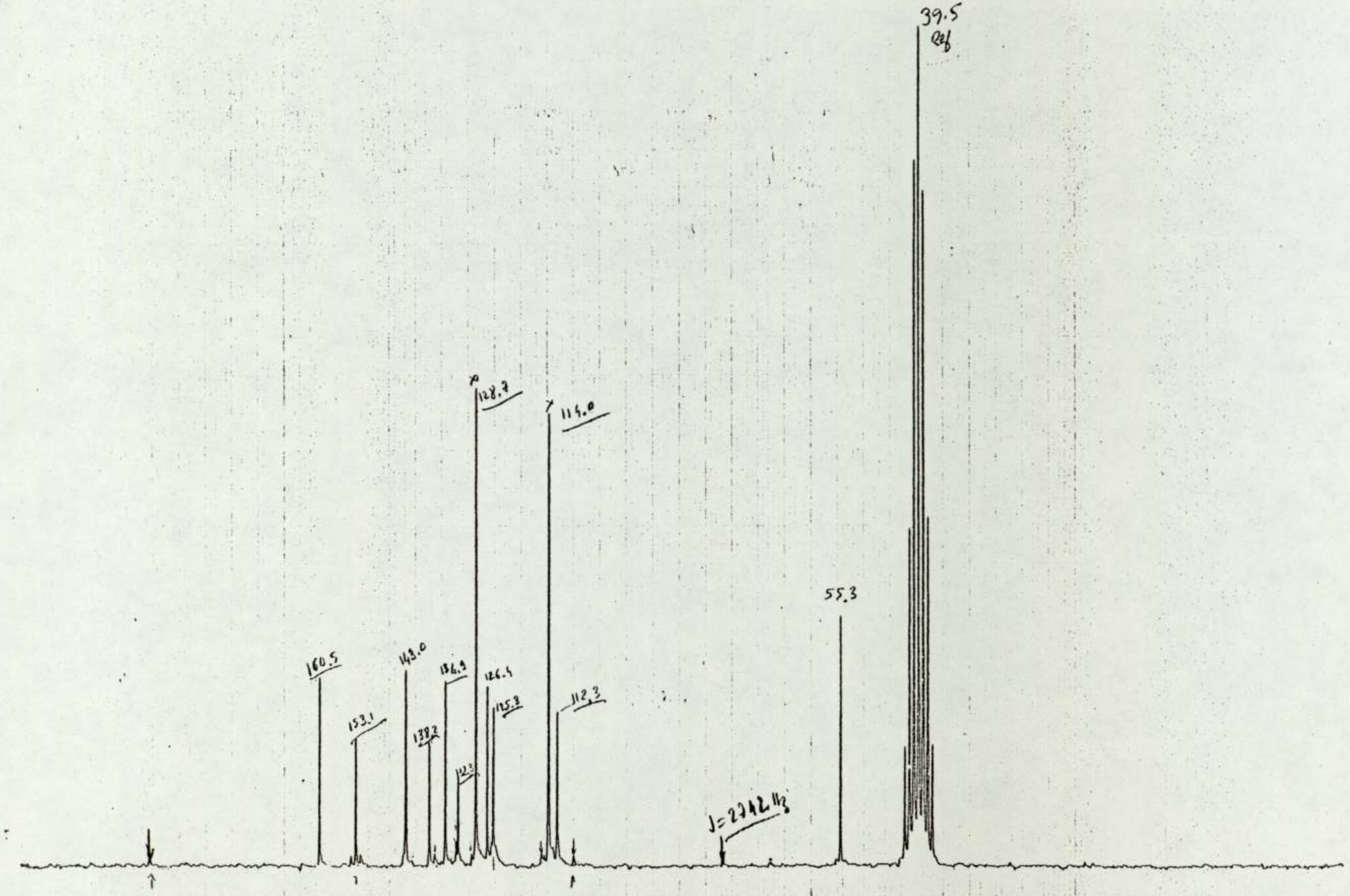


Figure 5.9 ^{13}C N.M.R. spectrum of p-methoxybenzaldehyde o-chloro-mercurio p-nitrophenylhydrazone

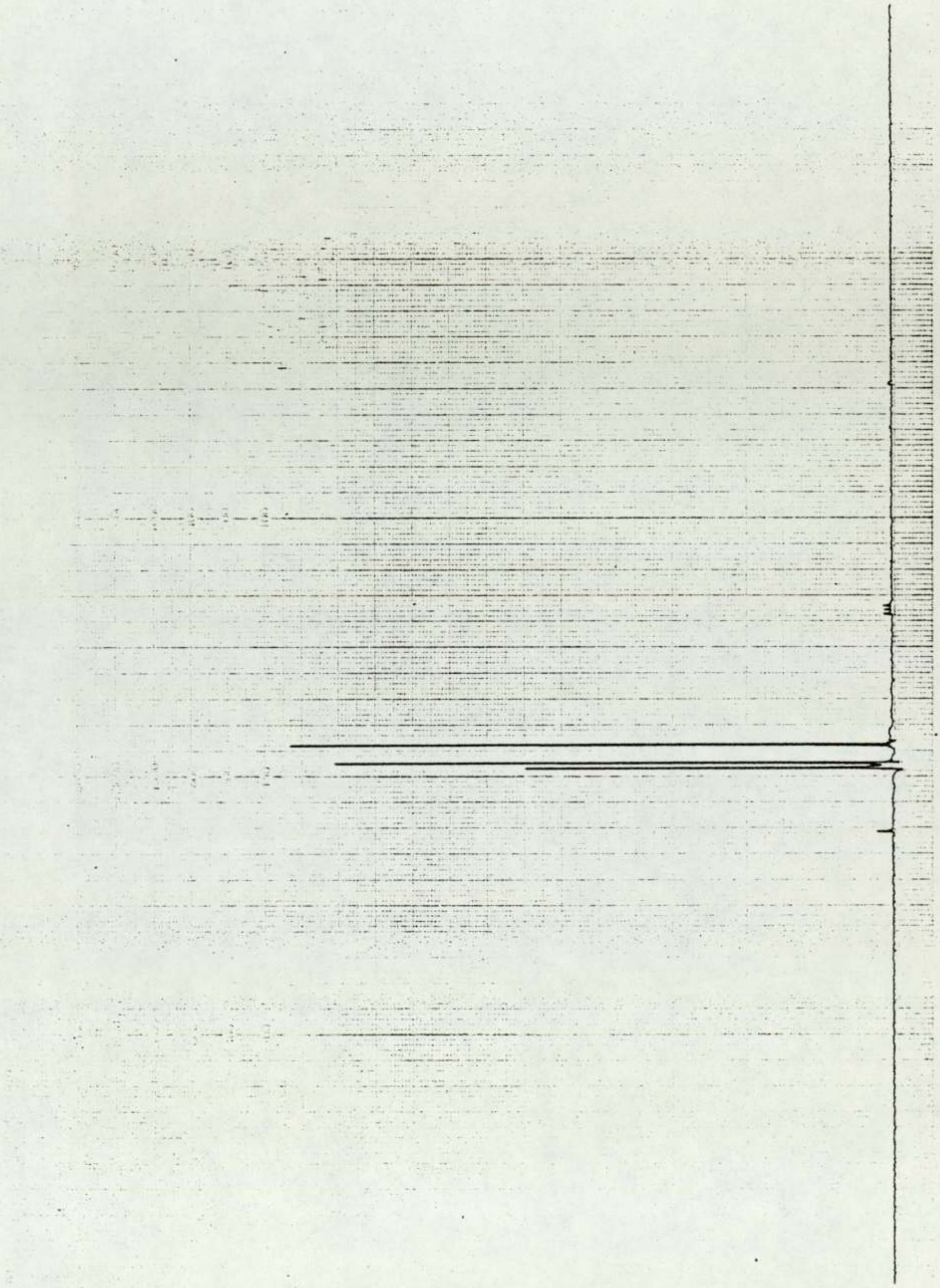


Figure 5.10 ^{13}C N.M.R. spectrum of azobenzene

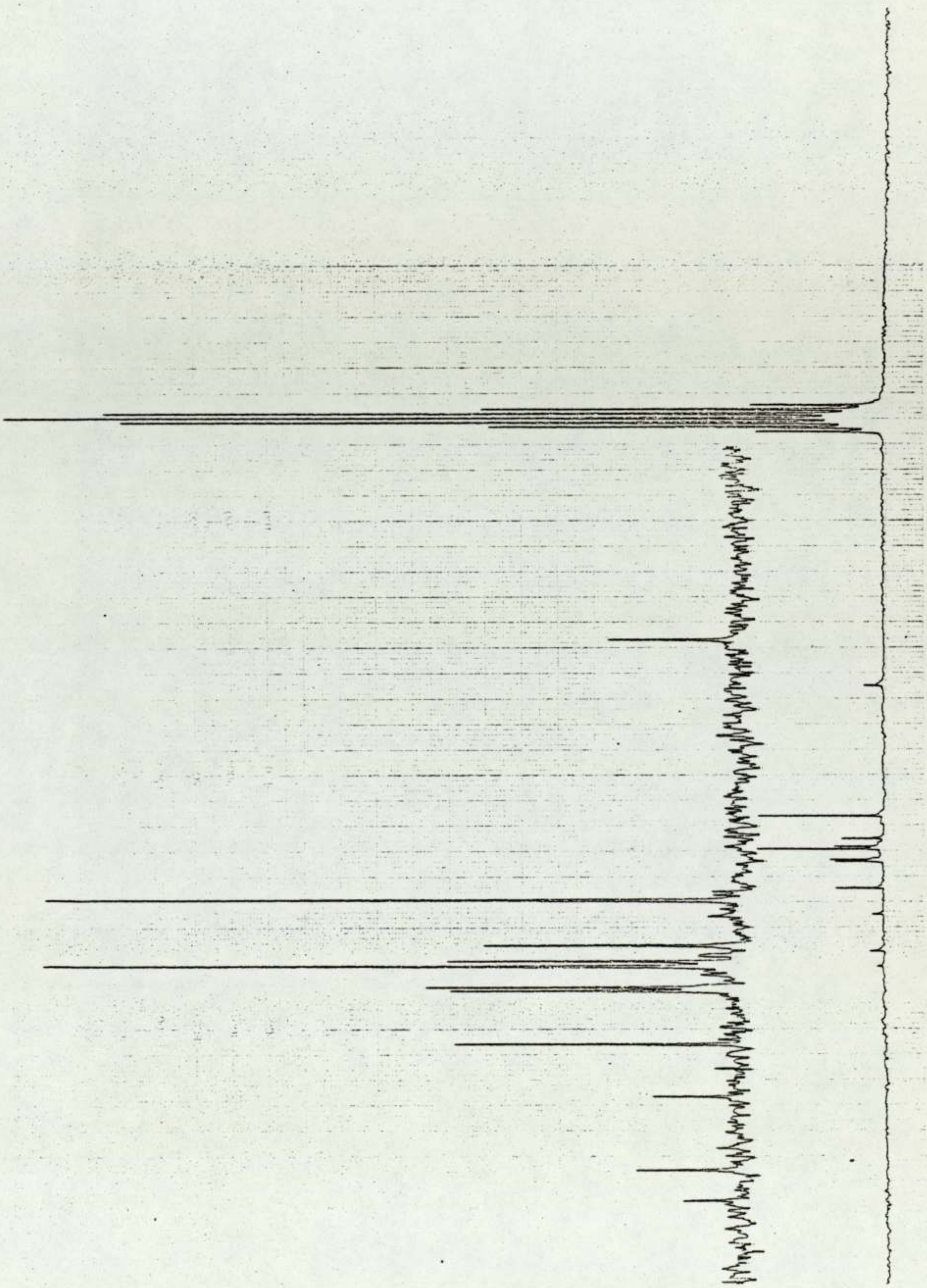


Figure 5.11 ^{13}C N.M.R. spectrum of mercurated azobenzene

Compared to the parent SB's, ipso-carbons experience substantial downfield (∿20 ppm) shift while the chemical shifts of meta-carbons is very similar to that of parent SB. The mercury atom in the monomeric ArHgCl is at least two two coordinate, since it is bonded to the substituent Cl and to the aryl group. The latter bonding is shown by the (^{199}Hg-^{13}C) couplings. In principle, the mercury atom can become three-coordinate by additional interaction of the internal ortho-ligand -CH=N-. With regard to the question of whether Hg-N coordination occurs in these complexes, the ^{13}C N.M.R. data are not very informative. The ^{13}C chemical shifts for the -CH=N nuclei in ArHgCl and free ligands (ArH) are almost the same.

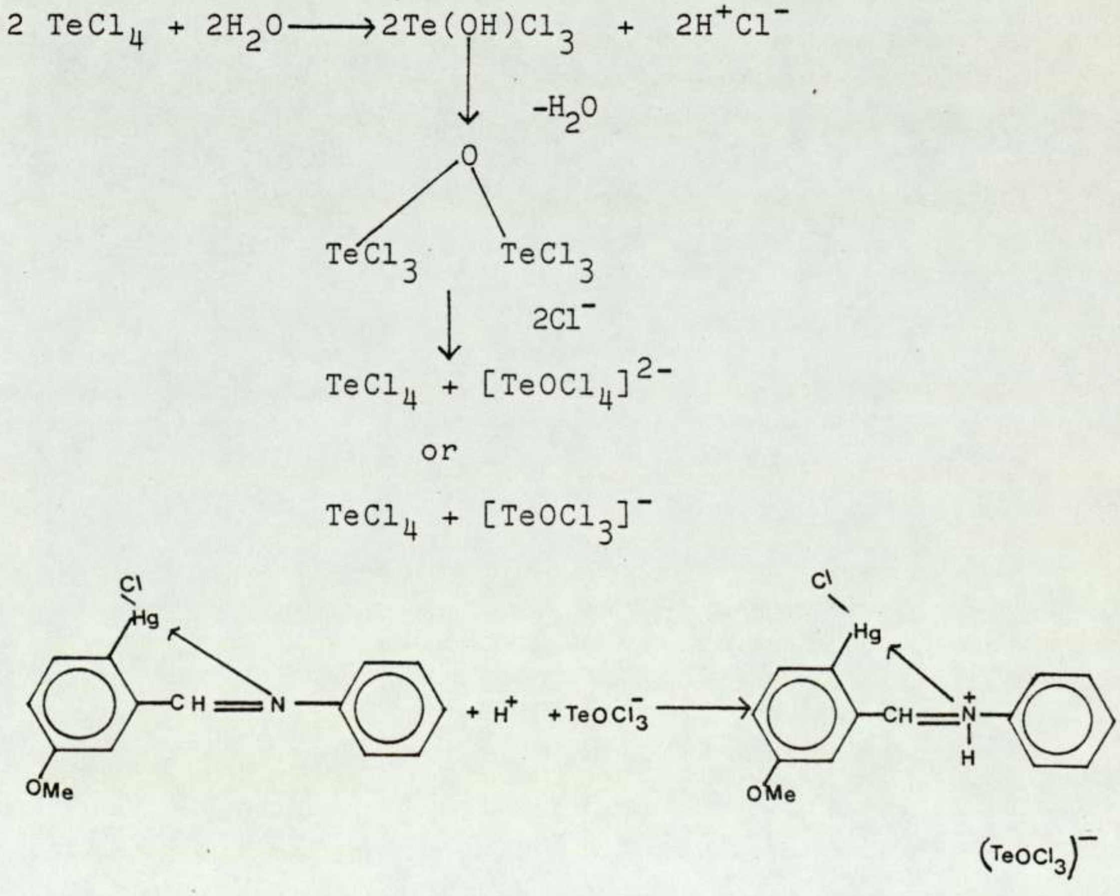
Although internal interactions have been reported for organomercury compounds, in the present case the ^{13}C N.M.R. results demonstrate that in solution such interactions can be inert on the N.M.R. time scale and thus determine the coordination geometry at the central mercury atom.

The additivity relationships used to determine the ^{13}C chemical shifts of the m-methoxybenzylideneaniline and 2,4-dinitrobenzylideneaniline do not compare closely with found values.

5.2.4. Transmetallation

After the successful synthesis and characterisation of the mercurated Schiff bases, transmetallation with tellurium tetrahalides was attempted.

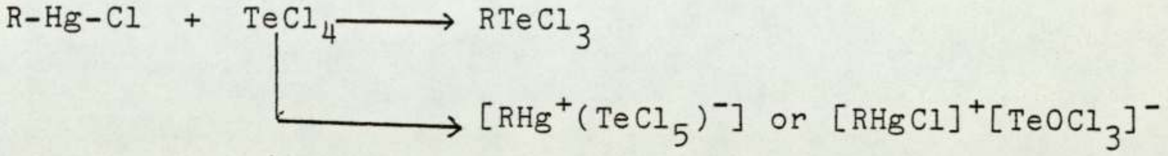
Transmetallation of the mercurated SB with tellurium tetrachloride was not successful. In this case a positive shift in the ν(C=N) was observed suggesting protonation of the base. This can most probably be attributed to the hydrolysis of the tellurium tetrachloride due to moisture present in the system. The protonation of the mercurated Schiff's base, probably proceeds as follows:



$$2\,TeCl_4 + 2H_2O \longrightarrow 2Te(OH)Cl_3 + 2H^+Cl^-$$

$$\xrightarrow{-H_2O} Cl_3Te{-}O{-}TeCl_3 \xrightarrow{2Cl^-} TeCl_4 + [TeOCl_4]^{2-} \text{ or } TeCl_4 + [TeOCl_3]^-$$

This is in contrast to reactions of tellurium tetrachloride with simple arylmercurials such as PhHgCl(164) and its ring substituted derivatives, which readily afford $TeCl_3R$-type derivatives (Scheme 6).



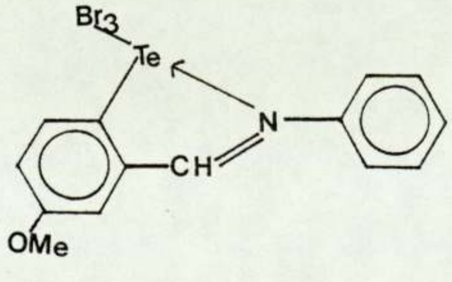
$$R\text{-}Hg\text{-}Cl + TeCl_4 \longrightarrow RTeCl_3$$

$$TeCl_4 \longrightarrow [RHg^+(TeCl_5)^-] \text{ or } [RHgCl]^+[TeOCl_3]^-$$

(Scheme 6)

Surprisingly, even when the transmetallation reactions were carried out under relatively anhydrous conditions, anionic complexes were isolated.

The reactions of tellurium tetrabromides with the Schiff base in 1:1 molar ratio in refluxing chloroform gave, upon concentration of the filtrate, brownish red solid (xiii). The compound melts with darkening at 180°C, and is soluble in chloroform, and methanol. The infra-red spectrum of the product supports the expected bonding mode of the bidentate organic group. The ν(C=N) occurs at 1624 m^{-1} in the tellurium compound. Such a lower shift in metal compound of SB indicates coordination to the azomethine nitrogen (Figure 5.3).



(xiii)

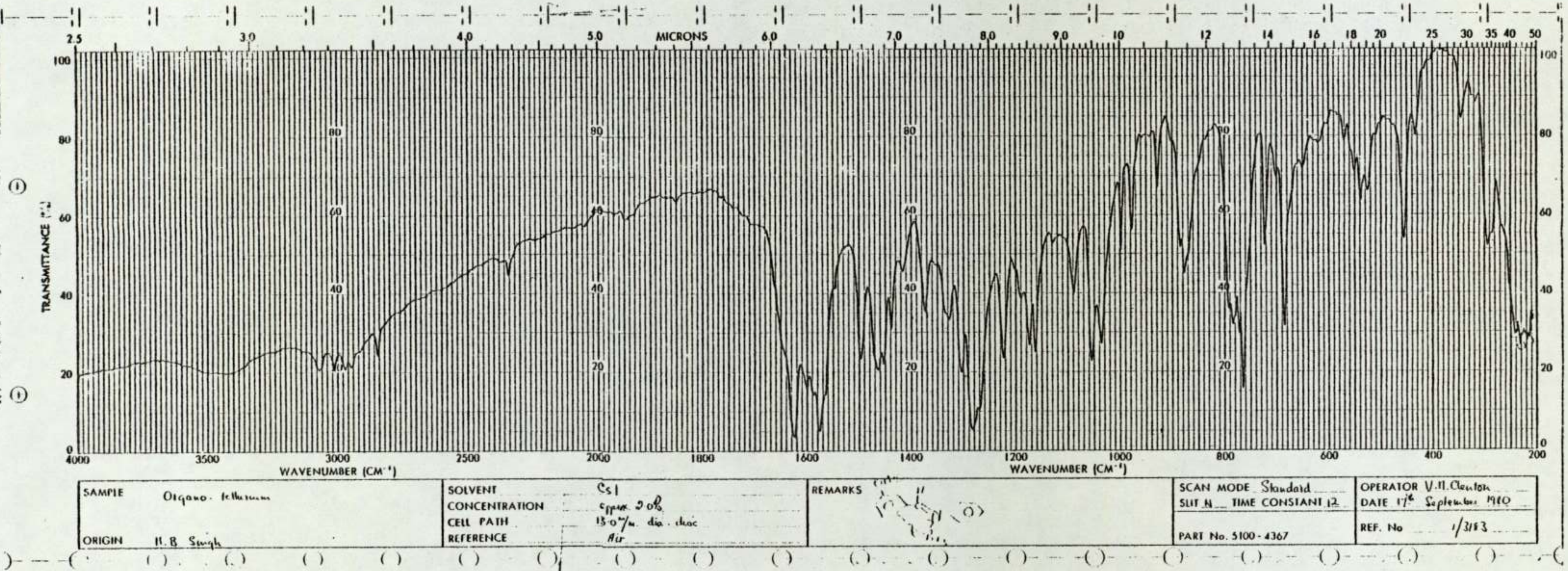
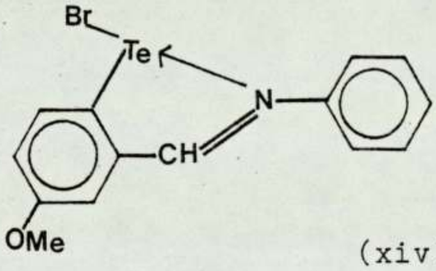


Figure 5.3 I.R. spectrum of (m-methoxybenzylideneaniline-C^2,N)tellurium(IV) tribromide

The fact that the metallation was successful when tellurium tetrabromide was used instead of the chloride leads to the conclusion that the basic cause of the failure is the acute sensitivity of tellurium tetrachloride to moisture. Hydrolysis of the tellurium tetrachloride is also promoted by SB (a strong Brönsted base).

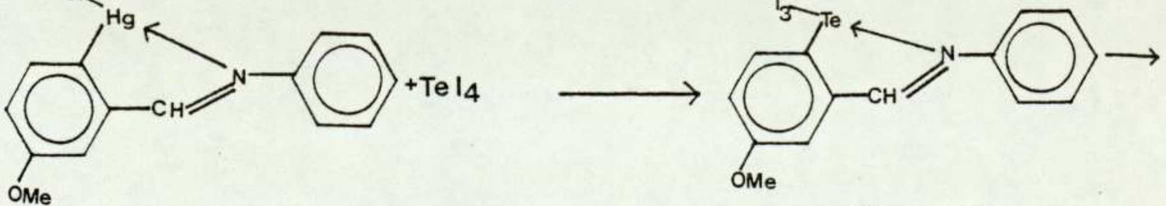
Reduction of the tribromide(xiii) with methanolic hydrazine hydrate at room temperature afforded the tellurenyl bromide (xiv). The infra-red spectrum shows similar features as found in the tribromide supporting the view that the skeleton is intact.



(xiv)

This deep-red coloured derivative melts with decomposition. The mass spectrum does not show the parent ion.

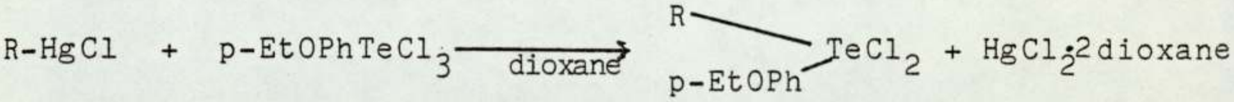
Treatment of the mercurated Schiff base with tellurium tetraiodide in dioxane or chloroform resulted in isolation of intractable black tar which could not be crystallised. This black oily substance results, probably, from the secondary decomposition of the <u>ortho</u>tellurated product (Scheme 7).



black oil

Scheme 7

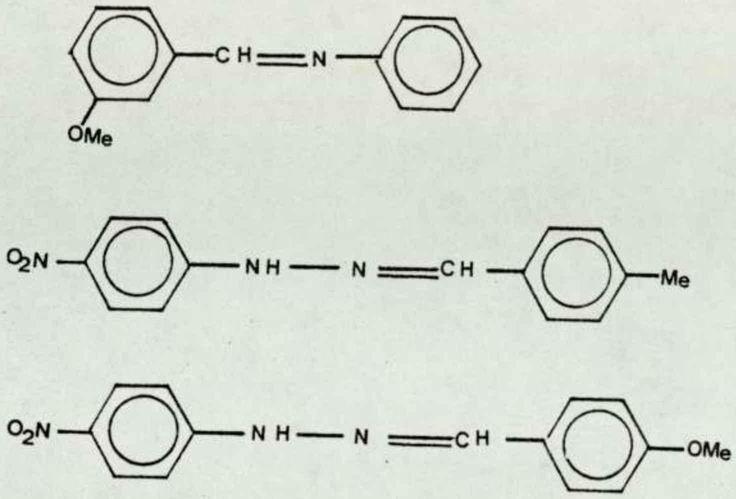
The dichloride derivatives (xv) were obtained by the action of (p-ethoxyphenyl)tellurium trichloride on the mercurated bases (Scheme 8) in refluxing dioxane (Table 5.4).



$$\text{R-HgCl} + \text{p-EtOPhTeCl}_3 \xrightarrow{\text{dioxane}} \begin{matrix}\text{R}\\ \text{p-EtOPh}\end{matrix} \text{TeCl}_2 + \text{HgCl}_2 \cdot 2\text{dioxane}$$

(xv)

R =



Scheme 8

In all these reactions, $HgCl_2$ is precipitated as dioxane complex. The dichlorides were sufficiently soluble in chloroform. The ^1H spectrum confirmed the metallation of the bases and the presence of the p-ethoxyphenyl group. The far infra-red spectra of these dichlorides were recorded. The tentative assignments for ν(Te-C) and ν(Te-Cl) are given in Table 5.6. Figure 5.4 shows I.R. spectrum of a typical dichloride.

5.2.5 Mass Spectra

The mass spectra of the mercurated Schiff bases show the parent ion peak and the characteristic fragmentation pattern

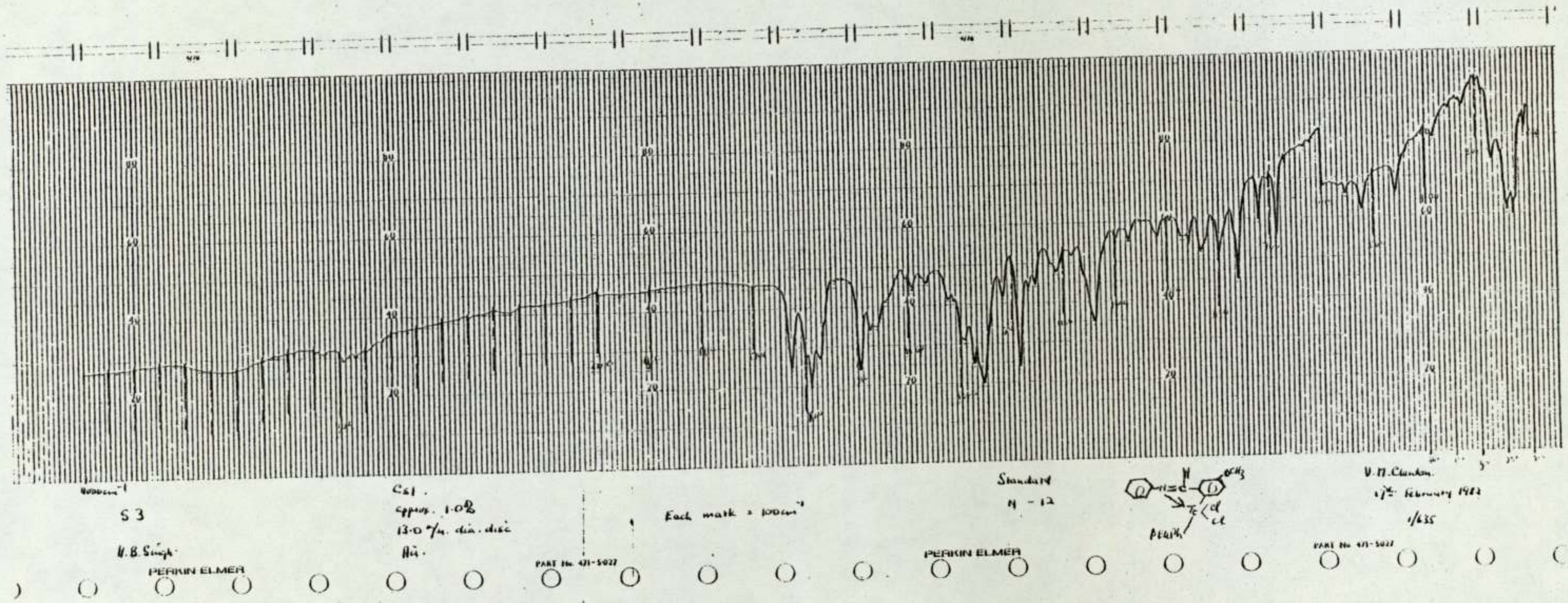


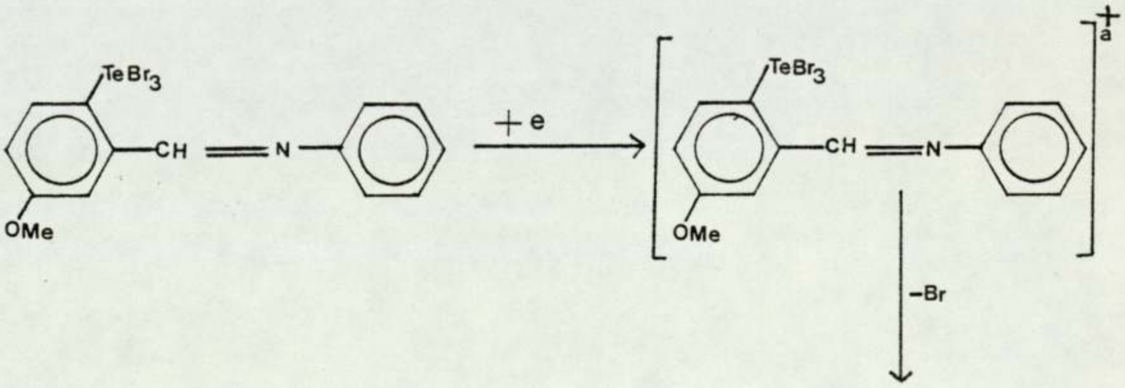
Figure 5.4 I.R. spectrum of an RR'$TeCl_2$ (R=p-EtPh, R'=m-$MeOC_6H_4CH:N-C_6H_5$)

of the parent Schiff bases$^{(165)}$, thus confirming the presence of the unaltered ligand. Some of the selected peaks from the spectrum of m-(methoxybenzylideneaniline-C^2,N)mercury(II)chloride (xi) are given below together with their relative abundance.

m/e = 450(20) M^+
m/e = 239(100) $HgCl^+$
m/e = 211(100)
m/e = 204(100) Hg^+
m/e = 133(70) $[C_8H_7NO]^+$
m/e = 77(100) $[C_6H_5]^+$

$[^{204}Hg, ^{35}Cl]$

In contrast the mass spectrum of the corresponding tribromide (Scheme 9) showed the highest peak at m/e = 502 (M-Br, ^{130}Te, ^{81}Br). The observed mass spectrum is in agreement with those reported by Musa$^{(166)}$. The fragmentation pattern is given below:



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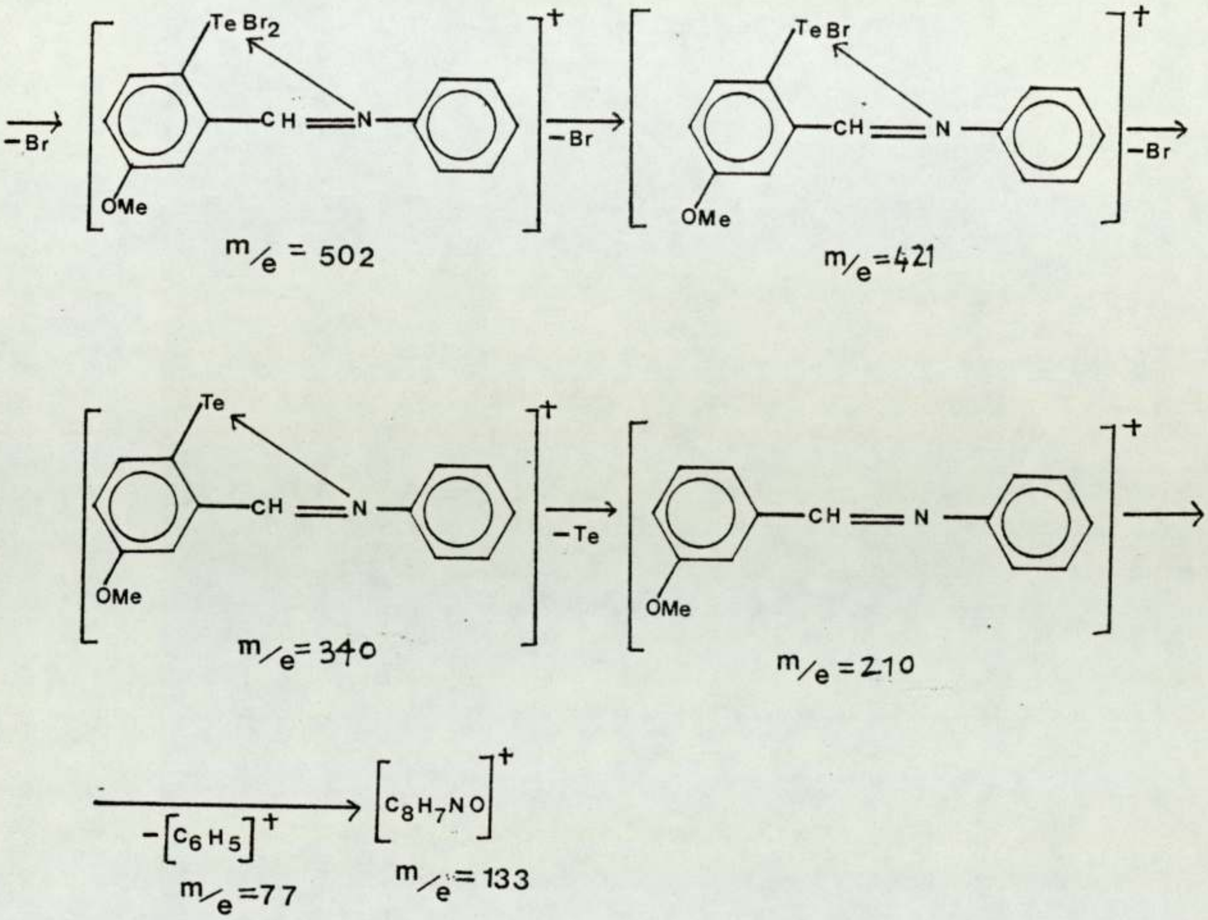
[a] Not observed


-Br
TeBr2
CH
N
OMe
m/e = 502
-Br
TeBr
CH
N
OMe
m/e = 421
-Br
Te
CH
N
OMe
m/e = 340
-Te
CH
N
OMe
m/e = 210
-[C6H5]+
m/e = 77
[C8H7NO]+
m/e = 133

CHAPTER SIX

ATTEMPTED INTRODUCTION OF TELLURIUM IN AROMATIC AND CONJUGATED SYSTEMS

6.0 Introduction

It was stated earlier (Chapter 1) that the initial aim of this project was to study charge-transfer in organotellurium chemistry and also to synthesise new organotellurium donors which may prove useful from the conductivity point of view. In this chapter, synthesis attempts based on structures of known organic conductors are described, however, most of the experiments must be regarded as exploratory.

Bechgaard(169) suggests that the molecules, giving rise to easily accessible oxidised or reduced ion radicals, can stabilize the open shell structures which in turn can form half-filled band conductors in the solid state. Generally, molecules having extended π-systems made from carbon pz or heteroatom pz orbitals, have been utilized for generating these stable open shell structures. Although the delocalised π-systems give rise to lower ionisation potentials and high electron affinities, on the other hand it has also been a difficult job to produce conducting solids from them. For example, the benzene cation(170) is known to exist in extreme conditions, whereas stable radical cations (i) of other arenes such as napthalene, triphenylene, pyrene, perylene and fluroanthene have been synthesised by anodic oxidation in presence of suitable anions(171,172).

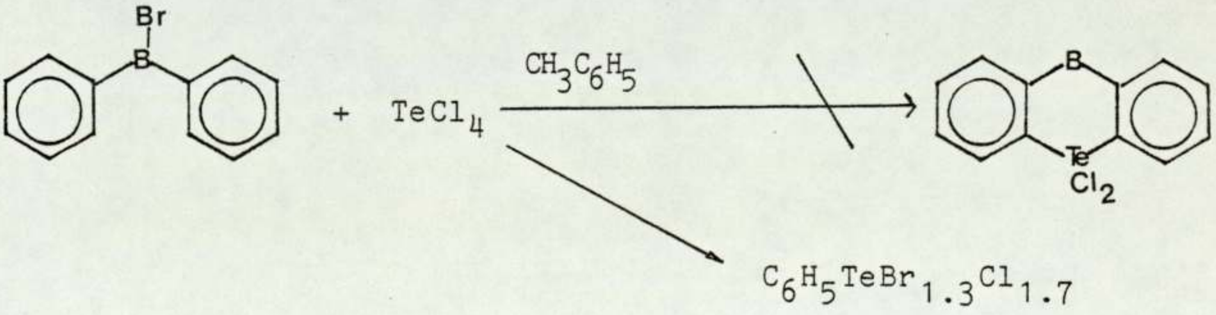
$[\mathrm{Aryl}]_2^{\cdot +}\ X^-$ $(X = ClO_4^-,\ BF_4^-,\ PF_6^-,\ AsF_6^-,\ SbF_6^-)$

(i)

All the complexes show a common structural principle. The radical cations are packed in stacks with short distances between the molecular planes. A view is held that more success could be expected if higher homologues of benzene and heteroaromatics containing heteroatoms such as N, P, O, S, Se and Te in the donor skeleton are employed.

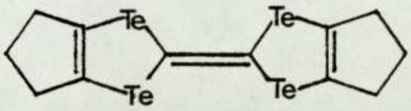
Perlstein et al$^{(173)}$ have demonstrated by empirical observations that those radical ions which form a mixed-valent high-conductivity state all contain additional 4n+2 local aromatic circuits not present in their neutral counterparts. It has been emphasised that this is a necessary condition for a molecule to form a mixed valent (partial charge-transfer) solid showing high conductivity.

As far as heteroaromatics containing tellurium are concerned, the literature is sparse. Zingaro et al$^{(174)}$ attempted the synthesis of one such compound. The reaction between equimolar quantities of diphenylboronbromide and tellurium tetrachloride (Scheme 1) in toluene led to isolation of only phenyltellurium trihalide.

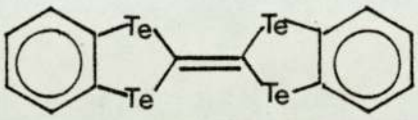


Scheme 1

Had this been successful, the central ring would have satisfied the Hückel 4n+2 rule for aromaticity. Two recent reports about the synthesis of organotelluriums with extended π-systems (ii, iii) which would obey Hückel's 4n+2 aromaticity rule have already been mentioned in Chapter 1(29,31).

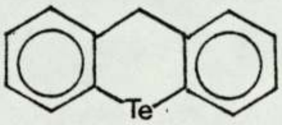


(ii)



(iii)

The aromatic tellurium compound chosen for study was the telluraxanthylium salt which could be derived from telluraxanthene. Sadekov and coworkers(175) were first to report the synthesis of telluraxanthene (iv) by intramolecular electrophilic cyclisation of 2-trichlorotelluriodiphenylmethane with subsequent reduction of the intermediately formed 10,10-dichlorotelluraxanthene.



(iv)

More recently a new syntheses of telluraxanthene has been reported by Lohner and Praefcke(176) involving 2,2'-dibromodiphenylmethane and n-butyllithium. While our collaborators at the University of Birmingham(177) were completing the X-ray diffraction analysis of telluraxanthene, it was published by the Russian group(178). The crystals of (iv) were orthorhombic; the molecular structure is given in Fig.6.1.

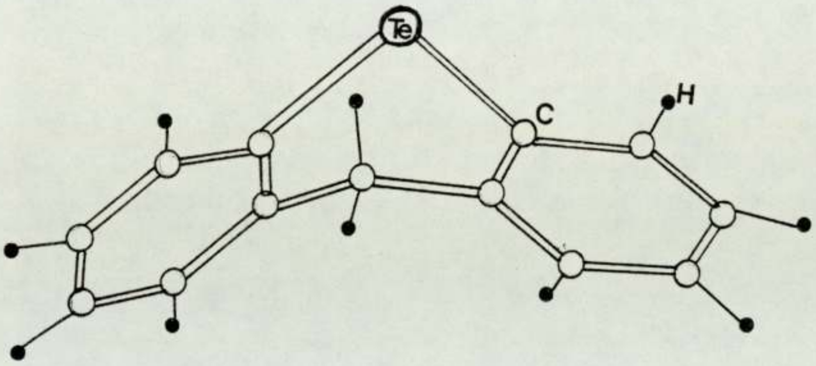
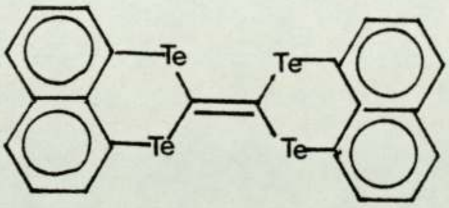


Figure 6.1 Diagram of the molecule of Telluraxanthene

The other strategy was to synthesise dinapthotetratelluraethylene (DNTTeE) (v) which, if successful, would have structural features in common with TTF etc.



(v)

6.1 Experimental

6.1.1 Synthesis of 2,2'-dibromodiphenylmethane(179)

6.1.1.1 3,3'-Dinitrodiphenylmethane

m-Nitrobenzylalcohol (10 g) and nitrobenzene (30 g) were dissolved in concentrated sulphuric acid (200 cm^3) on a water bath for 48 hours. After the reaction, the resulting mixture was poured upon cracked ice to give a white precipitate.

6.1.1.2 3,3'-Diaminodiphenylmethane

The base was prepared by two methods from 3,3'-dinitrodiphenylmethane:

3,3'-Dinitrodiphenylmethane (14 g) was mixed with powdered iron (30 g) and water (50 cm^3) in a porcelain dish. Concentrated acetic acid (2 cm^3) was added and the mixture was heated on a water bath with stirring. The reaction started in a few minutes with evolution of gas; the stirring was continued until most of the water had evaporated. The base was extracted with ether and the ethereal layer was dried over potassium hydroxide. The ether was evaporated on a rotatory evaporator to give a viscous oil with unreacted 3,3'-dinitrodiphenylmethane.

Better results were obtained by the method reported by Vlček and Rusina(180) which involves reduction by sodium borohydride catalysed by $Co^{2+}(bipy)_3$ complex.

Cobalt(II) chloride (2.77 g) was mixed with excess of bipyridyl (10 g) in ethanol and heated to reflux. The resulting solution was filtered and the filtrate evaporated to give the yellow-brown colour complex in quantitative yield.

3,3'-Dinitrodiphenylmethane (6.25 g) was dissolved in ethanol (100 cm^3) containing the cobalt complex (13.8 g). Sodium borohydride (0.9 g) dissolved in ethanol was added dropwise to the solution. After the completion of addition, the reaction mixture was poured into water (200 cm^3). The base was extracted with ether. The product which was obtained as a viscous oil, was immediately converted into its acetyl derivative.

6.1.1.3 3,3'-Diacetylaminodiphenylmethane

The diamine obtained from the experiment described above was dissolved in glacial acetic acid (20 cm^3) and acetic anhydride (15 cm^3). Heat was evolved, and the solution was refluxed for an additional 30 minutes. The resulting solution was poured into cold water to give a white crystalline derivative. The precipitate was filtered and recrystallised from ethanol, m.p. 191°C (lit. 193°).

6.1.1.4 3,3'-Diacetyl-6,6'-dibromodiphenylmethane

3,3'-diacetlydiphenylmethane (20 g) obtained as described above, was dissolved in glacial acetic acid (500 cm^3). Bromine (17 g) was added dropwise with stirring to the solution at 50°C during 30 minutes. The mixture was allowed to stand for a short time and then poured into cold water (2 l). Filtration and washing with cold water afforded a crystalline white compound. The white compound was recrystallised from acetic acid, m.p. 282°C (lit. 284).

6.1.1.5 3,3'-Diamino-6,6'-dibromodiphenylmethane

The diacetyl compound (60 g) in ethanol (250 cm^3) was stirred and refluxed.

Concentrated hydrochloric acid (200 cm^3) was added dropwise to the refluxing solution. After an hour's heating saponification was complete, and the solution entirely clear. Soon the hydrochloride of the base began to precipitate as fine colourless needles. The product was filtered off and washed with alcohol. The filtrate was evaporated almost to dryness on a water bath, ammonia was added and the base extracted with ether. Upon addition of hydrochloric acid to the ether solution, pure hydrochloride salt of the base was obtained.

6.1.1.6 2,2'-Dibromodiphenylmethane

The hydrochloride of the base (10 g) was mixed with water (30 cm^3) and hydrochloric acid (10 cm^3) and made into a paste. The mixture was cooled to 0^o and a cold saturated solution of sodium nitrite was gradually added until a test with starch-iodide paper indicated free nitrous acid. When almost all the hydrochloride was dissolved, it was poured into one litre of boiling alcohol, followed by a brisk evolution of nitrogen. The alcohol was distilled off, leaving a light brown oil, which was taken up with ether and dried over calcium chloride.

The solvent was removed on a rotatory evaporator and the residue was treated with concentrated sulphuric acid to remove the ethoxy derivative. The residue was distilled under a pressure of 1 mm. A colourless liquid was obtained in the range 140-160^o.

6.1.2 Telluraxanthene(176)

Freshly distilled 2,2'-dibromodiphenylmethane (5.0 g) was dissolved in dry ether (450 cm^3) in a dry box filled with dinitrogen. A solution of n-butyl lithium in hexane (35 cm^3 of 1.6 M) was added dropwise at room temperature. After completion of the addition, the resulting solution was refluxed for half an hour. After letting the reaction mixture cool to room temperature, tellurium powder (2.8 g) was added and the reaction mixture was again refluxed for another two hours. The resulting solution was poured into ice water and the compound was extracted with chloroform. The combined organic phases were dried over $MgSO_4$ and rotatory evaporated to afford crystals of telluraxanthene. The crystalline compound was treated with animal charcoal in methylenedichloride. Recrystallisation afforded pale yellow needles, m.p. 150° (lit. 151°).

6.1.3. 10,10-Dichlorotelluraxanthene

A stream of dry chlorine was passed through a solution of telluraxanthene (1.47 g) in benzene (20 cm^3) for 20 minutes after which most of the solvent was removed by distillation and the precipitate was removed by filtration, washed with petroleum ether to give the product, m.p. 250°(lit. 250°).

6.1.4 Telluraxanthone

A solution of dichlorotelluraxanthene (1.82 g) and potassium dichromate (1.47 g) in glacial acetic acid (20 cm^3) was refluxed for 8 hours, and the resulting solution was poured into ice water (200 cm^3). The precipitated 10,10-dichlorotelluraxanthone was removed by filtration, washed with water, dried and suspended in water (50 cm^3). Potassium metabisulphite (6.8 g) was added with stirring for 30 minutes. After stirring, the temperature was raised to $50^{\circ}C$. The mixture was cooled and the precipitated telluraxanthone was removed by filtration, washed with ice water and dried to give telluraxanthone. Recrystallisation from petroleum ether ($80-100^{\circ}$) gave large yellow crystals with m.p. 115° (lit. 116°).

6.1.5 Attempted Synthesis of Telluraxanthylium Tetrafluoroborate

To a suspension of lithium aluminium hydride (0.37 g) in ether in a properly dried flask, telluraxanthone (0.31 g) in ether was added slowly at room temperature under dinitrogen. The yellow colour of the solution disappeared. After completion of the addition, the reaction mixture was treated with ethyl acetate to decompose the unreacted $LiAlH_4$ and filtered on a sintered funnel.

To the filtered ethereal solution was added HBF_4 at -20°C and left to react. No precipitation was observed, even after two days.

6.1.6 Attempted Synthesis of Charge-Transfer Complex of Telluraxanthene with TCNQ

Telluraxanthene (0.29 g, 1 m mole) and TCNQ (0.20 g, 1 m mole) were refluxed and stirred in acetonitrile over 4 hours. Cooling the solution afforded a mixture of starting materials. Variation of quantities, time of reflux and volume of solvent failed to give a complex.

6.1.7 Preparation of 1,8-dibromonaphthalene(181)

6.1.7.1 8-Bromo-1-naphthoic acid

Naphthalic anhydride was converted to 8-bromo-1-naphthoic acid by the method reported by Rule and Pursell(182).

A solution of naphthalic anhydride (50 g) and sodium hydroxide (31 g) was warmed in water (1200 cm^3) and filtered. To the filtrate was added mercuric oxide (55 g) dissolved in warm acetic acid (40 cm^3) and water (150 cm^3). To the whole was added more acetic acid to form a brown suspension which was refluxed for 96 hours until evolution of carbon dioxide ceased. A test portion dissolved completely in aqueous sodium hydroxide solution and deposited no mercury on copper wire. Filtration and washing with water, alcohol and ether, followed by drying afforded a brown powder.

Anhydrous-8-hydroxymercuric-1-naphthoic acid (94 g) obtained as described above, was suspended in a mixture of glacial acetic acid and water (300 cm^3 + 50 cm^3). To the whole was added bromine (34 g) in concentrated aqueous sodium bromide (150 cm^3) gradually at 0°C while the reaction mixture was mechanically stirred. After completion of the bromine addition, the mixture was slowly heated to 90°C and poured with stirring into 3 l of cold water. The filtered precipitate was boiled out into 3 l of water until no more acid deposited on cooling. The yellowish plates after drying melted at 170° and were used without further purification.

6.1.7.2 1,8-Dibromonaphthalene

To an aqueous solution of 8-bromo-1-naphthoic acid (50 g) and sodium carbonate (1.06 g) was added silver nitrate (3.4g). The resulting silver salt was filtered, washed with water, methanol and finally with acetone and dried under vacuum over P_4O_{10}.

The silver salt (6.5 g) was suspended in dry carbon tetrachloride (50 cm^3) and to the suspension was added dropwise a solution of bromine (2.9 g) in dry carbon tetrachloride (19 cm^3). After 2 hours under reflux, the mixture was filtered and the filtrate treated with four portions of sodium bicarbonate to remove unreacted 8-bromo-1-naphthoic acid.

The solvent was evaporated to yield 1,8-dibromonaphthalene. The crude product was treated with animal charcoal in ethanol. Further recrystallisation from ethanol gave pure 1,8-dibromonaphthalene, m.p. 106° (lit. 109-110°).

6.1.8 Naphtho(1,8-C,D)1,2-ditellurole(183)

A solution of butyl lithium (4.27 g, 42 cm^3 of n-BuLi, 1.6 M in hexane) was added gradually to a solution of dibromonaphthalene (5.45 g) in tetrahydrofuran (90 cm^3) at room temperature under dinitrogen while the mixture was stirred. The solution was stirred for an additional 45 minutes; then the reaction mixture was cooled to -78°C and powdered tellurium (6.77 g) was introduced in a single addition; stirring was afterwards continued for 4 hours at this temperature and subsequently at room temperature for 1 hour. The mixture was treated carefully with water and dilute hydrochloric acid, and was allowed to stand overnight, after which it was filtered to remove the unchanged tellurium. The combined THF extracts were washed with water and dried over anhydrous sodium sulphate. Evaporation of the solvent afforded crude ditellurole which was recrystallised from CS_2 and hexane mixture as a greenish grey powder m.p. 200° (lit. 210°).

6.1.9 Attempt to React Ditellurole with Chloranil

Naphthoditellurole (0.38 g, 1 m mole) and chloranil (0.25 g, 1 m mole) were stirred and refluxed in acetonitrile (50 cm^3) for 1 hour. Cooling the reaction mixture afforded silver grey plates, m.p. 250-254^o(d).

6.1.10 Bis(p-ethoxyphenyltellurium)dichloromethane

To an emulsion of bis(p-ethoxyphenyl)ditelluride (2.4 g) in benzene (50 cm^3), benzyltributylammonium bromide (0.4 g), sodium hydroxide 50% (100 cm^3) and chloroform (50 cm^3) was added dropwise with vigorous stirring at 45^{o}C. The reaction was carried out for 5 hours until the whole solution became colourless; then the mixture was diluted with water. The organic layer was separated, washed with water and dried over $MgSO_4$. Evaporation of the solvent in vacuo yielded a viscous smelly product.

The aqueous layer, on acidification with dilute hydrochloric acid or tetrafluroboric acid, gave a white product. Recrystallisation from methanol afforded pure product m.p. 260^o(d).

6.1.11 Preparation of Bis(p-chlorophenyl)diselenide(184)

p-Chlorophenylaniline (13 g) in concentrated hydrochloric acid (20 cm^3) was cooled to 0^{o}C. To this mixture was added sodium nitrite (8 g) dissolved in cold water (20 cm^3). A solution of sodium acetate was added to neutralise the excess acid. Afterwards, potassium selenocyanate in water (75 cm^3) was added to the reaction mixture to give a precipitate of p-chlorophenylselenocyanate.

A solution of the selenocyanate (.002 mole) in ethanol was treated with an ethanolic solution of potassium hydroxide (.004 mole). After 5 minutes stirring, the mixture was diluted with water and the product was filtered and dried. The crude product was treated with charcoal and petroleum ether (30-40°) to give a deep yellow diselenide, m.p. 69-71°.

6.1.12 Attempts to react bis(p-chlorophenyl)diselenide with $|\overline{C}Cl_2$

The insertion reaction of dichlorocarbene to diselenide was done by a procedure described.

No colour change was noticed after 6 hours of stirring at 45°C and the diselenide was recovered on work up.

6.1.13 Preparation of Phenyl(trichloromethyl)mercury(185)

To a suspension of phenylmercury chloride (7.8 g) in chloroform (35 cm^3) and tributylbenzylammonium bromide (0.4 g), a solution of sodium hydroxide (10 g) and $KF.2H_2O$

(30 g) in water (40 cm^3) was added dropwise with vigorous stirring at room temperature. After two hours of stirring, the mixture was diluted with water. The organic layer was separated and dried over $MgSO_4$. Evaporation of the solvent on a rotatory evaporator afforded the crude product which was purified by washing with methanol and drying under vacuum, m.p. 108-109°(lit. 110-111°).

6.1.14 Attempted Preparation of Bis(p-EtOphenyltellurium) dichloromethane

In a dried, three-necked flask equipped with a reflux condenser, magnetic stirrer and nitrogen inlet, was charged phenyl(trichloromethyl) mercury (.01 mole) and sodium dried benzene (200 cm^3). Bis(p-ethoxyphenyl)ditelluride (.01 mole) was added quickly and the reaction mixture was heated to reflux for 10 hours. Filtration gave a red coloured solid which was soluble in dichloromethane and precipitated on adding n-pentane as white shiny plates, m.p. 150°. Evaporation of the filtrate afforded a viscous red-coloured liquid which solidified on adding n-hexane to give a slightly yellow solid m.p. 86-88°.

6.1.15 Attempt to Synthesise Tetrakis(p-ethoxyphenyl) tetratelluraethylene

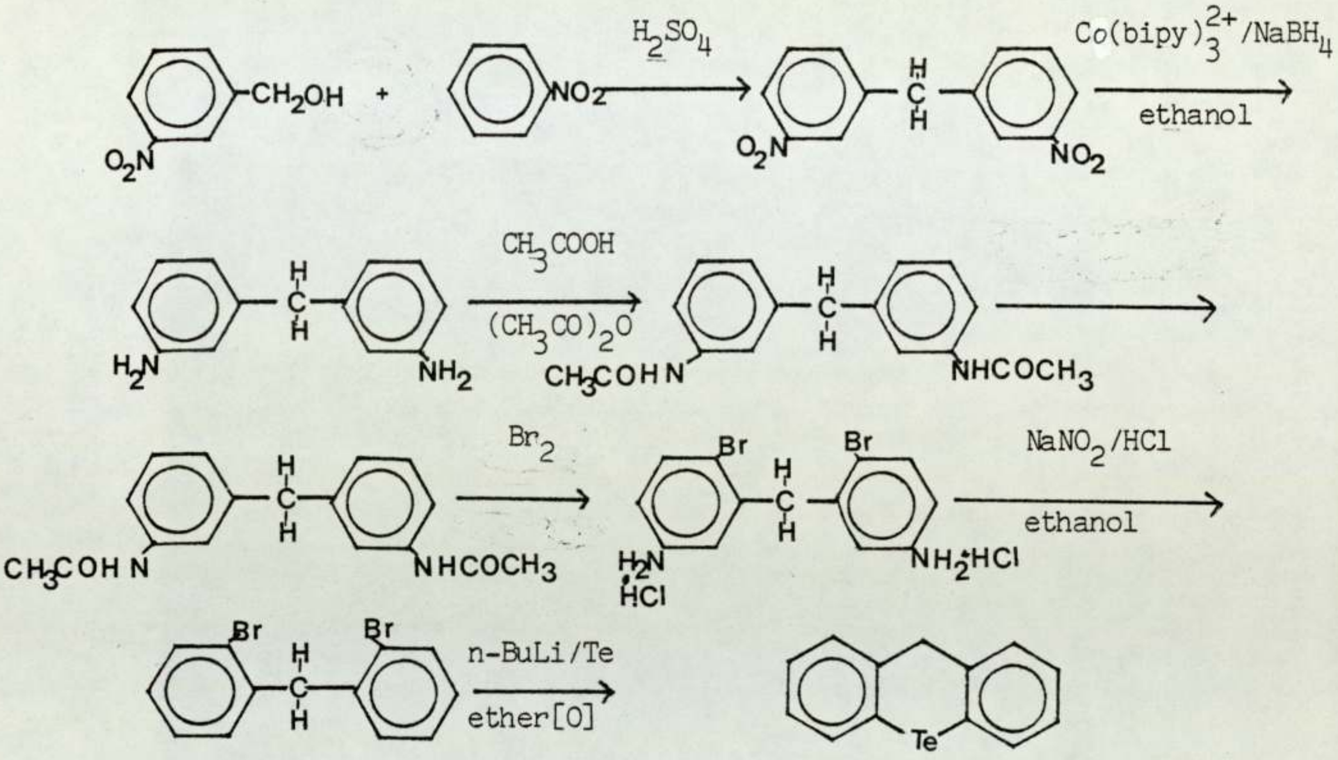
A solution of bis(p-ethoxyphenyl)ditelluride (6.2 g, 12.5 m mole) in benzene (5 cm^3) and ethanol (15 cm^3) was heated to reflux. To this solution was added dropwise a solution of sodium borohydride (0.75 g, 20 m mole) in N NaOH (17 cm^3). The solution mixture was colourless at the end of addition. Then tetrachloroethylene (1.0 g, 6.25 m mole) was added rapidly and the solution stirred. Soon after, red coloured ditelluride started precipitating. The work up of the reaction yielded an almost quantitative amount of ditelluride.

6.1.16 Attempt to Synthesise Dinaphthotetratelluraethylene

A solution of 1,8-dibromonaphthalene (4.26 g) in dry tetrahydrofuran (300 cm^3) was gradually added to n-butyllithium (.95 g, 9.3 cm^3 of 1.6 M n-BuLi in hexane) at -80° with vigorous stirring under dinitrogen. After half an hour of addition, powdered tellurium (1.9g) was added and the temperature was raised to 0°C. The temperature was again maintained at -80° and another lot of n-BuLi (0.95 g) was added, followed by addition of tellurium powder (1.9 g). To the reaction mixture was added tetrachloroethylene (1.2 g, .76 cm^3). This solution was stirred at -80° for 6 hours and then overnight at room temperature. Filtration and extraction of precipitate several times with CS_2 gave no solid and the black precipitate was characterised as tellurium powder.

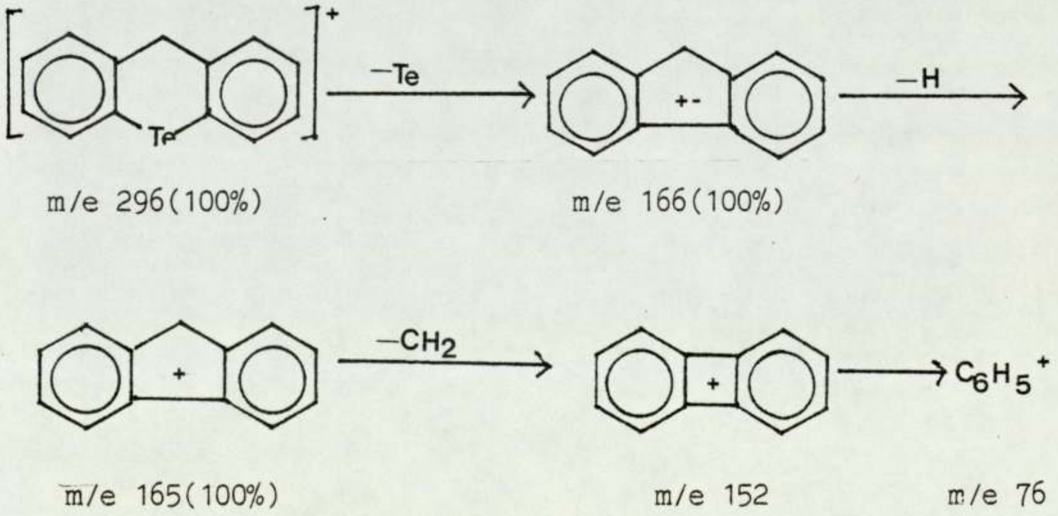
6.2 Results and Discussion

Telluraxanthene was prepared by the method of Lohner and Praefcke. The sequence of reactions is depicted by the following Scheme 2:



Scheme 2

This was characterised by m.p. 150° (lit. 151°C) and mass spectroscopy. The molecular ion peak was observed at m/e=296. The fragmentation pattern is given below (Scheme 3):



Scheme 3

Telluraxanthene itself seemed an interesting compound of which to study the donor properties. However, it failed to react with TCNQ. This was surprising since other tellurides formed CT complexes with TCNQ under rather mild conditions. However, it also failed to form a telluronium salt with methyl iodide(175). Structurally, it seems the basicity of the donor should be almost equal to diphenyl telluride which forms a CT complex with TCNQ. The appearance potential of telluraxanthene was measured by a mass spectroscopic method(74) and was found to be 10.25 eV which compares very well with the AP of diphenyl telluride (∼10 eV) determined by the same method. Figure 6.2 shows a plot of the relative abundance of telluraxanthene and argon as the exciting potential is varied from 8 eV to 70 eV. Table 6.1 gives the relative abundancies of telluraxanthene and argon.

The failure of complex formation by telluraxanthene can be due to two reasons; (1) it is actually very stable and a relatively poor donor, (2) steric factors may also be responsible for non-reactivity.

The synthesis of (telluraxanthylium)$^+$TCNQ$^-$ salt was attempted following a preliminary report by the Russian group(186). Scheme 4 shows the approach to the title compound.

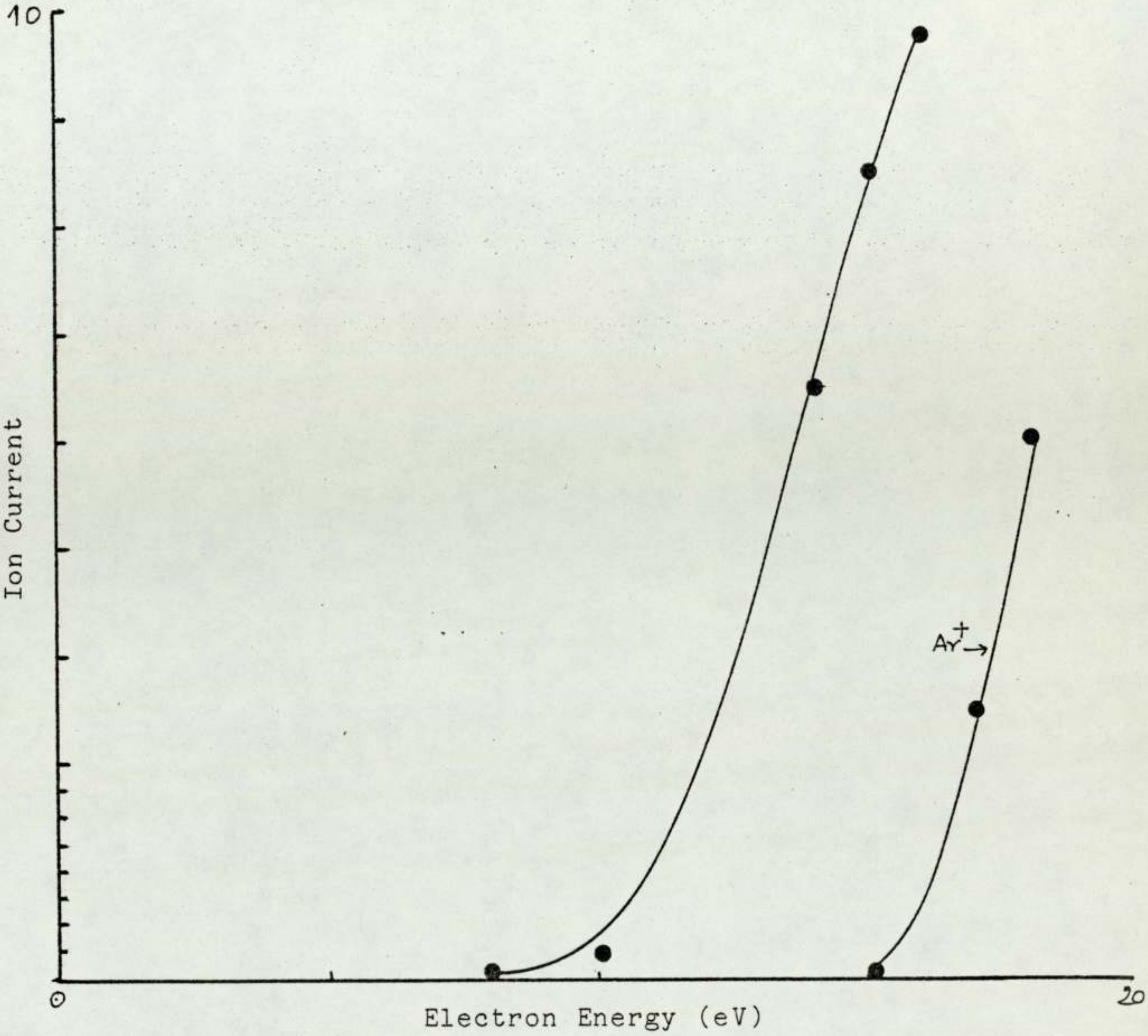
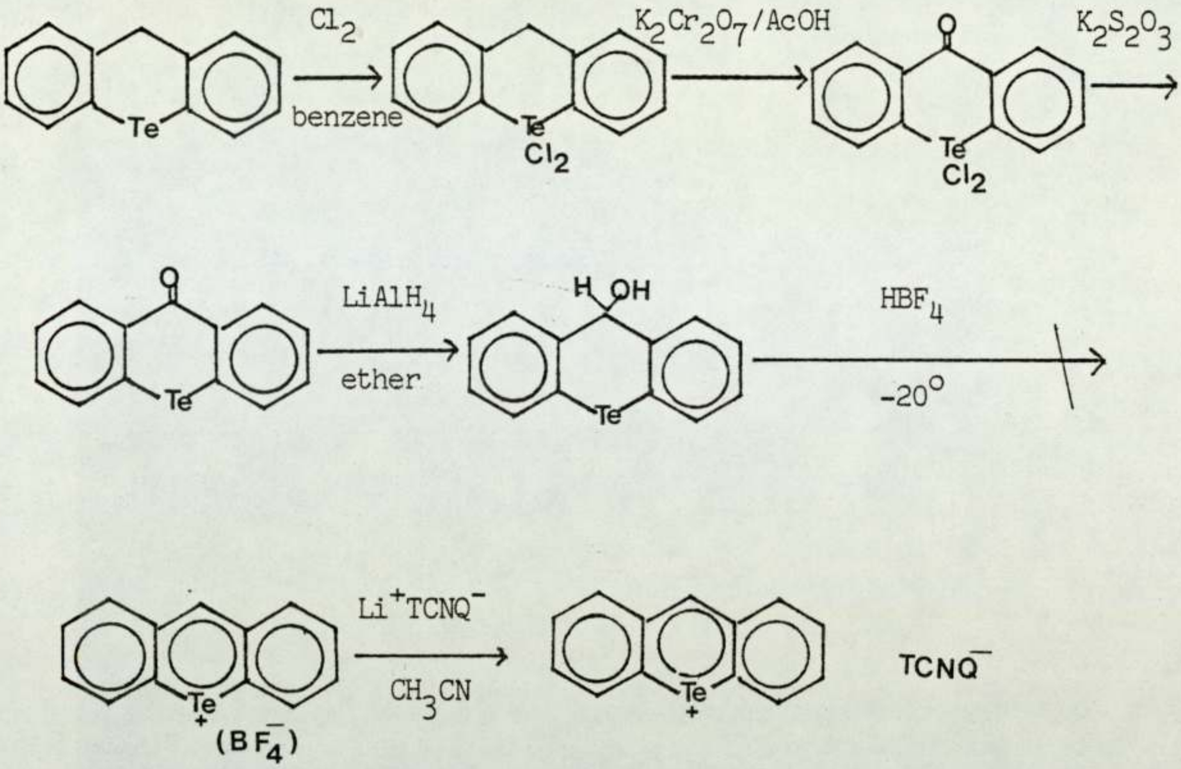


Figure 6.2 Graph of ion current against electron energy for telluraxanthene → (telluraxanthene)$^+$

Electron Energy (eV)	% Ion current	
	$C_{13}H_{10}Te^+$	Ar^+
70	100	76.25
20	54	21.25
19	32.5	12.5
18	20	5
17	11.5	2.5
16	.5	8.7
15	0	7.5
14	0	5.5
12	0	1.87
10	0	.25

Table 6.1 Ionisation efficiency data for '$C_{13}H_{10}Te$'



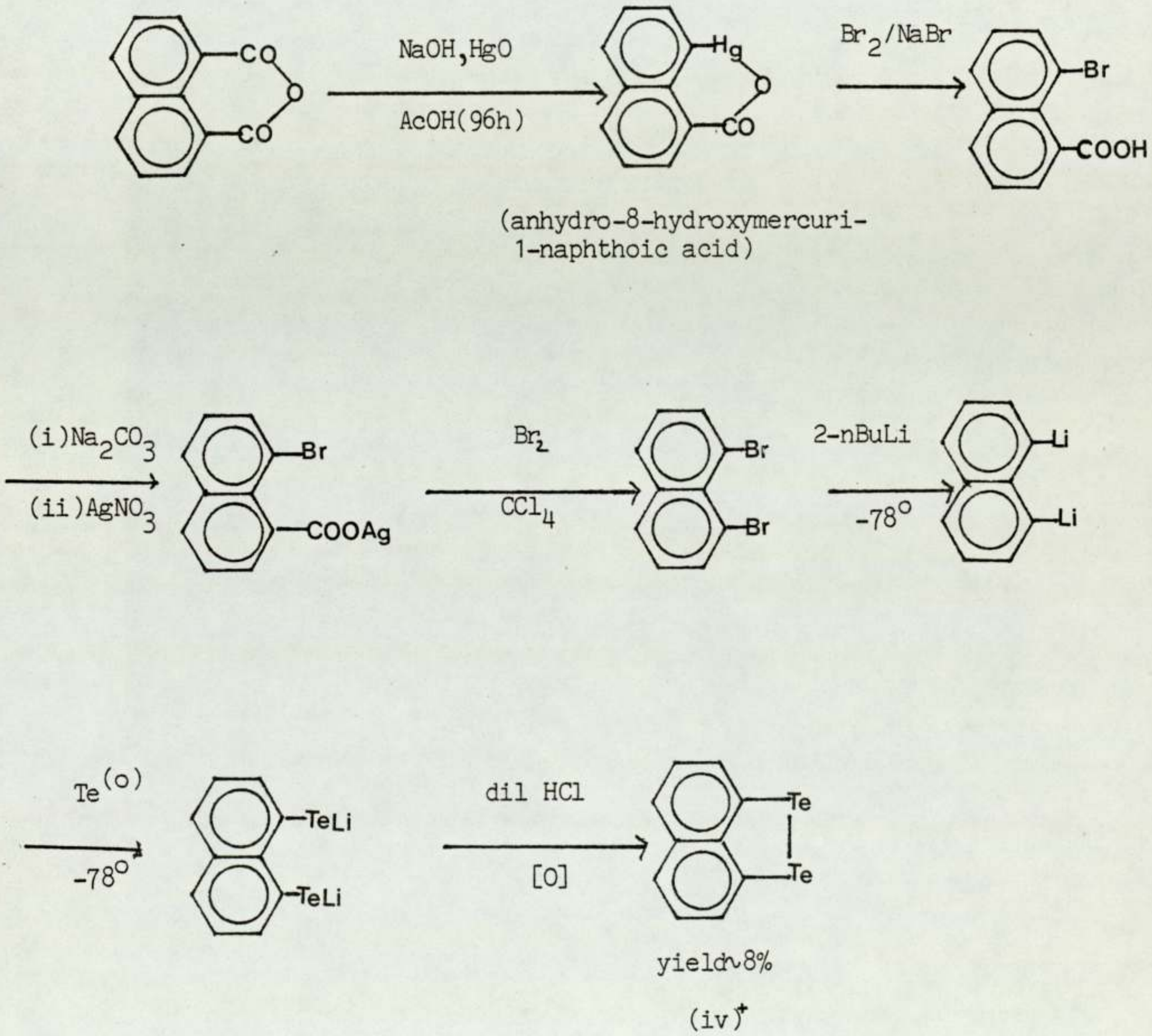
Scheme 4

10,10-Dichlorotelluraxanthene was obtained by passing dry Cl_2 gas to telluraxanthene. Then it was oxidised with potassium dichromate followed by reduction with potassium metabisulphite to get telluraxanthone. Telluraxanthone was recrystallised as yellow needles. All these intermediates were characterised by melting point determinations. On reduction with lithium aluminiumhydride, the yellow colour of the ethereal solution changed to colourless. After work up and adding hydrofluoric acid, no solid was obtained and not even a change in colour was observed. It appeared that no reaction took place, and the scheme could not be followed further.

It is still felt that the title compound can be prepared if the correct condition could be found.

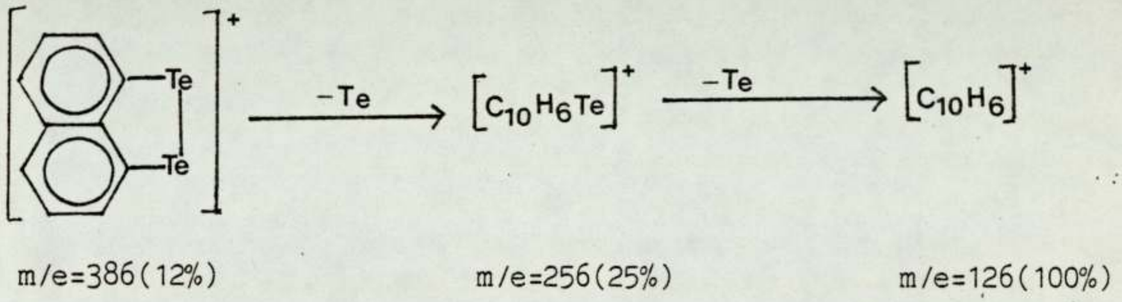
6.3 Attempted Synthesis of Dinaphthotetratelluraethylene

Naphtho(1,8-C,D)1,2-ditellurole was synthesised by the reported method(183). The Scheme 5 is illustrated below:



Scheme 5

Attempts to prepare 1,8-dibromonaphthalene by tetrazotization(187) of 1,8-diaminonaphthalene followed by addition of CuBr + HBr yielded a black residue from which only very low yields of 1,8-dibromonaphthalene could be obtained. The other procedure reported by Letsinger et al(181), though lengthy, gave better yields. The ditellurole was greenish grey in colour, fairly soluble in carbon disulphide. It was characterised by melting point and mass spectrum (Scheme 6). Table 6.2 gives the relative abundance of different fragments in molecular ion cluster.



Scheme 6, based on ^{130}Te

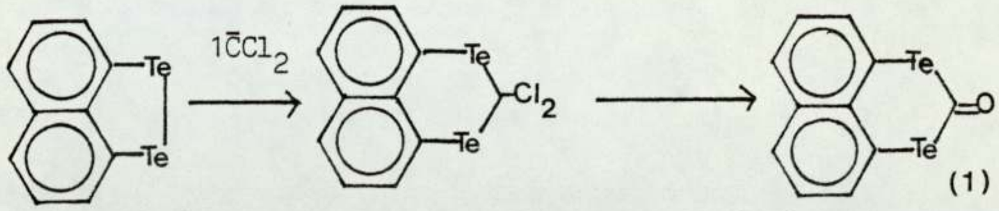
The reaction of the ditellurole with 'chloranil' provided a silvery-grey coloured flaky precipitate. This compound does not give an E.S.R. signal. The I.R. spectrum shows the presence of ν(CO). Elemental analysis was not as expected and could not be improved by recrystallisation. The CT complex of iv^{+} with TCNQ is reported to have good compact disc conductivity(183).

In order to try and obtain dinaphthotetratelluraethylene (DNTTeE) and related derivatives starting from ditellurole, an attempt was made to insert dichlorocarbene ($|\overline{C}Cl_2$) into

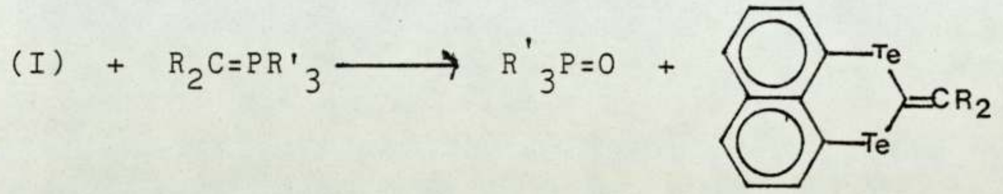
373	(2)
374	(6)
375	(5)
376	(17)
377	(16)
378	(36)
379	(25)
380	(66)
381	(28)
382	(100)
383	(12)
384	(92)
385	(9)
386	(50)
387	(5)

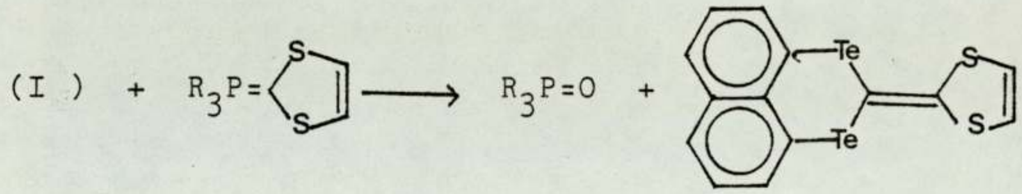
Table 6.2 Intensity ratio of molecular ion cluster (calculated)

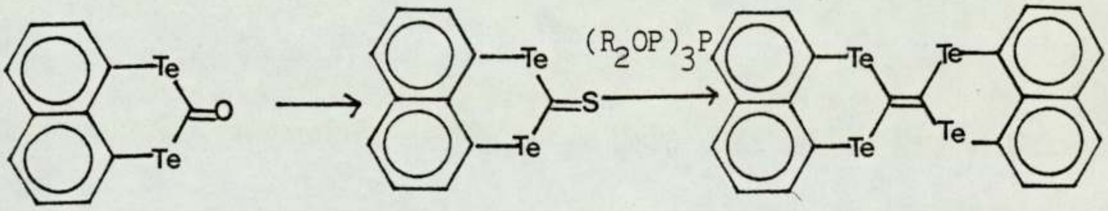
the Te-Te bond. This then could be converted to the title compounds by a Wittig reaction(188). Our approach to the title compounds is illustrated below:



(1)







6.4 Dichlorocarbene Insertion Into Te-Te Bond

Dichlorocarbene is simple to prepare and is known to undergo insertion into the Sn-Sn bond(189). Phenyl(trichloromethyl)-mercury was used to generate $|\bar{C}Cl_2$. Similar attempts to get dichlorocarbene insertion into the Te-Te bond by Petragnani and Schill led to isolation of products of indefinite composition(190). However, diazomethane reacted with diorganoditellurides to give telluroacetals (Eq 1).

$$\text{R-Te-Te-R} + CH_2N_2 \longrightarrow \text{RTe-}CH_2\text{-TeR} + N_2 \qquad \text{(Eq.1)}$$

It seemed possible that the phase-transfer technique could be used to do the reaction of dichlorocarbene with diorganoditellurides. The reagent ($1\bar{C}Cl_2$) is prepared in situ by a two phase system(191) involving reaction of chloroform with concentrated aqueous sodium hydroxide solution in the presence of quaternary ammonium compound as catalyst. In this instance tributylbenzylammonium bromide (Q^+) was used as catalyst. The scheme is shown in the following equations:

$$\begin{aligned}
&\text{NaOH(aq)} + \text{QBr(org)} &&\longrightarrow \text{Q(OH)(aq)} + \text{NaBr(aq)}\\
&\text{Q(OH)(aq)} &&\longrightarrow \text{QOH(org)}\\
&\text{QOH(org)} + CHCl_3\text{(org)} &&\longrightarrow H_2O + Q^+Cl_3C^-\text{(org)}\\
&Q^+Cl_3C^- &&\longrightarrow \text{QCl} + 1\bar{C}Cl_2
\end{aligned}$$

Due to the very low yield of the ditellurole and lengthy procedure of its preparation, insertion reactions were attempted with simple ditellurides. The reaction of bis-(p-ethoxyphenyl)ditelluride with $1\bar{C}Cl_2$ in the presence of the phase transfer catalyst provided a foul smelling, viscous oil (vii) from the organic phase in low yields of 10%. The most striking feature of the infra-red spectrum was the presence of a carbonyl group frequency and the absence of C-Cl stretching vibrations. Two strong bands at 1746 cm^{-1} and at 1670 cm^{-1} were observed which could be due to splitting of the carbonyl group frequency (Figure 6.3). The infra-red spectra of several tellurobenzoicacid-tellurophenyl esters have been

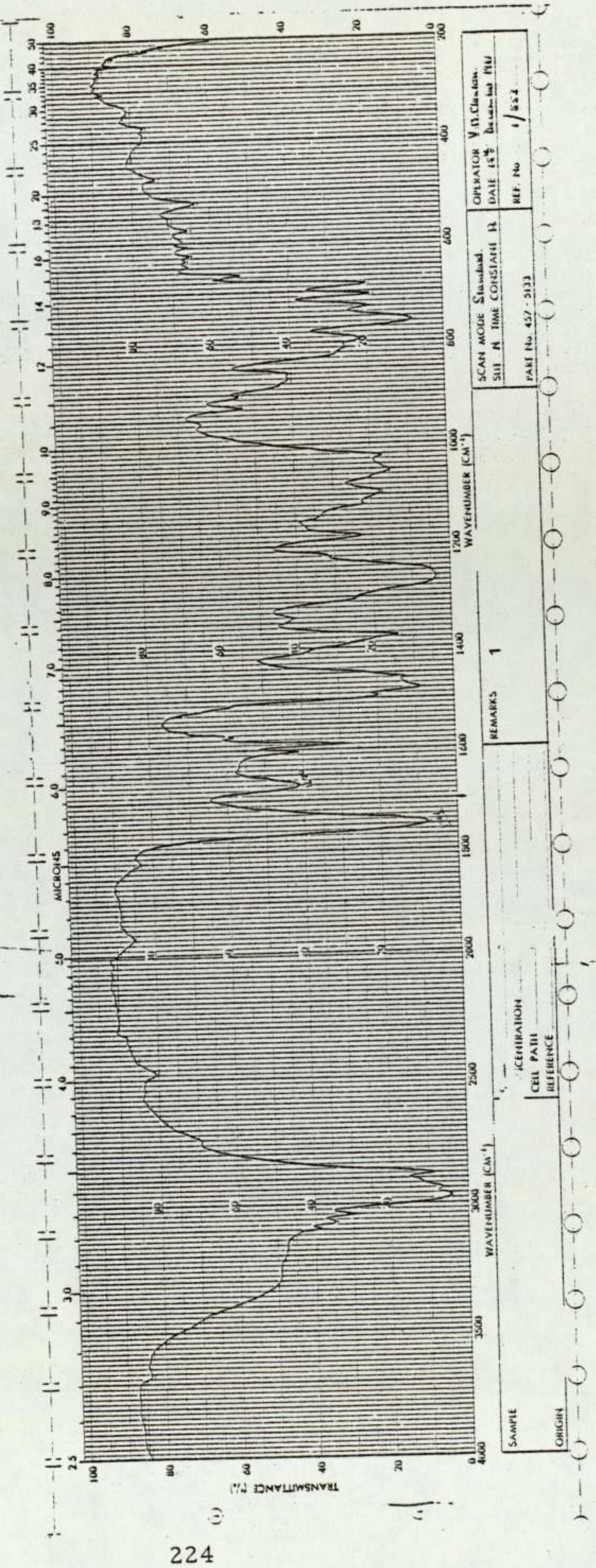
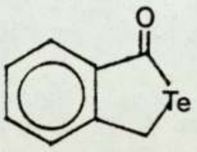


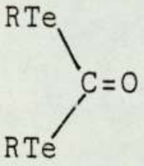
Figure 6.3 I.R. spectrum of $(p\text{-EtOPhTe})_2CO$

analysed in detail by Piette and Renson(192,193) who observed a splitting of the carbonyl band. Similar splitting of carbonyl band (1690, 1740 cm^{-1}) has been reported by Engman and Cava for tellurophthalide (vi) and has been attributed to Fermi resonance(107).



(vi)

On the basis of carbonyl band splitting (1670, 1746 cm^{-1}) which probably arises from Fermi resonance with the fundamental at 865 cm^{-1}, the following structure is proposed for (vii).



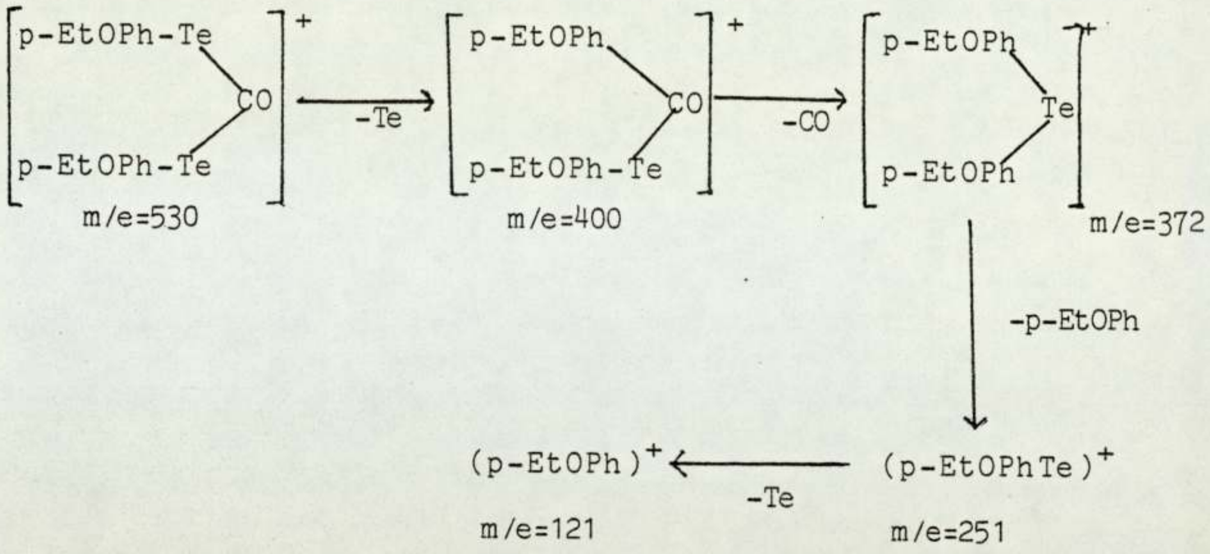
$(RTe)_2C=O$

(R=p-EtOPh)

(vii)

It appears that the dichlorocarbene derivative of the ditelluride is hydrolysed to give (vii).

The mass spectrum of (vii) showed a base peak at m/e=530 confirming the proposed structure. The fragmentation pattern is given below:



To characterise (vii) further, an attempt was made to prepare the hydrazone derivative. The reaction of (vii) with phenylhydrazine in ethanol yielded a red coloured compound. The infra-red spectrum showed absence of ν(CO) (Figure 6.4) but surprisingly ν(CN) was also not observed (which would be formed on treating with phenylhydrazine). The spectrum was found to be identical with the I.R. spectrum of the ditelluride. The mass spectrum confirmed that ditelluride had formed. The base peak was observed for R_2Te_2 at m/e=502. It appears that phenyl hydrazine had reduced the telluroacetal rather than forming a hydrazone derivative.

(vii) decomposed on standing for a long time.

The aqueous phase of the reaction on acidification with hydrochloric acid or tetrafluoroboric acid afforded a white compound (viii). Analytical data suggest an empirical formula of $(RTeO)_2O$. The infra-red spectrum of (viii) showed the presence of ν(Te=O) at 600 cm^{-1}(194) and ν(Te-O) at

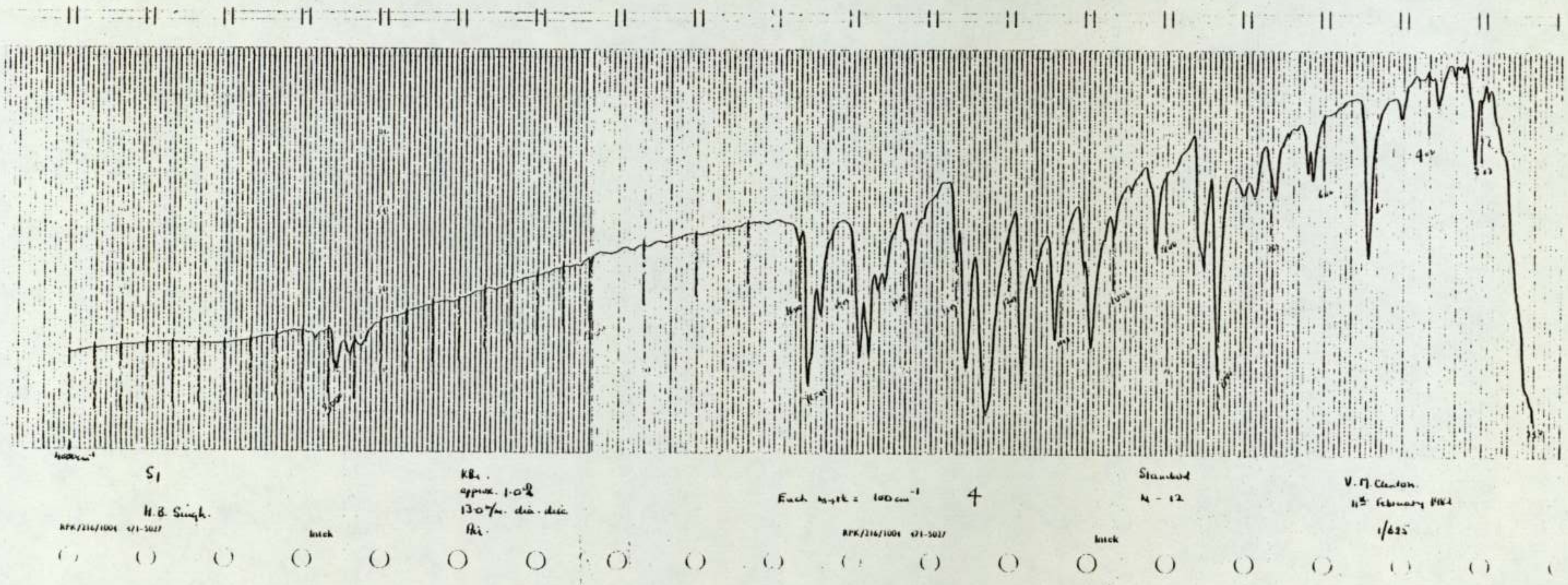
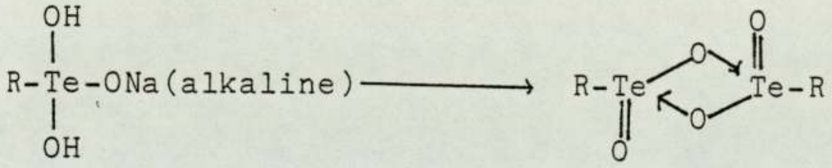


Figure 6.4 I.R. spectrum of $(p\text{-EtOPh})_2Te_2$

$\sim 285\ cm^{-1}$(194) (Figure 6.5). The mass spectrum (Scheme 7) showed a base peak at m/e 502 ($R_2Te_2^+$) indicating the probable polymeric nature of (viii). Reduction with hydrazine hydrate also afforded R_2Te_2. The fact that (viii) is fairly soluble and precipitates on acidification leads one to believe that the compound (viii) is molecular in alkaline medium and polymerises as pH decreases (shown below).



(viii)

To probe more deeply into the structure of (viii) several other oxygenated organotellurium compounds were prepared and their colour, melting point, I.R. and M.S. compared with (viii) and it was found that (viii) was different from the rest. The following organotellurium derivatives were prepared;

(I)  $R\text{-}\overset{O}{\overset{\|}{Te}}\text{-}O\text{-}\overset{O}{\overset{\|}{Te}}\text{-}R$ (195) , (II) R_2TeO(196) , (III) R_2TeO_2(197)

The low yield of (vii) and isolation of large quantities of the highly oxygenated derivative $(RTeO)_2O$, suggests that the ditelluride is affected by atmospheric oxygen. Work by others in our laboratory has independently demonstrated a reaction of ditellurides in solution with dioxygen capable of producing radical intermediates(198), hence the following scheme of equations might be responsible for production of (viii)

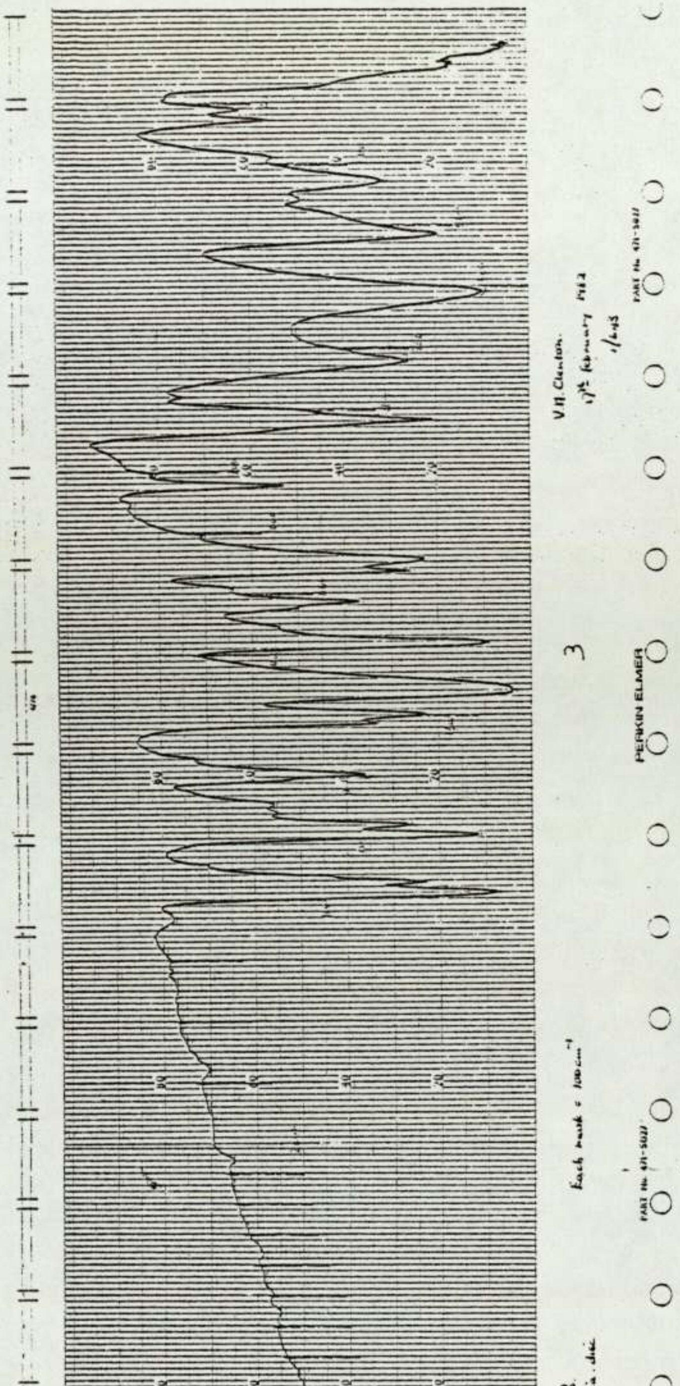
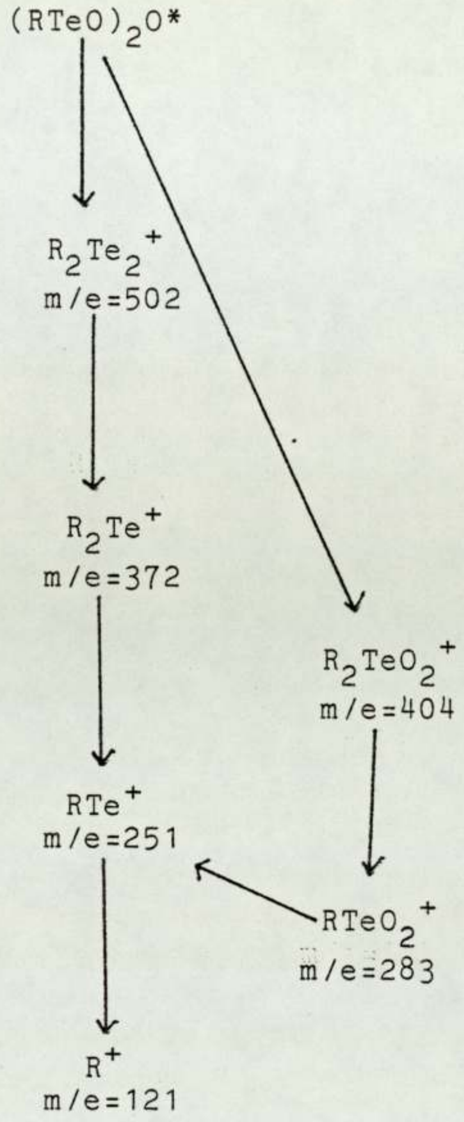
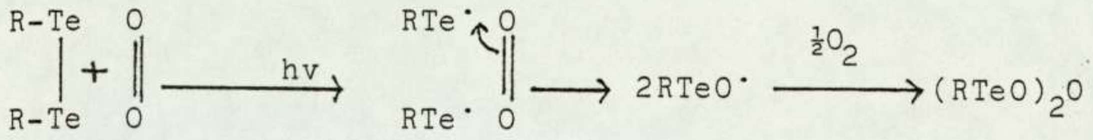


Figure 6.5 I.R. spectrum of $(p\text{-}EtOPhTeO)_2O$



* not observed
(based on ^{130}Te)

Scheme 7 Mass fragmentation pattern of (RTeO)$_2$O



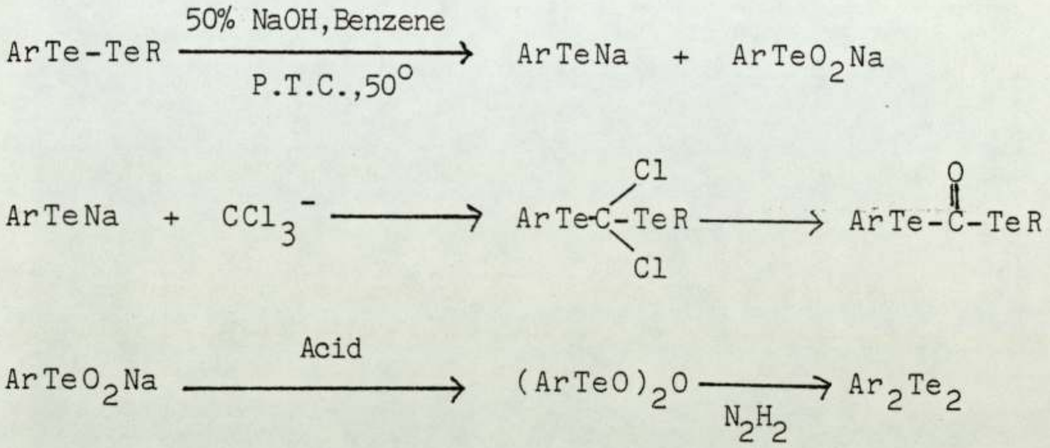
To ascertain the exact nature of the compound (viii) arrangements to measure ^{125}Te N.M.R. spectrum at different pH's are being made.

When the reaction was repeated in an inert atmosphere (solvents deoxygenated, and dry box used to maintain the absence of oxygen), the reaction period increased, but still ditelluride was scavenging O_2. It is certain that some oxygen will have got in during setting up the apparatus and perhaps during the course of the reaction. Two recent reports$^{(199,200)}$ which are in excellent agreement with our observations would be worth mentioning. The reaction between diarylditelluride and SeO_2 results in the insertion of Se between the Te atoms and also in the formation of highly oxygenated insoluble products. These are speculated to be as ditellurone or tellurinic acid anhydride.

The second report$^{(200)}$ explains the mechanism of the reaction. The authors claim that under phase transfer conditions, disproportionation of ditellurides takes place to give aryltellurolate anion which is responsible for the reaction (Eq. 2)

$$2ArTe\text{-}TeR \xrightarrow[\text{P.T.C.},N_2]{50\%\ \text{NaOH, THF}} 3ArTeNa + ArTeO_2Na \qquad (Eq.2)$$

In the light of the above evidence, the reactions of diaryl-ditelluride with dichlorocarbene could be represented as follows:



Bis(p-chlorophenyl)diselenide when treated with $|\overline{C}Cl_2$ by the same phase-transfer technique failed to react and was recovered as such.

In another experiment of insertion of $|\overline{C}Cl_2$, phenyl(trichloromethyl)mercury ($PhHgCCl_3$) was used for generating dichlorocarbene. The advantage over the first method consisted in direct formation of dichlorocarbene from organomercurial(201) without intermediate formation of trichloromethyl anion ($CCl_3^- \longrightarrow |\overline{C}Cl_2$) and also absence of aqueous sodium hydroxide, to which organotelluriums are susceptible to hydrolysis. The reaction of phenyl(trichloromethyl) mercury with bis-$(pEtOPh)_2Te_2$ yielded an oily compound which solidified upon addition of hexane.

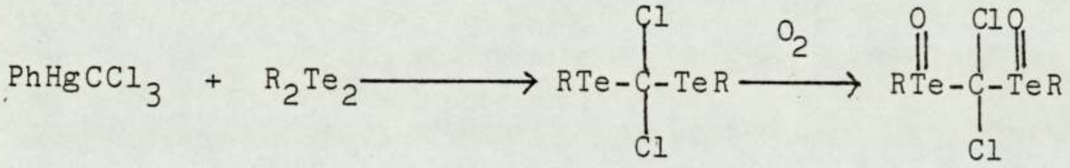
Elemental analysis was incomprehensible and the material could not be further purified.

Examination of the infra-red spectrum of the product showed a number of interesting features (Figure 6.6);

(i) Appearance of bands at 740 and 640 is assigned as a C-Cl stretching frequency.

(ii) A broad band at ~600 cm^{-1} which is characteristic of $\nu(Te=O)$.

From the above evidence it seems that insertion has taken place, however, the presence of $\nu(Te=O)$ shows that still a certain amount of ditelluride was reacting with oxygen. The possible reaction scheme is given below:



$$PhHgCCl_3 + R_2Te_2 \longrightarrow RTe-\overset{Cl}{\underset{Cl}{C}}-TeR \xrightarrow{O_2} R\overset{O}{\overset{\|}{Te}}-\overset{Cl}{\underset{Cl}{C}}-\overset{O}{\overset{\|}{Te}}R$$

Similar observations have been made by Petragnani et al$^{(190)}$.

6.5 Attempted Synthesis of Tetrakis(p-EtOPhenyltellurium)-ethylene

R_2Te_2 upon reduction with alkaline sodium borohydride is reported to give the reagent 'NaTeR'$^{(202)}$. It was hoped that the reaction of this reagent with tetrachloroethylene (TCE) may lead to the isolation of a tetratelluraethylene derivative (Scheme 8).

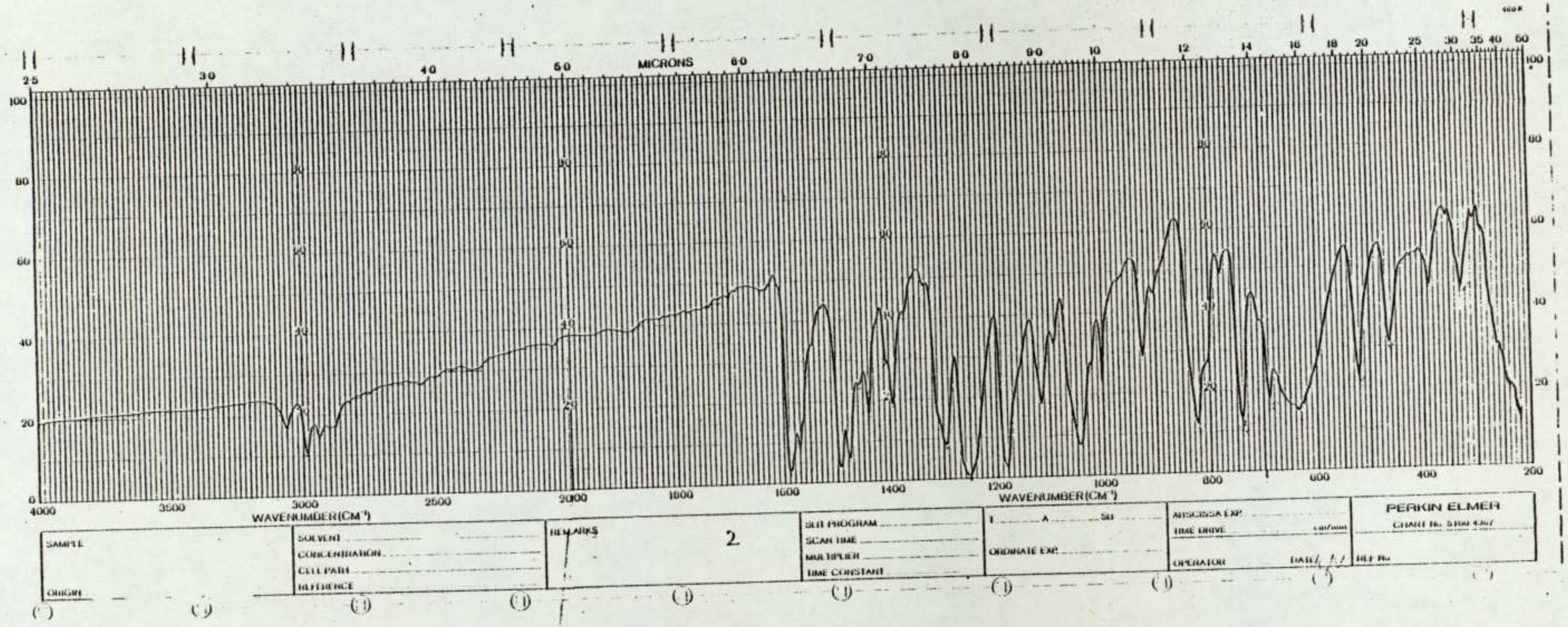
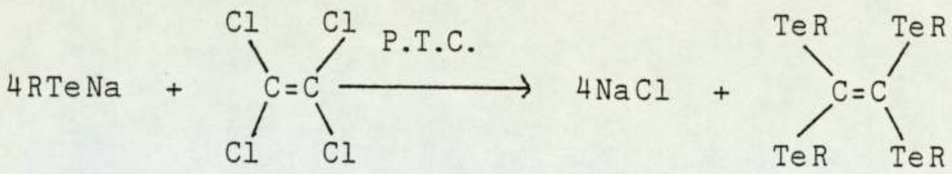
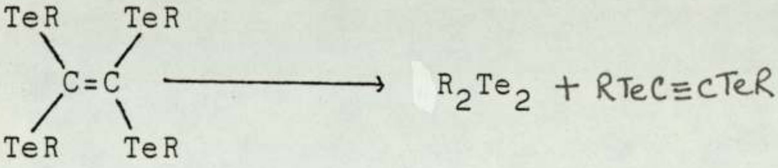


Figure 6.6 I.R. spectrum of $(p\text{-EtPhTeO})_2CCl_2$

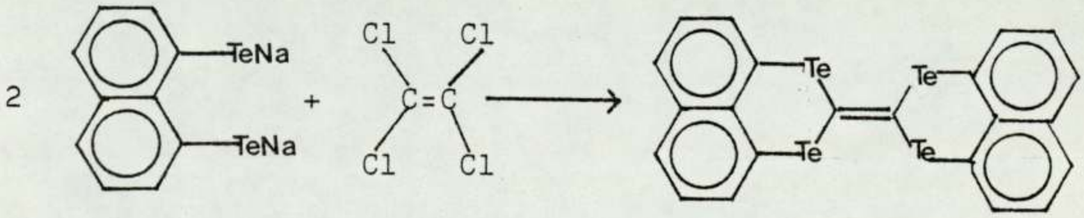


Scheme 8

But the addition of tetrachloroethylene to the boiling solution of 'NaTeR' resulted in the precipitation of ditelluride in almost quantitative yield:

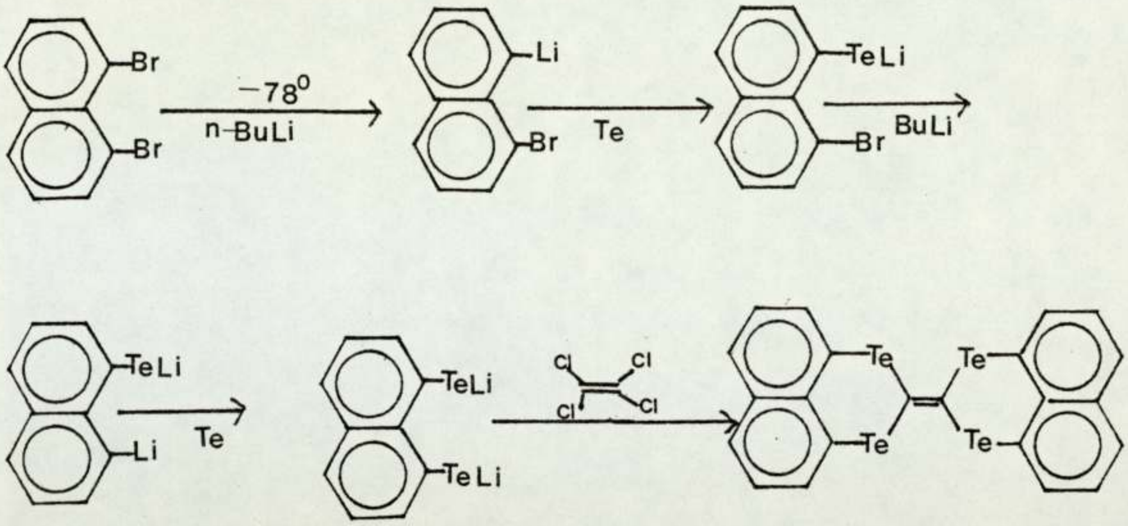


This reaction was therefore not attempted as previously desired, with naphtho(1,8-C,D)1,2-ditellurole i.e.,



6.6 Attempted Synthesis of Dinaphthotetratelluraethylene (DNTTeE)

The synthesis of (DNTTeE) was prompted by two recent reports of the synthesis of tetratellurafulvalene derivatives. The sequence of reactions is shown below:



The work up of the reaction gave tellurium powder as the only solid product.

Compound	m.p. ^{o}C	yield%	C% (calc)	H% (calc)	Te% (calc)
$(RTe)_2CCl_2$	86-88	25	38.5 (35.1)	3.6 (3.12)	-
$(RTeO)_2O$	260(d)	80	-	-	45.4 (46.7)
$C_{10}H_6Te_2$.chloranil	250-254(d)	90	58.5 (30.6)	4.0 (1.0)	-

Table 6.3 Analytical data and yields

$(RTe)_2CO$	R_2Te_2	$(RTeO)_2O$	$(RTeO)_2CCl_2$
3100	2960	3090	3060
3070	2920	3070	2980
2965		2990	
1746			
1670			
1605	1606	1595	1590
1590	1585	1570	1570
	1560		
1480	1490	1495	1490
	1470	1475	1475
	1450		
1375	1390	1395	1395
	1300	1310,1296	1300
1260	1285	1260	1255
	1250		
1095	1180	1180	1180
	1110	1130	1115
		1110	
1050	1045	1060,1040	1045
925	920	920	925
865	830	815	822
760,730	800	718	740
705	695	605	690
685	620		630
520	515	510	520
470	450	460,428	460,390
300	310	325	340
		310	305
		275	

Table 6.4 Infra-red data of bis(p-ethoxyphenyl)ditelluride and its derivatives

REFERENCES

1. C Kittel, "Intro to Solid State Physics", J.Wiley, New York, (1966).
2. J Bardeen, L N Cooper and J R Schrieffer, Phys.Rev., (1957), 108, 1175.
3. W A Little, Phys.Rev., (1964), A134, 1416.
4. F London, "Superfluids" Vol.I, J Wiley & Sons, New York,(1958).
5. A G MacDiarmid and A J Heeger in "Molecular Metals" edited by W E Hatfield, Plenum Press, New York, (1979).
6. M M Labes,P Love and L F Nichols, Chem.Rev.,(1979),79,1.
7. M J Cohen,S F Garito,A J Heeger,A G MacDiarmid,C M Mikulski, M S Saran and J Kleppinger, J.Amer.Chem.Soc.,(1976),98,3844.
8. D S Acker and W R Hertler, J.Amer.Chem.Soc.,(1962),84,3370.
9. R E Sorg,R A Sparks and K N Trueblood, Acta Cryst.,(1965), 18, 932.
10. Y Iida, Bull.Chem.Soc.Jpn., (1969),42,263.
11. L R Melby, Can.J.Chem., (1965),43,1448.
12. F Wudl,D Wobschall and E J Hufnagel, J.Amer.Chem.Soc., (1972), 94, 670.
13. L B Coleman,M J Cohen,D J Sandman,F G Yamagishi,A F Garito and A J Heeger, Solid State Commun., (1973),12,1125.
14. J B Torrance, Acc.Chem.Res., (1979),12,79.
15. T J Kistenmacher,T E Phillips and D O Cowan, Acta Cryst., (1974),B30,763.
16. F Denoyer,R Comés,A F Garito and A J Heeger, Phys.Rev.Lett., (1975),35,445.
17. A Andrieux,C Duroure,D Jérome and K Bechgaard, J.Phys.Lett., (1979),40,L-381.

18. D Jérome,M Ribault and K Bechgaard, New Sci., (1980),104.

19. K Bechgaard,C S Jacobsen,K Mortensen,H J Pedersen and N Thourp, Solid State Commun., (1980),33,1119.

20. R Comés and G Shirane in "Highly Conducting One Dimensional Solids" edited by J T Devreese,R P Evrard and V E van Doren, Plenum Press, New York, (1979),17.

21. Y Tomkiewicz and A Taranko, Phys.Rev.Lett., (1976),36,751.

22. G Soda,D Jérome,M Weger,J Alizon,J Gallice,H Robert,J M Farbe and L Giral, J.Physique, (1977),38,931.

23. A J Berlinsky,J F Carolan and L Weiler,Solid State Commun., (1974),15,795.

24. A W Addison,J P Barnier,V Gujral,Y Hoyano,H Huizinga and L Weiler in "Molecular Metals" edited by W E Hatfield, Plenum Press, New York, (1979),15.

25. F Wudl and D Nalewajek, J.Organometal.Chem., (1981)217,329.

26. M L Petrov,V Z Iaihev and A A Petrov,Russ.J.Org.Chem. (Engl. Transl.) (1979), 15, 2346.

27. M V Lakshmikantham,M P Cava,M Albeck,L Engman,F Wudl and E J Ahron-Shalom, J.Chem.Soc.,Chem.Commun., (1981),828.

28. S L Bender,M R Detty and N F Haley, Tetrahedron Lett., (1982), 23,1531.

29. F Wudl and E Ahron-Shalom, J.Amer.Chem.Soc., (1982),104,1154.

30. J S Bajwa,K D Berlin and H A Pohl,J.Org.Chem.,(1976),41,145.

31. K Lerstrup,D Talham,A Bloch,T Poeler and D Cowan, J.Chem.Soc., Chem.Commun., (1982),336.

32. D J Sandman,C J Stark and B M Foxman,Organometallics,(1982), 1,739.

33. D J Sandman, G P Hamill and W A Burke, Mol.Cryst.Liq.Cryst., (1982), 86, 79.

34. S L Bender, M R Detty, M W Fichtner and N F Haley, Tetrahedron Lett., (1983), 24, 237.

35. L Syper and A Sucharda-Sobczyk, Bull.Acad.Pol.Sci., (1975), 13, 563.

36. N S Dance, W R McWhinnie, J Mallaki and Z Monsaf-Mirzai, J. Organomet.Chem., (1980), 198, 131.

37. C A Heller, R A Zingaro and E A Meyers, Can.J.Chem., (1974), 52, 3814;
D P Rainville, R A Zingaro and J P Ferraris, Can.J.Chem., (1980), 58, 1133.

38. J Meinwald, D Dauplaise, F Wudl and J J Hauser, J.Amer.Chem. Soc., (1977), 99, 225.

39. W C Dunlap, Jr, "Methods of Experimental Physics", New York, Academic Press Inc., (1959).

40. D D Eley and J D Parfitt, Trans.Faraday Soc., (1955), 51, 1529.

41. A J Epstein and J S Miller, "Linear Chain Conductors", Scientific American, (1979), 241, 52.

42. R E Cobbledick, F W B Einstein, W R McWhinnie and F H Musa, J.Chem.Research(S), (1979), 145.

43. A I Vogel, "Practical Organic Chemistry", (London), (1970), 163.

44. F H Kruse, R W Sanftner and J F Suttle, Anal.Chem., (1953), 25, 500.

45. C H W Jones, R Schultz, W R McWhinnie and N S Dance, Can.J. Chem., (1976), 54, 3234.

46. J D McCullough, Inorg.Chem., (1975), 14, 2285.

47. S Cuthbertson and D D MacNicol, Tetrahedron Lett., (1975), 1893.

48. H D K Drew, J.Chem.Soc., (1926), 223.

49. G T Morgan and H D K Drew, J.Chem.Soc., (1920), 1462.

50. N Petragnani and M de Moura Campos, Chem.Ber., (1961), 94, 1759.

51. W H H Günther, J Nepywoda and J Y C Chu, J.Organometal.Chem., (1974), 74, 79.

52. G T Morgan and H D K Drew, J.Chem.Soc., (1925), 2307.

53. M G Patel, Ph.D. Thesis, University of Aston in Birmingham, (1972).

54. L S Efros and Z V Todres-Selektor, J.Gen.Chem.(USSR), (1957), 27, 1064.

55. E M Engler, Proc.3rd Int.Symposium on Organic Selenium and Tellurium Compounds, Ed:D Cagniaut and A Kirsch, Universite de Metz, (1979), 357.

56. J Tanaka, M Tanaka, T Kawai, T Takabe and O Maki, Bull.Chem.Soc. Jpn., (1976), 49, 2358.

57. Y Yumoto, R Nishioka and T Tanaka, Bull.Chem.Soc.Jpn., (1980), 53, 1247.

58. M R Bryce, A S Secco, J Trotter and L Weiler, Can.J.Chem., (1982), 60, 2057.

59. A N Bloch, T F Carruthers, T O Poehler and D O Cowan, "Chemistry and Physics of One-dimensional Metals", Ed:H J Keller, Plenum Press, New York, (1977), 47.

60. P A Lee, M J Rice and P W Anderson, Solid State Commun., (1977), 14, 703.

61. R Comés and G Shirane, "Highly Conducting One-dimensional Solids", Ed:J T Devreese, R P Evrard and V E van Doren, Plenum Press, New York, (1979), p.26.

62. R J H Clark, "Molecular Metals", Ed:W E Hatfield, Plenum Press, New York, (1979), p.385.

63. J S Chappell,A N Bloch,W A Bryden,M Maxfield,T O Poehler and D O Cowan,J.Amer.Chem.Soc.,(1981),<u>103</u>,2442.

64. G Cauquis and M Maurey-Mey,Bull.Soc.Chem.France, (1973),291.

65. A Gioabă,V Em Sahini and E Volanschi, J.Chem.Soc., Perkin Trans. II, (1977),529.

66. H Bock,G Brähler,D Dauplaise and J Meinwald, Chem.Ber.,(1981), <u>114</u>,2622.

67. B Lamotte and G Berthier, J.Chem.Phys., (1966),<u>63</u>,369; H F Chiu and B C Gilbert, J.Chem.Soc.,Perkin Trans.II, (1973),258.

68. I Davies,W R McWhinnie, N S Dance and C H W Jones, Inorg. Chim.Acta., (1978),<u>29</u>,L203.

69. C Knobler and R F Ziolo, J.Orgnaometal.Chem., (1979),<u>178</u>,423.

70. R H Jones and T A Hamor, J.Organometal.Chem., (1982),<u>234</u>,299.

71. R M Cheyne,C H W Jones and S Husebye,Can.J.Chem.,(1975),<u>53</u>, 1855 and references therein.

72. H D Smyth, Proc.Roy.Soc.(London),Ser.A,(1922),<u>102</u>,283.

73. F P Lossing,A W Tickner and W A Bryce,J.Chem.Phys.,(1951),<u>19</u>, 1254.

74. J W Warren,Nature,(1950),<u>165</u>,810.

75. F P Colonna,G Distefano,V Galasso,K J Irgolic,C E King and G C Pappalardo, J.Organometal.Chem.,(1978),<u>146</u>,235.

76. H M McConnell, B M Hoffman and R M Metzger,Proc.Natl.Acad.Sci., (1965),<u>53</u>,46.

77. D T Cromer and J T Waber,"International Tables for X-ray Crystallography" IV, The Kynoch Press,Birmingham,England, (1974),[Table 2.2B].

78. J A Ibers and W C Hamilton,Acta Crystallogr., (1964),<u>17</u>,781.

79. D T Cromer,"International Tables for X-ray Crystallography", IV, The Kynoch Press,Birmingham,England,(1974),[Table 2.3.1].

80. J D McCullough,Inorg.Chem.,(1975),14,2639.

81. F H Herbstein,"Perspectives in Structural Chemistry",J D Duiritz and J A Ibers,Ed:John Wiley and Sons, New York,(1971), Vol.IV,p.355.

82. A Bondi,J.Phys.Chem.,(1964),64,441.

83. L Pauling,"The Nature of the Chemical Bond",Cornell University Press, Ithaca,New York,(1960),p.260.

84. J S Lee,D D Titus and R F Ziolo,Inorg.Chem., (1977), 16, 2487.

85. D D Titus,J S Lee and R F Ziolo,J.Organometal.Chem.,(1976), 120,381.

86. J D Wright and Z A Ahmed,Acta Crystallogr.,(1981),B37,1852.

87. I Goldberg and U Shmeuli,Acta Crystallogr.,(1977),B33,2187.

88. A M Heyns and C W F T Pistorius,Spectrochim Acta,(1974), 30A,99.

89. S A Bell,J C Lancaster and W R McWhinnie,Inorg.Nucl.Chem.Lett., (1971),7,405.

90. A Z Al-Rubaie,W R McWhinnie,P Granger and S Chapelle,J. Organometal.Chem.,(1982),234,287.

91. G L Cote and H W Thompson,Proc.Roy.Soc.,(1951),210A,217.

92. H C Clark and R J O'Brien,Inorg.Chem.,(1963),2(5),1020.

93. W F Cooper,N C Kenny,J W Edmonds,A Nagel,F Wudl and P Coppens, J.Chem.Soc., Chem.Commun.,(1971),889; W F Cooper,J W Edmonds, F Wudl and P Coppens,Cryst.Struct.Commun.,(1974),3,23.

94. F Wudl,J.Amer.Chem.Soc.,(1981),103,7064.

95. G Y Chao and J D McCullough,Acta Crystallogr.,(1962),15,887.

96. C Knobler,J D McCullough and H Hope,Inorg.Chem.,(1970),9,797.

97. H Hope,C Knobler and J D McCullough,Inorg.Chem.,(1973),12,2665.

98. J D McCullough,Inorg.Chem.,(1973),12,2669.

98a. J D McCullough,Inorg.Chem.,(1975),14,1142.

99. F Einstein,J Trotter and C Williston,J.Chem.Soc.A,(1967),2018.

100. L Y Y Chan and F W B Einstein,J.Chem.Soc.,Dalton Trans.,(1972),316.

101. P H Bird,V Kumar and B C Pant,Inorg.Chem.,(1980),19,2487.

102. H Campsteyn,L Dupont,J Lamotte-Brasseur and M Vermeire,J.Heterocyclic Chem.,(1978),15,745.

547
504

103. K J Irgolic,"The Organic Chemistry of Tellurium",Gordon and Breach Science Publishers,(1974).

104. H J Gysling,H R Luss and D L Smith,Inorg.Chem.,(1979),18,2696.

105. D H R Barton and S W McCombie,J.Chem.Soc.,Perkin Trans.I,(1975),1578.

106. K Ramasamy and P Shanmugam,Z.Naturforsch.Teil B,(1977),32,605.

107. L Engman and M P Cava,J.Org.Chem.,(1981),46,4194.

108. R F Ziolo and W H H Günther,J.Organometal.Chem.,(1978),146,245.

109. V Kovočik,M Fedoroňko and I Ježo,Org.Mass.Spectrom.,(1973),7,449.

110. E J Moriconi and A J Fritsch,J.Org.Chem.,(1965),30,1542.

111. N Zumbulyadis and H J Gysling,J.Organometal.Chem.,(1980),192,182.

112. R H Vernon,J.Chem.Soc.,(1920),117,86.

113. G T Morgan and H Burgess,J.Chem.Soc.,(1928),321.

114. G T Morgan and H Burstall,J.Chem.Soc.,(1931),180.

115. T A Hamor and R H Jones, Private communications.

116. P Main,S J Fiske,S E Hull,L Lessinger,G Germain, J P Declercq and M M Woolfson, MULTAN 80, A system of computer programs for the automatic solution of crystal structures from X-ray diffraction data, Universities of York and Louvain,1980.

117. G M Sheldrick,SHELX,Program for crystal structure determination, University of Cambridge,1978.

118. N W Alcock,Adv.Inorg.Chem.Radiochem.,(1972),15,1.

119. H Pritzkow,Inorg.Chem.,(1979),18,311.

120. N W Alcock and W D Harrison,J.Chem.Soc.,Dalton Trans., (1982),1421.

121. N W Alcock and R M Countryman,J.Chem.Soc.,Dalton Trans., (1977),217.

122. K G K De Silva,Z Monsef-Mirzai and W R McWhinnie, J.Chem. Soc., Dalton Trans.,(1983) In Press.

123. R T Mehdi and J D Miller,J.Chem.Soc.,Dalton Trans.,(1983), 1071.

124. G M Sheldrik,SHELX 76, Program for crystal structure determination, University of Cambridge,(1976).

125. D J Sandman,J C Stark,M Rubner,L A Acampora and L A Samuleson, Proc.Sixth ICCOSS,Freiburg,Germany 4-8 Oct (1982).

126. N W Alcock and W D Harrison,J.Chem.Soc.,Dalton Trans., (1982),709.

127. P Shanmugam et al, Synthesis, (1978),545.

128. T K Raja,Indian J.Chem.,(1980),19B,812.

129. N R Ayyangar,S R Purao and B D Tilak,Indian J.Chem., (1978),16B,673.

130. S P Molnar and M Orchin,J.Organometal.Chem.,(1969), 16,196.

131. H Onoue and I Moritani,J.Organometal.Chem.,(1972).43, 431.

132. R L Bennett,M I Bruce,B L Goodall,M Z Iqbal and F G A Stone,J.Chem.Soc.,Dalton Trans.,(1972),1787.

133. M I Bruce,B L Goodall,M Z Iqbal,F G A Stone,R J Doedens and R G Little,J.Chem.Soc.,Chem.Commun.,(1971),1595.

134. I Omae,Chem.Rev.,(1979),79,287.

135. B Fitzsimmons,J.Chem.Soc.,Chem.Commun.,(1977),215.

136. M Baiwir,G Llabres,O Diederberg,L Dupont and J L Piette, Acta Crystallogr. Section B,(1974),30,139.

137. P Wiriyachitra,S J Falcone and M P Cava,J.Org.Chem., (1979),44,3957.

138. S A Gardner,J Organometal.Chem.,(1980),190,363.

139. A Brown,Ph.D. Thesis, University of Aston in Birmingham, (1980).

140. R N Butler and W B King,Chem. and Industry,(1975),647.

141. A I Vogel,"Practical Organic Chemistry",Longmans,London, (1970),653.

142. H E Cocksedge,J.Chem.Soc.,(1908),2175.

143. A Gutbier and F Flury,Z.Anorg.Allg.Chem.,(1902),32,108; M Damiens,Ann.Chim.,(1923),19,44.

144. A I Vogel,"Practical Organic Chemistry",Longmans,London, (1962),p.722.

145. S A Dias, A W Downs and W R McWhinnie,J.Chem.Soc.,Dalton Trans.,(1975),162.

146. W F Smith,Tetrahedron,(1963),19,445.

147. D P Powell and N Scheppard,J.Chem.Soc.,(1960),2519.

148. M Orchin and P J Schmidt,Coord.Chem.Rev.,(1968),3,345.

149. A D Ketley,L P Fisher,A J Berlin,C R Morgan,E H Gorman and T R Steadman,Inorg.Chem.(1967),6,657.

150. V G Tkalenko,A P Amarskaya,Yu V Kolodyazhniy,I D Sadekov and V I Minkin,Zh.Obshch.Khim.,(1973),43,1943.

151. R N Butler,"Synthetic Reagents",Ed:J Pizey,Ellis Horwood, Chichester,(1977),Vol.3.pp.318-323.

152. R J Cross and N H Tennent,J.Organometal.Chem.,(1973),61,33.

153. V G Tkalenko,A P Amarskaya,Yu V Kolodyazhnyi,I D Sadekov, V I Minkin and O A Osipov,Zh.Obsch.Khim.,(1973),43,1945.

154. L J Bellamy,"The Infra-red Spectra of Complex Molecules", Champman and Hall, London,(1975),p.300.

155. L J Bellamy,"The Infra-red Spectra of Complex Molecules", Champman and Hall,London,(1975),p.90.

156. R D Kross,V a Fassell and M Margoshes,J.Amer.Chem.Soc., (1956),78,1332.

157. Y Mikawa,R J Jacobsen and J W Brasch,J.Chem.Phys.,(1966), 45,4528.

158. P V Rolling,D D Kirt,J L Dill,S Hall and C Hollstrom, J.Organometal.Chem.,(1976),116,39.

159. L M Jackman and S Sternhell,"Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", Pergamon Press, Oxford,(1969),p.456.

160. Yu A Ustynyuk,V A Chertkov and I V Barinov,J.Organometal. Chem.,(1971),29,C53.

161. R N Butler and W B King,J.Chem.Soc.,Perkin I,(1976),986.

162. D F Ewing,Org.Magn.Reson.,(1979),12,499.

163. W Kitching,D Praeger,C J Moore,D Doddrell and W Adcock, J.Organometal.Chem.,(1974),70,339.

164. I B M Campbell and E E Turner,J.Chem.Soc.,(1938),37.

165. D J Elias and R G Gillis,Aust.J.Chem.,(1966),19,251.

166. F H Musa,Ph.D. Thesis, University of Aston in Birmingham, (1974).

167. N S Dance and W R McWhinnie,J.Chem.Soc.,Dalton Trans., (1975),1975.

168. W R McWhinnie and M G Patel,J.Chem.Soc.,(1972),199.

169. K Bechgaard,"The Physics and Chemistry of Low-Dimensional Solids",Ed:L Alcácer,D Reidel Publishign Company, (1980),247.

170. N Bartlett,R N Biagioni,G McCarron,B McQuillan and F Tanzella,"Molecular Metals",Ed:W E Hatfield,Plenum Press,(1979).

171. H P Fritz,H Gebauer,P Friedrich,P Ecker,R Artes and U Schubert,Z.Naturforsh.B,(1978),33,498.

172. C Kröhnke,V Enkelmann and G Wegner,Angew.Chem.Int. Ed.Engl.,(1980),19,912.

173. J H Perlstein,J A Van Allan,L C Isett and G A Reynolds, Ann.N.Y.Acad.Sci.,(1977),313,61.

174. D P Rainville and R A Zingaro,J.Organometal.Chem.,(1980), 190,277.

175. I D Sadekov,A A Ladatko and V I Minkin,Chem.Hetero.Comp., (1980),10,1342.

176. W Lohner and K Praefcke,J.Organometal.Chem.,(1981), 205,167.

177. R A Jones and T A Hamor,University of Birmingham, Private communications.

178. K Sh Karaev,N G Furmanova,N V Below,I D Sadekov,A A Ladatko and V I Minkin,J.Struct.Chem.,(1981),22(6),106.

179. L Thorp and E A Wildman,J.Amer.Chem.Soc.,(1915),37,372.

180. A A Vlaček and A Rusina,Pro.Faraday Soc.,(1961),161.

181. R L Letsinger,J A Gilpin and W J Vullo,J.Org.Chem., (1962),27,672.

182. H G Rule,W Purcell and R R H Brown,J.Chem.Soc.,(1934),168.

183. D Dauplaise,J Meinwald,J C Scott,H Temkin and J Clardy, Ann.N.Y.Acad.Sci.,(1977),313,382.

184. D L Klayman and W H H Günther,"Organic Selenium Compounds: Their Chemistry and Biology",J Wiley,N.Y.,(973).

185. M Fedorynski and M Makosza,J.Organometal.Chem.,(1973), 51,89.

186. I D Sadekov,A A Ladatko,E I Sadekova and V I Minkin, Khim.Geterotsikl.Soedin.,(1980),(2),275(Russ).

187. H H Hodgson and J S Whitehurst,J.Chem.Soc.,(1947),80.

188. G Wittig,Angew.Chem.,(1956),68,505.

189. D Seyferth and F M Armbrecht,Jr.,J.Amer.Chem.Soc.,(1967), 89,2790.

190. N Petragnani and G Schill,Chem.Ber.,(1970),103,2271.

191. W P Weber and Gökel,"Phase Transfer Catalysis in Organic Synthesis",Springer-Verlag,(1977).

192. J L Piette and M Renson,Spectrochim.Acta,Part A,(1973), 29,285.

193. M Renson and J L Piette,Spectrochim.Acta,(1969),20,1847.

194. R C Paul,R K Chadha,B S Bhandal and G Singh,Inorg.Chim. Acta,(1981),52,125.

195. P Thavornyutikarn and W R McWhinnie,J.Organometal.Chem.,(1973),50,135.

196. G T Morgan and F H Burstall,J.Chem.Soc.,(1930),2599.

197. L Engman nad M P Cava,J.Chem.Soc.,Chem.Commun.,(1982), 164.

198. A Z Al-Rubaie,Ph.D. Thesis,University of Aston in Birmingham,(1982).

199. N L M Dereu,R A Zingaro,E A Mayers and M Renson,Organometallics,(1982),1(1),111.

200. J V Comasseto,J T B Ferreira,J A Fontavillasval and A R M de Oliveira,"Synthesis of Aryl-Alkyl Tellurides Under Phase Transfer Conditions" Presented at the "4th International Conference on the Organic Chemistry of Se and Te" University of Aston in Birmingham,25-29 July(1983).

201. D Seyferth,M E Gordon,J Y P Mui and M Burlitch,J.Amer. Chem.Soc.,(1967),89,759.

202. K J Irgolic,J.Organometal.Chem.,(1980),203,367.