To The Memory of My Mother ....

SYNTHESIS AND PHYSICAL INVESTIGATION
OF
SOME ORGANOTELLURIUM COMPOUNDS

by

ALI ZAYED AL-RUBAIE

A thesis submitted for the Degree of
Doctor of Philosophy
in the
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Department of Chemistry

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SUMMARY

A new class of cyclic telluronium salt was prepared. Conductivity measurements of a range of these compounds in DMSO and DMF show that considerable ion pairing occurs in solution. The compounds show stability toward the reductive elimination of alkyl halides in solutions such as $CHCl_3$, DMSO and DMF. The idea of association of the telluronium salts is now firmly established, and is supported by mass spectral and molecular weight data. ^1H, ^{125}Te and ^{13}C NMR spectral data are presented. The ^{125}Te chemical shifts for the telluronium salts are measured in solvents with different polarity and are shown to correlate with the nature of the alkyl group and with the electronegativity of the anion substituent.

The crystal structure of 1-allyl-1-bromo-3,4-benzo-1-telluracyclopentane showed that the tellurium atom achieves an octahedral environment by the coordination of two additional bromine atoms from two different molecules. The allyl group and the bromine atom are in axial positions, normal to the benzo-1-telluracyclopentane ring and the two bromine atoms from the two neighbouring molecules occupy the other equatorial positions.

^{125}Te NMR is used to study the chemical exchange between diarylditellurides. The examination of a mixture of two diarylditellurides by ^{125}Te NMR confirms the existence of unsymmetrical diarylditellurides. It is shown that the exchange is slow, and that it is a thermal process. When dioxygen is present, radicals are formed which lead to CIDNP effects on ^{125}Te NMR and to new oxygenated products. NMR parameters (δ, J_{Te-Te}, $J_{^{13}C-^{125}Te}$) of ^{125}Te and ^{13}C of diarylditellurides are given.

Since there is considerable interest in preparation of unsymmetrical diarylditellurides in this study, attempts have been made to utilize a Lewis acid (CuX or HgX_2) to complex preferentially the unsymmetrical diarylditelluride. The spectroscopic data suggest that the unsymmetrical diarylditelluride complexes, $RR'Te_2.2MX_n$, have possibly been synthesised, but absolutely positive evidence cannot be provided since their X-ray structures are unavailable.

A range of charge transfer complexes of organotellurium compounds with TCNQ were prepared in order to clarify the ability of organotellurium compounds to act as an electron donors. Electronic absorption, infrared and ESR data are presented.

A convenient method of preparing tetraorganotellurium compounds appears to provide a general expedient method for the synthesis of these materials. The reaction of $C_8H_8TeI_2$, $C_4H_8TeI_2$ or $C_9H_{11}TeI$ with excess $NaBPh_4$ gave the corresponding tetraorganotellurium compound by a simple and rapid procedure for the phenylation of tellurium (IV) compounds. ^1H NMR, infrared and mass spectral data are presented.

Key words Telluronium Salts ^{125}Te NMR
Diarylditellurides Tetraorganotellurium

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This work was carried out between 1978 and 1981 at the University of Aston in Birmingham.
It has been done independently and has not been submitted for any other degree.

Ali

A.Z.AL-RUBAIE

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CHAPTER I

INTRODUCTION

Tellurium is a member of the Group VIB of the periodic system between selenium and polonium, which bears a definite resemblance to selenium and sulphur in many of its properties. The electronic structure of tellurium is $[Kr]\ 4d^{10}\ 5s^{2}\ 5p^{4}$, with an electronegativity on the Pauling scale of 2.1. Within this group the metallic nature increases as the atomic weight increases in proceeding from oxygen to polonium, which could be observed by looking at the insulator property of oxygen and sulphur, semiconductivity of selenium and tellurium and the more positively metallic nature of polonium. Tellurium exhibits common oxidation states of +I, +II, +IV, +VI and -II of these +IV is the most stable and a coordination number of 6 is common.

Tellurium has eight stable isotopes (^{120}Te, ^{122}Te, ^{123}Te, ^{125}Te, ^{126}Te, ^{128}Te and ^{130}Te) and about twenty one man-made unstable isotopes. These stable isotopes give rise to a series of mass spectral peaks for each ion containing one or more atoms of this element. Such isotope clusters are of great help in identifying tellurium containing ions.

In addition to its metallurigical and thermoelectric applications, tellurium and its derivatives have numerous applications in industry e.g. in rubber technology as a vulcanizing agent, in glass and ceramics for colouring, as an additive element to steel and copper for improving machinability, in fuses for explosives, in chemical reactions as a catalyst and as antioxidant in lubricating oils. Copper (I) halide ditelluride complexes(1) have possible potential as catalysts for the hydrocynanation of butadiene. More recently, hydrogen telluride(2)(3) was used as a reducing agent for organic nitro, nitroso, azo and azoxy compounds and also for reducing benzaldehyde to benzyl alcohol.

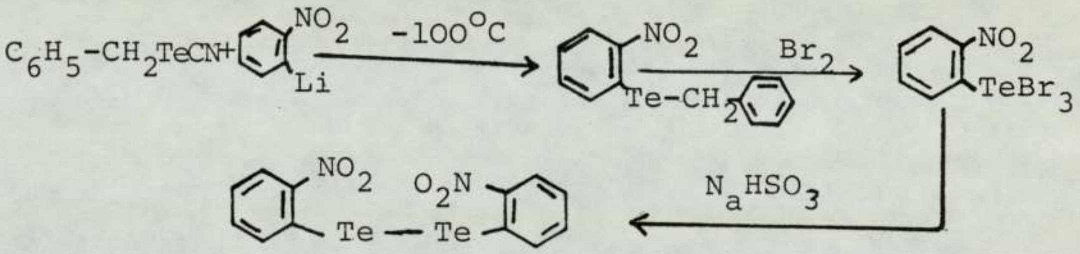
Organotellurium compounds have a history dating back to 1840 when Wöhler(4) prepared some dialkyltellurides. These were the first organic compounds of tellurium. The major theme of the present work is to synthesise new classes of organotellurium compounds and moreover, to investigate their physicochemical properties. A brief review of the chemistry of diorganylditellurides and triorganotelluronium salts is appropriate in this context.

I.(i) DIORGANYLDITELLURIDES (R_2 Te_2)

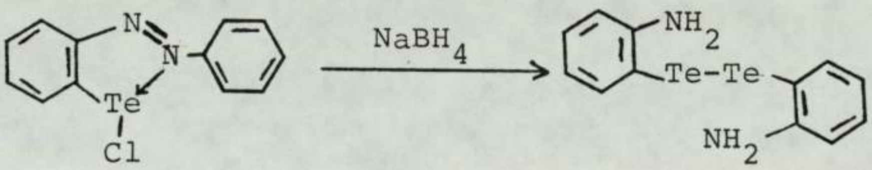
Diorganylditellurides, R - Te - Te - R, are useful intermediates for the synthesis of some classes of organotellurium compounds like diorganyltellurides, diorganyl tellurium dihalides, organyltellurium trihalides and transition metal complexes. They are orange to red in colour. The aromatic derivatives are more stable and much easier to handle than aliphatic members which in addition to their relative instability possess an obnoxious, persistent odour.

Dialkylditellurides can be obtained from sodium ditelluride and alkylhalides. The principal methods for synthesis of aromatic ditellurides are, the reducing of aryltellurium trihalides by means of several reducing agents (e.g. Na_2S , $Na_2S_2O_5$, hydrazine, ...), reducing of elemental tellurium with Grignard reagents in tetrahydrofuran (THF) in presence of oxygen, or with alkyl lithium compounds.

Recently, bis(o-nitrophenyl)ditelluride was obtained by reducing an aryltellurium tribromide by sodium hydrogen sulphite(5



The reduction of 2-phenylazophenyltellurium chloride by sodium borohydride in boiling methanol afforded red, crystalline bis(o-aminophenyl)ditelluride (6).



Diorganylditellurides are sensitive to atmospheric oxygen, diphenylditelluride was reported to react with oxygen at room temperature, and its alcoholic solution was at once decolourised by hydrogen peroxide; a white amorphous product was obtained on concentrating the liquid (7).

Bis(phenoxyphenyl)ditelluride produces a white, poorly characterised oxide (8), while the p-methoxyphenyl derivative under similar conditions gave rise to a yellowish green substance (9).

Determination of molecular weights of bis (p-methoxyphenyl) and bis(p-ethoxyphenyl)ditelluride in 8 per cent solution in camphor suggested a 30 per cent dissociation into radicals at 160°C(7). The ditellurides give, in benzene solution at room temperature, a molecular weight approximately 5 per cent less than that theoretically expected (9,10,11).

Farrar(7) observed that the molecular weight of diphenylditelluride indicated up to 30 per cent dissociation at 160°C, and he claimed that diphenylditelluride dissociated completely to radicals in solution:

$$\mathrm{Ph_2Te_2} \rightleftharpoons \mathrm{2PhTe^{\bullet}}$$

Petragnani and Moura Campus(12) assumed Farrar's idea to explain the mechanism of reaction between tellurium metal and phenylmagnesium bromide to describe the formation of diphenylditelluride and diphenyltelluride.

$$\begin{aligned}
&\mathrm{2PhMgBr} \longrightarrow \mathrm{2Ph^{\bullet} + 2MgBr^{\bullet}}\\
&\mathrm{2Ph^{\bullet} + 2Te} \longrightarrow \mathrm{2PhTe^{\bullet}}\\
&\mathrm{2PhTe^{\bullet}} \rightleftharpoons \mathrm{Ph{-}Te{-}Te{-}Ph}\\
&\mathrm{2MgBr^{\bullet} + Te} \longrightarrow \mathrm{Te(MgBr)_2}
\end{aligned}$$

$$\begin{aligned}
&\mathrm{Ph{-}Te{-}Te{-}Ph} \rightleftharpoons \mathrm{2PhTe^{\bullet}}\\
&\mathrm{2PhTe^{\bullet} + 2PhMgBr} \longrightarrow \mathrm{2Ph{-}Te{-}Ph + 2MgBr^{\bullet}}\\
&\mathrm{2MgBr^{\bullet} + Te} \longrightarrow \mathrm{Te(MgBr)_2}
\end{aligned}$$

It is known that solutions of diphenyldisulphide contain Ph — S radicals(13). Windle and Wiersema(14) observed no radicals from diselenides but did identify radicals from disulphides by the Electron Spin Resonance (ESR) technique.

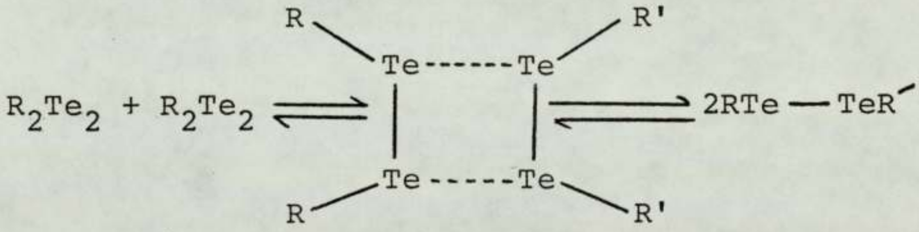
Thavornyutikarn(15) has concluded that the ditelluride is undissociated in organic solvents. The ESR spectrum of a solution of diphenylditelluride in benzene under conditions similar to those employed by Farrar did not indicate any radical species to be present and no signal corresponding to the $R\dot{T}e$ species was seen. The diffuse reflectance spectrum of diphenylditelluride and visible spectrum of a solution in chloroform were similar, indicating that the species in the solid and solution are similar.

The failure to synthesise the unsymmetrical diaryl ditellurides(15) cast doubt about the validity of Farrar's claim(7). Thavornyutikarn(15) had attempted to prepare unsymmetrical ditellurides by reducing a mixture of two different aryltellurium trichlorides using $Na_2S.9H_2O$ and $K_2S_2O_5$ as reducing agents, and by irradiating a benzene solution containing diphenylditelluride and bis(4-ethoxyphenyl) ditelluride.

Dance(16) gave the first evidence for the existence of unsymmetrical diarylditellurides, $R—Te—Te—R'$, by using mass and NMR spectroscopies. The mass spectrum of a mixture of Ph_2Te_2 and $(p\text{-}PhOC_6H_4)_2Te_2$ contained both parent ions $(Ph_2Te_2)^+$ and $((p\text{-}PhOC_6H_4)_2Te_2)^+$, in addition, $Ph—Te—Te—(C_6H_4OPh)^+$ was seen. Similar observations were made when intimate mixtures of other ditellurides were examined. ^{1}H NMR investigation of mixtures of solutions of two ditellurides showed the existence of unsymmetrical ditellurides. The possible mechanism$^{(16)}$ of the redistribution of R groups might go via radical mechanism, for which no positive proof was detected in these reactions.

$$R_2Te_2 \rightleftharpoons 2R\dot{T}e$$
$$R'_2Te_2 \rightleftharpoons 2R'\dot{T}e$$
$$R\dot{T}e + R'\dot{T}e \rightleftharpoons R-Te-Te-R'$$

or via a dimer intermediate,



Dance$^{(16)}$ showed no evidence that ditellurides spontaneously produced RTe$^{\bullet}$ radical and the dimer intermediate remained a distinct possibility.

Passmore$^{(17)}$ prepared perfluorobutyl pentafluoroethyl ditelluride, $C_4F_9Te-Te-C_2F_5$, in trace amount in a reaction between tetratellurium bis(hexafluoroarsenate) or hextatellurium bis(hexafluoroarsenate) and tetrafluoroethylene. The compound was identified by mass spectroscopy.

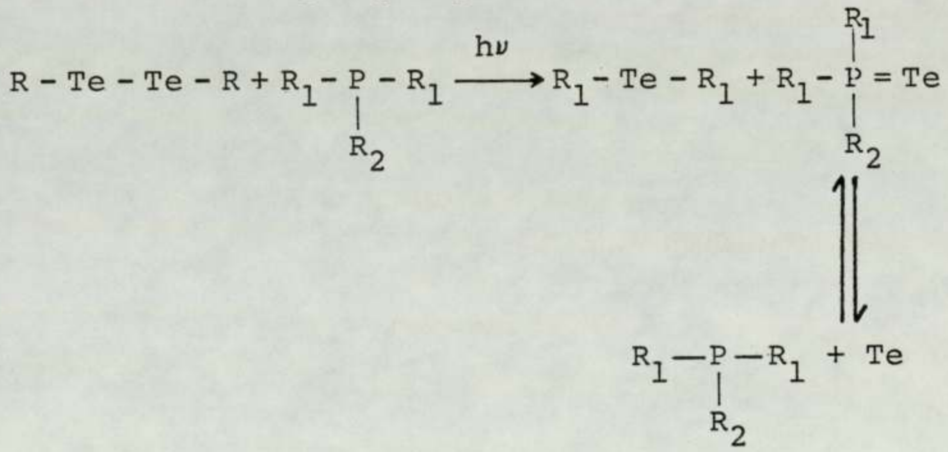
A very few studies have been made on photochemical reactions of diorganylditellurides. The first report on photochemistry of ditellurides was published by Spencer and Cava$^{(18)}$ in 1977. Irradiation of chloroform solution of dibenzylditelluride under oxygen yielded benzaldehyde (42%), toluene (21%), benzyl alcohol (21%), 1,2 - diphenylethane (7%) and tellurium.

$$PhCH_2-Te-Te-CH_2Ph \xrightarrow[O_2]{h\nu} PhCHO + PhCH_2OH + PhCH_2CH_2Ph + Te + CH_3Ph$$

In the absence of oxygen, dibenzylditelluride gives dibenzyl telluride and elemental tellurium powder under irradiation (19)

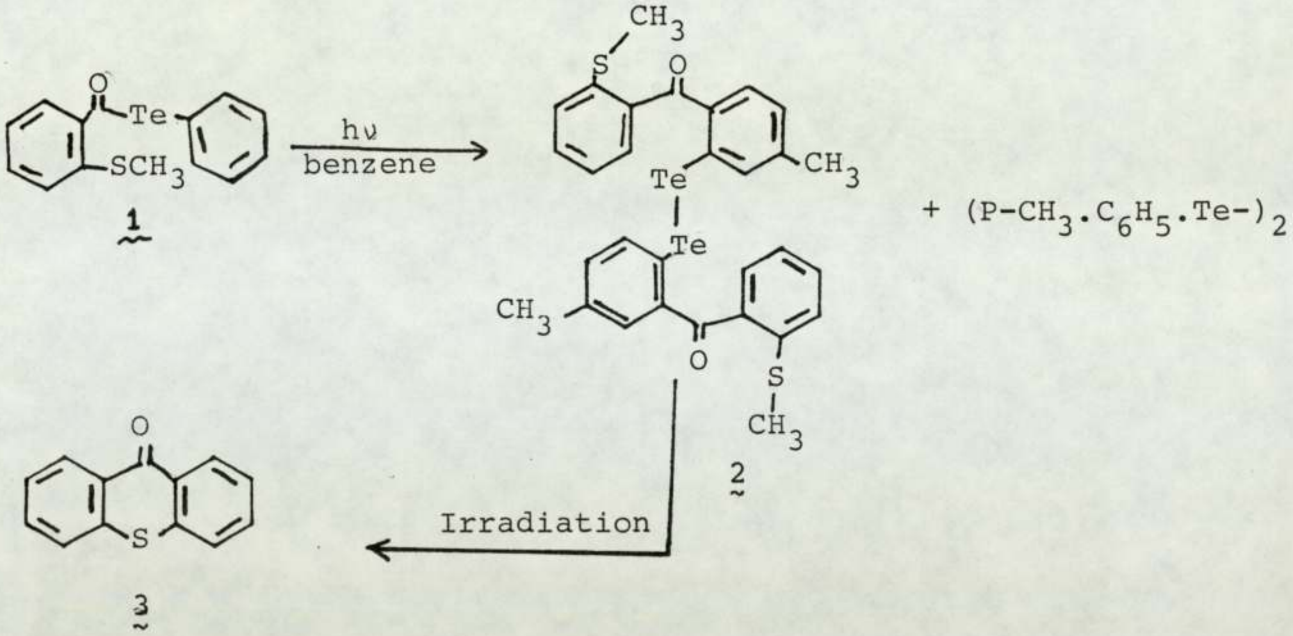
$$PhCH_2Te-Te-CH_2Ph \xrightarrow[N_2]{h\nu} PhCH_2TeCH_2Ph + Te$$

When diorgano ditellurides were photolysed in the presence of triorganyl phosphines, monotellurides and tellurium metal were produced. Tellurium was deposited only in some cases (19), in others it was reported to form a triorganyl phosphine telluride (20), which compounds are known (19,20) to be less stable and which rapidly equilibrate to triorganophosphine and elemental tellurium.



$$R-Te-Te-R + R_1-\underset{\displaystyle R_2}{\underset{|}{P}}-R_1 \xrightarrow{h\nu} R_1-Te-R_1 + R_1-\overset{\displaystyle R_1}{\overset{|}{\underset{\displaystyle R_2}{\underset{|}{P}}}}=Te \rightleftharpoons R_1-\underset{\displaystyle R_2}{\underset{|}{P}}-R_1 + Te$$

Irradiation of the tellurium - 4-methylphenyl 2-methylthio tellurobenzoate $\underset{\sim}{1}$ in dry benzene with mercury radiation produced, among other compounds bis(4-methylphenyl) ditelluride and the ditelluride $\underset{\sim}{2}$ via a radical mechanism, (22,23)



Irradiation of the solid ditelluride 2 with the light from a mercury lamp(22) or exposure of a chloroform solution of the ditelluride to daylight produced thioxanthone 3 (22, 23).

Diazomethane reacted with diselenides(24) under sunlight to furnish diselenoacetal, while the ditelluride reacted similarly with CH_2N_2, but did not require sunlight(24).

$$R-Se-Se-R + CH_2N_2 \xrightarrow{\text{sunlight}} R-Se-CH_2-Se-R$$

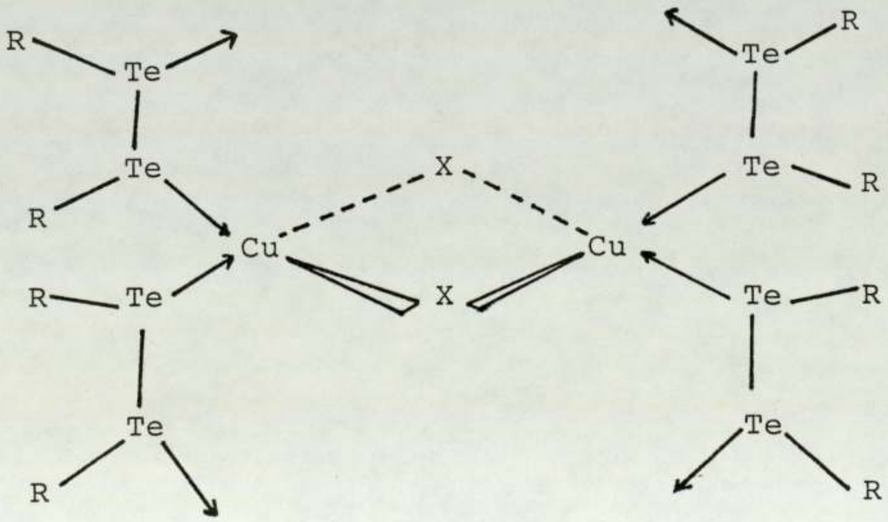
$$R-Te-Te-R + CH_2N_2 \longrightarrow R-Te-CH_2-Te-R$$

Diorganylditellurides formed complexes with a variety of metal ions. When diorganylditellrides react with transition metals they often undergo tellurium-tellurium bond cleavage to afford materials in which the RTe group bridges metal centres (e.g. $Pd(TeR)_2(PPh_3)$ (25)), but a few elements have been reported to give simple complexes with R_2Te_2, namely mercury ($Ph_2Te_2.HgCl$) (26),

$[(P\text{-}MeOC_4H_4)_2Te_2.H_gI_2]$(9), Uranium $(ph_2Te_2.UCl_5)$(27).

McWhinnie et.al.(28,29), reported the syntheses of simple ditelluride complexes with copper (I) halides, $R_2Te_2.CuX$, where R = ethyl, butyl, pentyl, phenyl and phenetyl; X = Cl, Br. They are non-electrolytes in acetonitrile. According to ^{125}Te Mössbauer data the complexes contain intact ditellurides with both tellurium atoms weakly coordinated to copper atoms. The tellurium atoms used their 5p orbitals for complexation with little change in their hybridization(29). It has been determined from Mössbauer studies of various tellurium containing compounds(30) that the p electrons imbalance in the tellurium-carbon is about 1.1 and the ditellurides have large quadrupole splitting, reflecting a considerable imbalance in the tellurium 5p orbital population.

The polymeric structure was proposed for ditelluride copper (I) halide complexes(29)



Possible structure for R_2Te_2CuCl

The copper chloride complexes, (o - $NH_2C_6H_6)_2Te_2.CuCl_n$ (n = 1,2), formed when either Cu_2Cl_2 or $CuCl_2$ dissolved in acetonitrile was mixed with diethyl ether solutions of the ditelluride. The complexes are 1:1 electrolytes in acetonitrile(6).

Diorganyl ditellurides have been reported to form a simple complex with mercury (II) halides of the stoichiometric composition $R_2Te_2.HgX_2$ and $R_2Te_2.2HgX_2$(31).

The structural studies of diorganylditellurides have been determined from X-ray crystallographic studies(32,33,34). In all ditellurides examined the C — Te — Te bond angles have been found to be between 90°-100°, indicating that the Te — C bonds have a higher degree of p-character and the C — Te - Te/Te — Te — C angles are dihedral.

The vibrational analysis of Me_2Te_2(35) and Ph_2Te_2(15) assumed a similar structure of these ditellurides. Bis (4-chlorophenyl)ditelluride is the first ditelluride whose structure has been determined by single crystal X-ray analysis(32). The two organic groups bonded to the tellurium atom form a dihedral angle of 70°. The hydrogen peroxide configuration is the most probable configuration(32). The structure of diphenylditelluride in solid state is the same with a dihedral angle of 88.5°. The Te — Te — C bond angles are 97.4° and 100.3°(33).

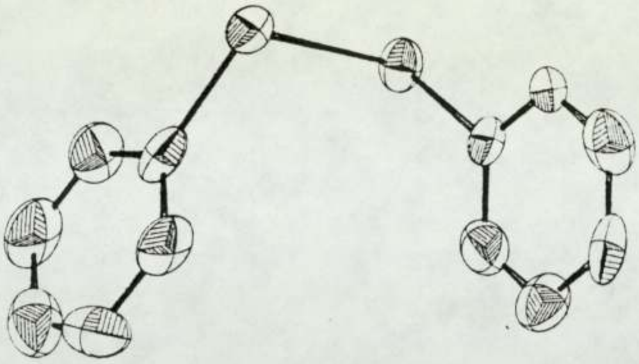


Fig (a). Ph_2Te_2

Piette[(36)] reported crystal data of some diorganylditellurides $(4\text{-}R\text{-}C_6H_4)_2Te_2$, R = H,$CH_3$, Cl, Br, which agreed with the above structures.

Recently, the structure of bis (4-methylphenyl) ditelluride was determined by three- dimensional X- ray analysis[(34)]. The molecule was characterized by the value of dihedral angle C —Te —Te/Te — Te — C of 85.7° and Te — C and Te — Te bond lengths of 2.13 and 2.69A°, respectively. The molecular structure is shown in the following figure.

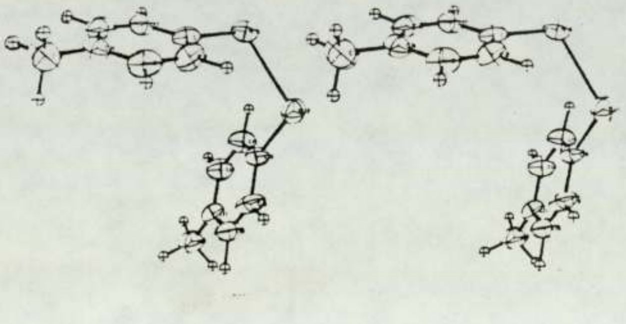


Fig (b). bis(P-tolyl)ditellurides

All these structures of diorganylditellurides have shown that the C — Te — Te bond angles have been found to be between 70° - 103°, indicating a high degree of p-character in the Te — C bonds. Evidence of the type of bonding involved also obtained from ^{125}Te Mössbauer studies which suggested that there may be a slightly lower degree of S character in the Te — Te bond than the Te — C bond(30).

I. (ii) TELLURONIUM SALTS

Triorganotelluronium salts, R_3TeX, have been known for nearly one hundred years. The examples of trialkyl, triaryl and mixed alkyl-aryl derivatives containing many different anions are plentiful.

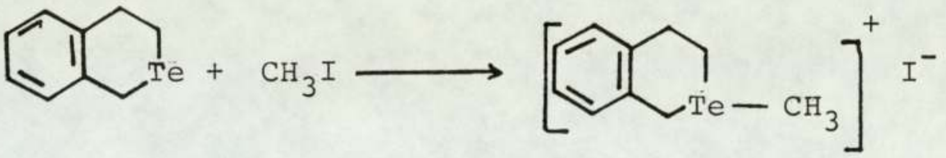
The synthesis of these compounds is mainly by the combination of diaryltellurides with alkyl halides, the reaction of tellurium tetrachloride with a Grignard reagent, or the reaction of diorganotellurium dichlorides with Grignard reagents.

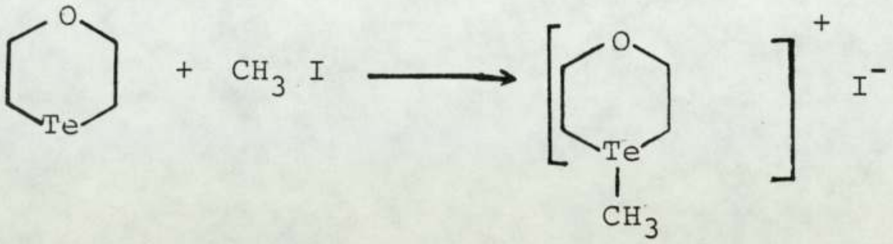
$$R_2Te + R'X \longrightarrow R_2R'TeX \quad (R' = \text{alkyl},\ R = \text{aryl})$$

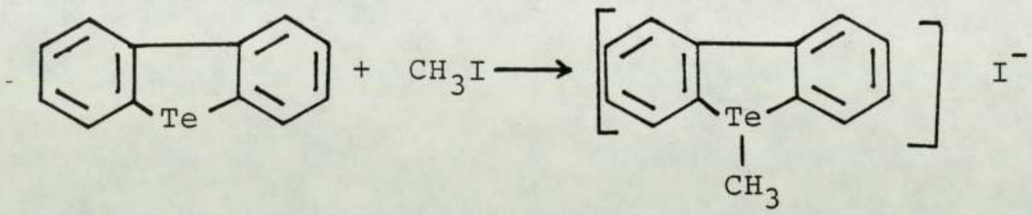
$$TeCl_4 + 3RMgX \longrightarrow R_3TeCl + 3MgClX$$

$$R_2TeCl_2 + R'MgX \longrightarrow R_2R'TeCl + MgClX$$

The cyclic tellurides undergo the same reactions given by diorganyltelluride, e.g. formation of cyclic telluronium salts(37,38,39) from telluroisochroman(37), 1 - Oxa - 4 - telluracyclohexane(38) and dibenzotellurophene(39):







Few physicochemical investigations have been carried out with these compounds in the solid state, and also their solution chemistry remains largely uncharacterised.

The thermal decomposition of triorganotelluronium halides(40) and pseudohalides(41) gives the organic halide (or pseudohalide) and the diaryl telluride.

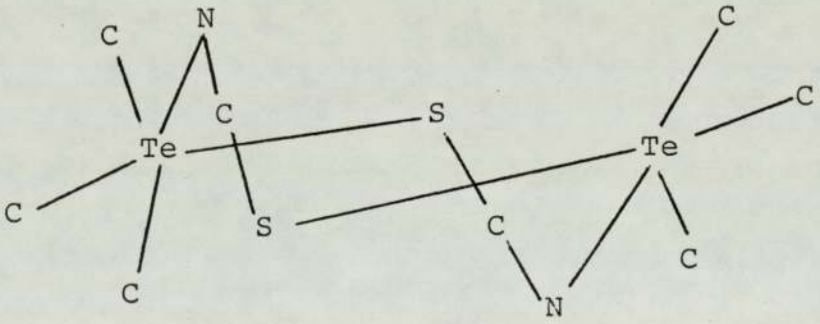
$R_3TeX \xrightarrow{\Delta} R_2Te + RX$ (X = halide or pseudohalide)

The recent studies on solid triorganotelluronium salts(42,46) have shown that these salts have relatively complex structures in the solid state thus suggesting limitation for the simple $R_3Te^+X^-$ ion-pairing model.

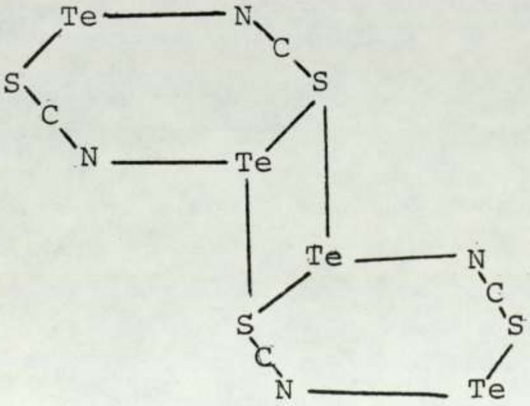
X-ray structural results showed that the solid organotellurium salt Ph_3TeNCS(42,43) exists as discrete dimer and tetramer formed from bridging NCS groups with intra Te....N and Te....S distances significantly shorter than the respective Van der Waals distances. In three independently determined structures the triphenyltelluronium cations have a pyramidal shape with C — Te — C angles ranging from 92° to 103°. Tellurium is both five and six coordinate in Ph_3TeNCS(42,43) while by contrast selenium in Ph_3SeNCS is only four coordinate(47). So the latter salt is monomeric while the former salt is oligomeric.

The tellurium atoms in the dimer, Ph_3TeNCS, are in 5-coordination(~square pyramidal) whereas both 5-coordination (~ square pyramidal) and 6-coordination (~ octahedral) occur in the tetramer. Thiocyanate bridging is in the three atom end-to-end mode with one of the groups bridging in the terminal single-atom mode as well.

The following diagrammatic structures of (c) Ph_3TNCS dimer and (d) Ph_3TeNCS tetramer gives more details:



(c) Ph_3TeNCS dimer



(d) Ph_3TeNCS tetramer

Triphenyltelluronium chloride is predominantly ionic in the solid state(48) and is composed of noncentrosymmetric dimers separated by Van der Waals distances. Two chloride ions bridge the Ph_3Te^+ ions with Te....Cl distances ranging from 3.142 to 3.234 Å .

The two tellurium atoms are each five coordinate and have a distorted square-pyramidal geometry. The $(C_6H_5)_3TeCl$ dimer is formed by sharing of a common basal edge by two square pyramids through bridging chloride ions. The Cl — Te — Cl angles are 90.84 and 92.28° while the Te — Cl — Te angles are 77.31 and 78.82°.

The following figure (e) gives more details about $(Ph_3TeCl)_2$.

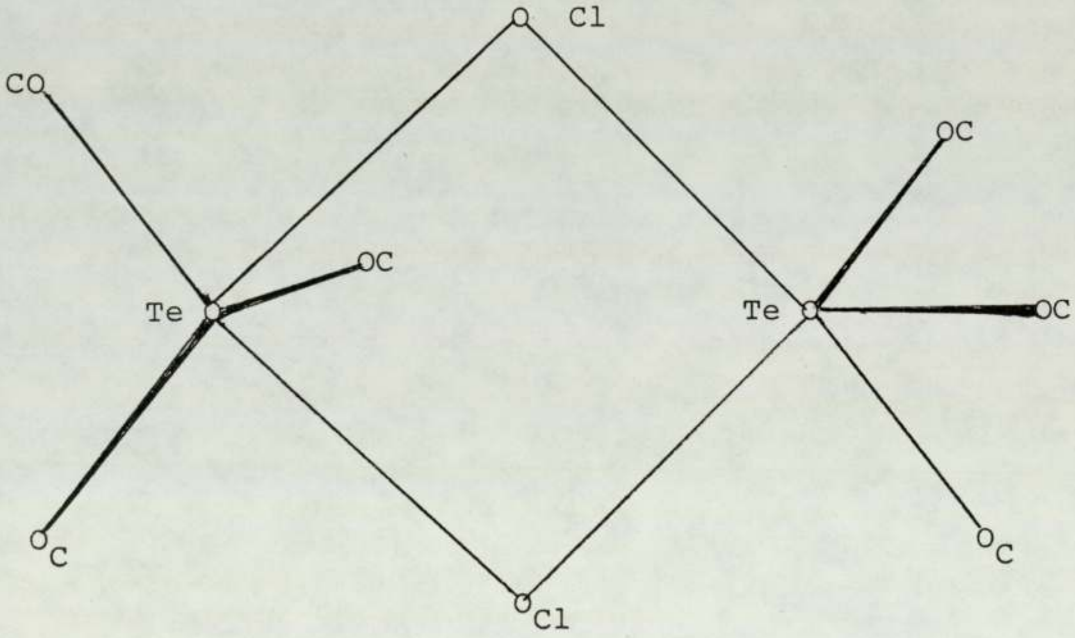


Fig (e) Ph_3TeCl dimer

The structures of a number of organotelluronium salts have shown that $(C_6H_5)_3TeCl$(48), $(C_6H_5)_3TeNCS$(42,43), which coexists with tetramers, and by contrast $(C_6H_5)SeCl.2H_2O$(49) are dimers. It has been noted that the unit cell of $(C_6H_5)_3TeNCO$ contains only tetramers and solvent of crystallization(44,45).

The telluronium salts have relatively complex structures due to the weak interaction between the tellurium atom and the anion. These interactions determine the structural features of the compounds and that the interactions are sensitive to the nature of both the cation and anion. The tellurium shows higher coordination number than does selenium or sulphur because of its expanded valence shell, and has the greater tendency for secondary interactions.

The secondary interactions which have been found in all structural determinations of telluronium salts(42,43,45,48), were absent in the trimethyltelluronium tetraphenylborate(51). Tellurium in this compound shows a three fold configuration and is therefore the first example of three coordinate tellurium IV. The lone pair electrons of tellurium in the absence of the secondary bonding interactions may have a greater stereochemical influence(51).

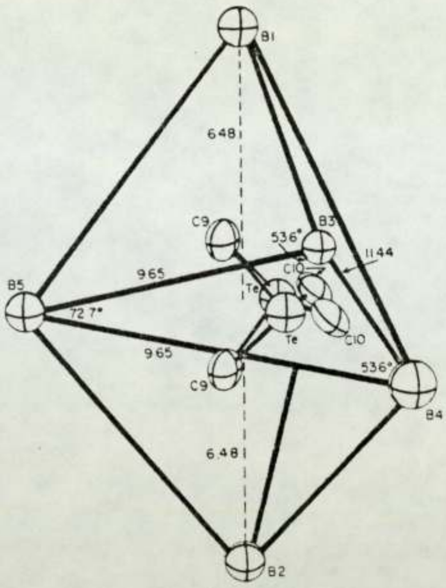
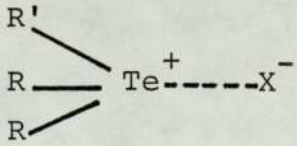


Figure (f) Trigonal-bipyramid cavity and cation disorder in $(CH_3)_3TeB(C_6H_5)_4$. The structure of this compound is dominated by the tetraphenylborate ion which has C_{2v} symmetry with normal interatomic distances and angles. The structure consists of layers of $B(C_6H_5)_4^-$ and $(CH_3)_3Te^+$ ions parallel to xy plane such that three $B(C_6H_5)^-$ ions surrounds each $(CH_3)_3Te^+$ ion. As a consequence a belt of phenyl rings from one anion and one each from two other anions surround each cation site. Boron is out of the planes of phenyl rings which are distorted from hexagonal geometry. The structure is layered such that a trigonal bipyramid of tetraphenylborate ions surrounds each cation site.

The solution chemistry of organotelluronium salts remains largely uncharacterized. Lederer(52) observed in 1916 that diarylmethyltelluronium salts decomposed in chloroform solution.

Kopf, et.al.(53) have shown that organotelluronium nitrosylates $R_3Te^+(R—C\genfrac{}{}{0pt}{}{\nearrow N-O}{\searrow N=O})^-$, exist in an ionic form in methanol solutions, but are apparently covalent in benzene solutions.

The conductivity measurements(54,55) indicate that all the telluronium salts, R_2MeTeX, are less than 1:1 electrolytes in dimethylsulphoxide (DMSO) and dimethylformamide (DMF) solutions. This indicated some degree of ion-pairing which may be represented as below:



Dance(54) observed that methyldiphenyltelluronium salts undergo dissociation in deuterochloroform solution to diphenyltelluride and methylhalide with a rate which is halogen dependent:

$$Cl < Br < I$$

The telluronium salts are covalent in chloroform and more ionic in DMSO and, to a lesser extent, DMF. Thus the following equilibria were shown to be shifted to right or left by selecting solvents of different polarity:

$$\underset{\text{"ionic"}}{Ph_2MeTe^+X^-} \rightleftharpoons \underset{\text{"covalent"}}{Ph_2MeTeX} \rightleftharpoons Ph_2Te + MeX$$

^{1}H.NMR spectra for Ph_2MeTeX (X = Cl, Br, I) in deuterochloroform changed with the time, a new methyl resonance appearing on standing and also the chemical shift of methyl group bonded to the tellurium atom was found to depend significantly on the anion(54).

Dance(54) studied kinetically the reaction of methyliodide with an excess of diphenyltelluride as a solvent at 35°C within the NMR spectrometer and the spectrum of the aliphatic resonance was recorded and integrated in time intervals until the reaction was complete. Immediately after mixing methyliodide and diphenyltelluride, the only aliphatic resonance was that due to CH_3I. However, within one minute a resonance at $\delta = 3.05$ ppm (covalent form) developed, followed by one at $\delta = 2.70$ ppm (ionic form). From these resonant positions, he assumed the species present to be those previously identified in chloroform (covalent) and DMSO (ionic). The plot of concentration of methylated products against time for the ionic form, is sigmoidal indicating that it arose from an intermediate. The "covalent" form is initially produced at a rate greater than the "ionic" form, but latterly the relative rates are reversed, which indicates that the "covalent" form is the intermediate involved. Methyliodide was eliminated from $Ph_2MeTe^+I^-$ rather than phenyliodide. There was no obvious thermodynamic explanation for these observations since methyl-and phenyl-halogen bonds are of similar strength(56) and Mössbauer measurements(30) have not shown great difference between tellurium-alkyl or -aryl bonds.

Musa(55) synthesised methyldiphenyltelluronium isothiocyanate, $Ph_2MeTeNCS$, and studied its behaviour in in solvents of different polarity. This compound gave conducting solutions in DMSO and DMF indicating 1:1 electrolytes.

The IR spectrum of $Ph_2MeTeNCS$ in $CDCl_3$ was different than in solid state. The initial solution gave a broad band due to ν(CN) centred on 2059 cm^{-1}, this decayed with time to be replaced by an extremely sharp band at 2161 cm^{-1} which proved that the telluronium salts decomposed to methylthiocyanate and diphenyltelluride (subsequently confirmed by ^{1}H NMR) as follows:

$$\mathrm{Ph_2MeTe(NCS)} \longrightarrow \mathrm{Ph_2Te + MeSCN}$$

Musa$^{(55)}$ obtained more kinetic data using ^{1}H NMR spectroscopy on these systems and suggested a mechanism for the reductive elimination reaction. The kinetic data indicated that two pseudo-first order processes were involved, the second (faster) which required the presence of diphenyltelluride and this did not become dominant until a reasonable concentration of diphenyltelluride built up. He postulated that the most probable mechanism for the initial stage of the reaction is one involving loss of methyl radical in a rate determining step:

$$\mathrm{MePh_2TeNCS} \xrightarrow{\text{slow}} \mathrm{M\dot{e}} + \mathrm{Ph_2\dot{T}eNCS}$$

followed by a sequence of fast steps.

$$\text{propagation}\ \left\{\begin{array}{lll} \mathrm{M\dot{e}} + \mathrm{(SCN)TePh_2Me} & \longrightarrow & \mathrm{MeSCN} + \mathrm{\dot{T}ePh_2Me} \\ \mathrm{\dot{T}ePh_2Me} & \longrightarrow & \mathrm{Ph_2Te} + \mathrm{M\dot{e}} \end{array}\right.$$

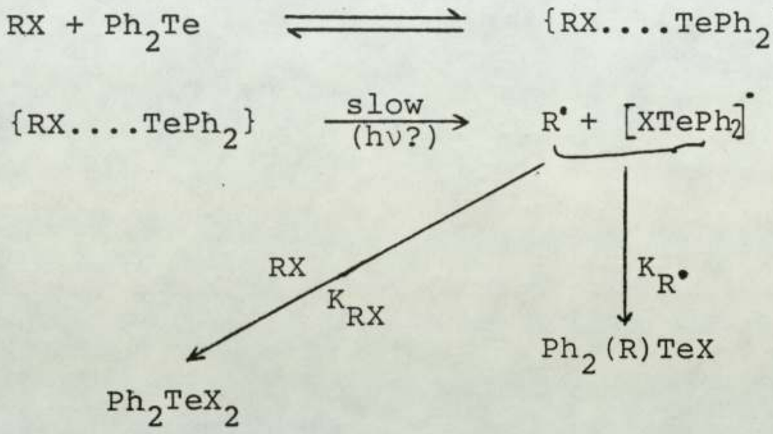
termination $\dot{Me} + (SNC)\dot{Te}Ph_2 \longrightarrow MeSCN + Ph_2Te$

More recently, McWhinnie et al.(57) studied in more detail the solution chemistry of triorganotelluronium salts $Ph_2(CH_3)TeX$ (where X = Cl, Br, I, PhCOO, NCS). Using ^1H NMR spectroscopy of chloroform solution showed that the rate of dissociation was in the order:

$I > Br \simeq NCS > Cl > PhCOO$

In the case of Cl and PhCOO an equilibrium was established, in other cases the dissociation was complete, thus the stability of the salt to dissociation in chloroform is inversely related to the electronegativity of the ligand atom of the anion. The IR data for solid $Ph_2MeTe(PhCOO)$ suggested a considerable interaction of the carboxylate with tellurium.

McWhinnie et.al.(57) have given positive evidence for a radical pathway in both oxidative addition of alkyl halides to Ph_2Te and reductive elimination of methylthiocyanate from $Ph_2MeTe(NCS)$ using electron spin resonance spectroscopy (ESR) and spin trapping experiments with phenyl (t-butyl)nitrone (PBN). The addition of PBN gave immediate evidence for free radicals after mixing of diphenyltelluride (2 moles) and organic halides (1 mole) with PBN which dissolved in pure de-oxygenated benzene. The experiments were carried out under very strictly anaerobic conditions, but if dioxygen were deliberately introduced the concentration of the trapped radicals increased. They proposed a mechanism for oxidative addition which involved the preformation of a charge transfer complex of the alkyl halide and diphenyltelluride as follows:



They concluded that oxidative addition of methylhalides to Ph_2Te proceeds along a radical pathway via the initial formation of a charge transfer complex, and the initial product of the oxidative addition is a covalent molecule from which, depending on the solvent, ionisation may occur.

The mass spectra of telluronium salts(54,58,59), Ph_2MeTeX (where X = Cl, Br, I, NCS, BF_4, PF_6, PhCOO) showed the thermolysis pathway is:

$$Ph_2MeTeX \longrightarrow Ph_2Te + MeX$$

A series of studies were carried out by Dance(54), Musa(55) and McWhinnie(57) on methyldiphenyltelluronium salts showed that reductive elimination might occur from an associated species in solution.

It is interesting to continue these investigations to explore the solution structure of telluronium salts which are stable to reductive elimination. Attempts will be used to synthesise stable telluronium salts and to obtain further evidence for, or against, the previous work.

CHAPTER II

GENERAL EXPERIMENTAL METHODS

Chemicals:

All chemicals were obtained from commercial sources and in purest available grades used when necessary. Tellurium tetrachloride and tellurium powder, the starting materials for many reactions, were supplied by British Drug Houses (BDH).

Solvents:

The solvents were obtained from commercial sources. They were purified according to literature methods, i.e. benzene, chloroform, ethanol, dioxane, dimethylsulphoxide, dimethylformamide and tetrahydrofuran (THF) (60).

Elemental Analysis:

Micro analysis for carbon, hydrogen, nitrogen and halogen were carried out by the Micro Analytical Laboratories of the Chemistry Department of Aston University. Tellurium analysis was carried out by the method of Suttle(61).

Physical Measurements:

(a) Infra-red Spectra

A Perkin-Elmer 457 spectrophotometer of range 4000-250 cm^{-1} and a Perkin-Elmer 599B spectrophotometer of range 4000-200 cm^{-1} were used. The solid specimens were prepared as Nujol Mulls supported between KBr plates, or examined as KBr discs or as CsI discs.

(b) Proton Nuclear Magnetic Resonance (^{1}H NMR) Spectra

Proton magnetic resonance spectra of solution of organotellurium compounds containing tetramethylsilane (TMS) as an internal standard were recorded on a Perkin-Elmer R14 spectrometer at 60 MHz.

(c) Te and ^{13}C Nuclear Magnetic Resonance Spectra

The tellurium-125 nuclear magnetic resonance spectra were measured on a Bruker WH 90C spectrometer of the Université de Rouen in France at 28.40 MHz, and tellurium-123 at 23.57 MHz, in the Fourier mode. 90° pulses were used. Carbon-13 spectra were measured on the same instrument at 22.63 MHz, the sample temperature was 26°C.

^{13}C chemical shifts are referred to TMS as internal reference. For tellurium, chemical shifts are referred to pure $(CH_3)_2Te$.

(d) Visible Solution Spectra

The visible solution spectra were recorded on a Unicam SP8-100 spectrophotometer using 1 mm pathway glass cells and 10 mm pathway silica cells.

(e) Conductivity Measurements

Solution conductivities were measured with a Mullard Conductivity bridge, using a standard conductivity cell with a cell constant of 1.46 with bright platinum plates.

(f) Osmometric Molecular Weight Measurements

Molecular weights were measured with a Knauer Vapour Pressure Osmometer using benzil as a reference compound.

(g) Mass Spectra

The Mass Spectra of all compounds were recorded on the AEI MS9 spectrometer at 70 eV.

(h) Electron Spin Resonance (ESR) Spectra

The Jeol, JES-PE, esr spectrometer was used to record the spectra of the samples.

(i) Melting Points

The melting points of all solid compounds were determined by a Gallenkamp melting point apparatus which is heated electrically.

(j) Raman Spectra

The Raman spectra in range of 300-26 cm^{-1} were recorded on the Coderg RS 100 Raman spectrometer at the Chemistry Department of the University of Leicester, using 6471A^o (15453 cm^{-1}) Kr laser excitation. All the samples were recorded in the crystalline solid state and in deoxygenated benzene.

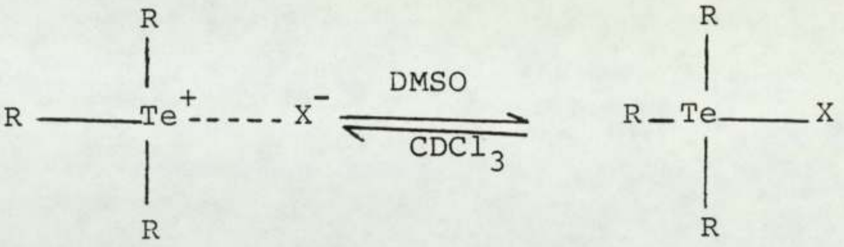
CHAPTER III

3.(i) INTRODUCTION

The recent literature contains several papers indicating a growing interest in organotelluronium salts; the solution behaviour of these compounds and their solid state structures have been studied. The crystal and molecular structures of telluronium salts are relatively sparce; in most cases studied there is evidence of positive anion-cation interaction. In $[(CH_3)_3Te]^+$ $[(CH_3)TeI_4]^-$ for example, both cationic and anionic tellurium atoms are in distorted six coordinate environments,(50) and in the case of triphenyltelluronium pseudohalides the cation-anion interaction is sufficient to impose dimeric or oligomeric structures of some complexity(43-48). In the case of $[(CH_3)_3Te]BPh_4$, the structural determination has shown an ionic compound(51).

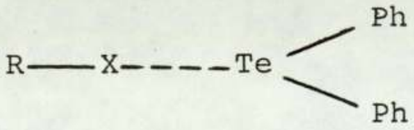
The values of the molar conductivity of $Ph_2MeTe^+X^-$ (X = Cl, Br, I, NCS and PhCOO) indicated that they are something less than 1:1 electrolytes in dimethylsulphoxide and dimethylformamide(55,57).

The results of measurements of telluronium salts, $PhMeTe^+X^-$, in chloroform and dimethylsulphoxide solution by ^1H NMR spectroscopy suggested that these compounds, in chloroform, formed a covalent form whereas in dimethylsulphoxide solution they exist as ionic forms:



The 'HNMR spectra of methyldiphenyltelluronium salts were recorded in chloroform and it was shown that the methyl singlets corresponding to methyl group which is attached to tellurium decayed with time to be replaced by new signals shown to arise from MeX (X = Cl, Br, I, NCS and PhCOO), also the Me — Te resonance was X dependent.(55,57)

Kinetic data(57) showed that the reaction of CH_3X with excess Ph_2Te (solvent) affords an equilibrium mixture of ionic and covalent forms of Ph_2MeTeX, the ionic species being formed via the covalent one. Spin trapping experiments with phenyl-t-butyl nitrone (PBN) indicated that oxidative addition of alkylhalide to Ph_2Te and reductive elimination of alkylhalides from $Ph_2MeTe^+X^-$ involved a radical pathway. A mechanism was proposed for oxidative addition which involved the initial formation of a charge transfer complex.



which was similar to some precedents in selenium chemistry(62).

The present work attempts to study the physicochemical properties of triorganotelluronium salts which are stable to the reductive elimination in order to explore the solution structure of these compounds.

The synthesis of a new class of cyclictelluronium salts is carried out in this work.

3.ii Experimental

Preparation of 1,1'-diiodo -3,4-benzo-1-telluracyclopentane

This compound was prepared according to the literature(63) with some modification. A mixture of ∝, ∝'-dibromo-o-xylene (10.6 g; 0.04 mol), tellurium powder (5.1 g; 0.04 g-atom) and sodium or potassium iodide (0.16 mol) in 2-methoxyethanol (~250 ml) was stirred and heated gently in an open beaker. Gentle boiling was continued for 30 minutes. Deionized water (300 ml) was added. The precipitate was collected by filtration, washed with water, rinsed with acetone and air dried. Recrystallization from hot 2-methoxyethanol gave orange-red and yellow-orange crystalline forms (∝- and β-form respectively). Recrystallization from DMF gave yellow-orange crystals (β-form).m.p266 - 228°C (∝) and 223 - 224°C (β). |Lit(63). 225°C (∝) and 222°C (β)|.

Found : C, 19.70; H, 1.70

$C_8H_8TeI_2$ requires: C, 19.79; H, 1.66

Synthesis of 3,4-benzo-1-telluracyclopentane

Sodium borohydride was added to a boiling methanolic solution of 1,1'diiodo - 3,4-benzo-1-telluracyclopentane until the orange colour had disappeared. The solution was filtered, then poured into 1L of water and extracted with ether. The combined ether extracts were washed with water, dried over $CaCl_2$, and concentrated to dryness on a rotary evaporator.

The yellow plates of 3,4-benzo-1-telluracyclopentane which melted at 43-44°C (Lit.(64) 44-46°C) were recrystallized from petroleum ether (60/80°C).

Found : C, 41.4; H, 3.50

C_8H_8Te requires: C, 41.4; H, 3.48

During the course of this work Gysling(65) prepared this compound by reduction of 1,1'-diiodo -3,4-benzo-1-telluracyclopentane by hydrazine.

Synthesis of 1-methyl-1-iodio-3,4-benzo-1-telluracyclopentane

Excess of fresh distilled methyliodide (6 ml) and 3,4-benzo-1-telluracyclopentane (2.32 g; 0.01 mole) were placed in flask flushed with dry nitrogen. An exothermic reaction took place, giving a pale yellow crystals which, recrystallized from a mixture solution of ethanol and water (3:1), gave bright white crystals which decomposed at 190-192°C.

Found : C, 28.9; H, 2.90

$C_9H_{11}TeI$ requires: C, 28.9; H, 2.79

The following telluronium salts were prepared by similar oxidation addition reaction of appropriate alkylhalide with 3,4-benzo-1-telluracyclopentane

1-Ethyl-1-iodo -3,4-benzo-1 -telluracyclopentane

The white precipitate formed after 2 hours m.p. 185-186°C(d).

Found : C, 31.2; H, 3.60

$C_{10}H_{13}TeI$ requires: C, 31.0, H, 3.40

1-Allyl-1-bromo-3,4-benzo-1-telluracyclopentane

An exothermic reaction took place. The white crystals melted with decomposition at 166-168°C.

Found : C, 37.2; H, 3.90

$C_{11}H_{13}TeBr$ requires: C, 37.5; H, 3.70

1-Benzyl-1-bromo-3,4-benzo-1-telluracyclopentane

A pale yellow precipitate formed immediately after mixing which recrystalized from a mixture solution of ethanol and water (3:1) to afford white crystals which decomposed at 170-172°C.

Found : C, 44.6; H, 3.90; Br, 20.4

$C_{15}H_{15}TeBr$ requires: C, 44.7; H, 3.80; Br, 19.8

1-Phenacyl-1-bromo-3,4-benzo-1-telluracyclopentane

3,4-benzo-1-telluracyclopentane (2.32 g; 0.01 mol) and phenacylbromide (2.0 g; 0.01 mol) were mixed, and sufficient dry diethylether added. The reaction flask was then stoppered and left overnight. The resulting white solid was washed with diethylether and dried under vacuum over P_2O_5. White crystals of the compound were obtained after recrystallization from a mixture solution of ethanol and water (3:1). M.p. (dec.) 166-168°C.

Found : C, 44.7; H, 3.70; Br, 20.9

$C_{15}H_{15}OTeBr$ requires: C, 44.6; H, 3.50; Br, 18.6

Synthesis of 1-methyl-3,4-benzo-1-telluracyclopentane-perchlorate

To 1-methyl-1-iodo-3,4-benzo-1-telluracyclopentane (0.37 g; 0.001 mol) which was dissolved in hot ethanol (20 ml) was added an aqueous solution of silver perchlorate (0.21 g; 0.001 mol). The resulting solution was stirred for 2 hours, and then the solution heated for 15 minutes with stirring, after which the hot solution was filtered and the yellow precipitate of silver iodide was collected. The solution was evaporated at room temperature. The white needles of 1-methy-3,4-benzo-1-telluracyclopentane perchlorate were recrystalized from a mixture solution of ethanol and water (4:1) and decomposed at 179-182°C.

Found : C, 29.9; H, 2.90

$C_9H_{11}O_4TeCl_4$ requires: C, 31.1, H, 3.20

Synthesis of 1-methyl-3,4-benzo-1-telluracyclopentane tetraphenylborate

Two methods of preparation were developed:

(a) The appropriate $C_9H_{11}TeI$ (0.37 g; 0.001 mol) dissolved in hot ethanol was mixed with an ethanolic solution of sodium tetraphenylborate (0.34 g; 0.001 mol) forming a voluminous precipitate. Stirring was continued for 2 hours, after which the suspension was boiled with stirring for 15 min. On cooling the solution to room temperature, a solid settled and was collected, washed with ethanol and water and dried in a vacuum over P_2O_5. The white precipitate of $C_{33}H_{31}BTe$ was recrystallized from DMF/H_2O to give white crystals. m.p. 208°C (d).

(b) By mixing equimolar portions of hot solutions $C_9H_{11}TeCl$ (0.28 g; 0.001 mol) (ethanol/water) and sodium tetraphenylborate (0.34 g; 0.001 mole) (ethanol) and stirring for one hour at room temperature, the compound was formed. After separation and washing with ethanol and water, the white crystals were recrystallized from a mixture of DMF and water. m.p. 208-210°C (d).

Found : C, 69.6; H, 5.20

$C_{33}H_{31}BTe$ requires: C, 70.0; H, 5.50

Synthesis of 1-phenyl-3,4-benzo-1-telluracyclopentane tetraphenylborate

A mixture of 1,1'-diiodo-3,4-benzo-1-telluracyclopentane (2.42 g; 0.002 mol) with $NaBPh_4$ (3.42; 0.01 mol) and dry ethanol (100 ml) were placed into 250 ml round bottomed flask equipped with magnetic stirring bar, and condenser. The reaction mixture was heated to reflux with stirring for 3-4 hours, after which the hot solution was filtered and the white crystals of $C_{38}H_{33}BTe$ collected in quantative yield, washed with water and methanol and recrystallized from water and DMF to m.p. 184°C (d).

Found : C, 72.0; H, 5.20

$C_{38}H_{33}BTe$ requires: C, 72.6; H, 5.20

Synthesis of 1-(1'-bromo-2'-butene)-1-bromo-3,4-benzo-1-telluracyclopentane

1.4-dibromo-2-butene (0.46 g; 0.002 mol) and C_8H_8Te (0.43 g; 0.002 mol) were dissolved in absolute ethanol.

A white precipitate was formed within one hour. The resulting solid was collected, washed with ethanol and dried over P_2O_5 under vacuum. Attempts for recrystallization from a mixture of ethanol and water produced decomposition, and so the compound was used without further purification. m.p. 135-137°C (d).

Found : C, 27.7; H, 2.10; Br, 36.6

$C_{12}H_{14}TeBr_2$ requires: C, 35.8; H, 2.98; Br, 34.1

Unsatisfactory elemental analysis for this compound does not agree with the emprical formula. In ^{13}C NMR, there is no signal due to - CH = CH -.

Synthesis of 1,1'-dibromo-3,4-benzo-1-telluracyclopentane

C_8H_8Te (0.5g) in carbon tetrachloride (50 ml) was treated with bromine (0.3 g) in carbon tetrachloride and stirred at room temperature for 30 minutes. The solution was filtered to afford very pale yellow crystals which were recrystallized from 2-methoxyethanol to m.p. 244-246°C.

Found : C, 24.7; H, 2.10; Br, 36.6

$C_8H_8TeBr_2$ requires: C, 24.5; H, 2.05; Br, 40.8

During the course of this work, Gysling(65), prepared this compound with m.p. of 230°C.

Attempts to prepare the telluroxide from the above compound were not successful.

An aqueous suspension of silver oxide mixed with solution of $C_9H_{11}TeI$ in order to precipitate silver iodide and form the telluronium hydroxide, which could be combined with hydrofluoric acid to form $C_9H_{11}TeF$, was not successful

The attempted preparation of other telluronium salts from 1,4-dibromo-2-butene

Di(p-ethoxyphenyl)telluride (1.85 g; 0.005 mol) which was prepared according to the literature(66) refluxed with 1,4-dibromo-2-butene (1.1 g; 0.005 mole) in ethanol for one hour. The solution was allowed to cool at room temperature. On cooling pale yellow crystals were obtained which melted at 126-128°C. It was found that the product was bis(p-ethoxyphenyl)tellurium dibromide.[Lit.(66) m.p.127

Found : C, 36.5; H, 3.50; Br, 30.0

$C_{16}H_{18}TeBr_2$ requires: C, 36.3; H, 3.40; Br, 30.2

The reaction of 1,4-dibromo-2-butene with diphenyltelluride carried out as above led to the formation of Ph_2TeBr_2. m.p. 201-203°C. (Lit(67) 203-204°C).

3.(ii). RESULTS

3.(ii)a. Solubility

The cyclic telluronium salts are soluble in DMSO and DMF. With the exception of 1-methyl-iodo -3,4-benzo-1-telluracyclopentane, 1-ethyl-1-iodo -3,4-benzo-1-telluracyclopentane and 1-allyl-1-bromo-3,4-benzo-1-

telluracyclopentane, they are not soluble in chloroform. All cyclic telluronium salts were found to be insoluble in ethanol, acetonitrile, nitromethane, benzene, toluene, ether, carbon tetrachloride and petroleum ether.

3.(ii)b. Conductivity Measurements

The molar conductivity of each cyclic telluronium salt in dimethylsulphoxide (DMSO) and N,N'-dimethylformamide (DMF) is shown in table I. Conductivity at various concentrations in DMSO and DMF were also measured Fig. 1 and 2.

3.(ii)c. Infrared Spectra

The infra-red spectra of all cyclic telluronium salts in a range of 4000-200 cm^{-1} in KBr discs are presented in table 2.

The infra-red spectra of 1-methyl-1-iodio-3,4-benzo-1-telluracyclopentane and 1-(trideuteromethyl)-1-iodo -3,4-benzo-1-telluracyclopentane in KBr discs are represented in figures 3 and 4. The IR spectra of 1-methyl-3,4,-benzo-1-telluracyclopentane perchlorate both as a Nujol mull and as KBr disc in range of 4000-200 cm^{-1} are shown in figures 5 and 6.

The infra-red spectrum of 1-phenacyl-1-bromo-3,4-benzo-1-telluracyclopentane in KBr disc is represented in figure 7.

3.(ii)d. ^1H NMR Spectra

The ^1H NMR spectra were obtained for cyclic telluronium salts in $CDCl_3$, DMSO-d_6 and DMF-d_7 are presented in table 3.

There are two types of aliphatic resonances in these compounds, one is due to the alkyl group and the other due to the presence of two methylene groups. The position of the alkyl resonances in chloroform, dimethylsulphoxide and dimethylformamide remained unchanged.

The initial spectrum of 1-methyl-1-iodo -3,4-benzo-1-telluracyclopentane in $CDCl_3$ showed in the aliphatic region a singlet methyl resonance at $\delta = 2.42$ ppm (relative to TMS) with satellites corresponding to ^1H - ^{125}Te coupling (J = 24.5 Hz) and four resonances at $\delta = 4.12$, 4.36, 4.88 and 5.12 ppm due to the methylene groups. The position of methyl resonances remained unchanged after 30 hours, as presented in figures 9 and 10.

3.(ii)e ^{13}C NMR Spectra

The ^{13}C NMR spectra for some of the cyclic telluronium salts were measured in $CDCl_3$, DMSO-d_6, and DMF-d_7. The results are given in table 4.

3.(ii)f ^{125}Te NMR Spectra

^{125}Te chemical shifts for some of cyclic telluronium salts were obtained in $CDCl_3$, DMSO-d_6 and DMF-d_7 using pure dimethyltelluride as external reference, the results are tabulated in table 5.

3.(ii)g Molecular Weight Measurements

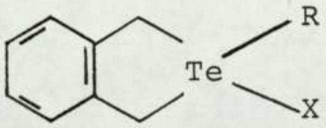
The molecular weight measurement of 1-methyl-iodo-3,4-benzo-1-telluracyclopentane was carried out in chloroform at 25°C and the results are shown in table 6.

3.(ii)h Mass Spectra

The mass spectra for all cyclic telluronium salts are tabulated in tables 7-15. These tables contain only the important ions and the ions of high relative abundance.

TABLE (1)

Conductivity measurements on solution of cyclic-telluronium salt:

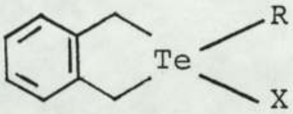


R	X	Solvent/Molar conductivity (ohm^{-1} cm^2 mol^{-1})	
		DMSO	DMF
$-CH_3$	I	32.6	64.0
$-CH_2CH_3$	I	30.8	61.8
$-CH_2-CH=CH_2$	Br	33.6	61.2
$-CH_2-Ph$	Br	31.0	45.3
$-CH_2-\overset{O}{\overset{\|\|}{C}}-Ph$	Br	-	32.1
$-CH_3$	BPh_4	21.9	43.8
Ph	BPh_4	-	46.1
$-CH_2-CH=CH-CH_2Br$	Br	35.6	-

Solutions were 10^{-3} M

TABLE (2a)

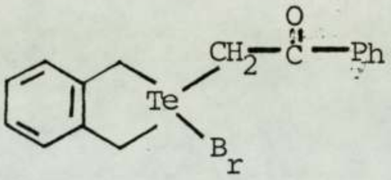
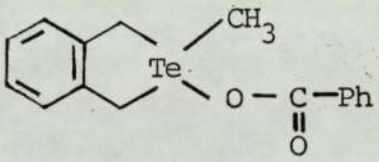
IR Data for Tellurium-Carbon Vibrations of Tellurium Salts:



R	X	ν (cm^{-1})
CH_3	I	538 (w)
CH_2 CH_3	I	538 (w)
- CH_2 - CH = CH_2	Br	535 (w)
- CH_2Ph	Br	538 (w)
$CH_2\overset{O}{\overset{\|\|}{C}}Ph$	Br	472 & 482 (w)
CH_3	Br	535 (w)
CH_3	ClO_4	540 (w)
Ph	BPh_4	460 (m)
CD_3	I	520; 500 (m)
- CH_2 - CH = CH - CH_2Br	Br	475 (w)

TABLE (2b)

IR data of cyclic telluronium salts. Solution spectra were obtained in chloroform solution.

Compounds	$\nu(CO)_{cm^{-1}}$	ν (CO)	(Te - C_{alkyl}) solid
	1660 ----- 1660		482, 472
	1600 ----- 1600	1365 ----- 1365	530*

* Data from ref 59

TABLE (3)

^1H NMR data of Cyclic Telluronium Salts.

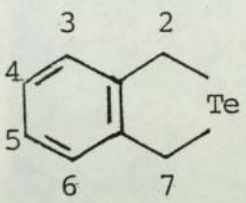
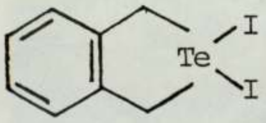
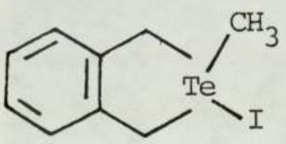
Compound	Solvent	Chemcial Shifts, ppm TMS = 0 ppm	Coupling constant Hz
	$CDCl_3$	H(2,7): 4.65(s); H(3,4,5,6): 7.15-7.3 (m)	24.0
	DMSO	H(2,7): 4.45(s); H(3,4,5,6): 7.05-7.2 (m)	24.0
	DMSO	H(2,7): 4.75(s); H(3,4,5,6): 7.2-7.5 (m)	24.0
	DMF	H(2,7): 2.42(s); H(3,4,5,6): 7.00-7.45 (m)	25.5
	$CDCl_3$	CH_3: 4.42(s); H(2,7): 4.1, 4.38, 4.88, 5.1; H(3,4,5,6): 6.9-7.3 (m)	24.6
	DMSO	CH_3: 1.98(s); H(2,7): 3.77, 4.02, 4.17, 4.42; H(3,4,5,6): 6.8-7.3 (m)	24.0
	DMF	CH_3 2.25(s); H(2,7): 4.03, 4.2, 4.5, 4.78; H(3,4,5,6): 7.2-7.45 (m)	23.8

TABLE (3) cont'd

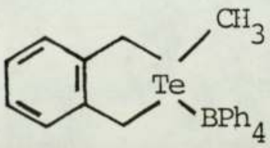
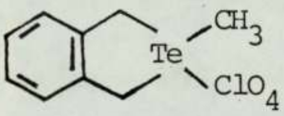
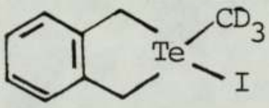
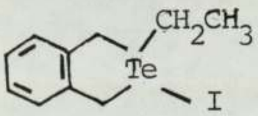
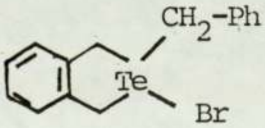
Compound	Solvent	Chemical Shifts, ppm TMS = 0 ppm	Coupling constant Hz
	DMSO	CH_3: 2.05(s); H(2,8): 3.48, 4.11, 4.20, 4.45; H(3,4,5,6): 6.8-7.2 (m); H(Ar): 7.2-7.5 (m)	18.6
	DMSO	CH_3: 1.98(s); H(2,7): 3.82, 4.06, 4.21, 4.47; H(3,4,5,6): 7-7.5 (m)	22.4
	DMSO	H(2,7): 3.89, 4.12, 4.30, 4.52; H(3,4,5,6): 7.1-7.5 (m)	-
	DMSO	CH_3: 2.30(t); CH_2: 2.6-2.8(q); H(2,7): 3.9, 4.15, 4.28, 4.53; H(3,4,5,6): 7.20-7.45 (m)	18.0
	DMSO	CH_2: 2.83(s); H(2,7): 3.95, 4.1, 4.2, 4,45; H(Ar): 7.0-7.20 (m)	-

Table (3) cont'd

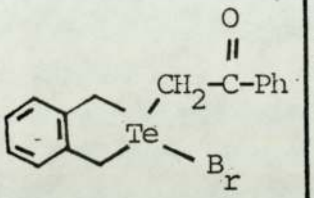
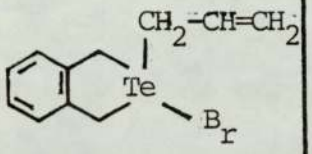
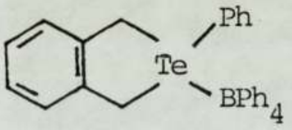
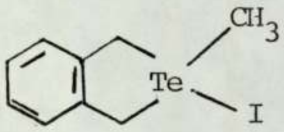
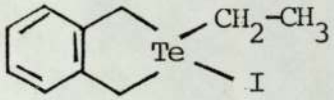
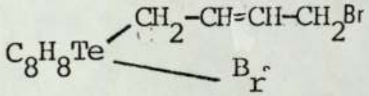
Compound	Solvent	Chemical Shifts ppm TMS = 0 ppm	Couplings constants Hz
	DMSO	CH_2: 1.32(s); H(2,7): 3.95, 4.21, 4.36, 4.61; H(Ar): 7.2-7.5 (m)	21.2
	DMSO	CH_2(a): 3.0-3.2(d); CH_2(c): 4.44-3.66(d): CH; 4.86-5.42(q) H(2,7): 3.44, 3.62, 3.62, 3.84; H(3,4,5,6): 6.72-7.28 (m)	-
	DMSO	H(2,7): 3.95, 4.21, 4.35, 4.61; H(3,4,5,6): 6.8-7.10 (m) H(Ar): 7.12-7.60 (m)	-

TABLE (4)

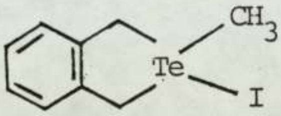
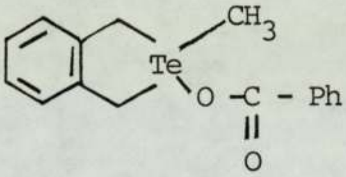
^{13}C NMR data for telluronium salts. $\delta\ ^{13}C \pm 0.1$ ppm internally referred to TMS.

Compounds	Solvents	$\delta^{13}C_1$	$\delta^{13}C_2$	$\delta^{13}C_3$	$\delta^{13}C_4$	Other $\delta^{13}C$
	$CDCl_3$	36.7	138.4	127.9	130.1	7.1
	DMSO	34.4	138.7	126.6	129.1	5.6
	DMF	*	133.3	133.3	135.6	13.6
	$CDCl_3$	36.0	138.9	127.7	129.4	10.9; 21.9
	DMF	*	145.6	132.9	135.0	15.3; 25.1
	DMSO	34.3	139.2	129.1	129.9	20.6; 27.3

* In DMF the CH_2 - fall in a solvent line.

TABLE (5)

Molecular weight data for some cyclic telluronium salts.

Compounds	Monomer	Dimer	Observed
	373	746	742
	367	734	731*

* Data from reference 59.

TABLE (6)

^{125}Te NMR data for some telluronium salts.

Reference $(CH_3)_2Te$.

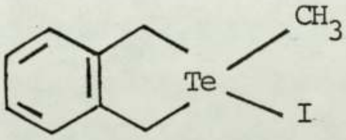
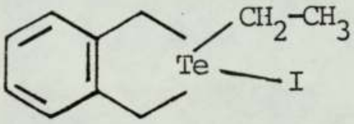
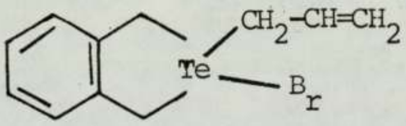
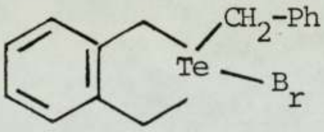
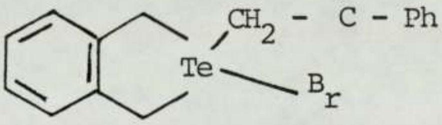
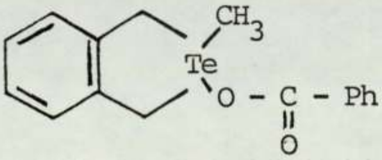
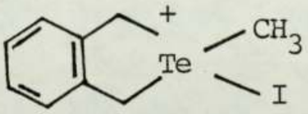
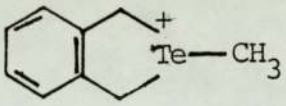
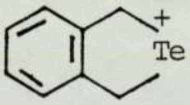
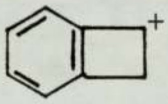
Compounds	Solvents	δ ^{125}Te ppm
	$CDCl_3$ DMSO DMF	652.0 651.4 652.2
	$CDCl_3$ DMSO DMF	706.4 708.9 -
	DMSO	688.3
	DMSO	722.3
	DMSO DMF	693.5 680.1
	$CDCl_3$	687.0

TABLE (7)

Mass spectra for $C_9H_{11}TeI$ relative to ^{130}Te.

Species	m/e	R.I
	376	4
	249	6
	234	100
$PhTe^+$	207	100
	104	100
MeI	142	100
I^+	127	100

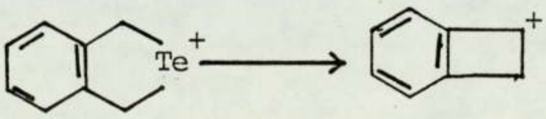
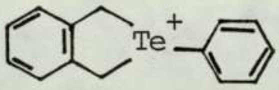
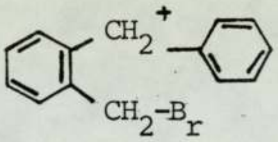
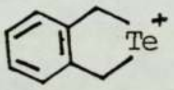
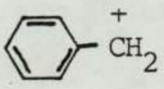
46.2 metastable for 

TABLE (8)

Mass spectra for 1-benzyl-1-bromo-3,4-benzo-1-telluracyclopentane relative to ^{130}Te, ^{81}Br (24 ev).

Species	m/e	R.I
	309	3
	260	9$^{(a)}$
	234	100
Ph-CH_2-Br	172	100
Ph_2^+	154	25
$C_8H_8^+$	104	100
	91	95
Br^+	81	100
Ph^+	77	100
$C_5H_5^+$	65	100

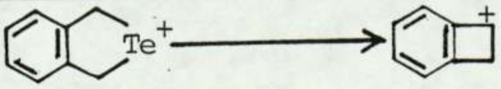
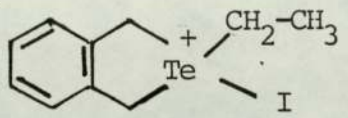
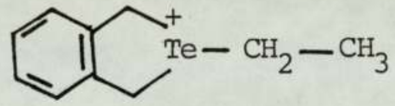
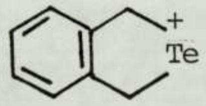
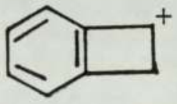
46.2 metastable for 

TABLE (9)

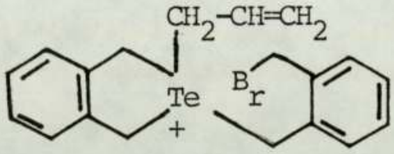
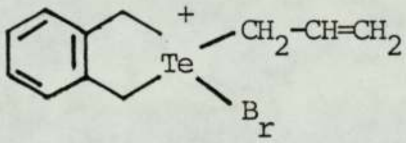
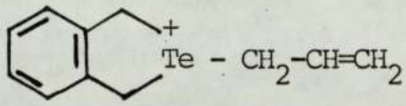
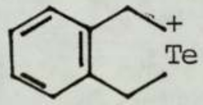
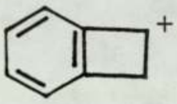
Mass spectra for $C_{10}H_{13}TeI$ relative to ^{130}Te and ^{127}I.

Species	m/e	R.I
	390	3.5
	263	15
	234	100
$PhTe^+$	207	11
$CH_3-CH_2-I^+$	156	100
Te^+	130	70
	104	100
Ph_2^+	154	64
I^+	127	100
Ph^+	77	100

46.2 metastable for

TABLE (10)

Mass spectra for $C_{11}H_{13}TeBr$ relative to ^{130}Te, ^{81}Br.

Species	m/e	R.I
	460	3
	356	25
	275	8
	234	100
$PhTe^+$	207	49
$CH_2=CH-CH_2Br$	121	100
	104	100
Br^+	81	100
Ph^+	77	100

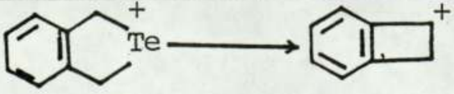
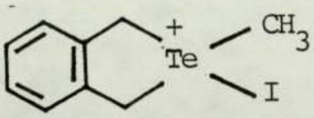
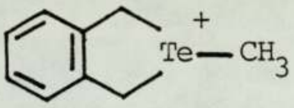
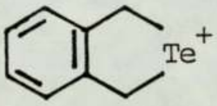
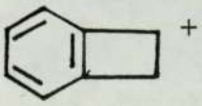
46.2 metastable for 

TABLE (11)

Mass spectra for $C_9H_9O_4TeCl$, relative to ^{130}Te, ^{35}Cl.

Species	m/e	R.I
	284	3
	249	4
	234	100
$PhTe^+$	207	11
Ph_2^+	154	12
	104	100
CH_3ClO_4	115	8
Ph^+	77	100

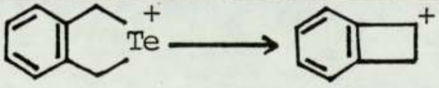
46.2 metastable for 

TABLE (12)

Mass spectra for $C_{16}H_{15}OTeBr$, relative to ^{130}Te, ^{81}Br.

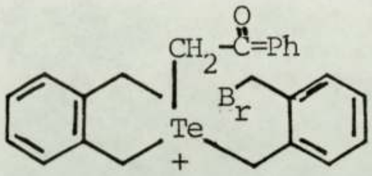
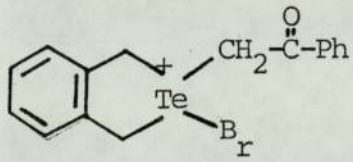
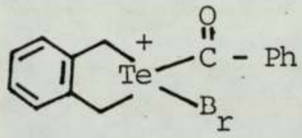
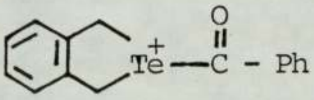
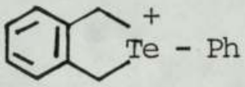
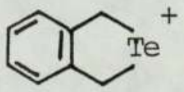
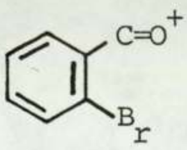
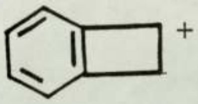
Species	m/e	R.I
	538	4
	434	40
	420	7
	339	20
	311	5
	234	100
$PhTe^+$	207	69
$Ph - CO - CH_2 - Br^+$	200	100
	185	100

TABLE (12) cont'd

Species	m/e	R.I
$C_6H_5CO^+$	106	100
	104	100
$C_7H_7^+$	91	100
Br^+	77	100
$C_5H_5^+$	65	100
$C_4H_3^+$	51	100
CO^+	39	100

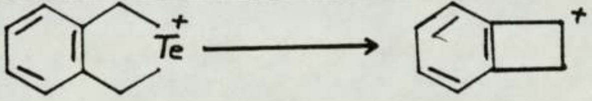
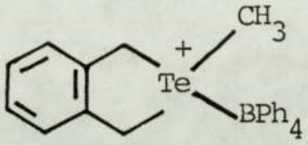
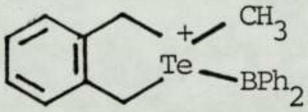
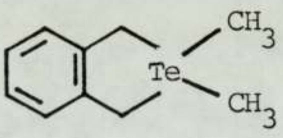
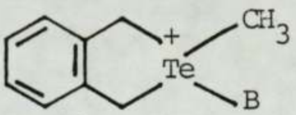
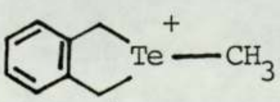
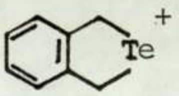
46.2 metastable for 

TABLE (13)

Mass spectra for $C_{33}H_{31}BTe$, relative to ^{130}Te, ^{11}B.

Species	m/e	R.I	Species	M/e	R.I
			$BC_{12}H_{10}^+$	165	30
	568	4	$BC_8H_6^+$	133	25
		–	$C_8H_8^+$	104	off scale
	414	2			
			BPh^+	88	25
Ph_4B^+	319	11			
			Ph^+	77	off scale
	264	8			
	260	12			
$Ph_3B^+CH_3$	257	10			
	249	40			
BPh_3^+	242	40			
	234	off scale			
$PhTe^+$	207	15			

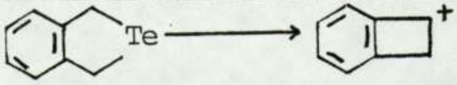
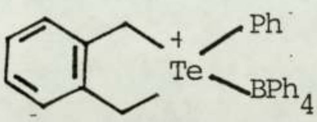
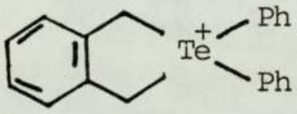
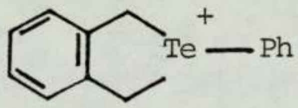
46.2 metastable for 

TABLE (14)

Mass spectra for $C_{38}H_{33}BTe$ relative to ^{130}Te, ^{11}B.

Species	m/e	R.I	Species	m/e	R.I
	630	0.8	$BC_{10}H_8^+$	139	off scale
$Ph_2Te_2^+$	414	14	$B(C_{10}H_6)^+$	137	off scale
			$BC_8C_6^+$	113	off scale
	388	4	$C_8H_8^+$	104	off scale
Ph_4B^+	319	6	Ph_+	77	off scale
	311	9			
Ph_2Te^+	284	off scale			
Ph_3B^+	242	off scale			
$PhTe^+$	207	off scale			
$BC_{12}H_{10}^+$	165	off scale			
$BC_{12}H_8^+$	163	off scale			
Ph_2^+	154	off scale			

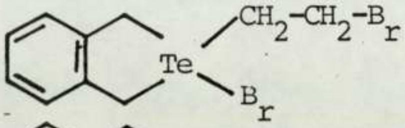
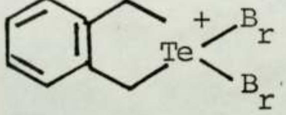
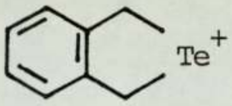
46.2 metastable for $C_8H_8Te^+ \longrightarrow C_8H_8^+$

85.5 metastable for $Ph_2Te^+ \longrightarrow Ph_2^+$

151 metastable for $Ph_2Te^+ \longrightarrow PhTe^+$

TABLE (15)

Mass spectra for $C_{12}H_{14}TeBr_2$ relative to ^{130}Te, ^{81}Br.

Species	m/e	R.I
	427	21.8
	396	2.7
	234	100
$C_8H_8Br^+$	185	41.8
$PhTe^+$	207	9.5
$C_8H_8^+$	104	100
Br^+	81	74
Ph^+	77	100

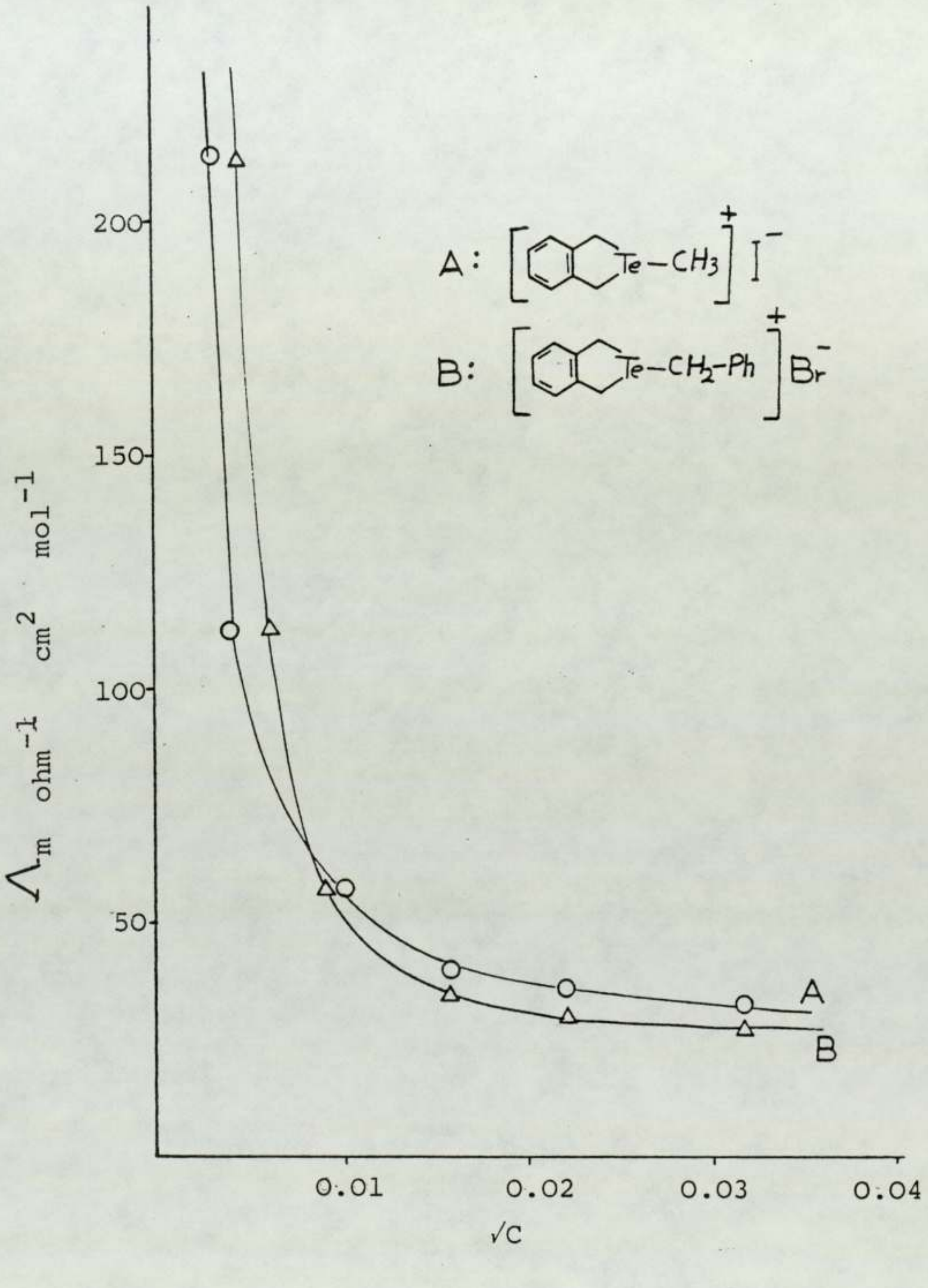


Figure 1 Conductivity of some telluronium salts in DMSO

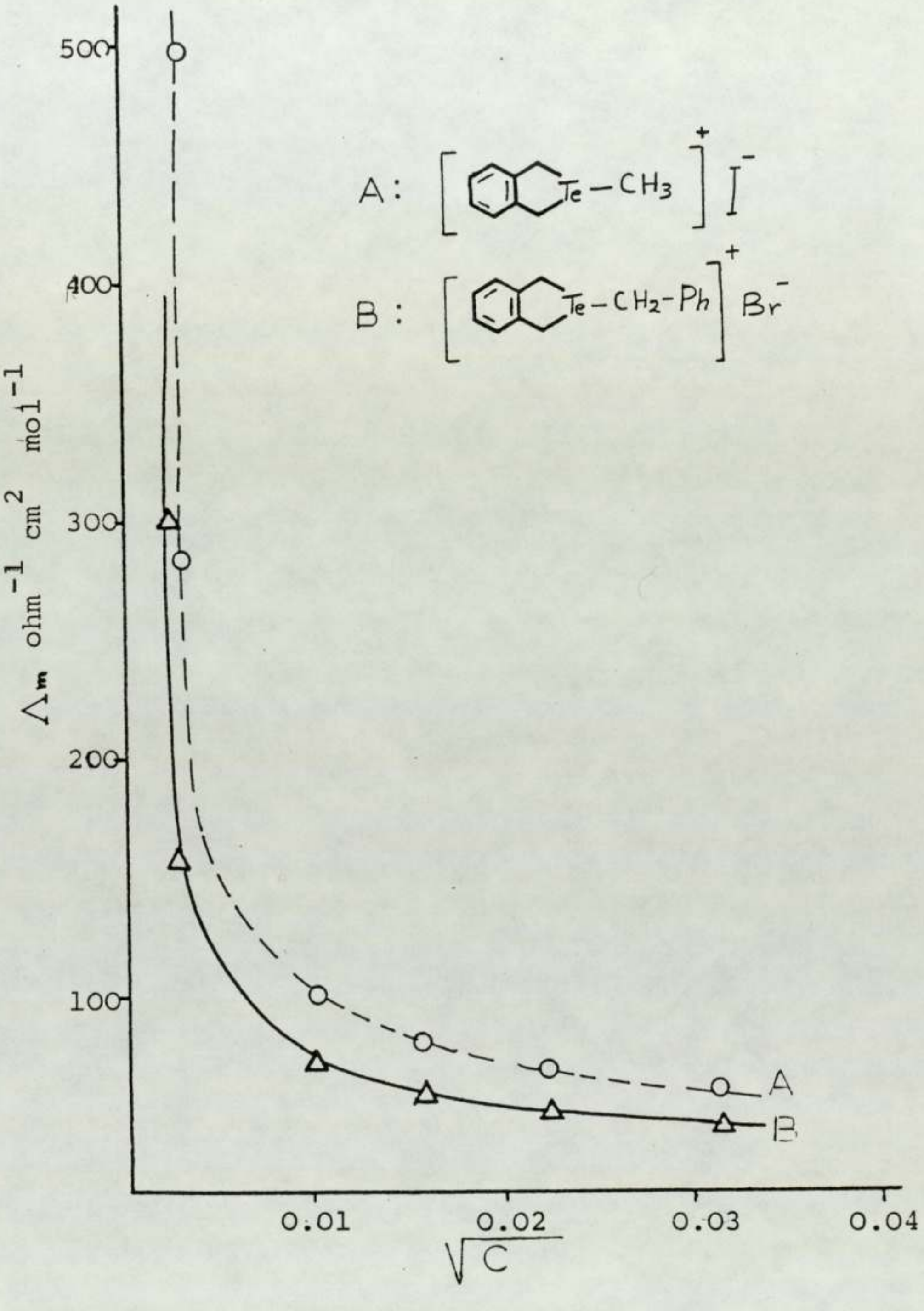
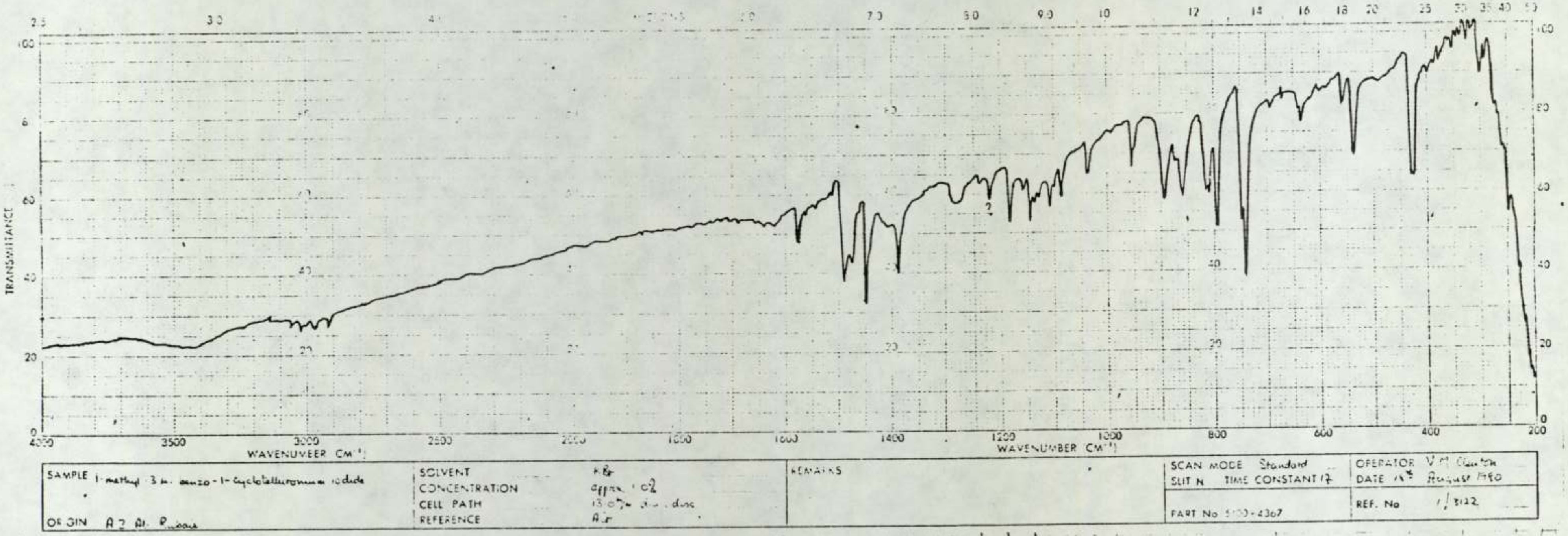


Figure 2 Conductivity of cyclic telluronium salts in DMF



SAMPLE 1-methyl-3H-benzo-1-cyclotelluronium iodide

ORIGIN A. Z. Al. Rubaie

SOLVENT KBr

CONCENTRATION approx 1%

CELL PATH 13 mm dia. disc

REFERENCE Air

SCAN MODE Standard

SLIT N TIME CONSTANT 1/2

OPERATOR V. M. Clanton

DATE 13th August 1980

REF. No 1/3122

PART No 5100-4367

Figure 3 Infra-red spectrum of $C_9H_{11}TeI$

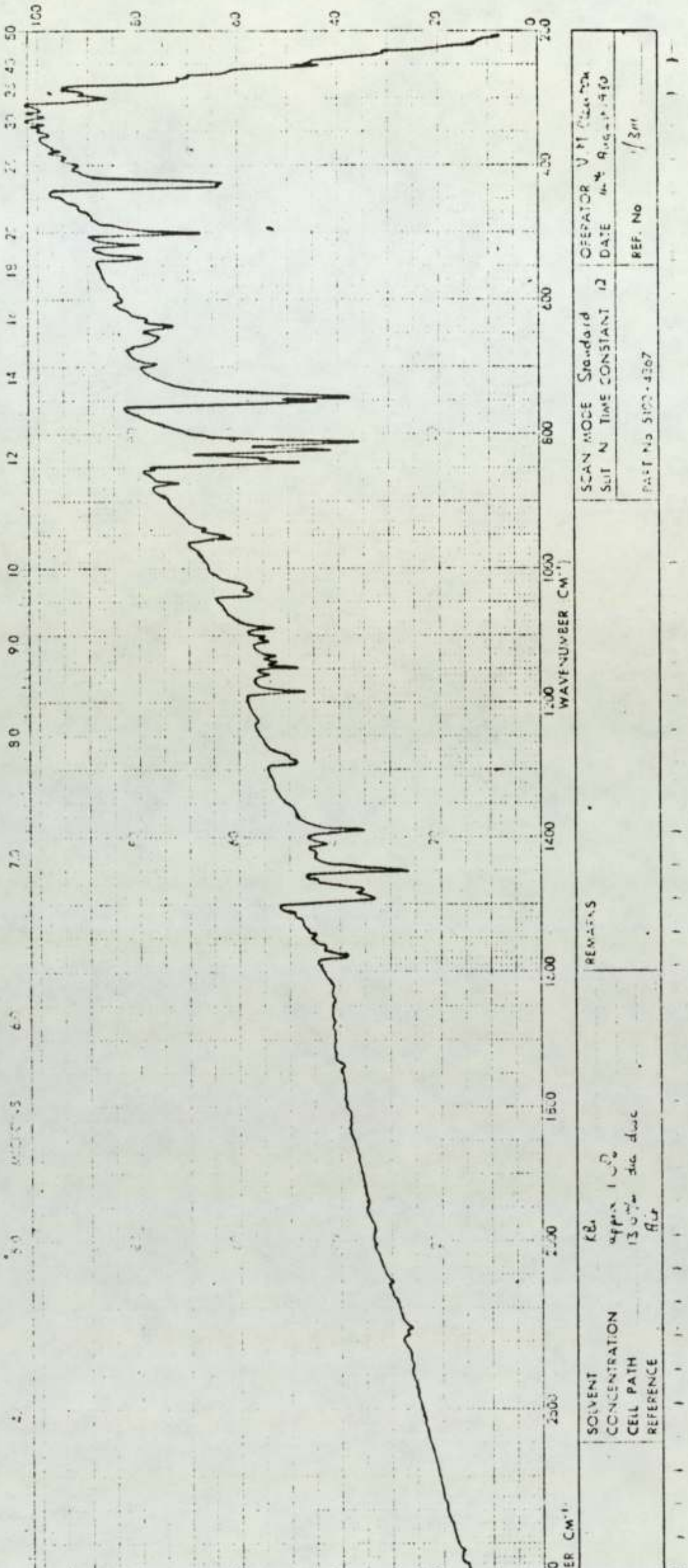


Figure 4 Infra-red spectrum of $C_8H_8Te.CD_3I$

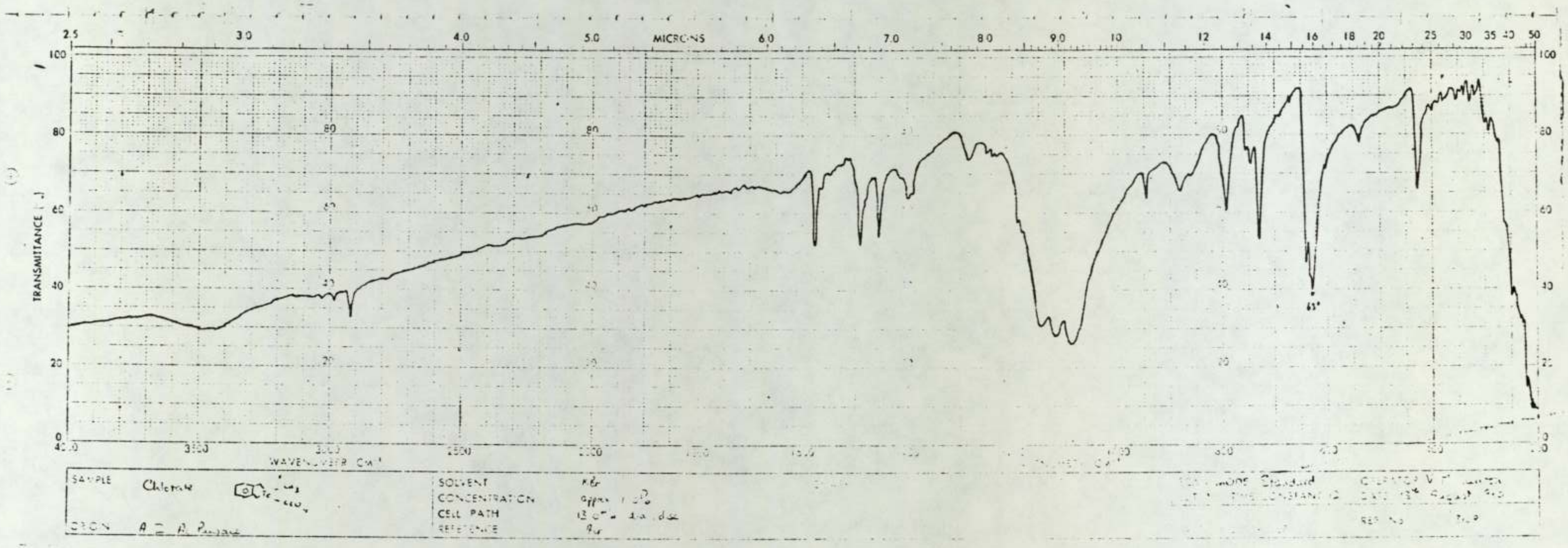


Figure 5 IR spectrum of 1-methyl-3,4-benzo-1-telluracyclopentane perchlorate as KBr disc

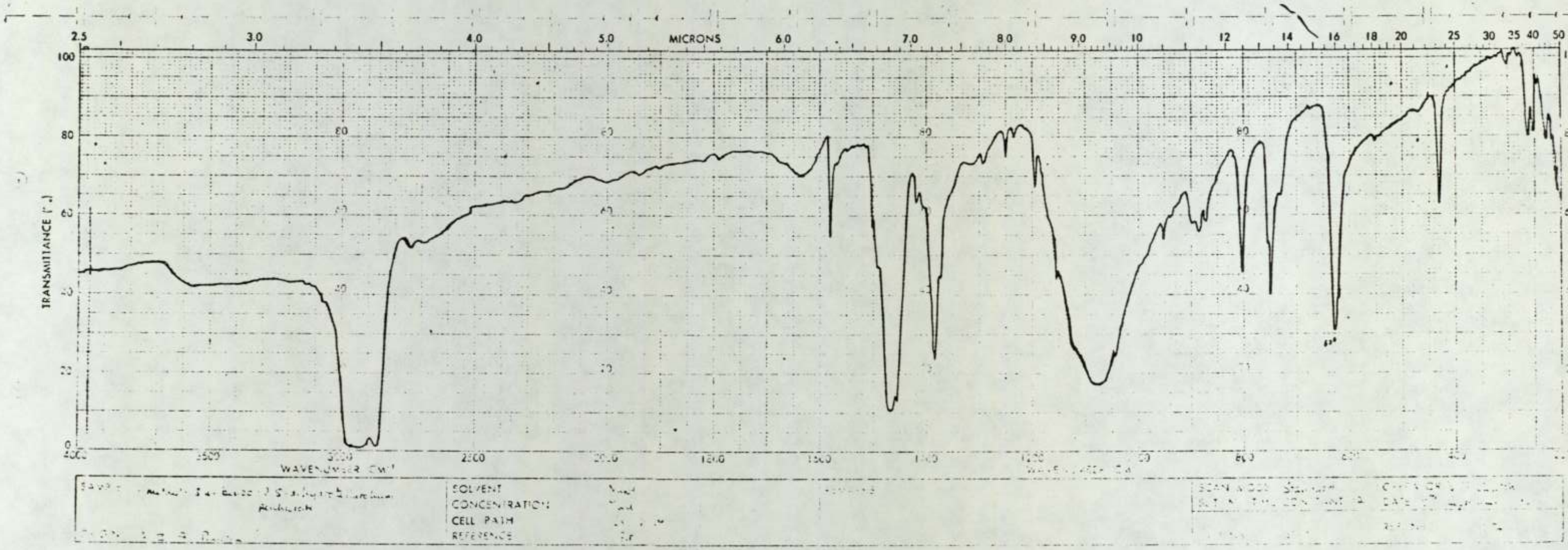


Figure 6 IR spectrum of 1-methyl-3,4-benzo-1-telluracyclopentane perchlorate as a Nujol mull

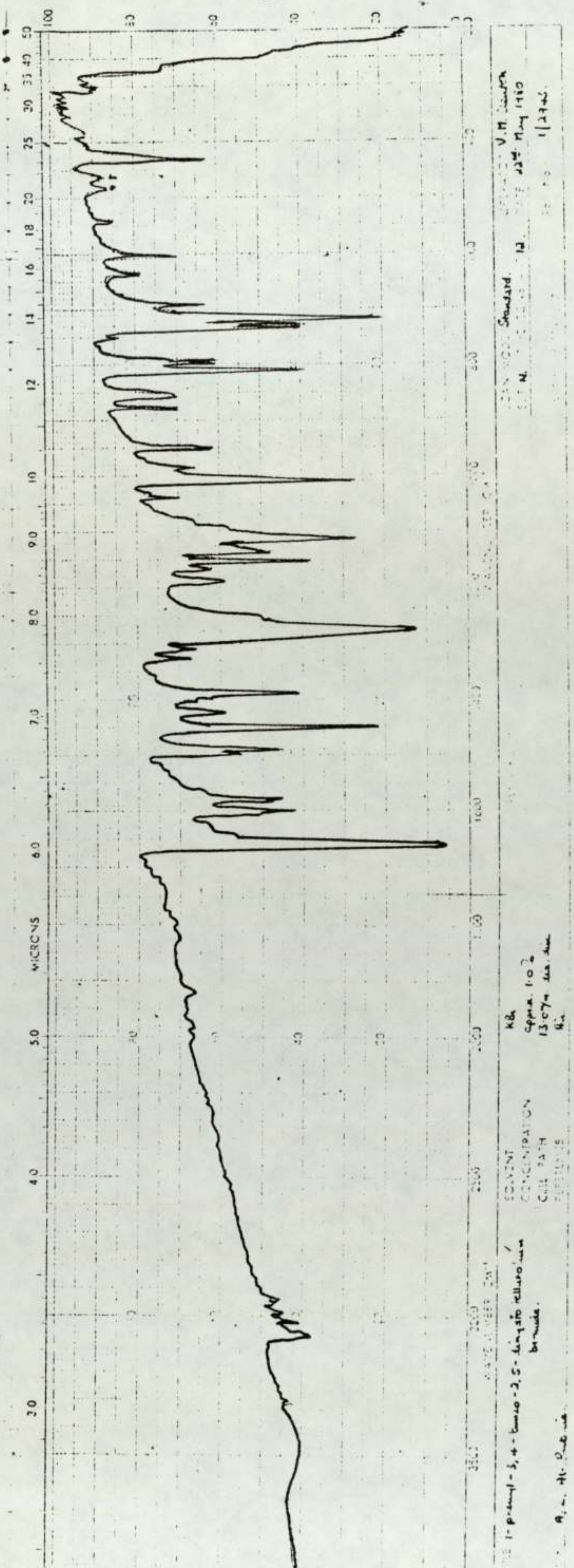


Figure 7 IR spectrum of 1-phenacyl-1-bromo-3,4-benzo-1-telluracyclopentane

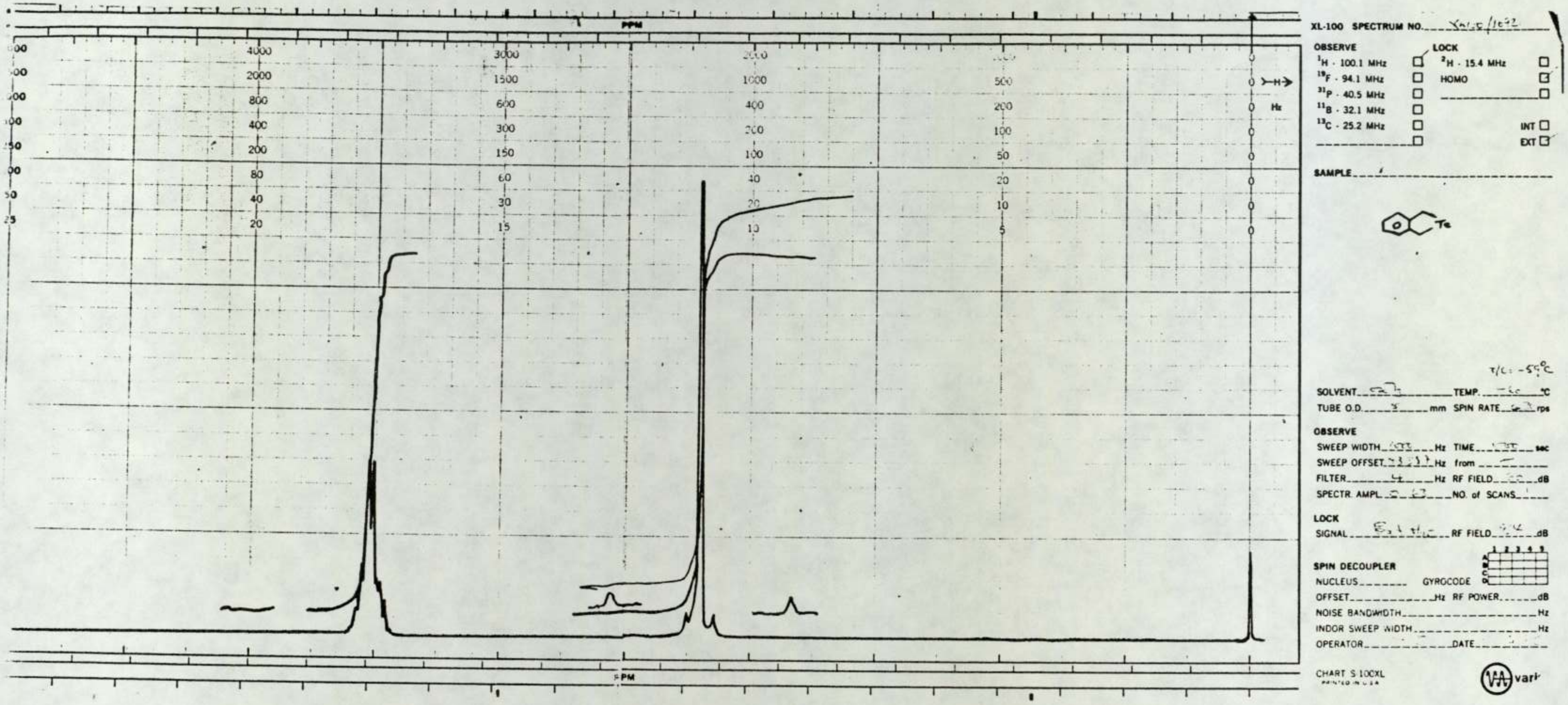


Figure 8 ^1H NMR spectrum of C_8H_8Te in $CDCl_3$ at -59°C

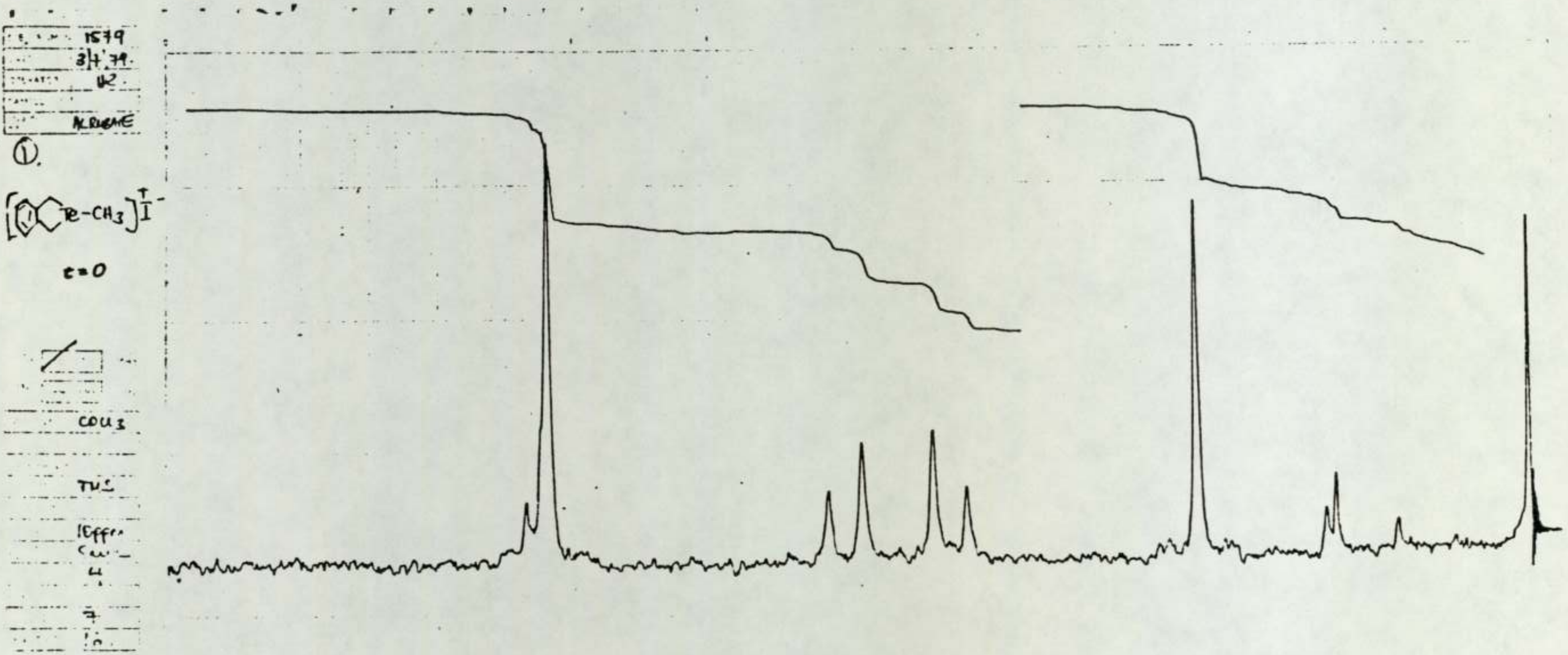


Figure 9 ^1H NMR spectrum of $C_9H_{11}TeI$ in $CDCl_3$ immediately after mixing

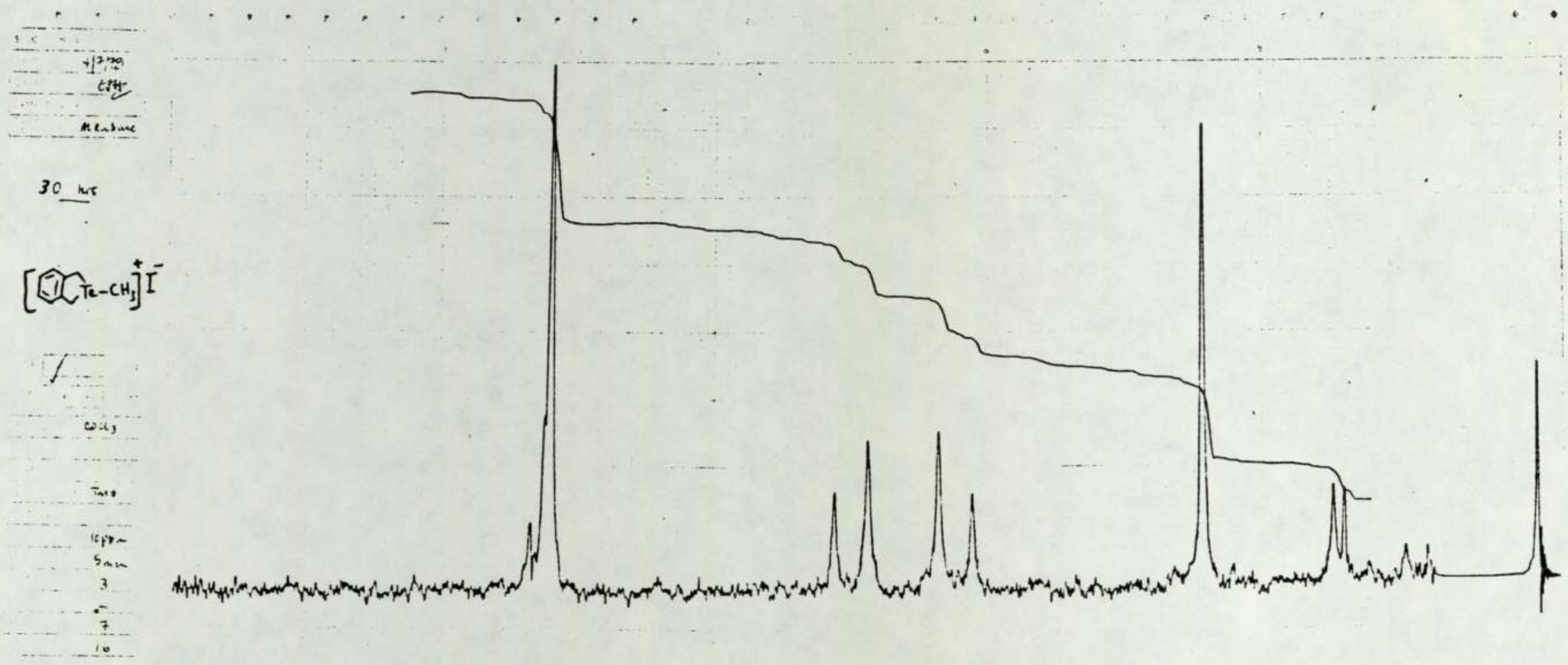
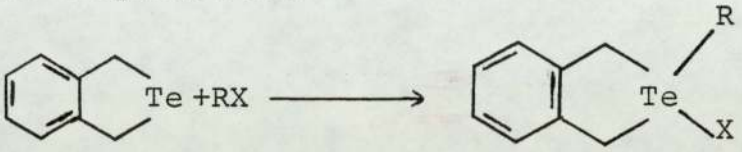


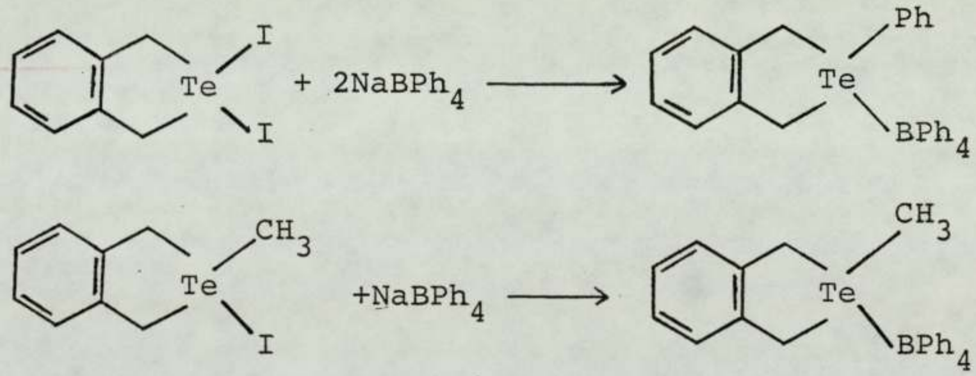
Figure 10 ^{1}H NMR spectrum of $C_9H_{11}TeI$ in $CDCl_3$ after 30 hours

3.(iii) DISCUSSION

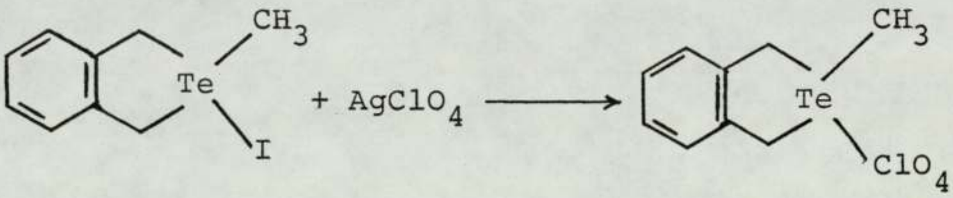
A series of new stable cyclic telluronium salts have been prepared by reaction of 3,4-benzo-1-telluracyclopentane with appropriate alkylhalides,



reaction of 1,1-diiodo-3,4-benzo-1-telluracyclopentane or 1-methyl-1-iodo-3,4-benzo-1-telluracyclopentane with sodium tetraphenylborate.



and reaction of a cyclic telluronium salt with silver perchlorate,



The molar conductivity of each telluronium salt was determined in dimethylsulphoxide (DMSO) and N,N'-dimethylformamide (DMF). The results are presented in table (1). The values of the molar conductivity indicate that the compounds are less than 1:1 electrolytes in both solvents. Conductivites are also measured as a function of concentration, in DMSO and DMF solutions. Plots of molar conductance against (concentration)$^{\frac{1}{2}}$ are typical of weak electrolytes, figures 1 and 2. All the telluronium compounds produced very similar results, hence only two examples are described on figures 1 and 2. It would appear that there is ion pairing in these compounds, indicating there is some attractive interaction between the tellurium and anion atoms.

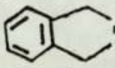
The infra-red spectra of cyclic telluronium salts show ν(Te-C$_{alkyl}$) occuring between 472-540 cm^{-1}, the results are shown in table 2.

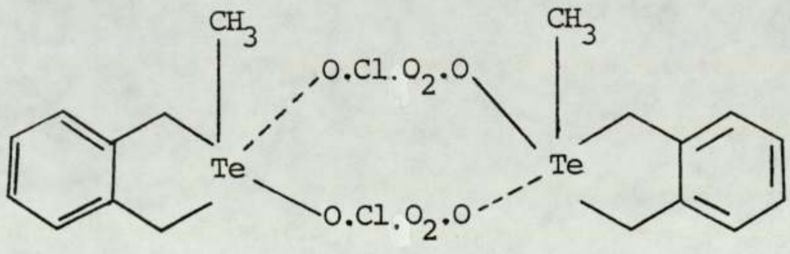
Comparison of the infra-red spectra of 1-methyl-1-iodo-3,4-benzo-1-telluracyclopentane and 1-(trideuteromethyl)-1-iodo-3,4-benzo-1-telluracyclopentane indicate many bands are shifted on deuteration. The assignment of bands in the infra-red spectrum of these compounds is much simplified by application of isotopic substitution techniques. The large difference in mass between -CH$_3$ and -CD$_3$ will produce shifts of the relevant bands. The isotopic substitution technique can therefore indicate whether previous vibrational assignments have been correct.

It is therefore possible to state that the band at 538 cm^{-1} split and shifted to 520 and 500 cm^{-1} on deuteration, is the Te-CH$_3$ stretching mode and also the band at 556 cm^{-1} shifted to 540 cm^{-1}. Bands at 1220 cm^{-1} to 940 cm^{-1} and bands at 893 and 860 cm^{-1} are shifted to 668 and 640 cm^{-1}

respectively and are attributed to the CH_3 vibrational rock modes fig 3 and 4. McWhinnie et. al.(57) examined some IR data for $Ph_2(CH_3)$.TeI and $Ph_2(CD_3)$.TeI and they have included literature data for $(CH_3)_2TeI_2$ and $(CD_3)_2TeI_2$ on their assignment.

The existence of extra bands is due to a lowering of the symmetry by intermolecular interaction; if there is more than one molecule within the unit cell then factor group splitting becomes possible, and would explain the observation of apparent splitting of the $\nu(Te-CH_3)$ and the presence of an extra CH_3 mode, figures 3 and 4.

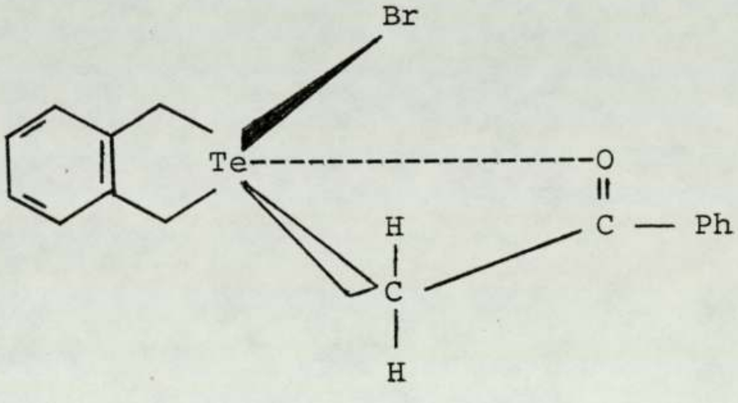
The IR spectrum of ( Te-CH_3)ClO_4 as a Nujol mull shows bands typical of the ionic perchlorate group centred on 1075 cm^{-1} together with a sharp band at 628 cm^{-1} . However, when this compound pressed into a KBr disc the broad band split into 3 components at 1145, 1120 and 1085 cm^{-1}; also the sharp band at 628 cm^{-1} splits into 640 and 630 cm^{-1} as shown in figures 5 and 6. The splitting is well resolved and may be attributed to a lowering of the symmetry for the perchlorate group in a new polymorphic form of the crystal. A reasonable explanation of the above observation is that the anion and cation interact via tellurium-oxygen bonding, in the high pressure modification of material possibly to give a dimer of the type,



The literature describes similar behaviour for perchlorate groups in an organic compound(69), co-ordination and organometallic compounds (70).

The infra-red spectra of 1-phenacyl-1-bromo-3,4-benzo-1-telluracyclopentane in solid and solution state were recorded and are given in table 2. The band at 1660 cm^{-1} corresponding to ν(CO) and frequency at 482 cm^{-1} due to Te-C$_{alkyl}$ vibration were observed in solid state which were similar to those obtained in solution state spectrum recorded in chloroform, figure 7. The IR spectrum of this compound remained unchanged with time. This indicates that this compound did not undergo decomposition to telluride and alkylhalide.

There are slight lowerings of the frequency of ν(C = O) in the infra-red spectrum compared with ν(C = O) for acetophenone (1668 cm^{-1}) (54). This may be due to the coordinates of carbonyl oxygen to the tellurium atom, in which the phenacyl group is acting as unsymmetrical bidentate (54).



The molecular weight measurements were not possible due to the low solubility of this compound in common organic solvents.

Mallaki (59) observed that the IR spectra of

$C_{16}H_{16}O_2Te$ in the solid state and in chloroform solution showed bands at 1600 and 1365 cm^{-1} corresponding to $\nu(C = O)$ were similar in both states.

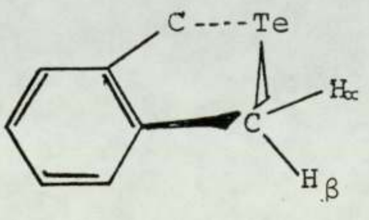
The ^{1}H NMR spectrum of each cyclic telluronium salt was recorded in a suitable solvent. There are two types of aliphatic resonances of these compounds, one is due to the alkyl group and the other due to the presence of two methylene groups. The two methylene groups in all cyclic telluronium compounds give a quartet, generally 1:3:3:1, table 3, while in 1,1-diiodo-3,4,-benzo-1-1-telluracyclopentane and 3,4-benzo-1-telluracyclopentane, a methylene singlet at $\delta = 4.75$ ppm ($J_{^{1}H\,-\,^{125}Te} = 34.67$ Hz) and $\delta = 4.65$ ppm ($J_{^{1}H\,-\,^{125}Te} = 22.85$ Hz) respectively in DMSO-d_6 was observed.

The ^{1}H NMR spectrum of 3,4-benzo-1-telluracyclopentane in $CDCl_3$ has been investigated over the temperature range $-59^{\circ}C$- + $33,7^{\circ}C$. The compound shows only one singlet resonance for the protons of methylene groups at 4.42 ppm which has satellite peaks for ^{125}Te and ^{1}H coupling ($J = 22.5$ Hz) over the entire range of temperature. Thus, either the molecule is planar or inversion about the methylene carbon atom is still fast on the NMR time scale at $-59^{\circ}C$, figure 8. The X-ray crystallography of $C_8H_8TeI_2$ (71) showed that the configuration is distorted octahedral, with I_2 in the axial positions normal to the benzo-1-telluracyclopentane ring. The nine-member hetero ring is planar in $C_8H_8TeI_2$.

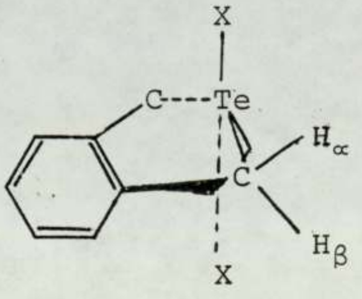
All cyclic telluronium salts produced very similar results, hence only the spectrum of $C_9H_{11}TeI$ is illustrated in figures 9 and 10.

The aliphatic region contains several peaks; the singlet resonance appearing at $\delta = 2.4$ ppm is due to the methyl group which has satellite peaks caused by coupling between ^{125}Te and ^{1}H ($J = 24.6$ Hz) and which is therefore due to the methyl group attached to the tellurium atom. There is quartet in ratio of 1:3:3:1 appearing at 4.14, 4.38, 4.88 and 5.13 ppm corresponding to the splitting of two inequivalent protons in methylene groups.

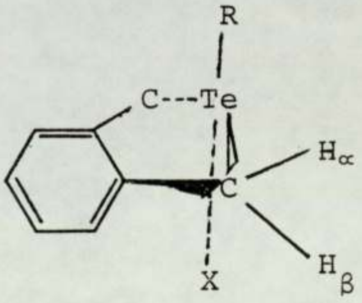
In the case of the telluronium salt, the presence of an organic group on the tellurium atom clearly removes the equivalence of the two protons within each methylene group. By contrast the fact that two extra, but identical bonds, are formed when the dihalides are prepared will retain the equivalence of the methylene protons. It is therefore to be expected, and indeed is analytically useful, that the telluronium compound gives the more complex methylene NMR spectrum.



$\alpha \equiv \beta$



$\alpha \equiv \beta$



$\alpha \not\equiv \beta$

It is obvious to conclude that the alkyl or aryl group affects the relative configurations of protons in methylene groups of the telluronium salt. Furthermore, the proton methylene resonances in deuterated telluronium salt $C_9H_8D_3TeI$ shift to higher fields compared with the methylene resonances of $C_9H_{11}TeI$, table 3, which indicates the effect of a deuterated methyl group on the chemical shifts of methylene groups, table 3.

The spectra of $C_9H_{11}TeI$ were recorded immediately after the compound had been dissolved in deuterochloroform, and the position of the methyl group remained unchanged even after more than 60 days.

Spectra of $C_9H_{11}TeI$ in DMSO were similarly recorded. The position of methyl resonances were observed to be constant with time. The methyl singlet resonance appearing at $\delta = 2.25$ ppm has satellite peaks caused by coupling between ^{125}Te and ^{1}H ($J = 24$ Hz), and there is a quartet appearing at $\delta = 4.03$, 4.30, 4.52 and 5.78 ppm. The same observation was made for all cyclic telluronium salts which indicates the stability of these compounds to the reductive elimination which had been observed for another series of telluronium salts Ph_2MeTeX (X = Cl, Br, I, NCS and PhCOO)$^{(54,55,57)}$.

1-methyl-3,4-benzo-1-telluracyclopentane tetraphenylborate showed a sharp singlet signal in DMSO-d_6 at $\delta = 2.05$ ppm a quartet at 3.86, 4.10, 4.20 and 4.46 ppm, multiplet at 6.82-7.05 ppm, while 1-phenyl-3,4-benzo-1-telluracyclopentane tetraphenylborate showed a quartet at 3.95, 4.20, 4.35 and 4.62 ppm, multiplet at 6.70-7.02 ppm and multiplet at 7.02-7.70 ppm. In both compounds the cation phenyl-proton multiplet is downfield from the anion phenyl-proton multiplet, consistent with the large deshielding effect expected for cations.

Carbon-13 NMR data for a number of cyclic telluronium salts were obtained in deuterated chloroform, DMSO and DMF, table 4. The ^{13}C NMR showed that the two carbon atoms in the methylene groups are equivalent.

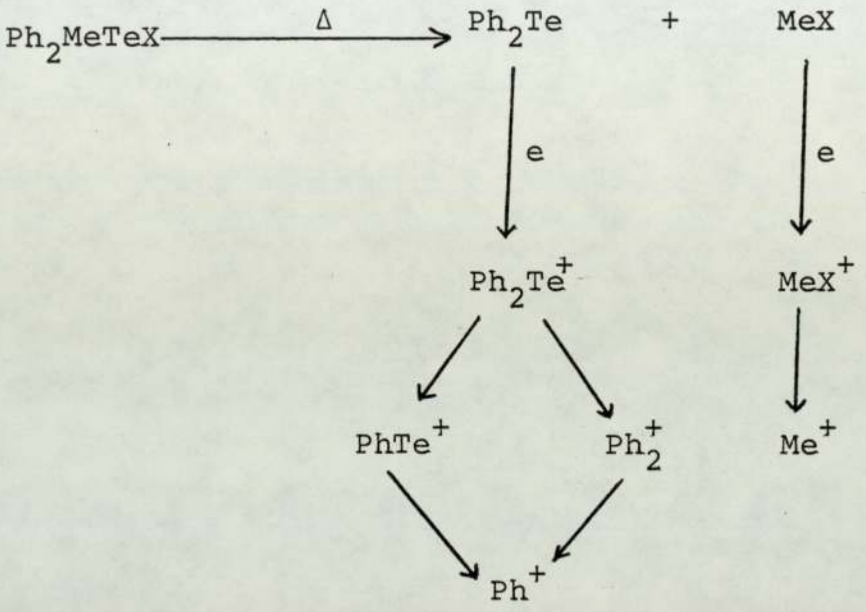
The molecular weights of 1-methyl-1-iodo-3,4-benzo-1-telluracyclopentane and 1-methyl-3,4-benzo-1-telluracyclopentane benzoate were determined in chloroform at 25°C and the values are presented in table 5, and indicate that these compounds exist as dimers.

The ^{125}Te chemical shifts for some cyclic telluronium salts have been measured, in which single signals are observed. As was mentioned before, the molecular weight data, table 5, showed that some cyclic telluronium salts are dimers in chloroform solution. The ^{125}Te NMR shows no tellurium-tellurium coupling even after 15 days in $CDCl_3$; this must mean that the two tellurium atoms within the dimer are equivalent. It may also be concluded that these compounds are symmetric dimers in solutions. The tellurium-125 chemical shifts of these compounds increase strongly with the increasing length of alykl group which means that the tellurium chemical shifts of benzo-1-telluracyclopentane are sensitive to substituent effect. The ^{125}Te chemical shift of 1-ethyl-1-iodo-3,4-benzo-1-telluracyclopentane is 708.9 ppm which is greater than the ^{125}Te chemical shift of 1-methyl-1-iodo-3,4-benzo-1-telluracyclopentane (652.2 ppm) as shown in table 6. The tellurium-125 chemical shifts are less sensitive to the nature of the anion and a correlation between anion electronegativities and tellurium chemical shifts is observed; table 6 shows that the benzoate in 1-methyl-3,4-benzo-1-telluracyclopentane benzoate induces the largest downfield shift, iodine in 1-methyl-3,4-benzo-1-telluracyclopentane the smallest shift (687.0 and 652.0 ppm respectively). The solvent effect has been studied by changing the solvent. Comparisons with information on ion-pair formation from conductivity studies in DMSO and DMF showed that these telluronium salts are 1:1 electrolytes and that there is ion pairing in these compounds. This led to the conclusion that solvent separated ion-pairs are formed in these compounds, while contact ion-pair formation seems to be relatively insignificant. A change of solvent does not affect the chemical shifts; for example, the tellurium-125 chemical shift for $C_9H_{11}TeI$ in $CDCl_3$, DMSO-d_6 and DMF-d_7 are 652.0, 651.2 ppm and 652.2 ppm respectively and does not change with different solvents.

The thermal decomposition of triorganotellurium halides is well known(40) and triphenyltelluronium pseudohalides have been shown to decompose in a similar fashion on heating(41).

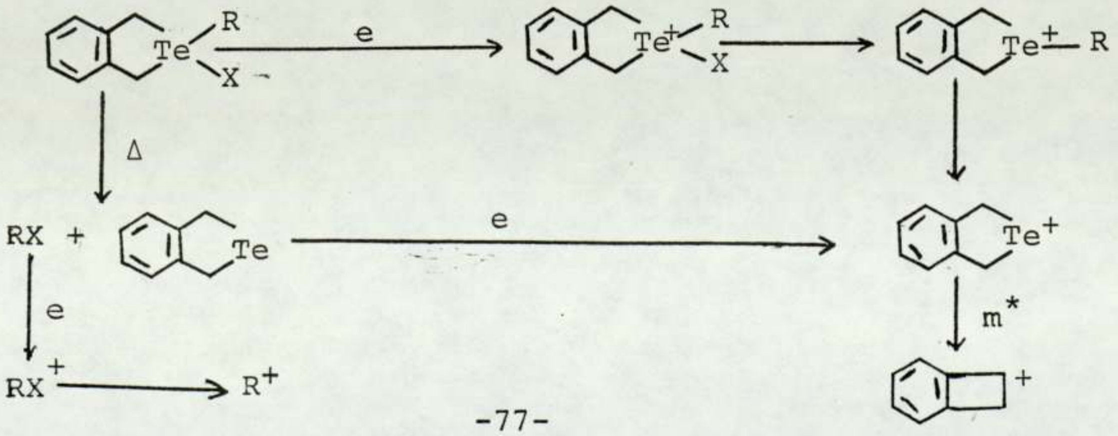
$$R_3Te^+X^- \xrightarrow{\text{heat}} R_2Te + RX$$

Mass spectroscopy has previously been used for the characterisation of a series of $Ph_2MeTe^+X^-$ (X = Cl, Br, I, NO_3, NCS and PhCOO)(54,55,57). The highest observed mass for this series was diphenyltelluride. In all cases the decomposition involving thermolysis of the telluronium salts to give diphenyltelluride and MeX was observed. The fragmentation patterns are represented as follows:



In principle, the fragmentations in the spectra of cyclic telluronium salts should follow the expected thermolysis of triorganotelluronium salts. The mass spectra of these cyclic telluronium salts in general closely resemble those of diphenylmethyltelluronium salts tables 7-15.

The fragmentation patterns of these cyclic telluronium salts may be represented by following scheme:



All these ions are indicated in the mass spectra of telluronium salts, tables 7-15.

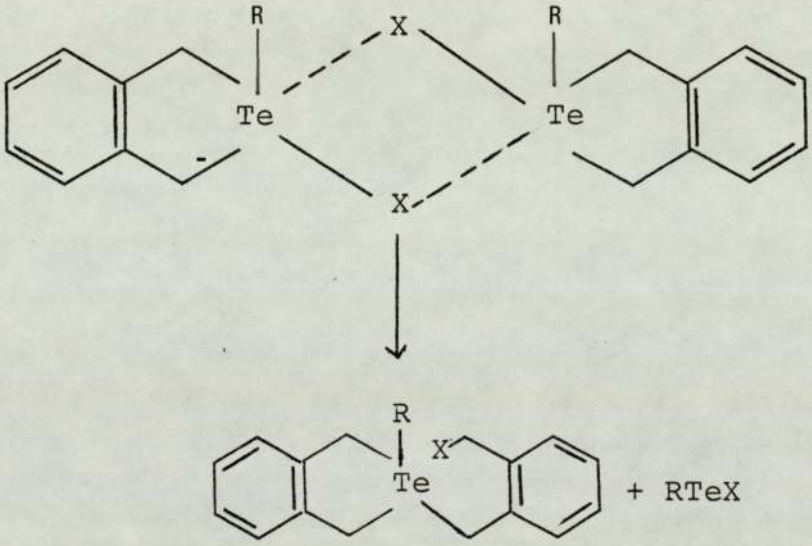
Unfortunately there was no evidence to support all steps in the scheme from the meta-stable ions. However, there is evidence for the step of eliminating tellurium from $C_8H_8Te^{+}$ to form $C_8H_8^{+}$ from the metastable ion at m/e = 46.2 for all the cyclic telluronium salts.

Cuthbertson(64) has reported that the pyrolysis of 3,4-benzo-1-telluracyclopentane was carried out at 500°C in a low pressure stream of He gas (0.4-0.5 mmHg) to give benzocyclobutene. It is obvious that the observation of a benzocyclobutene cation in the mass spectra of cyclic telluronium salts and in the pyrolysis of C_8H_8Te suggests the ready elimination of a tellurium atom from the cyclic telluride.

The most important features of the mass spectra, (as can be seen in tables 7-15) of cyclic telluronium salts are that there were also unexpected organo and organotellurium ions which means that there are several possible routes for the fragmentation of cyclic telluronium salts.

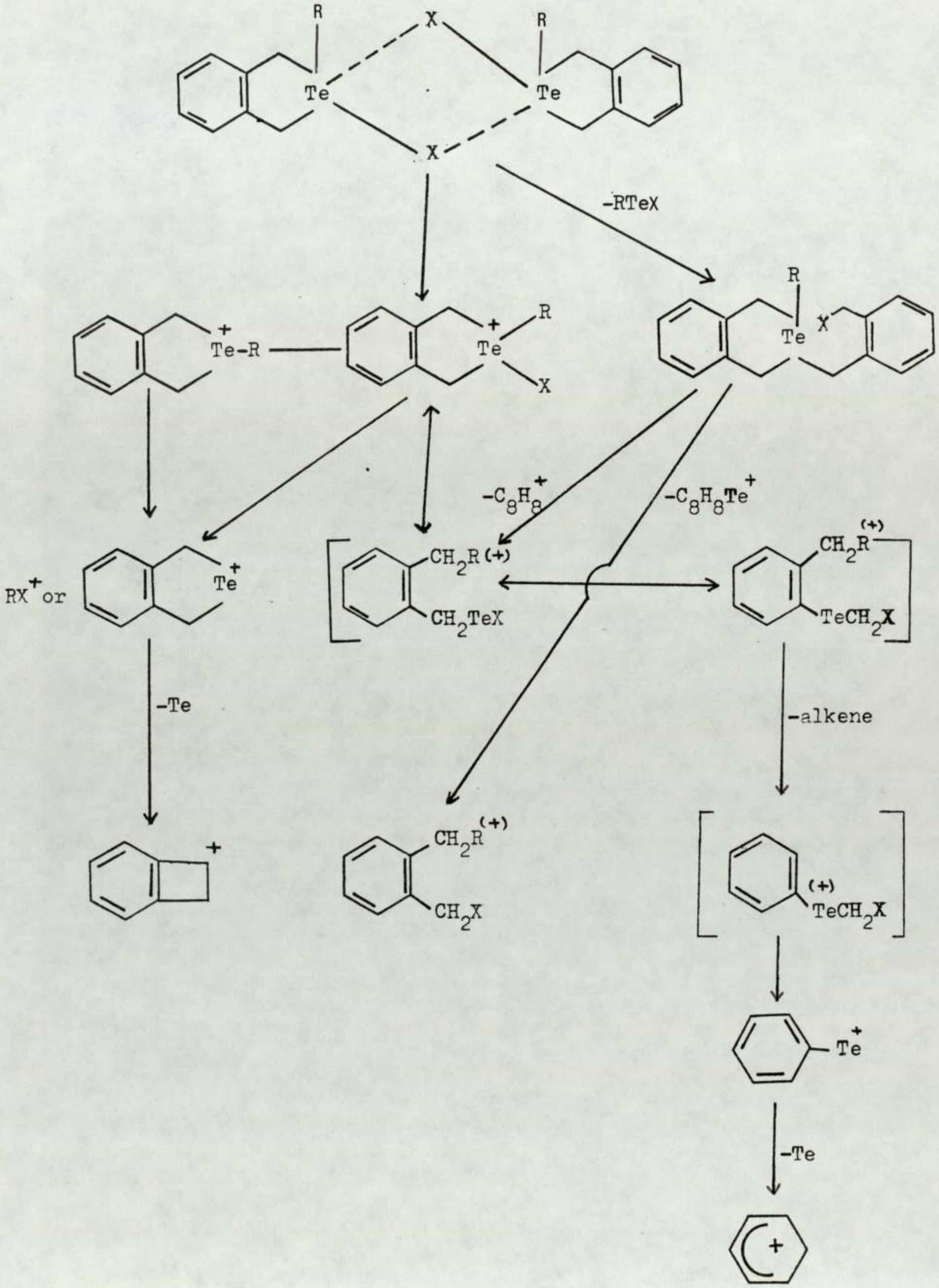
The mass spectra of $C_8H_8RTe^{+}X^{-}$ (where R = allyl, and phenacyl; X = Br) showed ions appearing at higher mass charge ratios than that corresponding to the monomer telluronium salt ion. Thus the spectra of these two cyclic telluronium salts (table 10 and 12) clearly indicate that the telluronium salts are associated and the original molecule must be at least a dimer. The molecular weight data, table 6, showed that some cyclic telluronium salts exist as dimers in chloroform solution.

The lost fragment from a supposed dimer (in allyl and phenacyl derivatives) is consistent with the molecular weight of allyltellurium bromide and phenacyltellurium bromide. The peaks which are observed at 460 and 538 correspond to $C_{19}H_{13}TeBr^+$ and $C_{24}H_{23}OTeBr^+$ respectively, (table 10 and 12). This may be illustrated by the following scheme:

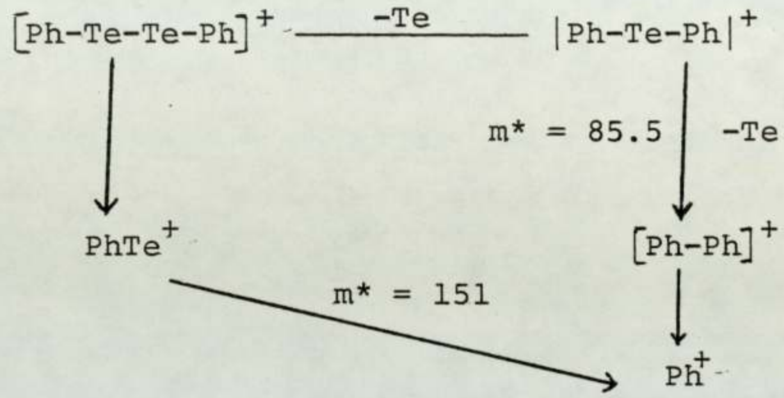


Another very interesting feature of the mass spectra of cyclic telluronium salts is the formation of the unexpected $PhTe^+$, Ph^+ and ∝-benzo-∝-bromo-o-xylene cations, tables 7-15. The $PhTe^+$ and Ph^+ ions are common to all mass spectra of cyclic telluronium salts while the identification of the ∝-benzo-∝-bromo-o-xylene cation was confirmed by the determination of the accurate molecular mass with an error of less than 0.5 ppm.

A possible scheme for the fragmentation of the telluronium salts is shown below. It is necessary to postulate some species which are not actually detected e.g. $PhTe^+CH_2X$.


R
X
R
Te
Te
X
-RTeX
R
Te-R
Te
R
X
R
Te
X
$-C_8H_8^+$
$-C_8H_8Te^+$
$CH_2R^{(+)}$
CH_2TeX
$CH_2R^{(+)}$
$TeCH_2X$
RX^+ or
Te
-Te
-alkene
$CH_2R^{(+)}$
CH_2X
$TeCH_2X$
Te
-Te

The mass spectrum of $C_{38}H_{33}BTe$ indicated the formation of diphenylditelluride which was very interesting, table 13. Diphenylditelluride showed the expected fragmentation of the ditellurides.



Some stages are supported by the observation of metastable ions as indicated.

The most important characteristic ions in mass spectra of $C_{38}H_{33}BTe$ and $C_{33}H_{31}BTe$ (table 13 and 14) are $C_{10}H_{11}Te^+$ and $C_{20}H_{18}Te^+$ respectively which indicate the formation of tetraorganotellurium compounds. These ions are presumably formed via further phenylation reactions in the source of the spectrometer which afford a tetraorganotellurium compound.

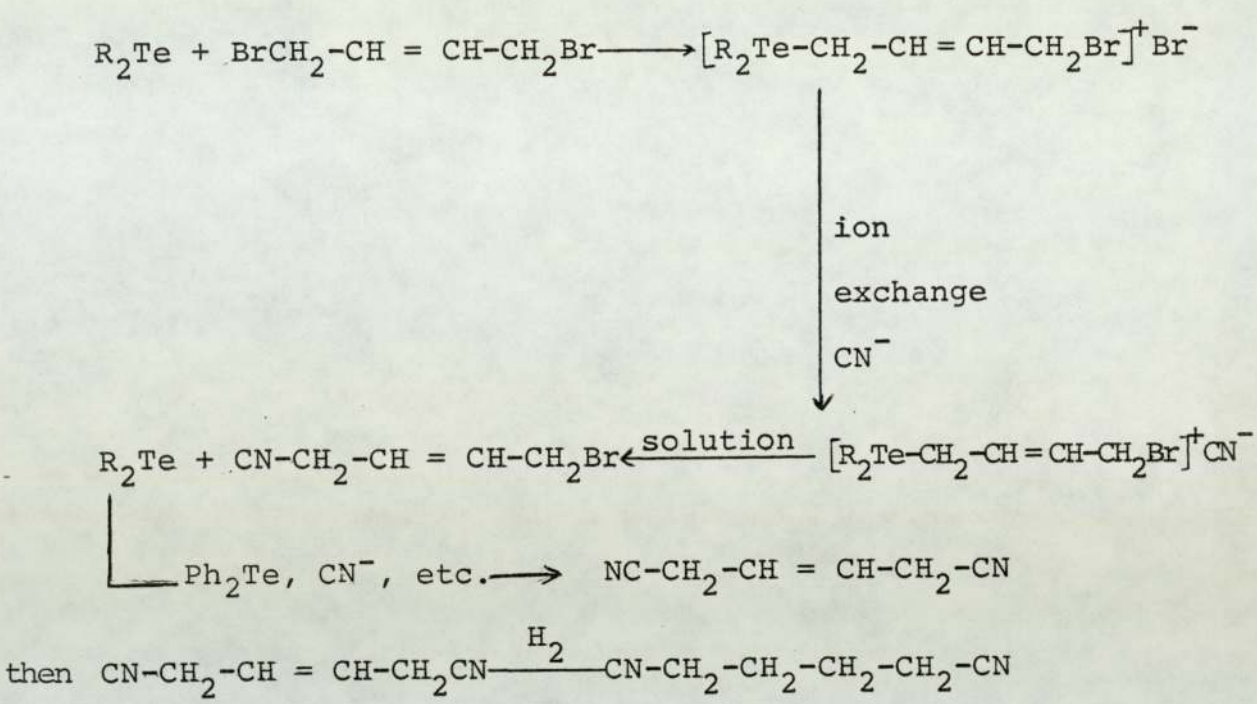
The question arises what would happen if more forcing conditions are used in the reaction between $C_8H_8TeI_2$ and $NaBPh_4$ and is it possible to form a tetraorganotellurium compound under these conditions? Details will be discussed in chapter six.

The following points can be drawn from the analysis of the mass spectral data in tables 7-15:

1. Molecular ions are almost always observed.
2. The original molecules of cyclic telluronium salts must be polymers or at least dimers because there were ions appearing at higher m/e than the corresponding monomer molecules.
3. The formation of phenyl, phenyltelluride and diphenylditelluride by mass spectroscopy is very interesting.
4. In general the decomposition of cyclic telluronium salts involved thermolysis in a similar fashion as the thermal decomposition of $R_3Te^+X^-$.
5. The association of telluronium salts is now firmly established and supported by mass spectral and molecular weight data.

Given that aryltellurides are very easily transformed to telluronium salts which are decomposed in chloroform solution to aryltelluride and alkylhalide, now leads us to study the reaction of diaryltelluride with 1,4-dibromo-2-butene in order to form a telluronium salt. The cyanation of this telluronium salt may take place by ion exchange to obtain after repetition 1,4-dicyano-2-butene which may be used as an intermediate for the preparation of nylon after hydrogenation of the double bond in this compound.

The general hypothesis can be summarised by the following equations:



$$R_2Te + BrCH_2\text{-}CH = CH\text{-}CH_2Br \longrightarrow [R_2Te\text{-}CH_2\text{-}CH = CH\text{-}CH_2Br]^+Br^-$$

$$\Big\downarrow \text{ion exchange } CN^-$$

$$R_2Te + CN\text{-}CH_2\text{-}CH = CH\text{-}CH_2Br \xleftarrow{\text{solution}} [R_2Te\text{-}CH_2\text{-}CH = CH\text{-}CH_2Br]^+CN^-$$

$$\xrightarrow{Ph_2Te,\ CN^-,\ etc.} NC\text{-}CH_2\text{-}CH = CH\text{-}CH_2\text{-}CN$$

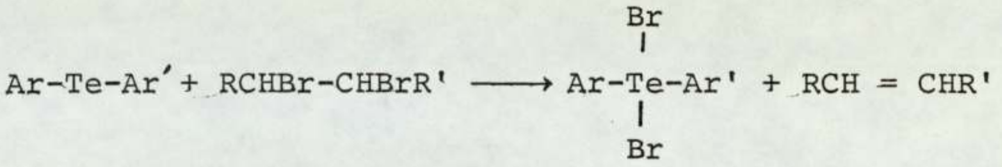
$$\text{then } CN\text{-}CH_2\text{-}CH = CH\text{-}CH_2CN \xrightarrow{H_2} CN\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CN$$

During the course of this study Marinelli(72) utilized the same idea for cynation of arylhalide with NaCN in the presence of $Ni[P(C_6H_5)_3]_3$.

When refluxing a solution of diphenyltelluride or di(p-ethoxyphenyl)telluride with 1,4-dibromo-2-butene in ethanol for one hour the corresponding diphenyltellurium dibromide or bis(p-ethoxyphenyl)tellurium dibromide was obtained in very good yield.

McWhinnie et. al.(57) gave positive evidence for radical pathways in oxidative addition of alkylhalides to R_2Te and they showed that the products depended on the stability of alkyl radicals; thus 1,4-dibromo-2-butene which generates an allylic radical gave entirely Ph_2TeBr_2.

Petragnani(73) has studied the reaction of diphenyltelluride with ethylbromide to obtain ethenes:



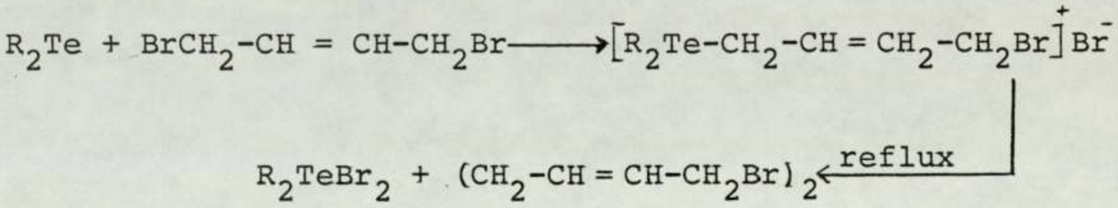
$$\text{Ar-Te-Ar}' + \text{RCHBr-CHBrR}' \longrightarrow \text{Ar-}\underset{\text{Br}}{\overset{\text{Br}}{\text{Te}}}\text{-Ar}' + \text{RCH} = \text{CHR}'$$

and he found that a solution of diphenyltelluride in allylbromide was heated at 180°C in a sealed tube for 3 hours gave rise to a diphenyltellurium dibromide and probably diallyl:

$$Ph_2Te + 2CH_2{=}CH\text{-}CH_2Br \longrightarrow Ph_2TeBr_2 + (CH_2 = CH\text{-}CH_2)_2$$

In this connection it is interesting to point out that the reaction of allylbromide and 1,4-dibromo-2-butene and C_8H_8Te, when performed at room temperature, gives rise to the corresponding cyclic telluronium salt, as confirmed by X-ray crystallography (see below).

It seems likely, therefore, in reaction of diaryltelluride and 1,4-dibromo-2-butene, that a telluronium species was initially formed and upon refluxing, diaryltellurium dibromide and possibly butadiene or $(\text{-}CH_2\text{-}CH = CH\text{-}CH_2Br)_2$ were formed.



$$\begin{tikzcd} R_2Te + BrCH_2\text{-}CH = CH\text{-}CH_2Br \arrow[r] & {[R_2\overset{+}{T}e\text{-}CH_2\text{-}CH = CH_2\text{-}CH_2Br]Br^-} \arrow[d] \\ & R_2TeBr_2 + (CH_2\text{-}CH = CH\text{-}CH_2Br)_2 \arrow[u, phantom] \end{tikzcd}$$

$$\xleftarrow{\text{reflux}}$$

The reaction of benzo-1-telluracyclopentane with allyl bromide afforded a telluronium salt at room temperature which was confirmed by X-ray crystallography.

X-ray crystallography was provided by Dr A.T. Hamor (University of Birmingham) and is now discussed.

The Crystal Structure of 1-Allyl-1-Bromo-3,4-Benzo-1-Telluracyclopentane

Structural studies on a variety of organotellurium compounds have revealed inter-molecular bonding effects of various types and strength. In organotellurium diiodides(74-81), interactions of the type Te....I, I....I have been shown to be very pronounced whereas in corresponding bromides either a very weak effect(82) or complete absence(83) of such effect has been reported. In dimethyl tellurium dichloride(84), however, a fairly strong interaction between a tellurium atom of one molecule and one chlorine on each of two neighbouring molecules has been described.

It is well established that tellurium (IV) in its many and varied compounds possesses a four-, five-, or six-fold configuration. The triorganotelluronium salts, R_3TeX, are no exception, and the recent structural studies on these compounds show tellurium to have a five- or sixfold configuration.

A relatively small number of telluronium salt structures have been reported. The telluronium salts have relatively complex structures due to the weak interaction between the tellurium atom and the anion. These interactions determine the structural features of the compounds and the interactions are sensitive to the nature of both the cation and anion. In triphenyltelluronium pseudohalides the cation-anion interaction is sufficient to impose oligomeric structures of some complexity and fascination, but in trimethyltelluronium tetraphenylborate(51), the structural determinations show an ionic compound and the absence of the secondary interactions, which had previously been found in the structural determination of other telluronium salts(42,43,45,48).

A preliminary report of the structural study of a stable triorganotelluronium salt relevant to this study is given in this work.

The structural data were provided by Dr T. A. Hamor and R. Jones (University of Birmingham), with whom we are collaborating.

The structure of 1-allyl-1-bromo-3,4-benzo-1-telluracyclopentane, $C_{11}H_{13}TeBr$, has been determined by single-crystal X-ray diffraction methods. The salt crystallizes in the space group Pbac of the Orthorhombic system.

Final cell dimensions and intensities were measured with a Eraf Nonius CAD4 computer-controlled 4 circle diffractometer.

Some 1262 unique reflections with $I > 2.5\ \delta\ (I)$ were considered to be observed and were used in the analysis.

The structure was solved from a three-dimensional Patterson syntheses from which the position of the tellurium atom was found. All other atoms were found from several difference syntheses. Upon the refinement, it was found that the geometry of atom of C9, C10 and C11 became unacceptable. Computation of difference synthesis showed that there was disorder in the side chain. Positions of the disordered atoms were found from this difference synthesis. In the final stage of refinement the disordered allyl group was subject to constrained refinement with slack constraints, also the hydrogen atoms in the benzo-1-telluracyclopentane moity atoms Te, C1-C9 were placed. The final R value was 5.17 %.

The benzo-1-telluracyclopentane cations were geometrically placed and atoms Te C1-C9 were refined with anisotranic term factors whilst C10, C10', C11, C11' were given isotronic term factors. The final R value was 5.37 %.

Bond lengths and angles are given in tables 16, 17 and 18 respectively.

TABLE (16a)

Distances about tellurium in $C_{11}H_{13}TeBr$, Å.

esd x 10^3 in parentheses

Te-C1	2.165 (15)
Te-C8	2.145 (15)
Te-C9	2.180 (16)
C1-C2	1.466 (18)
C2-C3	1.390 (20)
C3-C4	1.350 (20)
C4-C5	1.366 (24)
C5-C6	1.357 (11)
C6-C7	1.390 (23)
C7-C2	1.356 (22)
C7-C8	1.495 (21)
C9-C10	1.485 (26)
C10-C11	1.366 (35)
C9-C10'	1.520 (29)
C10'-C11'	1.311 (35)

TABLE (16b)

Te-Br distances, Å.

Te-Br (A)	3.326
Te-Br (B)	3.365
Te-Br (C)	3.368

Crystal data:

$C_{11}H_{13}TeBr$ M_w = 352.73   Orthorhombic Pbca.

a = 9.617 (12)   b = 25.586 (7)   c = 9.680 (3)

u = 2387.99 $Å^3$ z = 8 D_c = 1.962 g cm^{-3}

F(000) = 1327.97; MoKα λ = 0.71069 Å ; μ(Mo-Kα) = 55.90 cm^{-1}

TABLE (17)

Bond Angles in $C_{11}H_{13}TeBr$, deg.

C1-Te-C8	83.1 (6)
C1-Te-C9	95.7 (6)
C8-Te-C9	95.3 (8)
Te-C1-C2	107.4 (1)
Te-C8-C7	106.7 (1)
C1-C2-C3	120.0 (1.4)
C1-C2-C7	119.4 (1.4)
C3-C2-C7	120.6 (1.4)
C2-C3-C4	120.6 (1.6)
C3-C4-C5	120.1 (1.8)
C4-C5-C6	120.5 (1.8)
C5-C6-C7	119.2 (1.7)
C6-C7-C2	119.6 (1.5)
C6-C7-C8	120.4 (1.5)
C2-C7-C8	120.0 (1.4)
Te-C9-C10	119.1 (1.4)
Te-C9-C10	115.3 (1.6)
C9-C10-C11	125.5 (3.0)
C9-C10'-C11'	123.6 (3.3)

TABLE (18)

Angles about tellurium atom in degrees.

Br (A)-Te-Br (B)	118.56
Br (A)-Te-Br (C)	99.67
Br (A)-Te-C7	98.64
Br (A)-Te-Cl	78.34
Br (A)-Te-C8	162.65
Br (A)-Te-Br (C)	103.65
Br (B)-Te-C2	78.19
Br (B)-Te-Cl	160.85
Br (B)-Te-C8	78.45
Br (C)-Te-Cl	80.63
Br (C)-Te-C7	179.10
Br (C)-Te-C8	80.63
Cl-Te-C7	95.70
Cl-Te-C8	83.10
C8-Te-C7	95.30

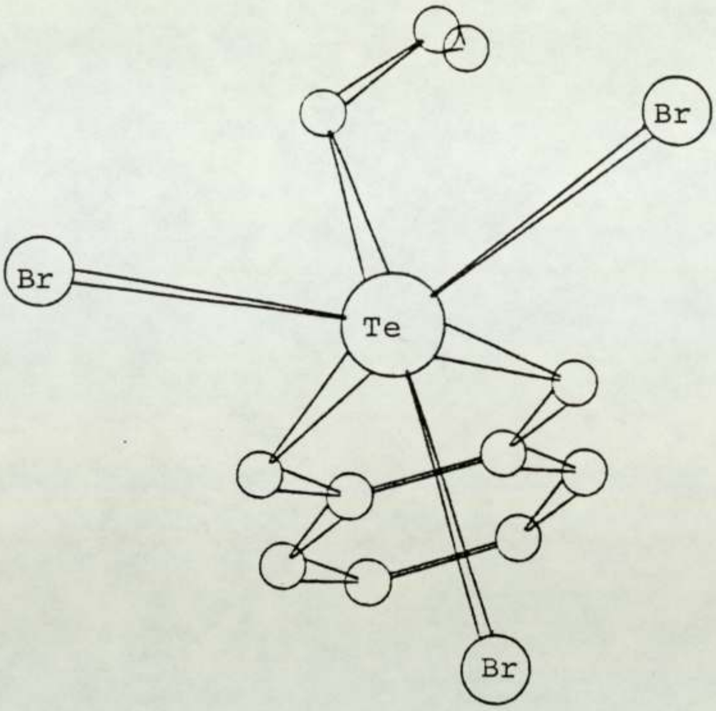


Figure 11 The molecule of $C_{11}H_{13}TeBr$

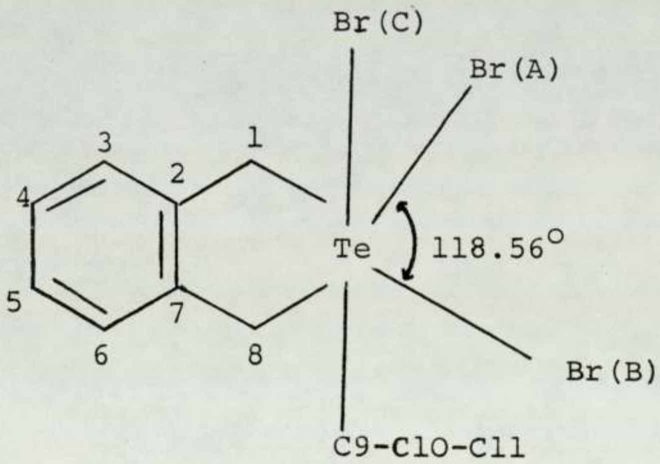


Figure 12 Atom labelling scheme

The crystal structure of 1-allyl-1-bromo-3,4-benzo-1-telluracyclopentane showed that the tellurium atom in this compound achieves an octahedral environment by the coordination of two additional bromine atoms from two different molecules. The molecule is shown in figure 11. Bond distances and angles within the molecule are listed in tables 16-18.

The allyl group, $-CH_2-CH = CH_2$, and Br (C) atom are in axial positions normal to the benzo-1-telluracyclopentane ring. Carbon atoms 1 and 8 of the ring system and two bromine atoms, Br (A) and Br (B), from two neighbouring molecules occupy the equatorial positions(85).

The Te-C distances of 2.145 (15) Å and 2.165 (15) Å are identical to those i the 1-thia-4-telluracyclohexane-4,4-dibromide(82) and in 1,1-diiodo-3,4-benzo-1-telluracyclopentane(71). The angle between these bonds is 83.1 (6)°, which is greater than the corresponding angles in dibenzotellurophene (81.7 (2)°)(86) and dibenzotellurophene diiodide (81.8 (2)°)(78), and smaller than the corresponding angles in 1,1-diiodo-3,4-benzo-1-telluracyclopentane (86.0 (5)°)(71) and 1-thia-4-telluracyclohexane-4,4-dibromide (99.4 (6)°)(82) which is presumably due to the differences in C-C bond lengths.

The Te-C-C angles, 106.7 (1.0) and 107.4 (1)°, are similar to those in $C_8H_8TeI_2$ (106.7 an 106.9° respectively) and are slightly smaller than the corresponding angles in $C_8H_8OTeI_2$(76), $C_{12}H_8TeI_2$(78) and $C_{12}H_8Te$(86).

The intermolecular Te......Br distances of 3.326, 3.365 and 3.368 Å are appreciably shorter than the sum of the van Der Waal's radii (Pauling) for these atoms which is equal to 4.15 Å.

The Te......Br distances have a mean value of 3.350 Å which is significantly longer than the value of 2.50 Å obtained from single bond radii(87). A survey of the non ionic dibromide, R_2TeBr_2 (82,83), and tribromide (88,89) shows these compounds to be essentially monomeric with weak but significant Te....Br interactions down to 3.591 Å (82). By comparison, the Te-Br distances in $C_{11}H_{13}TeBr$ are significantly less than the Van der Waal's distance of 4.15 Å and they are longer than the sum of the normal, single-bond radii (2.51 Å for Te-Br)(87) which indicates an ionic interaction between the tellurium atom and bromine atoms.

The six C-C distances in the benzene portion of the nine-membered ring have a mean value of 1.368 Å which is slightly smaller than in the corresponding diiodide (1.383 Å)(71). The two nonaromatic C-C distances are slightly smaller than in the corresponding diiodide (1.507 and 1.513 Å respectively). The mean C-C-C angle for all C-C-C angles in the nine-membered ring is 120.04°, which is almost equal to the mean C-C-C angles in $C_8H_8TeI_2$ (120.0 (4)°)(71), the smallest angle is 119.6° (C5-C6-C7) and the largest, 120.6° (C3-C2-C7 and C2-C3-C4). The Br-Te-Br angles are 118.56, 99.67 and 103.65 respectively, table 18.

The octahedral configuration about the tellurium atom is completed by the formation of secondary intermolecular bonds with a bromine atom in each of two neighbouring molecules. The secondary bonds form angles of 162.65 and 160.85° with the carbon atoms opposite them (i.e. C1 and C8).

Bromine-tellurium-carbon angles range from 78.34 to 80.63.

The allyl group which is normal to benzo-1-telluracyclopentane ring shows the Te-C distance equals 2.18 (15) Å which is greater than Te-C1 and Te-C8 distances. The C9-C10 distances are similar to single C-C bonds. The C10-C11 distances have a mean value of 1.338 Å which is identical to a simple double bond (1.337 Å).

CHAPTER IV

4.(i) INTRODUCTION

Tellurium has two isotopes with a nuclear spin $I = \frac{1}{2}$ which are available for investigation i.e. ^{123}Te and ^{125}Te. There is less interest in ^{123}Te NMR spectroscopy. This arises from its lower natural abundance 0.87% compared with 7% for ^{125}Te and its inherent low sensitivity. As a consequence, it has receptivity of 0.88 relative to ^{13}C while ^{125}Te has a receptivity of 12.5.

The first indirect observation of tellurium NMR was by McFarlane(90,91) who determined tellurium-125 chemical shifts by the heteronuclear double resonance technique and found them to parallel closely the ^{77}Se shifts in analogous compounds(91). The tellurium shielding decreased as the electronegativity of substituents increased(91).

^{125}Te- and ^{1}H- chemical shifts and ^{J}Te-H coupling constants were reported. The Te-H coupling constants have values between 24 and 36 Hz for a range of organotellurium compounds(92). The direct observation of the tellurium NMR resonance allowed better understanding of some chemical properties of this element(65, 92-99). The presence of two active isotopes ^{123}Te and ^{125}Te allows measurements of the tellurium-tellurium coupling constant even in cases in which the tellurium atoms are chemically equivalent. This possibility has been used to determine the structure in oleum solutions of different tellurium polyatomic cations(95,96). High resolution ^{123}Te

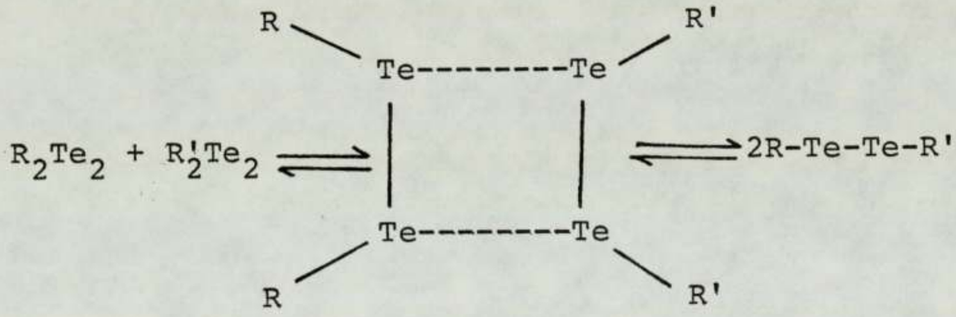
and ^{125}Te Fourier Transform NMR spectroscopy has been used to identify all the series $(Te_nSe_{4-n})^{2+}$ (n = 1-4) in Te-Se oleum system(96) and also to characterize the previously known Te^{4+}, Te_4^{2+} and $(Te_2Se_4)^{2+}$ cations(95,96).

It has been observed that the tellurium (II) organometallic species are in slow exchange on NMR time by using ^{125}Te, ^{13}C and ^1H nuclei(97). The ^{125}Te chemical shifts, which are dependent to a certain extent on solvent, concentration and temperature, and the ^{125}Te-'H coupling constants for the heterocyclic 1,3-dihydro-benzo[c]tellurophene and its dihalooxidation products have been observed by ^{125}Te NMR when saturated DMF solutions of the dichloride and of the dibromide are mixed. The halogen exchange rate is slow on the NMR time scale(65). Recently, Praefck(98) determined tellurium-125 NMR resonances of nine cyclic and acyclic phenyltellurium compounds by direct method.

Farrar(7) claimed that diorganylditellurides are dissociated completely into radicals in organic solvents, and supported his claim with molecular weight values, obtained cryoscopically in camphor, but Thavornyutikarn(15) examined the ESR spectra of solutions of diarylditellurides under similar conditions, and observed no signal corresponding to $R\dot{T}e$ species and he also found that the visible solution spectrum and diffuse reflectance spectrum of diphenylditelluride were very similar, indicating that the diphenylditelluride is largely undissociated in solution.

Thavornyutikarn(15) reported that a mixture of two diarylditellurides could only be separated into the original components, after dissolving in benzene, by the use of column chromatography, and interpreted this as evidence that no radical species $RTe^{\cdot}$ were present. Furthermore, there is no evidence from ^{125}Te Mössbauer spectrosocpy that the Te-Te bond is particularly weak in these compounds(30).

More recent work(16) demonstrated an exchange reaction between ditellurides R_2Te_2 and R'_2Te_2 and provided the first evidence for the existence of unsymmetrical diarylditellurides, R-Te-Te-R', using mass and proton NMR spectroscopy. The possible mechanism of redistribution of R groups might go via a dimer intermediate rather than via radical mechanism.



The following work was designed to study the diarylditellurides in solution in more detail. It shows that tellurium NMR is a powerful tool for the investigation of such a system and furthermore, has found that dioxygen naturally dissovled in solvents gives radical species and leads to the formation of new oxotellurium compounds.

4.(ii) EXPERIMENTAL

Preparation of Diarylditellurides

The diarylditellurides used in this study were synthesised by literature methods:

Diphenylditelluride (7)

Phenyltellurium trichloride (0.01 mole) was reduced by 0.08 mole of $Na_2S.9H_2O$. The mixture was heated with stirring in a boiling water bath for 30 min. The resulting mixture was diluted with ice-water, and the precipitate of diphenylditelluride was filtered off, washed with water, dried over P_4O_{10} in a vacuum desiccator, and recrystallized from petroleum ether or benzene. The yield of orange red crystals, which melted at 54-55°C (lit. 53-54°C (67a) and 66-67°C (7,100)) was quantitative.

Bis(p-methylphenyl)ditelluride (101)

p-Methylphenyltellurium trichloride (0.01 mole) was suspended in water (20ml). Potassium metabisulphite (0.05 mole) in water (10 ml) was then added slowly to the solution at 0°C with continuous stirring, to give orange needle crystals after recrystallization from petroleum ether (30/40°C). The ditelluride melted at 50-52°C (Lit. 52.5°C (7), 51-52°C (101)). The yield was quantitative.

Bis(p-ethoxyphenyl)ditelluride (10)

p-Ethoxyphenyltellurium trichloride (0.01 mole) was reduced by potassium metabisulphite (0.05 mole). The golden crystalline ditelluride was obtained in quantitative yield, and had a melting point between 102-104°C (Lit. 107-108°C (10); 104-106°C (101)).

Bis(p-Chlorophenyl)ditelluride (102)

A mixture of p-chlorophenylmercuric chloride (which was prepared according to the literature (103)) and tellurium tetrachloride was refluxed for 4 hours in dry dioxane. On cooling the colourless plates of the complex compound of mercuric chloride with dioxane were filtered off, and dioxane was vacuum-distilled from the filtrate. The residue crystallized from a large volume of benzene to remove traces of mercuric chloride. The material was then recrystallized from a mixture of benzene/petroluem ether to obtain a white substance which melted at 224-226°C (lit.(102) 225°C).

p-Chlorophenyltellurium trichloride was reduced by sodium sulphide. The orange red crystals of bis(p-chlorophenyl)ditelluride were obtained with a melting point of 115°C (Lit.(102) 114°C).

Attempts to prepare bis (2-nitrophenyl)ditelluride by the reaction of a Grignard reagent o-$N_2OC_6H_4MgBr$ with tellurium powder in the presence of oxygen (104) and also from the reaction of o-nitrophenylmercuric chloride with tellurium tetrachloride in dry dioxane were not successful. During the course of this work, Cava (5), prepared this compound.

Investigation for free radical of diarylditellurides in solution and solid

i) Visible irradiation of a solution of bis(p-ethoxyphenyl)ditelluride, t-butylbromide and phenyl-t-butylnitrone(PBN), $C_6H_5CH = \overset{O}{\overset{\uparrow}{N}}-C(CH_3)_3$, in an equi-molar ratio in benzene at room temperature, was carried out overnight in the presence of air; no signal for free radicals was observed. After the addition of ethanol to the solution and irradiation overnight, a white precipitate formed and the solution gave positive evidence for free radicals.

A solution of bis(p-ethoxyphenyl)ditelluride, t-butylbromide, and spin trap (PBN) in benzene in the dark under dry nitrogen and gave no free radical signal, even after the addition of ethanol and under the same conditions there was no free radical observed.

ii) Spin trap (PBN) was added immediately to the boiling bis(p-ethoxyphenyl)ditelluride in benzene and then cooled at room temperature. No free radical could be detected.

iii) Solid diarylditelluride, $(p\text{-}RC_6H_4)_2Te_2$, where $R = H, CH_3, Cl, C_2H_5O$, did not give any free radical signal from fresh solid specimens or from those which had been stored for about two months.

iv) Solid diphenylditelluride gave free radical signal when stored for several months and white spots formed.

Diarylditellurides In Benzene Solution

Diphenylditelluride in benzene gives a white precipitate formed after three days in daylight. A similar precipitate was formed for solutions of bis(p-methylphenyl), bis(p-chlorophenyl) and bis(p-ethoxyphenyl)ditelluride in benzene. It was noted that when the solutions were put aside the colour became less intense until a pale yellow solution in contact with a white solid remained. Elemental analysis of the white solid suggests an empirical formula "$(RTeO)_2O$" (R = aryl). Infra-red analysis shows strong band centred on 550 cm^{-1} which is very characteristic of ν(Te-O).

Visible Spectra of Diarylditellurides

Diarylditellurides were dissolved in benzene or in chloroform of 10^{-3}M concentration. Different concentration ranges between 0.01-0.05M of bis(p-ethoxyphenyl)ditelluride in benzene and in chloroform were reported.

Molecular Weights Of Ditellurides

The molecular weights of diarylditellurides were measured by vapour pressure osmometry in benzene at 45°C and chloroform at 25°C, table 1.

Raman Spectra of Diarylditellurides

The Raman spectra in range of 300-26 cm^{-1} were recorded on the Coderg SR100 Raman Spectrometer at the University of Leicester, using 6471A°Kr laser excitation.

All the samples were recorded in the crystalline solid state and in deoxygenated benzene, and are presented in table 3 and figure 3.

^{13}C NMR Spectra of Ditelluride Mixtures

To study the exchange reaction, the ^{13}C NMR spectra of the two following mixtures have been examined:

i) $(p\text{-}ClC_6H_6)_2Te_2 + (p\text{-}EtOC_6H_4)_2Te_2$

ii) $(p\text{-}CH_3C_6H_4)_2Te_2 + (p\text{-}EtOC_6H_4)_2Te_2$

The ^{13}C NMR chemical shifts of these two equi-molar mixtures show no differences from the individual pure compounds and the spectra are the sum of the contributions from each component. Table 4 presents some ^{13}C NMR parameters for pure diarylditellurides in $CDCl_3$.

^{125}Te NMR Spectra of Ditelluride Mixtures

The following mixtures have been studied:

i) $(p\text{-}ClC_6H_4)_2Te_2 + (p\text{-}EtOC_6H_4)_2Te_2$

ii) $(p\text{-}CH_3C_6H_4)_2Te_2 + (p\text{-}EtOC_6H_4)_2Te_2$

iii) $(p\text{-}CH_3C_6H_4)_2Te_2 + (p\text{-}ClC_6H_4)_2Te_2$

When equi-molar mixtures are prepared in $CDCl_3$ without special care (e.g. no removal of dioxygen from solvent) and examined in a conventional 10 mm tube four lines are observed, the chemical shifts and intensities of lines which are presented in table 5. The labelling of the lines is from low field to high field and typical spectra are represented in figure 4.

The solvent effect has been studied both by changing the solvent and by investigating the dilution effect with mixtures (i) and (ii) in C_6D_6 and $CDCl_3$.

Four lines are observed which are assigned to the two symmetrical species and the other to the unsymmetrical one. The $^{125}Te\underline{\quad}^{125}Te$ spin-spin coupling constant is observed and gives an AB case which results from the unsymmetrical species. The coupling constants are solvent and concentration dependent and allow the assignment of different lines to different species in mixtures (i) and (ii);

Mixture (i)

Line A, $(p\text{-}EtOC_6H_4)Te$–; Line B, $(p\text{-}EtOC_6H_4)_2Te_2$;

Line C, $(p\text{-}ClC_6H_4)_2Te_2$; Line D, $(p\text{-}ClC_6H_4)Te$–.

Mixture (ii)

Line A, $(p\text{-}EtOC_6H_4)_2Te_2$; Line B, $(p\text{-}EtOC_6H_4)Te$–;

Line C, $(p\text{-}CH_3C_6H_4)Te$–; Line D, $(p\text{-}CH_3C_6H_4)_2Te_2$.

In mixture (iii), the assignments followed from the data for (i) and (ii);

Mixture (iii)

Line A, $(p\text{-}ClC_6H_4)_2Te_2$; Line B, $(p.ClC_6H_4)Te$–;

Line C, $(p.CH_3C_6H_4)Te$–; Line D, $(p.CH_3C_6H_4)_2Te_2$.

In the latter case the resonance of the symmetrical species are very close to those of pure compounds in the same solvent.

4.(iii) RESULTS

The visible spectra for diarylditellurides in benzene and chloroform are shown in figure 1. The absorption maxima are the same in both solvents.

The molecular weights data for diarylditellurides are listed in table 1.

Elemental analysis of $(RTeO)_2O$ is represented in table 2. The ESR spectrum for $(p\text{-}EtOC_6H_4)_2Te_2$ is represented in figure 2.

The Raman data below 300 cm^{-1} of diphenylditelluride, bis(p-ethoxyphenyl)ditelluride and a mixture of both ditellurides are tabulated in table 3. The Raman spectrum of solid diphenylditelluride is shown in figure 3.

The ^{13}C NMR data for diarylditellurides in $CDCl_3$ are represented in table 4.

The ^{125}Te chemical shifts for $CDCl_3$ solutions referred to external $(CH_3)_2Te$ at 26°C together with intensity in percent of the total intensity for the three mixtures studied are shown in table 5.

The solvent effect has been studied both by changing the solvent and by investigating the dilution effect with mixture (i) and mixture (ii). Table 6 presents data in C_6D_6 compared with $CDCl_3$, and table 7 illustrates the effect of dilution in two different solvents.

The coupling constants for the unsymmetrical ditellurides are gathered into table 8.

Table 9 represents the variation of rate of exchange of ditellurides in $CDCl_3$ (mixture (i)) with time after mixing. The chemical shifts and intensities percent of mixture (i) in $CDCl_3$ in the absence of oxygen and light are presented in table 10.

The ^{125}Te NMR spectra of equi-molar mixtures of diarylditellurides are illustrated in figures 4, 5, 6, and 7.

TABLE (1)

The molecular weight of diarylditellurides determined osmometrically in benzene and chloroform.

Compounds	In benzene at 45°C	In chloroform at 25°C
$(C_6H_5)_2Te_2$	431	-
$(p\text{-}CH_3C_6H_4)_2Te_2$	456	723
$(p\text{-}EtOC_6H_4)_2Te_2$	630	472
$(p\text{-}ClC_6H_4)_2Te_2$	428	-

TABLE (2)

The elemental analysis of $(RTeO)_2O$.

Compounds	Found %		Required %	
	C	H	C	H
$(C_6H_5TeO)_2O$	31.7	2.30	31.6	2.20
$(p.CH_3C_6H_4TeO)_2O$	34.5	3.00	34.6	2.91

TABLE (3)

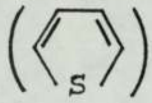
Raman data for diarylditellurides in benzene solution.

Compounds	$\nu(Te\text{-}Te)\,cm^{-1}$	$\nu(Te\text{-}Te)\,cm^{-1*}$
$(C_6H_5)_2Te_2$	173 m	167 vs
$(p\text{-}EtOC_6H_4)_2Te_2$	188 m	186 vs
$(C_6H_5)_2Te_2$ + $(p\text{-}EtOC_6H_4)_2Te_2$	170.5, 174.5 and 185 w	-

* data from reference 15

TABLE (4)

NMR spectral parameters of some diarylditellurides in $CDCl_3$.

	$\delta^{125}Te$	$T_1(^{125}Te)$ sec.	$\delta^{13}C_1$	$\delta^{13}C_2$	$\delta^{13}C_3$	$\delta^{13}C_4$	Other 13C
$(C_6H_5)_2Te_2$	420.8		108.0	137.6	129.2	128.0	
$(p.CH_3C_6H_4)_2Te_2$	432.2	1.4	104.3	138.3	130.2	138.3[a]	20.7
$(p.ClC_6H_4)_2Te_2$	451.8		105.4	139.4	129.7	135.1	
$(p.EtOC_6H_5)_2Te_2$	456.0	1.7	92.4	140.5	115.6	159.7	63.1, 14.
 $_2Te_2$	264.1						

$\delta^{125}Te$ ± 0.2 in ppm externally referred to pure $(Me)_2Te$ and $\delta^{13}C$ ± 0.1 in ppm internally referred to TMS. Temperature 26°C.

(a) ±0.3 ppm.

TABLE (5)

^{125}Te chemical shifts in ppm at 26°C and intensity for the three studied mixtures in $CDCl_3$.

	Mixture (i)		Mixture (ii)		Mixture (iii)	
	$\delta^{125}Te$	I%	$\delta^{125}Te$	I%	$\delta^{125}Te$	I%
A	475.2	24	459.3	24	451.5	26
B	462.7	20	456.3	25	446.9	26
C	455.3	32	433.9	25	436.8	26
D	444.3	24	430.5	26	431.6	22

TABLE (6)

Same as Table 5 but in C_6D_6. $\Delta\delta = \delta$ in $CDCl_3$ - δ in C_6D_6.

	Mixture (i)			Mixture (ii)		
	$\delta^{125}Te$ ppm	I%	$\Delta\delta$	$\delta^{125}Te$	I%	$\Delta\delta$
A	473.5	23	1.7	457.7	19	1.6
B	460.3	15	2.4	455.7	24	0.6
C	450.6	35	4.7	431.4	27	2.5
D	438.5	27	5.8	429.0	30	1.5

TABLE (7)

Effect of dilution on mixture (i) in C_6D_6, concentration divided by 4 and mixture (ii) in $CDCl_3$ concentration divided by 3.

				Dilute Soln		
		δTe	I%	δTe	I%	Δδ
Mixture (i)	A	473.5	23	469.1	26	4.4
	B	460.3	14	456.1	18	4.2
	C	450.6	35	445.5	33	5.1
	D	438.5	27	433.7	23	4.8
Mixture (ii)	A	459.3	24	457.3	23	2.0
	B	456.3	25	453.8	23	2.5
	C	433.9	25	431.9	24	2.0
	D	430.5	26	428.3	30	2.2

TABLE (8)

One bond coupling constant between ^{125}Te and ^{125}Te in dissymmetrical species.

	Species	Split lines	Solvent	$^{1}J_{^{125}Te-^{125}Te}$ Hz
(i)	$EtOC_6H_4TeTeC_6H_4Cl$	A and D	$CDCl_3$	170
		A and D	C_6D_6	175
		A and D	dilute C_6D_6	178
(ii)	p-$EtOC_6H_4TeTeC_6H_4-CH_3$	B and C	C_6D_6	207

TABLE (9)

Evolution of mixture (i) in $CDCl_3$ with Time after mixing.

Time after mixing/min.	δA	IA%	δB	IB%	δC	IC%	δD	ID%
0	474.7	20.5	462.1	20.5	454.7	35	443.7	24
20	475.2	24	462.7	18	455.3	32	444.3	26
∞	475.3	23.5	462.7	18	455.3	33	444.4	25.5

TABLE (10)

Chemical shifts and intensities of mixture (i) in $CDCl_3$ when O_2 and light are removed

	δA	IA%	δB	IB%	δC	IC%	δD	ID%
Ordinary	475.2	24	462.7	20	455.3	32	444.3	24
Without O_2	471.2	27	459.3	23	450.3	23	440.0	27
Without O_2 and without light	469.6	25	457.9	25	448.5	25	438.5	25

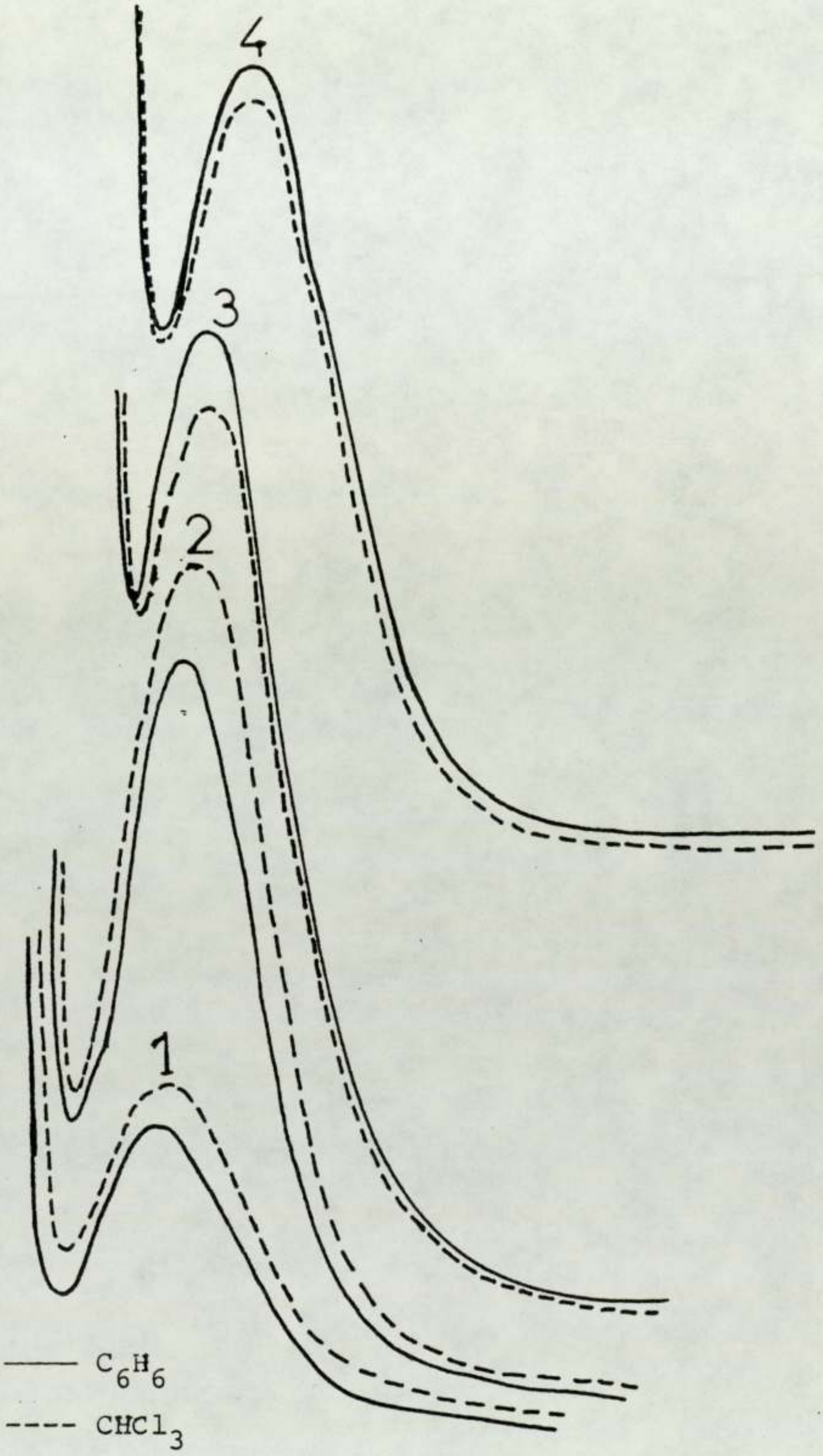


Figure 1 Visible spectra of diarylditellurides, $(4\text{-}R.C_6H_4Te\text{-})_2$, in benzene and in chloroform (1:R = H, λ_{max} = 405, 2:R = Cl, λ_{max} = 400, 3:R = C_2H_5O λ_{max} = 380 and 4:R = CH_3, λ_{max} = 405_{nm}).

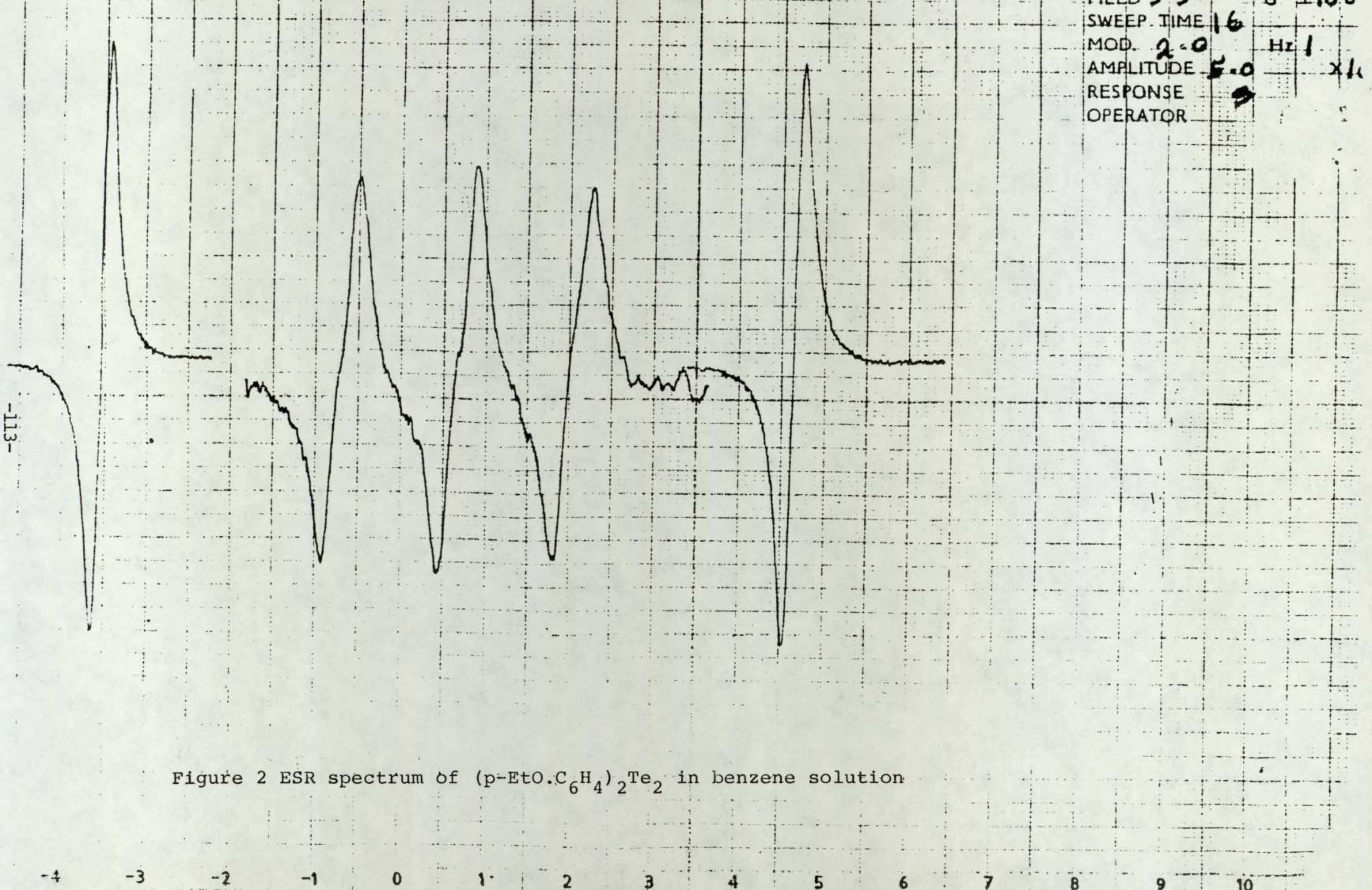


Figure 2 ESR spectrum of (p-EtO.$C_6H_4)_2Te_2$ in benzene solution

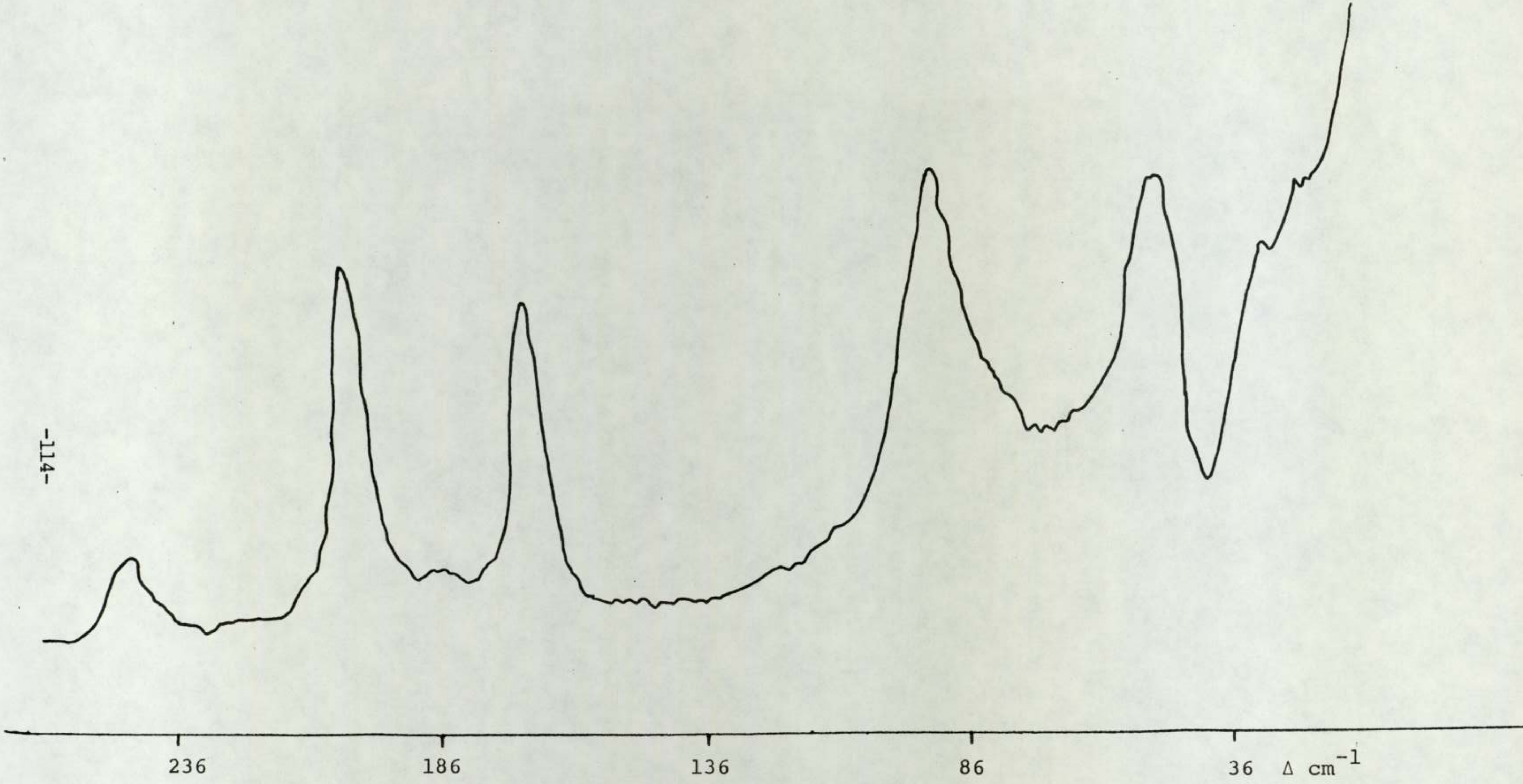


Figure 3 Raman spectrum of diarylditelluride

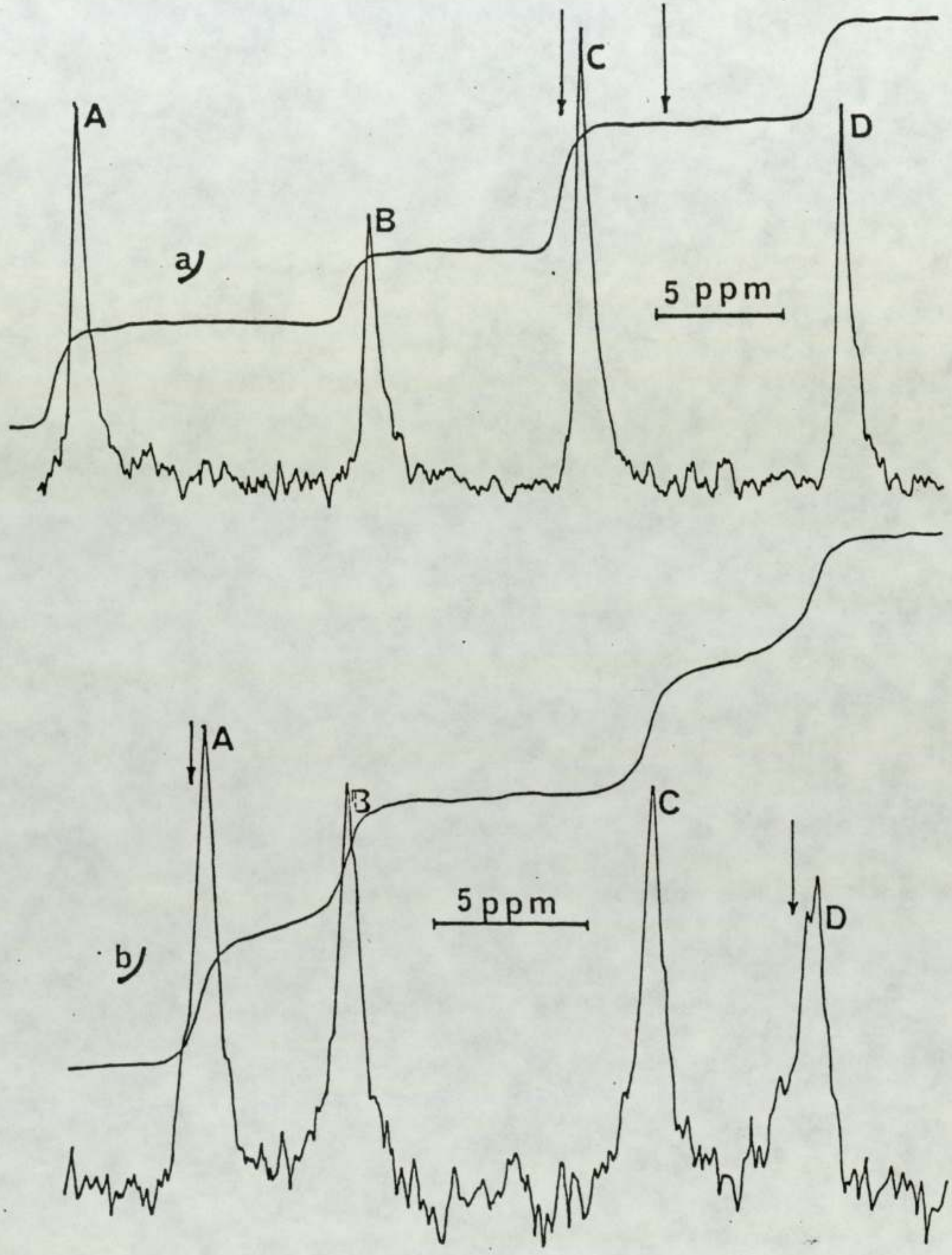


Figure 4 ^{125}Te NMR spectra of equi-molar mixture:

(a) mixture (i) $(p\text{-ClC}_6H_4)_2Te_2$ + $(p\text{-EtO.C}_6H_4)_2Te$

(b) mixture (ii) $(p\text{-ClC}_6H_4)_2Te_2$ + $(p\text{-CH}_3C_6H_4)_2Te_2$

Arrows indicate the resonance positions of pure compounds.

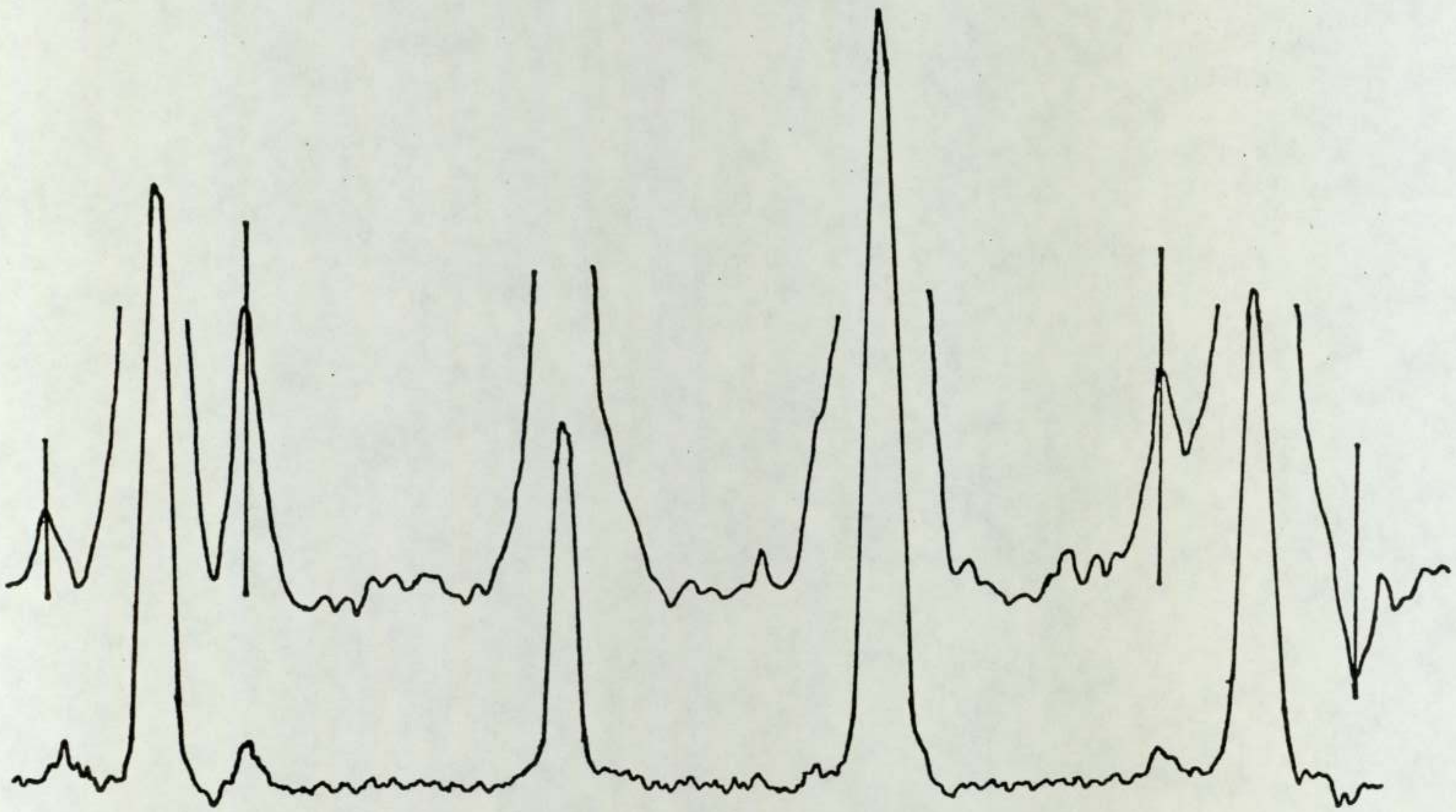


Figure 5 ^{125}Te NMR spectra of mixture (i) in C_6D_6 showing anomalous AB case arising from R-^{125}Te-^{125}Te-R'

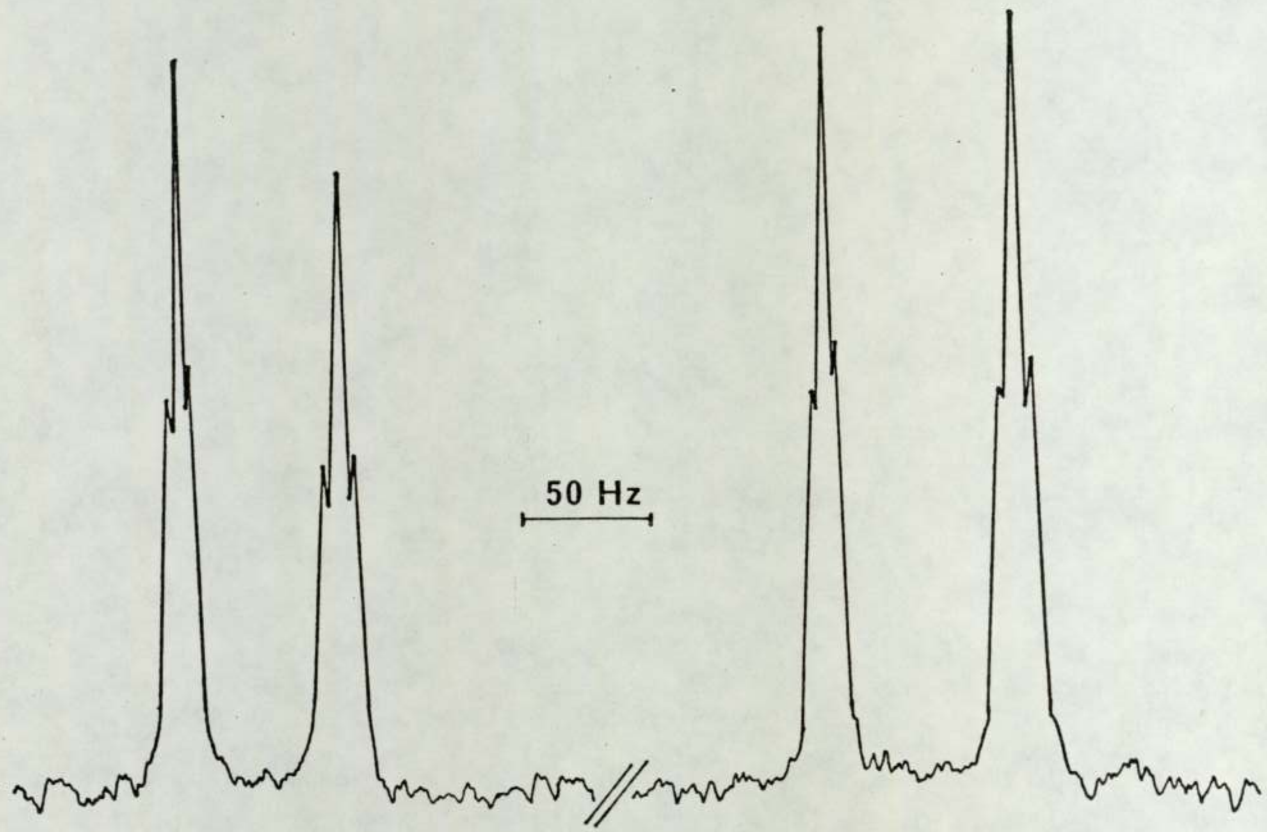


Figure 6 Undecoupled ^{125}Te NMR spectra of mixture (i) in C_6D_6 showing the three bonds ^{125}Te-^{1}H coupling constant

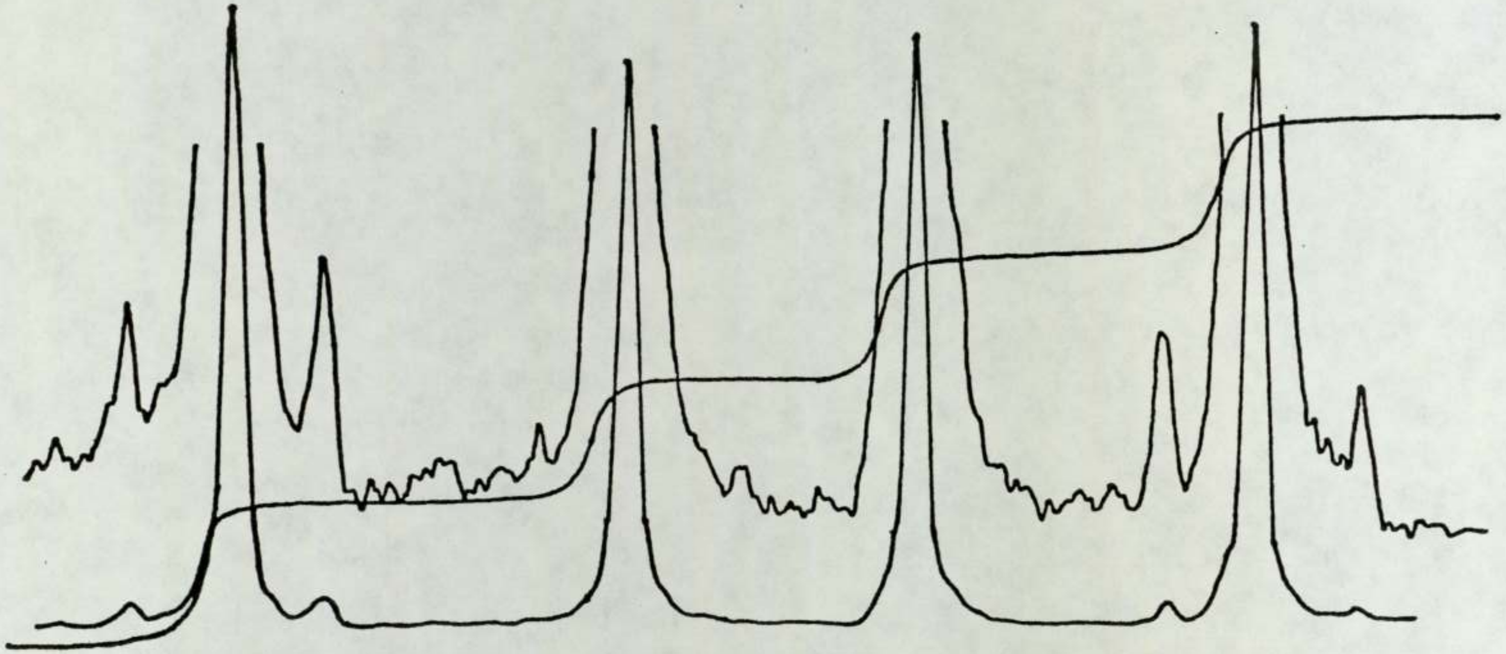


Figure 7 ^{125}Te NMR spectra of mixture (i) in $CDCl_3$ without dioxygen

4.(iv) DISCUSSION

There are two examples of unsymmetrical ditellurides known in the literature (16,17).

The compounds selected for this study were $(C_6H_5)_2Te_2$, $(p\text{-}EtOC_6H_4)_2Te_2$, $(p\text{-}CH_3C_6H_4)_2Te_2$ and $(p\text{-}ClC_6H_4)_2Te_2$.

Visible spectra of diarylditellurides, fig 1, show no difference to some extent in absorption maxima for each ditelluride in benzene and in chloroform. Moreover Thavornyutikarn(15) showed that the diffuse reflectance spectrum of diphenylditelluride and visible spectrum of a solution in chloroform were similar. Thavonyutikarn's work(15) together with this result may indicate that the diarylditellurides are largely undissociated in solution or a more reasonable interpretation is that the dissociation is largely incomplete in solution. The absorption maximum for diphenylditelluride in benzene and in chloroform is 405 nm which agrees well with the previous works(7,15).

There was no ESR signal from fresh solid specimens of diarylditellurides or from those which had been stored for a long time (~60 days) which casts doubt on the possibility of the diarylditellurides to dissociate completely or partially to radicals in the solid state. Furthermore, it has been found that the visible solution spectrum and diffuse reflectance spectrum of Ph_2Te_2 were very similar(15).

The irradiation of benzene solutions of diphenylditelluride, bis(p-methoxyphenyl)ditelluride by visible light in the presence of air formed a white precipitate which is identified by IR and elemental analysis as μ-Oxo-bis(aryloxotellurium iv.)

$$R_2Te_2 \xrightarrow{h\nu/O_2} (RTeO)_2O$$

This may be evidence to suggest that visible light plays an important rôle in the reaction of ditellurides in solution with dioxygen.

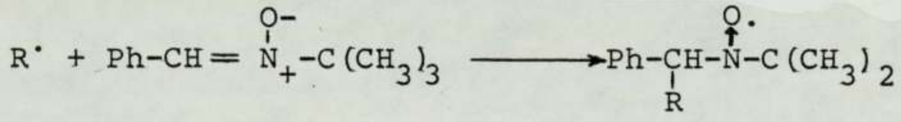
Recently two indirect techniques for the detection and identification of low concentrations of free radicals in reacting systems have been developed; CIDNP (105) (this will be mentioned in detail later in the chapter) and spin trapping. The former depends on the strong polarization of certain nuclear spin by the unpaired electron during the molecule's existence as a free radical. The latter involves trapping of a reactive free radical by an addition reaction to produce more stable radicals detected by ESR.

As it was mentioned before, Thavornyutikarn (15) examined the ESR spectra of solutions of diarylditellurides under conditions similar to those employed by Farrar, and observed no signal corresponding to RTe$^{\bullet}$ species, which might be because of low concentration of the radicals or due to an unfavourable relaxation effect.

In the present work, phenyl-t-butylnitrone (PBN) was used as a spin trap, which was initially introduced by Janzen$^{(106,107)}$. Janzen and Blackburn$^{(108)}$ showed the ability of PBN to trap the methyl, ethyl, n-butyl, phenyl and benzyl radical from the photolysis of organolead, -tin, and -mercury compounds. In the photolysis of $(p\text{-}EtOC_6H_4)_2Te_2$, in presence of PBN and t-butylbromide in benzene solution, it was hoped to produce organotellurium radicals which would capture bromine radicals from t-butylbromide and the t-butyl radical would be trapped by PBN. The sequence of the reaction may be represented by the following scheme:

$$R'_2Te_2 \xrightarrow[O_2]{h\nu} 2R'Te^{\bullet}(?)$$

$$R'Te^{\bullet} + RX \longrightarrow RR'TeX + R^{\bullet}$$



$$R^{\bullet} + Ph\text{-}CH{=}\overset{\overset{\displaystyle O^-}{|}}{N}_{+}\text{-}C(CH_3)_3 \longrightarrow Ph\text{-}\underset{\underset{\displaystyle R}{|}}{CH}\text{-}\overset{\overset{\displaystyle O^{\bullet}}{\uparrow}}{N}\text{-}C(CH_3)_2$$

No signal could be detected when $(p\text{-}EtOC_6H_4)_2Te_2$ and (PBN) in benzene was photolysed in the presence of t-butylbromide and air, but a free radical was detected by ESR after the addition of the ethanol and irradiation of the mixture by visible light, fig (2). The addition of ethanol gives immediate evidence for a free radical. Thus the observation of a signal indicates the presence of radicals in the reaction mixture. The hyperfine coupling constants a_N(14.68) and $a_{\beta H}$(1.76) are in agreement with previous work(57) in which a t-butyl radical was trapped by PBN. This may suggest that the spin trap (PBN) reacts with a t-butyl radical and also that the presence of ethanol (or dioxygen dissovled in ethanol) accelerates the formation of radicals such as RTeO$^{\cdot}$. White spots are formed in solid diphenylditelluride after leaving it for a long time in daylight which gives a free radical ESR signal. The IR shows ν(Te-O) vibration at 550 cm^{-1}; also NMR spectra show the presence of spurious peaks namely two different phenyl resonances.

Visible irradiation of diarylditellurides in benzene at room temperature did not produce tellurium, while Millington(19) proved that UV irradiation of solutions of diethyl and dibenzyl ditellurides under the same conditions produced dialkyltelluride and tellurium.

Molecular weight data, which were obtained in benzene and chloroform at 45^{o}C and 25^{o}C respectively, table 1, shows the effect of organic solvents, temperature, presence of light and dioxygen on the variation of these data. The molecular weight of these diarylditellurides determined in boiling chloroform was half the molecular weight of these compounds(109).

The molecular weight data, suggest that there may be (complete or partial) association or dissociation of diarylditellurides taking place in specific solvents and at particular temperatures together with the effect of dioxygen and the presence of light. It seems likely that diarylditellurides might be partially dissociated to radicals under certain conditions, and these radicals react with atmospheric dioxygen or with dioxygen dissolved in the solvent to form new oxygenated tellurium compounds such as $(RTeO)_2O$.

$$(RTeO)_2O \xleftarrow{O_2} 2(2RTe^{\cdot}) \rightleftharpoons 2R_2Te_2 \rightleftharpoons (R_2Te_2)_2$$

The other possibility is that the dioxygen initiates the formation of radicals. It may be noted that Morgan et. al.(9,11) obtained molecular weight data of $(p\text{-}EtOC_6H_4)_2Te_2$ and $(p\text{-}CH_3C_6H_4)_2Te_2$ in freezing benzene which were in agreement with the expected values for undissociated molecular species.

The investigation of ^1H NMR spectra of mixed solutions of two diarylditellurides and the mass spectra for a mixture of diarylditellurides, prepared either by melting the ditellurides together or dissolving in benzene and evaporating to dryness, gave the first evidence of unsymmetrical ditellurides, R-Te-Te-R', which formed through redistribution reactions(16).

To study the exchange reaction in more detail, the ^{13}C NMR spectra were examined for the two following mixtures;

(i) $(p\text{-}ClC_6H_4)_2Te_2 + (p\text{-}EtOC_6H_4)_2Te_2$

(ii) $(p\text{-}CH_3C_6H_4)_2Te_2 + (p\text{-}EtOC_6H_4)_2Te_2$

The ^{13}C chemical shifts of these two equi-molar mixtures show no differences from the individual pure compounds and the spectra are the sum of the contributions from each component, thus no conclusion may be drawn as to the nature of exchange since there is no interaction between the aryl groups. The values obtained from ^{13}C NMR data for pure diarylditellurides in $CDCl_3$ are given in table 4. The literature reports ^{13}C data only for diphenylditelluride(106,110) and these values (table 4) agree with the previously reported values. These results allow the assignment of the carbons using published increments for the phenyl ring(111). The coupling constant $^{13}C-^{125}Te$ is found to be independent of concentration and equal to 322 ± 1 Hz in p-ethoxy derivative and 304 ± 1 Hz in the p-methyl derivative. By contrast the $J_{^{125}Te-^{125}Te}$ is dependent on concentration and its value ranges from 213 to 223 Hz for bis(p-ethoxyphenyl)ditelluride. The other $^{125}Te-^{125}Te$ coupling constants lie within the range 257-269 Hz.

When equi-molar mixtures are prepared in $CDCl_3$ without special care (e.g. removal of dioxygen from the solvent), four lines were instantaneously observed, the ^{125}Te chemical shifts and intensities of which are presented in table 5. The labelling of the lines is from low field to high field and typical spectra reproduced in figure 4. These experiments show positive proof that the exchange reaction occurs.

The exchange is not fast since individual lines are observed; however, the resonances cannot be assigned directly as their position does not always correspond to to those of the pure compounds given in table 4. The other interesting feature is that the line intensities are not as would be expected for a slowly exchanging system. Since they are equi-molar mixtures, a pair of lines of equal intensity should arise from the unsymmetric specie, RTe-TeR', and a further pair of lines with components of equal intensity should arise from the remaining symmetric species (R_2Te_2 + R'_2Te_2).

Dance$^{(16)}$ estimated an "equilibrium constant" (K) of average value 4 from the integration of spectra for solutions containing different ratios of two symmetrical ditellurides;

$$\underset{(a)}{R_2Te_2} + \underset{(b)}{R'_2Te} \longrightarrow \underset{(c)}{2R\text{-}Te\text{-}Te\text{-}R'}$$

$$K = \frac{[c]^2}{[a]\,[b]}$$

It was shown that the equilibrium constant (K) is independent of temperature and the exchange reaction is under entropy control and that ΔH for such a reaction must be insignificant, so if Dance$^{(16)}$ is correct, the line intensities should be equal. In fact the predicted relationships are not observed (table 5) and the effect is most marked with mixture (i).

The solvent effect has been studied both by changing the solvent and by investigating the dilution effect with mixtures (i) and (ii). Table 6 represents data in

C_6D_6 compared with $CDCl_3$, and table 7 illustrates the effect of dilution in two different solvents.

Dilution leads to a deshielding effect of the same order for all resonances together with a slight change in intensities. Change of solvent does not affect chemical shifts to the same extent, but intensities change.

The anomalous intensities and anomalous AB spectrum observed for mixture (i) in C_6D_6 (fig 5) may have one of several origins: a CIDNP effect(105), a pulse effect(110) in an exchanging system or a dynamic effect in the acquisition of the decay. The last possibility is rapidly eliminated using a waiting time equal to $10T_1$ between each scan. The pulse length also has no effect, since use of a smaller pulse angle of about 10^{o}, which is below the value proposed by Ernst et.al.(112), leads to the same spectra. A CIDNP effect remains possible with a net effect as it appears on the main lines and probably a multiplet effect as it appears from the AB pattern.

The fact that ^{J}Te-Te may be measured means that the exchange is very slow with an upper limit for its rate about $(^{J}\text{Te-Te})^{-1}$ or 4×10^{-3} sec^{-1}. It has been attempted to observe the establishment of the equilibrium by measuring spectra just after mixing and at different time intervals later. The results for mixture (i) in $CDCl_3$ are presented in table 9. The chemical shifts are immediately established but the intensities observed in the first measurement show that the system has not reached equilibrium and this result confirms the slow rate of this exchange. The rates of exchange depend on the mixture and solvent. Mixture (ii) in C_6D_6 has a line width of 4 Hz and allows the measurement of ^{J}Te-H (fig 6) which is 4.5 Hz for lines A and C and 6 Hz for lines B and D. This leads to a rate of exchange of less than 0.3 sec^{-1}. For the other mixtures the measurement of the proton-tellurium coupling constant is impossible and the line widths are greater. Mixture (i) in C_6D_6 has a line width of 20 Hz in $CDCl_3$ of 12 Hz. Mixture (ii) has a line width of 20 Hz in $CDCl_3$, thus in those cases the exchange rate is faster.

All the lines of mixture (ii) in C_6D_6 begin a sudden and complete collapse at 45°C which may be attributed to the decomposition of the ditellurides. On the cooling of the same mixture, new species and 12 lines are formed which are at the moment very difficult to interpret. Similar results have been observed by Celotti(97) for $TeCl_2/TeBr_2$ mixtures.

The CIDNP effect implies the existence of a free radical process in the exchange. It was mentioned before that solutions of diarylditellurides stored in the laboratory without special care gives eventually, a white precipitate which covers the wall of the container. A similar precipitate was noted during attempts to obtain molecular weight data, by vapour phase osmometry, for solutions of individual ditellurides in benzene. It was noted that when the experimental solutions were put aside the colour became less intense until, ultimately, only a pale yellow solution in contact with a white solid remained.

The rate of decolourization of a diarylditelluride solutions is in the following order:

$$(p\text{-}EtOC_6H_4)_2Te_2 < (p\text{-}ClC_6H_4)_2Te_2 < (p\text{-}CH_3C_6H_4)_2Te_2 < (C_6H_5)_2Te_2$$

Elemental analysis of the white solid suggests an empirical formula "$(RTeO)_2O$" (R = aryl). Infra-red analysis shows strong bands centred on 550 cm^{-1} which are very characteristic of ν(Te-O)$^{(113)}$. Thus the products certainly contain oxygen. The free radical signal obtained from a mixture of $(p.EtOC_6H_4)_2Te_2$, PBN and t-butylbromide in the presence of air, ethanol and light indicates the formation of radical intermediates such as $RTeO^{\cdot}$ which may capture the bromide. The same experiment when carried out under dry nitrogen and the absence of light gave no free radical signal; even after the addition of ethanol free radicals were not observed. Furthermore, white spots were observed in very old specimens of Ph_2Te_2 which also gives ESR signal. So it is reasonable to predict that dioxygen, together with visible light, played an important rôle in formation of intermediate radicals. Work by others in our laboratory has independently demonstrated a reaction of ditellurides in solution with dioxygen capable of producing radical intermediates$^{(114)}$, hence it is necessary to accept that dioxygen dissolved in organic solvents may play a rôle in producing the spectroscopic data described above.

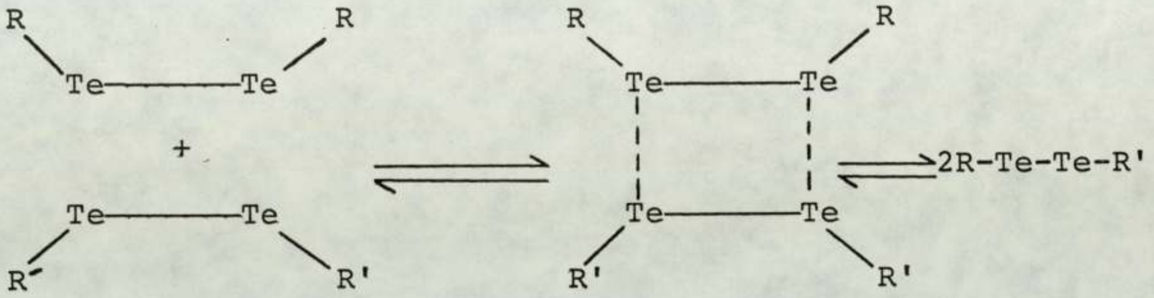
To evaluate the effect of dioxygen on the exchange reaction a sample of mixture (i) with degassed $CDCl_3$ has been prepared. The resulting spectrum shows that the intensities of lines A and D of the unsymmetric species are equal, as are lines B and C corresponding to the symmetric species. The results are summarised in table 10 and shown in figure 7 are consistent with Dance's work(16).

It has also been attempted to determine whether or not the exchange may be photochemically initiated (as the reaction of diarylditelluride with dioxygen). For this purpose a 10 mm sample tube was painted black and the appropriate quantities (equi-molar) of the ditellurides were weighted into the tube. The solids were then covered with degassed $CDCl_3$ in the dark and sealed into the tube. The resulting spectral data are given in table 10.

The exchange reaction occurs without photochemical assistance and line intensities are similar to those for the previous sample in degassed solvent. The small difference that is observed may arise from a possible influence of light, but it is at the limit of precision of the measurements. The exchange is a thermal process rather than a photochemical process.

No evidence that ditellurides spontaneously produce RTe' radicals is obtained as Farrar claimed. The data demonstrate that the reaction may be disturbed by dioxygen dissolved in the solvent, and that care must be taken in the studies of chemical mechanisms in tellurium chemistry. This may lead to new investigations of previous dielectric studies (115) and the ^{13}C relaxation measurements (116).

The dimeric intermediate mechanism of exchange reaction of diarylditellurides remains a distinct possibility:



These results, together with previous work (16), confirm that unsymmetrical ditelluride can exist and the exchange reaction between two symmetrical ditellurides is a slow reaction which depends on the mixture, concentration and solvent. Moreover, the exchange reaction is a thermal process and the exchange may be disturbed by dioxygen.

The Raman spectra of Ph_2Te_2 and $(p\text{-}EtOC_6H_4)_2Te_2$ showed tellurium-tellurium stretching frequencies at $\Delta\nu = 167$ and $186\ cm^{-1}$, (15) while $(C_6F_5)_2Te_2$ (16) showed two bands to be candidates for ν(Te-Te) at $\Delta\nu = 173$ and $186\ cm^{-1}$, which are within the range observed by Thavornyutikarn (15). The ν(Te-Te) was observed to be to some extent sensitive to a change of aryl group in diarylditellurides. These frequency shifts may be attributed to the electronic effect of aryl groups, to crystal effects, or to the differing degree of coupling with other vibrations e.g. ν(Ph-Te).

In the following work an attempt is made to study the exchange reaction of an equi-molar mixture of diphenylditelluride and bis(p-ethoxyphenyl)ditelluride in deoxygenated benzene by Raman spectroscopy, in order to clarify the existence of the unsymmetrical ditelluride, (p-EtOC$_6$H$_4$-Te-Te-C$_6$H$_5$), which will exhibit a different Te-Te stretching frequency from symmetric ditellurides. This is expected because of the effect of aryl groups in the Te-Te bond.

The Raman spectrum of an equi-molar mixture of $(C_6H_5)_2Te_2$ and $(p\text{-}EtO.C_6H_4)_2Te_2$ (prepared in deoxygenated benzene) has been examined and showed that the exchange reaction between the two ditellurides had taken place. Three weak to medium bands at 170.5, 174.5 and 185 cm^{-1} were instantaneously observed representing the Te-Te stretching frequency of $(C_6H_5)_2Te_2$, $(p\text{-}EtO.C_6H_4)_2Te_2$ and p-Eto.C$_6$H$_4$-Te-Te-C$_6$H$_5$ respectively. The labelling of these bands is presented in table 3. In fact this result is explained by the exsistence of the equilibrium between all three ditellurides which has been previously mentioned. The Raman spectrum of solid $(C_6H_5)_2Te_2$ shows a band at $\Delta\nu = 169$ cm^{-1} for ν(Te-Te) which is the same value as that observed by Thavornyutikarn(15), fig 3.

Medium bands at 173 and 188 cm^{-1} were observed for solutions of individual diphenylditelluride and bis(p-ethoxyphenyl)ditelluride in deoxygenated benzene and are assigned to tellurium-tellurium stretching frequency table 3, which are within the range observed by Thavornytikarn(15).

CHAPTER V

5. (i) INTRODUCTION

Diorganoditellurides form complexes with a variety of metal ions. The compounds of the group I and II metals are of the type $(RTe)_nM$, $n = 1$ or 2. Silicon, germanium, tin and lead all form compounds having the general formula $R_3M\text{-}TeR'$, or $R_3M\text{-}TeM'R_3$ (M, M' = group IV element; R = organic group or H; R' = Li, H or organic group). The compounds with other metallic elements are complexes, in which diorganyltellurides, diorganylditellurides, or organotelluro groups serve as ligands.

When diorganylditellurides react with transition metals, they often undergo tellurium-tellurium bond cleavage to afford material in which the RTe group bridges metal centres. The first reported method to use diarylditellurides as reagents to form bridging $M(\mu\text{-}TeAr)_2M$ linkages via oxidative addition reactions was introduced by Hieber and co-workers$^{(117,118)}$.

$$2Fe_3(CO)_{12} + 3Te_2(p\text{-}MeO.C_6H_4)_2 \longrightarrow$$

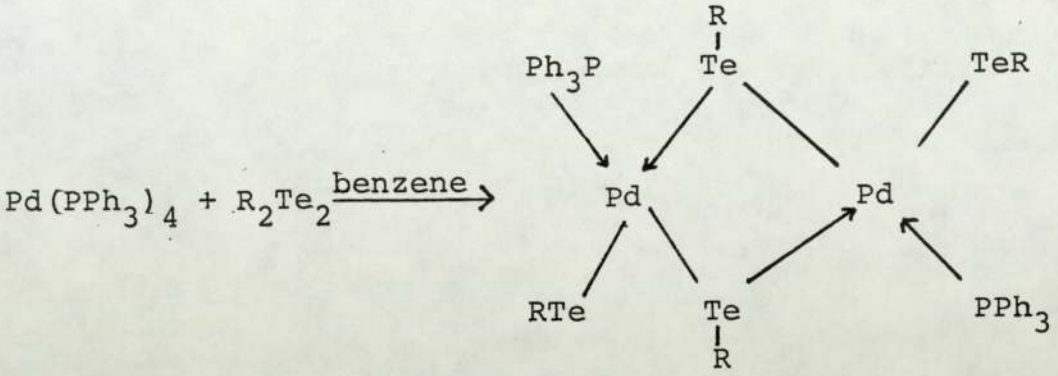
$$3(OC)_3Fe(\mu\text{-}Te(p\text{-}MeO.C_6H_4))_2Fe(CO)_3 + 6CO.$$

Baddley and co-workers$^{(119,120)}$ later demonstrated that a terminal M-TeAr bond could be formed by analogous reactions, the dimeric complexes with the bridging bonding mode being formed under more forcing conditions:

$$[\pi CpFe(CO)_2]_2 + Ph_2Te_2 \xrightarrow[\text{reflux}]{\text{benzene}} \pi CpFe(CO)_2TePh \text{ ———}$$

$$\xrightarrow[\text{IR lamp}]{\text{benzene, reflux}} \pi Cp(CO)Fe(\mu\text{-}TePh)_2Fe(CO)\pi Cp$$

Recently Chia and McWhinnie(25) reported an interesting complex incorporating both terminal and bridging aryl tellurol ligands:



The above complexes were decomposed by carbon monoxide to give R_2Te_2, palladium and triphenylphosphine(25).

A few elements have been reported to give simple complexes with diorganylditellurides namely mercury (II)(31,121) copper (I)(6,28,29), and uranium (V)(27) in which the tellurium-tellurium bond remains intact.

Dance and Jones(31) have prepared three general types of mercuric halide complex with diarylditellurides by reaction of the components in ethanol, characterization being by ^{125}Te Mössbauer and far infra-red spectroscopies. The type of complex isolated depends on the stoichiometry of the reaction and the mercuric halide used.

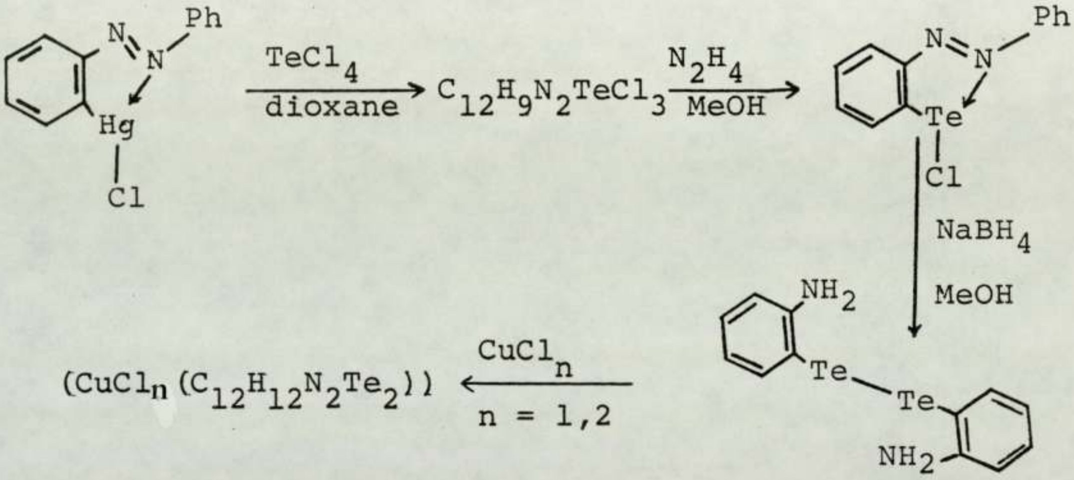
^{125}Te Mössbauer spectra of $R_2Te_2.HgX_2$ indicated that the tellurium atoms are two coordinate and that all Te sites are equivalent, thereby suggesting that the diarylditelluride is weakly complexed in such adducts.

Complexes of cuprous halides with diarylditellurides,

$Ar_2Te_2.CuX$, (X = Cl, Br; Ar = Ph, p-EtO.C_6H_4) have been prepared by addition of an equi-molar amount of Ar_2Te_2 in ether solution to an acetonitrile solution of cuprous halide under a nitrogen atmosphere, orange to red precipitates of the complexes being obtained on cooling the reaction solutions$^{(28,29)}$. According to their colour the complexes contain intact ditellurides this is supported by the assignment of a ν (Te-Te) absorption for $Ph_2Te_2.CuCl$ at 170 cm^{-1} in its far infra-red spectrum. This latter absorption is apparently enhanced by coordination, the corresponding band for the solid diphenylditelluride occuring at 169 cm^{-1} in its Raman spectrum. The occurrence of a νCu-Cl at 230 cm^{-1} in far infra-red indicates the presence of bridging rather than terminal chloro ligands $^{(29)}$. ^{125}Te Mössbauer spectral data of $R_2Te_2.CuX$ showed that the Te-Te bonds remain intact. The chemical isomer shifts (δ) are all the same within the experimental error and are similar to the values for the free ditellurides, indicating that the tellurium atoms use their 5p orbitals for complexation with little change in their hybridization.

Comparison of the quadrupole splitting of Cu(I) complexes with those of Hg(II) complexes [$(p\text{-}EtO.C_6H_4)_2Te_2.HgX_2$; X= Cl, Br; Δ = 8.9-9.5 mm sec^{-1} for the Cu(I) complexes vs. 5.1 mm sec^{-1} for the Hg(II) complexes.] indicates that Hg(II) has greater Lewis acidity than Cu(I) with respect to this ditelluride ligand.

A complex of di(o-aminophenyl) ditelluride with CuCl has also been reported (6). The molar conductivity of CuCl($C_{12}H_{12}N_2Te_2$) in acetonitrile indicated a 1:1 electrolyte (6). This new ditelluride was prepared by borohydride reduction of (2-phenylazophenyl-C,N') tellurium chloride (6):



The copper chloride complexes, $(2\text{-}H_2N.C_6H_4)_2Te_2.CuCl_n$ (n = 1,2) were formed when an ethereal solution of the ditelluride was mixed with an acetonitrile solution of CuCl or $CuCl_2$ under nitrogen. The molar conductivities indicate the complexes to be 1:1 electrolytes in acetonitrile.

In chapter four ^{125}Te NMR spectroscopy was used to study the chemical exchange between diarylditellurides. It was shown that the exchange is slow, and is a thermal process. These observations confirm that unsymmetrical ditellurides can exist. All attempts to separate the unsymmetrical ditellurides from symmetrical species by fractional crystallization or by chromatography were not successful and resulted in the isolation of the original symmetrical species (16).

The question which arises from this work and previous works (15,16) is "Will a Lewis acid (Hg (II) and Cu (I) halide) complex preferentially with unsymmetrical ditellurides, R-Te-Te-R', by the reaction of a mixture of two diarylditellurides with Lewis acid?"

Musa (6) recently prepared (phenylazophenyl-C, N') tellurium chloride which represents one of the few examples of organyl tellurenyl halides and is also an example of a nitrogen-tellurium bond. The structure of this compound has been determined by X-ray crystallography (6) and gives Te-N bond length as 2.23 Å and the Te-C (II) bond length as 2.04 Å which is the shortest known for an organotellurium compound.

^{125}Te Mössbauer spectrum of tellurenyl chloride showed that the value of the chemical isomer shift of 0.63 mm sec^{-1} is relatively large compared with other Te (II) compounds, e.g. for Ph_2Te_2 it is 0.18 mm sec^{-1} (30) and is also larger than the value of 0.46 mm sec^{-1} obtained for the anion p-EtO.$C_6H_4TeI_2^-$. Furthermore, the quadrupole coupling constant value of 11.76 mm sec^{-1} deviates from the value for Te (II) compounds which should be of the order of 14 mm sec^{-1} (30), this means that there is some other mechanism for the withdrawal of p-electrons from the tellurium. Musa (6) proposed that there is a positive π-interaction between tellurium and the chelate ring according to Mössbauer data.

In the early 1960s, a new powerful π-molecular acceptor was discovered (122,123), namely tetracyano-p-quinodimethane (TCNQ). The TCNQ radical forms organic semiconductors with a large number of cations. When strong π-molecular donor and acceptor molecules (e.g. TCNQ) react, they often form ion-radical salts and charge transfer compounds with considerably higher conductivities.

McWhinnie and co-workers(57) postulated that the formation of a charge transfer complex in the reaction between Ph_2Te and MeX was intermediate in the formation of telluronium salts.

It was hoped, as part of the present work to examine the ability of tellurium (II) compounds in azobenzene derivatives to act as π-molecular donors to an acceptor molecule such as TCNQ.

5. (ii). EXPERIMENTAL

Preparation of diarylditellurides

The diarylditellurides used in this work were synthesised by literature methods e.g. Ph_2Te_2 (7) and $p\text{-}EtO.C_6H_4)_2Te_2$ (10). All materials had satisfactory melting points and spectra (IR and NMR).

Preparation of copper (I) halides:

Copper (I) chloride and bromide were prepared as follows:

Copper (II) chloride (12 g) was dissolved in degassed water (40 ml), stirred under a nitrogen atmosphere, and an aqueous solution of sodium sulphite (24 g) was added dropwise over a period of 30 min. The solution slowly changes colour from green to pale yellow. The solution was decanted from the white precipitate of copper (I) chloride. The precipitate was washed with distilled water, absolute ethanol, and dry diethyl ether. The solvents were all degassed prior to use and the solution kept in dry boxes at all times.

The copper (I) chloride was vacuum dried and stored under nitrogen.

Copper (I) bromide was prepared similarly, starting with 19 g. of copper (II) bromide.

Sulphur dioxide was also used as a reducing agent in preparing copper (I) halides.

Preparation of Diarylditelluride-Copper (I) halide Complexes:

$Ph_2Te_2.2CuX$ and $(p\text{-}EtO.C_6H_4)_2Te_2.2CuX$ (where X = Cl

Br) were prepared by the literature method (29).

Preparation of Unsymmetrical Diarylditelluride - Copper (I) halide Complexes:

Diphenylditelluride (2mM) and bis(p-ethoxyphenyl)-ditelluride (2mM) were dissolved in dry diethylether under dry nitrogen. Copper (I) chloride or bromide (2mM) was dissolved in propionitrile under nitrogen atmosphere. To this solution was added dropwise the solution of the ditellurides. The solution was warmed to 30-40°C and stirred for 15 minutes; orange to red precipitates of the complex being obtained on cooling the reaction solution.

Preparation of Diarylditelluride-Mercury (II) halide Complexes:

Mercury (II) chloride and bromide complexes of diphenylditelluride and bis(p-ethoxyphenyl)ditelluride were prepared by following the method of Davies (1).

Preparation of Unsymmetrical Diarylditelluride-Mercury (II) halide Complexes:

0.5mM of diphenylditelluride and 0.5mM of bis(p-ethoxyphenyl)ditelluride were dissolved in the minimum propionitrile under nitrogen. To this solution was added a solution of mercury (II) chloride (1mM) in propionitrile. The resulting solution was refluxed and stirred for 30 minutes, and the yellow precipitate filtered. The compound was washed with ethanol, then vacuum dried m.p. 180°C.

Mercury (II) bromide complex was prepared as described above. The same preparations were carried out in ethanol to afford yellow materials.

Preparation of the Azobenzene Derivaties of Tellurium:

All the azobenzene derivatives of tellurium prepared are known compounds except the tellurenyl bromide.

The method employed for preparation of (2-phenylazophenyl-C,N') tellurium (IV) trichloride, (2-phenylazophenyl-C,N') tellurium (II) chloride, (2-phenylazophenyl-C,N') tellurium (IV) tribromide and di(o-aminophenyl) ditelluride were according to literature sources (6).

Preparation of (2-phenylazophenyl-C,N')-tellurium (II) bromide:

4.3 g of (2-phenylazophenyl-C,N') tellurium (IV) tribromide was dissolved in methanol (60 ml) and heated under reflux. A solution of hydrazine hydrate (0.8 g) in methanol (30 ml) was added slowly to the refluxing solution. The hot solution was filtered and cooled to afford brown crystals of the product of m.p. 78°C, in quantitative yield.

Found: C, 37.0; H, 2.20; N, 7.20, Br, 19.8

$C_{12}H_9N_2TeBr$ requires: C, 37.0; H, 2.33; N, 7.21; Br, 20.5

Preparation of 1:1 Charge Transfer Complex of (2-phenylazophenyl-C,N') Tellurium (II) bromide and TCNQ

A mixture of 0.39 g of (2-phenylazobenzene-C,N')-tellurium (II) bromide and 0.21 g of tetracyano-p-quinodimethane (TCNQ) in dry acetonitrile (30 ml) was stirred and refluxed under a nitrogen atmosphere for 2-3 hours. A small quantity of blue-black crystals were deposited from this reaction during the period of the reflux and on cooling. The acetonitrile was removed on a rotary evaporator to give blue-black crystals. This precipitate was washed with small amounts of acetonitrile, m.p. 90-92°C.

The following charge transfer complexes were prepared by a direct reaction between TCNQ and the organotellurium compounds according to the above method:

1:1 Charge Transfer Complex of (2-phenylazophenyl-C,N')-tellurium (II) Chloride and TCNQ:

Reddish-black precipitate was formed, m.p. 119-120°C.

1:1 Charge Transfer Complex of 3,4-benzo-1-telluracyclopentane and TCNQ :

Blue-black precipitate was formed, m.p. 169-171°C.

1:2 Charge Transfer Complex of di(o-aminophenyl)ditelluride and TCNQ :

Brown-black precipitate was formed, m.p. 105-106°C.

5.(iii). RESULTS

Analysis:

Elemental analysis for diarylditelluride complexes and TCNQ complexes are shown in tables 1 and 2 respectively.

Mass Spectra:

Mass spectra of (p-Eto.C_6H_4)(C_6H_5)Te_2.2HgX_2 and (p-EtO.C_6H_4)(C_6H_5)Te_2.CuX (X = Cl, Br) are presented in tables 3, 4, 5 and 6.

Raman Spectra:

Raman spectra of diarylditelluride complexes with Hg(II) and Cu(I) halides are presented in tables 7, 8 and 9.

Visible Spectra of Organotellurium (II)-TCNQ Complexes:

The visible spectra of TCNQ, $C_{12}H_9N_2$TeCl. TCNQ, $C_{12}H_9N_2$TeBr.TCNQ, $C_{12}H_{12}N_2$Te.TCNQ and C_8H_8Te.TCNQ in acetonitrile are shown in figure 3.

ESR Spectra:

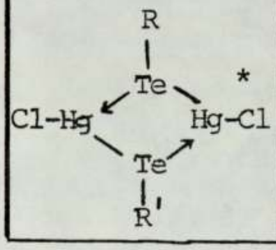
ESR sepctra of solids $C_{12}H_9N_2$TeX.TCNQ (X = Cl, Br) $C_{12}H_{12}N_2Te_2$.TCNQ and C_8H_8Te.TCNQ are presented in figures 4, 5, 6 and 7, and their spectra in acetonitrile solution are shown in figures 8, 9 and 10.

Infra-red Spectra:

IR spectra of p-EtO.C_6H_4Te-TeC_6H_5.2CuBr and p-EtO.C_6H_4.Te-Te-C_6H_5.2$HgCl_2$ are presented in figures 1 and 2.

TABLE (1)

Elemental analysis of ditelluride - Hg (II) and Cu (I) halides complexes.

Complex	Found %				Required %			
	C	H	X	Te	C	H	X	Te
$RR'Te_2.2CuBr$	22.9	2.00	-	33.7	22.7	1.90	-	34.5
$RR'Te_2.2CuCl$	24.1	2.50	-	-	25.8	2.20	-	-
$RR'Te_2.2HgCl_2$	16.7	1.50	-	24.9	16.8	1.42	14.23	25.6
$RR'Te_2.2HgBr_2$	13.9	1.00	-	20.4	14.3	1.20	27.22	21.7
 *	18.3	1.60	8.10	26.6	18.16	1.50	7.67	27.5

R = Ph; R' = (p-EtO.C_6H_4)

* Prepared in ethanol.

<u>TABLE (2)</u>

Elemental analysis of 1:1 charge transfer complexes.

	Found				Required			
Complex	% C	% H	% X	% N	% C	% H	% X	% N
$C_{12}H_9N_2TeCl.TCNQ$	51.1	2.3	-	16.6	52.6	2.3	-	15.3
$C_{12}H_9N_2TeBr.TCNQ$	49.8	2.20	13.4	14.10	48.62	2.21	12.40	14.1
$C_8H_8Te.TCNQ$	54.2	2.70	-	13.0	55.09	2.75	-	12.8

TABLE (3)

Mass spectra of $(p\text{-}EtO.C_6H_4)(C_6H_5)Te_2.2CuBr$, relative to ^{130}Te, ^{81}Br, ^{16}O.

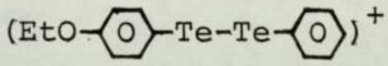
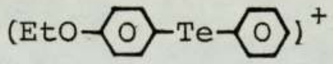
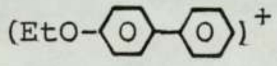
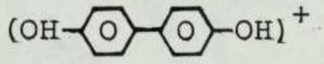
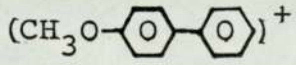
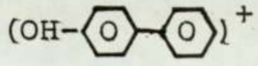
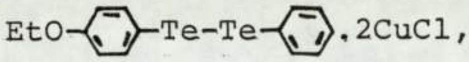
Ions	m/e	R.I%
$(EtO\text{-}C_6H_4)_2Te_2^+$	502	1.0
	458	4.5
$Ph_2Te_2^+$	414	2.1
$(p\text{-}EtO.C_6H_4)_2Te^+$	372	100
	328	100
Ph_2Te^+	284	3.0
	198	77
	186	85
	184	100
	169	100
Ph_2^+	154	45
Br^+	81	55
Ph^+	77	100

TABLE (4)

Mass spectra of , relative to ^{130}Te, ^{35}Cl, ^{16}O.

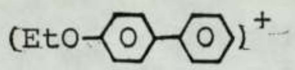
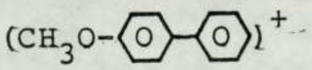
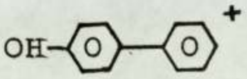
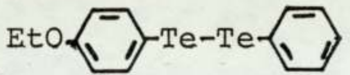
Ions	m/e	R.I (%)
$(p\text{-}EtO.C_6H_4)_2Te_2^{+}$	502	1.2
$(p\text{-}EtO.C_6H_4Te\text{-}TeC_6H_5)^{+}$	458	7.0
$Ph_2Te_2^{+}$	414	2.2
$(p\text{-}EtOC_6H_4)_2Te^{+}$	372	80
$(p\text{-}EtOC_6H_4Te.C_6H_5)^{+}$	328	100
$(p\text{-}CH_3O.C_6H_4)_2^{+}$	214	100
	198	77
$(p\text{-}HO.C_6H_4)_2^{+}$	186	100
	184	100
	169	100
Ph_2^{+}	154	100
Ph^{+}	77	95
Cl^{+}	35	75.3

TABLE (5)

Mass spectra of  $.2HgCl_2$, relative to ^{130}Te, ^{35}Cl, ^{203}Hg.

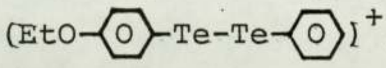
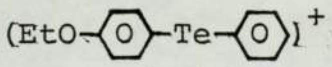
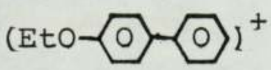
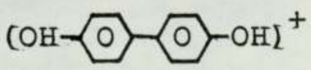
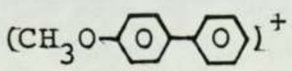
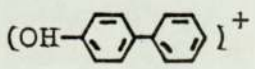
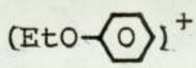
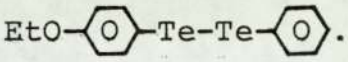
Ions	m/e	R.I (%)
$(p\text{-}EtO.C_6H_4)_2Te_2^+$	502	24.6
	458	47.5
$Ph_2Te_2^+$	414	13.1
$(p\text{-}EtO.C_6H_4)_2Te^+$	372	100
Ph_2Hg^+	356	32.8
	328	100
$PhHgCl^+$	315	26.2
$PhHg^+$	279	50.8
$HgCl_2^+$	277	57.8
$(p\text{-}EtO.C_6H_4)_2Te^+$	251	100
$HgCl^+$	237	8.2
$(p.CH_3O.C_6H_4)_2^+$	214	100
$PhTe^+$	207	100
	198	100
	186	100
	184	100
	169	100
	121	100
Te^+	130	100
Ph^+	77	100

TABLE (6)

Mass spectra of  $.2HgBr_2$, relative to ^{130}Te, ^{81}Br, ^{16}O, ^{203}Hg.

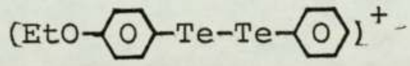
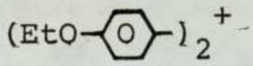
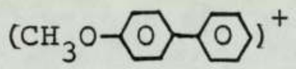
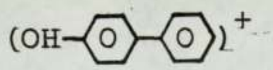
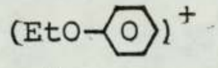
Ions	m/e	R.I (%)
$(p\text{-}EtO.C_6H_4)_2Te_2^+$	502	1.0
	458	2.2
$Ph_2Te_2^+$	414	2.0
$p\text{-}EtO.C_6H_4\text{-}HgBr^+$	404	1.8
$(p\text{-}EtO.C_6H_4)_2Te^+$	372	42
$HgBr_2^+$	363	10.5
$PhHgBr^+$	359	5
$(p\text{-}EtO.C_6H_4\text{-}Te\text{-}C_6H_5)^+$	328	4
Ph_2Te^+	284	1.8
	242	44
	184	54
	169	100
Ph_2^+	154	14
	121	1.6
Br^+	81	12
Ph^+	77	5

TABLE (7)

Raman spectra of diorganoditelluride - Copper (I) halide complexes.

$(p\text{-}EtO\text{-}C_6H_4)_2Te_2.2CuCl$	$(p\text{-}EtOC_6H_4)_2Te_2.2CuBr$	$RR'Te_2.2CuCl^*$	Assignment
206m	206m		ν(Te-Ph)
186vs	186vs		ν(Te-Te)
156m	162m	169vvs	ν(Te-Cu)
116w	116w		
92w	87w		
47m	69m	R = Ph;	
		$R = (p.EtOC_6H_4)$	

* The Raman data of this compound could not be obtained since it was decomposed by laser beam.

TABLE (8)

Raman assignments for diorganoditelluride-mercuric chloride complexes.

$Ph_2Te_2.2HgCl_2$	$(p\text{-}EtO.C_6H_4)_2Te_2.2HgCl_2$	$RR'Te_2.HgCl_2$	Assignment
279 vw	288 vw	280 vw	ν(Hg-Cl)
253 w	-	251 w	ν(Te-C)
216 w	204 w	206 w	Phenyl X
160 m	-	-	
141w	148 w	144w	Phenyl X
130 m	133 w	-	=
120 vs	110 vs	119 vs	ν(Te-Hg)
88 m	99 w	-	unassigned
69.5 w	55 m	60 m	
32 s	31 s	35 s	

R = Ph; R' = $(p\text{-}EtO.C_6H_4)$

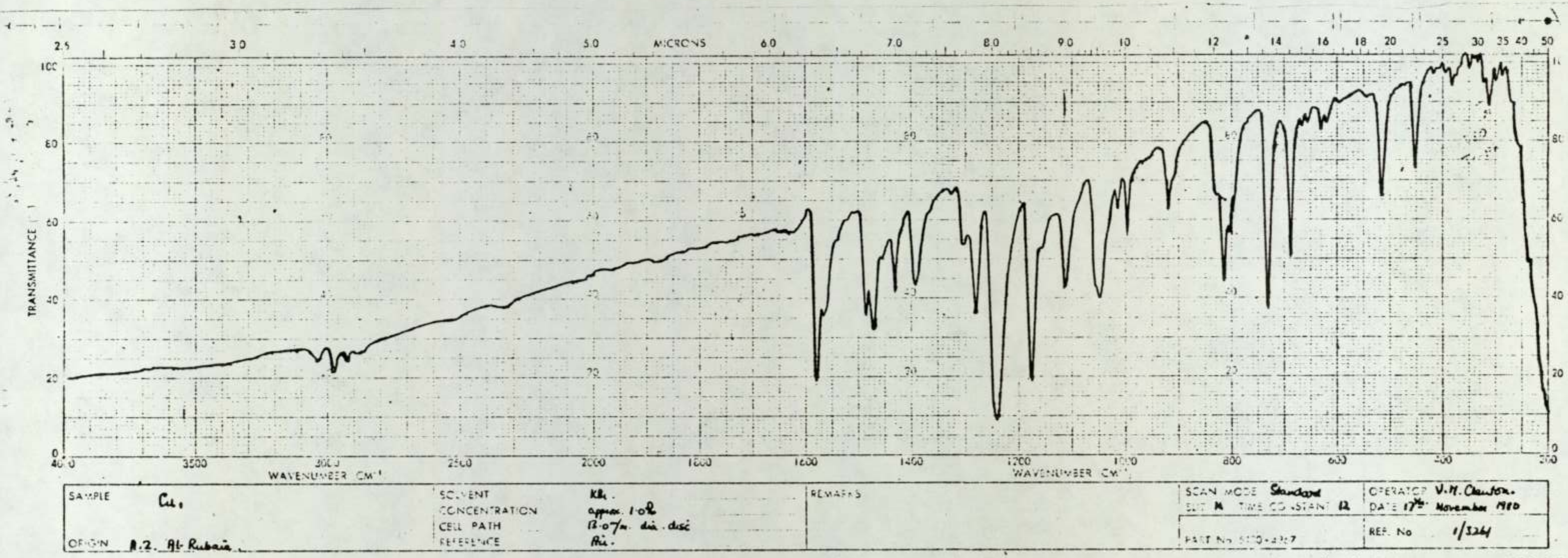
TABLE (9)

Raman assignments for diorganoditelluride-mercuric bromide complexes.

$Ph_2Te_2.2HgBr_2$	$(EtO.C_6H_4)_2Te_2.2HgBr_2$	$RR'Te_2.2HgBr_2$	Assignment
256 w	254 w	256 w	ν (Te-C)
216 w	-	204 vw	ν (Te-C)
186 w	-	186 vw	
141 w			
120 vs	133 vs	133 vs	ν (Te-Hg)
90.5 w			
99.5 w	54 w	53 w	unassigned
51.5 w	34 m	38.5 m	
31 s			

R = (C_6H_5)

R' = $(p\text{-}EtO.C_6H_4)$



SAMPLE Cu₁

ORIGIN A.Z. Al-Rubaie.

SOLVENT KBr.

CONCENTRATION approx. 1·0%

CELL PATH 13·0 m/m. dia. disc

REFERENCE Air.

REMARKS

SCAN MODE Standard

SLIT M TIME CONSTANT 12

PART No 5120-4267

OPERATOR V.M. Clanton.

DATE 17th November 1980

REF. No 1/3261

Figure 1 Infra-red spectrum of (p-EtO.$C_6H_4TeTeC_6H_5 . 2CuBr$

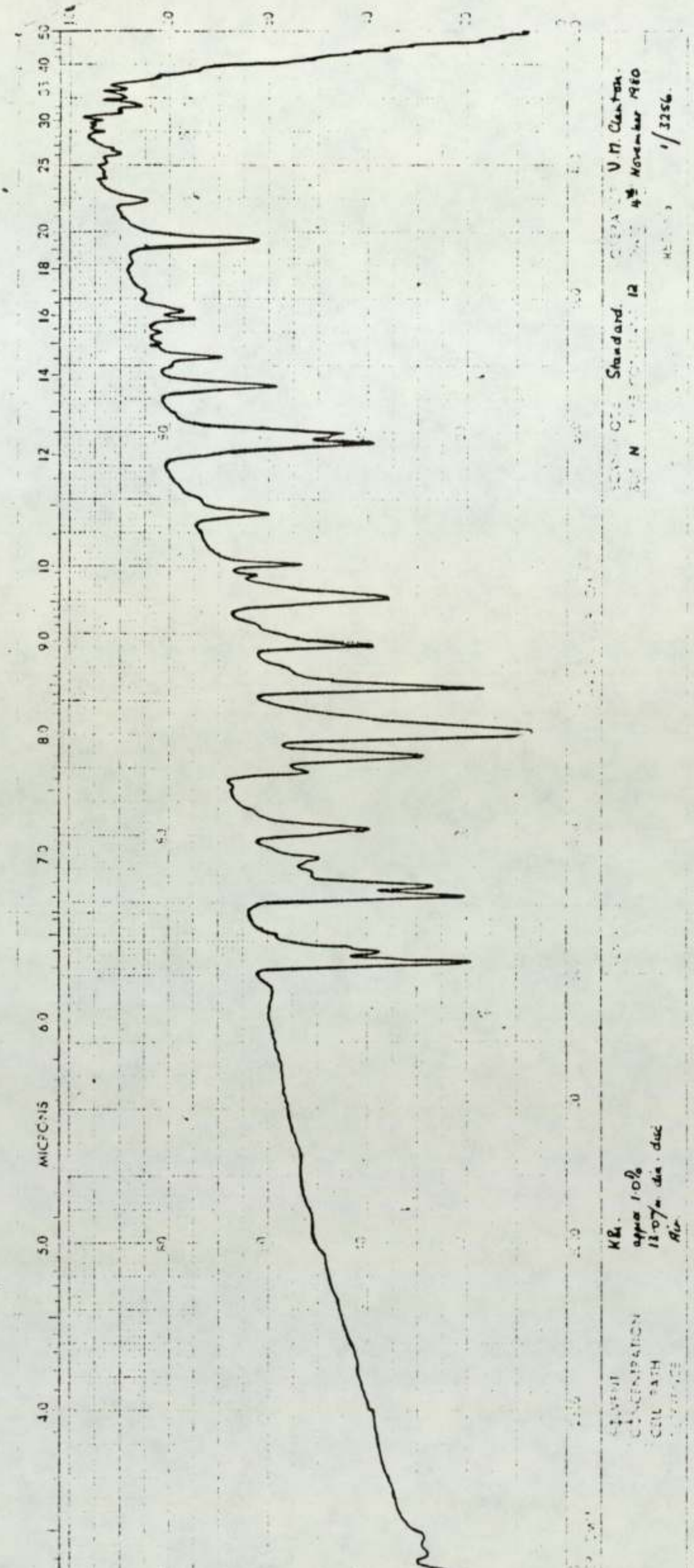


Figure 2 Infra-red spectrum of (p-EtO.C_6H_4)TeTe$C_6H_5 \cdot 2HgCl_2$

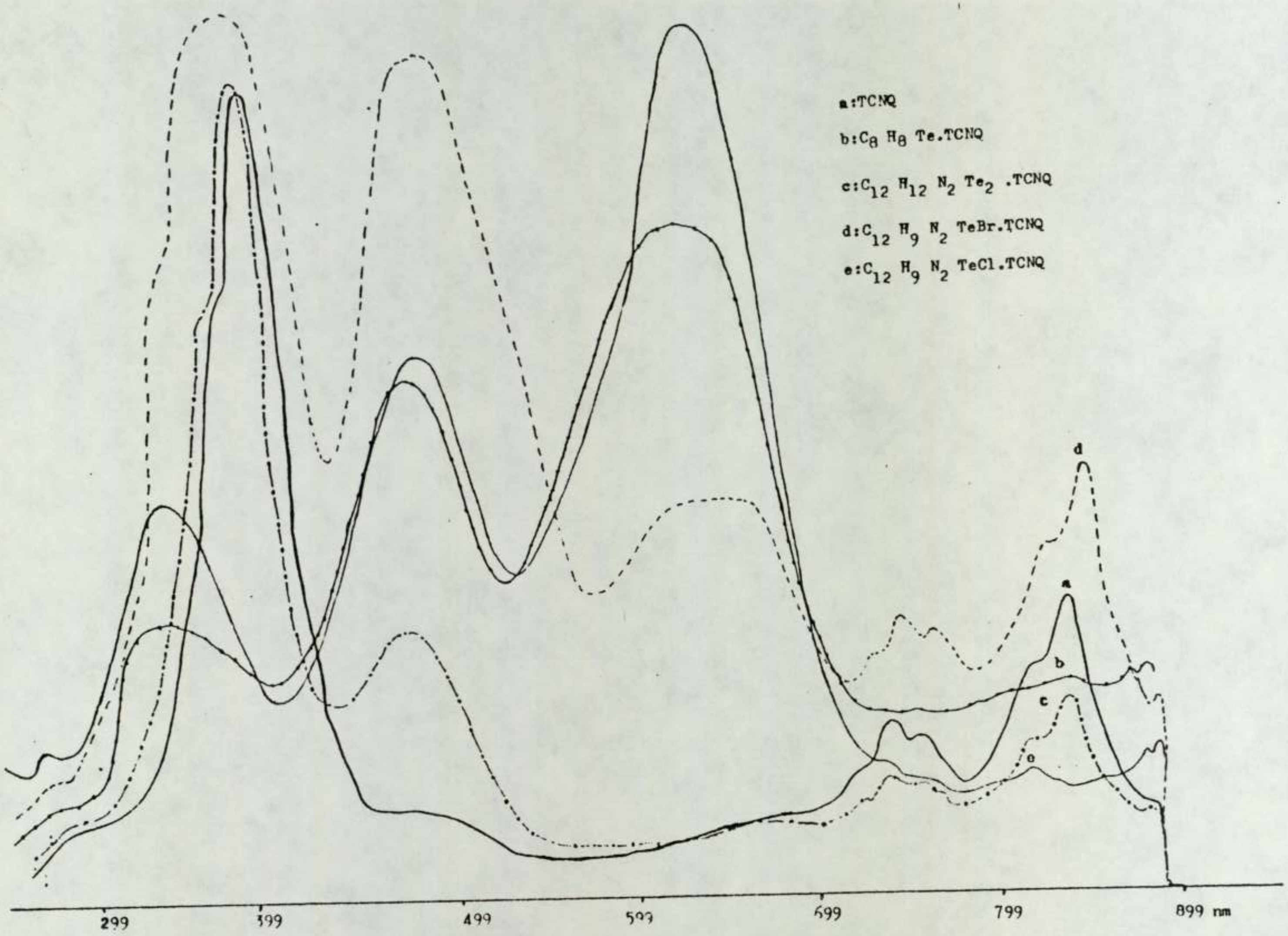


Figure 3 Electronic spectra of TCNQ complexes in acetonitrile

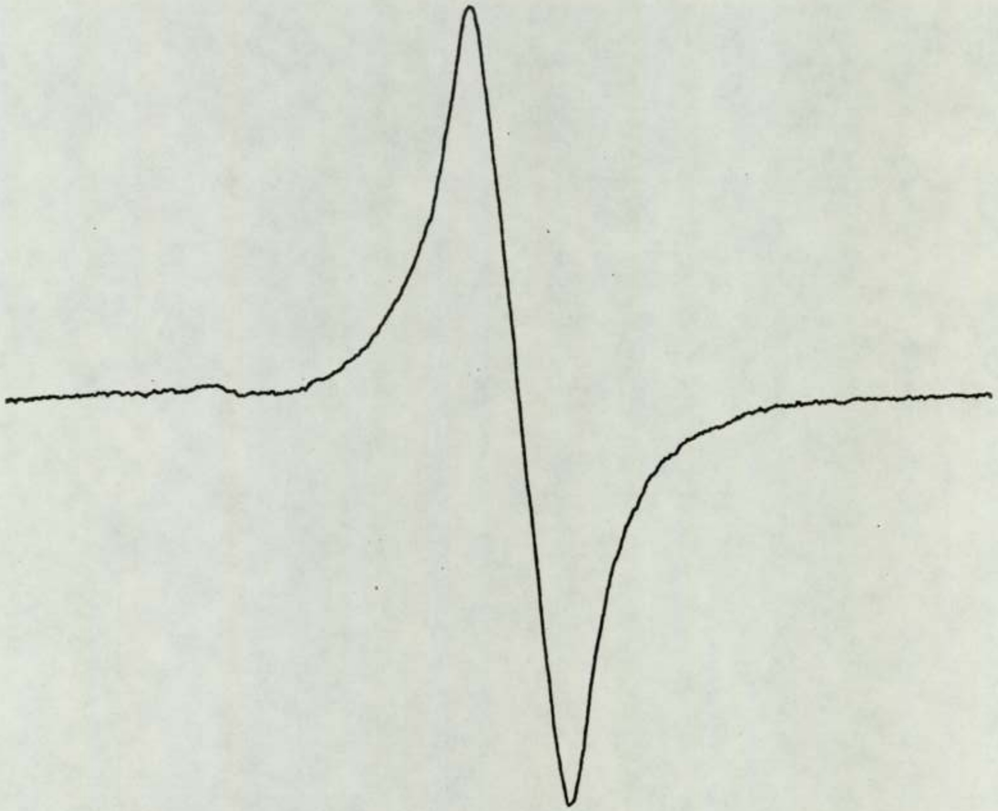


Figure 4 ESR absorption of $C_{13}H_9N_2TeCl.TCNQ$ complex at room temperature

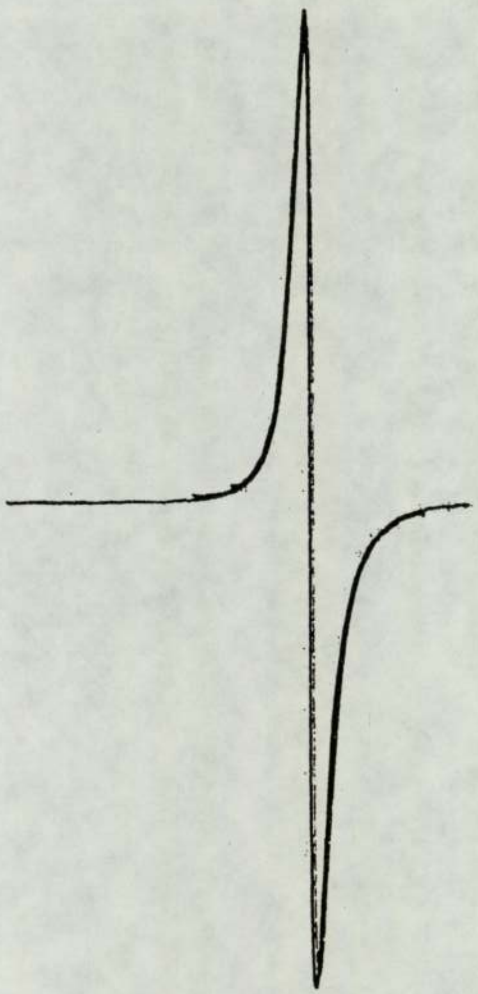


Figure 5 ESR spectrum of $C_{12}H_9N_2TeBr{\cdot}TCNQ$ complex at room temperature

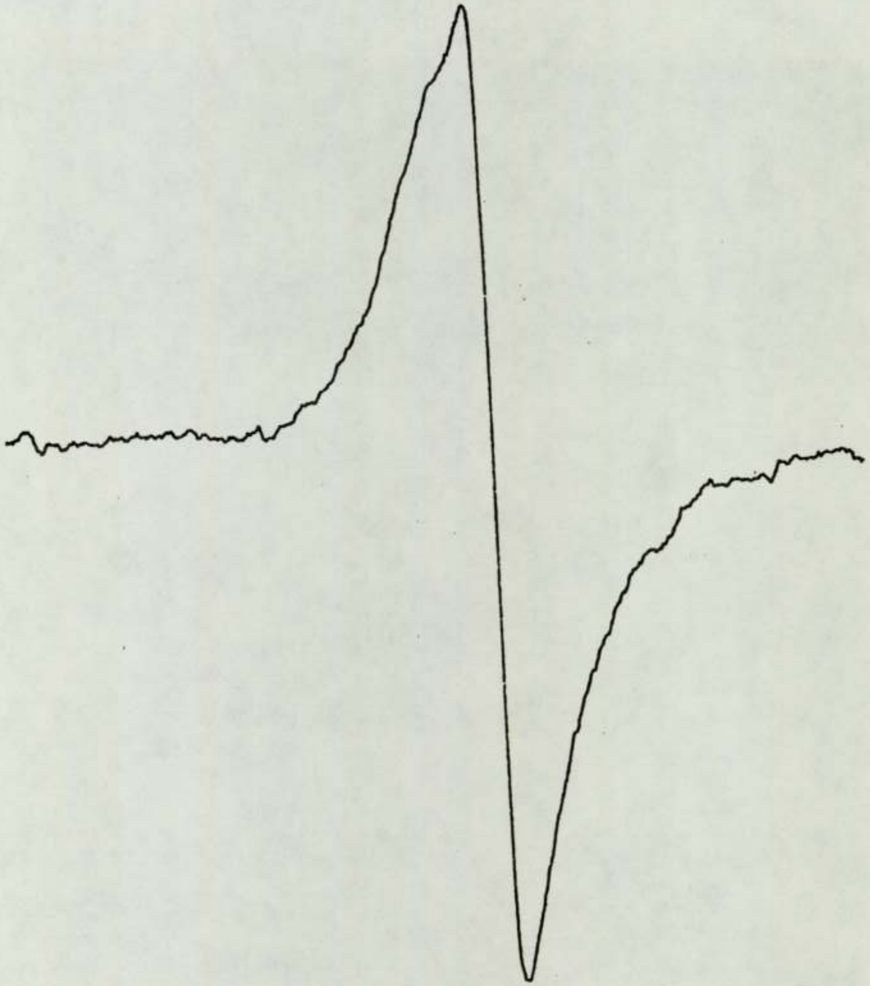


Figure 6 ESR spectrum of $C_8H_8Te.TCNQ$ complex at room temperature

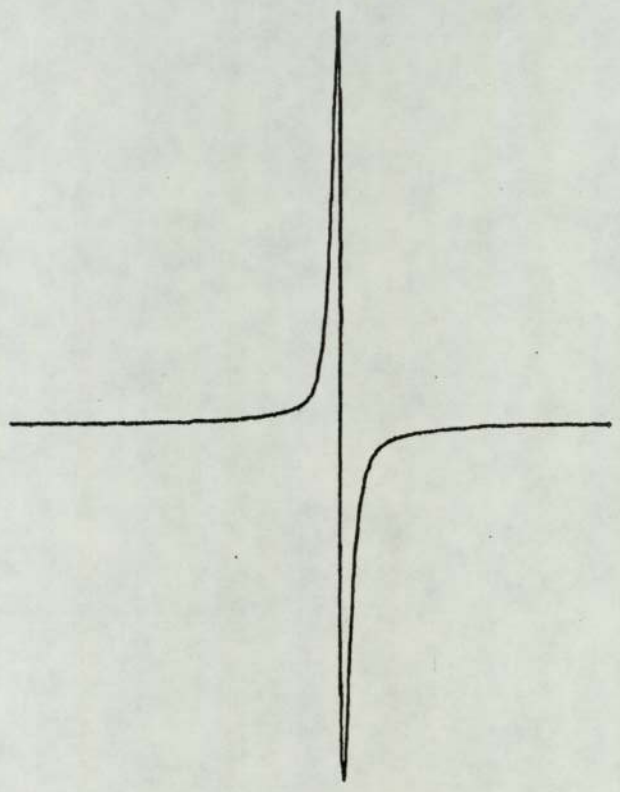


Figure 7 ESR spectrum of $C_{12}H_{12}N_2Te_2TCNQ$ complex at room temperature

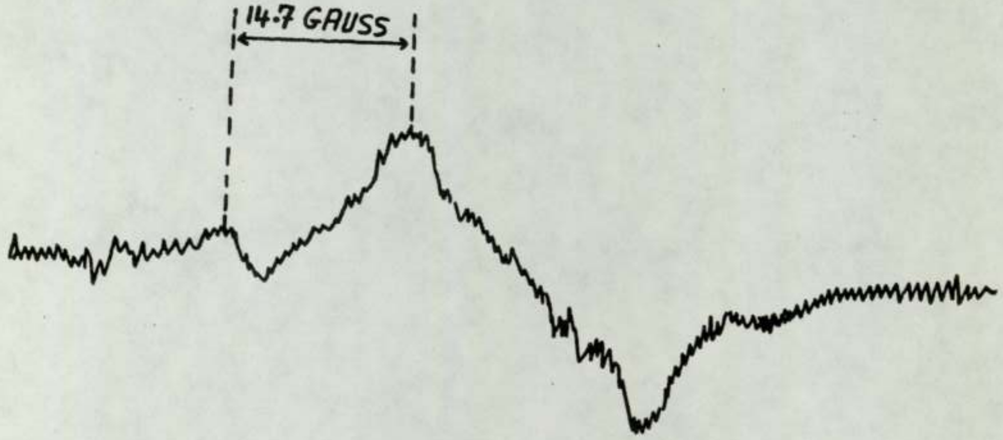


Fig. 8 ESR spectrum of $C_{12}H_{12}N_2TeCl.TCNQ$ complex in acetonitrile solution at room temperature. The N^{14} hyperfine splitting is about 14.7 gauss.

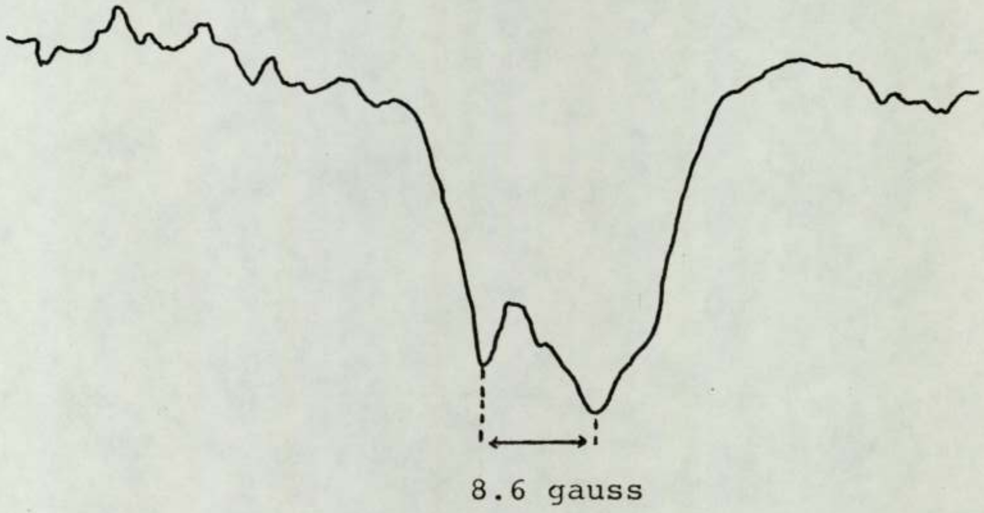


Figure 9 ESR spectrum of $C_8H_8Te.TCNQ$ complex in acetonitrile solution

$g = 2.0014$

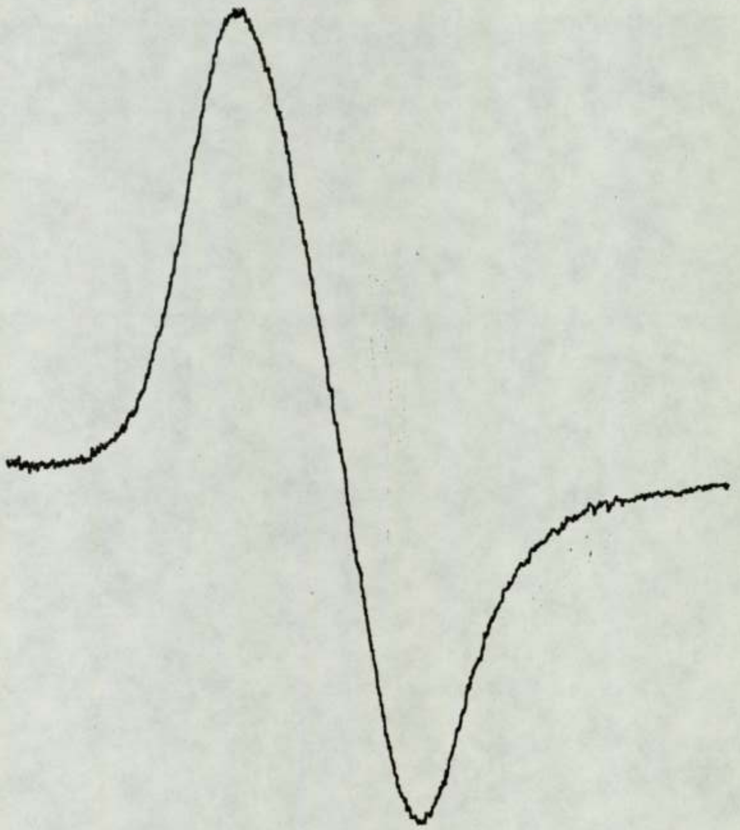


Figure 10 ESR spectrum of $C_{12}H_9N_2TeBr.TCNQ$ complex in acetonitrile solution in room temperature

5.(iii). DISCUSSION

5.(iii)a. Diarylditelluride-Copper (I) and Mercury (II) Complexes

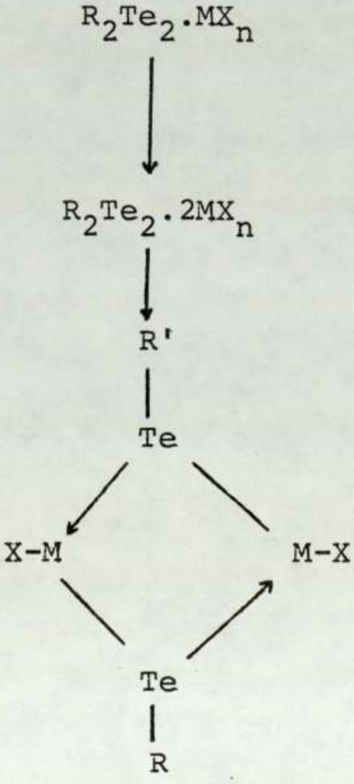
Although cleavage of Te-Te bonds in reactions of diarylditellurides with transition metal substrates to give bridging or terminal TeR^- ligands is an established reaction for these derivatives, they can also coordinate to metals with this bond intact. Simple diarylditelluride complexes with copper (I) halides and mercury (II) halides were reported (28,29,31) in which Te-Te bonds remain intact. The ^{125}Te Mössbauer spectra of $R_2Te_2.CuX$ indicate that both tellurium atoms are weakly coordinated to copper (I), while those of $R_2Te_2.HgX_2$ indicate that there is only one distinct tellurium site, and that the tellurium atom is trigonally coordinated.

As was previously mentioned, the existence of unsymmetrical diarylditellurides in organic solvents, such as benzene was confirmed. It was hoped in this study to utilize a Lewis acid (CuX or HgX_2) to complex preferentially the unsymmetrical diarylditelluride, RTe-TeR'. Therefore, a mixture of Ph_2Te_2 and $(p\text{-}EtO.C_6H_4)_2Te_2$ was reacted with CuX and HgX_2 where X = Cl, Br according to the literature.

The good elemental analyses of these complexes, table 1, suggest the following empirical formulae; $RR'Te_2.2CuX$, $RR'Te_2.2HgX_2$ and $[(RTeHgX)(R'TeHgX)]$ (where R = Ph and R' = $(p\text{-}EtO.C_6H_4)$). The cleavage of Te-Te in in some mercuric halide complexes to give a product with PhTe and p-EtO.C_6H_4Te bridges, may be attributed to the use of more forcing reaction conditions and using ethanol as solvent which promotes radical formation (see chapter 4).

In contrast Davies$^{(29)}$ reported that the reaction of an ethereal solution diarylditelluride with an acetonitrile solution of CuCl under nitrogen gave an orange-red 1:1 complex of general formula R_2Te_2.CuX. In this work, the reaction of a mixture of diarylditelluride with CuX in propionitrile instead of acetonitrile affords a complex of stoichiometry RR'Te_2.2CuX.

The formation of the complexes between the mixture of diarylditellurides (Lewis base) and metal halides (Lewis acid) may be illustrated by the following scheme:



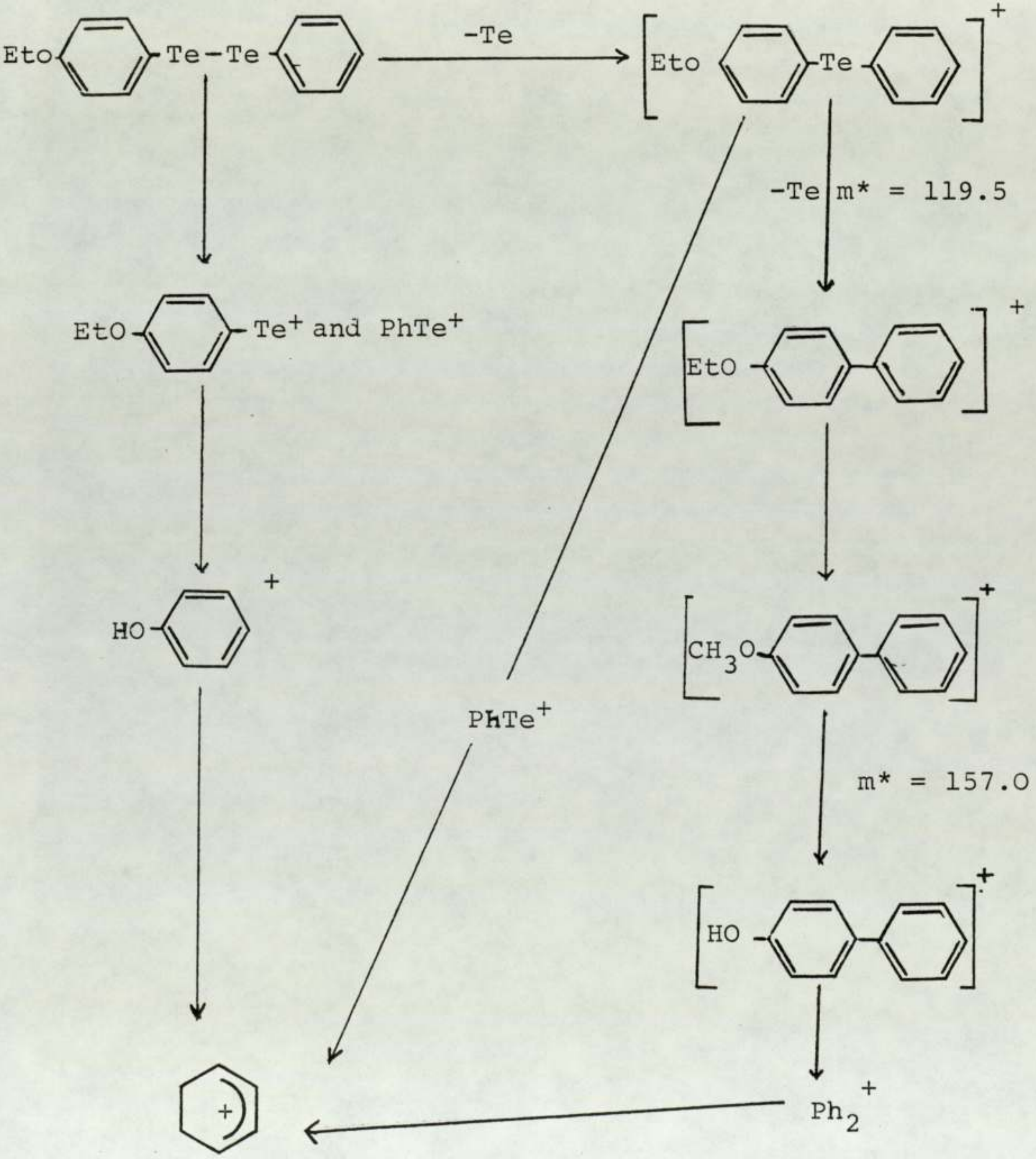
From the above scheme it seems that when a metal halide reacts with a ditelluride a 1:1 complex ratio is obtained. By changing the solvent, a further mole of metal halide reacts with the corresponding ditelluride and 1:2 complexes are obtained. In addition to changing the solvent, if more forcing conditions are subsequently employed, complexes with the bridging bonding mode are formed. In our laboratory there are analogous reactions of diarylditellurides with TCNQ and I_2 which also gave 1:2 complexes. Thus the 1:2 ratio is quite common in the reaction of ditellurides.

In the mass spectra of $RR'Te_2.2CuX$ (where R = Ph, $R' = p\text{-}EtO.C_6H_4$ and X = Cl, Br), tables 3 and 4, some ions were observed, which indicate the presence of the parent ions $Ph_2Te_2^+$, $(p\text{-}EtO.C_6H_4)_2Te_2^+$ and $(PhTe\text{-}Te\text{-}C_6H_4.OEt)^+$. Also, as well as Ph_2Te^+, $(p\text{-}EtO.C_6H_4)_2Te^+$, ions of the mixed telluride are noted, $(phTeC_6H_4.OEt)^+$, which arise from the elimination of one tellurium atom from the corresponding ditelluride. These observations confirm the existence of unsymmetrical ditellurides in the complexes. Furthermore, the presence of Ph_2^+, $(p\text{-}EtO.C_6H_4)_2^+$ ions, in addition to $(Ph\text{-}C_6H_4.OEt)^+$ ion, were observed. Some stages are supported by the observation of metastable ions for both symmetrical and unsymmetrical species.

Analogous results were obtained from the mass spectra of $RR'Te_2.2HgX_2$ complexes, table 5 and 6 which undergo the same fragmentation pattern.

It is possible, therefore, that the existence of $RR'Te_2$ may arise from the redistribution reaction which was also noticed by Dance(16).

So if unsymmetrical ditellurides are synthesised the probable fragmentation pattern is as follows:



However, the evidence for the step of $R\text{-}Te^{+}\text{-}R \longrightarrow R\text{-}R^{+}$ was supported by the metastable ions at m/e = 157.7 and m/e = 83.5 of $(p\text{-}EtO.C_6H_4)_2Te_2$ and Ph_2Te_2 respectively and that of $(CH_3O.C_6H_4)_2^{+} \longrightarrow (HO.C_7H_4)_2^{+}$ was supported by the metastable ion at m/e = 161.5 of bis(p-ethoxyphenyl)ditelluride.

The infrared spectra of cuprous chloride and mercuric chloride with mixtures of diarylditelluride in region 4000-250 cm^{-1} are shown in figures 1 and 2 and are very similar. By comparison of the infrared spectra of the free ligands (Ph_2Te_2 and $(p\text{-}EtO.C_6H_4)_2Te_2$) and the complexes, it is noted that the coordination does not affect the internal modes of the free ligands on complexation. The infrared spectra confirmed the presence of the Ph and $(p\text{-}EtO.C_6H_4)$ groups, which do not preclude a mixture of Ph_2Te_2 and $(p\text{-}EtO.C_6H_4)_2Te_2$ complexes. Thus, no conclusions may be drawn from infrared spectra as to the unique existence of $RR'Te_2$.

The Raman spectra of $(p\text{-}EtO.C_6H_4)_2Te_2.2CuCl$ and $(p\text{-}EtO.C_6H_4)_2Te_2.2CuBr$ complexes, table 7, show bands at 186, 187, 156 and 162 cm^{-1} which are of interest. Two assignments need to be considered, the copper-tellurium and tellurium-tellurium stretching frequencies. In fact $\nu(Te\text{-}Te)$ for $(p\text{-}EtO.C_6H_4)_2Te_2$ has been reliably assigned at 186 cm^{-1} from Raman spectra(15). This may lead to the assumption that the medium bands at 156 and 162 cm^{-1} are due to $\nu(Cu\text{-}Te)$.

However, Davies and McWhinnie(29) assigned bands at at 170 cm^{-1} ($Ph_2Te_2.CuCl$) and 180 cm^{-1} ($Et_2Te_2.CuCl$) to both ν(Cu-Te) and ν(Te-Te) and explained that the tellurium-tellurium mode is activated on coordination and coincides with the ν(Cu-Te) band.

Unfortunately, Raman spectroscopic data of $Ph-Te-Te-C_6H_4OEt.2CuX$ could not be obtained since these compounds decomposed immediately when placed in the laser beam even using spinning cell. This may be because they strongly absorbed the energy at 6471 Å . However, only the very strong band at 169 cm^{-1} for these complexes was obtained.

Raman spectra of $Ph_2Te_2.2HgCl_2$, $(p\ EtO.C_6H_4)_2Te_2.2HgCl_2$ and $PhTe-TeC_6H_4OEt.2HgCl_2$ complexes, tables 8 and 9, contain intense peaks at 120, 110 and 119 cm^{-1} respectively. Dance and Jones$^{(31)}$ have assigned ν(Te-Hg) at Δ = 100-140 cm^{-1} in a series of organotellurium-mercury (II) halide complexes.

The strong band of the tellurium-tellurium stretching vibration could not be observed. This may be explained by the suggestion that stronger co-ordination shifts ν(Te-Te) to lower frequency, possibly overlapping with intense ν(Hg-Te), and it is possible that the Te-Te bond remains intact within the complex. Dance and Jones$^{(31)}$ showed that the ^{125}Te Mössbauer parameters indicate that there is only one distinct tellurium site, and that the tellurium is trigonally coordinated in ditelluride-mercury (II) complexes.

Therefore, the R-Te-Te-R' molecule can be considered to be either strongly bonded to mercuric halide, or cleavage of Te-Te bond takes place to give tellurol derivative of RTeHgX and R'TeHgX groups. It is felt to be probable that unsymmetrical ditelluride-mercuric halides are formed, in which both Te-Te remain essentially similar to those in free ditelluride.

The results can be summarised as follows. The good analytical data give an empirical formula of $RR'Te_2.2MXn$. From the infrared spectra the presence of the appropriate R and R' groups are confirmed but they do not preclude a mixture of the R_2Te_2 and R'_2Te_2 complexes. Fragments due to ${R_2Te_2}^+$, ${R'_2Te_2}^+$ are observed in all the mass spectra of the complexes. The Raman data give reasonable evidence for ν(Te-Te) and ν(Te-M) (where M = Cu, Hg).

It may therefore be concluded that unsymmetrical diarylditelluride-mercury (II) and copper (I) halide complexes, $RR'Te_2.2MX_n$, have been synthesised, but, absolutely positive evidence cannot be provided.

5.(iii)b. Charge Transfer Complexes of Organotellurium Compounds with TCNQ :

TCNQ is a well known strong electron acceptor which forms stable crystalline anion radical salts of the $M^{+}TCNQ^{-\cdot}$ type and complex salts of $(M^{+})_2(TCNQ)_3^{--\cdot}$ and $M^{+}(TCNQ)^{-\cdot}$, which contain the formally neutral TCNQ and the anion radical $TCNQ^{-\cdot}$ (124).

The purpose of the present work is to clarify the ability of organotellurium (II) compounds to act as electron donors in reaction with TCNQ.

Tellurium (II)-TCNQ complexes were prepared by a direct reaction of TCNQ and tellurium (II) compounds in dry acetonitrile where blue-black and red-black crystals are obtained.

The absorption spectra of neutral TCNQ and anion radical $TCNQ^{\bar{\cdot}}$ in acetonitrile between 899-299 nm are illustrated in figure 3. The absorptions at 841 and 474 nm are assigned to TCNQ(124,125). The complex salts of TCNQ have been found to be completely dissociated(124,125), thus giving spectra consisting of these independent TCNQ and $TCNQ^{\bar{\cdot}}$ molecules. The electronic absorption spectra show a similarity of the neutral TCNQ and the anion radical $TCNQ^{\bar{\cdot}}$, figure 3.

The electronic absorption spectra have peaks centred on 841, 749 and 474 nm which are typical of the TCNQ molecule. Furthermore, new bands at 629 nm for C_8H_8Te, $C_{12}H_{12}N_2Te_2$ and $C_{12}H_9N_2TeCl$-TCNQ complexes and at 646 nm for $C_{12}H_9N_2TeBr$-TCNQ complex are observed. These new bands are very strong in TCNQ complexes of C_8H_8Te, $C_{12}H_9N_2TeCl$ and $C_{12}H_9N_2TeBr$ and weak in the $C_{12}H_{12}N_2Te_2$.TCNQ complex, figure 3. This may be because of the planar structure of (phenylazophenyl)tellurium chloride which has been determined by X-ray crystallography(6). Moreover, it is known that there is a positive π—interaction between tellurium and the chelate ring in the tellurenyl chloride which may lead to bond formation between the tellurenyl halide (Donor) and TCNQ (Acceptor). One would think that the high conductivity is associated with crystal structures in which the planar molecules are packed face-to-face, with segregated stacks of cations and TCNQ's. The π-overlap and charge transfer interaction between adjacent molecules in the stacking direction are strong, causing their unpaired electrons to be partially delocalized along these one-dimensional molecular stacks and enabling them to conduct in that direction. These new strong bands, figure 3, correspond to the planar structure of tellurenyl halides and C_8H_8Te(71) and to the charge transfer transition between anion radical and tellurium (II) compounds.

The electronic absorption specturm of $C_{12}H_{12}N_2Te_2$.TCNQ in acetonitrile is essentially the same as that of the tellurenyl halides and C_8H_8Te complexes. The spectrum, shown in figure 3, has a weak peak at 629 nm compared with the other complexes.

The infrared spectra of the TCNQ-tellurium (II) complexes are compared with the spectra of the component alone; the spectra of the complexes are quite similar to a superposition of the spectra of the components. There are slight shifts in frequency and some alterations of the intensity which reflect the molecular association. There is a change in the C≡N frequency. However, it appears that no strong interactions are involved; no intermolecular bonds have been greatly changed during the formation of the complexes.

A complete electron transfer can take place in the ground state for molecules with great donating and accepting power. The system, then, is paramagnetic and to show free radical behaviour; ESR is observed in such systems and indicates the presence of unpaired electrons in such crystalline materials(126).

Strong, and in general sharp, ESR signals in solid tellurium (II)-TCNQ complexes were detected, figures 4-7. The g-value of ESR absorption by unpaired electron in $C_{12}H_9N_2TeCl.TCNQ$ is 2.0047 and for the corresponding complex $C_{12}H_9N_2TeBr.TCNQ$ is 2.0042, while for $C_8H_8Te.TCNQ$ and $C_{12}H_{12}N_2Te_2.TCNQ$ are 2.0035 and 2.0027 respectively. The g-value measurements, which agree with values reported in the literature, are close to the free electron value (2.0023)(126). The ESR spectra obtained for solid tellurium (II)-TCNQ complexes do not exhibit hyperfine structures (figures 4-7).

The ESR spectra of tellurium (II)-TCNQ complexes in acetonitrile solution are shown in figures 8-10. The g-values of $C_{12}H_9N_2TeCl$, $C_{12}H_9N_2TeBr$ and C_8H_8Te complexes of TCNQ are 2.0200, 2.0216 and 2.0014 respectively. The hyperfine structure could be seen only in $C_{12}H_9N_2TeCl$-TCNQ complex, figure 8, which shows three peaks with a splitting constant of 14.78 gauss. In figure 9, the sample shows two peaks of a splitting constant of 8.6 gauss. The appearance of the hyperfine structure of 3 or 2 peaks in acetonitrile solution may be due to the weak association of the TCNQ radical with the organotellurium molecule. The ESR spectra of these complexes in acetonitrile are weaker than in the solid state.

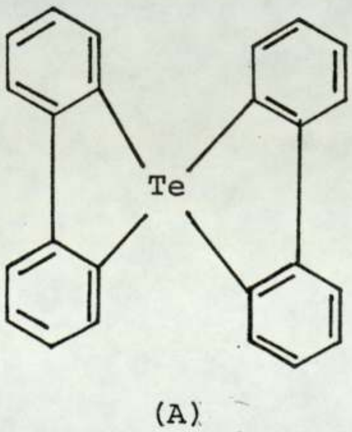
More extensive work is being carried out in our group to synthesise new classes of organotellurium-TCNQ complexes and to study the ability of various classes of organotellurium compounds to act as a strong electron donors.

CHAPTER VI

TETRAORGANOTELLURIUM (IV) COMPOUNDS

6.(i) INTRODUCTION

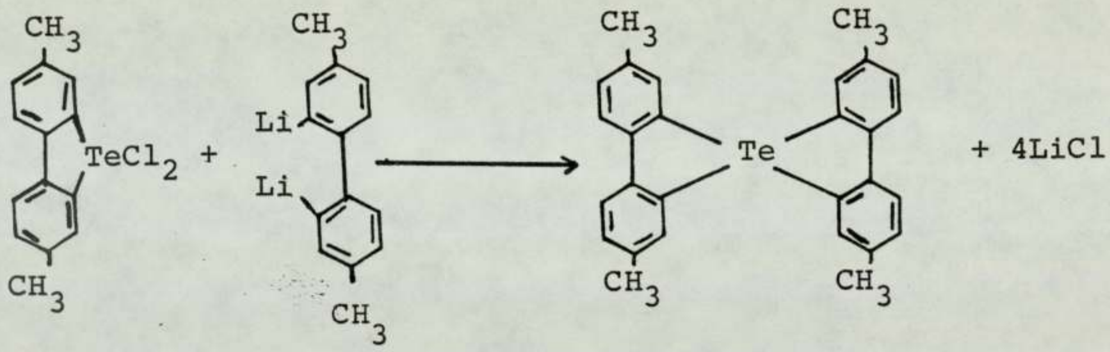
A few examples of tetraorganotellurium compounds are known. Marquardt and Michaelis (127) in 1888 made an unsuccessful attempt to prepare a tetraorganyltellurium compound by reaction of tellurium tetrachloride and diethyl zinc and they obtained only triethyltelluronium chloride. Wittig and Fritz (128) succeeded in preparing tetraphenyltellurium in 1952. They synthesised this compound from tellurium tetrachloride and an excees of phenyl lithium as yellow crystals, which melted at 104-6°C with decomposition. This compound can also be prepared from the reaction of triphenyltelluronium chloride or diphenyltellurium dichloride with an excess of phenyl lithium. The reactions were carried out in anhydrous ether under an inert atmosphere of nitrogen. Hellwinkel and Fahrbach (129) reacted hexamethoxy tellurium, tetramethoxy tellurium and tellurium tetrachloride with 2,2'-biphenylylene dilithium and isolated bis(2,2'-biphenylylene) tellurium (A) in yields ranging from 40-55 percent.



(A)

This compound, which crystallised as yellow needles and melted at 214°C, is much more stable than tetraphenyltellurium. The same authors reported in later publications the preparation of bis(2,2'-biphenylylene)tellurium (A) by new routes in acceptable yields(39,130).

Bis(4,4'-dimethyl-2,2'-biphenylylene)tellurium was prepared according to the following equation in 48 per cent yield(130).



Nefedou(131) and Wheeler(132) obtained ^{125m}Te-tetraphenyltellurium by β-decay of ^{125}Sb in $Sb(C_6H_5)_5$ and $(C_6H_5)_4SbCl$. Tetrakis(pentafluorophenyl)tellurium which decomposed at 210°C, was the product of the reaction between tellurium tetrachloride and pentafluoroPhenyllithium as reported by Cohen and coworkers(133).

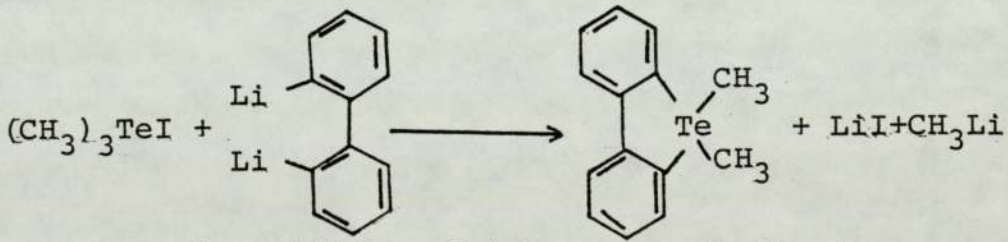
Tetraalkyl and dialkyldiaryltellurium compounds are thermally unstable and have not yet been isolated. Hellwinkel and Fahrbach(39) showed that these compounds exist in solution. Tetraalkyltellurium compounds have been prepared by the alkylation of tellurium tetrachloride and trialkyltellurorium iodides with lithioalkanes:

$TeCl_4 + 4RLi \longrightarrow R_4Te + 4LiCl$

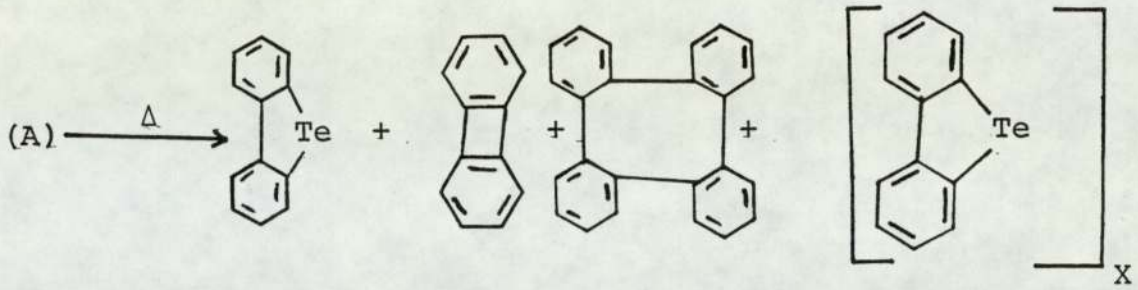
$R_3TeI + RLi \longrightarrow R_4Te + LiI$

(where R = CH_3, C_4H_9)

Dimethyl-2,2'-biphenylylene tellurium was prepared from the reaciton between trimethyltellurorium iodide and 2,2'-biphenylylene dilithium. The formation of this compound requires an exchange of methyl group, which is removed as methyl lithium, from an aromatic group.



The thermal stability of tetraorganyltellurium compounds increases in the series alkyl, phenyl, 2,2'-biphenylylene. The tetraalkyl derivatives decompose at room temperature while tetraphenyltellurium is stable to 115°C. Cohen and his group(132) have shown that tetrakis(pentafluorophenyl) tellurium produced the respective telluride and bis(pentafluorophenyl) when heated in a sealed tube at 200-220°C. Bis(2,2'-biphenylylene)tellurium remains largely unchanged when heated to 210°C. At 260°C, in a vacuum, decomposition takes place according to the following reaction:



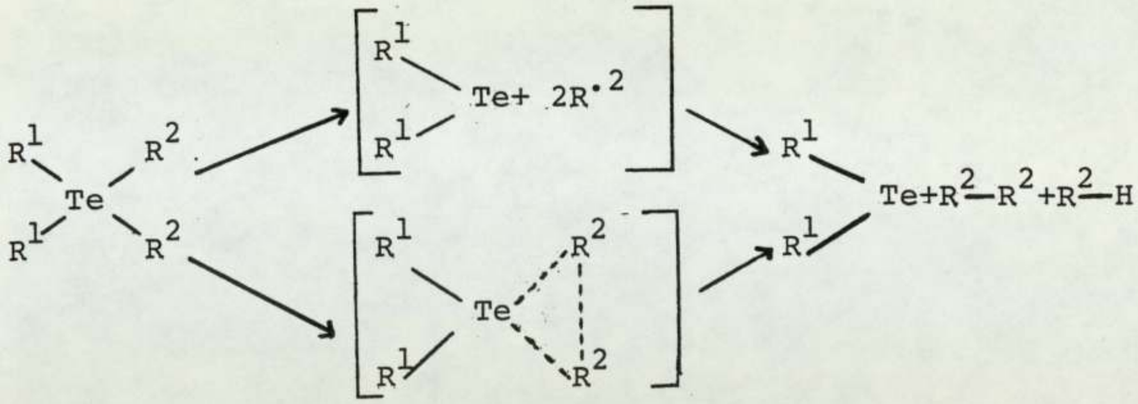
+ higher polyphenylylene compounds.

The corresponding 4-methyl substituted derivative behaves similarly.

Barton$^{(134)}$ has investigated the mechanism of the thermal decomposition of tetraaryltellurium under a variety of conditions. Tetraphenyltellurium decomposed at 140°C in vacuo in a sealed tube to diphenyltelluride (92%), biphenyl (89%) and benzene (10%). Similar decomposition experiments under a nitrogen atmosphere but at 80°C in the presence of toluene, triethylsilane, furan or styrene gave similar results indicating little radical trapping. Only a trace of polymer was observed during the decomposition of Ph_4Te in styrene.

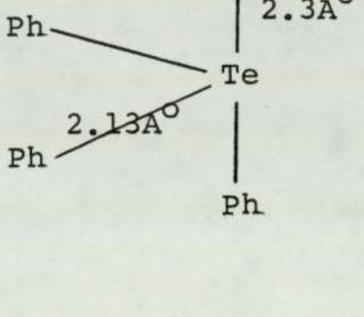
Tetrakis(4-methylphenyl)tellurium likewise decomposed on melting (124-127°C) to give bis(4-methylphenyl)telluride and 4,4'-dimethylbiphenyl with only a small amount of toluene.

These results indicated that radicals, which can be trapped, were not formed during the decomposition reaction. The decomposition of $(C_6H_5)_4Te/(4\text{-}CH_3\text{-}C_6H_4)_4Te$ and $(C_6H_5)_4Te/(C_6D_5)_4Te$ yielded large quantities of mixed biaryl and unsymmetric diaryltellurides.



Barton, Glover and Ley(134) concluded "that tetraaryltellurium compounds exchange ligands by a fast non-radical process prior to decomposition to diaryltellurium and biaryl. The decomposition process itself is concerted, does not involve radicals, and represents an interesting procedure for the formation of carbon-carbon bonds".

The X-ray crystallography of $(C_6H_5)_4Te.C_6H_6$(135) showed that a trigonal bipyramidal arrangement of the four phenyl groups around the tellurium atom took place, as shown in the following scheme:



No bond angles were given. Only bond lengths for the Te-C axial as 2.3A° and Te-C equatorial as 2.13A° were given. This structure was in fact similar to that found for diphenyltellurium dibromide(136). Hellwinkel and Fahbrach(130) investigated the ^{1}H NMR spectrum of bis(4,4-dimethyl-2,2-biphenylylene) tellurium. The compound showed only one peak for the methyl hydrogen atoms in the range -55°C to room temperature. This result is inconsistent with a trigonal bipyramidal structure. The authors proposed a rapid interconversion of the trigonal bipyramid into another trigonal bipyramid as an explanation for the equivalence of the methyl groups, those formerly in axial positions then occupying equatorial sites. A tetrahedral arrangement with a stereochemically inactive lone electron pair was also mentioned as a possible cause for the equivalence of the methyl groups.

As was seen in chapter three, the formation of a tetraorganotellurium compound through the thermal decompositon of $C_{38}H_{33}BTe$ and $C_{33}H_{31}BTe$ was observed by mass spectrometry.

The main objective of this work was to attempt to prepare new classes of tetraorganotellurium compound by using sodium tetraphenylborate as a phenylation agent.

6.(ii) EXPERIMENTAL

Reaction of 1,1-diiodo-3,4-benzo-1-telluracyclopentane with sodium tetraphenylborate:

A new rapid and facile reaction for the phenylation of tellurium (IV) using sodium tetraphenylborate appears to provide a general method for the synthesis of tri- and tetraorganotellurium (IV) and is as follows:

A mixture of 1,1-diiodo-3,4-benzo-1-telluracyclopentane (2.42 g; 0.002 mol.) with $NaBPh_4$ (3.42 g; 0.01 mol.) and dry ethanol was placed into 250 ml round-bottomed flask equipped with magnetic stirring bar and condenser. The reaction mixture was heated to reflux with stirring for 3 hours, after which the hot solution was filtered and the crystals of 1-phenyl-3,4-benzo-1-telluracyclopentane tetraphenylborate collected (m.p. 184°C (d.)).

The solution was evaporated using vacuum at room temperature. White crystals of 1,1'-diphenyl-3,4-benzo-1-telluracyclopentane were obtained in reasonable yield, washed with a small amount of water and methanol and dried in vacuum over P_4O_{10}, m.p. 179°C (d.).

New Method for the Preparation of 1,1-diiodo-1-telluracyclopentane

The preparation of 1,1-diiodo-1-telluracyclopentane has been reported(137,138). The earliest methods give poor yields and the procedure required close attention for long periods. The following new method was used to prepare this compound.

Excess of 1,4-dibromobutane (6.5g; 0.03 mol.), tellurium powder (2.55 0.02g-atom), excess of sodium iodide and 2-ethoxyethanol

(~100 ml.) were placed in an open beaker. The reaction mixture was heated gently with stirring. Gentle boiling afforded a heavy orange-red precipitate. After addition of 200 ml of deionised water to the cold mixture, which caused additional precipitation, the precipitate was collected by filtration, washed with water, rinsed with acetone, and air dried.

The filtrant giving a quantitative yield for 1,1-diiodo-1-telluracyclopentane of 90-95%. Recrystallization of the reaction product from 2-ethoxyethanol yielded an orange-red crystalline form which melted at 152°C. (Lit.(137,138) 149-150°C).

Found: C, 22.2; H, 3.70

$C_4H_8TeI_2$ requires: C, 22.2; H, 3.70

Reaction of 1,1'-diiodo-1-telluracyclopentane with sodium tetraphenylborate

To a solution of $C_4H_8TeI_2$ (4.37 g; 0.01 mol) in 25 ml of ethanol was added a solution of $NaBPh_4$ (6.84$_g$; 0.02 mol.) in ethanol. The resulting solution was refluxed for 7 hours. After 30 minutes, the reaction mixture contained a white precipitate. The hot solution was filtered and the white crystals of 1-phenyl-1-telluracyclopentane tetraphenylborate collected, washed with water and ethanol and recrystallised from water and DMF, m.p. 214°C(d).

Found: C, 70.1; H, 5.50

$C_{34}H_{33}BTe$ requires: C, 70.4; H, 5.70.

The solution was concentrated to dryness on a rotary evaporator. The resulting white powder was washed with a minimum amount of ethanol and dried over P_2O_5 in vacuo. m.p. 246°C (d).

Reaction of 1-methyl-1-iodo-3,4-benzo-1-telluracyclopentane with sodium tetraphenylborate

A mixture of 3.73g (0.01 mol.) of $C_9H_{11}TeI$ and 3.42g (0.01 mol) of $NaBPh_4$ and 2-ethoxyethanol (~100 ml) were placed into a 200 ml round-bottomed flask equipped with a magnetic stirring bar and a reflux condenser. The reaction mixture was heated to reflux under stirring for 8 hours. After cooling, the precipitated tellurium powder was filtered off. The filtrate afforded toluene, 3,4-benzo-1-telluracyclopentane and other products which could not be identified. G.L.C. determinations of toluene (Carbowax 20M on chromosorb W 80-100 mesh) were on Pye Unicam CDG chromatograph with F.I.D..

6.(iii). RESULTS

1. SOLUBILITY

The tetraorganotellurium compounds are soluble in DMSO, DMF, Acetone and slightly soluble in dichloromethane, nitrobenzene, chloroform and nitromethane.

2. CONDUCTIVITY MEASUREMENTS

The molar conductivity of each compound in dimethylsulphoxide (DMSO) and dimethylformamide (DMF) are shown in Table 1. Conductivity at various concentrations in DMSO and DMF were also measured, Figs 1 and 2.

3. INFRA-RED SPECTRA

The infra-red spectra of tetraorganotellurium and the corresponding telluronium salts in the range of 4000-200 cm^{-1} in CsI discs are shown in Figs. 3, 4, 5 and 6.

4. ^{1}H NMR SPECTRA

The ^{1}H NMR specta of $C_{38}H_{33}BTe$ and $C_{20}H_{18}Te$ were obtained in DMSO and are presented in Figs. 7 and 8.

5. MASS SEPCTRA

The mass spectra of $C_{16}H_{18}Te$ and $C_{34}H_{33}BTe$ were obtained in DMSO and are shown in Tables 2 and 3.

TABLE 1

The Elemental Analysis of Tetraorganotellurium Compounds

Compound	Found %		Requires%	
	C	H	C	H
$C_{20}H_{18}Te$	61.4	4.60	61.2	4.67
$C_{16}H_{18}Te$*	39.0	3.90	56.9	5.33

* Unsatisfactory elemental analysis was due to the decomposition of this compound in storage

TABLE 2

Molar Conductivities of Some Tetraorganotellurium Compounds

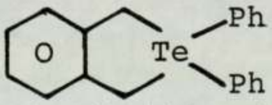
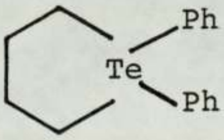
Compounds	Solvent/Molar Conductance $\text{moh}^{-1}\ \text{cm}^{-2}\ \text{mol}^{-1}$	
	DMSO	DMF
	18.98	42.05
	28.03	55.19

TABLE 3

Mass Spectra of $C_{16}H_{18}Te$ Relative to ^{130}Te

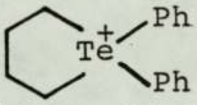
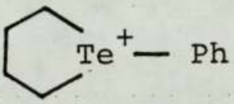
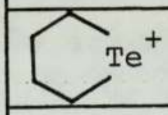
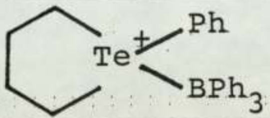
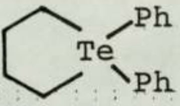
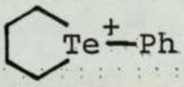
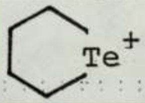
Ions	m/e	R.I.(%)
$Ph_2Te_2^+$	414	44
	340	51
Ph_2Te^+	284	23
	263	56
Ph Te^+	207	50.3
	186	29
Ph_2^+	154	100
Te^+	130	23
Ph^+	77	100
$C_4H_8^+$	56	100

TABLE 4

Mass Spectra of $C_{34}H_{33}BTe$ Relative to ^{130}Te

Ions	m/e	R.I. (%)
	505	9
$Ph_2Te_2^+$	414	100
	340	11
$(C_6H_5)_4B^+$	319	12.5
	263	Off scale
	186	100
$(C_6H_5)_3B^+$	242	Off scale
$PhTe^+$	207	Off scale
$B\ C_{12}H_{10}^+$	165	Off scale
$B\ C_{12}H_8^+$	163	Off scale
$B\ C_{10}H_6^+$	137	Off scale
Ph_2^+	154	Off scale
^{130}Te	130	Off scale
$B\ C_8H_6^+$	113	Off scale
Ph^+	77	Off scale
C_4H_8	56	Off scale

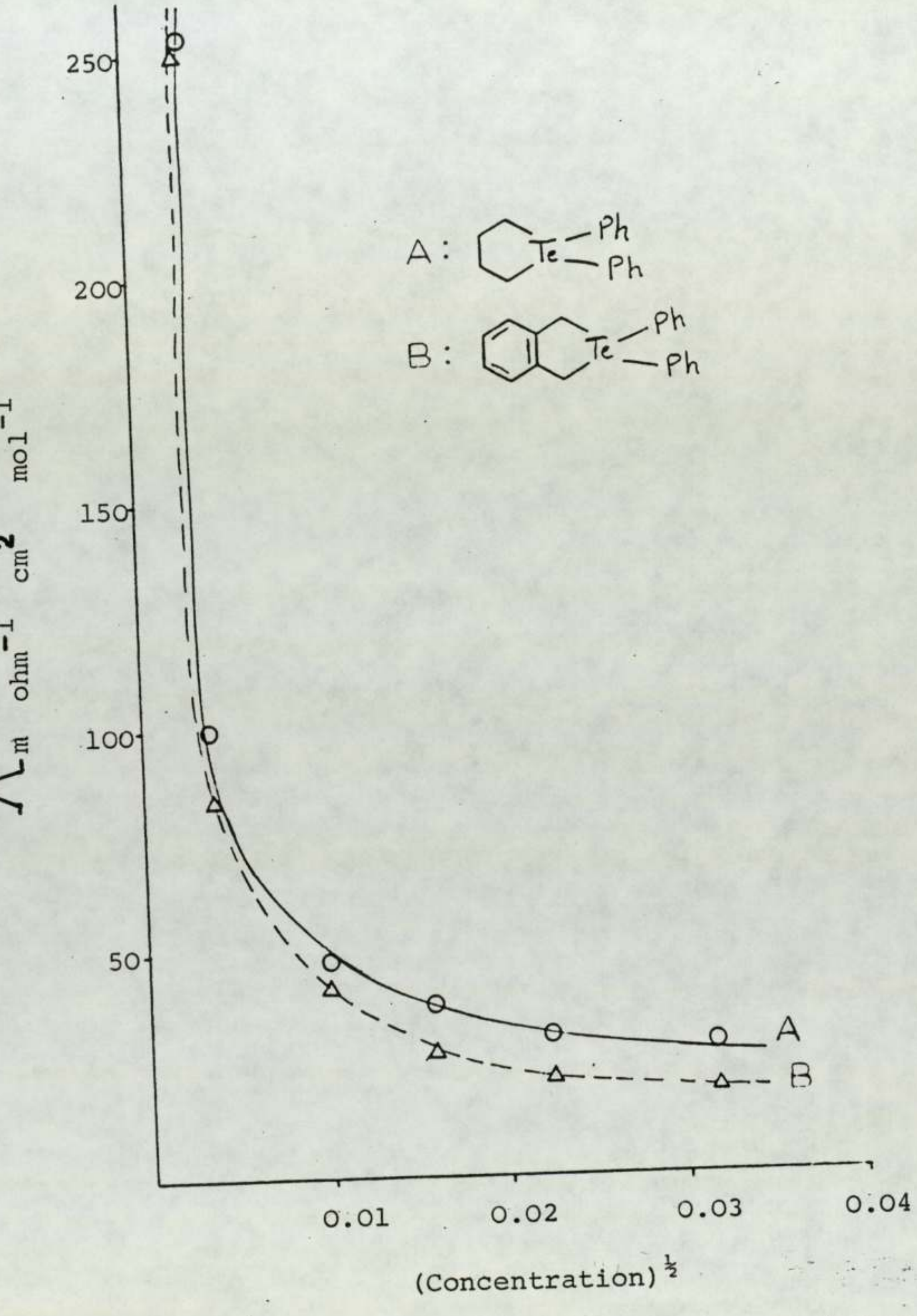


Figure 1 A plot of malor conductivity vs (concentration)

in DMSO for tetraorganotellurium

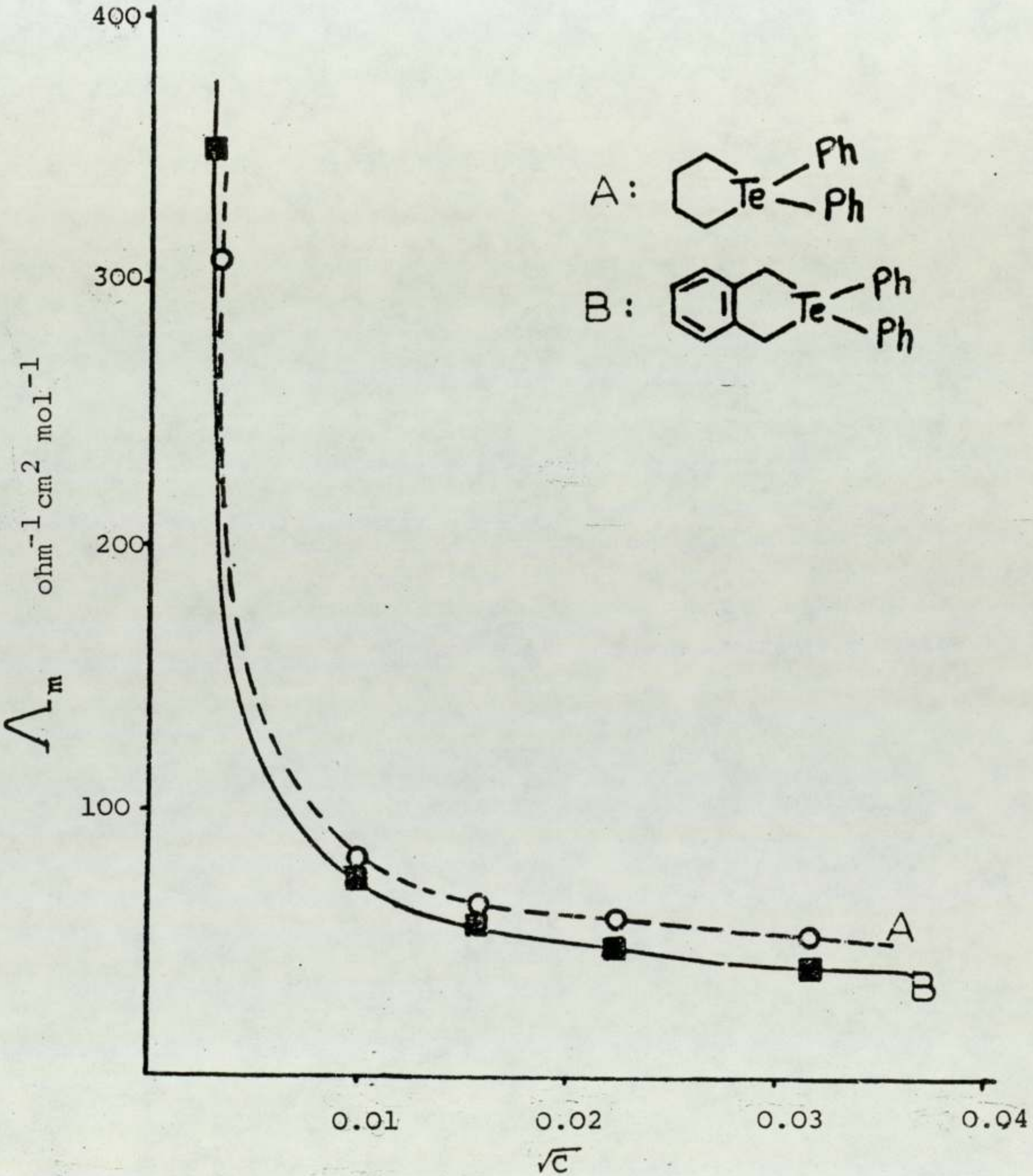
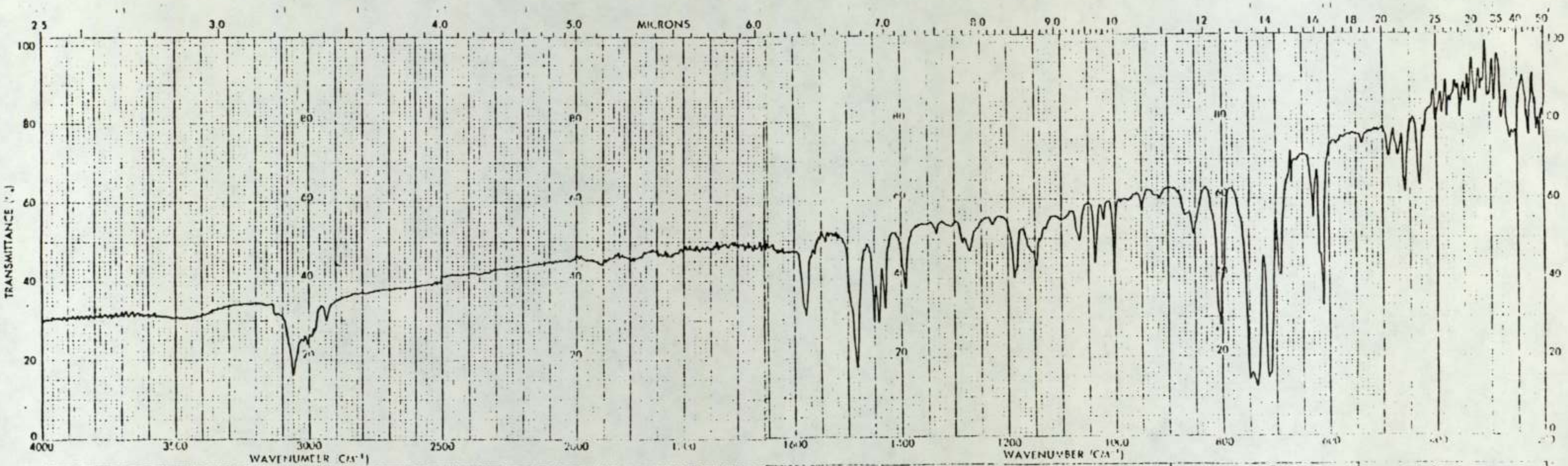


Figure 2 A plot of molar conductivity vs (concentration)$^{\frac{1}{2}}$ in DMF.



SAMPLE 82.
ORIGIN A.Z. Al-Rubaie.

SOLVENT CsI.
CONCENTRATION approx. 1.0%
CELL PATH 13 mm. dia. disc.
REFERENCE Air.

REMARKS

SCAN MODE Standard
SLIT N TIME CONSTANT
CHART No. STD-4367

OPERATOR V.H. Claxton.
DATE 12th August 1981
PEI No 1/341

Figure 3 Infra-red spectrum of 1,1'-diphenyl-3,4-benzo-1-telluracyclopentane

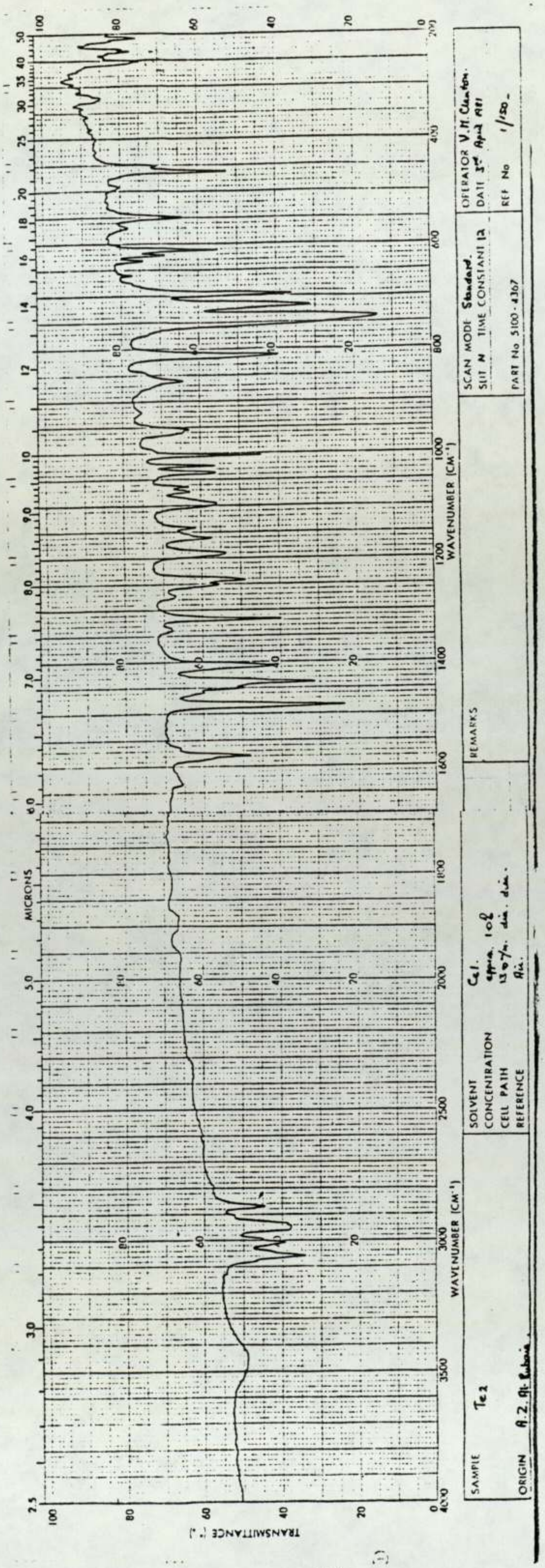
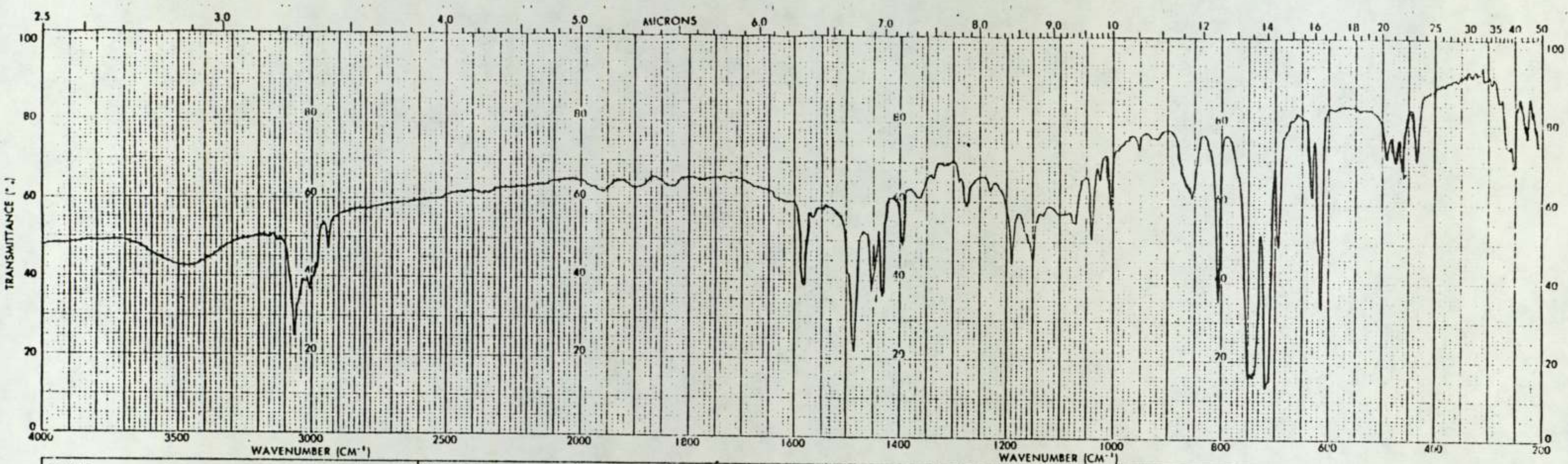


Figure 4 Infra-red spectrum for 1,1'-diphenyl-1-telluracyclopentane



SAMPLE B1

ORIGIN A. Z. Al-Rubaie.

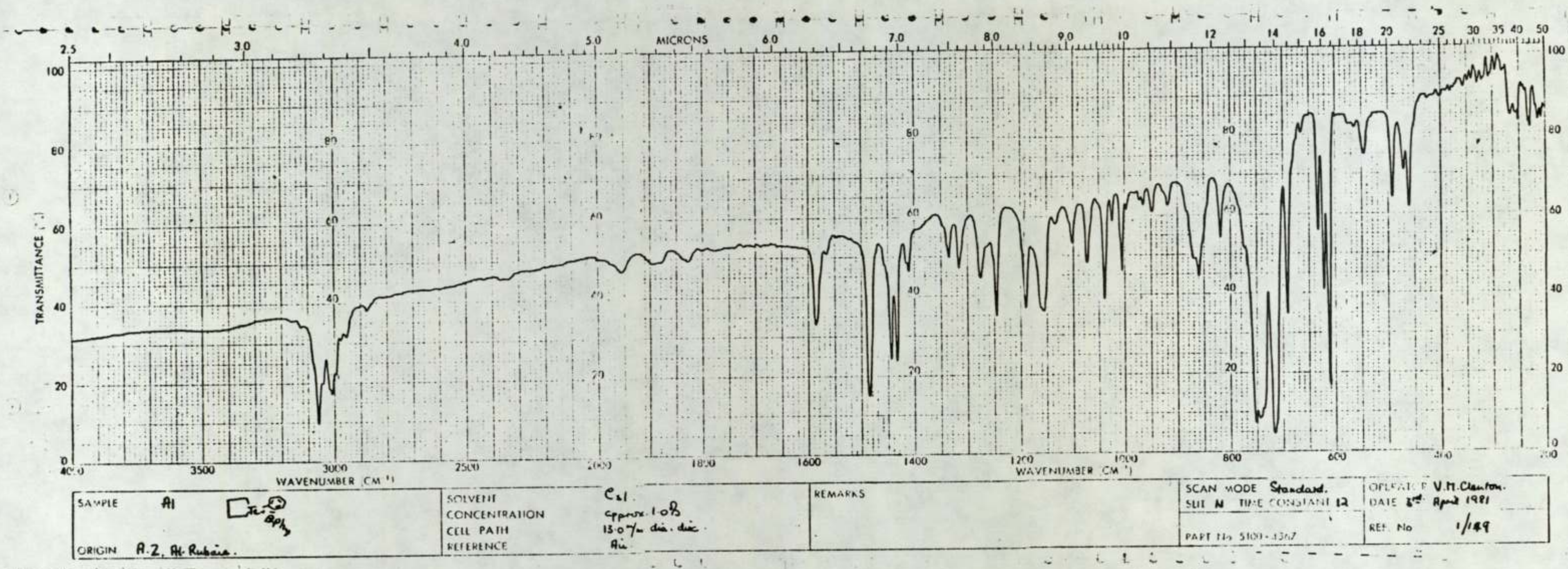
SOLVENT CsI.
CONCENTRATION appra 1·0%.
CELL PATH 13·0 ?m. dia. disc.
REFERENCE Air.

REMARKS

SCAN MODE Standard.
SLIT N TIME CONSTANT 12
PART No 5100-4367

OPERATOR V.M. Clanton.
DATE 3rd October 1980
REF. No 1/3^{20}2a

Figure 5 Infra-red spectrum of 1-phenyl-3,4-benzo-1-telluracyclopentane tetraphenylborate



SAMPLE A1

ORIGIN A.Z. Al-Rubaie.

SOLVENT CsI.

CONCENTRATION approx. 1.0%

CELL PATH 13.0 ㎜ dia. disc.

REFERENCE Air

REMARKS

SCAN MODE Standard.

SLIT N TIME CONSTANT 12

PART No 5100-3367

OPERATOR V.M. Clanton.

DATE 3rd April 1981

REF. No 1/149

Figure 6 Infra-red spectrum of 1-phenyl-1-telluracyclopentane tetraphenylborate

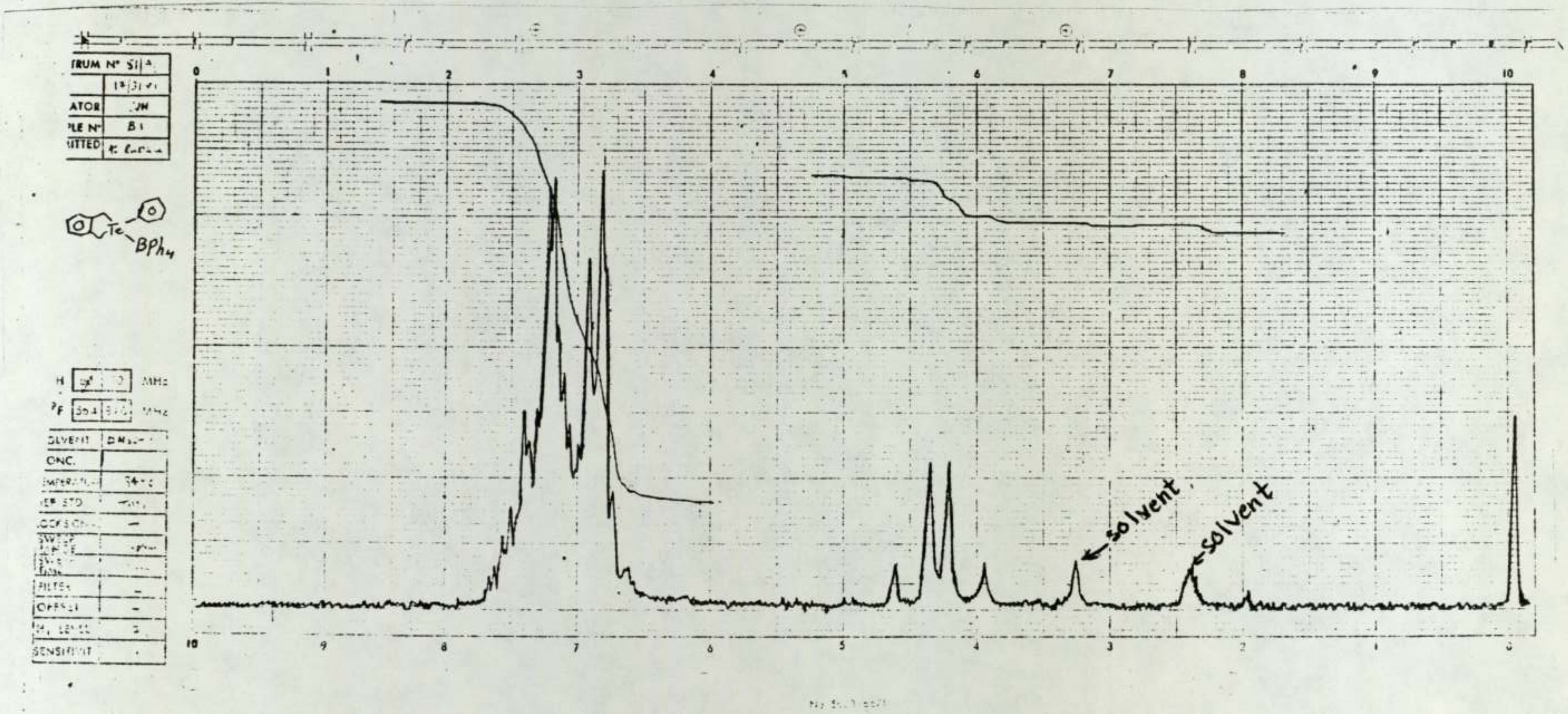


Figure 7 ^1H NMR spectrum of $C_{38}H_{33}BTe$

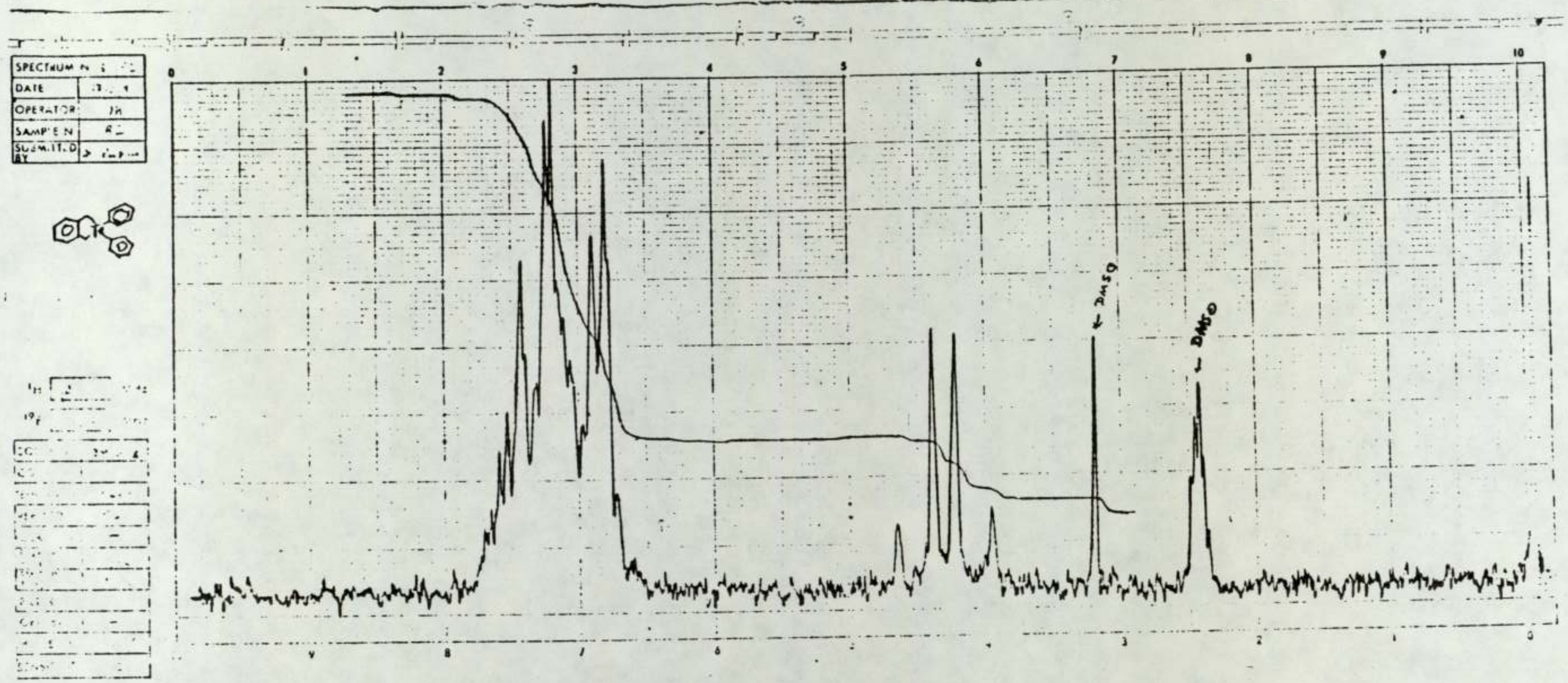


Figure 8 ^1H NMR spectrum of $C_{20}H_{18}Te$

6. (iv). DISCUSSION

This work gives a convenient method of preparing tetraorganotellurium compounds by the cleavage of Te-I bonds with sodium tetraphenylborate and replacing these bonds by Te-Ph bonds.

The reaction of sodium tetraphenylborate with $C_8H_8TeI_2$, $C_4H_8TeI_2$ or $C_9H_{11}TeI$ gave the corresponding tetraorganotellurium compound by a simple, rapid and facile procedure for the phenylation of tellurium (IV) compounds. The few examples of tetraorganotellurium compounds have been prepared by very difficult methods and the reaction must be carried out in anhydrous conditions under an inert atmosphere of nitrogen gas.

Tetraorganotellurium compounds decompose on melting to give diaryltelluride and biaryls as the major products(39,128-130, 133). Alkyl containing species decompose similarly.

Most synthetic methods for biaryls require halogen-substituted aromatic compounds as starting materials. It involves heating an aryl halide with copper powder or with activated copper bronze. Such a reaction may be effected by palladium chloride in an acetic acid-sodium acetate medium(139,140), lead tetra-acetate in trifluoro-acetic acid(143), $FeCl_3$(142) and some similar reagents(142,143).

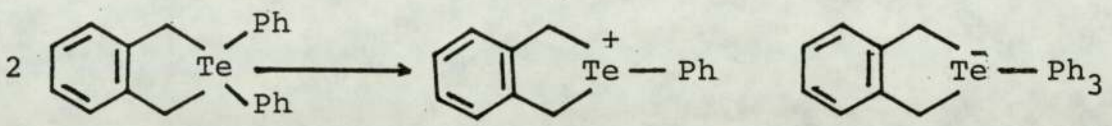
The selectivity is often unsatisfactory, and the coupling of toluene promoted by $Pd(OAC)_2$. Six possible isomeric dimethylbiphenyls are obtained(140) and the yield of the desired product is often reduced by side reactions, e.g. acetoxylation.

As can be seen the important use of tetraorganotellurium compounds is to synthesise biaryl compounds by a selective route and in good yields.

The elemental analysis of 1,1-diphenyl-3,4-benzo-1-telluracyclopentane is in good agreement with the calculated value for $C_{20}H_{18}Te$. Unsatisfactory elemental analysis of 1,1-diphenyl-1-telluracyclopentane, Table 1, was achieved due to the decomposition of this compound on standing for 3-5 weeks (i.e. wating time for this particular analysis). It is known that tetralkyl and dialkyldiaryltellurium are thermally unstable and have not yet been isolated and these compounds exist in solution.

The conductivity was studied as a function of concentration i.e. molar conductance against $\sqrt{C}$, and the plots are typical of weak electrolytes, as shown in Figs. 1 and 2. The molar conductivity measurements of these compounds ($C_{20}H_{18}Te$ and $C_{16}H_{18}Te$) at 10^{-3}M in DMSO and DMF (Table 2) indicate that they are less than 1:1 electrolytes, but if the formula is doubled, the molar conductance (Λm) is quite good for 1:1 electrolytes.

Therefore, a possible explanation is that these tetraorganotellurium compounds may exist as dimers in DMSO and DMF solutions. It is known from Barton's work(134) that the tetraaryltellurium compunds exchange ligands by a fast non-radical process, which indicates probably that the following equilibrium can be established:

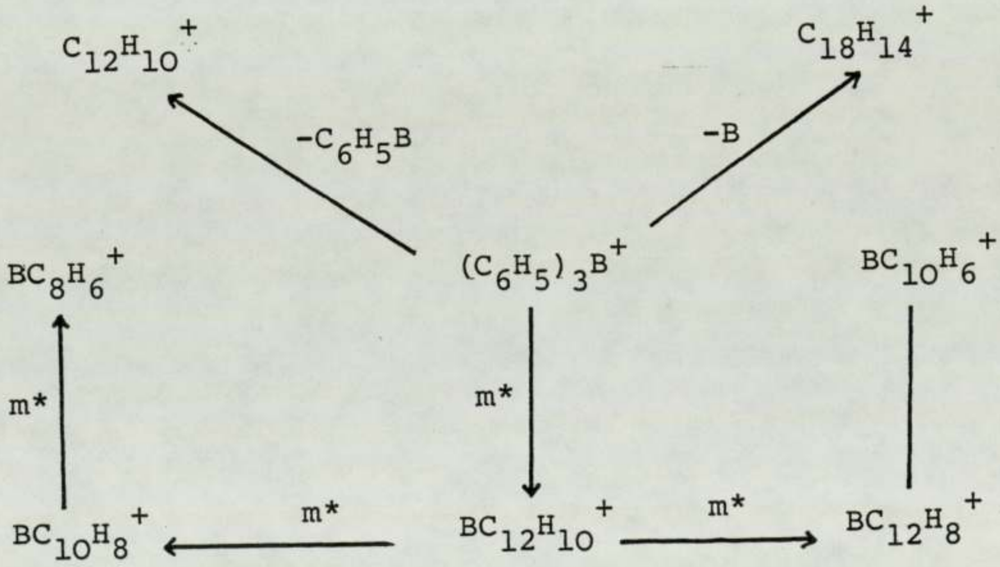


Another reason for these values may be contamination with a trace amount of a tetraphenylborate telluronium salt, however the ^{11}B NMR spectrum of $C_{16}H_{18}Te$ does not show any signal for the presence of boron.

The mass spectrum of $C_{16}H_{18}Te$ shows the presence of the tetraorganotellurium, m/e=340 and its decomposition products. This gives m/e at 263, 186 and 58 corresponding to $C_4H_8Te^{+}\cdot Ph$, $C_4H_8Te^{+}$ and $C_4H_8^{+}$ ions respectively. Unfortunately there was no evidence to support the decomposition of $C_{16}H_{18}Te$ from the metastable ions. The decomposition involved thermolysis of this compound to diphenylditelluride, diphenyltelluride, and $PhTe^{+}$ ions, table 3, which was supported by the observation of a metastable ion at 150.8 for the $Ph_2Te^{+} \longrightarrow PhTe^{+}$ step.

Fragmentation in the spectrum of $C_{34}H_{33}BTe$ shows a high m/e ratio of $C_{28}H_{28}BTe^{+}$ at 505 together with the presence of tetraorganotellurium, m/e=340, Table 4. The spectrum of this compound indicated the formation of diphenylditelluride which showed the expected fragmentation of the ditellurides. The mass spectra of $C_{38}H_{33}BTe$ and $C_{20}H_{18}Te$ show the same fragmentation (Chapter 3). On reconsidering the analytical data, the results for $C_{20}H_{18}Te$ agrees well with its calculated value and therefore, leads to the conclusion that this compound contains only a trace amount of tetraphenylborate telluronium salt.

The fragmentation pattern of the tetraphenylborate entity may be represented by the following scheme:



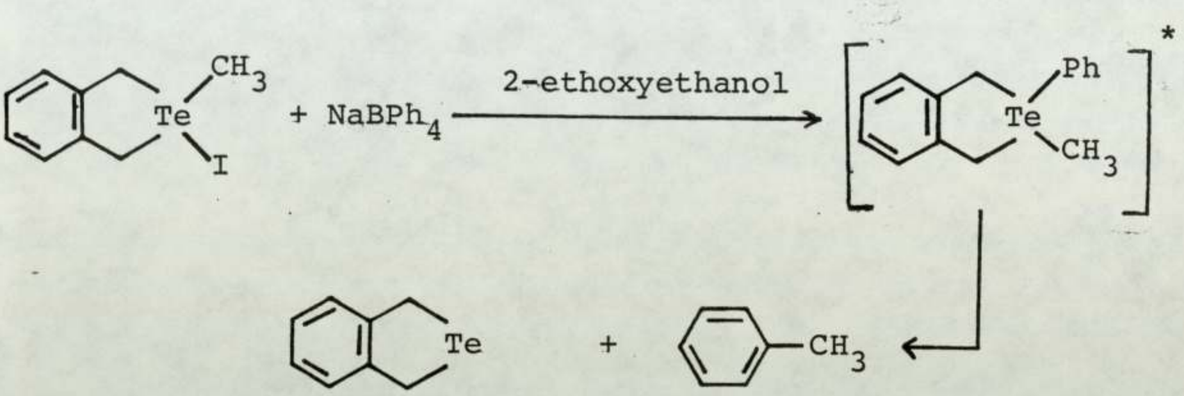
This scheme involves the production of metastable ions (m*) whose presence was observed.

Infra-red spectra of 1,1-diphenyl-3,4-benzo-1-telluracyclopentane and 1,1-diphenyl-1-telluracyclopentane show modes at 255 and 252 cm^{-1} respectively which are characteristic of ν(Te-Ph)(15,144,145), as shown in Figs. 3 and 4. These bands are also noted in the corresponding telluronium salts ($C_{38}H_{33}BTe$ and $C_{34}H_{33}BTe$) at 258 and 259 cm^{-1} respectively, Figs. 5 and 6. These data could be interpreted to suggest that two compounds have one species in common, probably the telluronium cation.

The new compound ($C_{20}H_{18}Te$) shows a ^{1}H magnetic resonance quartet signal in DMSO-d_6 at 3.96, 4.22, 4.39 and 4.66 ppm in 1:3:3:1 ratio due to the inequivalent protons in the methylene groups, a multiplet at 6.7-7.0 ppm and a multiplet at 7.0-7.72 ppm in about 7:2 ratio. The ^{1}H NMR spectrum of the corresponding telluronium salt, $C_{38}H_{33}BTe$, in DMSO-d_6 was obtained and the spectrum consisted of a quartet of the protons in the methylene groups appearing at 3.95, 4.21, 4.35 and 4.62 ppm, a multiplet at 6.7-7.02 ppm and a multiplet at 7.02-7.70 ppm in about 29:4 ratio. The aromatic:aliphatic ratio of $C_{20}H_{18}Te$ is completely different from that of the corresponding telluronium salt. Moreover, the aromatic proton resonances are shifted down compared with the spectrum obtained for the telluronium salt ($C_{38}H_{33}BTe$). The results of the ^{1}H NMR investigations show clearly that the two substances are different, Figs. 7 and 8.

The result of refluxing a mixture of 1-methyl-1-iodo-3,4-benzo-1-telluracyclopentane and $NaBPh_4$ in 2-ethoxyethanol is the formation of toluene and 3,4-benzo-1-telluracyclopentane.

Clearly, this result suggests that the tetraorganotellurium was formed and undergoes thermal decomposition with toluene and telluride as major products.



In this connection it should be noted that tetraaryltellurium decomposes in a similar way to afford diaryltelluride and biaryls as major products$^{(134)}$.

In summary then, it may be concluded that, from the elemental analysis, ^{1}H NMR, ^{11}B NMR, mass spectral and conductivity data tetraorganotellurium compounds are formed when $C_8H_8TeI_2$, C_4H_8TeI or $C_9H_{11}TeI$ are reacted with a tetraphenylborate. Such compounds, however, may well be ionic.

The new reaction reported in this work for the formation of Te-C bond (i.e. tri- and tetraorganotellurium compounds) appears to provide a general and expedient method for the synthesis of tetraorganotellurium compounds. This synthetic method may be of general utility in organotellurium chemistry.

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