SOME INVESTIGATIONS OF ORGANOTELLURIUM CHEMISTRY

by

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-9.NOV72 156113

A thesis submitted for the degree of
Doctor of Philosophy
of the
University of Aston in Birmingham

October, 1972

SUMMARY

Diaryl ditellurides, R_2Te_2 (R = Ph, p-$CH_3C_6H_4$, p-$CH_3OC_6H_4$, p-$C_2H_5OC_6H_4$, p-$PhOC_6H_4$ and 1-Naphthyl were prepared. The IR and Raman spectra of these compounds between 400-40 cm^{-1} are presented. Detailed assignments of the spectra of Ph_2Te_2 are attempted. The tellurium-tellurium stretching frequency in all cases is identified between 167-187 cm^{-1}. The evidence from these spectroscopic data suggested that the structure of diaryl ditellurides have C_2 skeletal symmetry. There is no evidence to support previous claims that diphenyl ditelluride readily dissociates into radicals in solution. Attempts to prepare unsymmetrical diaryl ditellurides were unsuccessful.

The infrared and where possible the Raman spectra between 400-40 cm^{-1} of five classes of aryltellurium trihalides, $RTeX_3$ (R = Ph, p-$CH_3C_6H_4$, p-$CH_3OC_6H_4$, p-$C_2H_5OC_6H_4$aand p-$PhOC_6H_4$ (X = Cl, Br and I) are presented. The tellurium-halogen vibrational modes are indicated and detailed assignments for spectra of $PhTeX_3$ are offered. The low frequency data and other physical evidence suggested the compounds are associated to some degree with dimeric structures the most probable for chlorides and iodides in which the tellurium atom has coordination number five. There is evidence that some bromides, notably $PhTeBr_3$, (p-$CH_3C_6H_4$)$TeBr_3$ and (p-$PhOC_6H_4$)$TeBr_3$ are more associated. The structures are best described as involving donor-acceptor interaction between X^- and $RTeX_2^+$.

The infrared and Raman spectra of aryltellurium oxyhalides, RTeOX (R = Ph, p-$C_2H_5OC_6H_4$, X = Cl, Br) are presented. The tellurium oxygen vibrational modes of the compounds are assigned. p-Phenetyltellurium trichloride was hydrolysed with 10% sodium carbonate solution, the products obtained are RTeOOH, and $(RTeO)_2O$ when the previous one was acidified with dilute acetic acid. The assignment of tellurium oxygen vibrational modes of these products are also given. $PhTeCl_3$ and $(p\text{-}C_2H_5OC_6H_4)TeCl_3$ both reacted with pyridine in benzene gave $RTeCl_4^-$ PyH^+. The mechanism of hydrolysis of aryltellurium trihalides with water is suggested.

The micro-analysis method of tellurium in organotellurium compounds by atomic absorption spectroscopy is developed. The compounds were decomposed with concentrated nitric acid and perchloric acid, and the absorption of aqueous solutions was recorded. Telluric acid AR grade is used as a standard.

This work was carried out between 1969 and 1972 at the University of Aston in Birmingham. It has been done independently and has not been submitted for any other degree.

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ACKNOWLEDGEMENTS

I wish to express my thanks to Dr. W. R. McWhinnie for his guidance and encouragement throughout this study.

My thanks are also due to Dr. A. V. Golton for help with the computation and presentation of the infrared-data, Dr. D. M. Adams of the University of Leicester and Dr. G. Davidson of the University of Nottingham for access to the Raman spectrophotometers. I am grateful for the assistance from the technicians of the Department of Chemistry. I am indebted to the Colombo Plan for a scholarship and Chiengmai University (Thailand) for study leave.

Finally, I thank my wife, Primprow, for her patience and understanding at all times.

ABBREVIATIONS

as = Asymmetric
bipy = α,α'-Bipyridyl
br. = Broad
DMF = Dimethylformamide
dpm = di-(Bipyridyl)amine
Et = Ethyl
Fig = Figure
m = Medium intensity
Me = Methyl
M.P. = Melting Point
m.s = Medium-strong intensity
Ph = Phenyl
Py = Pyridine
s = Strong intensity
sh = Shoulder intensity
tmtu = Tetramethylthiourea
tu = Thiourea
ug = Microgram
v.s = Very-strong intensity
vw = Very-weak intensity
w = Weak intensity
X = Halogen (Cl, Br and I)

SYMBOLS

ν = Stretching vibration
$\Delta\nu$ = Raman frequency shift
I = Spin quantum number of nucleus

CONTENTS

1. W. R. McWhinnie and P. Thavornyutikarn, J. Organometal. Chem., 1972, 35, 149.
2. W. R. McWhinnie and P. Thavornyutikarn, J. C. S. (Dalton), 1972, 551.

CHAPTER I

INTRODUCTION

Tellurium belongs to group VIB, the oxygen group, with the electronic structure of $[Kr]\,4d^{10}5s^{2}5p^{4}$ and has an electronegativity of 2.01 (Pauling Scale). With an electronic structure approaching the configuration of the xenon atom the inert gas, the element shows more non-metallic chemistry than metallic chemistry. The element has s, p and d orbitals available for use in bonding so it can form more than four sigma bonds to other atoms. In addition to these s, p and d orbitals, sulphur and selenium have the ability to use $d\pi$ orbitals for hybridization. Tellurium exhibits valencies of -2, 2, 4 and 6 of these 4 is the most stable, and a coordination number of 6 is common. Tellurium differs from its analogues sulphur and selenium which have oxidation states of -II, II, IV and VI all of which are relatively stable and the coordination numbers 2, 4 and 6 are common.

Tellurium (-II): The fact that tellurium has oxidation state of (-II) in Te^{2-} ion shows its tendency to complete the inert gas configuration, of which it lacks two electrons.

Tellurium (II) can form compounds in which it has coordination number of 2 or 4. The stereochemistry of tellurium (II) with two bonds is an angular shape for examples hydrogen telluride and tellurium dibromide,

Fig. 1(a). The molecule of $TeBr_2$ has been shown by an electron diffraction to be angular.[1]

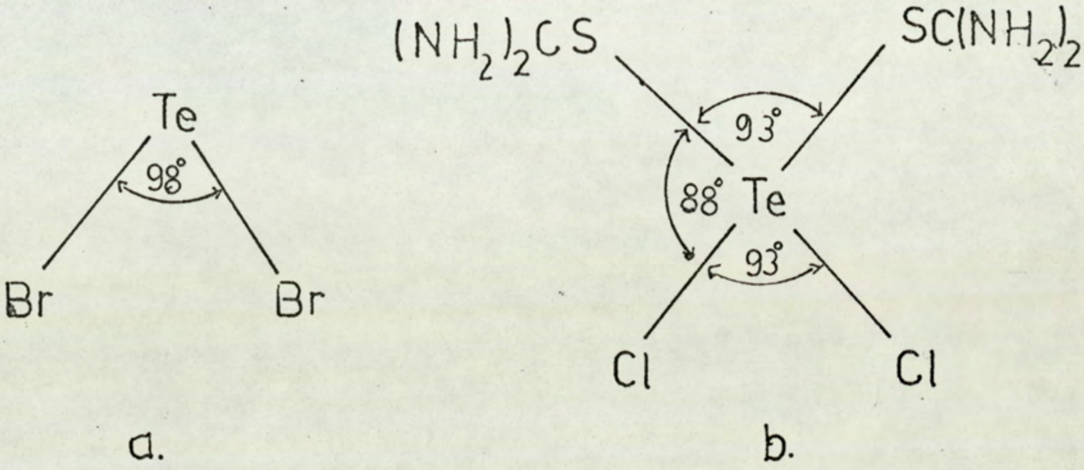


Fig. 1(a) The structure of $TeBr_2$;
(b) The structure of <u>Cis</u>-Te(tu)$_2$Cl$_2$.

With four bonds it is square planar for example <u>Cis</u>-Te(tu)$_2$Cl$_2$ Fig. 1(b). Though the stereochemistry of tellurium (II) may be termed "planar", for Te(tmtu)$_2$Cl$_2$ there appear to be only three normal bonds, the fourth is very long. The complex is virtually 3-coordinated. This is the "<u>trans</u>" effect exerted by one ligand on that "trans" to it. This effect is shown again in C_6H_5Te(tu) Cl[3] Fig. 2 which is also effectively 3-coordinated.

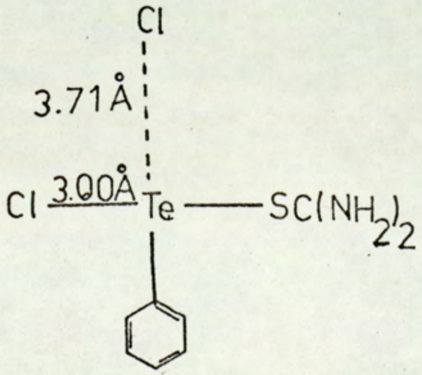


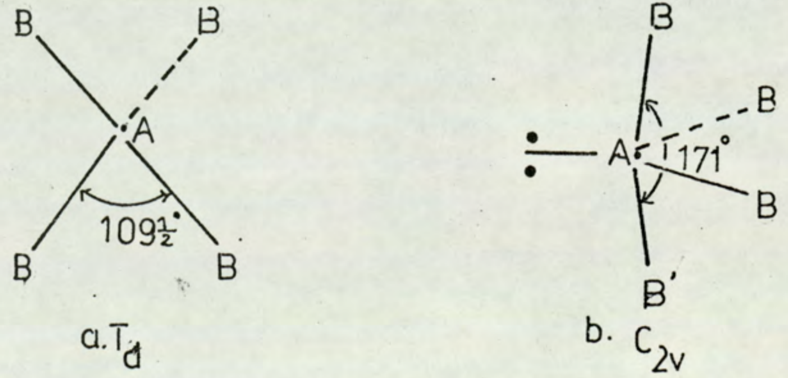
Fig. 2. The structure of C_6H_5Te(tu)Cl.

The Te----Cl bond opposite the phenyl group is virtually vaccant.

The effect is probably due to use of a single p orbital for bonding at 180° so that if one ligand is more strongly bound then the other must be less.[4]

When tellurium shows an oxidation state IV, the electronic structure will be $[\mathrm{Kr}]4d^{10}5s^{2}$. The presence of this non-bonding pair in the compounds of tellurium (IV) will create a distorted tetrahedral shape for compounds with 4 bonds such as the halides, MX_4. The molecules become a ψ-trigonal bipyramidal shape with one equatorial position occupied by an unshared pair of electrons.

This is explained by the Valence-Shell Electron-Pair Repulsion (VSEPR) Theory[5] or Electron Pair Repulsion Theory.[6] For a molecule of four atoms, AB_4 the shape of the molecule which is most stable; having the minimum electrostatic repulsion between the electron-dense regions in the bonds is a tetrahedron. Fig. (3a).



a. T_d b. C_{2v}

Fig. 3(a) Tetrahedron, AB_4; (b) Trigonal bipyramid, AB_4.

The angles between B-A-B are 109° 28'. The configuration of the molecule is also that of the highest symmetry. A good example is the methane (CH_4) molecule.

When the central atom is replaced by an atom which has an unshared pair of electrons, the molecule is no longer of the tetrahedral shape. Since the lone pair is attracted to the central atom nucleus instead of being subject to be fields of two nuclei as is a bonding pair, the lone pair electron density is concentrated closed to the central atom.

The lone pair electrons then exert a greater repulsive effect than bonding electron pairs causing a distorted molecular shape. The structure with minimum repulsive effect is adopted which is the trigonal bipyramidal shape. The unshared pair of electrons occupied one of the equatorial positions, Fig. (3b), since at this position the unshared pair electrons made 90° angle with only two AB' bonds, otherwise if it took the apical position it would made 90° angle with three AB bonds. Which will exert a greater repulsive effect. The AB' bonds will be longer than AB bonds inorder to further reduce the repulsive effect from the lone pair electrons. The typical example of this type structure is tellurium tetrachloride ($TeCl_4$) in the vapour phase.

Tellurium (VI) State: The compounds of this oxidation state are not stable as those of sulphur and selenium. The coordination number of tellurium is six whereas those of sulphur and selenium are four.

The first organotellurium compound was prepared by Wohler in 1840,[7] since then about 300 papers have been published[8] which deal with various aspects of organotellurium chemistry. This amount, when compared with organoselenium and organosulphur of its analogues, is surprisingly little. Especially the amount of publications in the field of organosulphur chemistry, one can appreciate the numbers in one year from the Specialist Periodical Report[9] covering both theoretical and synthetic aspects.

The works on the mechanisms and reactions of organotellurium chemistry are very limited and obscure. Very little is known about the structures of organotellurium compounds, and only a limited amount of work on spectroscopic and other physical properties has been done. Before 1960, there had been no infrared study of organotellurium compounds. Fritz and Keller[10] were the first to develope a systematic study of infrared spectra of organotellurium compounds. The spectra of tellurides $(CH_3)_2Te$, $(C_2H_5)_2Te$, $(C_6H_5)_2Te$, $CH_3TeC_6H_5$, dihalides $(CH_3)_2TeI_2$, $(C_2H_5)_2TeI_2$, $(C_6H_5)_2TeCl_2$, monohalides $(CH_3)_3TeI$, $(C_2H_5)_3TeI$, $(C_2H_5)_2CH_3TeI$, $(C_6H_5)_3TeI$, trihalides $C_6H_5TeCl_3$, ditelluride $(C_6H_5)_2Te_2$ and tetraphenyltelluride $(C_6H_5)_4Te$ were examined to 250 cm^{-1}.

In the present work six diaryl ditellurides, R_2Te_2 (R = Ph, p-MeC_6H_4, p-$MeO.C_6H_4$, p-$EtO.C_6H_4$, p-$PhO.C_6H_4$ and 1-Naphthyl were investigated with the objective of determining the structure of the molecules. Examination of the vibration spectra with the particular object of identifying tellurium-tellurium stretching frequency ν(TeTe) by the well known and established infrared and Raman spectroscopic methods. The reason these compounds were chosen was that diaryl ditellurides are very useful intermediates in the preparation of other classes of organotellurium compounds. The more understanding of these compounds will be of benefit for the studies of other compounds. Furthermore, diaryl ditellurides are good examples of molecules containing metal to metal bonds. The effect on the Te-Te bond strength of various aryl groups is also of interest. Though the presence of aryl groups in the molecule will made the spectra more complicated, but the compensation is that they are comparatively stable and crystalline solid state at room temperature, which made it easy to handle compared to those dialkyl ditellurides which are liquid and sensitive to moisture and temperature.

A part from a limited investigation by Fritz and Keller[10] in which the infrared spectrum of diphenyl ditelluride was examined to 250 cm^{-1}, the only examinations of ditelluride reported are those of Chen and George[11] and Sink and Harvey[12] on dimethyl ditelluride.

Farrar[13] claimed that diphenyl ditelluride dissociated to radicals in solution, and Petragnani and Moura Compus[14] assumed this idea to explain the mechanism of reaction between tellurium metal and phenylmagnesium bromide. They proposed the following mechanism to describe how diphenyl ditelluride and diphenyl telluride were obtained.

$$2C_6H_5MgBr \longrightarrow 2C_6H_5\cdot + 2BrMg\cdot$$
$$2C_6H_5\cdot + 2Te \longrightarrow 2C_6H_5Te\cdot$$
$$2C_6H_5Te\cdot \longrightarrow C_6H_5TeTeC_6H_5$$
$$2BrMg\cdot + Te \longrightarrow Te(MgBr)_2$$

$$2C_6H_5MgBr + Te \longrightarrow C_6H_5TeTeC_6H_5 + Te(MgBr)_2$$

followed by:-

$$C_6H_5TeTeC_6H_5 \longrightarrow 2C_6H_5Te\cdot$$
$$2C_6H_5Te\cdot + 2C_6H_5MgBr \longrightarrow 2C_6H_5TeC_6H_5 + 2BrMg\cdot$$
$$2BrMg\cdot + Te \longrightarrow Te(MgBr)_2$$

$$C_6H_5TeTeC_6H_5 + 2C_6H_5MgBr \longrightarrow 2(C_6H_5)_2Te + Te(MgBr)_2$$

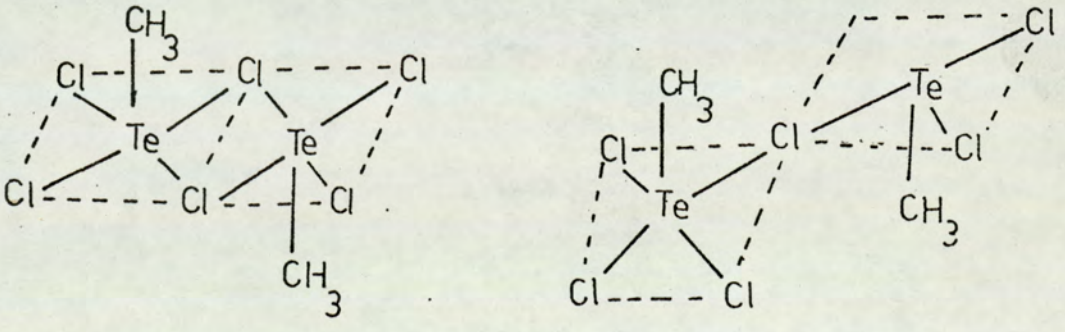
Schoberg and coworkers[15] reported that solution of diphenyl disulphide dissociation to radicals. Windle and Wiersema[16] observed no any radicals of diselinide but radicals of disulphides by Electron Spin Resonance technique.

The organotellurium halides are another interesting series for structural investigations. In the present work five classes of aryltellurium trihalides; $RTeX_3$ (R = Ph, p-MeC_6H_4, p-$MeO.C_6H_4$, p-$EtO.C_6H_4$, and p-$PhO.C_6H_4$; X = Cl, Br and I) were investigated with the objective to establish the structure of trihalides and assignment of vibrational spectra especially the tellurium-halogen vibrational modes by vibrational spectroscopy. Though the presence of aryl groups will complicate the low frequency vibrational spectra but the ease of preparation and handling and the possibility of examing a wide range of compounds provide a compensation.

Though the vibrational spectroscopic technique is a powerful tool for the structural investigation. Some ambiguous and indecisive cases can occur for the interpretation of the spectra of complex molecules. A very good example is shown by the studies of tellurium tetrachloride.[17,18] Both covalent structures based on the Ψ-trigonal bipyramid ($TeCl_4$)[17a] and ionic structures ($TeCl_3^+Cl^-$)[18] were proposed for tetrachloride solid state. Despite a number of earlier attempts[19] to determine the crystal structure of tetrachloride by the X-ray crystallographic method, only recently the structure was shown by the X-ray method[20] to be monoclinic crystals containing Te_4Cl_{16} units based on a

Tl_4Cl_4 cubane-like structure. The coordination number of each tellurium atom is six by virtue of three normal covalent bonds(2.3 A) and three much longer bonds(2.9 Å).

For stoichiometrically similar organotin compounds, $RSnX_3$ (R = Me, X = Cl, Br, I) the molecules are tetrahedral and monomeric in the gas phase.[21] The presence of an unshared pair electrons in tellurium atom, as previously described stereochemistry of aryltellurium trihalides are expected to have a distorted tetrahedral shape. Chen and George[22] reported methyltellurium tribromide molecule to be associated to dimer in benzene solution, and tellurium-bromide vibrational modes were assigned. Wynne and George[23] suggested methylselenium tribromide is dimeric in methylene chloride with D_{2h} symmetry. Wynne and Pearson[24] also reported methyltellurium trichloride is a dimer in benzene and possible in solid state with the structure of either A or B of Fig. 4.



A. B.

Fig. 4. The possible configuration of CH_3TeCl_3 dimer A and B.

They did not observe any lattice absorption in CH_3TeCl_3, and ruling out the ionic formulation $[CH_3TeCl_2^+]Cl^-$. Cryoscopic study in benzene shows an increased order of polymerization with $CH_3TeCl_3 < CH_3SeCl_3 < CH_3TeBr_3$. Kobelt and Paulus[25] determined the structure of adduct between $TeCl_4$ and C_2H_4 to be polymer chains by the X-ray method. The molecules are bridge through Te-Cl-Te bonds. Tellurium atom has coordination number 5.

The ligands are at the corners of pyramid having an approximately four fold axis, the tellurium atom being situated very nearly in the centre of the base plane of pyramid as shown in Fig. 5,

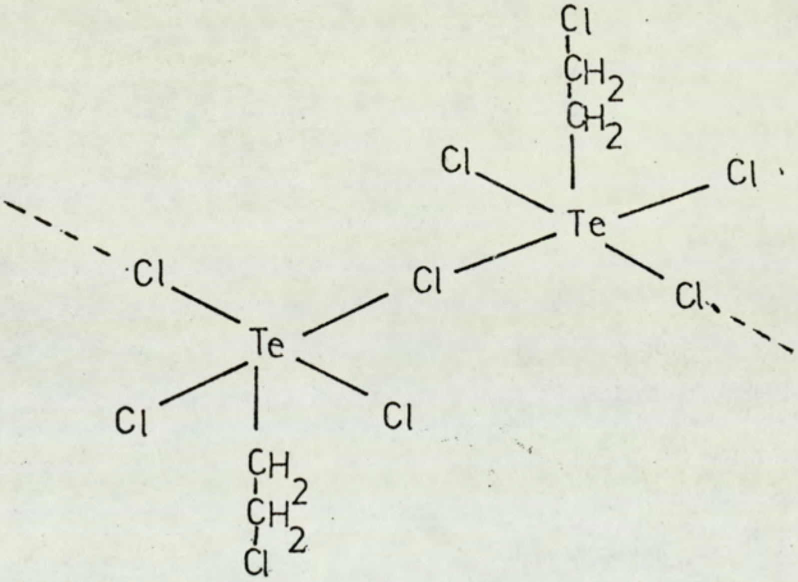


Fig. 5. Structure of p-chloroethyltellurium trichloride.

with tellurium-chloride terminal bonds 2.386 Å, and tellurium-chloride bridging bonds 2.717 Å .

It is also important to compare aryltellurium trichloride with dialkyl and diaryltellurium dihalides (R_2TeX_2), and trialkyl-and triaryltellurium halides (R_3TeX), since they are organotellurium(IV) halides.

Christofferson and McCullough[26] determined the crystal structure of diphenyltellurium dibromide by the X-ray crystallographic technique to be a monomer and a slightly distorted trigonal bipyramidal shape with tellurium atom at centre, two bromide atoms at axial positions and two phenyl groups plus the unshared pair electrons at equatorial positions. The angle between Br-Te-Br' is 178° as shown in Fig. 6(a).

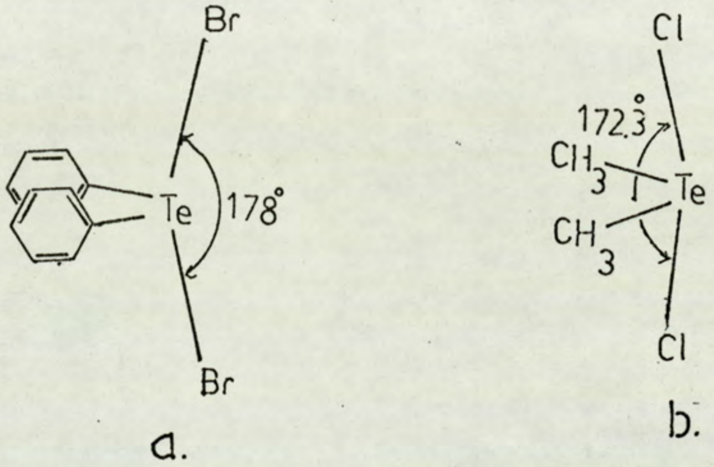


Fig. 6(a) The configuration of Ph_2TeBr_2;
(b) The configuration of $(CH_3)_2TeCl_2$.

Christofferson et al[27] reported the crystal structure of dimethyltellurium dichloride similar to diphenyltellurium dibromide, with the exception that in this case Cl-Te-Cl angle is bent towards the methyl group, while is the previous case Br-Te-Br angle is bent away from organic group. Choa and McCullough[28] found the crystal structure of di-p-chlorodiphenyltellurium diodide $(p\text{-}ClC_6H_4)_2TeI_2$ which again similar to dimethyltellurium dichlorides and bromides of dialkylselenide and dialkyltelluride. Hayward and Hendra[29] using infrared and Raman spectroscopy, had assigned the tellurium-halogen stretching frequencies for Me_2TeX_2 (X = Cl, Br and I).

Mcwhinnie and Patel[30] investigated series of diaryltellurium dihalides found that all the compounds have

ψ-trigonal bipyramidal structures with axial halogen atoms regardless of the nature of the substituents in the aryl ring, and tellurium-halogen vibrational modes were assigned in all cases.

There are no crystallographic studies on the structure of trialkyl- and triaryltellurium halides but Chen and George[22] reported $(CH_3)_3TeBr$ to be ionic and it behaves as a strong electrolyte in dimethylformamide and Hope[31] determined the crystal structure of $(CH_3)_3SeI$ to be built up of pairs of selenonium and iodide ions. Thus made to believe the structure of R_3TeX be also ionic $R_3Te^+X^-$.

There is a theory which is important to the present work by Wynne and Pearson.[24] They proposed a unifying theory concerning factors affecting the state of aggregation of group VI halides and organohalides which rationalize the interesting range of structure and solution behaviour of organochalcogen(IV) and chalcogen(IV) halides. According to this theory the various coordination numbers of tellurium atom in the series $(CH_3)_nTeCl_{4-n}$ compounds can be explained by two assumptions. First, bonding is assumed to be primarily through p orbitals, leading to a maximum coordination number of 6 for tellurium where three three-centre four-electron bonds are found. Second, the methyl group is proposed to exhibit a strong "trans" bonding effect causing no bonding for the coming group in opposite direction. This is supported by various evidences from literature as shown in Table 1.

TABLE 1

Coordination Numbers in the Solid State and State of Aggregation in Benzene Solution for Tellurium Tetrachloride and Tri-, Di-, and Monomethyltellurium Chlorides.

	CN	STATE OF AGGREGATION IN BENZENE
$TeCl_4$	$(6)^a$	Trimer, Tetramers.
CH_3TeCl_3	$(5)^a$	Monomer, dimers.
$(CH_3)_2TeCl_2$	4	Monomers.
$(CH_3)_3TeCl$	3	Ionic, insoluble.

a = Predicted.

The tellurium in solid tellurium tetrachloride would be predicted to be surrounded by six chlorides. Then the substitution of Cl by CH_3 eliminates the possibility of bonding "trans" to the methyl group thus lowering the coordination number of tellurium to 5 in CH_3TeCl_3. Substitution of two methyl groups for Cl reduced the number of nearest neighbours to 4 in $(CH_3)_2TeCl_2$. Last, when three methyl groups are connected to tellurium, no sites for nearest neighbours are present resulting the $(CH_3)_3Te^+$ ion. The state of aggregation in benzene, also can be explained by the "trans" bond lengthening effect. Thus, due to the "trans" bond lengthening effect, no sites are available for bridging in $(CH_3)_2TeCl_2$ so the compound is monomeric. One bridging site "trans" to Cl is available in CH_3TeCl_3 thus it is able to form dimer. The existance of $TeCl_4$ as trimers and tetramers is probably due to a combination of the increased availability of bridging sites to two and the increased partial positive on tellurium due to replacement of CH_3 by Cl.

The coordination numbers for tellurium depends on the number of organo group present, whereas the degree of association seems to depend on the nature of the bridging group.

The coordination number of tellurium atom in tellurium tetrachloride was predicted to be six. Which was proved to be corrected by Buss and Krebs.[20] The prediction of five coordination number for tellurium in CH_3TeCl_3 was later supported by their work on methyltetrahalogen (tetramethylthiourea)tellurium(IV) compound.[32] This compound was found to be square pyramidal structure (Fig.7) from infrared evidence, in which tellurium atom is 5 coordination.

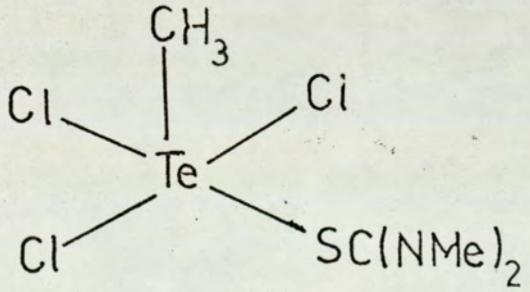


Fig. 7. The configuration of $CH_3Te\ SC(NMe)_2\ Cl_3$.

As previously indicated the infrared spectrum of phenyltellurium trichloride[10] is the only vibrational spectroscopy investigation of aryltellurium trihalides, which assigned bands at 290 cm^{-1} attribute to tellurium-chloride vibrational modes and bands between 487 and 455 cm^{-1} were assigned to tellurium-phenyl vibrations.

The first tellurium ylide was prepared by Freeman and Lloyd[33] by thermodecomposition between diazotetraphenylcyclopentadiene and diphenyltelluride. The ylide is shown in Fig. 8. The analogue sulphonium[34] and selenium[35] ylides were also obtained by the same reaction.

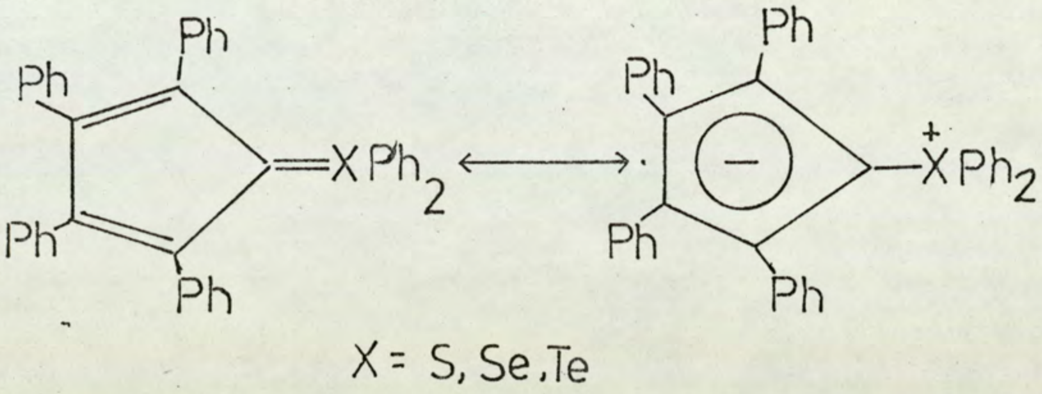


Fig. 8. The sulphonium, selenium and tellurium ylides.

It is of interest to study the hydrolysis of aryltellurium trihalides, since the products contain tellurium-oxygen bonds. No infra-red study of organotellurium compounds containing tellurium to oxygen bonds has previously been made.

The mechanism of the hydrolysis with water and alkali is unknown. The fact that aryltellurium trihalides have been investigated, it would not so difficult to identify the tellurium-oxygen vibrational modes. Aryltellurium oxyhalides is believed to be the intermediate of the reduction of aryltellurium trihalides.

Morgan and Kellet[36] claimed to have obtained 4-methoxyphenyltellurium trihydroxide by hydrolysing the trichloride with 2N. NaOH and acidifying the mixture with acetic acid. When 2-methyl-4-methoxyphenyltellurium trichloride and 4-methoxyphenyltelluriumtribromide treated with water white hydroxide were obtained. Morgan and Drew[37,38] reported that moist air hydrolysed 3-hydroxy-4-methoxyphenyltellurium trichloride when dissolved in organic solvent, and also methylene bis(tellurium trichloride) was hydrolysed by cold water to a white amorphous oxide or oxychloride. Reichel and Kirschbaum[39] found that 4-ethoxy and 4-hydroxyphenyltellurium trichloride were hydrolysed to tellurinic acids by sodium hydroxide and acidified with sulphuric acid. Petragnani and Vicentini[40] systematically studied the hydrolysis of aryltellurium trihalides. Their investigation showed that the trichlorides and tribromides are easily hydrolysed to oxyhalides. The triodides were stable towards cold water, only 4-methoxyphenyltellurium triodide yielded oxyiodide when boiled with water. Tellurinic acid anhydrides were formed when the trihalides were treated with 10% sodium carbonate solution and acidified with acetic acid.

It is inevitable in one stage of the work on organotellurium chemistry, the analysis of tellurium metal content is necessary. So far the methods[41,42,43] reported in the literature are either time consuming or more sample is needed. The present work, the method of analysis of tellurium in organotellurium compounds by atomic absorption spectroscopy is developed.

CHAPTER II

EXPERIMENTAL

1. CHEMICALS:

All chemicals were obtained from commercial sources and "AnalaR" grade reagents were used when necessary. Tellurium tetrachloride($TeCl_4$) which is the important starting material was supplied by British Drug House(B.D.H.) in a sealed bottle and was found to be of a more satisfactory quality than that supplied by other manufacturers. Phenylmercuric chloride from every manufacturers was found to contain some impurity. The compound was purified by recrystallization from ethanol.

2. SOLVENTS:

All solvents were obtained from commercial sources. If pure solvents were needed, they were purified according to literature methods, i.e. nitromethane,[44] dimethylformamide,[45] benzene,[46a] chloroform,[46b] methanol[46c] and dioxane[46d].

3. ANALYSIS:

Microanalysis for carbon, hydrogen and nitrogen were carried by Mr. Abbott, Microanalytical Department, University of Reading, Dr. F. Strauss, 10 Carlton Road, Oxford, A. Bernhardt, Max Planck Institute fur Kohlenforschung, Mulheim(Ruhr), West Germany and Mrs. B Taylor of this Department. Tellurium were analysed according to the method developed in Chapter VI.

4. PHYSICAL MEASUREMENTS:

(a) INFRARED SPECTRA:

(i) 4000-250 cm^{-1}

Spectra in this range were recorded on a Perkin-Elmer Spectrophotometer model 457. Solid state specimences were prepared as Nujol mulls supported between KBr plates, CsI plates or polythene plates, or examined as KBr dises pressed in a KBr matrix, depending on the nature of compounds. The spectra were recorded on medium speed, normal slit and with reference to air.

(ii) 410-200 cm^{-1}

Spectra in this range were recorded on a Perkin-Elmer Spectrophotometer model 225. Solid state samples were prepared as Nujol mulls supported between CsI plates or polythene plates if the compounds attacked CsI plates. For samples in polythene cells, the polythene cells were used to compensate in addition to the attenuator. The spectra were recorded on slit programme 5.0, speed 0.1 fast and pen travelling 10 sec.

(iii) 400-40 cm^{-1}

The far-infrared spectra(400-40 cm^{-1}) were obtained with a R.I.I.C. FS720-FS200 Fourier Spectrophotometer. The spectra were not recorded instantly as with a conventional double-beam spectrophotometer. The transmitted intensity of an interfering beam of radiation was recorded for a total of 1024 positions of a moving mirror; using a Golay detector. The form of the resulting interferogram is a function of the spectral distribution of the radiation entering the detector. A Fourier cosine transform was computed by the University ICL 1905 computer using a programme written by RIIC and modified to out put drawn spectra on a graph plotter. A resolution of 2 cm^{-1} on the computed spectra was obtained. A detailed description of this instrument, its operation and problems encountered in its used has been reported by Thomson.[47] An interferogram (i.e. a continuous recording of a voltage proportional to the transmitted out of the Golay detector) was traced for each run. Any data tapes in which a "Spike" appeared in the interferogram elsewhere except at the zero path difference position were rejected, since these tapes were found to give meaningless spectra when computed. Each sample was obtained in separated data tape by causing the moving mirror to move in both directions through zero path position. The interferometer was calibrated with the spectrum of water vapour by comparing with the literature wavenumber value.

The solid samples were prepared as Nujol mulls with different solid concentration, this was done by using a 0.1 mm spacer between polythene plates in one run and then repeating without a spacer. The mulls were supported in polythene cells, these in turn were placed in a vacuum-tight cell holder.

Each samples was run at least in duplicate with different physical conditions. In some cases if unsatisfactory spectra were obtained, the measurements were carefully replicated according to the following. The spectra were consulted first, if the spectra indicated too much radiation was absorpted, the repeat mulls were made thinner and can be checked from the less value of gain and vice versa. The liquid cells were used for liquid samples. The cells were made by inserting a brass 10 mm thick, having a hole the same size as the window of cell holder, between the polythene plates in a vacuum-tight holder.

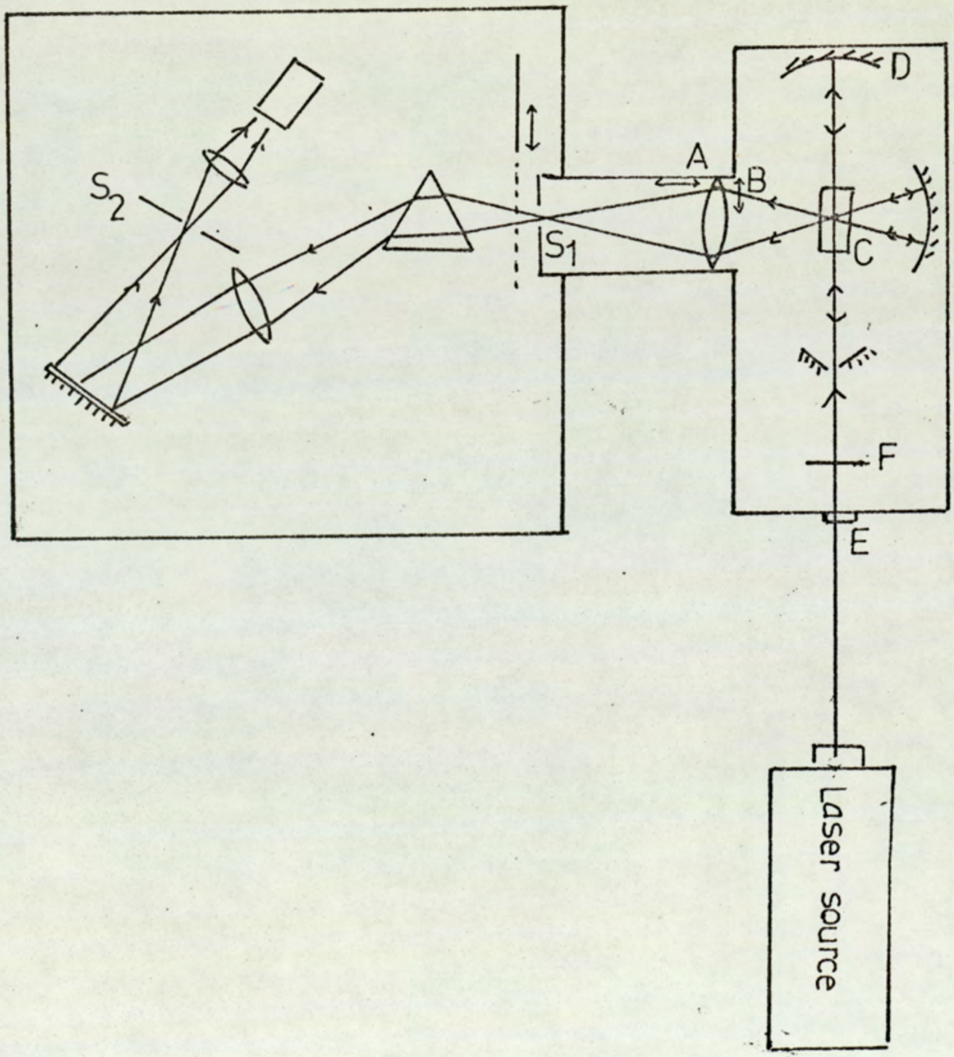
The background spectra of polythene cells showed a sharp band at 72 cm^{-1} and another weak and broad absorption centre at about 380 cm^{-1}, these are bands attribute by polythene and recognisable from the single-beam computed spectra. Background spectra of liquid solvents were also obtained for comparision. The interior of the interferometer was evacuated below 0.05 torr for each run.

(b) RAMAN SPECTRA:

The Raman spectra in the range of 400-40 cm^{-1} reported in Chapter III were recorded on the Coderg PH1 Raman Spectrophotometer at the University of Leicester, using 6328 nM He-Ne laser excitation. Those reported in Chapter IV and V were recorded on the Cary 81 Raman Spectrophotometer at the University of Nottingham, using 6328 nM He-Ne laser excitation.

All the samples were recorded in crystalline solid state. For Cary 81 spectrometer the samples were recorded directly from the sample bottles dimeter of ¼" and ½", filling the crystals in a pyrex glass solid cell or filling the crystals in the metallic hollow holder. The samples must make perfect contact with the sample window, in the cases of a sample bottle and a solid cell a drop of paraffin oil was needed to connect the two surfaces. It was found that ground crystals gave poor spectra, so original crystalline solids were used. p-Phenoxyphenyltellurium tribromide (needle yellow crystals) gave the best spectrum. The dark brown or black compounds gave no usable results.

The instructional manual for the operation of the Coderg PH1 Spectrophotometer is not published in English and the instrument is not very well known compared to the Cary 81 Spectrophotometer. Thus the procedure used to obtain Raman spectra of solids will be described here. The simplified optical system of the Coderg PH1 Spectrophotometer is shown schematically in figure below.



The laser source containing a mixture of helium and neon gases which emits nearly all of its radiation in a coherent line at 6328 nM in the red region of the visible spectrum. A few non-lasing emission lines of neon are also excited, but these can be removed by placing a thin-film interference filter at F before the beam strikes the sample. The He-Ne laser used in this work produced a total out put power between 40 and 85 mW. The laser was switched on and allowed to stabilize for one hour before recording the spectra.

The solid samples were introduced in glass capillary tubes weighing between 5 and 10 mg without grinding. The sample is mounted on the clay at C and is illuminated by the laser beam. A sample capillary was adjusted to get maximum reflectance enter the spectrometer. Setting the photomultiplier to 1 Kv, the amplifier time constant at 3, and the amplifier gain at 5, the chart recorder was switched on and the recorder gain set at 1. Then opened the slits to 4, and scanned monochromator until movement of the recorder pen showed a strong Raman line in the sample had been located. Then the monochromator was scanned slowly to get the maximum intensity for the chosen line. The position of the sample in relation to the laser beam was then adjusted using the ecentrics provided at the base of the sample holder until no further increase in the signal to background intensity ratio could be observed. The scattered light was focussed on the spectrometer entrance slit by controlling A and B. Then intermediate slit S_2 was gradually closed until a sharp reduction in the signal intensity was observed. This adjustment reduced the amount of stray light reaching the photometer. By choosing suitable values for these parameters, and for the slit widths, photomultiplier voltage and recorder gain, a spectrum was obtained for each sample.

The wavenumber of the spectrometer was calibrated with laser lines obtained by reflection from potassium bromide.

(c) X-RAY POWDER PHOTOGRAPHS:

All the X-ray photographs were obtained from the "SOLUS-SCHALL" London, generator and "Phillips" camera and X-ray tube, using Cu-$K_\alpha$radiation as a source. The d values of each line in the photograph was measured in Amstrong(Å) by Cu-$K_\alpha$ruler. The times of exposure varied from 30 minutes to 3 hours, this depended on the nature of the samples.

(d) NUCLEAR MAGNETIC RESONANCE (NMR) SPECTRA:

All ^{1}H n.m.r. spectra at 100 MHz were recorded on Perkin-Elmer R 14 Spectrometer of the University of Birmingham. Appropriate solvents were chosen for each sample and TMS (tetramethylsilane) was used as an internal reference.

(e) ELECTRON SPIN RESONANCE (ESR) SPECTRA:

The Hilger and Watts microspin instrument was used to record the spectra of samples. The instrument is operated on the X-band frequency.

(f) MASS SPECTRA:

The mass spectra of all compounds were recorded on AE1 MS9 Spectrometer at 70 eV with the exception three spectra which were recorded at lower voltage.

(g) DIFFUSE REFLECTANCE SPECTRA:

The spectra in the range of 55,000 to 11,500 cm^{-1} were obtained from Unicam SP800 Spectrophotometer. The diffuse reflectance unit was installed in the sample chamber. The solid samples were smeared on filter papers, using magnesium carbonate as reference.

(h) VISIBLE SOLUTION SPECTRA:

The visible solution spectra in the range of 35,000 to 11,500 cm^{-1} were recorded on Unicam SP800 Spectrophotometer using 1 cm silica cells.

(i) CONDUCTIVITY MEASUREMENTS:

Molar conductivity of all compounds were measured at room temperature with a Henelec Conductivity bridge using a Mullard standard conductivity cell type E 7591/B of cell constant 1.36.

(j) MELTING POINTS:

The melting points of all solid compounds were determined by a Gallenkamp Melting-Point Apparatus. The thermometers were calibrated with organic compounds of known melting points.[46e]

(k) THIN LAYER CHROMATOGRAPHY:

Thin layer chromatography on silica (Keiselgur G) was used to determine the number of species present in certain solutions.

CHAPTER III

DIARYL DITELLURIDES

INTRODUCTION

Diaryl ditllurides are useful intermediates for the synthesis some classes of organotellurium compounds. The ditellurides are good simple examples of compounds containing metal to metal bonds. X Redox Reactions A vibrational spectroscopy study of these compounds will be of benefit for the understanding of their chemistry. This technique was used to investigate some diaryl ditellurides, R_2Te_2 (R = Ph, p-tolyl, p-MeO.C_6H_4, oh p-EtO.C_6H_4, p-PhO.C_6H_4, and 1-Naphthyl) with the objective to establish the structure of the ditllurides and in particular to identify the tellurium-tellurium stretching frequency, ν(Te-Te). The bond strength variation of tellurium-tellurium bonds in the ditellurides with various aryl groups was also of interest. As already indicated, apart from the examination of Ph_2Te_2[10] by infrared down to 250 cm^{-1} the only work on ditelluride is that on dimethyl ditelluride.[11,12] It was also of interest to investigate the behaviour of Ph_2Te_2 in solutions since diphenyl ditelluride has been suggested[13] to substantially dissociate to radicals in solutions.

EXPERIMENTAL

PREPARATION OF DIARYL DITELLURIDES

All the ditellurides prepared are known compounds. The methods employed are according to the literature sources with modifications in some cases.

Diphenyl ditelluride

The method reported by Farrar[13] is tedious and needs a pure phenyltellurium trichloride to start with. So Morgan and Drew's[38] method was used for this preparation.

Crude phenyltellurium trichloride(2.9 g) was suspended in water(20 ml). The mixture was reduced by the solution of potassium metabisulphite(5.3 g) in water(10 ml). The solution was slowly added at 0° C with continuous stirring. The orange precipitate appeared, after the solution was used up stirring was continued for another hour. The product was filtered and dried over P_4O_{10} in a vacuum desiccator. The ditelluride was then recrystallized from petroleum ether(30/40°). This yielded orange needle crystals (0.7 g) which melted at 65-66° C (lit.[13] 66-67° C).
(Found: C,36.0; H,2.4; $C_{12}H_{10}Te_2$ requires: C,35.2; H,2.5%).

Bis-p-tolyl ditelluride

The same procedure as that used in the preparation of diphenyl ditelluride was employed.

p-Tolyltellurium trichloride(2.3 g) was reduced by potassium metabisulphite(5.6 g), to give orange needle crystals(0.8 g) after recrystallization from petroleum ether(30/40°). The ditelluride melted at 51-52° C (lit.[13] 52.5° C).

The following preparations were carried out according to the methods given in literature.

Bis-p-anisyl ditelluride[36,39]

p-Anisyltellurium trichloride(5.0 g) was reduced by potassium metabisulphite(4.0 g) at 0° C. The deep brown crystals of ditelluride(1.6 g) was obtained after re-crystallization from petroleum ether(40/60°). The compound had a melting point between 56.5-58° C (lit. 60° C). This compound is unstable in air and decomposes slowly.
(Found: C,39.4; H,3.6; $C_{16}H_{18}O_2Te_2$ requires: C,38.6; H,3.6%).

Bis-p-phenetyltellurium ditelluride[36,39]

p-Phenetyltellurium trichloride(6.0 g) was reduced by potassium metabisulphite(11.3 g). The golden crystalline ditelluride(2.3 g) was obtained, and had a melting point between 104-106° C (lit. 107-108° C).
(Found: C,39.4; H,3.6; $C_{16}H_{18}O_2Te_2$ requires: C,38.6; H,3.6%).

The trichloride can also be reduced by hydrated sodium sulphide($Na_2S.9H_2O$).[48] This method is less tedious and need no control of the temperature at 0° C.

Di-p-phenoxytellurium ditelluride[48]

p-Phenoxyphenyltellurium trichloride(4.0 g) was reduced by potassium metabisulphite(6.6 g) to afford deep violet crystals(3.0 g) which melted at 84-86° C (lit. 87-88° C). The ditelluride decomposed slowly in petroleum ether solution affording an insoluble yellowish compound.
(Found: C,49.2; H,3.0; $C_{24}H_{18}O_2Te_2$ requires: C,48.7; H, 3.1%).

Di-1-naphthyltellurium ditelluride[49]

1-Naphthyltellurium trichloride(3.6 g) was reduced by hydrated sodium sulphide($Na_2S.9H_2O$) to give a red crystalline product(1.3 g). The compound had a melting point between 120-121 °C (lit.123.5-124 °C). After one year storage it became yellowish, however, pure material was obtained again after recrystallization. A small amount of a yellowish insoluble compound was also observed. (Found: C,47.0; H,2.8; $C_{20}H_{14}Te_2$ requires: C,47.1; H,2.7%).

ATTEMPTS TO PREPARE UNSYMMETRICAL DITELLURIDES

Reduction the mixture of p-MeO.$C_6H_4TeCl_3$ and p-EtO.$C_6H_4TeCl_3$ with $Na_2S.9H_2O$

A mixture of p-MeO.$C_6H_4TeCl_3$(0.34 g), p-EtO.C_6H_4-$TeCl_3$ (0.35 g) and $Na_2S.9H_2O$(7.2 g) was heated in a water bath at about 95° C for 30 minutes. A brown precipitate appeared the mixture was then diluted with cold water and cooled, and filtered, and the precipitate was then dried over P_4O_{10} in a vacuum desiccator. The brown product(0.56g) obtained was shown to be only the mixture of the two ditellurides by thin layer chromatography.

Reduction the mixture of p-MeO.$C_6H_4TeCl_3$ and p-EtO.$C_6H_4TeCl_3$ with $K_2S_2O_5$

A mixture of p-MeO.$C_6H_4TeCl_3$(0.34 g) and p-EtO.$C_6H_4TeCl_3$(0.35 g) was reduced by potassium metabisulphite(1.11 g) at 0 °C. The yellow colour of the trichlorides changed to brown. The crude product was recrystallized from petroleum ether(40/60°). The compound obtained showed only two components on the thin layer chromatography.

Reduction the mixture of p-Me.$C_6H_4TeCl_3$ and p-MeO.$C_6H_4TeCl_3$ with $K_2S_2O_5$

A mixture of p-$MeC_6H_4TeCl_3$(0.33 g) and p-MeO.$C_6H_4TeCl_3$(0.34 g) was suspended in water and reduced by potassium metabisulphite(1.11 g) at 0° C. An oily mass of brown product was obtained. The product was recrystallized from petroleum ether(30/40°), but only an oily liquid was obtained which was shown to be of two components on the thin layer chromatography using carbon tetrachloride as solvent. This was confirmed by ^{1}H n.m.r. spectroscopy.

UV Irradiation of the mixture of bis-p-tolyl ditelluride and bis-p-anisyl ditelluride in carbon tetrachloride

Bis-p-tolyl ditelluride(0.22 g) and bis-p-anisyl ditelluride(0.24 g) were dissolved in carbon tetrachloride (25 ml). The solution was irradiated with U.V. radiation for 6 hours in a U.V. reaction vessel. The white precipitate was observed, and the red-brown colour of the ditellurides became colourless. This product was filtered and dried, the filtrate had a smell resembling that of carbon tetrachloride plus hydrogen chloride. The filtrate was shaken with water affording a white precipitate. After filtration the aqueous filtrate showed acidity with blue litmus paper and silver chloride was precipitated upon adding silver nitrate solution. The white product separated from carbon tetrachloride melted at 165-185° C. The first white product obtained contained at least p-tolyltellurium trichloride and p-anisyltellurium trichloride from the i.r. spectrum. The thin layer chromatography failed to identify the contents of the mixture owing to unsuitable solvents.

UV Irradiation the mixture of diphenyl ditelluride and bis-p-phenetyl ditelluride in benzene

A benzene solution(15 ml) of a mixture of diphenyl ditelluride(0.08 g) and bis-p-phenetyl ditelluride (0.09 g) was irradiated by U.V. in a U.V. reaction vessel for 6 hours. The red brown solution remained unchange though a little black precipitate was observed at the bottom of the flask. The solution was made concentrated by evaporation, and was proved to be the mixture between the two original ditellurides by thin layer chromatography and column chromatography. The infrared spectrum of individual fraction from column chromatography also identified the corresponding original ditellurides.

INVESTIGATION FOR FREE RADICAL OF DIPHENYL DITELLURIDE IN SOLUTION

Visible spectra of diphenyl ditelluride

Diphenyl ditelluride was dissolved in ethanol and carbon tetrachloride of $5x10^{-4}$M concentration.

Validity of Beer's Law

Three different concentrations of diphenyl ditelluride in carbon tetrachloride were prepared; $5x10^{-4}$M, 10^{-3}M, and $2x10^{-3}$M.

ESR Spectrum

The solutions of diphenyl ditelluride in ethanol and carbon tetrachloride were used for an electron spin resonance study.

RESULTS

The IR and Raman spectra below 400 cm^{-1} of diphenyl ditelluride are presented in Fig. 9 and 10 respectively, and tabulated in Table 2. All other ditellurides are tabulated in Table 3.

The infrared spectra of all diaryl ditellurides above 400 cm^{-1} are identifiable with the modes of the organic groups, R in R_2Te_2 and no further discussion is needed.

Bis-p-anisyl ditelluride and bis-p-phenoxyphenyl ditelluride decomposed immediately to elemental tellurium when placed in a laser beam. These were the only two compounds which strongly absorpted radiation at 15,803 cm^{-1} (6328 Å) the frequency of the He-Ne laser. See Fig. 11.

The diffuse reflectance spectra(v.s. $MgCO_3$) of the six ditellurides investigated are shown in Fig. 11.

Proton NMR Spectra

The proton NMR spectra of both $(p\text{-}EtO.C_6H_4)_2Te_2$ and $(p\text{-}MeO.C_6H_4)_2Te_2$ in carbon tetrachloride were recorded. For bis-p-phenyl ditelluride the centre of resonance of the triplet methyl of ratio 1:2:1, J = 15Hz is at 8.6 τ. Methylene show quartet of ratio 1:2:2:1, J = 25Hz at 6.0 τ. The two protons at ortho position relative to the ethoxy group show doublet of ratio 1:1, J = 10Hz at 3.31 τ, and also doublet for the two meta protons at 2.32 τ with ratio 1:1 and J = 10Hz.

For bis-p-anisyl ditelluride the singlet of methyl group is at 6.22 τ; the doublet of two ortho protons is at $3.32\,\tau$, with ratio of 1:1, J = 15Hz; and the doublet for two meta protons is at $2.35\,\tau$, with ratio 1:1, J = 15Hz.

Mass Spectra

The mass spectra of bis-p-phenetyl ditelluride, bis-p-anisyl ditelluride, phenyl-p-anisyltelluride, and and bis-p-anisyl ditelluride are tabulated in Table 4, 5, 6 and 7 respectively.

Diphenyl ditellurides in Solution

The visible spectra of diphenyl ditelluride in ethanol and in carbon tetrachloride are shown in Fig. 12. The absorption maxima are at 24,600 cm^{-1} in both solvents.

The visible spectrum of the ditelluride in carbon tetrachloride at various concentrations is shown in Fig. 13. The solutions obey Beer's Law; a straight line was obtained by plotting concentration versus absorbance at 24,600 cm^{-1}, affording εmax 937 $Lmol^{-1}$.

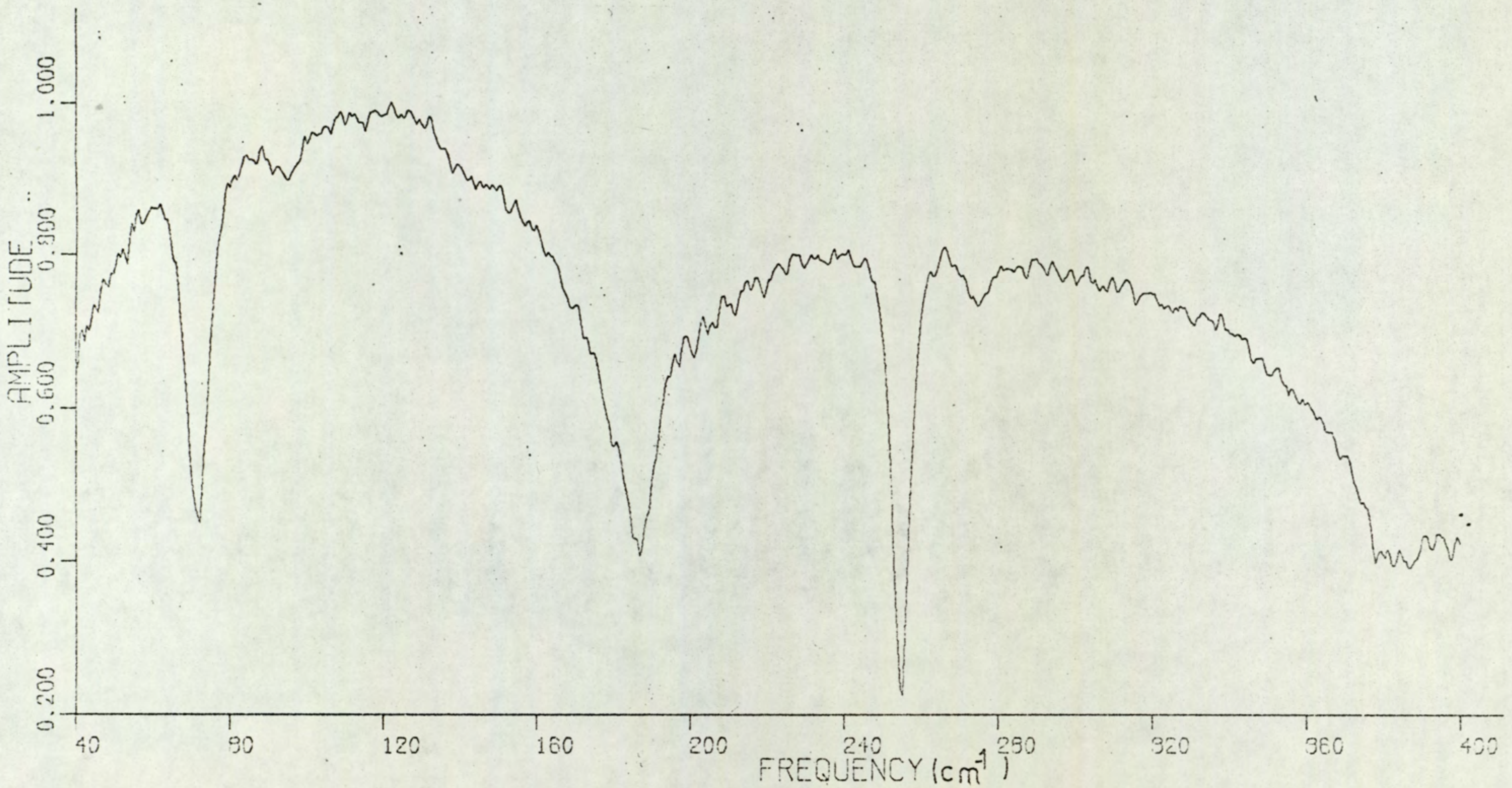


Fig. 9. Far-infrared spectrum of Ph_2Te_2

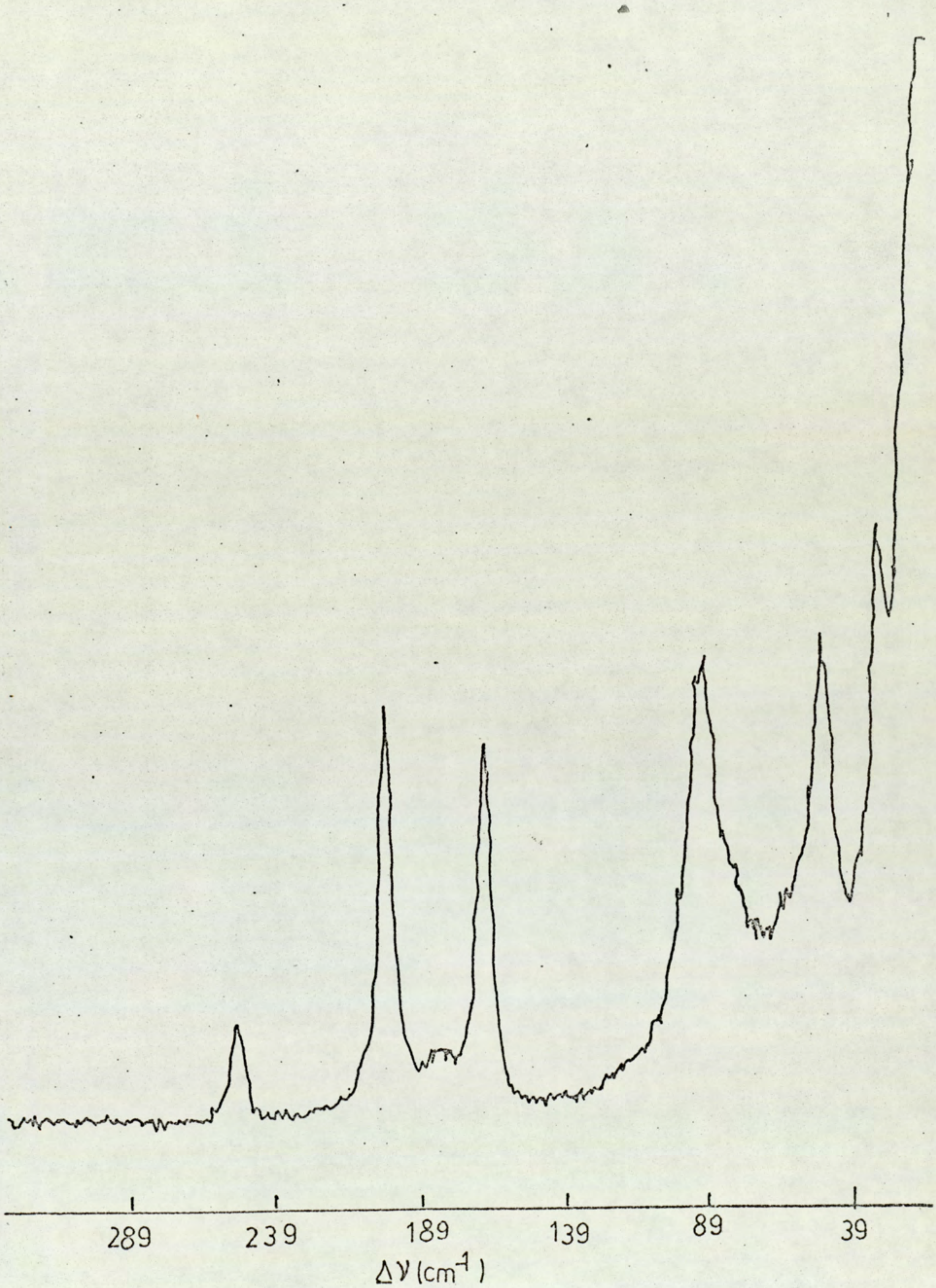


Fig. 10. Raman spectrum of Ph_2Te_2.

TABLE 2

The Low Frequency (<400 cm^{-1}) Vibrational Spectra of Crystalline Diphenyl Ditelluride

Infrared (cm^{-1})	Raman $\Delta\nu$(cm^{-1})	Assignment
398 w		Phenyl w
350 w		Phenyl w'
274 w		Phenyl u
255 s	253 w-m	ν_{as}(TePh) or phenyl t
202 (sh)	204 vs	ν_s(TePh) or phenyl t'
188 s	183 w, (sh)	Phenyl x
169 (sh)	167 vs	ν(TeTe)
146 w		Phenyl x'
94 w	92 s	Unassigned
	51 s	Unassigned

TABLE 3

Low Frequency Vibrational Spectra of Some Diaryl Ditellurides

$(p\text{-}MeO.C_6H_4)_2Te_2$ IR(cm^{-1})	$(p\text{-}PhO.C_6H_4)_2Te_2$ IR(cm^{-1})
375 m	400 m
316 m-s	348 w
310 (sh)	287 m-s
223 s[a]	275 m-s
213 s[a]	192 s
178 s[b]	185 s[b]
140 w	145 w

TABLE 3-Continued

$(p\text{-}MeC_6H_4)_2Te_2$		$(p\text{-}EtO.C_6H_4)_2Te_2$		$(1\text{-}Naphthyl)_2Te_2$	
IR(cm^{-1})	Raman($\Delta\nu$)	IR(cm^{-1})	Raman($\Delta\nu$)	IR(cm^{-1})	Raman($\Delta\nu$)
		380 m			
		313 vs		274 w	
		232 w	226 (sh)	258 w	
275 w		204 s	206 w	240 s	238 w
232 s	231 w	186 m^{b}	186 vvs^{b}	234 s	233 w
197 (sh)	197 m	166 (sh)	165 w	184 s^{b}	187 vs^{b}
184 s		140 (w)			135 w
156 (sh)	169 vs^{b}			126 w	
	65 w				64 m
	51 w				

a In n-heptane solution these bands appear at 217 cm^{-1} and 205 cm^{-1}.

b Bands to which stretching of the Te-Te bond is considered to contribute.

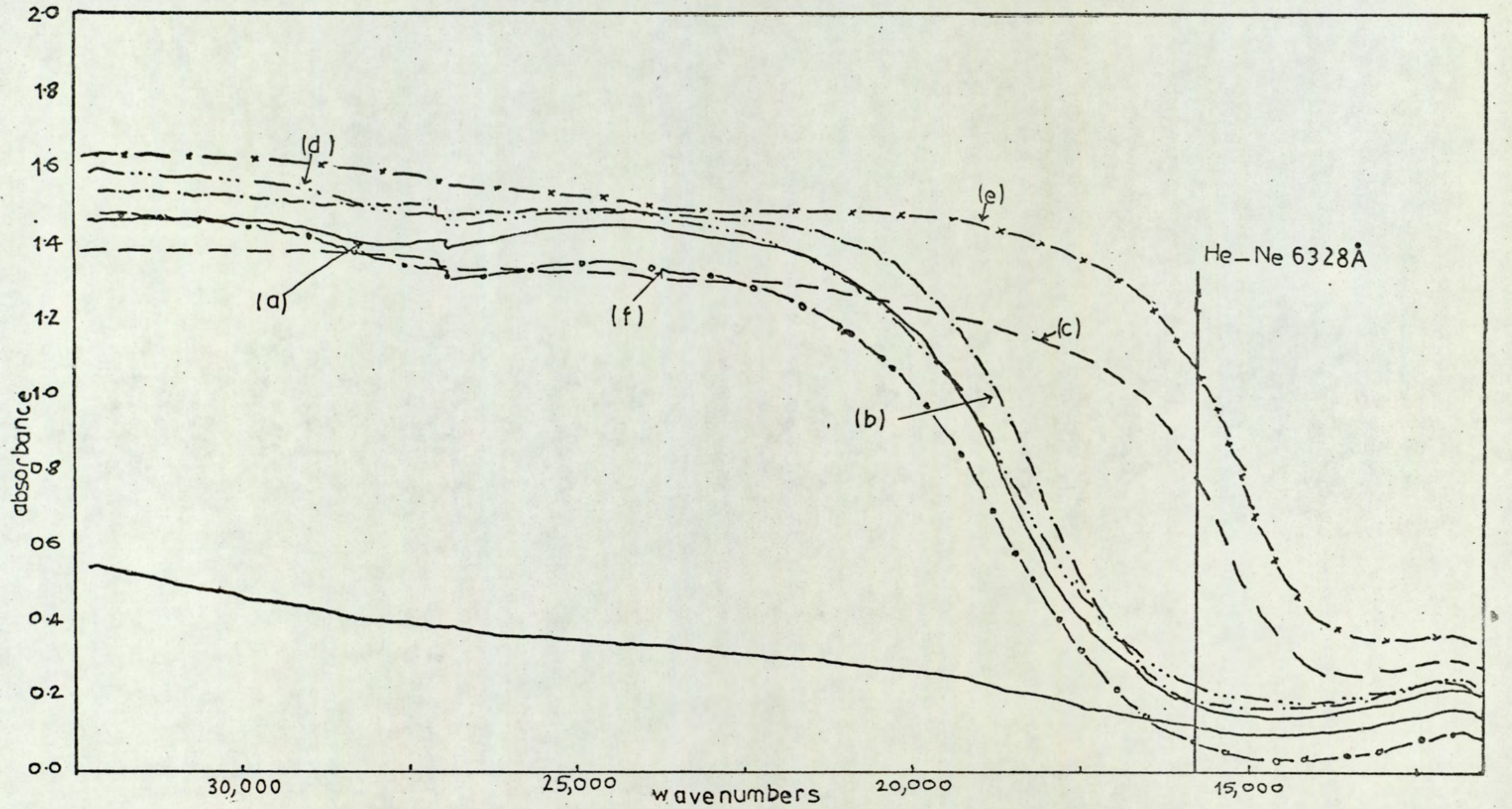


Fig.11. Diffuse reflectance spectra of ;(a) Ph_2Te_2;(b) $(p\text{-}MeC_6H_4)_2Te_2$;(c) $(p\text{-}MeO.C_6H_4)_2Te_2$;(d) $(p\text{-}EtO.C_6H_4)_2Te_2$;(e) $(p\text{-}PhO.C_6H_4)_2Te_2$;(f) $(1\text{-}Naphthyl)_2Te_2$

TABLE 4

The Mass Spectrum of $(p\text{-EtO.C}_6H_4)_2Te_2$ Relative to ^{130}Te

m/e	Relative Abundance (%)	ions
502	7	parent ion
372	43	$(p\text{-EtO.C}_6H_4)_2Te^+$
280	15	-
274	10	-
251	40	$(p\text{-EtO.C}_6H_4)Te^+$
242	100	$(p\text{-EtO.C}_6H_4)_2^+$
223	56	-
214	24	-
213	53	-
189.3	-	metastable
186	63	-
185	63	-
161.5	-	metastable
157	32	-
154	16	-
128	12	Te^+
126	16	Te^+
94	21	-
93	27	-
92	17	-
65	65	-
64	17	-
63	28	-
28	27	N_2^+
18	46	H_2O^+

TABLE 5

The Mass Spectrum of $(p\text{-MeO.}C_6H_4)_2Te_2$ Relative to ^{130}Te

m/e	Relative Abundance %	ions
474	7	parent ion
344	28	$(p\text{-MeO.}C_6H_4)_2Te^+$
237	61	$(p\text{-MeO.}C_6H_4)Te^+$
214	100	$(p\text{-MeO.}C_6H_4)_2^+$
199	97	-
185.5	-	metastable
171	26	-
128	14	Te^+
113.2	-	metastable
107	9	-
92	38	-
77	32	$C_6H_5^+$
64	42	-
63	56	-
18	35	H_2O^+

TABLE 6

The Mass Spectrum of $C_6H_5TeC_6H_4.OMe$ Relative to ^{130}Te

m/e	Relative Abundance %	ions
314	16	parent ion
237	4	$(p\text{-}CH_3O.C_6H_4)Te^+$
207	3	$(C_6H_5)Te^+$
184	47	$p\text{-}CH_3O.C_6H_4\text{-}C_6H_4^+$
169	25	-
155.2	-	metastable
141	15	metastable
118.3	-	-
107.8	-	metastable
107	3	$C_7H_7O^+$
77	28	$C_6H_5^+$
51	19	-
39	33	-
28	15	N_2^+
18	100	H_2O^+

TABLE 7

The Mass Spectuum of $(p\text{-MeO.C}_6H_4)_2Te$ Relative to ^{130}Te

m/e	Relative Abundance %	ions
354	5	parent ion
237	11	$p\text{-MeO.C}_6H_4Te^+$
214	77	$(p\text{-MeO.C}_6H_4)_2^+$
199	100	-
185.2	-	metastable
171	24	-
147.2	-	metastable
128	11	Te^+
92	20	-
77	17	$C_6H_5^+$
64	22	-
63	31	-
28	8	N_2^+
18	60	H_2O^+

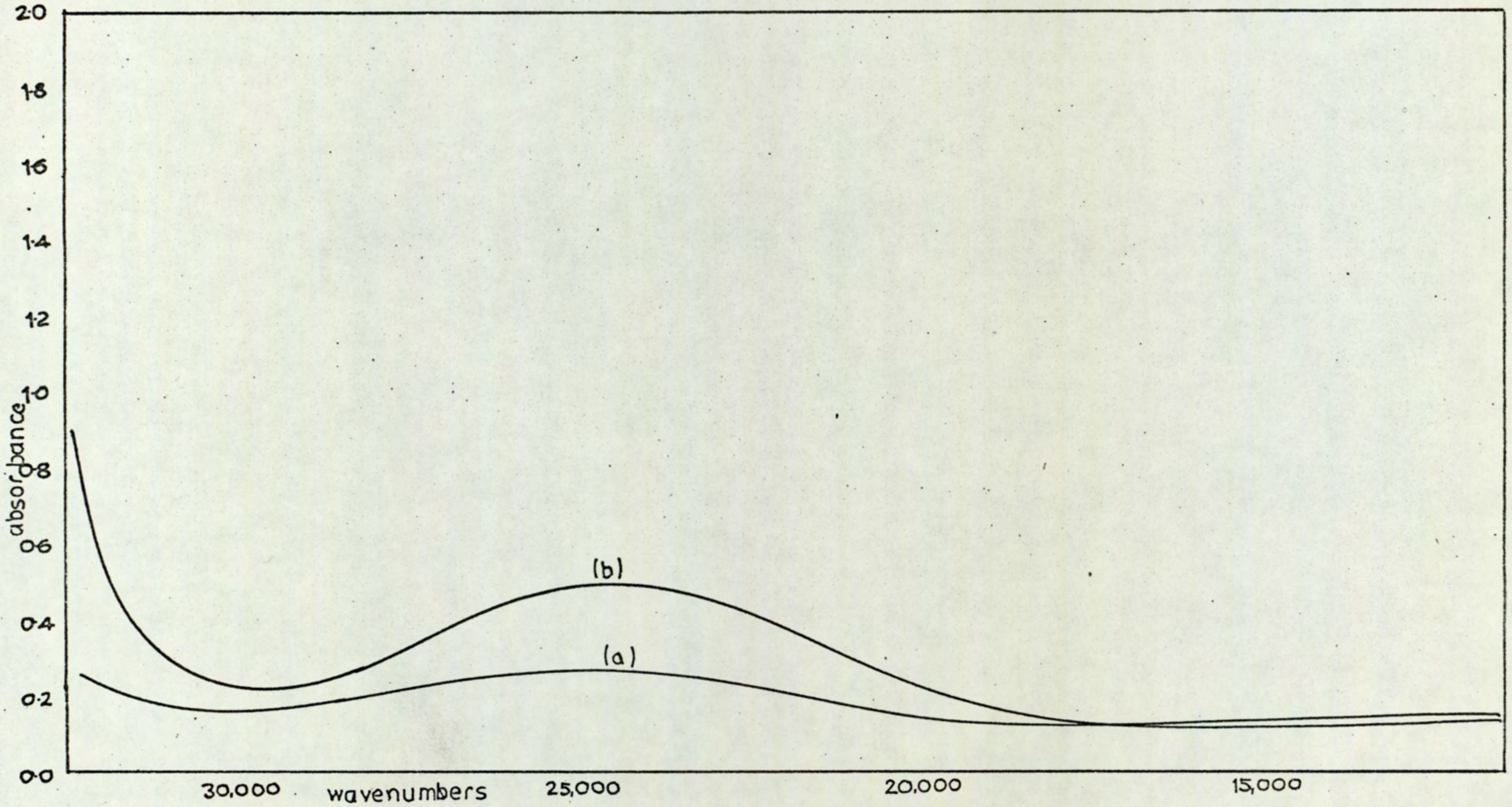


Fig. 12. Visible spectra of Ph_2Te_2; (a) in ethanol $5x10^{-4}M$; (b) in CCl_4 $5x10^{-4}M$

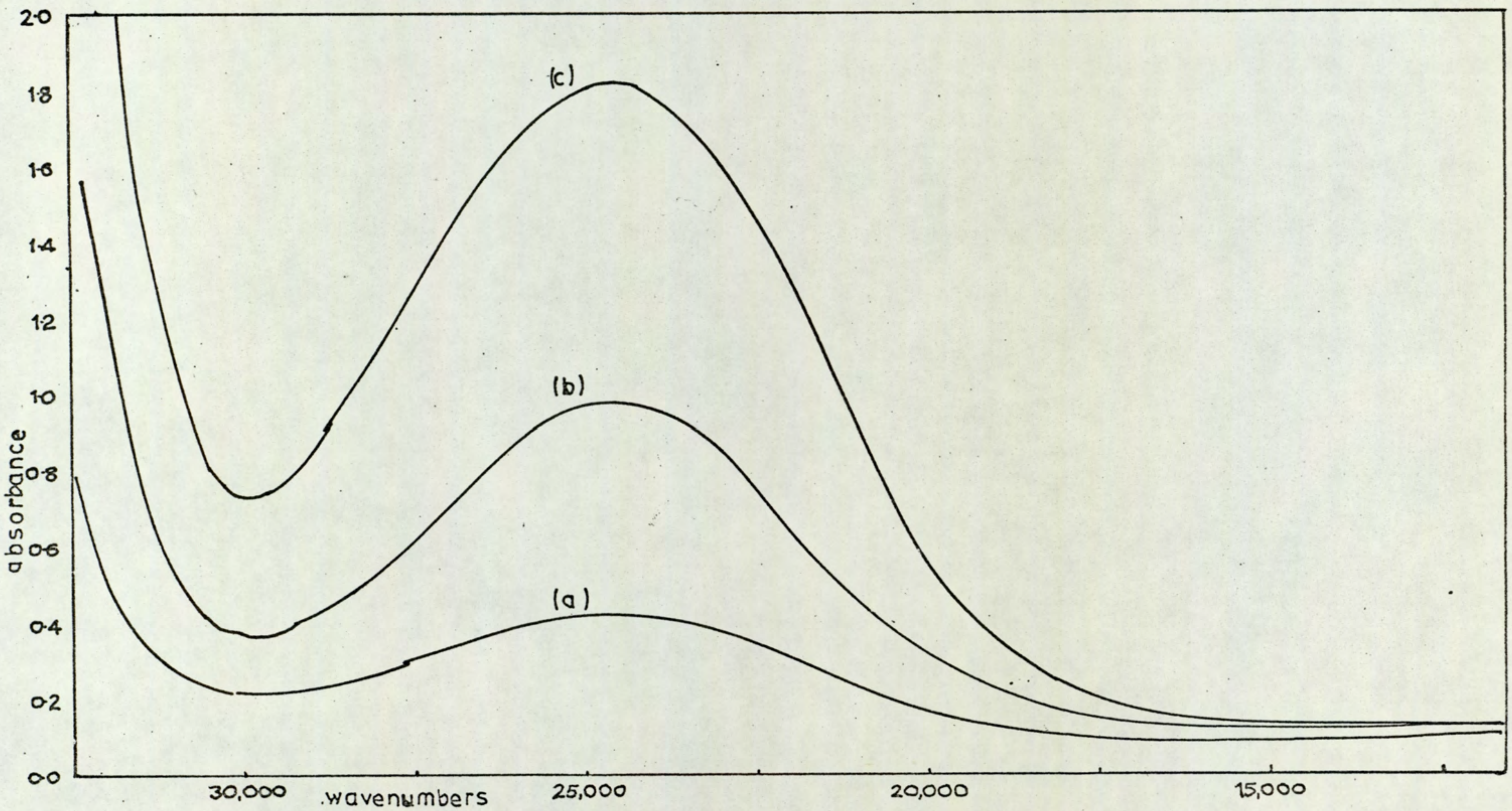


Fig.13. Visible spectra of Ph_2Te_2 in CCl_4; (a)$5x10^{-4}$M;(b)10^{-3}M;(c)$2x10^{-3}$M

DISCUSSION

The infrared spectra of phenyl compounds have been extensively studied, and they are now reasonably well understood. The low vibrational frequencies of phenyl compounds can be assigned satisfactorily according to Whiffin;[50] who considered the compounds as monosubstituted benzenes, PhX. The bands in this lower frequency region are "X-sensitive" modes. Thus their frequencies vary with the nature of the substituent in the molecule PhX. This approach had been applied satisfactorily for spectra of group IVA phenyl compounds.[51] An alternative approach for assignment of bands at low frequency is to consider them to be either of "X-Ph stretching" or "bending" vibrations since the low frequency "X-sensitive" vibrations involve stretching or bending of the X-phenyl bonds but this assignment is an approximate one.[52] The latter approach had been satisfactorily used for tin-phenyl vibrations in organotin compounds.[53]

The data for diphenyl ditelluride (Table 2) at low frequency will be considered first. These vibrational frequency modes may be assigned according to Whiffin and the bands can assigned as Table 2 labelling with Whiffin's notation. Alternatively some low frequency modes may be assigned as skeletal vibrations i.e. the deformation of the C-Te-Te-C skeleton. In the diphenyl ditelluride case the assignment of some low frequency modes as skeletal vibration of the C-Te-Te-C unit gives a more imformative interpretation.

The weak bands at 398 and 350 cm^{-1} were assigned to the phenyl w and phenyl w' modes respectively; the non X-sensitive out-of-plane ring deformation was always found occuring near 400 cm^{-1}. The weak band at 274 cm^{-1} was assigned for phenyl u (in-plane ring rotation against Te). The strong IR band at 255 cm^{-1} and a weak-medium Raman band counterpart at 253 cm^{-1} were assigned as νas(TePh) or phenyl t ("M-Ph stretching" vibration). The position of the frequency of i.r. of this mode depends on the mass of the metal. In this case it is expected that asymmetric stretching vibration will be strongly infrared active. The shoulder of IR band at 202 cm^{-1} and a strong band of Raman at 204 cm^{-1} counterpart were assigned as νs(TePh) or phenyl t'. It is again as expected that symmetric stretching vibration of tellurium-phenyl will be strongly Raman active. The strong IR band at 188 cm^{-1} and a weak Raman counterpart at 183 cm^{-1} were assigned as phenyl x (out-of-plane ring bending). The study of the diphenyltellurium dihalides[30] suggested that the strong IR band at 188 cm^{-1} with a very weak Raman counterpart is the characteristic of the Whiffin x mode in phenyltellurium compounds. The weak IR band at 146 cm^{-1} was assigned as phenyl x' mode. The bands at lower frequency were not assigned, since these can arise from the lattice vibrations of the crystals and the low frequency skeletal modes.

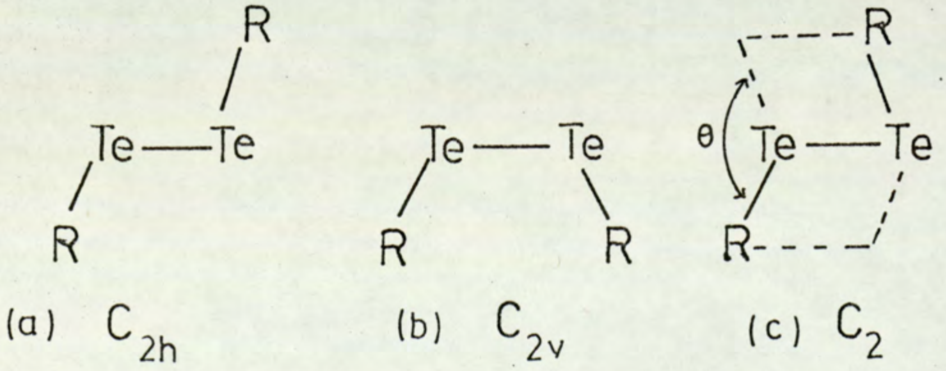
Finally, the strongest Raman band at 167 cm^{-1} with a shoulder IR counterpart at 169 cm^{-1} were assigned as ν(TeTe), the tellurium-tellurium stretching vibrational mode. The tellurium-tellurium stretching frequency is expected below $\Delta\nu = 200$ cm^{-1}. For the fact that the crystal structure of bis(p-chlorophenyl) ditelluride[54] has the Te-Te bond length of 2.70 Å, which is less than the covalent single bond length (2.74 Å), means that one cannot assume the Te-Te bond to be weak. On simple mass considerations, it is believed that ν(SnSn) in Me_6Sn_2 and Ph_6Sn_2 may be comparable to ν(TeTe) in Me_2Te_2 and Ph_2Te_2. Brown et al[55] suggested that ν(SnSn) = 190 cm^{-1} in Me_6Sn_2, and Bullimer et al[56] have reliably assigned Raman frequency of 140 cm^{-1} for ν(SnSn) in Ph_6Sn_2. Chen and George[11] suggested a weak IR band at 122 cm^{-1} for ν(TeTe) in Me_2Te_2 but Sink and Harvey[12] unambiguously assigned the strongest Raman band at 188 cm^{-1} to be the correct value for ν(TeTe). Thus the assignment for ν(TeTe) in Ph_2Te_2 is in a region comparable with that of ν(SnSn). The fact that the ν(TeTe) frequency in Ph_2Te_2 is slightly lower than that in Me_2Te_2, as expected for the heavier phenyl, appears consistent. Dodd et al[57] have also assigned ν(TeTe) at 167 cm^{-1} in $F_5Te-TeF_5$.

It has not attempted to analyse in detail the vibrational data of the more complex ditellurides since the presence of one more substituent in benzene ring would complicate the spectra in the lower frequency region. However it does appear very reasonable to assign the strongest Raman band below $\Delta\nu$ = 200 cm^{-1} as ν(TeTe), which is indicated in Table 3. In the case of $(p\text{-}MeO.C_6H_4)_2Te_2$ and $(p\text{-}PhO.C_6H_4)_2Te_2$ the assignments rely on IR data alone. The Raman data of these two ditellurides could not be obtained since they were the only two ditellurides which decomposed to elemental tellurium when placed in the laser beam. The reason for this decomposition is that they strongly absorbed the energy at 15,803 cm^{-1}

(6328 Å) see Fig. 11. It is, however, to be noted that the IR bands of these two compounds at $\sim$180 cm^{-1} in Table 3 certainly contain contributions from aromatic ring modes. All the ν(TeTe) of these six diaryl ditellurides were identified between 187 to 167 cm^{-1}.

The ν(TeTe) is observed to be sensitive to the changing of R in R_2Te_2 to some extent. However, it would be unwise to say that these frequency shifts are wholly attributable to the electronic effect of R since the shifts of ν(TeTe) could equally well arise from the crystal effects or from differing degree of coupling with other vibrations e.g. ν_s(TePh). In the case of (p-MeO.$C_6H_4)_2Te_2$ for which whose IR solution spectrum was obtained considerable shifts of some bands on change of phase were noted (Table 3).

The linear structure is impossible for a ditelluride, because tellurium is believed to use p orbitals for bonding. Thus the structure may be the one with configuration of either C_2 or C_{2h}, or C_{2v} symmetry which is the configuration between the limiting planar cases of those C_{2h} and C_{2v} as shown below.



(a) C_{2h} (b) C_{2v} (c) C_2

The skeletal configuration of a ditelluride; (a) C_{2h}, (b) C_{2v} and (c) C_2 symmetry.

The fact that many coincidences are observed between IR and Raman data (Table 2 and 3) eliminates a skeletal structure of C_{2h}. A skeletal structure of C_{2v} symmetry should has comparable IR intensity for both νas(Te-C) and νs(Te-C), whereas skeletal structure of C_2 symmetry would probably produce more intensity for νas(Te-C) and less intensity for νs(Te-C) in the IR and the reversal of this intensity relationship in the Raman spectrum. Thus, by accepting this argument, the assignments of Table 2 completely support a skeletal structure of C_2 symmetry with a relatively large dihedral angle. The good classical example for molecule of C_2 symmetry is hydrogen peroxide. This type of structure was found for $(p\text{-}ClC_6H_4)_2\text{-}Te_2$[53] which is isomorphous with the analogous diselenides whose dihedral angle between the planes containing the selenide to carbon bonds was 74.5°. The vibrational analysis of Me_2Te_2[12] was consistent with a structure of C_2 symmetry with a dihedral angle in the region of 82°.

The NMR spectra of $(p\text{-}MeO.C_6H_4)_2Te_2$ and $(p\text{-}EtO.C_6H_4)_2Te_2$ show the chemical shifts for methyl and methylene as is generally known. The chemical shifts and the spin-spin coupling of the protons in benzene ring of the two ditellurides are the same though the environments are different. There was no evidence observed for the spin-spin coupling between Te and H nuclei of benzene ring. Both ^1H and ^{125}Te have the spin quantum number of $\frac{1}{2}$, one might therefore expect the possibility of coupling between these two nuclei. A spin-spin coupling between ^{125}Te and ^1H nuclei in an Me-Te compound (J(Me-Te) = 20.7 Hz) has been reported.[57]

Some ions were indicated in the mass spectra of $(p\text{-EtO.C}_6\text{H}_4)_2\text{Te}_2$, $(p\text{-MeO.C}_6\text{H}_4)_2\text{Te}_2$, $p\text{-MeO.C}_6\text{H}_4\text{TeC}_6\text{H}_5$, and $(p\text{-MeO.C}_6\text{H}_4)_2\text{Te}_2$ in Table 4, 5, 6 and 7 respectively. From these tables it is obvious that the most prominent ions were $(p\text{-EtO.C}_6\text{H}_4)_2^+$, $(p\text{-MeO.C}_6\text{H}_4)_2^+$, $p\text{-MeO.C}_6\text{H}_4\text{-C}_6\text{H}_5^+$, and $(p\text{-MeO.C}_6\text{H}_4)_2^+$ which corresponded to the elimination of either one or two tellurium atoms. The very important ions are $(p\text{-EtO.C}_6\text{H}_4)\text{Te}^+$ and $(p\text{-MeO.C}_6\text{H}_4)\text{Te}^+$ which were the fragments obtained by the disruption of Te-Te bonds of the ditellurides.

There are two general points which can be drawn from the analysis of the data in Table 4 and 5. Firstly, the Te-C bonds in the ditellurides are weaker than Te-Te bonds because the ions corespond to the breaking of Te-C bonds are more abundance. Secondly, the fragmentation pattern of the two ditellurides can be shown as follows:

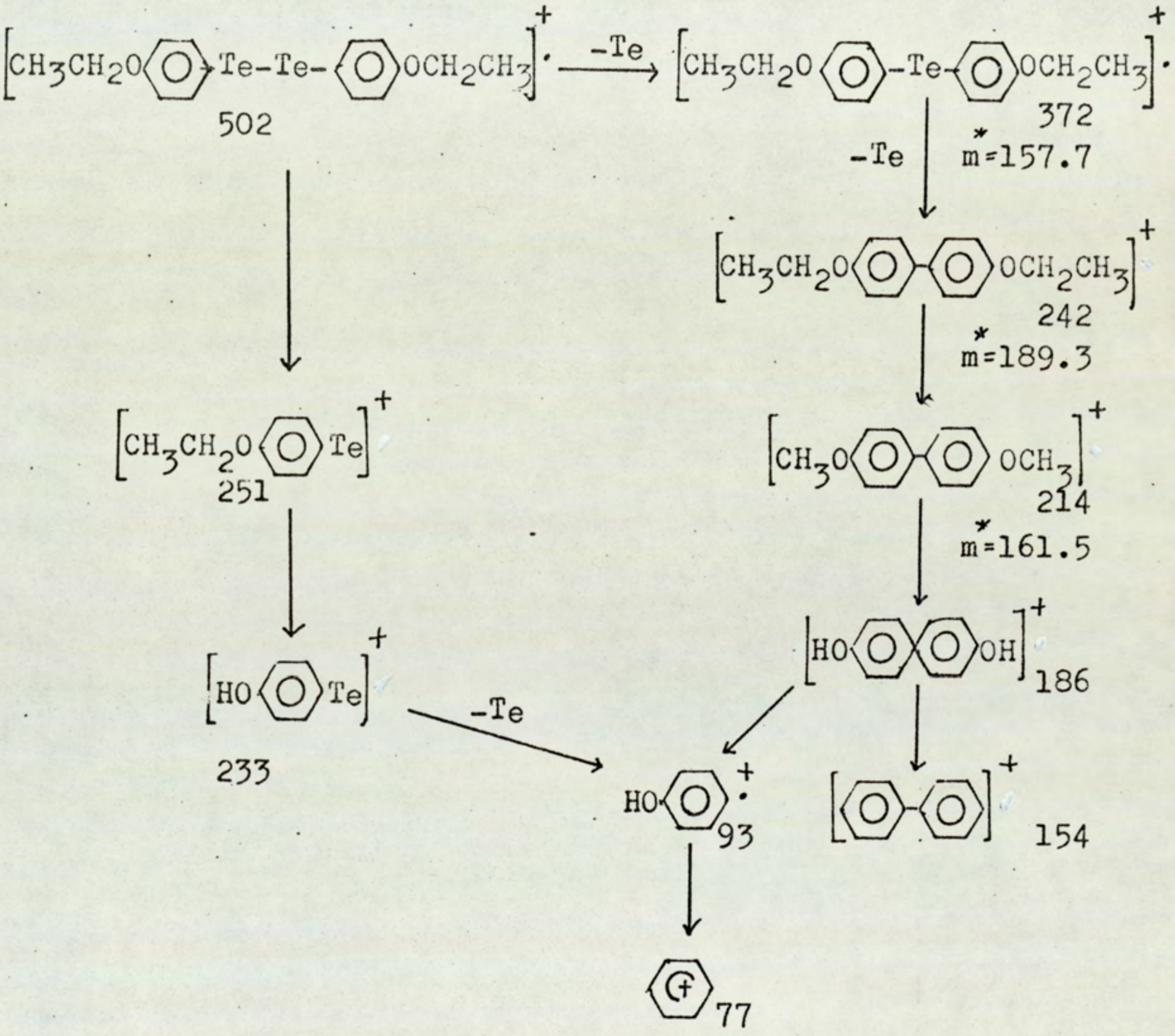
$$\text{R-Te-Te-R} \xrightarrow{+e} \text{R-Te-Te-R}^{+} + 2e \qquad \text{(a)}$$

$$\begin{tikzcd}
& \text{R-Te-R}^{+} \arrow[r, "-\text{Te}", "\text{m}"'] & \text{R-R}^{+} & \text{(b)} \\
\text{R-Te-Te-R}^{+} \arrow[ur, "\text{Te}"] \arrow[dr] & & & \\
& \text{RTe}^{+} + \text{RTe} & & \text{(c)}
\end{tikzcd}$$

where R is $p\text{-EtO.C}_6\text{H}_4$ or $p\text{-MeO.C}_6\text{H}_4$.

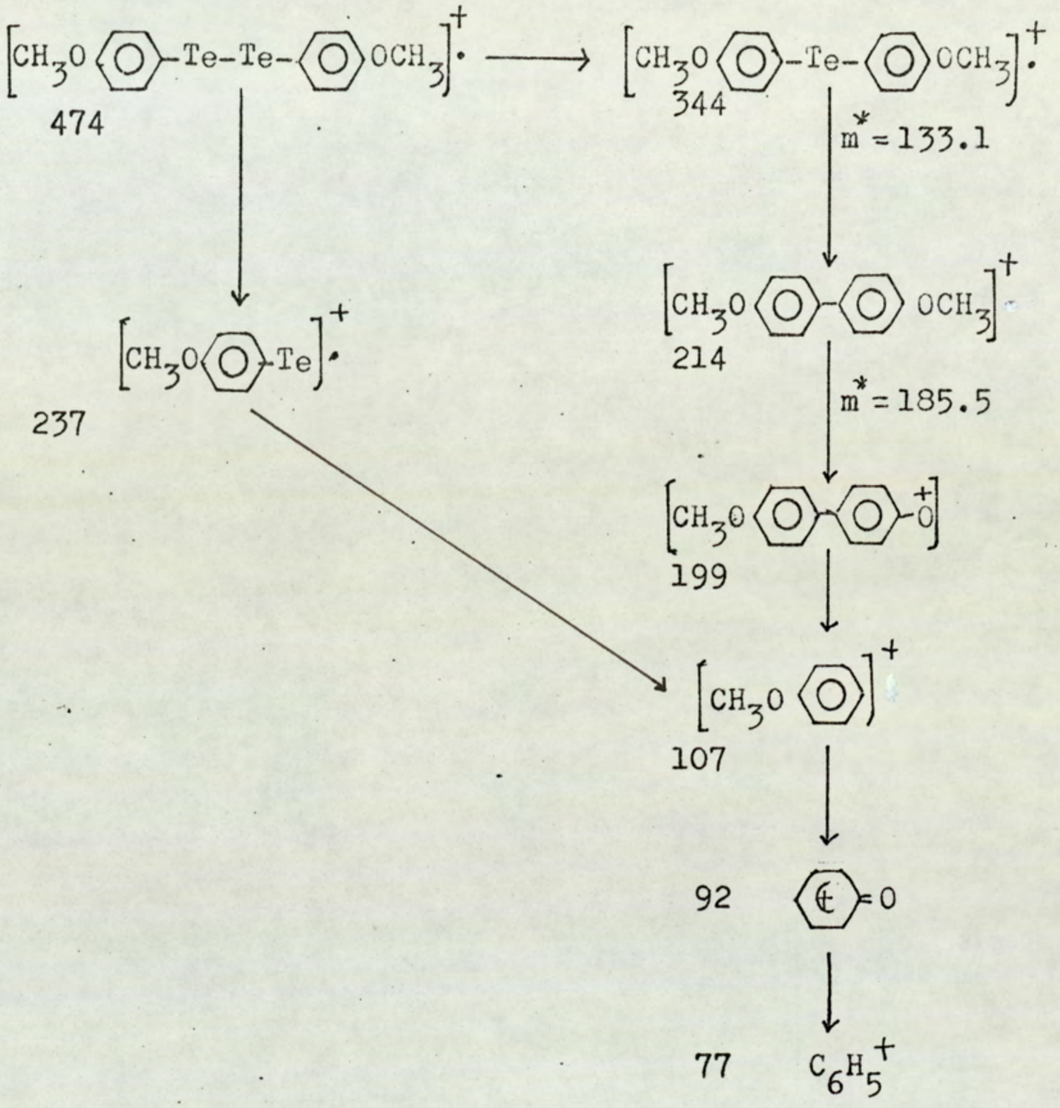
The path (b) is more favoured than path (c). In both ditellurides (Table 4 and 5) the stage $\text{R-Te-R}^{+} \longrightarrow \text{R-R}^{+}$ is further confirmed by the detection of metastable ions at mass-charge ratio of 157.7 and 131.1 for bis-p-phenetyl ditelluride and bis-p-anisyl ditellurides respectively. This observation is firmly supported by the recent mass spectra study of RTe-TeR (R = Ph, p-tolyl).[59]

The further fragmentations of the organic ions are complicated because they are more than one possible way. The most probable fragmentation pattern of bis-p-phenetyl ditelluride is shown below:



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

For bis-p-anisyl ditelluride the probable fragmentation pattern is as following:



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

As already mention, it is observed that ν(TeTe) is sensitive to some extent to the presence of R in R_2Te_2. The fact that RTe^+ ions are also observed in mass spectra suggest the possibility of establishing more positively the existence or non-existence of a relationship between ν(TeTe) and the Te-Te bond strength. This is possible if the unsymmetrical diaryl ditellurides can be synthesized.

Consider the fragmentation process:

$$\text{R-Te-Re-R} + e \longrightarrow \text{RTe}^{+} + \text{RTe} + 2e$$

The appearance potential for RTe^{+} is a (eV)

therefore $a = D(\text{R-Te-Te-R}) + I_1(\text{RTe})$

Where D is the bond dissociation energy(Te-Te) and I_1 is the ionization potential of RTe.

The fragmentation for R'TeT.R' is

$$\text{R'-Te-Te-R'} + e \longrightarrow \text{R'Te}^{+} + \text{R'Te} + 2e$$

and $b = D(\text{R'Te-TeR'}) + I_2(\text{R'Te})$

Now if RTeTeR' were synthesized.

$$\text{R-Te-Te-R'} + e \longrightarrow \text{RTe}^{+} + \text{R'Te} + 2e$$

or $$\text{R-Te-Te-R'} + e \longrightarrow \text{R'Te}^{+} + \text{RTe} + 2e$$

hence

$$c = D(\text{RTeTeR'}) + I_1(\text{RTe})$$

$$d = D(\text{RTeTeR'}) + I_2(\text{R'Te})$$

Since appearance potentials a, b, c and d are measurable, the unknown ionzation potentials can be eliminated.

$$a-c = D(\text{RTeTeR}) - D(\text{RTeTeR'})$$

$$b-d = D(\text{R'TeTeR'}) - D(\text{RTeTeR'})$$

Then the order of increasing Te-Te bond dissociation energy in RTeTeR, RTeTeR' and R'TeTeR' can be arranged and compared with the order of $\Delta\nu$ values from the Raman spectra.

The unsymmetrical diaryl ditellurides are unknown. The fact that compounds of the type RTeH and RTeX (X = halogen) are either unknown or of limited stability prevents a similar route of synthesis of unsymmetrical diselenides.[60]

$$\text{RSeX} + \text{R'SeH} \longrightarrow \text{RSeSeR'} + \text{HX}$$

It has been claimed that Ph_2Te_2 dissociated to radicals in solution,[13] and this idea has been adopted to explain the postulate of a radical mechanism for the formation of Ph_2Te_2 and Ph_2Te when phenylmagnesium bromide reacts with elemental tellurium.[14]

Thus, on the assumption that radicals may be produced the benzene solution of both Ph_2Te_2 and $(p\text{-}EtO.C_6H_4)_2Te_2$ was irradiated with U.V. for 6 hours. Thin layer chromatography showed that the solution contained only the two symmetrical starting ditellurides.

The reduction of the mixtures of $(p\text{-}MeO.C_6H_4)TeCl_3$ and $(p\text{-}EtO.C_6H_4)TeCl_3$, and of $(p\text{-}MeC_6H_4)TeCl_3$ and $(p\text{-}MeO.C_6H_4)TeCl_3$ by $Na_2S.9H_2O$ or $K_2S_2O_5$ agents gave only the mixtures of symmetrical ditellurides in each cases.

In one case the U.V. irradiation of the carbon tetrachloride solution containing $(p\text{-}MeC_6H_4)_2Te_2$ and $(p\text{-}MeO.C_6H_4)_2Te_2$ affords the mixture of products which contained at least the trichlorides of the starting ditellurides. This reaction occured because carbon tetrachloride is easily decomposed to radicals by U.V. irradiation.

$$CCl_4 \longrightarrow CCl_3^{\cdot} + Cl\cdot$$

The chloride radicals then attacked the ditellurides. A number of products can be produced by this photochemical reaction.

Thus the failure to synthesize the unsymmetrical diaryl ditellurides casts doubt about the validity of Farrar's claim;[13] he suggested that Ph_2Te_2 was substantially dissociated to radicals in chloroform solution. Diphenyl ditelluride was slightly soluble ($< 10^{-3}$M) in ethanol, but the visible spectra showed absorption maximum at 24,600 cm^{-1} which agrees well with that reported by Farrar at 24,570 cm^{-1} in chloroform. Also substitution of less polar solvent, carbon tetrachloride, for chloroform gives solutions which obey Beer's Law (Fig. 13) with λ max = 24,600 cm^{-1} and ε max = 937 $Lmol^{-1}$. This result agrees very well with Farrar's data for chloroform solution for which ε max = 930. Although the resolution is not very good the diffuse reflectance spectrum of solid diphenyl ditelluride (Fig. 11) is very similar indeed to the visible solution spectrum (Fig. 12). Farrar suggested that since Beer's Law is obeyed by dilute chloroform solution of Ph_2Te_2 it meant that the dissociation is largely complete. But, from the data of the present work, it would suggest that dissociation in the solid state, and in ethanolic, chloroform and carbon tetrachloride solutions is largely incomplete. It was further confirmed that there was not any paramagnetic species to be detected from Ph_2Te_2 solutions by the failure to observe an e.s.r. signal.

Thus it seems very unlikely that the ditelluride will readily dissociate into radicals as propose in one step of the reaction mechanism between phenylmagnesium bromide and tellurium.[14] Recently Haller and Irgolic[61] suggested the possibility of the radicals participating in this reaction. If this is true, it would be only a one-way reaction; the ditelluride can be formed from the coupling of the two radicals and once it is formed it cannot dissociate to radicals again.

CHAPTER IV

ARYLTELLURIUM TRIHALIDES

INTRODUCTION

There are many works on the structural investigation of dialkyl and diaryltellurium dihalides, and trialkyl and triaryltellurium monohalides. The structures of these compounds are now well established and understood. But there has not been any work on aryltellurium trihalides except the limited infrared investigation of $PhTeCl_3$.[10]

Five classes of aryltellurium trihalides were investigated by vibrational spectroscopy with the objective of identifying the tellurium-halogen vibrational modes and also, possibly the structures of the compounds. Though the presence of an aryl group will complicate the spectra of compounds but the possibility of examining a wide range of compounds offers some compensation, and it is the hope that this study may contribute to the greater understanding of the chemistry of aryltellurium trihalides.

For alkyltellurium trihalides, methyltellurium trihalides have been the subject of some investigations. Chen and George[22] investigated $MeTeBr_3$, and Wynne and George[23] studied some selenium analogues of the methyltellurium trihalides. Wynne and Pearson[24,32] have published two papers on CH_3TeCl_3 which are relevant to the present work.

EXPERIMENTAL

Most of the compounds are known and the methods of preparation were carried out according to literature procedures.

PHENYLTELLURIUM TRIHALIDES

Phenyltellurium trichloride

Farrar's method[13] for the preparation of phenyltellurium trichloride was first used: Phenylmercuric chloride(0.05 g) and tellurium tetrachloride(5.43 g) was mixed with dry dioxane(40 ml), and refluxed for 1½ hours with exclusion of moisture. The solution was cooled and fitered, then the filtrate was evaporated under reduced pressure until dryness. The solid product was recrystallized from sym-tetrachloroethane, the crystals obtained were recrystallized again from benzene. The final crystals were always contaminated with small amounts of greyish material which was difficult to remove by purification, and the compound melted below the reported melting point.

The same result was obtained regardless of the number of attempts and with various conditions.

Finally phenyltellurium trichloride was synthesized indirectly which is similar to the synthesis of aryltellurium tribromide and tri-iodide; phenyltellurium trichloride obtained after recrystallization from tetrachloroethane as above was reduced by potassium metabisulphite (see preparation of Ph_2Te_2 in Chapter III) to diphenyl ditelluride.

Diphenyl ditelluride(0.4 g) was dissolved in carbon tetrachloride(20 ml), and chlorine gas was bubbled through the cooled solution at 0° C with continuous stirring. The red brown solution changed to light brown and finally a white precipitate appeared. The white product (0.5 g) was filtered and dried, and had a melting point between 214-17° C without further recrystallization (lit.[13] 215-18° C).

(Found: C,22.5; H,1.55; $C_6H_5Cl_3Te$ requires: C,23.2; H,1.6%).

It was found later that phenyltellurium trichloride which was synthesized from diphenyl ditelluride (obtained from reduction of crude phenyltellurium before recrystallization from sym-tetrachloroethane) was not colourless even when recrystallized from benzene. It is pale yellowish but the compound still melted at correct melting point.

Phenyltellurium trichloride is very soluble in warm benzene; this observation is in contrast to Farrar's who reported that a large quantity of warm benzene had to use for dissolving about one gram of the compound. Phenyltellurium trichloride when stored in sample tube and exposure to light changed to a slightly greyish solid. So a small amount of $PhTeCl_3$ in a watch glass was irradiated by a U.V. lamp in a dark room. During the first hour the colour changed to brown, after continued irradiation for another 1½ hours the colour was more intense. However it was found that only the sample surface underwent colour change, and the melting point did not change.

Phenyltellurium tribromide

There are no details of phenyltellurium tribromide in the paper of Petragnani and Vicentini,[40] except the brief mention that it was prepared.

Bromine in carbon tetrachloride was slowly added to a solution of diphenyl ditelluride(0.81 g) in carbon tetrachloride which was cooled at about 10° C and magnetically stirred. The solution of diphenyl ditelluride changed from brown to yellow with the precipitation of a yellow compound, excess bromine was added, this was done by observing the existence of bromine colour in the solvent. The mixture was continuously stirred for another 30 minutes. The precipitate was filtered and dried, and recrystallized from glacial acetic acid. Yellow crystals(0.79 g) were obtained, and the crystals melted at 227-29° C dec.
(Found: C,16.2; H,1.15; $C_6H_5Br_3Te$ requires: C,16.2; H,1.15%).

Phenyltellurium tri-iodide

This unknown compound was synthesized by the same procedure as those of phenyltellurium tribromide. Diphenyl ditelluride(0.39 g) was dissolved in carbon tetrachloride, and the solution was cooled and maintained at 3-5° C. Iodine (0.72 g) in carbon tetrachloride was added slowly while the solution of ditelluride was continuously stirred. The mixture was stirred for an hour after all iodine solution added. Filtered and dried, the red brown product was recrystallized from benzene-petroleum ether(60/80°) yielded brown crystals(0.31 g) which melted at 180-81° C dec.
(Found: C,12.5; H,0.85; $C_6H_5I_3Te$ requires: C,12.3; H,0.85%).

If the iodine solution was added to the solution of diphenyl ditelluride at 10-15° C a black precipitate was obtained. On carefully examining the black precipitate, it was found to consist of black and red-brown compounds. The mixture was recrystallized from benzene red-brown and black crystals were obtained again. No suitable solvent was found to enable the separation of two compounds to be achieved.

The black crude product was refluxed with excess thiourea in benzene for 1 hour, the hot mixture was filtered and the filtrate yielded dark-yellow gilttering crystals after setting aside. The infrared spectrum of the crystals showed no evidence of sulphur-metal bonds.

An interesting observation was made for the filtrate from the dark-yellow product. First the solution was blue, but standing some benzene evaporated and the volume reduced; the solution became green. A few drops of concentrated nitric acid was added and the solution changed to red.

When a large quantity of crude phenyltellurium tri-iodide was recrystallized from benzene black precipitate was separated from benzene solution when the filtrate set aside for cooling. To avoid this the time of heating of tri-iodide in benzene must be very short.

p-Tolyltellurium trihalides

Both p-tolyltellurium tribromide and tri-iodide are unknown, and they were synthesized by parallel methods to those of phenyltellurium tribromide and tri-iodide.

p-Tolyltellurium trichloride

p-Tolyltellurium trichloride was prepared by two procedures.

1. Direct procedure[13]

p-Tolylmercuric chloride(3.2 g), tellurium tetrachloride(2.7 g) and dry dioxane(20 ml) were refluxed for 1½ hours. The solution was cooled and the $HgCl_2 \cdot$ dioxane crystals filtered off, and the filtrate was evaporated to dryness. The crude product was first recrystallized from sym-tetrachloroethane and finally recrystallized from dry benzene. The colourless crystals(1.2 g) melted at 187-188° C dec. (lit. 181-182° C).

(Found: C,25.7; H,2.1; $C_7H_7Cl_3Te$ requires: C,25.9; H,2.2%).

2. Indirect procedure

The procedure was carried out similar to the synthesis of phenyltellurium trichloride. Bis-p-tolyl ditelluride(0.6 g) was dissolved in carbon tetrachloride, and the solution was oxidized by chlorine gas. The white powder product(0.5 g) was obtained, and melted at 197-200° C dec.

(Found: C,25.9; H,2.1; $C_7H_7Cl_3Te$ requires: C,25.9; H,2.1%).

p-Tolyltellurium tribromide

To a cold solution of bis-p-tolyl ditelluride (0.62 g) in carbon tetrachloride at 10 C° bromine in carbon tetrachloride was slowly added. The red brown ditelluride solution changed to yellow and a yellow precipitate separated out, at which point excess bromine solution was added. The solution was stirred for another 30 minutes, after which the product was filtered and dried. The product was recrystallized from glacial acetic acid to yield yellow plate-like crystals(0.46 g) and melted at 215-216° C dec.

(Found: C,18.8; H,1.65; $C_7H_7Br_3Te$ requires: C,18.3, H, 1.55%).

p-Tolyltellurium tri-iodide

Iodine(1.02 g) in carbon tetrachloride was added into a cold solution of bis-p-tolyl ditelluride(0.44 g) in carbon tetrachloride at 5° C which was continuously stirred. Stirring continued for 30 minutes after all the iodide solution was added. The red brown crude product was filtered and dried, and recrystallized from benzene. The product was red brown needle crystals(0.65 g) and melted at 175-176° C dec.

(Found: C,14.6; H,1.5; $C_7H_7I_3Te$ requires: C,14.0; H,1.15%).

p-ANISYLTELLURIUM TRIHALIDES

p-Anisyltellurium trichloride[36,39]

A mixture of anisyl(10.4 g), tellurium tetrachloride(13.5 g) and chloroform or carbon tetrachloride (100 ml) was refluxed for 2 hours. The yellow crystals obtained(10.7 g) were recrystallized from chloroform to afford yellow plates which melted at 196-197° C dec. (lit. 190° C).

(Found: C,24.2; H,2.05; $C_7H_7Cl_3OTe$ requires: C,24.6; H, 2.05%).

p-Anisyltellurium tribromide[49]

Bromine in carbon tetrachloride was slowly added to an ice-cold solution of bis-anisyl ditelluride(1.4 g) in carbon tetrachloride, and excess bromine solution was added.

The mixture was continuously stirred for another hour after which the yellow product was filtered and dried. The product was recrystallized from glacial acetic acid and yielded yellow crystals(1.16 g) which melted at 189-190° C dec. (lit. 188-189° C).
(Found: C,17.6; H,1.4; $C_7H_7Br_3OTe$ requires: C,17.7; H, 1.15%).

p-Anisyltellurium tri-iodide[49]

To a cold solution of bis-p-anisyl ditelluride (1.3 g) in carbon tetrachloride, iodine(2.3 g) in carbon tetrachloride was slowly added. The temperature of the solution was maintained at 5-10° C. The solution was stirred for another hour. The crude product obtained was recrystallized from benzene to yield black needle-like crystals(1.0 g) of tri-iodide which melted at 131-32° C (lit. 131-133° C).
(Found: C,13.7; H,1.1; $C_7H_7I_3OTe$ requires: C,13.7; H,1.15%).

p-PHENETYLTELLURIUM TRIHALIDES

p-Phenetyltellurium trichloride[37,39]

Phenetol(17.0 g), tellurium tetrachloride(12.0 g) and chloroform or carbon tetrachloride(100 ml) were mixed together and refluxed for 2 hours. Yellow crystals(14.7 g) were obtained and melted at 184-187° C dec. (lit. 182-183° C). without further recrystallization.
(Found: C,26.8; H,2.55; $C_8H_9Cl_3OTe$ requires: C,27.1, H, 2.55%).

p-Phenetyltellurium tribromide[49]

Bis-p-phenetyl ditelluride(2.0 g) reacted with excess bromine in carbon retrachloride. The product was recrystallized from glacial acetic acid afforded yellow crystals which melted at 197-206° C (lit. 195-205° C). (Found: C,19.3; H,1.9; $C_8H_9Br_3OTe$ requires: C,19.7, H,1.85%).

p-Phenetyltellurium tri-iodide[49]

Bis-p-phenetyl ditelluride(1.0 g) reacted with iodine(1.6 g) in carbon tetrachloride. The product obtained was recrystallized from benzene afforded black needle crystals(0.8 g) which melted at 133-34° C (lit. 133-134° C). (Found: C,15.7; H,1.45; $C_8H_9I_3OTe$ requires: C,15.3; H, 1.45%).

p-PHENOXYPHENYLTELLURIUM TRIHALIDES

p-Phenoxyphenyltellurium trichloride[48]

A mixture of diphenyl ether(18.7 g), tellurium tetrachloride(23.8 g) and dry chloroform(15 ml) was heated under reflux for 26 hours. One hour after the reaction was started a pink precipitate was observed. The product obtained after the mixture was filtered was a very sticky pink mass which after setting aside for sometime solidified.

The reaction was repeated many times by varying the time and conditions; i.e. different batch of diphenyl ether and tellurium tetrachloride, dry chloroform or carbon tetrachloride. This reaction did not reproduce the reported method which said the yellow crystals of the trichloride was readily separated from the solution.

The solidified pink product was refluxed again with dry chloroform(30 ml) for 20 hours and yielded a yellow-pink precipitate which was filtered and dried. The yellow crystals were obtained after recrystallization from carbon tetrachloride and melted at 155-156° C (lit. 156-157° C). It was noted that the colour of the trichloride obtained from each recrystallization vary from pale-yellow to deep yellow.
(Found: C,36.1; H,2.15; $C_{12}H_9Cl_3OTe$ requires: C,35.8; H,2.25%).

p-Phenoxyphenyltellurium tribromide[49]

Bis-p-phenoxyphenyl ditelluride(0.68 g) was bromogenolyzed with excess bromine in carbon tetrachloride. The product(1.9 g) was recrystallized from glacial acetic acid to yield yellow crystals which melted at 204-205° C (lit. 206.5-207° C).
(Found: C,26.5; H,1.65; $C_{12}H_9Br_3OTe$ requires: C,26.5; H, 1.7%).

p-Phenoxyphenyltellurium tri-iodide[49]

Bis-p-phenoxyphenyl ditelluride(0.5 g) was reacted with iodine(0.76 g) in carbon tetrachloride. The crude product(1.17 g) was recrystallized from benzene-petroleum ether(60/80°) to afford a reddish brown crystals which melted at 161-162° C (lit. 160.5-161° C).
(Found: C,22.2; H,1.45; $C_{12}H_9I_3OTe$ requires: C,21.3; H, 1.35%).

Synthesis of 1-Naphthyltellurium trichloride[49]

To synthesize 1-naphthyltellurium trichloride 1-naphthylmercuric chloride had to be prepared first.[62]

α-Naphthylamine(14.3 g) and conc. hydrochloric acid(80 g) was diazotized with $NaNO_2$(9 g). Then the filtrate was reacted with mercuric chloride(27 g) and yielded a yellow product($C_{10}H_7N_2Cl_3H_9$).

$C_{10}H_7N_2Cl_3H_9$(35 g) was mixed with acetone(220 ml) and reacted with copper powder(11.2 g). Dark brown 1-naphthylmercuric chloride was obtained, and melted at 189-191° C. A mixture of 1-naphthylmercuric chloride(7.2 g), tellurium tetrachloride(5.4 g) and dioxane(40 ml) was refluxed for 2 hours. The dioxane mercury chloride complex which precipitated on cooling was removed by filtration. The filtrate was evaporated until a viscous oil was obtained. Petroleum ether(60/80°) was added to the oil and left overnight; the oil solidified and was separated by filtration and dried on a porous plate. The crude trichloride(7.2 g) was yellow-green. The product was very difficult to recrystallize from glacial acetic acid because the trichloride is readily hydrolysed by moisture. However some yellow crystals were obtained by avoiding prolong heating the solution and melted at 174-182° C.

Attempts to Synthesize Aryltellurium Tribromides Directly

1. The synthesis of phenyltellurium tribromide

A mixture of phenylmercuric chloride(3.0 g), tellurium tetrabromide(4.5 g) and dry dioxane(30 ml) was refluxed with magnetic stirring for 3 hours with exclusion of moisture. The solution was black and there were some undissolved compounds. The mixture was cooled and filtered, and the filtrate was evaporated to dryness. The yellow-black crude product was recrystallized twice from glacial acetic acid in order to get yellow crystals of the tribromide. The yield was very poor only a small quantity was obtained

2. The synthesis of p-anisyltellurium tribromide

A mixture of anisol(3.2 g), tellurium tetrabromide(4.4 g) and dioxane(50 ml) was refluxed with exclusion of moisture for 6 hours. The black solution was cooled and filtered, and the filtrate was evaporated to dryness under vacuum. The crude product was dried after which it was recrystallized twice from glacial acetic acid. The yellow crystals of tribromide(0.5 g) was obtained which melted at 186-189°C. The percentage yield was 10% compared to 41% of the indirect method.

If carbon tetrachloride was used as a solvent there was no reaction.

ATTEMPTS TO SYNTHESIZE A TELLURIUM YLIDE

Bis-p-phenetyltellurium dichloride had to be prepared first.[37] A mixture of phenetol(60.72 g) and tellurium tetrachloride was refluxed for 8 hours at 180-190°C. Petroleum ether(80/100°) was added to the solution and left overnight. The crude brown product obtained after filtration was recrystallized from methanol and yield white needle crystals(12.8 g) which melted at 107-108 °C. The attempt to prepare a tellurium ylide precursor

$(p\text{-}EtO.C_6H_4)_2TeICH_2C_6H_5$ employed the procedure of Lederer.[63]

A solution of bis-p-phenetyltellurium dichloride (9.25 g) in benzene(200 ml) under N_2 gas was taken and stirred. A Grignard reagent of benzyl bromide(10.8 g), magnesium(1.53 g) and dry ether(50 ml) was added rapidly. The expected white solid of $(p\text{-}EtO.C_6H_4)_2TeBrCH_2C_6H_5$ was not obtained. The organic layer was evaporated to afford an yellow oil which when set aside for some days yielded a pale yellow precipitate. The precipitate was recrystallized from ethanol and white crystals were obtained. This was found to be bis-p-phenetyl telluride by a mixed melting point with the known telluride. Separation by thin layer chromatography of the yellow oil showed that it was a mixture of bis-p-phenetyl telluride, dibenzyl and other unidentified compounds.

RESULTS

1. Synthesis

Four unknown compounds were synthesized these are phenyltellurium tribromide and tri-iodide, and p-tolyltellurium tribromide and tri-iodide.

Pure phenyltellurium trichloride and p-tolyltellurium trichloride can be prepared indirectly; chlorogenolysis of the corresponding ditellurides.

$RTeBr_3$ (R = Ph, and $MeO.C_6H_4$) can be synthesized directly from the reaction between tellurium tetrabromide and phenylmercuric chloride or anisol but the reactions were slow, and it was difficult to obtain the products in a pure state and yields were very poor.

The method of synthesis of $(p\text{-}PhO.C_6H_4)TeCl_3$ could not repeated. A modified method was used to obtain the compound.

2. The solubilities of the phenyltellurium trihalides

The solubilities of the phenyl-compounds in benzene were qualitatively investigated, and the order of solubility was $PhTeCl_3 \gg PhTeI_3 > PhTeBr_3$.

3. Conductivity Measurements

The molar conductivity of the phenyl and p-tolyltellurium trihalides in DMF are shown below:

$PhTeCl_3$	31.28	$ohm^{-1}cm^2mol^{-1}$
$PhTeBr_3$	42.16	"
$PhTeI_3$	102.48	"

p-$MeC_6H_4TeCl_3$	39.44	$ohm^{-1}cm^2mol^{-1}$
p-$MeC_6H_4TeBr_3$	42.16	"
p-$MeC_6H_4TeI_3$	68.00	"

b. The conductivity of p-$MeC_6H_4TeCl_3$ at various concentrations in DMF are given as following:

$1 \times 10^{-3}M$	27.88	$ohm^{-1}cm^2mol^{-1}$
$5 \times 10^{-4}M$	31.01	"
$4 \times 10^{-4}M$	32.98	"
$2.5 \times 10^{-4}M$	36.99	"
$1 \times 10^{-4}M$	71.40	"
$5 \times 10^{-5}M$	119.68	"

The graph plotting $\sqrt{C}$ versus molar conductance is shown in Fig. 14.

4. Vibrational spectra

The IR and Raman spectra at low-frequency(below 400 cm^{-1}) of phenyltellurium trichloride, -tribromide and -tri-iodide are tabulated in Table 8, the IR spectra are shown in Fig. 15, 16, 17 and Raman spectra are shown in Fig. 18, 19 and 20.

For other aryltellurium trihalides, $RTeX_3$ (R = p-tolyl, p-$MeO.C_6H_4$, p-$EtO.C_6H_4$ and p-$PhO.C_6H_4$; X = Cl, Br and I) the low-frequency vibrational spectra are tabulated in Table 9 and the tellurium-halogen vibrational modes are given in Table 10.

The tri-iodides absorbed strongly at 6328 Å and showed signs of decomposition in the laser beam therefore only limited data are reported.

The infrared spectra of all aryltellurium trihalides above 400 cm^{-1} are identifiable with the modes of the organic groups, R, in $RTeX_3$ and need not be further discussed.

5. X-ray powder photographs

The d-spacing values of all trihalide compounds are tabulated in Table 11, 12, and 13. The quality of the photographs were poor especially for the tribromides.

6. Mass spectra

The mass spectra of aryltellurium trihalides $RTeX_3$ (R = Ph, p-tolyl and p-EtO.C_6H_4; X = Cl, Br and I) are tabulated in Table 14, 15 and 16. The mass spectrum of phenyltellurium trichloride at 10 eV is tabulated in Table 17. These tables contain only the important ions and the unidentified ions of high relative abundance.

7. ^1H n.m.r. spectra

There was no suitable solvent for aryltellurium trihalides to investigate the compounds by ^1H n.m.r.. However, two compounds p-anisyl and p-phenetyltellurium trichloride were dissolved in methyl cyanide and p-phenetyltellurium trichloride dissolved in ethanol in order to investigate the aromatic protons which are not interfered with by the protons in these two solvents.

For p-anisyltellurium trichloride in methyl cyanide the two protons which are at the meta position to the methoxy group show a doublet of ratio 1:1 at 1.65 τ, J = 10Hz and the other two protons which are at the ortho position to the methoxy group show a doublet of ratio 1:1

at 2.83 τ, J = 10Hz.

For p-phenetyltellurium trichloride in methyl cyanide the two protons which are at meta position to the ethoxy group show a doublet of ratio 1:1 at 1.70 τ, J = 10Hz; and the other two protons which are at ortho position to the ethoxy group show a doublet of ratio 1:1 at 2.87 τ, J = 10Hz. It was also the same for the compound in ethanol solution except that the signal for the two protons at the meta position to ethoxy group is shifted to 1.62 τ.

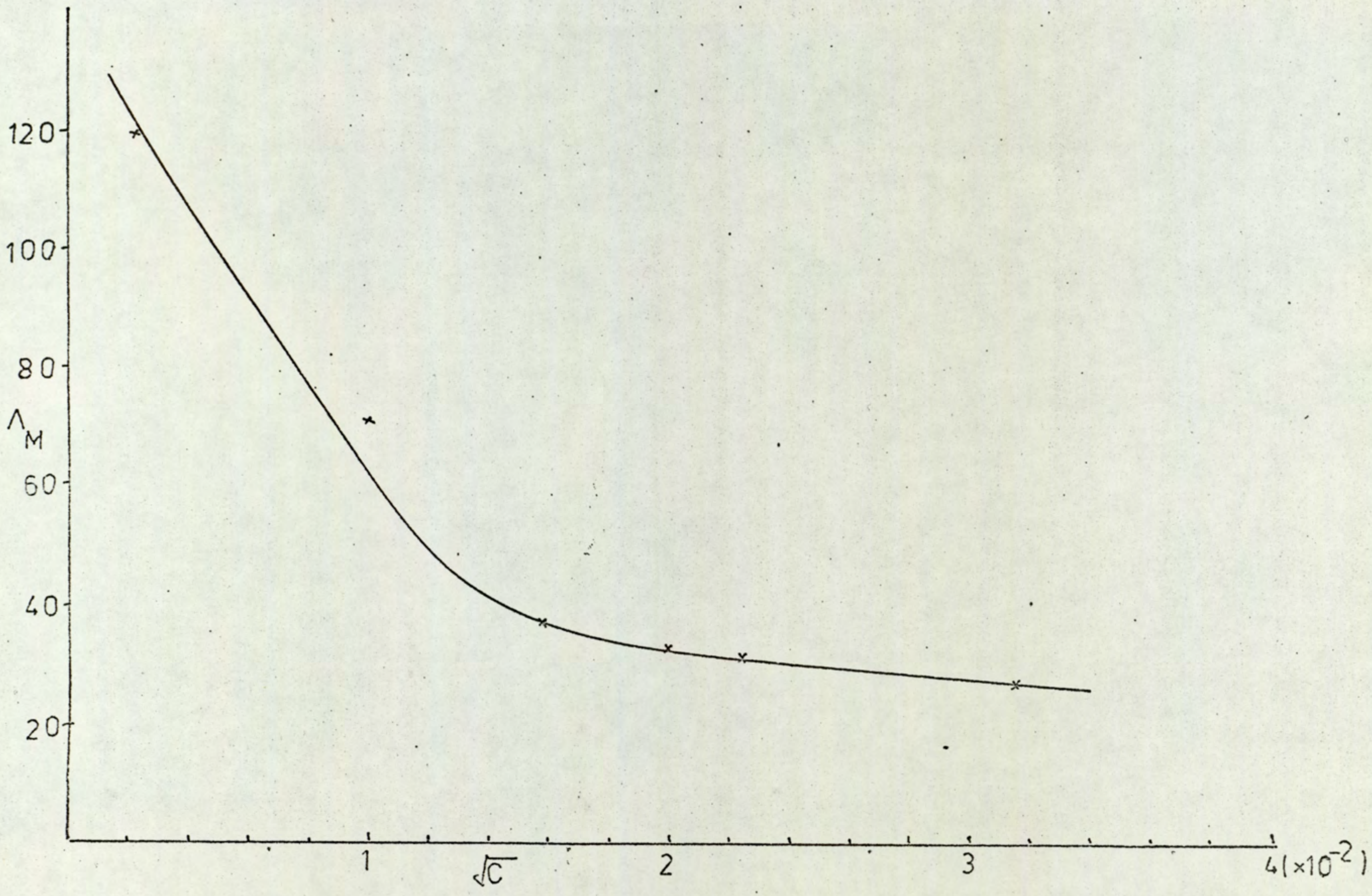


Fig.14. $(p\text{-}MeC_6H_4)TeCl_3$ in dimethylformamide

TABLE 8

The Low-frequency Vibrational Spectra of Phenyltellurium Trihalides

$PhTeCl_3$		$PhTeI_3$		$PhTeBr_3$		Assignment
i.r. (cm^{-1})	Raman	i.r. (cm^{-1})	Raman	i.r. (cm^{-1})	Raman	
337 s	342 s	169 s	168 s	220 sh		ν(Te-X) terminal
317 sh	318 m			213 s	210 sh	
306 s	303 m	158 s	153 s	198 m	198 vs	
178 s	174 w	97 m	94 m	134 m	132 w	ν(Te-X)bridge + $\delta(TeX_2)$
153 sh	143 m	86 m		123 m	120 vw	
				113 sh		
260	263 m	250sh		260 ms		ν(Te-Ph) i.e. phenyl t and t' modes
255 m	256	247 m	241			
250		241	238 m		234 m	
206 m			205			Phenyl x and u modes
		196 m		185 m		
		100 m				
				93 w		Unassigned

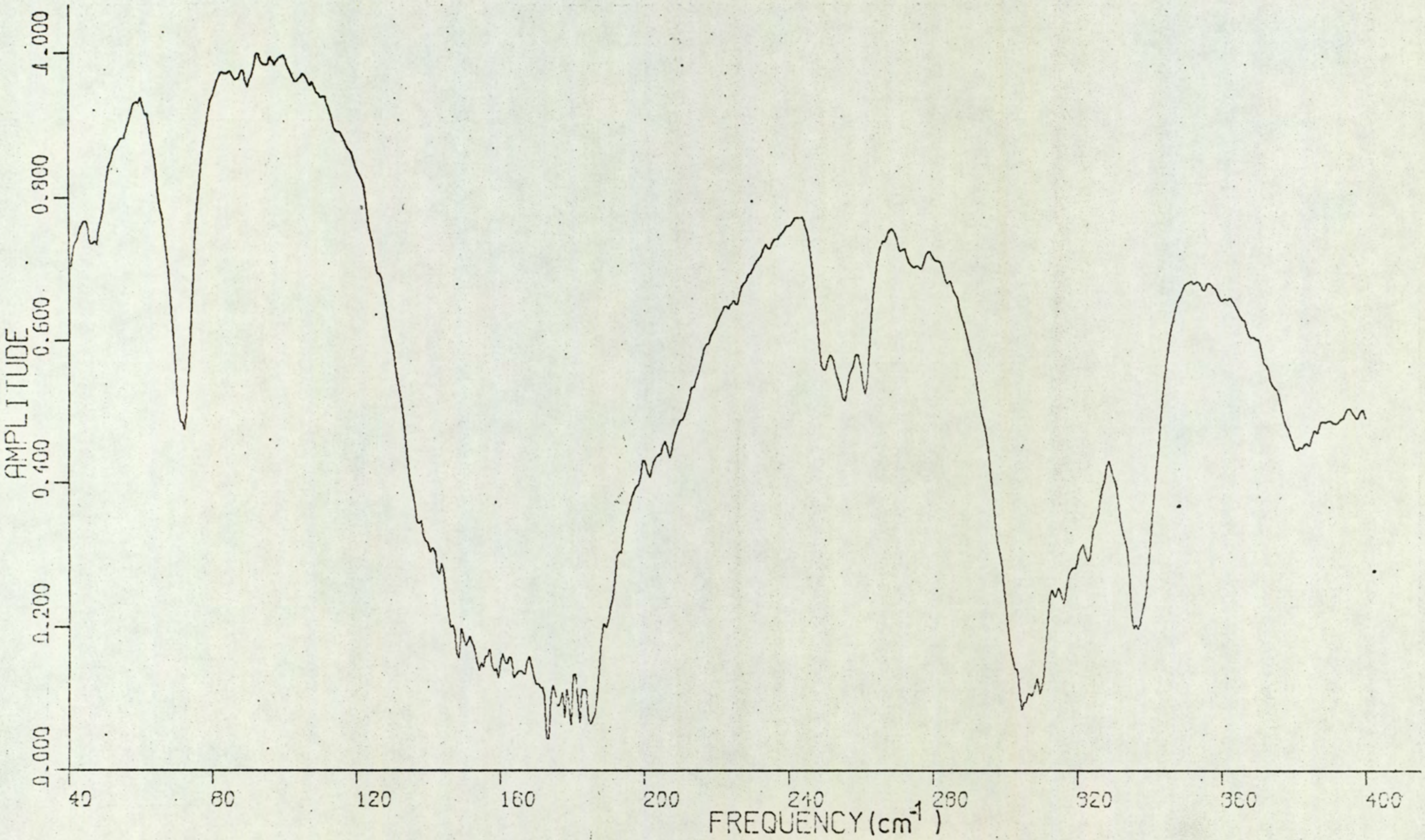


Fig.15. Far-infrared spectrum of $PhTeCl_3$

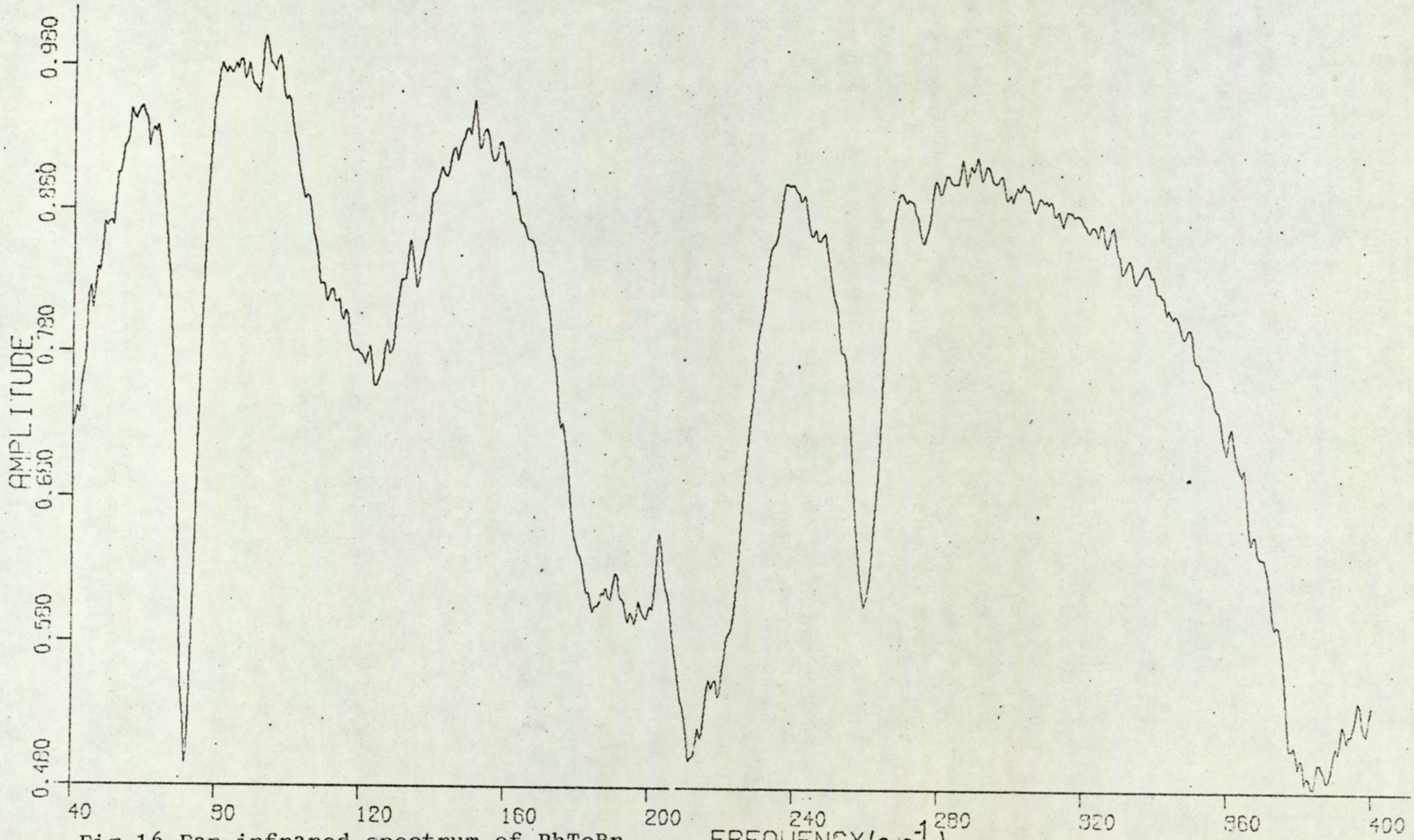


Fig.16. Far-infrared spectrum of $PhTeBr_3$

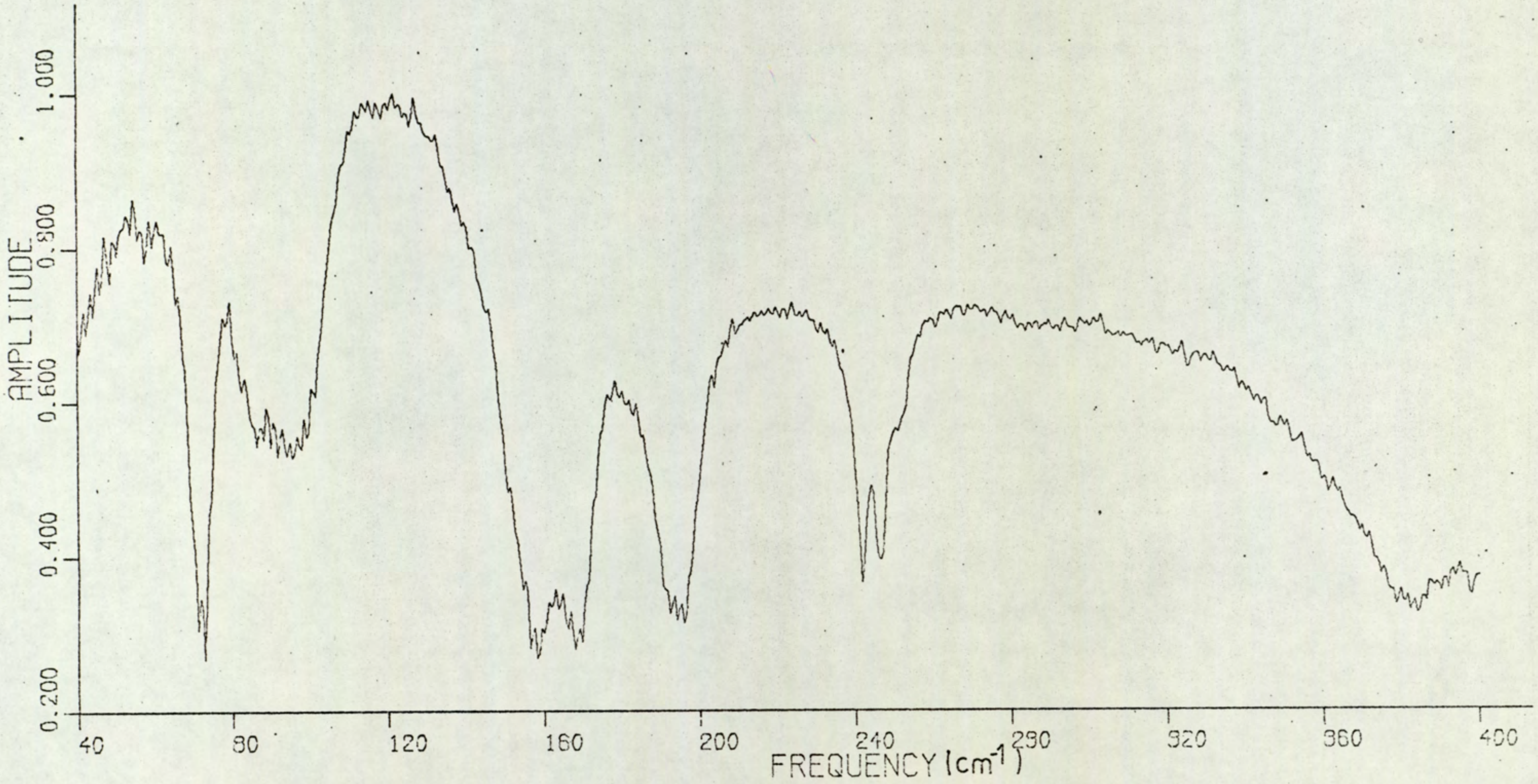


Fig.17. Far-infrared spectrum of $PhTeI_3$

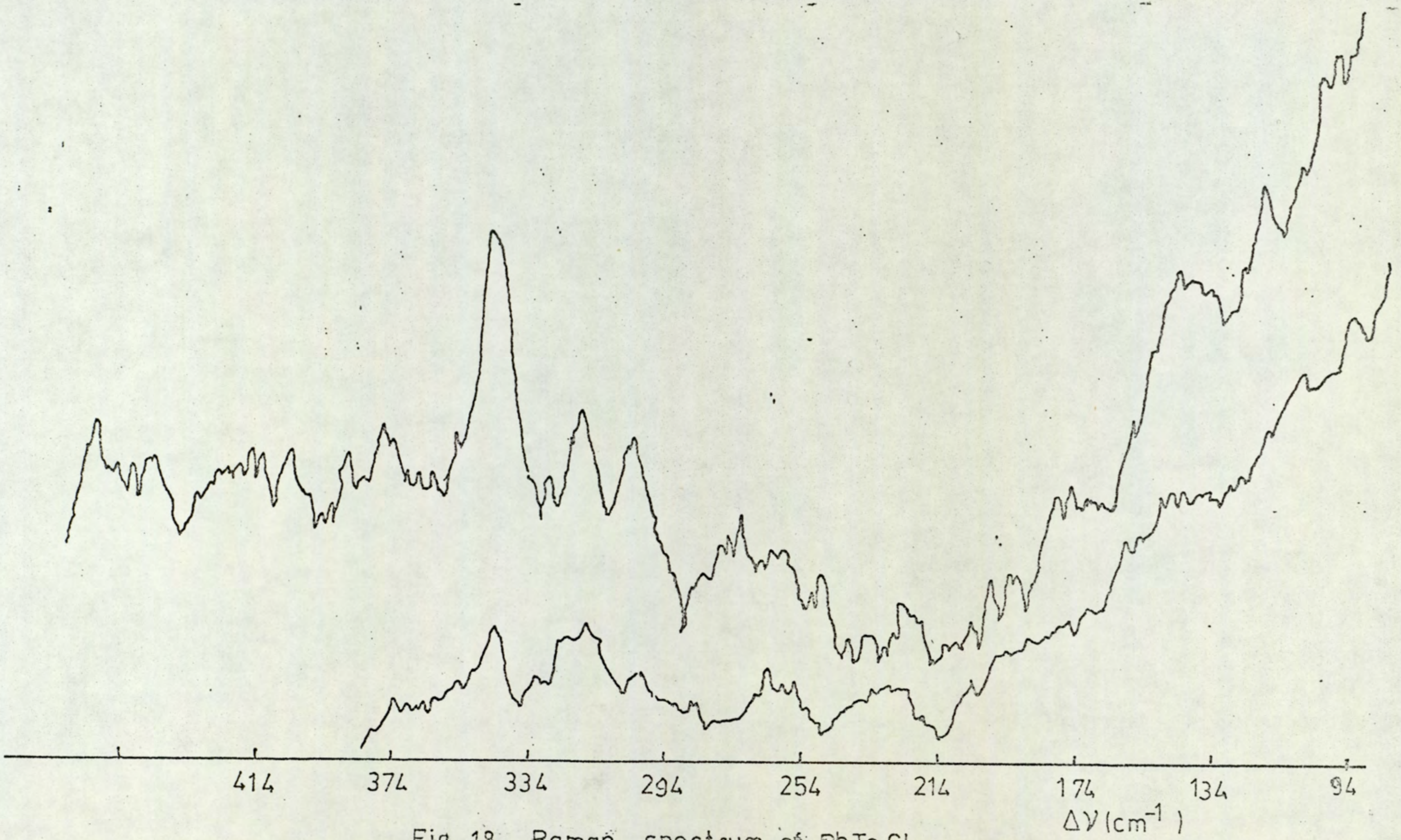


Fig. 18. Raman spectrum of $PhTeCl_3$.

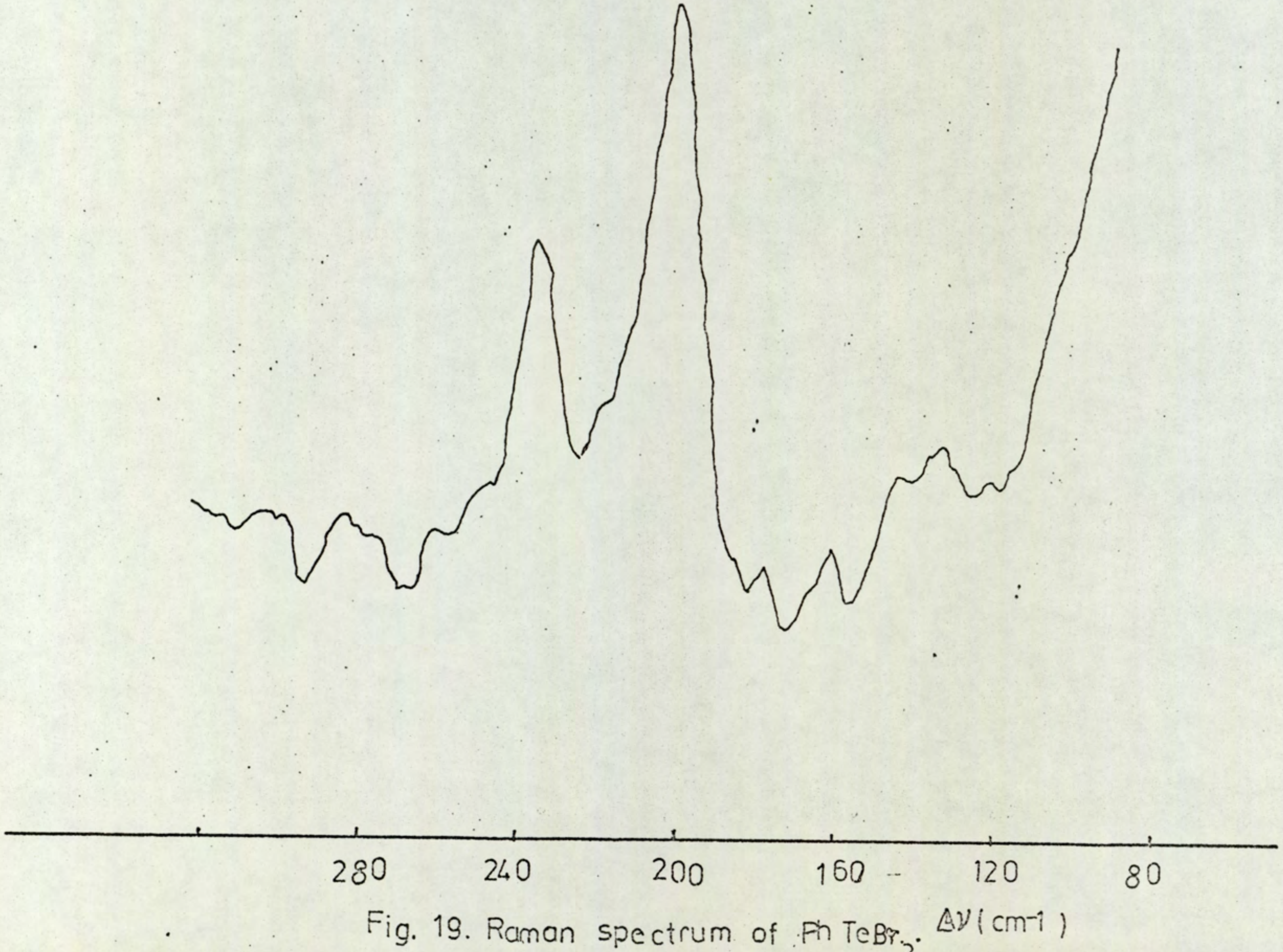


Fig. 19. Raman spectrum of Ph TeBr$_3$.

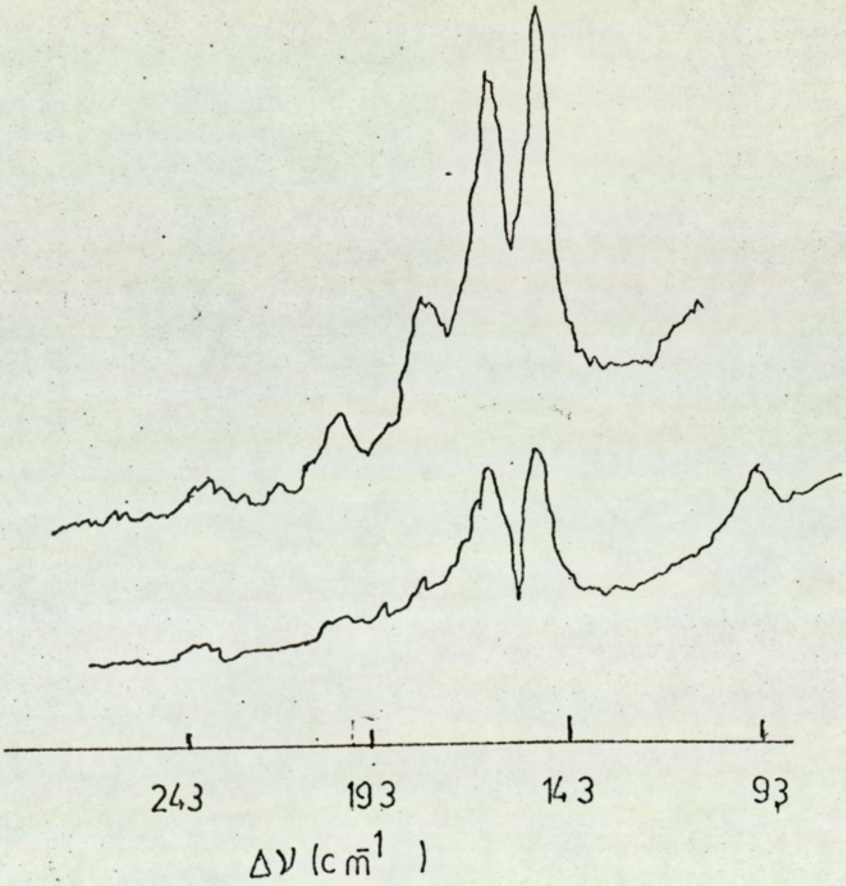


Fig. 20. Raman spectrum of $PhTeI_3$.

TABLE 9

Infrared and Raman Spectra(below 400 cm^{-1}) of Aryltellurum Trihalides

(p-tolyl)$TeCl_3$		(p-tolyl)$TeBr_3$		(p-tolyl)TeI_3	
i.r.(cm^{-1})	Raman	i.r.(cm^{-1})	Raman	i.r.(cm^{-1})	Raman
369 w	375 w	294 w		284 w	
336 sh	341 s	242 m	246 s	230 m	
318 sh	316 w	236 m-s		218 m-s	
304	303 w	220 m-s	219 m	178 v-s	
244 m-w	248 w-m	204 v.s	199 v.s	155 v.s	
219 m-w	213 w-m		181 w	106 w	
180 s	179 m	141 w	141 m.w	86 m	
152 m	164 m	126 m.s	131 m.w	63 w	
	136 m	113 m.s	103 sh		
90 w	92 s	86 w	87 m		

TABLE 9--<u>Continued</u>

(p-MeO.C_6H_4)$TeCl_3$		(p-MeO.C_6H_4)$TeBr_3$		(p-MeO.C_6H_4)TeI_3	
i.r.(cm^{-1})	Raman	i.r.(cm^{-1})	Raman	i.r.(cm^{-1})	Raman
323 s	329 s	316 m		320 m	
	301 m	236 m.s	235 s	313 m	
295 s*	298 m		230 sh	293 m	
228 s	228 m	213 s	209 m	216 m	
211 s.br	198 w	192 m.s		200 m	
180 s	186 w	180 w.sh	181 m	164 v.s	
148 s	139 w.m	136 m	128 w	154 v.s	
93 w		115 m.s		140 m	
		89 w	96 w	101 sh	
			76 m	91 m.s	

* unresolved shoulder of m-w intensity to high wave number.

TABLE 9--Continued

$(p\text{-}EtO.C_6H_4)TeCl_3$		$(p\text{-}EtO.C_6H_4)TeBr_3$		$(p\text{-}EtO.C_6H_4)TeI_3$	
i.r.(cm^{-1})	Raman	i.r.(cm^{-1})	Raman	i.r.(cm^{-1})	Raman
334 s	330 s	380 w		378 w	
326 s	327 s	311 m		316 m	
318 s		260 m	262 m.w	246 m	
298 s	305 m	254 m		204 m	
252 w	260 w	218 s	216 s	174 s	
227 w		206 v.s		154 m.s	
179 s		194 v.s	192 w.m	133 sh	
146 s		164 v.w	154 m	94 m	
110 w		126 s	135 m		
		104 v.s	105 m.w		
			95 m.s		

TABLE 9--Continued

$(p\text{-}PhO.C_6H_4)TeCl_3$		$(p\text{-}PhO.C_6H_4)TeBr_3$		$(p\text{-}PhO.C_6H_4)TeI_3$	
i.r.(cm^{-1})	Raman	i.r.(cm^{-1})	Raman	i.r.(cm^{-1})	Raman
326 s		394 w		353 w	
334 s	339 s	357 w			
320 s		306 m	306 w		
311 s	315 m.s	296 w		296 m	
268 w		284 w		280 w.m	
216 m		270 w	275 w	206 m.s	
199 s		244 w		190 m	
172 s	179 w	231 s		162 s	
	161 w	224 m.s	224 s	154 s	
137 m	129 w	211 s		144 sh	
	73 w	200 m	204 v.s	94 m.s	
		194 s	190 s		
		186 m			
		136 m	133 m		
		120 w.s			
			100 w		
			68 m		
			55 s		
			41 sh		

TABLE 10

Tellurium-Halogen Vibrations of Aryltellurium Trihalides

R	$RTeX_3$				
	X = Cl		X = Br		X = I
	i.r.(cm^{-1})	Raman	i.r.(cm^{-1})	Raman	i.r.(cm^{-1})
p-MeC_6H_4	336 s	341 s	220 ms	219 m	178 s
	318 sh	316 w	204 vs	199 vs	155 s
	304 s	303 w	126 ms	131 mw	
	180 s	179 m	113 ms		
	152 m				
p-$MeO.C_6H_4$	323 s	329 s	213 s	209 m	164 s
	295 s	301 m	192 ms		154 vs
		298 m			
	180 s	186 w	136 m		91 ms
	148 s	135 m	115 ms		
p-$EtO.C_6H_4$	334 s	330 s	218 s	216 s	174 s
	326 s	327 s	206 vs		154 ms
	318 s		194 vs	192 mw	94 m
	298 s	305 m	126 s	135 m	
	179 s		104 vs	105 mw	
	146 s				
p-$PhO.C_6H_4$	334 s	339 s	224 m	224 s	162 s
	320 s	315 m-s	211 s	204 vs	154 s
	311 s		194 s	190 s	94 m-s
	175 s	179 w	136 m	135 m	
			120 m-s		

TABLE 11

'd'-Spacing from the X-ray Powder Photographs of Phenyltellurium Trihalides

PhTeX$_3$		
X = Cl	X = Br	X = I
		11.5 s
	9.2 s	
7.0 s		7.0 s
5.3 s		5.2 w
4.7 w	4.7 m	
3.75 s	3.8 w	3.65 s
	3.6 w	
3.43 s	3.4 m	
	3.28 m	
	3.18 w	
2.95 m		2.91 s
2.72 w		2.75 w
	2.67 s	2.67 m
2.55 m	2.55 w	2.55 w
2.28 w	2.28 w	2.33 m
2.17 w		
	2.05 m	
1.91 w	1.94 w	1.95 s
1.88 s	1.82 m	1.90 s
1.73 w		1.75 w

TABLE 12

'd'-Spacing from the X-ray Powder Photographs of p-Tolyl and p-Anisyltellurium Trihalides

$(p\text{-}MeC_6H_4)TeX_3$			$(p\text{-}MeO.C_6H_4)TeX_3$		
X=Cl	X=Br	X=I	X=Cl	X=Br	X=I
	13 s	13 s		13 s	
8.6 s					11 s
	7.2 w	7.6 m	7.6 w		
6.6 w		6.7 w	7.2 m	6.7 s	6.6 w
5.7 s		5.5 s		5.7 m	
4.8 m	4.7 w		5.2 w	5.1 w	5.2 w
4.3 w		4.1 s	4.8 m		4.7 m
3.9 w		3.85 m	4.4 w	4.3 m	4.3 m
3.75 s			3.85 m		3.80 s
3.6 w		3.6 m	3.75 m	3.65 m	
		3.32 m	3.45 m	3.50 m	3.40 w
3.25 s	3.15 s	3.15 s	3.35 m		
		3.05 s	3.10 w	3.10 s	3.10 w
2.88 w					2.95 w
2.75 w	2.73 w	2.72 w			2.80 s
2.65 w			2.72 m	2.65 m	2.67 w
2.55 w		2.55 s	2.50 s	2.50 m	
2.46 w	2.40 w	2.45 s	2.42 s		
2.38 w			2.35 s	2.3 w	2.20 w
2.33 w		2.33 w	2.17 s		2.15 w
		2.15 w	2.12 s		2.08 w
		2.05 m	2.05 w		2.03 w
		2.02 w	1.98 m		1.92 w
		1.96 w	1.88 w		1.86 w
		1.92 w	1.86 w	1.85 w	1.82 w
		1.82 w	1.67 w		1.78 w
1.72 w		1.78 w	1.58 w		
1.70 w	1.68 w	1.67 w			

TABLE 13

'd'-Spacing from the X-ray Powder Photograph of p-Phenetyl and p-Phoenoxyphenyltellurium Trihalides

$(p\text{-}EtO.C_6H_3)TeX_3$			$(p\text{-}PhO.C_6H_4)TeX_3$		
X=Cl	X=Br	X=I	X=Cl	X=Br	X = I
12 s			10 s	9.5 s	
	9.0 s		6.5 s	6.7 m	
8.6 s			5.6 w	5.7 m	
	7.2 s			5.2 m	
6.6 w	6.8 w		4.7 s		4.3 w
5.7 w	5.8 w	5.6 w	3.85 m		3.82 m
5.3 w	5.4 m		3.35 w	3.35 w	
4.9 m			3.30 w		3.25 m
4.6 m	4.7 s		3.15 w		3.05 w
4.1 w	4.4 w	4.1 m	2.95 w		
3.75 m	3.75 m	3.80 m	2.80 m	2.85 s	2.85 w
		3.60 m	2.62 w	2.75 m	2.6 w
3.32 s	3.40 m	3.45 m	2.55 w	2.52 s	
			2.35 m	2.40 s	
3.18 w	3.20 m	3.22 w	2.25 m	2.30 m	
3.10 w	3.08 m	3.08 w		2.12 w	2.12 w
3.05 w			2.05 w	2.05 w	2.0 w
2.94 m	2.90 m	2.95 w		1.93 m	1.93 w
2.82 m		2.85 w	1.88 w		
2.67 m	2.65 s	2.68 w	1.75 w		
2.55 w	2.53 s	2.55 w	1.72 w		
2.30 s	2.37 w	2.35 w			
2.21 w	2.24 w	2.23 w			
2.13 w	2.08 w	2.10 m			
2.03 w					
1.95 w	1.95 w	1.97 m			
1.90 m	1.90 w	1.92 w			
1.82 w					
1.74 w					
1.71 w					

TABLE 14

Mass Spectra of Phenyltellurium Trihalides Relative to ^{130}Te, ^{35}Cl, ^{79}Br

$PhTeCl_3$		$PhTeBr_3$		$PhTeI_3$	
m/e	R.A.(%)	m/e	R.A.(%)	m/e	R.A.(%)
444	1	327	2	334	4
335	3				
284	5	284	26	284	28
277	31			254	9
242	100				
207	58	207	9	207	13
165	8	186	5	1	
154	11	154	69	154	79
130	13			130	3
113	55				
77	50	77	60	77	100
51	96	51	32	51	91
36	56	28	26	28	8
18	20	18	100	18	31

TABLE 15

Mass Spectra of p-Tolyltellurium Trihalides Relative to ^{130}Te, ^{35}Cl, ^{79}Br

$p\text{-}MeC_6H_4TeCl_3$		$p\text{-}MeC_6H_4TeBr_3$		$p\text{-}MeC_6H_4TeI_3$	
m/e	R.A.(%)	m/e	R.A.(%)	m/e	R.A.(%)
442	2	442	3	348	52
348	5	379	2		
312	47	312	43	312	2
291	8	300	10		
256	21			255	100
221	18	221	26	221	44
182	100	182	78	182	4
168	21	167	31		
154	11			130	5
126	40				
91	100	91	97	91	92
77	22				
65	95	65	44	65	39
51	33			51	10
39	53	39	19	39	93
36	68				
28	13	28	21		
18	40	18	100		

TABLE 16

Mass Spectra of p-Ethoxyphenyltellurium Trichlorides
Relative to ^{130}Te, ^{35}Cl, ^{79}Br

p-EtO.$C_6H_4TeCl_3$		p-EtO.$C_6H_4TeBr_3$		p-EtO.$C_6H_4TeI_3$	
m/e	R.A.(%)	m/e	R.A.(%)	m/e	R.A.(%)
372	43	430	3		
286	30	372	27	378	33
		331	15	372	58
251	25	289	25	251	42
		254	56		
242	84	251	37		
		242	37	242	70
223	44	223	41	223	42
213	68				
		208	56		
186	94	202	88	186	75
185	100	200	88	185	78
		186	37		
156	53	185	42	157	46
138	30	175	12	93	55
130	12	159	35		
94	36	130	19		
93	28	93	100		
77	14	77	94	77	8
65	89	65	62	65	100
39	44	39	96	39	58
38	36				
29	52	28	19	28	8
18	36	18	62	18	8

TABLE 17

Mass Spectra of Phenyltellurium Trichloride at 10 eV Relative to ^{130}Te, and ^{35}Cl

m/e	R.A.(%)
441	17
335	5
284	3
277	5
242	100
207	14
77	5

DISCUSSION

1. Synthesis

The product of the synthesis of phenyltellurium trichloride[13] from the reaction of phenylmercuric chloride and tellurium tetrachloride always contained an impurity which was very difficult to remove; also it gave a very low yield after recrystallization. The reaction did not occur as smoothly as reported regardless of various changes of the factors (i.e. purity of dioxane, tellurium tetrachloride and time of refluxing). Phenylmercuric chloride from commercial sources was found to be impure. Though phenylmercuric chloride obtained from recrystallization was used for the synthesis of phenyltellurium trichloride the reaction still could not be reproduced. So there was a doubt that the failure might arise from phenylmercuric chloride. The compound was prepared from sulphinic acid in Farrar's report.[64] But commercial phenylmercuric chloride is believed to be synthesized from aniline.

A modified method was used to prepare pure phenyltellurium trichloride in which the crude phenyltellurium trichloride was reduced to diphenyl ditelluride, and then the ditelluride was oxidized with chlorine gas back to the trichloride. The ditelluride obtained from the reduction of the trichloride (which had been recrystallized first from sym-tetrachloroethane) was found to be pure while that obtained from the direct reduction of the crude trichloride after evaporation of dioxane contained some impurity. So the trichloride obtained from the ditelluride in the later case had to be recrystallized from benzene to get a pure compound. Phenyltellurium trichloride is very soluble in warm benzene which is in contrast to Farrar's[13] observation that a large quantity of benzene was needed to dissolve the trichloride. The reason of the difficulty is believed to be that the trichloride containing some impurity which is very difficult to dissolve in benzene. Recently a direct method of synthesis of diphenyl ditelluride[61] has been published which should be very suitable for the synthesis of pure phenyltellurium trichloride.

The above modified method for the synthesis of phenyltellurium trichloride was also found to be suitable for the synthesis of p-tolyltellurium trichloride.

When diphenyl ditelluride was oxidized by iodine at 10-15° C a black benzene-soluble material was obtained. Careful inspection showed this to be a mixture of phenyltellurium tri-iodide and a second substance. There was no suitable solvent for the separation of the two substances. At first it was believed that the black material may be the intermediate phenyltellurenyl iodide, PhTeI. Very few tellurenyl compounds are known and only one organotellurenyl halide, (2-napthyl)TeI, has been reported.[65]

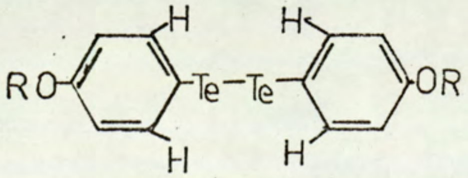
Later it was found that when phenyltellurium tri-iodide was recrystallized from benzene, if the heating of the solution is prolonged, the warm filtrate after setting aside for cooling produces a black substance. This black material is not soluble in hot benzene which is probably metallic tellurium obtained from the decomposition of the tri-iodide.

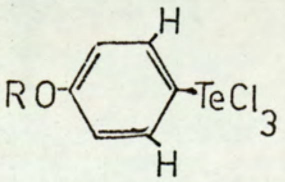
Thus the most probable explanation is that the black material is metallic tellurium which was obtained when diphenyl ditelluride was over oxidized by iodine at 10-15° C, and the observation that the substance was benzene-soluble may be wrong, since the black substance could be obtained from the decomposition of the tri-iodide in benzene solution.

A point of interest from these five classes of aryltellurium trihalides which does not seem to have previously drawn comment is that, with the exception of the group $RTeX_3$ ($R = p\text{-}MeO.C_6H_4\text{-}$) the bromide has a higher melting point than the other two members.

2. ^{1}H n.m.r. spectra

An interesting observation from the ^{1}H n.m.r. spectra of p-methoxyphenyl and p-ethoxyphenyltellurium trichloride is that the two protons which are meta to the ethoxy or methoxy group resonate at about 1.60τ. This chemical shift differs from those of p-methoxy and p-ethoxyphenyl ditelluride in which the two protons in the same positions resonance at about $2.30\ \tau$ (Chapter III). The shifts to lower fields of these two protons in the trichlorides are due to the neighbour anisotropy effect due to the replacement of a less electronegativity tellurium by more electronegative chlorine atoms.





$R = C_2H_5, CH_3$

There is not any evidence of the possibility of spin-spin coupling between aromatic protons and tellurium atoms (^{125}Te, I = $\frac{1}{2}$).

3. Solubilities and conductivity measurements

The solubilities of the phenyl-compounds in benzene were qualitatively investigated, and is in an order of $PhTeCl_3 \gg PhTeI_3 > PhTeBr_3$. This is in contrast to the behaviour of the methyl series where the order of solubilities was $MeTeCl_3 > MeTeBr_3 > MeTeI_3$ (insoluble).[24] In general it was found that tri-iodide is more soluble than the bromide within a given group.

In polar solvents such as dimethylformamide some ionic dissociation occured. The values of the molar conductivity, Λ_M increasing for $RTeX_3$ in the order X,Cl < X, Br < X, I (e.g. for 10^{-3} M solution $PhTeCl_3$, Λ_M = 31; $PhTeBr_3$, Λ_M = 42; $PhTeI_3$, Λ_M = 102 ohm^{-1}cm^{2}mol^{-1}. When molar conductivity, Λ_M was plotted against (concentration)$^{\frac{1}{2}}$ for $(p\text{-}MeC_6H_4)TeCl_3$ non-linear graph was obtained as shown in Fig. 14. This graph was typical of a weak electrolyte but the literature for $TeCl_4$ and $TeBr_4$[17(b),18(a)] advises caution in interpreting these data. Therefore a simple ionic model for the solid state structures was not considered for aryltellurium trichlorides.

4. X-ray powder photographs

The X-ray powder data were of poor quality, particularly for the bromides, however the following isomophous systems may be noted. $PhTeCl_3$ and $PhTeI_3$; $(p\text{-}MeC_6H_4)TeCl_3$ and $(p\text{-}MeC_6H_4)TeI_3$; $(p\text{-}EtO.C_6H_4)TeCl_3$, (p-EtO.$C_6H_4$)$TeBr_3$, and (p-EtO.$C_6H_4$)$TeI_3$. In other cases the data do not enable definite conclusions to be drawn. When careful examination of the i.r. spectra (4000-400 cm^{-1}) showed considerable differences between $PhTeBr_3$ and $PhTeX_3$ (X = Cl, I); the spectra of all three p-methoxyphenyltellurium trihalides differed in detail and (p-PhO.C_6H_4)TeI_3 differed from other two members of the group. By contrast the i.r. spectra (4000-400 cm^{-1}) of the p-tolyl and p-ethoxylphenyl series were identical. Thus there is correlation betweem observed spectral differences and the more positive conclusions from the X-ray data.

5. Mass spectra

The most important features of the mass spectra (Table 14, 15 and 16) of $RTeCl_3$ (R = Ph, p-tolyl and p-EtO.C_6H_4) are that there were ions appearing at higher mass-charge ratio than the correspond monomer trichlorides which would be the parent ions if the compounds were monomers. Thus the spectra clearly indicated that the trichlorides are associated.

For the tribromides and tri-iodides of these series the mass spectra (Table 14, 15 and 16) showed only ions below the mass-charge ratio which corresponded to the monomer, $RTeX_3$.

Careful examination of the spectra (Table 14, 15 and 16) the following results could be drawn with some confidence.

1. Parent ions were not observed in all cases, even when the spectra of the trichloride compound (Table 17) were recorded at 10 eV, 5½, and 4½ eV there were no such

ions observed.

2. In general the aryltellurium tribromides and tri-iodides were more easily decomposed than the trichlorides in the same series. This suggests that the tellurium-bromide and tellurium-iodide bonds are weaker than tellurium-chloride bonds.

3. Tellurium-carbon bonds are stronger than tellurium-halogen bonds.

4. The fragmentation patterns of these aryltellurium trihalides are as following:

$$(R\text{-}TeX_3)_n + e \longrightarrow (RTeX_3)_n^+ + 2e$$

$$(RTeX_3)_n^+ \longrightarrow RTeX_3^+ \longrightarrow RTeX_2^+ \longrightarrow RTeX^+ \longrightarrow RTe^+ \longrightarrow R^+ \qquad \underline{(a)}$$

$$\begin{tikzcd}
(RTeX_3)_n^+ \arrow[r] & R\text{-}Te\text{-}Te\text{-}R^+ \arrow[r] \arrow[d] & RTe\text{-}R^+ \arrow[r] & R\text{-}R^+ \arrow[r] & R^+ \quad \underline{(b)} \\
 & RTe^+ \arrow[d] & & & \\
 & R^+ & & & \\
 & \underline{(c)} & & &
\end{tikzcd}$$

where R = Ph, p-MeC_6H_4 and p-EtO.C_6H_4;
X = Cl, Br and I
n $\geqslant$ 2

There was the evidence of these ions from the spectra except for $RTeX_3^+$. Unfortunately there was not evidence to support the scheme from the meta-stable ions. However, the evidence for the step of

$$R\text{-}Te\text{-}I^+ \longrightarrow RTe^+$$

was supported by the metastable ion at 141.5 of $p\text{-}MeC_6H_4TeI_3$, and the step of

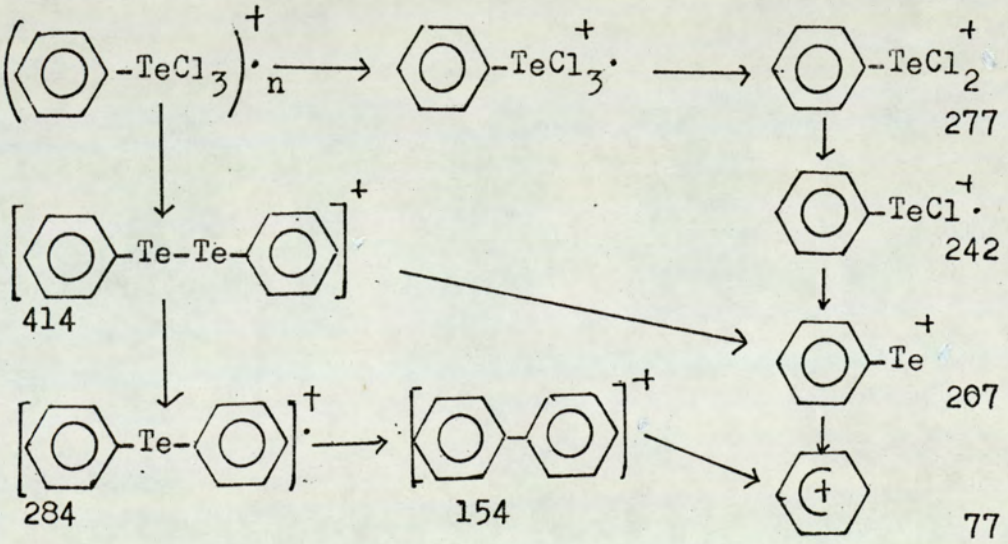
$$R\text{-}Te\text{-}R^+ \longrightarrow R\text{-}R^+$$

was supported by the metastable ion at 109.2 of the same tri-iodide.

The fragmentation pattern of the ditellurides has been discussed in Chapter III.

In general for the trichlorides path (a) was more favoured than (b) and (c) but for the tribromides and tri-iodides the favoured route was in an order of (c) > (b) > (a).

An illustrated example of the fragmentation pattern is shown by $PhTeCl_3$:-



The mass-charge ratio ions observed from the spectrum are indicated by the figures.

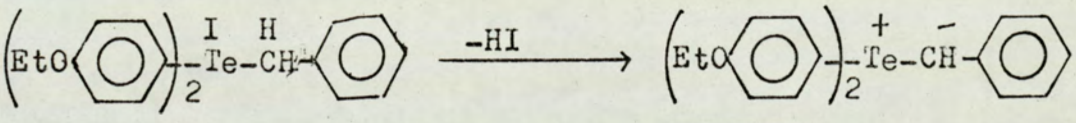
5. The most important evidence from the mass spectra is that aryltellurium trihalides <u>must be polymers or at least dimers</u>. There were two main reasons, the first was that the ions at higher mass-charge ratio than the

monomer molecule were observed. The second was the observation of ditelluride ions. These ions could not occur from the monomer molecule except from the dimer or polymer molecule by breaking the tellurium-halogen bonds and forming tellurium-tellurium bonds.

The formation of the ditellurides by mass spectroscopy is very interesting, as the ditellurides are usually obtained from the reduction of the trihalides.

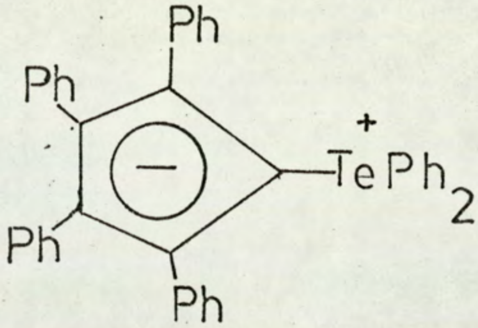
Tellurium ylide

An attempt to prepare a tellurium ylide of the formula II. This could be achieved if the compound(I) was prepared by the application of the method to synthesize



(I) (II)

triphenyltellurium iodide[66] which was obtained from the reaction between diphenyltellurium dichloride and phenylmagnesium bromide. But the synthesis of compound(I) failed possibly due to the unstable nature of benzylmagnesium bromide when this reagent was reacted with bis-p-phenetyltellurium dichloride. The choice of a more suitable secondary alkyl bromide for the grignard reagent might gave the satisfactory compound. The first tellurium ylide has been recently reported.[33]



6. Vibrational spectra

Fritz and Keller[10] have suggested the bands between 455 and 487 cm^{-1} were assigned to a tellurium-phenyl vibration, ν(TePh), and a band at about 290 cm^{-1} was attributed to the tellurium-chloride vibrations. Their assignments are unaceptable and wrong. Simple mass considerations between tellurium and tin which are comparable in magnitude suggests that the ν(TePh) and ν(TeCl) bands may occur in a similar position to that of the ν(SnPh) and ν(SnCl) bands i.e. at ~ 250-236 cm^{-1},[21] and at the region of 385-318 cm^{-1} [21] respectively. Vibrational spectroscopy of organotin compound is well established and reliable.

The interpretation of a more complex molecule by vibrational spectroscopy should be made with caution because sometimes there is a possibility that ambiguous conclusions may be drawn which is clearly indicated in the case of $TeCl_4$.[17,18]

The fact that many coincidence are observed between i.r. and Raman data indicate that the molecules of the aryltellurium trihalides have very low symmetry. From the evidence of the mass spectra analysis and the low solubility of the compounds in organic solvent suggest the molecules are associated in the solid state. A X-ray crystallographic investigation of the structure of 2-chloroethyltellurium trichloride[25] has clearly shown to be a polymeric structure containing·pentacoordinate tellurium.

Phenyltellurium trihalides

The data (Table 8) for $PhTeCl_3$ do not agree exactly with those of Fritz and Keller[10] who failed to report a band at 337 cm^{-1}, however Wynne and Pearson[24] reported bands at 338 and 315 cm^{-1} for $MeTeCl_3$.

It is convenient to discuss the phenyl compounds separately from the other aryltellurium compounds since the ring vibrations may be identified with more certainly in these cases.[50] Again it was found that the assignments following Whiffin's notation for monosubstituted benzenes,[50] and the alternative approach for the t and t' modes which could be designated "metal-phenyl stretching" modes as is common practice in organotin chemistry[53] gave a satisfactory interpretation of the spectra.

The assignments of the phenyl compounds were given in Table 8.

Both the high frequency i.r. data and the X-ray data indicate that $PhTeBr_3$ may differ structurally from the other two members of the group. Also the higher melting point and reduced solubility in benzene indicate a greater molecular complexity for $PhTeBr_3$. This is in contrast to the methyltellurium trihalides where the tri-iodide was considered to have the highest degree of association.[24] Therefore the trichloride and tri-iodide were considered as isomorphous in structure.

The i.r. spectrum of the tri-iodide was relatively simple and the easier to interpret. The data was compatible with a structure based on "$PhTeI_2^+$ units" associated via iodide bridges to give a five co-ordinate tellurium atom in agreement with the theory of Wynne and Pearson.[24] This theory has already been mentioned (see introduction).

Thus the higher frequency i.r. bands at 169 cm^{-1} and 158 cm^{-1} (with Raman counterpart at 168 and 153 cm^{-1} respectively) are assigned to the stretching of the short tellurium-iodine bonds of "$PhTeI_2^+$", and the lower frequency bands at 97 cm^{-1} and 86 cm^{-1} (with Raman counterpart at 94 cm^{-1}) are assigned to both stretching vibrations involving the bridge bonds and also, possibility, deformation vibrations of "$PhTeI_2^+$". The assignments of the higher frequency bands to the stretching of the short tellurium-iodine bond and the lower frequency bands to the stretching of the longer or bridge tellurium-iodine are expected. This is shown in the case of $TeCl_4$[18(b)] where the i.r. at the higher frequency bands are assigned to the short tellurium-chlorine bonds and the low frequency bands assigned to the long tellurium chloride bonds.

The assignments of tellurium-iodine stretching at 169 and 158 cm^{-1} are comparable to those of tin-iodine[21] stretching at 207-170 cm^{-1} region for phenyltin compounds as expected from simple mass considerations.

The i.r. bands at 247 and 241 cm^{-1} with the Raman counterpart at 241 and 238 cm^{-1} respectively plus an i.r. shoulder at 250 cm^{-1} are assigned to ν(Te-Ph), the tellurium-phenyl stretching modes i.e. the phenyl t and t' modes (ring modes) which are labeled according to Whiffin's notation.[50] For a substituent of the mass of tellurium, it is the phenyl t and t' modes which are most reasonably termed tellurium-phenyl stretching vibrations, but, as calculations on simple monohalogeno-benzene[52] demonstrate, such a description is approximate. These vibrational modes are "X-sensitive" their frequencies depend on the mass of X in the PhX and both are i.r. and Raman active. Thus simple mass considerations suggest that the ν(Te-Ph) will occur in the frequency region which is comparable to the ν(Sn-Ph). For the monophenyl compounds the ν(Sn-Ph) shows at ∼ 250-236 cm^{-1}.[21] Therefore the assignments of ν(Te-Ph) at 247 and 241 cm^{-1} agree with this comparision. This assignments are also supported by the ν(Te-Ph) at 255 cm^{-1} in Ph_2Te_2 (Chapter III). In fact the assignments of the ν (Te-Ph) in $PhTeI_3$ agree very well with the frequencies of ν (Te-Ph) in Ph_2TeX_2 (X = Cl, Br and I) by McWhinnie and Patel[30] who assign the frequencies in the region of 272-248 cm^{-1} to ν (Te-Ph) or phenyl t and t' modes.

The i.r. band at 196 cm^{-1} and Raman band at 205 cm^{-1} are assigned to both the phenyl x and u modes (x, out-of-plane ring bending and u, in-plane ring rotation against Te respectively). Both of the phenyl x and phenyl u modes are "X sensitive" modes, and in this case they are unable to be identified from each other.

Thus by similar considerations the i.r. and Raman data in Table 8 of both $PhTeCl_3$ and $PhTeBr_3$ are assigned as indicated in the Table 8. For $PhTeCl_3$ the assignments of the bands i.r. at 337, 317, and 306 cm^{-1} to the ν(Te-Cl) terminal tellurium-chlorine bands are comparable to the region of the ν(Sn-Cl) at 385-381 cm^{-1} [21] in the alkyl- and phenyl-tin halides.

For $PhTeBr_3$ the assignments of the i.r. bands at 220, 213, and 198 cm^{-1} to the ν(Te-Br) terminal are again comparable to the region of ν(Sn-Br) at 264-222 cm^{-1} in alkyl-and phenyl-tin halides.[21] The positions of the three tellurium-bromide modes (i.e. ν(Te-Br), 226 and 202 cm^{-1}; ν(Te-Br) bridge, 133 cm^{-1}) reported by Chen and George[22] for $MeTeBr_3$ are in good agreement with those assigned for $PhTeBr_3$ in Table 8.

When the structure of $PhTeI_3$ is considered to be built up from the "$PhTeI_2^+$" units associated via iodine bridges to give a five co-ordinate tellurium atom it does not imply the structure to be ionic, but it is convenient to regard the structure as being built up from $RTeX_2^+$ and X^- units to give the molecular types illustrated in the Fig. 21. The appearance of three bands in the 340-300 cm^{-1} region for $PhTeCl_3$ probably reflects coupling of vibrations of "$PhTeCl_2^+$" groups within a molecular unit or between chromophores within the unit cell, since the isomorphism of $PhTeCl_3$ and $PhTeI_3$ does not enable us to interpret the greater band multiplicity for ν(TeCl) than for ν(TeI) in terms of structural differences. The phenyl t modes are also affected by coupling in the case of the trichloride and tri-iodide as shown by the complexity of the bands.

Although there are many coincidences between the i.r. and Raman frequencies for $PhTeCl_3$ and $PhTeI_3$, some differences of the order of 5-10 cm^{-1} are noted and in this respect the data for $TeCl_4$ and $TeBr_4$[18(c)] are similar. From this vibrational data it cannot be concluded that a centrosymmetric structure exists for the molecule of phenyltellurium compounds. But the final judgement for the symmetry of the molecule must be reserved until a detailed X-ray study is available since as implied in the above discussion of coupling of the ν(TeX), the observed spectra more properly reflect the symmetry of the unit cell.

Several structures may be built up from the donor-acceptor interactions of $PhTeX_2^+$ and X^- units which agree with the theory of Wynne and Pearson.[24] The structures have five-co-ordinate tellurium atoms and the absence of bonds to halogens in positions trans to the phenyl groups (see introduction). This process of building up the structures also accounts for the differing degrees of association of the molecules, thus if $PhTeCl_3$ and $PhTeI_3$ are at least dimers, $PhTeBr_3$ may be a trimer as illustrated in Fig. 21.

Other aryltellurium trihalides

A detailed analysis of the spectra of the more complex trihalides was not attempted since the spectra will be complicated by the presence of more complex organic group, R in $RTeX_3$. However, the tellurium-halogen vibrations of these aryltellurium trihalides are assigned and shown in Table 10. The assignments of bands below 200 cm^{-1} to tellurium-halogen modes, must be made with caution since both lattice modes and low-frequency vibrations of complex

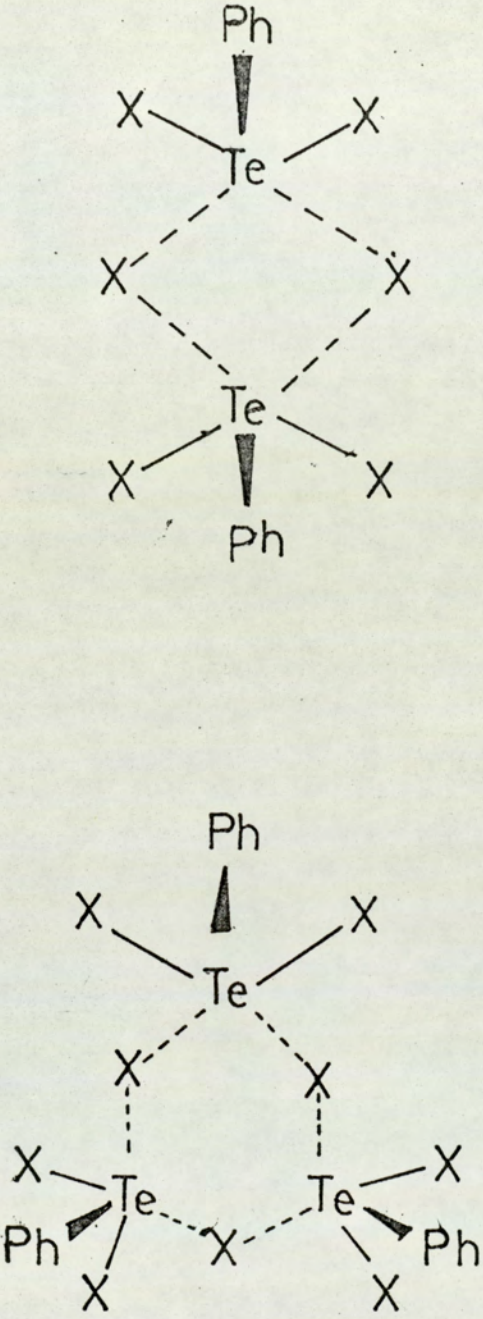


Fig.21. Illustration of typical structures resulting from donor-acceptor interaction of X^- and $PhTeX_2^+$

organic group R in $RTeCl_3$ complicate the spectra. Also, there is the possibility that both long and short tellurium-halogen bonds may be present, as in $TeCl_4$, stretching vibrations associated with the long bonds and deformation modes associated with the short bonds may occur in similar regions. Thus, particularly in the case of the trichlorides, when two vibrations below 200 cm^{-1} are assigned as tellurium-halogen modes (Table 10), it is probable that one is a deformation mode. The above arguments about the possibility of a deformation mode may be occur below the frequency of 200 cm^{-1} is also true for the assignment in Table 8.

For these aryl compounds, though the presence of more complex aryl groups will give greatly complicated spectra, it may be concluded that a pattern very similar to that for phenyl compounds emerges. Thus, in general, there is more evidence of vibrational coupling for the chlorides than the bromides and iodides and also agreement between IR and Raman tellurium-halogen frequencies is less precise for the chlorides than for the bromides. The relative simplicity of the i.r. data for iodides is again noted, though this time it is difficult to assign confidently tellurium-halogen modes below 100 cm^{-1} due to the presence of the more complex aryl groups. Again the structures of the iodides may be considered to be built up from the $RTeI_2^+$ and I^- units and the dimeric molecules are the most probable. It is also believed that the structures of the chlorides and bromides may be understood in similar terms.

It was noted that the assignments of the frequencies for tellurium-halogen vibrations in diaryltellurium dihalides[30] whose molecules are monomers and the structures being a pseudo trigonal bipyramid, the highest ν(Te-X) are much lower than the highest ν(Te-X) in aryltellurium trihalides. The i.r. tellurium-halogen vibrations in R_2TeX_2 are between 287 and 129 cm^{-1} in contrast to 337 and 91 cm^{-1} for $RTeX_3$.

The conclusions that may be ligimately drawn from this study are as follows. There is good evidence to suggest that $PhTeBr_3$ is more associated than $PhTeCl_3$ and $PhTeI_3$, and that similar conclusions are valid for $(p\text{-}MeC_6H_4)TeBr_3$ and $(p\text{-}PhO.C_6H_4)TeBr_3$. However it is not generally true that the bromide is the most complex member of any series $RTeX_3$, the structure being a function of both R and X. The evidence from i.r. and Raman data, and the behaviour of their solubility, and particularly from the mass spectra it is believed that the most probable structure for the chlorides and iodides is the dimer represent in Fig. 21; this is in agreement with the theory of Wynne and Pearson.[24] However, more complex structures are possible in which the co-ordination number of the tellurium remains five and in which no halogen atom trans to the organic groups(R) is present. The structural variety possible for the compounds is best understood if each structure is considered to be built up from donor-acceptor interaction between $RTeX_2^+$ and X^-.

Soon after this work had been finished Wynne and Pearson[67] published a paper which is relevant to this work. Their assignments for ν(Te-Cl) terminal in $MeTeCl_3$ agree very well with those frequency for $PhTeCl_3$ in Table 8. They also reported an i.r. spectrum for $(p\text{-}MeO.C_6H_4)TeCl_3$ the agreement of bands below 400 cm^{-1} is good except two bands.

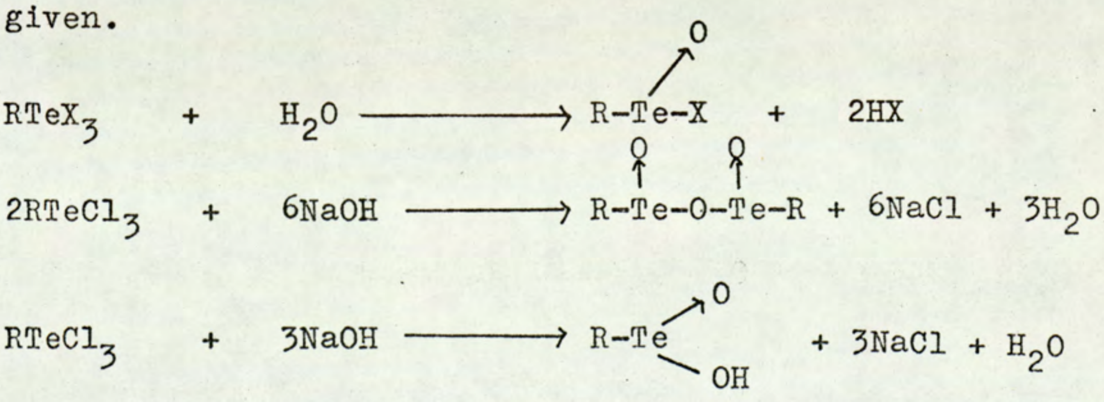
They have not reported a band at 211 cm^{-1} but a band at 128 cm^{-1} whereas in this study there is a band at 211 cm^{-1} and not at 128 cm^{-1}, in fact the position at 128 cm^{-1} obscured by the broad band at 148 cm^{-1}. However, in this work five spectra of $(p\text{-}MeO.C_6H_4)TeCl_3$ were obtained at various sampling conditions and all were in agreement.

CHAPTER V

HYDROLYSIS OF ARYLTELLURIUM TRIHALIDES

INTRODUCTION

The hydrolysis of aryltellurium trihalides has been the subject of some investigations.[36,39,40] There is general agreement that the hydrolysis in neutral agueous media affords aryltellurium oxyhalides, RTeOX for X = Cl and Br although reported melting points differ. The hydrolysis of $RTeI_3$ (R = aryl) in hot water leads to indefinite products except in the case of R = p-MeO.C_6H_4 where RTeOI was obtained.[40] The use of an alkaline medium has variously been reported to afford $RTe(OH)_3$[36] (R = p-MeO.C_6H_4), RTe(O).OH[39] and $(RTeO)_2O$.[40] In all cases the products of the alkaline hydrolysis were acidified with dilute acid before analysis. The products are now generally accepted to be anhydrides. No attempt has been made to discuss the structures of these hydrolysis products. The machanism of hydrolysis of aryltellurium trihalides is unknown, except for one speculative scheme which has been given.



$$RTeX_3 + H_2O \longrightarrow R\text{-}\overset{O\nearrow}{Te}\text{-}X + 2HX$$

$$2RTeCl_3 + 6NaOH \longrightarrow R\text{-}\overset{O}{\overset{\uparrow}{Te}}\text{-}O\text{-}\overset{O}{\overset{\uparrow}{Te}}\text{-}R + 6NaCl + 3H_2O$$

$$RTeCl_3 + 3NaOH \longrightarrow R\text{-}Te\begin{smallmatrix}\nearrow O\\ \searrow OH\end{smallmatrix} + 3NaCl + H_2O$$

In the present study it is hoped to gain more insight into the probable course of the reaction, and to extend the vibrational spectroscopic investigation to these hydrolysis products with the objective of assigning tellurium-oxygen vibrational modes. No tellurium-oxygen vibrations have been previously reported in the literature.

EXPERIMENTAL

The starting aryltellurium trihalides were obtained as described in Chapter IV.

Although the reactions were carried out parallel to Petragnani and Vicentini,[40] in view of the fact that the previously reported methods have not been complete agreement, the details of the experimental methods are described.

Only the hydrolysis of phenyl- and p-ethoxyphenyl tellurium trihalides were studied in the present work. The completion of the hydrolysis reactions was checked by the precipitation of the released halide as the silver salt. The filtrates were acidified with dilute nitric acid and then excess silver nitrate solution was added followed by warming. The silver halide salts were filtered by using a sintered glass crucible, and dried in an oven at ~ 120° C until constant weight was obtained.

HYDROLYSIS IN NEUTRAL MEDIA

Phenyltellurium oxychloride

Phenyltellurium trichloride(0.84 g) was

magnetically stirred with cold water(20 ml) for 45 minutes. The white powder like product(0.57 g) was filtered and dried over P_4O_{10} in a vacuum desiccator. The product had shrank between 226-28° C (lit.[40] M.P. 250° C)
(Found: C,28.90; H,1.99; C_6H_4ClOTe requires: C,28.10; H,1.95%).

The filtrate was analysed for the released chloride as silver chloride(0.77 g) which corresponded to (0.82 g) the release of two moles of chloride per mole of $PhTeCl_3$. It was also noted that the product is slightly soluble in cold water.

2. Phenyltellurium oxybromide

Phenyltellurium tribromide(0.53 g) was magnetically stirred with cold water(25 ml) at room temperature for 2½ hours. The deep yellow colour of tribromide changed to almost colourless in 5 minutes. The pale yellow product(0.28 g) was filtered and dried over P_4O_{10} in a vacuum desiccator. The product had a melting point between 218-22° C (lit.[40] 247-49° C). The behaviour of melting; it changed to clear semi-solid but not into liquid phase.
(Found: C,26.85; H,2.20; C_6H_4BrOTe requires: C,24.05; H, 1.80%).

Analysis of the filtrate for bromide ion as silver bromide(0.47 g) confirmed the release of two moles of bromide(0.56 g) per one mole of $PhTeBr_3$. It was also noted that PhTeOBr is slightly soluble in cold water.

Attempted preparation of phenyltellurium oxyiodide

When phenyltellurium tri-iodide was magnetically stirred with cold water at room temperature for 46 hours. The colour of the tri-iodide was not changed, and the analysis of the filtrate indicated only a slight reaction to have occured.

The reaction was repeated where phenyltellurium tri-iodide was heated under reflux with water, and continuously stirred for 6 hours. The product obtained was a mixture of brown compound and tellurium metal.

p-Ethoxyphenyltellurium oxychloride

Recrystallized p-ethoxyphenyltellurium trichloride(1.03 g) was stirred with cold water(40 ml) at room temperature for 30 minutes. The yellow trichloride changed to white in 3 minutes. The white powder like product(0.92g) was filtered and dried over P_4O_{10} in a vacuum desiccator. The product had a melting point between 222-25° C (lit.^{40} 224-26° C). At the melting point the product became semi-solid but did not changed to liquid.
(Found: C,32.5; H,2.28; $C_8H_9ClO_2Te$ requires: C,32.0; H,3.00%).

Analysis of the filtrate for chloride ions as silver chloride(0.83 g) confirmed the release of two moles of chloride(0.83 g) per mole of (p-EtO.C_6H_4)$TeCl_3$.

When the same reaction was carried out for different times(2½ hours and 6 hours) the same products were obtained.

Reaction of p-ethoxyphenyltellurium trichloride with water

When different batches of unrecrystallized p-ethoxyphenyltellurium trichloride,[39] which was believed to be pure, were used for the preparation of p-ethoxyphenyltellurium oxychloride, the products obtained had different behaviour which should be noted.

(1) p-Ethoxyphenyltellurium trichloride(1.78 g) was stirred with cold water(50 ml) for 20 minutes. The white product(1.36 g) was obtained, and had a melting point between 219-221° C (lit.[40] 224-26° C).
(Found: C,32.50; H,2.83; Cl,10.97; $C_8H_9ClO_2Te$ requires: C,32.0; H,3.00; Cl,11.80%).

Analysis of the filtrate confirmed the release of two moles of chloride per mole of the trichloride.
(Found: AgCl,1.40 g; Calculated: AgCl,1.42 g).

(2) p-Ethoxyphenyltellurium trichloride(0.89 g) was stirred with cold water(50 ml) for 2½ hours. The white powder like product(0.66 g) was filtered and dried <u>in vacuo</u> over P_4O_{10}. The product had no melting point but decomposed at 278°C to dark grey compound.
(Found: C,31.62; H,2.92; $C_8H_9ClO_2Te$ requires: C,32.00; H,3.00%).

Analysis of the filtrate for chloride ions confirmed the release of two moles of chloride per mole of the trichloride.
(Found: AgCl,0.70 g; Calculated: AgCl,0.71 g).

p-Ethoxyphenyltellurium oxybromide

(1) p-Ethoxyphenyltellurium tribromide(0.40 g) was stirred with cold water(50 ml) for 4 hours. After the reaction started for 5 minutes there was no visible change of the yellow colour of the trichloride, after 40 minutes the yellow colour changed to pale yellow. The yellowish product(0.22 g) was filtered and dried <u>in vacuo</u> over P_4O_{10}, and had a melting point between 210-15° C (lit.[40] 233-36° C). (Found: C,29.77; H,3.34; $C_8H_9BrO_2Te$ requires: C,27.9; H,2.6%).

Analysis of the filtrate for bromide ions confirmed the release of two moles of bromide per mole of the tribromide.
(Found: AgBr,0.32 g; Calculated: AgBr,0.31 g).

(2) p-Ethoxyphenyltellurium tribromide(0.30 g) was stirred with cold water(60 ml) over night. The pale yellowish product(0.17 g) was filtered and dried, and had no melting point but at 210° C started to decompose to dark grey.
(Found: C,29.77; H,3.12; $C_8H_9BrO_2Te$ requires: C,27.90; H,2.61%).

Analysis of the filtrate for bromide confirmed the release of two moles of bromide per mole of the tribromide.
(Found: AgBr,0.23 g; Calculated: AgBr,0.23 g).

(3) p-Ethoxyphenyltellurium tribromide(0.59 g) was stirred with cold water(50 ml) for 45 minutes with no visible change of the colour. The mixture was then warmed

to 50° C causing the rapid change of the colour. The yellowish product(0.35 g) was filtered and dried, and had no melting point but decomposed at 270° C.
(Found: C,29.77; H,3.34; $C_8H_9BrO_2Te$ requires: C,27.90; H,2.61%).

Analysis of the filtrate for bromide confirmed the release of two moles of bromide per mole of the tribromide.
(Found: AgBr,0.44 g; Calculated: AgBr,0.49 g).

p-Ethoxyphenyltellurium oxyiodide

(1) p-Ethoxyphenyltellurium tri-iodide(1.7 g) was heated under reflux with water(50 ml) for 4 hours. The black crystals changed to red brown. The red-brown product (1.0 g) was filtered and dried in a vacuum desiccator over P_4O_{10}, and had a melting point at 170° C. The product is soluble in acetone and methanol.
(Found: C,24.8; H,2.27; $C_8H_9IO_2Te$ requires: C,24.5; H,2.32%).

(2) p-Ethoxyphenyltellurium tri-iodide(0.38 g) was stirred with cold water(30 ml) for 49 hours. After stirring for an hour the pale yellow particles started to appear. The pale yellow product(0.21 g) was filtered and dried in a vacuum desiccator over P_4O_{10}, on griding the colour changed to red brown.
(Found: C,24.3; H,2.00; $C_8H_9IO_2Te$ requires: C,24.5; H,2.3%).

Analysis of the filtrate for iodide ion confirmed the release of two moles of iodide per mole of the triiodide.

(Found: C,24.3; H,2.00; $C_8H_9IO_2Te$ requires: C,24.5; H,2.3%).

(3) p-Ethoxyphenyltellurium tri-iodide(1.06 g) was stirred with cold water(50 ml) for 54 hours. The pale yellow product(0.70 g) was filtered and dried, and had a melting point between 160-161° C.

The filtrate was analysed for iodide ion as silver iodide(0.38 g) and compared to the expected amount (0.78 g) if two moles of iodide were released per mole of the tri-iodide.

(Found: C,19.6; H,1.9%).

When the infrared spectrum of the product was carefully examined it showed to be a mixture of $(p\text{-}EtO.C_6H_4)TeI_3$ and $(p\text{-}EtO.C_6H_4)Te(O)I$ rather than the hoped for $[(p\text{-}EtO.C_6H_4)TeI_2]_2O$, because both the carbon and hydrogen analysis and the amount of the iodide ion released suggested the product to be $[(p\text{-}EtO.C_6H_4)TeI_2]_2O$.

HYDROLYSIS IN ALCOHOLIC SOLVENTS

p-Ethoxyphenyltellurium oxychloride

p-Ethoxyphenyltellurium trichloride(0.89 g) was dissolved in ethanol(75 ml) and excess water(10 ml) added, the white product precipitated immediately. The mixture was stirred for 2½ hours then the white powder like product (0.69 g) was filtered and dried. The product had no melting point but decomposed at 280°C.

(Found: C,31.62; H,2.92; $C_8H_9ClO_2Te$ requires: C,32.00; H,3.00%).

Analysis of the filtrate confirmed the release of two moles of chloride per mole of the trichloride. (Found: AgCl,0.69 g; Calculated: AgCl,0.71 g).

Water(10 ml) was added to a solution of p-ethoxyphenyltellurium trichloride(0.89 g) in methanol(75 ml). No immediate precipitation was seen but on stirring slow precipitation occured. After stirring for 30 minutes the white product(0.61 g) was filtered and dried. The product had no melting point but shrank at 235° C and decomposed at 270° C.
(Found: C,32.11; H,3.55; $C_8H_9ClO_2Te$ requires: C,32.00; H,3.00%).

ATTEMPTS TO ISOLATE INTERMEDIATE PRODUCTS

(1) p-Ethoxyphenyltellurium trichloride(0.89 g) was stirred with cold water(50 ml) for 6 minutes. The colour of the trichloride changes from yellow to white. The white powder like product(0.79 g) was filtered and dried, and had a melting point between 222-224° C (lit.[40] 224-26° C).
(Found: C,24.42; H,2.20; $C_8H_9ClO_2Te$ requires: C,32.00; H,3.00%).

Analysis of the filtrate as silver chloride (0.59 g) compared to expected(0.71 g) amount if two moles of chloride per mole of the trichloride were released.

(2) p-Ethoxyphenyltellurium trichloride(0.89 g) was dissolved in ethanol(50 ml) to which water(0.09 g) was added and stirred for 30 minutes there was no visible change. Another amount of water(0.29 g) was further added and continuously stirred for 10 minutes and still there was no visible change, so more water(0.97 g) was added the white precipitate appeared immediately. The white product

(0.39 g) was filtered, washed with hot acetone and dried, and had no melting point but decomposed at 275° C to dark grey compound.

(Found: C,23.04; H,1.95%).

The careful examination of the i.r. spectrum of the product indicated a mixtures of the trichloride and oxychloride.

HYDROLYSIS IN ALKALINE MEDIA

The experiments were restricted to the p-ethoxyphenyltellurium trihalides which were treated with 10% sodium carbonate solution.

(1) Recrystallized p-ethoxyphenyltellurium trichloride(1.14 g) was stirred with 10% sodium carbonate solution(40 ml) at room temperature for 2½ hours. The reaction mixture was divided into two parts: (a) the white product was filtered and dried in a vacuum desiccator over P_4O_{10}; (b) the mixture was acidified with dilute acetic acid and the stirring was continued for another hour after which the second product was filtered and dried in vacuo over P_4O_{10}. Analysis of the two combined filtrates for chloride ion showed all three moles of chloride were released per mole of the trichloride.

(Found: AgCl,1.31 g; Calculated: AgCl,1.26 g).

Product (a) had a melting point between 199-201° C (shrank) and decomposed between 235-40° C; product (b) had a melting point between 234-238° C decomposed (lit.[40] 206-210° C).

(Found: product(a) C,33.9; H,3.50%; and product(b) C,34.7;

H,3.47%).

Product(a), which shows ν(OH) at 3060 cm^{-1} (hydrogen bonded) has an analysis corresponding closely to that expected for $(p\text{-}EtO.C_6H_4)TeO(OH)$. $C_8H_{10}O_3Te$ requires: C,34.1; H,3.6%. Product(b) correspond to the "anhydride" $[(p\text{-}EtO.C_6H_4)TeO]_2O$: $C_{16}H_{18}O_5Te_2$ requires: C,35.1; H,3.3%.

(2) Recrystallized p-ethoxyphenyltellurium trichloride(0.60 g) was stirred with 10% sodium carbonate solution(30 ml) for 30 minutes. The white product(0.17 g) was filtered and dried <u>in vacuo</u> over P_4O_{10}, and had a melting point at 220°C (shrank) and melted with decomposition between 240-45° C. The product showed ν(OH) at 3060 cm^{-1} (hydrogen bonded).

Analysis of the filtrate for chloride ion showed the release of all three moles of chloride per mole of the trichloride.

(Found: AgCl,0.65; Calculated: AgCl,0.72 g).

(Foung: C,31.53; H,3.69%).

(3) Recrystallized p-ethoxyphenyltellurium trichloride(0.61 g) was stirred with 10% sodium carbonate solution(30 ml) for 30 minutes. The mixture was acidified with dilute acetic acid and the white product(0.42 g) was filtered and dried. The product had melting point between 200-203° C.

(Found: C,33.86; H,3.34%).

(4) p-Ethoxyphenyltellurium trichloride(0.89 g) was stirred with 10% sodium carbonate solution(25 ml) for 30 minutes. The mixture was acidified with dilute acetic acid, and the white product(0.65 g) was filtered and dried.

The product had a melting point between 206-210°C (lit.[40] 206-210°C).

(Found: C,32.64; H,3.04%).

Analysis of the filtrate as silver chloride showed three moles of chloride per mole of the trichloride were released.

(Found: AgCl,1.04 g; Calculated: AgCl,1.08 g).

ATTEMPTS TO ISOLATE INTERMEDIATE PRODUCT

It was hoped to isolate the intermediate between the trichloride and the hydrolysed product by varying of time.

(1) p-Ethoxyphenyltellurium trichloride(0.89 g) was stirred with 10% sodium carbonate solution(30 ml) for 5 minutes. The mixture was acidified with dilute acetic acid, and the white product(0.65 g) was filtered and dried. The product had a melting point between 235-40°C decomposed.

(Found: C,24.42; H,2.15%).

When the same reaction was carried out for 7 minutes the same product was obtained.

The careful examination of the i.r. spectra shows a mixture of the trichloride and the "anhydride" in both cases.

(2) p-Ethoxyphenyltellurium trichloride(1.05 g) was stirred with 10% sodium carbonate solution(50 ml) for an hour. The mixture was acidified with dilute acetic acid, and the white product(0.65 g) was filtered and dried. The product had a melting point between 205-15°C, and decomposed at 236-38°C.

(Found: C,31.47; H,2.38%).

The filtrate was analysed for chloride ion as silver chloride showed three moles of chloride per mole of the trichloride were released.

HYDROLYSIS IN ACID MEDIA

p-Ethoxyphenyltellurium trichloride(1.0 g) was stirred with 10% hydrochloride acid solution for 30 minutes, and the white product(0.73 g) was filtered and dried. The product had no melting point but decomposed at 270° C.
Found: C,32.64; H,3.04% with corresponds to p-EtO.C_6H_4Te(O)Cl: Calculated: C,32.00; H,3.00%. The i.r. spectrum of the product was identical with that of (p-EtO.C_6H_4)Te(O)Cl .

REACTION BETWEEN (p-EtO.C_6H_4)$TeCl_3$ WITH H_2O_2

p-Ethoxyphenyltellurium trichloride(0.52 g) was stirred with a mixture of hydrogen peroxide(20 vol. 10 ml), 10% sulphuric acid solution(10 ml) and water(10 ml) for 1½ hours. The white product(0.36 g) was filtered and dried, and had a melting point between 221-24° C.

Analysis of the filtrate for chloride ion showed two moles of chloride per mole of the trichloride were released. The i.r. spectrum of the product was identical to that of (p-EtO.C_6H_4)TeOCl.

ATTEMPTS TO PREPARE (p-EtO.C_6H_4)Te(S)Cl

The attempts to prepare the analogous sulphur compounds, RTe(S)X of RTe(O)X.

(1) Hydrogen sulphide gas was bubbled through a clear solution of p-ethoxyphenyltellurium trichloride (0.89 g) in absolute ethanol(75 ml) for 5 minutes. The colourless solution changed to orange immediately and black oily liquid was observed at the bottom of the flask. The solution was set aside for 30 minutes, then some orange precipitate appeared and the black oil solidified, and the orange product(0.26 g) was filtered and dried. When the orange product was recrystallized from petroleum ether (80/100°) the crystals obtained was proved to be $(p\text{-}EtO.C_6H_4)_2Te_2$ from both melting point and i.r. spectrum evidence. The black solid was also identified to be the ditelluride.

(2) Hydrogen sulphide gas was bubbled through a clear solution of p-ethoxyphenyltellurium trichloride (0.89 g) in absolute ethanol(75 ml) which had been saturated with nitrogen gas for 15 minutes. The colourless solution changed immediately to orange and cloudy then to clear orange with black oily liquid and finally at the end of 15 minutes the brown precipitate appeared. The orange crystals was filtered and dried, and proved to be $(p\text{-}EtO.C_6H_4)_2Te_2$ again.

REACTION OF ARYLTELLURIUM TRICHLORIDES WITH PYRIDINE

(1) Reaction of $PhTeCl_3$ with pyridine

Freshly distilled pyridine(2.0 ml) was added to a mixture of phenyltellurium trichloride(0.50 g) and dry benzene(80 ml), the white product precipitated immediately and the mixture was set aside for 48 hours. The white product(0.6 g) was filtered and dried. The product was treated with acetone to yield an insoluble residue of phenyltellurium oxychloride. The acetone solution was concentrated under vacuum then was treated with petroleum ether(40/60°) to give white crystals(0.15 g) (a). Further treatment of the filtrate with petroleum ether afforded a second crop of white crystals(b). Solids(a) and (b) had a melting points between 245-247° C dec, and 113-114° C respectively. Solid (a) dissolved in acetone, methanol alcohal and nitromethane.

Product (a) proved to be pyridinium phenyltetrachlorotellurate (IV), $PyH^+ . PhTeCl^-$.
(Found: C,31.5; H,3.12; N,3.14. ν(NH) = 3220, 3165 cm^{-1}; $\Lambda_M(10^{-3}$ in $MeNO_2)$ = 90 $ohm^{-1}cm^2mol^{-1}$; $C_{11}H_{11}Cl_4NTe$ requires: C,31.0; H,2.60; N,3.3%).

Product (b) contained no nitrogen and was a non-electrolyte in nitromethane (Λ_M = 7 $ohm^{-1}cm^2mol^{-1}$) and was identified as a reaction product of $PhTeCl_4^-$ and acetone i.e. $Ph(CH_3CO.CH_2)TeCl_2$.
(Found: C,32.1; H,3.34; N,0.00. ν(CO) = 1705 cm^{-1} v.s. TGA showed the lost of two organic groups $C_9H_{10}Cl_2OTe$ requires: C,32.5; H,3.01%).

(2) Reaction of $(p\text{-}EtO.C_6H_4)TeCl_3$ with pyridine

Freshly distilled pyridine(2.0 g) was added to a mixture of p-ethoxyphenyltellurium trichloride(1.78 g) and dry benzene(150 ml). The yellow solution and crystals changed to a white precipitate immediately on addition of pyridine. The mixture was set aside for 24 hours, and the white product(1.54 g) was filtered and dried. The filtrate was analysed for chloride ion as silver chloride(0.05 g). A portion of product(0.82 g) was treated with acetone to yield an insoluble residue of p-ethoxyphenyltellurium oxychloride. The acetone solution was concentrated under vacuum distillation then was treated with petroleum ether (40/60°) to give white crystals(0.46 g). The crystals had a melting point between 214-216° C dec.

The crystals proved to be pyridinium p-ethoxyphenyltetrachlorotellurate(IV), $PyH^+ (p\text{-}EtO.C_6H_4)TeCl_4^-$. (Found: C,33.3; H,3.27; N,3.0; Te,26.7. ν(NH) = 3220, 3165 cm^{-1}. $\Lambda_M(10^{-3}$ in $MeNO_2)$ = 77 $ohm^{-1}cm^2mol^{-1}$. $C_{13}H_{15}NO_2Te$ requires: C,33.2; H,3.20; N,3.0; Te,27.1%).

HYDROLYSIS OF $(p\text{-}EtO.C_6H_4)TeCl_4^-$. PyH^+

When pyridinium p-ethoxyphenyltetrachlorotellurate (IV) was stirred with cold water for 1½ hours the product obtained was identified as $(p\text{-}EtO.C_6H_4)TeCl$, and pyridine was released.

REACTION OF $(p\text{-}EtO.C_6H_4)TeCl_3$ WITH ANILINE

A benzene solution of freshly distilled aniline was added to a mixture of benzene and p-ethoxyphenyltellurium trichloride produced a white precipitate. This product was not analysed but the i.r. spectrum of the crude product indicated the present of aniline salt.

REACTION OF $(p\text{-}EtO.C_6H_4)TeCl_3$ WITH Ph_3P

When a benzene solution of triphenylphosphine was added to a benzene solution of p-ethoxyphenyltellurium trichloride an orange solution was obtained. The orange solution was identified as $(p\text{-}EtO.C_6H_4)_2Te_2$ which is soluble in benzene.

REACTION OF $PhTeCl_3$ WITH $(Ph)_4AsCl$

A solution of phenyltellurium trichloride(0.31 g) in absolute ethanol(10 ml) was added to a solution of tetraphenylarsonium chloride(0.42 g) in absolute ethanol (75 ml). The white precipitate appeared immediately. The white product(0.66 g) was filtered and dried, and had a melting point between 205-208° C.

The product proved to be $(Ph_4As^+)(PhTeCl_4^-)$.
$\Lambda_M(10^{-3}$ in $MeNO_2) = 58$ $ohm^{-1}cm^2mol^{-1}$.
(Found: C,49.6; H,3.6; $C_{30}H_{25}AsCl_4Te$ requires: C,49.5; H,3.4%).

LEWIS ACIDITY OF ARYLTELLURIUM TRICHLORIDE

In the molecules of aryltellurium trichloride, $RTeCl_3$ the tellurium(IV) atom has vaccant 4f[68(a)] orbitals which may be used for bonding by accepting a pair of electrons from electron donor molecules. The fact that tellurium tetrachloride formed complex with thiourea, $TeCl_4.2tu$ and $TeCl_4.6tu$, pyridine, $TeCl_4.2py$ et al[68(b)] suggest the possibility of using 4f orbitals for bonding.

Reaction of (p-EtO.C H)TeCl with α,α′-bipyridyl

To a solution of p-ethoxyphenyltellurium trichloride(0.36 g) in benzene added a solution of α,α′-bipyridyl(0.16 g) in benzene. A white precipitate appeared immediately, and the white product(0.33 g) was filtered and dried after set aside for an hour. The product had a melting point between 237-240° C.

The product is probablely $(p\text{-EtO.C}_6H_4)TeCl_4^-$. bipyH$^+$.
(Found: C,38.96; H,3.49; N,4.74. ν(NH) = 3220,3160 cm^{-1}
Λ_M = 92 ohm^{-1}cm^{2}mol^{-1}. $C_{18}H_{18}Cl_4N_2OTe$ requires: C,39.45; H,3.50; N,5.1%).

Reaction of $(p\text{-EtO.C}_6H_4)TeCl_3$ with 1, 10-phenantrolene

A benzene solution of 1, 10-phenantrolene hydrate (0.20 g) was added to a benzene solution of p-ethoxyphenyltellurium trichloride(0.36 g) to afford a white product (0.30 g). The product had a melting point between 245-250° C, and most probablely is $p\text{-EtO.C}_6H_4TeCl_4^-$. Phen H$^+$.
(Found: C,43.40; H,3.43; N,5.03. ν(NH) = 3200 cm^{-1}
Λ_M = 59 ohm^{-1}cm^{2}mol^{-1}. $C_{20}H_{18}Cl_4N_2OTe$ requires: C,41.40; H,3.45; N,4.90%).

Reaction of $(p\text{-EtO.C}_6H_4)TeCl_3$ with di(2-pyridyl)amine

A benzene solution of di(2-pyridyl)amine(0.26 g) was added to a benzene solution of p-ethoxyphenyltellurium trichloride(0.20 g) to afford a white product(0.50 g) which melted at 165-170° C.

The product is probablely $(p\text{-EtO.C}_6H_4)TeCl_4^-$. dpm H$^+$.
(Found: C,39.94; H,3.79; N,6.81. Λ_M = 52 ohm^{-1}cm^{2}mol^{-1}
$C_{18}H_{19}Cl_4N_3OTe$ requires: C,38.40; H,3.59; N,7.47%).

REDUCTION OF P-ETHOXYPHENYLTELLURIUM OXYCHLORIDE

A mixture of p-ethoxyphenyltellurium oxychloride (1.30 g) and sodium sulphide hydrated(10.5 g) was heated in a water bath for 30 minutes. Cold water was added to the mixture which after cooling the red brown precipitate (1.30 g) was filtered and dried. The product proved to be bis-p-ethoxyphenyl ditelluride.

RESULTS

Spectroscopic data for phenyltellurium oxyhalides, $PhTe(CH_2COCH_3)Cl_2$ and pyridinium phenyltetrachlorotellurate (IV) are tabulated in Table 18. The Raman spectra of both PhTe(O)Cl and PhTe(O)Br gave unsatisfactory results. The IR spectra (800-250 cm^{-1}) of $PhTeCl_3$, $PhTeBr_3$, PhTe(O)Cl, PhTe(O)Br, and the low-frequencies(400-40 cm^{-1}) of PhTe(O)Cl, PhTe(O)Br, $PhTe(CH_2COCH_3)Cl_2$, and $PyH^+PhTeCl_4^-$ are shown in Fig. 22, 23, 24, 25, 26, 27, 28 and 29 respectively. A Raman spectrum of $PhTeCl_4^-PyH^+$ is also shown in Fig. 30.

The vibrational spectra (800-40 cm^{-1}) of $(p\text{-}EtO.C_6H_4)Te(O)X$ (X = Cl, Br and I), $(p\text{-}EtO.C_6H_4)Te(O)OH$, and $[(p\text{-}EtO.C_6H_4)TeO]_2O$ are tabulated in Table 19. The compound $(p\text{-}EtO.C_6H_4)Te(O)I$ absorbed at the laser frequency and it was not possible to obtain a Raman Spectrum.

The low-frequency(400-40 cm^{-1}) IR and Raman spectra of pyridinium phenyltetrachlorotellurate(IV), pyridinium p-ethoxyphenyltetrachlorotellurate(IV), tetraphenylarsonium phenyltetrachlorotellurate(IV), and tetraphenylarsonium chloride are tabulated in Table 20. The IR and Raman spectra of $(C_5H_5NH^+)(p\text{-}EtO.C_6H_4TeCl_4^-)$, $(Ph_4As^+)(PhTeCl_4^-)$ and Ph_4AsCl are shown in Fig. 31, 32, 33, 34, and 35 respectively.

The "d"-spacing values from the X-ray powder photographs of p-ethoxyphenyltellurium oxychloride which had a melting point and no melting point are tabulated in Table 21.

In general the rate of hydrolysis of aryltellurium trihalides is in an order of $RTeCl_3 > RTeBr_3 \gg RTeI_3$.

In the case of the hydrolysis of $(p\text{-}EtO.C_6H_4)TeCl_3$ where scrupulous attention to the purity of the starting material had not been paid, products showing different behaviour on heating were obtained.

The hydrolysis of phenyl- and p-ethoxyphenyltellurium trihalides in neutral media yielded the oxyhalide compounds in agreement with Petragnani and Vicentini.[40] However, there was little agreement in the observed melting points. The hydrolysis of $(p\text{-}EtO.C_6H_4)TeI_3$ afforded $(p\text{-}EtO.C_6H_4)Te(O)I$ which, apart from $(p\text{-}MeO.C_6H_4)Te(O)I$,[40] is the only oxy-iodide to be prepared to be date.

The product of alkaline hydrolysis of $(p\text{-}EtO.C_6H_4)TeCl_3$ after treatment with acetic acid was confirmed to be $[(p\text{-}EtO.C_6H_4)TeO]_2O$. However, another product can be obtained which according to the infrared spectrum contains OH bonds and the analysis corresponds to $(p\text{-}EtO.C_6H_4)TeO(OH)$. The compound is converted to the anhydride on treatment with dilute acetic acid.

The hydrolysis of aryltellurium trihalides in acid media, 10% hydrochloric acid afforded the same products of those the hydrolysis in neutral media. There is no reaction between aryltellurium trihalides with hydrogen peroxide in acid media. The products obtained were identified to be the oxyhalides.

The attempts to isolate intermediate product between $RTeX_3$ and RTeOX failed. When aryltellurium trichloride reacted with pyridine in benzene solution the pyridinium salts of formula $(PyH^+)(RTeCl_4^-)$ were obtained.

The compounds have a molar conductivity in nitromethane solution characteristic of an 1:1 electrolyte. The reaction of $PhTeCl_3$ with Ph_4AsCl in absolute alcohol afforded $(Ph_4As^+)(PhTeCl_4^-)$ which is also an 1:1 electrolyte in nitromethane. Recrystallization of $(PyH^+)(PhTeCl_4^-)$ from an acetone containing medium led to the isolation of the new compound $Ph(CH_2COCH_3)TeCl_2$.

The reaction between $RTeX_3$ with aniline in benzene solution afforded the white to pale yellow products but these compounds were not analysed.

An attempt to use triphenylphosphine(Ph_3P) to break the halogen bridge in $RTeX_3$ resulted in the reduction of the trihalide to the ditelluride. It was hoped that the analogous sulphur compounds, RTe(S)X, to RTe(O)X could be prepared. The ethanolic solution of $RTeX_3$ was treated with dry H_2S gas, the chloride was immediately reduced to the ditelluride.

The investigation of the Lewis acidity of $RTeX_3$ by the reaction between $RTeX_3$ and Lewis base (i.e. α,α'-bipyridyl, 1, 10-phenantrolene and di(bipyridyl)amine led to the products which were believed to be similar to those of pyridinium salts. The analysis of the unrecrystallized product; from the percentage of carbon and hydrogen and the molar conductivity in nitromethane solutions were characteristic as an 1:1 electrolyte suggested the most probable products are $(RTeCl_4^-)(bipyH^+)$, $(RTeCl_4^-)(Phen.H^+)$ and $(RTeCl_4^-)(dpmH^+)$.

TABLE 18

The Low-frequency Vibrational Spectra of Phenyltellurium Compounds

PhTe(O)Cl	PhTe(O)Br	Assignment
715s	704s	Tellurium-oxygen modes
605s	592s	
498s	495s	
424s	411s	
312m-s	304s	
259m-s	251s	Phenyl t or ν(TePh)
234m-s	234m	Phenyl u
207m	208m	Phenyl u'
196m		Phenyl x
	165s	Phenyl x'
277s	185s	ν(Te-halogen)
150m	136m	δ(Te-halogen)

TABLE 18-Continued

$PhTe(CH_2COCH_3)Cl_2$	$PyH^+(PhTeCl_4^-)$		Assignment
	i.r.(cm^{-1})	Raman	
260^+s	264s	256sh	Phenyl t or ν(TePh)
masked	masked		Phenyl u
214s			Phenyl u'
	182sh		Phenyl x
160m			Phenyl x'
		249m-s	
260^+s	284m	280s	ν(Te-halogen)
250s	227v.s.	220br.,sh	
	152m		δ(Te-halogen)
530m			ν(Te-alkyl)
131m			Other bands
117w			

$^+$ overlap of bands

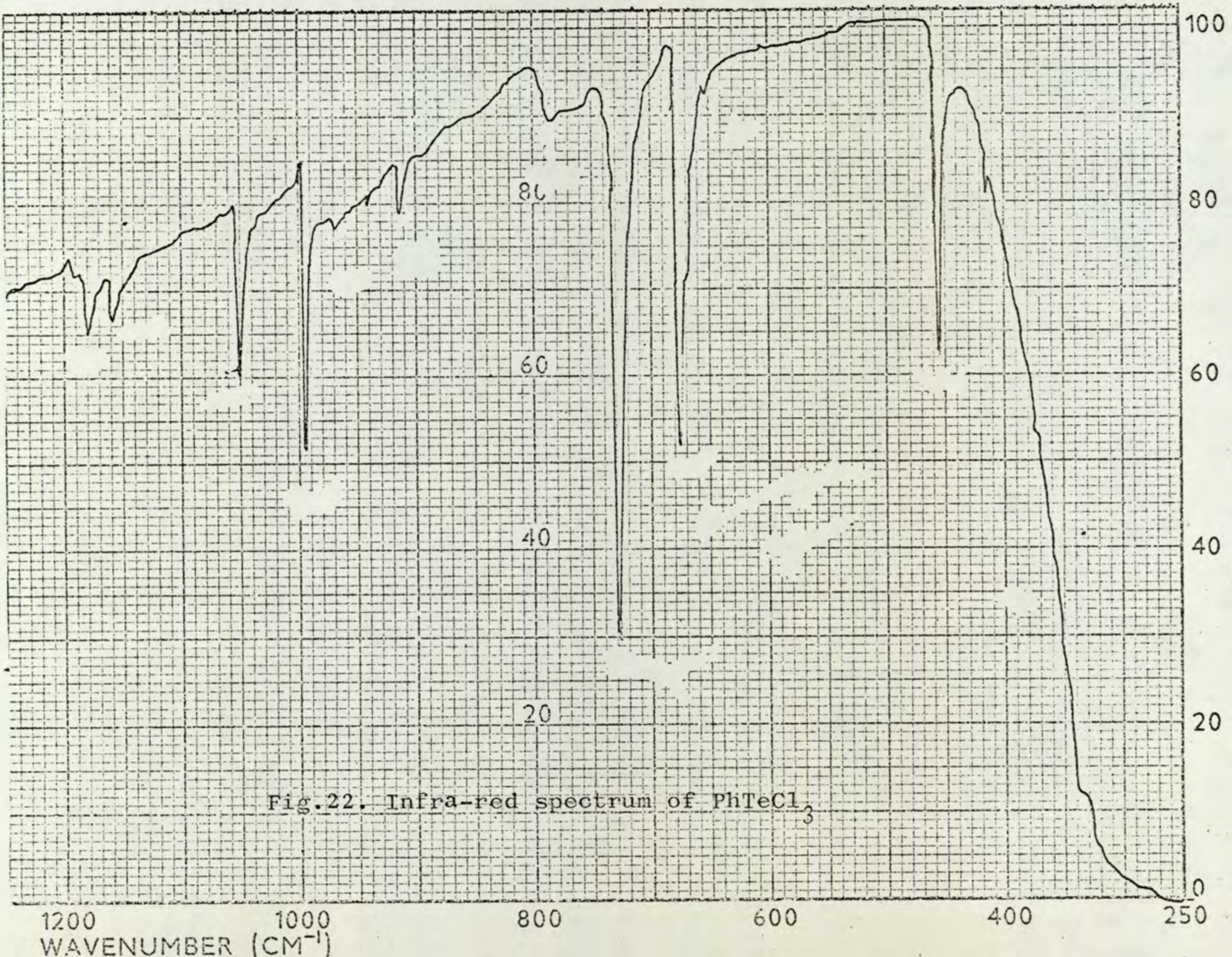


Fig.22. Infra-red spectrum of $PhTeCl_3$

Fig.23. Infra-red spectrum of $PhTeBr_3$

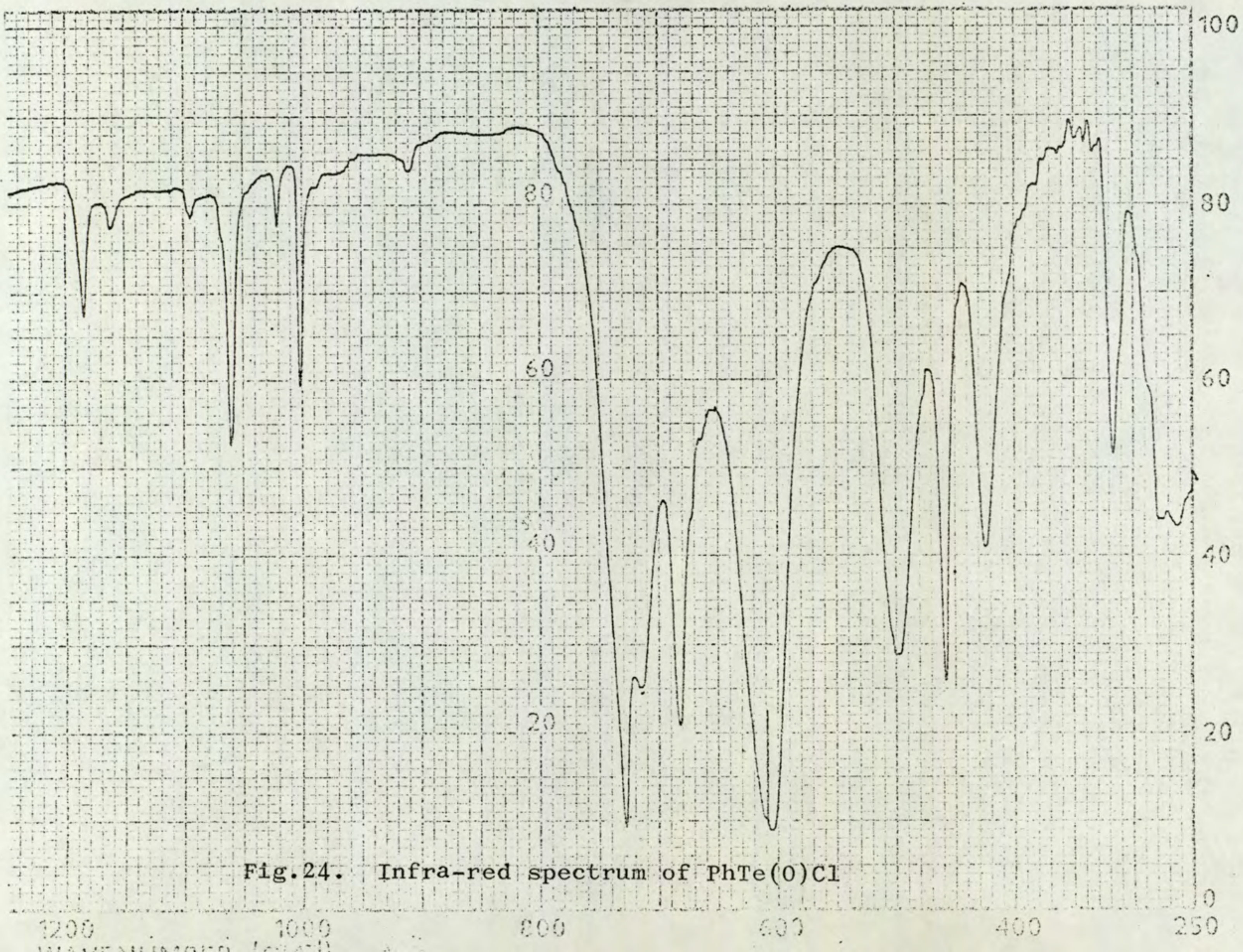


Fig.24. Infra-red spectrum of PhTe(O)Cl

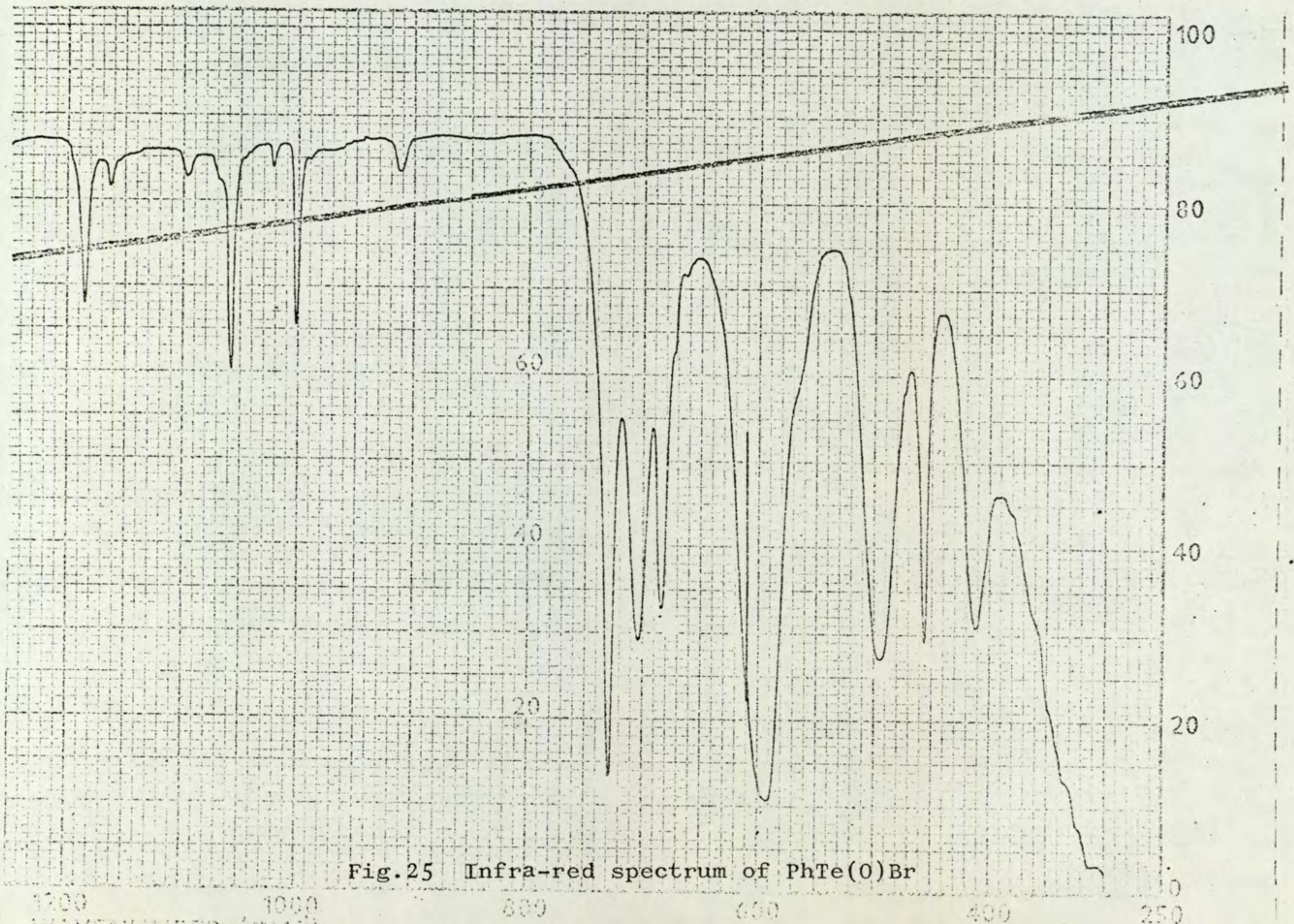


Fig.25 Infra-red spectrum of PhTe(O)Br

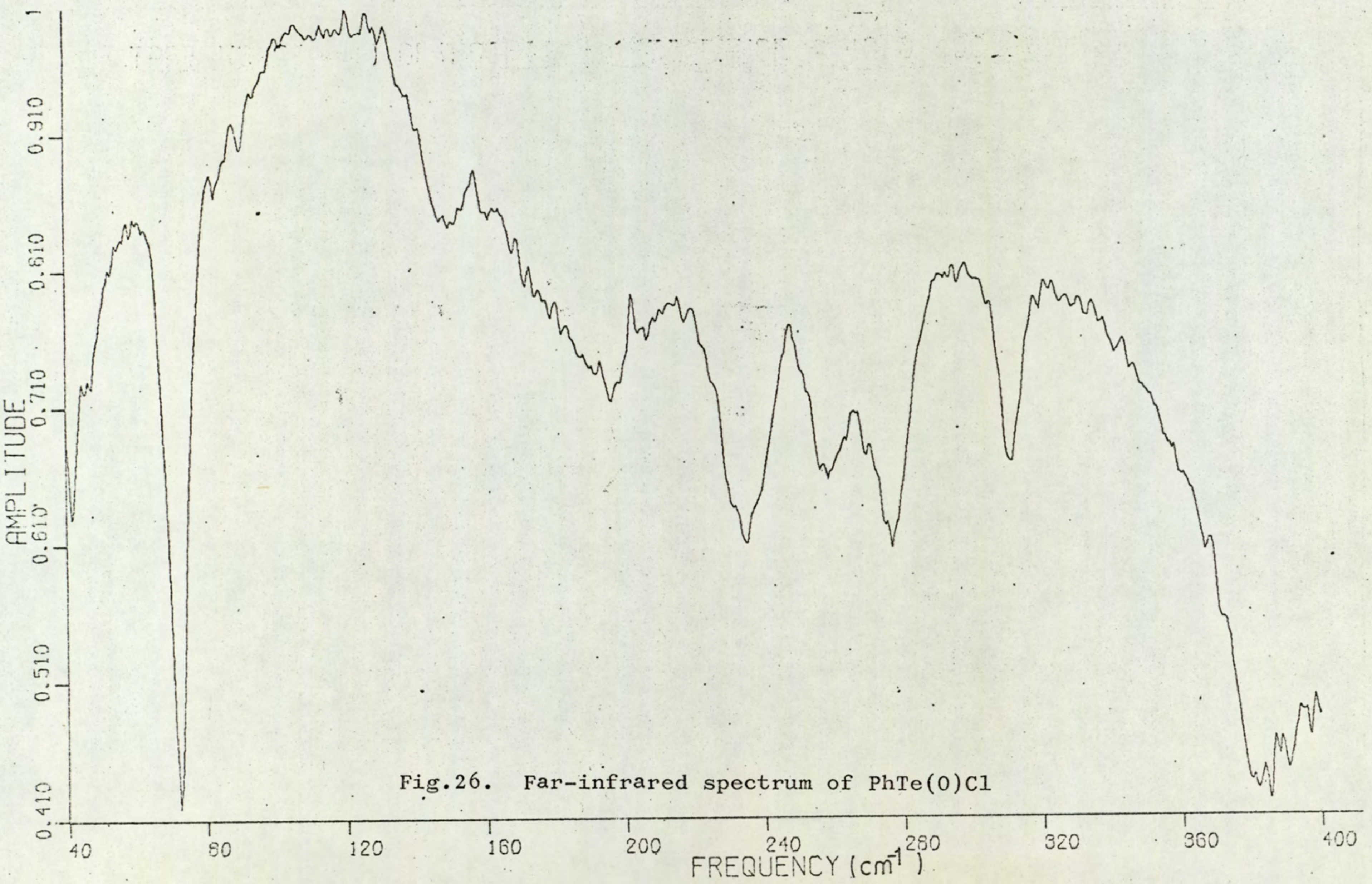


Fig.26. Far-infrared spectrum of PhTe(O)Cl

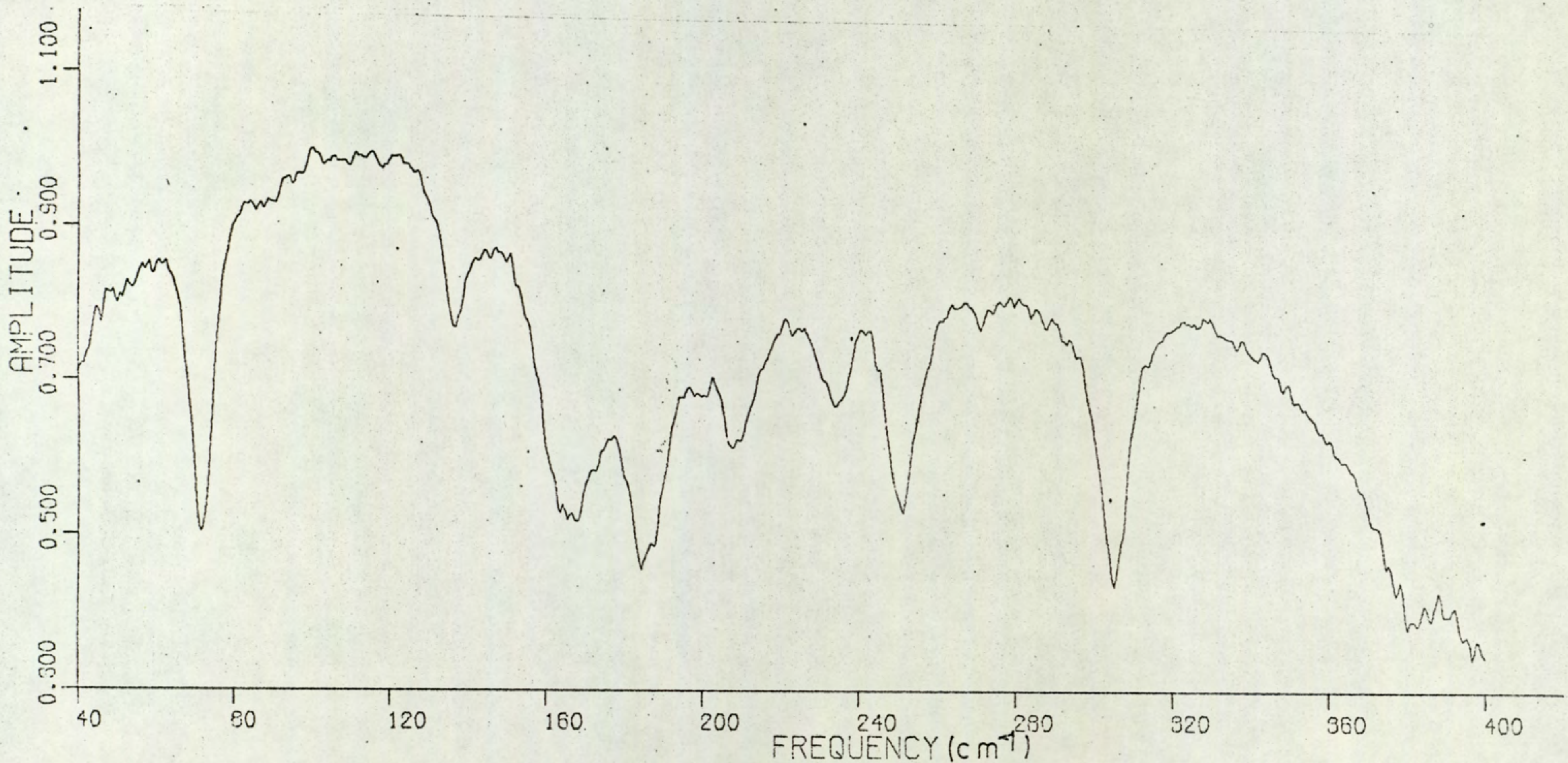


Fig.27. Far-infrared spectrum of PhTe(O)Br

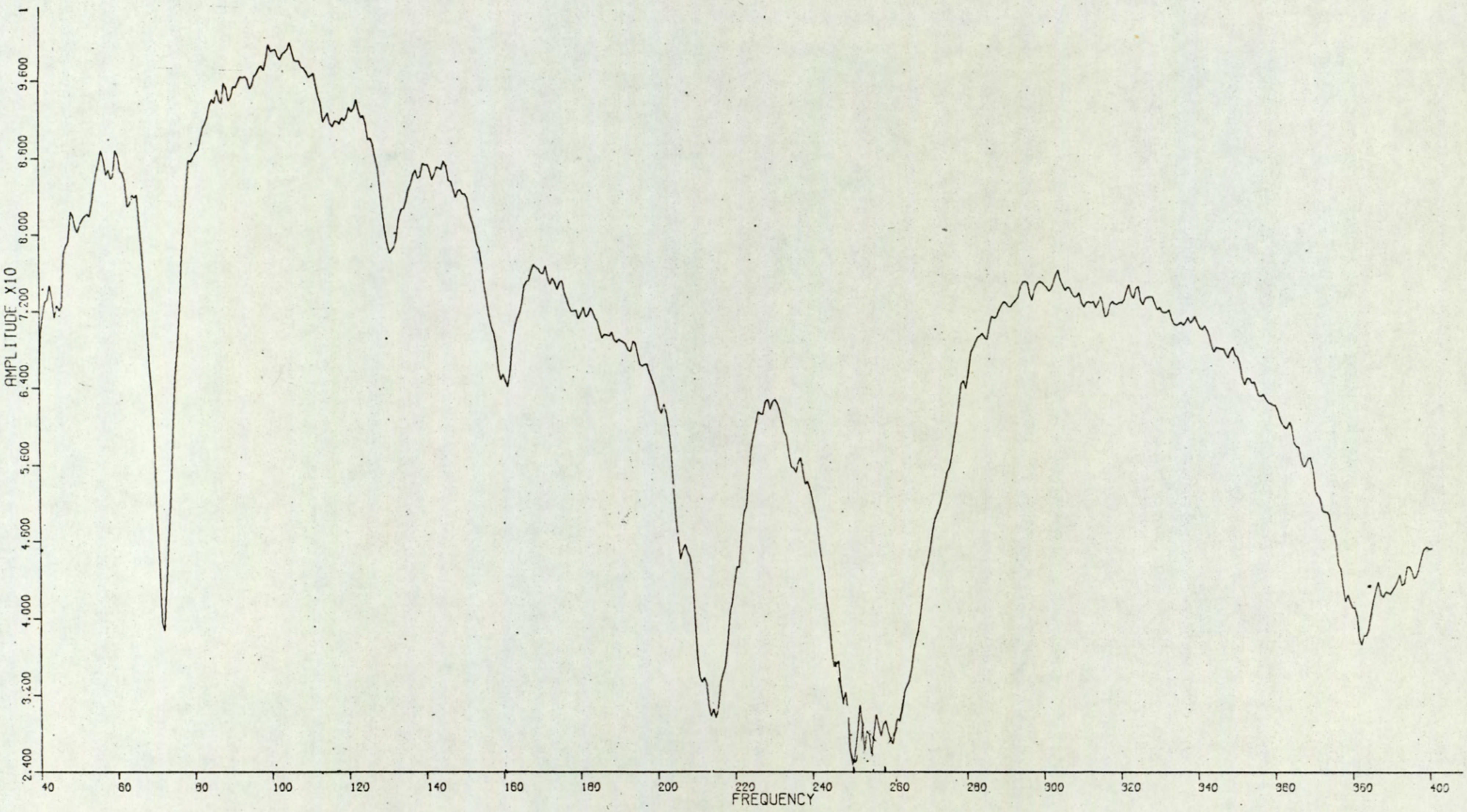


Fig.28. Far-infrared spectrum of Ph(C H_3COCH_2)$TeCl_2$

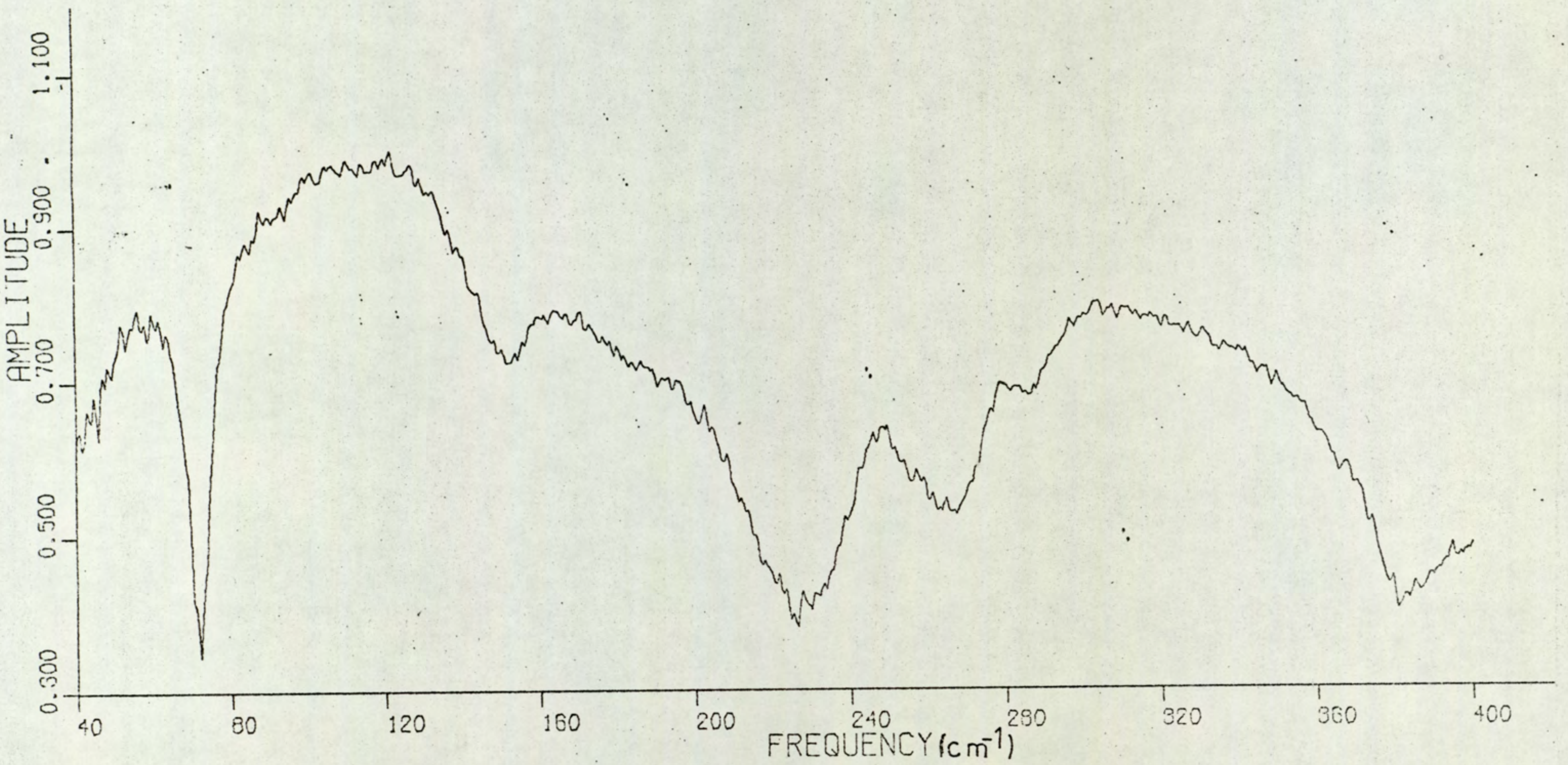


Fig. 29. Far-infrared spectrum of $(PhTeCl_4^-)(PyH^+)$

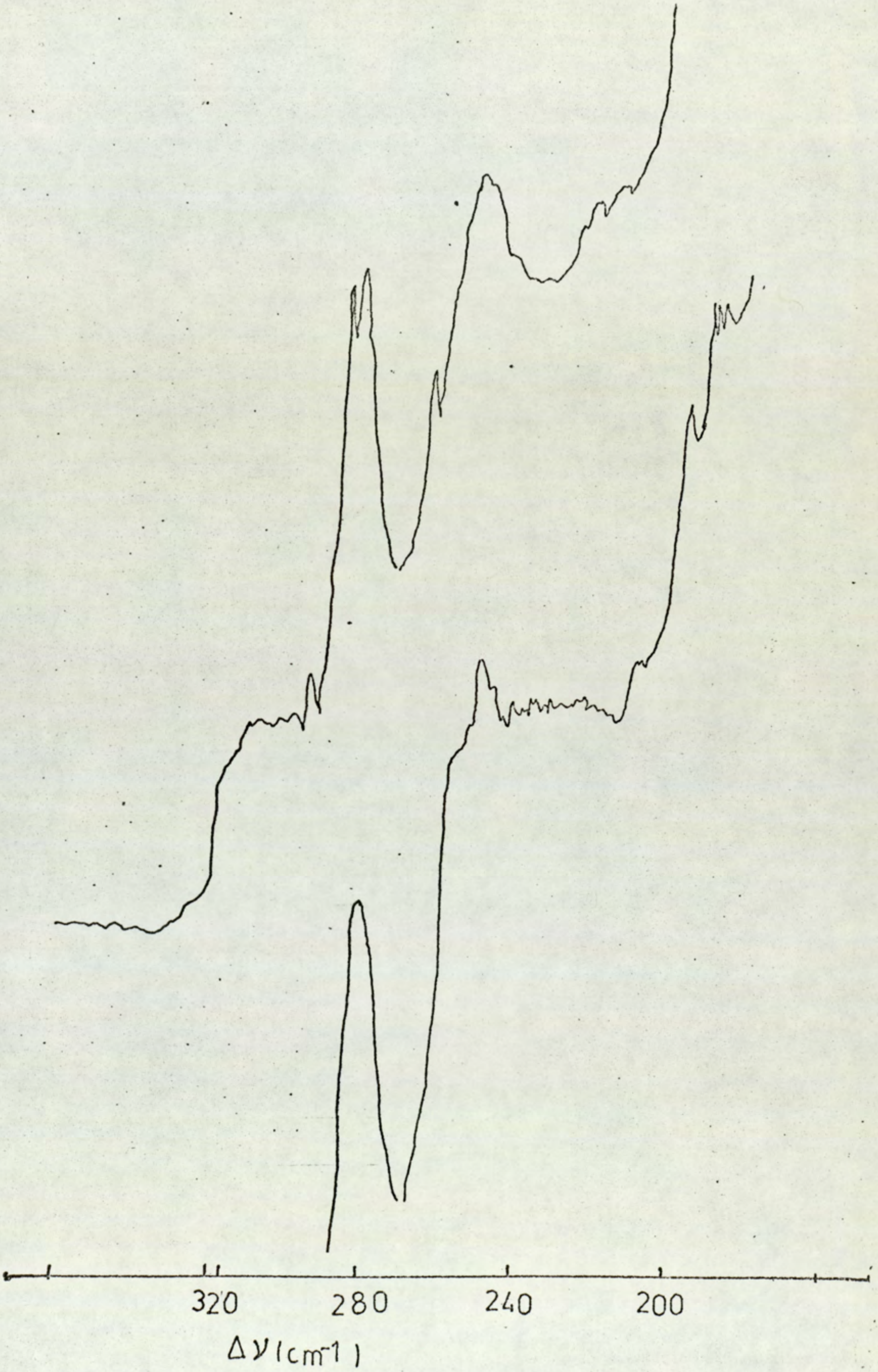


Fig.30. Raman spectrum of $(PhTeCl_4^-)(PyH^+)$

TABLE 19

Low frequency Vibrational Spectra of some p-Ethoxyphenyltellurium Compounds

RTe(O)Cl		RTe(O)Br	RTe(O)I	Assignment
(i.r.)	Raman	(i.r.)	(i.r.)	
719s		704s	688m	Te–O modes
602s	603m	590s	575s	
500s[+]		505sh	482s	
425s	425s	415s	400m	
308s	313w	303s	298 w-m	
248s	249v.s.	187v.s.	115w(?)	(TeX)
145w	145w			(TeCl)
323s	323w	321s	318m	Bands arising from R = p-EtO.$C_6H_4^-$
272s	271w	264m	264w-m	
217m		218s	218m	
205m			180s	
168m	168s[*]	153m	172sh	
139w			137m	
119m	121m	100w-m		
87m				
		57w-m		

TABLE 19-Continued

$RTeCl_3$+10%Na_2CO_3[a] (i.r.)	$RTeCl_3$+10%Na_2CO_3[b] (i.r.)	Assignment
715s	705s	Te-O modes
695sh	680s	
568s	555s	
380m-s	393m-s	
-	-	ν(TeX)
		δ(TeCl)
302s	312m-s	Bands arising from R = p-EtO.C_6H_4-
236s	264s,br.	
218s	227s	
	192s	
174s	172sh	
148w		
112m	118m-s	

a Without acidification with acetic acid

b After acidification with acetic acid

+ Mixed with R mode

* Overlap with laser line.

TABLE 20

The Low-frequency Vibrational Spectra of Organotetrachlorotellurates (IV)

$(C_5H_5NH)(PhTeCl_4)$		$(C_5H_5NH)(p\text{-}EtO.C_6H_4.TeCl_4)$		Assignment
i.r.	Raman	i.r.	Raman	
284m	280s	284s	284s	A_1^+
	249m-s		254s	B_1^+
227v.s.	220br.,sh.	231v.s.	228br.,sh	E^+
264s	256sh	262s	262sh	"R" modes
182sh		211s		
152m		147m		

TABLE 20- Continued

(Ph_4As) $(PhTeCl_4)$		$Ph_4As.Cl$	Assignment
i.r.	Raman	i.r.	
280s,sh.	284v.s.		A_1^+
	248s		B_1^+
227 sh	220br.sh.		E^+
396w			Ph_4As^+
363s		363s	
350s		350s	
345s		345s	
260s			"R" modes
250m			
235m-s			

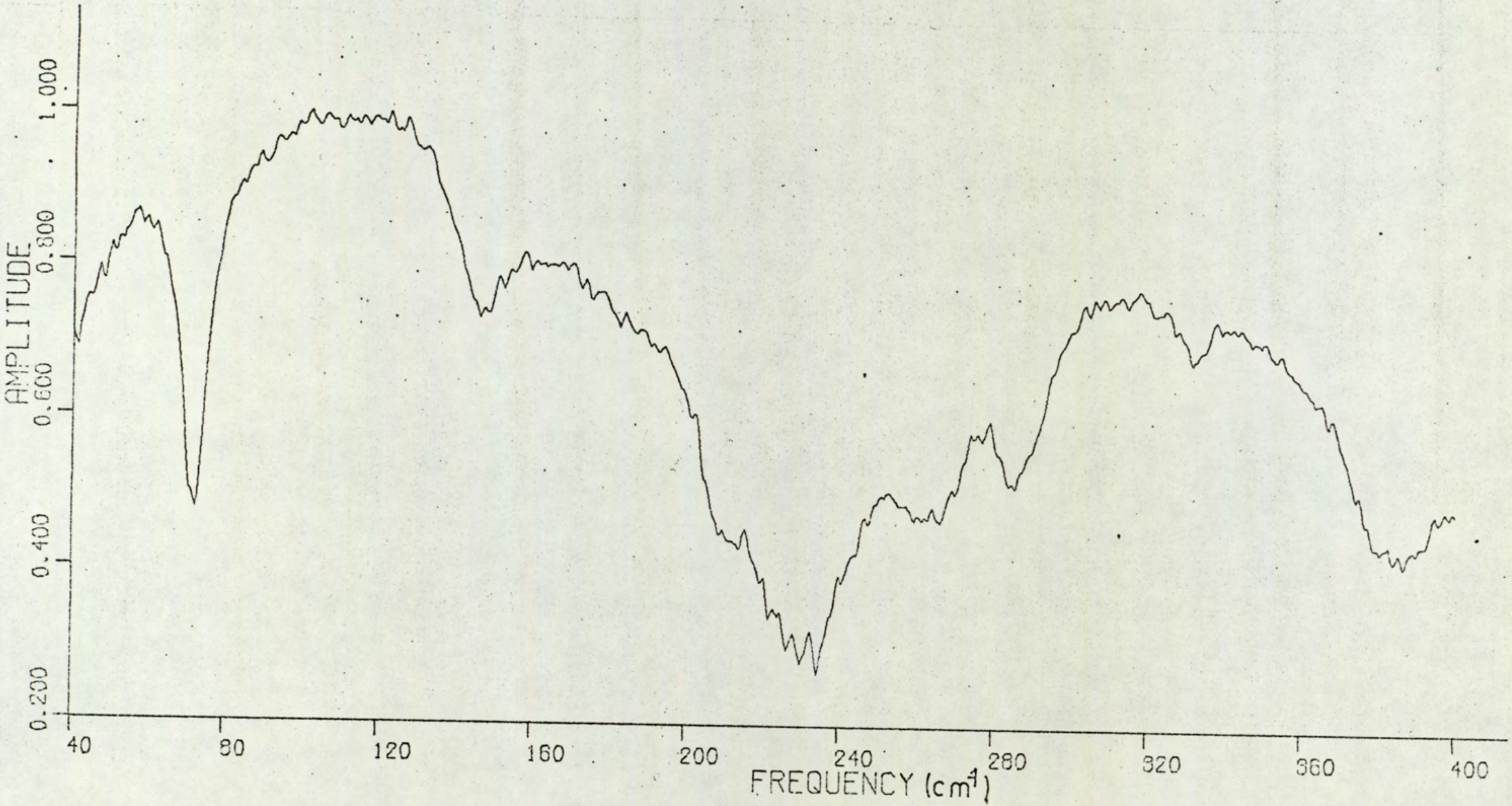


Fig.31. Far-infrared spectrum of $(p\text{-EtO.C}_6H_4TeCl_4^-)(PyH^+)$

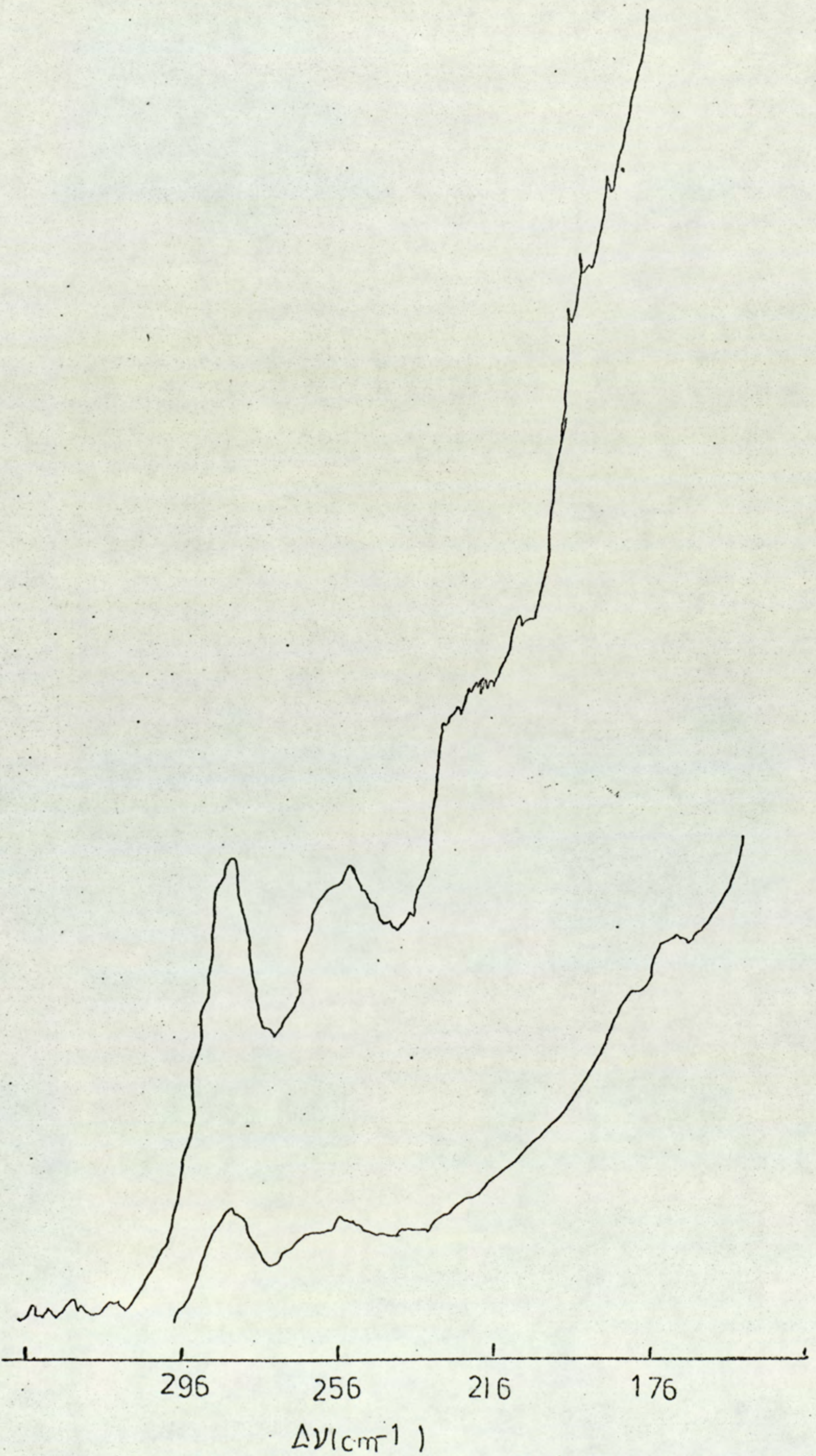


Fig.32. Raman spectrum of $(p\text{-EtO.C}_6H_4TeCl_4^-)(PyH^+)$

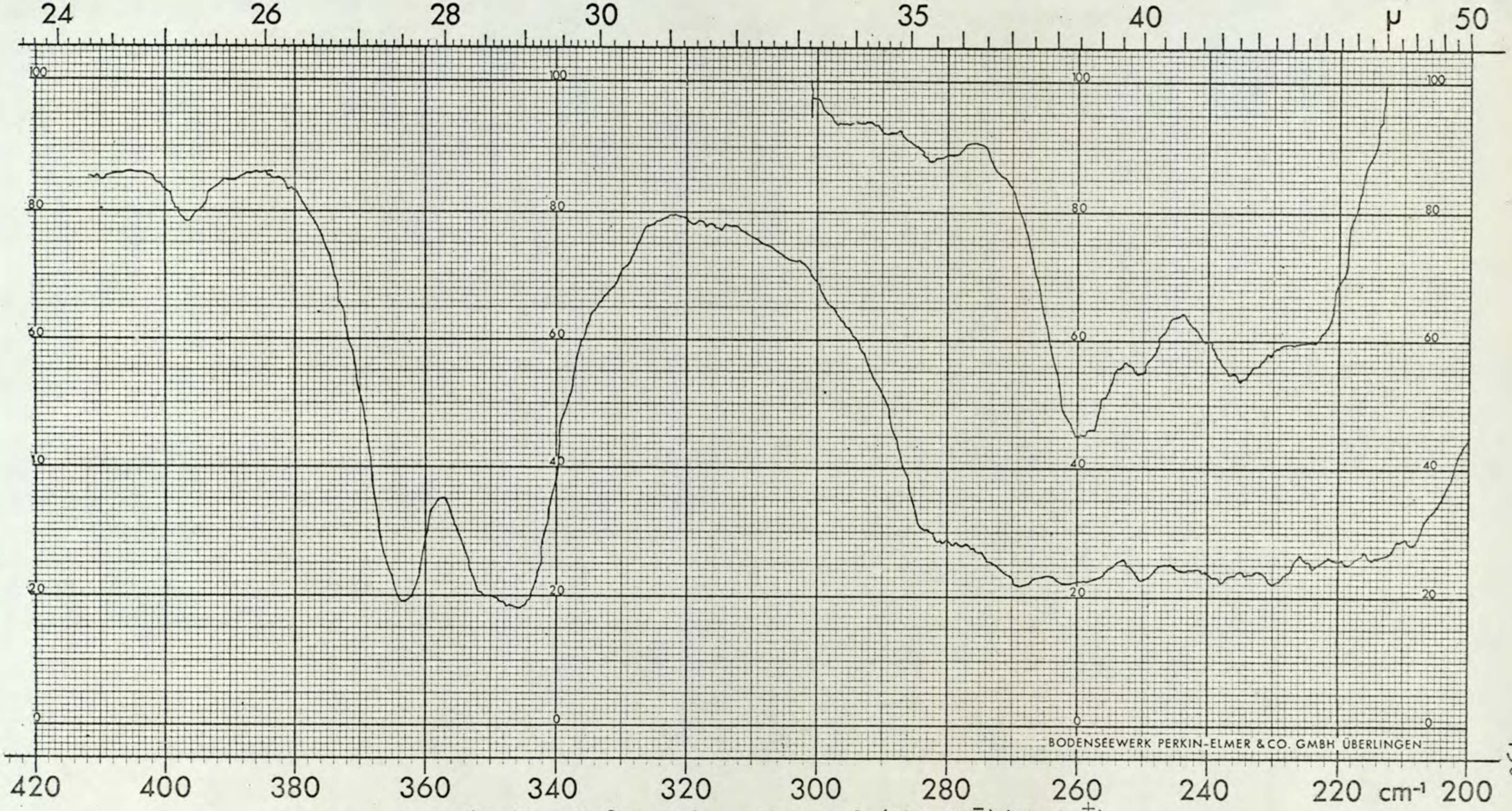


Fig.33. Infra-red spectrum of $(PhTeCl_4^-)(Ph_4As^+)$

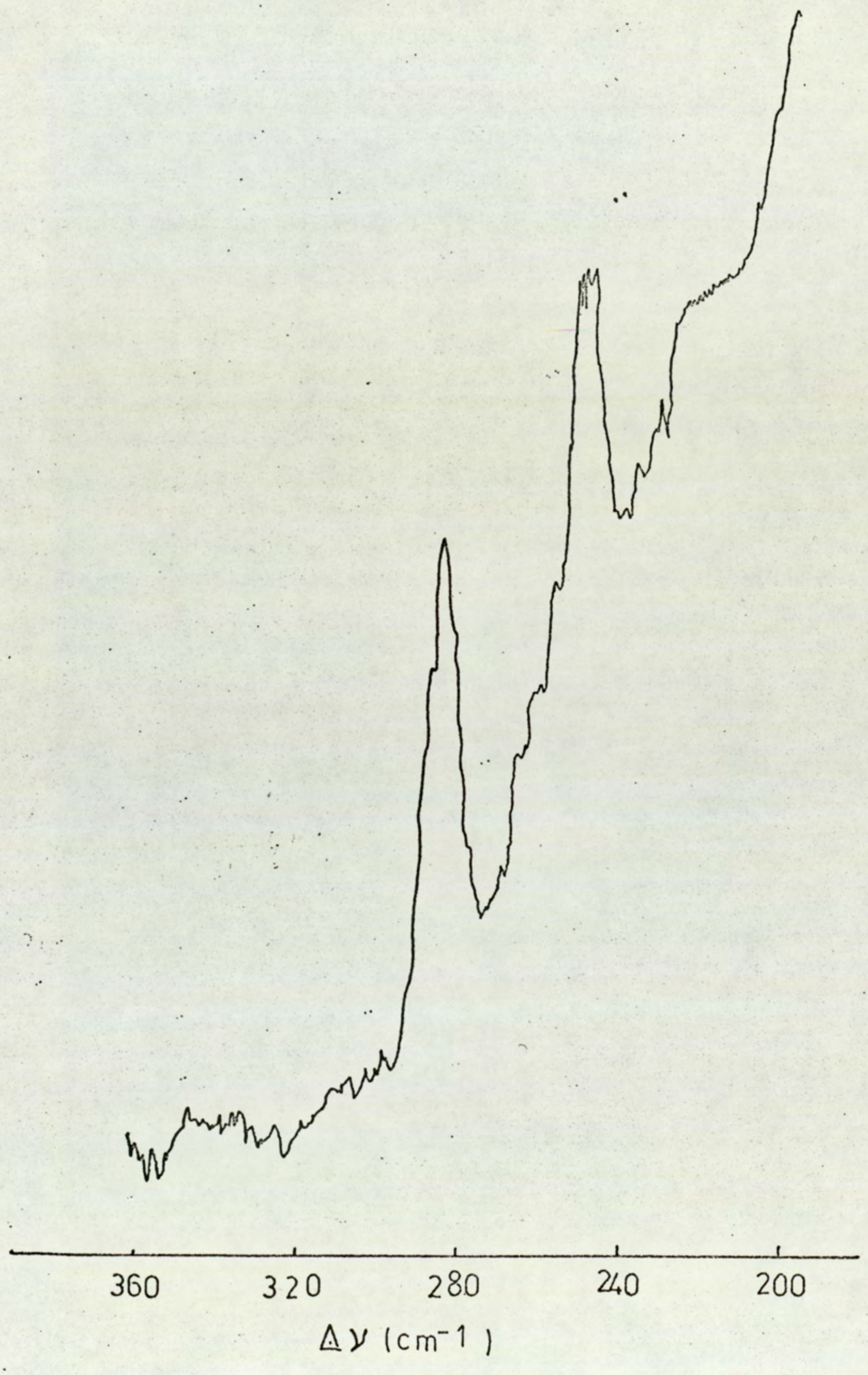


Fig. 34. Raman spectrum of $(PhTeCl_4^-)(Ph_4As^+)$

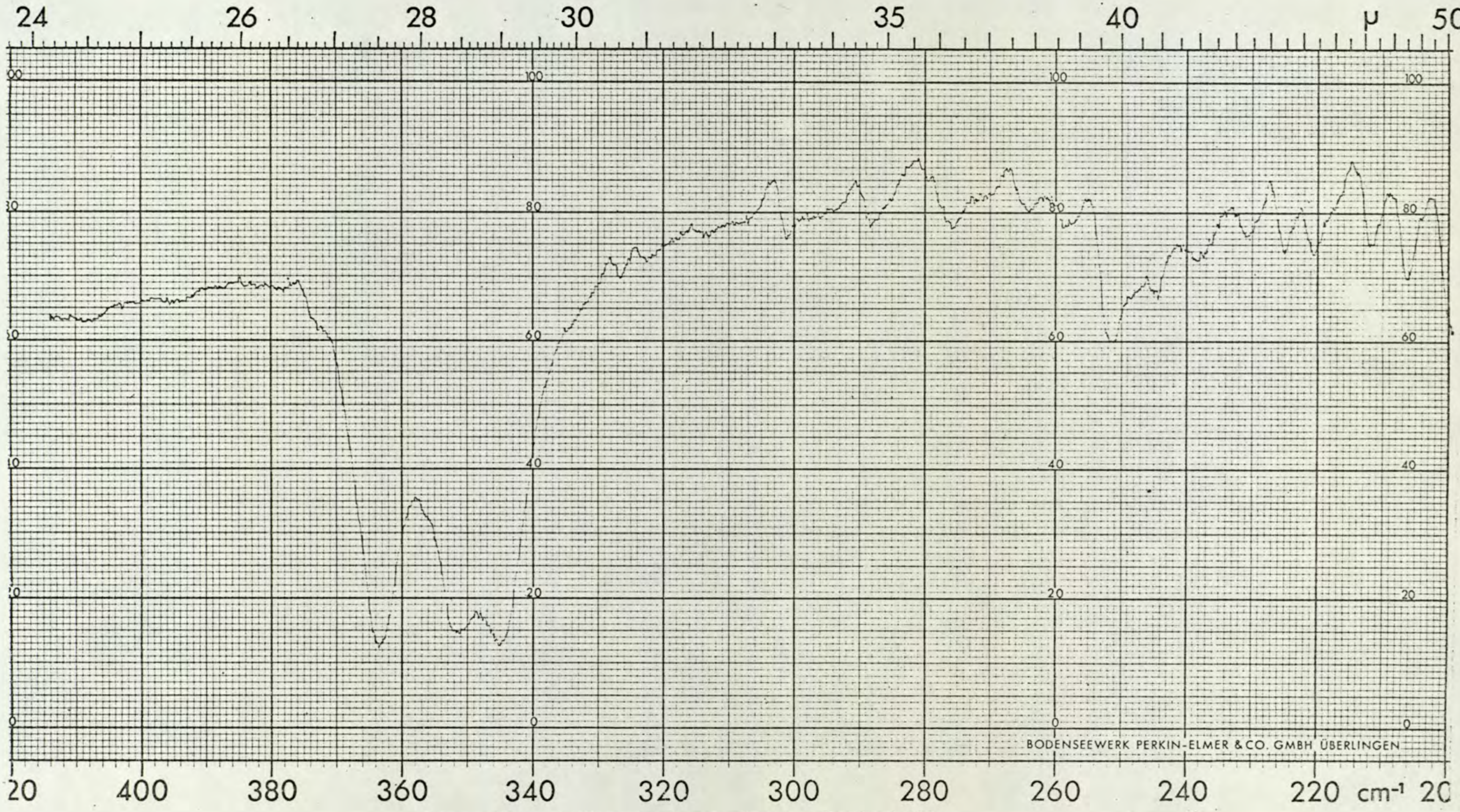


Fig. 35. Infra-red spectrum of Ph_4AsCl

TABLE 21

'd'-Spacing from the X-ray Powder Photographs of

$(p\text{-}EtO.C_6H_4)Te(O)Cl$

Melted	Not melted	Not melted*
	13 s	
11 s		11 s
9.2 s	9.5 s	9.4 s
5.7 s	6.1 s	5.8 s
5.2 w	5.4 w	5.3 w
4.7 w	4.8 m	4.8 m
	4.0 s	
3.9 s	3.8 s	3.92 s
3.7 s	3.6 w	3.72 s
3.55 w		3.50 w
	3.35 w	
	3.20 w	3.28 w
		3.12 w
2.92 s	2.98 s	2.92 s
	2.75 m	2.72 w
	2.68 m	2.65 w
	2.60 m	2.55 w
2.38 m	2.40 m	2.35 s
2.29 m	2.32 s	2.30 s
2.12 w	2.10 s	2.12 m
2.08 w		2.08 m
1.96 m	1.97 s	1.97 m

* obtained from addition of water to the alcoholic solution of $(p\text{-}EtO.C_6H_4)TeCl_3$.

DISCUSSION

Synthesis

It was found that in general the preparative results were reproducible and parrallel those of Petragnani and Vicentini,[40] however, there are some different points of detail. There is the observation of the different behaviour on heating the compounds. In the case of p-ethoxyphenyltellurium oxychloride it was found that unless scrupulous attention was paid to the purity of the starting material the product obtained showed no definite melting point. When p-ethoxyphenyltellurium oxychloride was obtained from the recrystallized p-ethoxyphenyltellurium trichloride the product had a melting point between 224-26 °C whereas the product obtained from the unrecrystallized starting material had no melting point. This observation is noted as Reichel and Kirschbaum[39] reported the melting point of $(p\text{-EtO.C}_6H_4)\text{TeOCl}$ to be in the region of 400-500° C. The i.r. spectra of the melted and unmelted compounds are identical, and the two compounds have satisfactory carbon and hydrogen analysis, but careful examination of the X-ray powder photographs (Table 21) shows slightly differences between the two, though the compounds are isomorphous. This is a very surprising result because one would expected that if a compound containing impurity it will melt at a lower temperature than the purer one.

It was agreed that the hydrolysis of phenyltellurium tri-iodide led to an undefined product. However, the hydrolysis of p-ethoxyphenyltellurium tri-iodide afforded p-ethoxyphenyltellurium oxyiodide which apart from (p-MeO.C_6H_4)TeCl[40] is only oxy-iodide to be prepared to date. Petragnani and Vicentini[40] claimed that the aryltellurium tri-iodides are not hydrolysed by cold water, this is wrong since it was found that both cold and hot water could be used to hydrolyse the tri-iodide, except a longer period is needed for the hydrolysis by cold water.

Attempts to isolate the intermediate products between the trihalides and oxyhalides were made by varying the time of stirring between the trihalides and water, and the trihalides in ethanol and water. The results were that if less time was used incomplete hydrolysis was obtained. This were shown by the very low carbon percentage and on careful examination of the i.r. spectra of the products proved to be a mixture of the starting trihalides and the oxyhalides. In one case for the hydrolysis of p-ethoxyphenyltellurium tri-iodide it was found that one mole of iodine were released per mole of the tri-iodide and believed that the product may be an intermediate of formula $[(\text{p-EtO.}C_6H_4)\text{TeI}]_2\text{O}$. However spectroscopic analysis showed the product to be a mixture of (p-EtO.C_6H_4)TeI_3 and (p-EtO.C_6H_4)Te(O)I instead.

For p-ethoxyphenyltellurium trichloride the hydrolysis was not completed within 5 minutes when the compound was stirred with cold water. Both phenyl- and p-ethoxyphenyltellurium tribromide took about 5 minutes for the yellow colour to change to white when they were stirred with cold water. Thus the observation of Petragnani and Vicentini[40] that both the trichloride and bromide are immediately hydrolysed seem unlikely to be correct. The fact that the tribromide was recrystallined from glacial acetic acid (Chapter IV) showed that the compound is not immediately hydrolysed by moisture. Therefore in this observation, the conclusion is that the hydrolysis of the trihalides by water is in an order $RTeCl_3 > RTeBr_3 \gg RTeI_3$. The trichlorides are more easily hydrolysed than the tribromides and in turn the tri-iodides.

The rate of the hydrylysis of aryltellurium trihalides by water can be explained in the term of steric effect. The tellurium atom in the molecules of aryltellurium trihalides has vaccant 4f orbitals[68(a)] having low energy enough for bonding by accepting a lone pair electrons from oxygen in water molecule forming an unstable intermediate. The size of ionic radius of the halides is in an order $Cl < Br < I$. Therefore the trichlorides are easily attacked by water molecule than the tribromides and in turn the tri-iodides. Also greater electronegativity of chlorine leads to higher effective charge on tellurium which again will favour attack by the nucleophile.

The hydrolysis of p-ethoxyphenyltellurium trichloride in alkaline media (10% Na_2CO_3 solution) yielded $[(p\text{-}EtO.C_6H_4)TeO]_2O$ after treatment with acetic acid. This is in agreement with the result of Petragnani and Vicentini.[40] However another product may also be resproducibly prepared which, according to infra-red data, contains OH bonds and the analysis of which corresponds to $(p\text{-}EtO.C_6H_4)TeO(OH)$. The compound is converted to the anhydride on treatment with dilute acetic acid.

When the reactions were carried out over various time of less than 2 hours, the products obtained after treatment with dilute acetic acid showed lower carbon percentages than the expected one. This implied that the reaction was not complete. However, in one case when the trichloride was stirred with 10% sodium carbonate solution for 30 minutes. The product obtained without prior treatment with dilute acetic acid, according to infrared spectrum, contained OH bonds and analysis corresponded to $(p\text{-EtO.C}_6H_4)Te(OH)_3$. The similar compound, $(p\text{-MeO.C}_6H_4)Te(OH)_3$ has been reported by Morgan and Kellet.[36] But there is no further evidence for the existance of three hydroxide groups.

The failure to isolate any product of the hydrolysis corresponding to a stage intermediate between $RTeX_3$ and RTe(O)X thus the intervening stages appear to be fast, the limited solubility of $RTeX_3$ in water is probably the rate determining factor. In an attempt to use a Lewis base other than water to break the bridging halogen bonds in $RTeX_3$, pyridine were reacted with phenyl- and p-ethoxyphenyltellurium trichlorides.

The product obtained are pyridinium salts, $RTeCl_4^-.PyH^+$ instead of an expected compound, $RTeCl_3.Py$. The explanation is that although the reagents were supposedly "dry" they contained sufficient water to hydrolyse some $RTeX_3$ to RTe(O)X. The hydrogen chloride released reacted with $RTeX_3$ to yield $RTeCl_4^-$ which was subsequently isolated as a pyridinium salt. Recrystallization of $(PyH^+)(RTeCl_4^-)$ from an acetone containing medium led to the isolation of the new compound $Ph(CH_3COCH_2)TeCl_2$. The condensation of mono-organotellurium trihalides with methyl ketones is well known[69] yet, surprisingly, this example of the reaction has not been previously reported. Interestingly enough the p-ethoxyphenyl- salt did not give the corresponding compound when treated under the same conditions. The formation of aryltetrachlorotellurate(IV) was further supported by the preparation of $(Ph_4As^+)(PhTeCl_4^-)$ by direct reaction between Ph_4AsCl and $PhTeCl_3$. This reaction a chloride was supplied by Ph_4AsCl where in the case of the reaction with pyridine hydrogen chloride was generated by the hydrolysis of $RTeX_3$.

In $RTeX_3$ the tellurium atom has the possibility of accepting a pair of electrons to the vaccant 4f orbitals.[68(a)] Thus it acts as a Lewis acid and the atom or molecule which donates a lone pair of electrons is a Lewis base. The reaction of $RTeX_3$ and some Lewis base i.e. α,α'-bipyridyl, 1, 10-phenanthrolene and di-(bipyridyl)diamine in bezene solution yielded unexpected products, which according to the analysis are most probablely $(RTeCl_4^-)(bipyH^+)$, $(RTeCl_4^-)(phenH^+)$ and $(RTeCl_4^-)(dpmH^+)$. These products in fact are similar to those affording from the reaction of $RTeX_3$ with pyridine.

The belief that the process of the reduction of $RTeX_3$ to R_2Te_2 involves an intermediate RTe(O)X is now confirmed from the reduction of RTe(O)X which yielded R_2Te_2.

MECHANISM OF HYDROLYSIS

A possible scheme for the hydrolysis of an aryltellurium trihalide is given in (5-1)

$$\mathrm{R.TeX_3} \xrightarrow{\mathrm{H_2O}} \underset{\text{(A)}}{\mathrm{RTeX_3.H_2O}} \xrightarrow{\mathrm{-HCl}} \underset{\text{(B)}}{\mathrm{RTeX_2(OH)}} \xrightarrow{-\frac{1}{2}\mathrm{H_2O}}$$

$$\underset{\text{(C)}}{\mathrm{(RTeX_2)_2O}} \xrightarrow[\text{etc}]{\mathrm{H_2O,\ -HCl}} \mathrm{RTe(O)X} \qquad (5\text{-}1)$$

It had been hoped to isolate an intermediate compound corresponding to (C) but it was found that either RTe(O)X or a mixture of $RTeX_3$ and RTe(O)X were obtained by varying the time and conditions. Thus if stages corresponding to (B) and (C) are involved in the reaction, the intermediates must be short-lived. Compound (A) should be monomeric and would arise from nucleophillic attack on tellurium in $RTeX_3$ by water to break the halogen bridge bonds. There was a possibility to use other nucleophiles, L, and to demonstrate the feasibility of forming monomeric compounds $RTeX_3.L$ direct from the trihalide. It was indeed sucess but not in the way as expected. Ions $RTeCl_4^-$ were prepared by the reaction of $RTeX_3$ and HCl which had been generated in situ from the hydrolysis of another portion of $RTeX_3$ by water. Further support for the concept of a monomeric first intermediate is derived from the work of Wynne and Pearson[67] who recently demonstrated that the product obtained from the reaction of $MeTeCl_3$ and tetramethylthiourea to be $MeTeCl_3$(tmtu) having a five co-ordinate tellurium atom and is a monomeric molecule. The hydrolysis of $RTeCl_3$ or RTe(O)X in alkaline media yielded the same products, hence the initial stage of reaction probably follows a scheme similar to (5-1). However another compound was isolated directly from the alkaline medium before treatment with dilute acetic acid. This compound has a formula of $(\text{p-EtO.C H })\text{TeO(OH)}$ and it was converted to $[(\text{p-EtO.C}_6\text{H}_4)\text{TeO}]_2\text{O}$ on acid treatment. Therefore the most probable scheme for the alkaline hydrolysis is that of (5-2).

$$\text{RTe(O)X} \xrightarrow[\text{H}_2\text{O}]{\text{OH}^-} \underset{(\text{D})}{\text{RTe(OH)}_3} \xrightarrow[-\text{H}_2\text{O}]{} \underset{(\text{E})}{\text{RTe(O)OH}} \xrightarrow[-\frac{1}{2}\text{H}_2\text{O}]{\text{H}^+} \underset{(\text{F})}{\tfrac{1}{2}\,(\text{RTeO})_2\text{O}} \qquad (5\text{-}2)$$

Reichel and Kirschbaum[39] did infact with good analytical data, claim to have isolated the compound formulated as RTe(O)OH but their products were treated with dilute sulphuric acid before separation. However in several of the experiments of the present work, the compounds obtained after alkaline hydrolysis without treatment with dilute acetic acid have the analytical data which were intermediate between RTe(OH)_3 and RTe(O)OH. It was very interesting that in one case the alkaline hydrolysis of RTeX_3 afforded a compound whose analyses corresponding to RTe(OH)_3. This reaction was carried out for 30 minutes. If RTe(OH)_3 is genuine compound it will be another intermediate compound has been isolated. However, one could not ignore it because as in the scheme (5-2) RTe(OH)_3 is an expected compound. Morgan and Kellet[36] did claim that they had prepared RTe(OH)_3 by the alkaline hydrolysis of RTeX_3 but the product was acidified with dilute acetic acid.

It was also observed that in several experiments of alkaline hydrolysis of $RTeX_3$ where the stirring times were less than two hours, the products obtained after acidification with dilute acetic acid had the carbon percentages which were intermediate between $RTeX_3$ and $(RTeO)_2O$. But they had no any OH bonds observed from the infrared spectra. Therefore the staged (D) to (E) and to (F) must be fast in the reaction on addition of acid. Otherwise in the absence of acid the stage to form compound (F) is prohibited and the rate to form compound (E) is slow. Compound (D) is expected to be less stable than compound (E) by the elimination of water to form a stable compound (E). In organic chemistry it is well known that compound containing three hydroxide groups in one carbon atom is unstable compound.

INFRA-RED SPECTRA

The assignments of the infrared bands of PhTe(O)Cl, PhTe(O)Br, $Ph(CH_2COCH_3)TeCl_2$ and $(PyH^+)(PhTeCl_4^-)$ are given in Table 18. The i.r. spectra of PhTe(O)Cl and PhTe(O)Br at higher frequency are very similar, and this implies the compounds to be isostructural. By comparision of the i.r. spectra with starting compounds i.e. $PhTeCl_3$ and $PhTeBr_3$, the tellurium-oxygen vibrational modes were assigned with some confidence and they were straightforward. For i.r. and Raman bands at frequencies below 400 cm^{-1} of the above phenyl compounds the assignments of Table 18 for Phenyl<u>t</u> or ν(TePh), Phenyl <u>u</u> and <u>u</u>', Phenyl <u>x</u> and <u>x</u>', ν(Te-X) and δ(Te-X) using Whiffin's notation[50] can be done with confidence and readiness by comparision with the assignments for $PhTeX_3$ in Chapter IV and particularly the detailed assignments of Ph_2TeX_2.[30] The assigned bands agree very well with those for Ph_2TeX_2, except the ν(TeX) vibrational modes. The assignments of ν(TeX) for all phenyl compounds in Table 18 are lower than assigned the frequencies for ν(TeX) terminal in the parent trihalides. They are infact in the region between the ν(TeX) terminal and bridge, and near the ν(TeX) modes of Ph_2TeX_2. However for pyridinium salt the lower frequency of ν(TeCl) is expected for an anionic complex compared with a neutral species. Both Phenyl <u>u</u> modes in $Ph(CH_3COCH_2)TeCl_2$ and $(PyH^+)(PhTeCl_4^-)$ are masked by the other bands near by. The spectrum of $Ph(CH_3COCH_2)TeCl_2$ is unremarkable and is consistent with the established distorted four co-ordinated structure of other diorganotellurium dihalides.[30] The assignment of ν(Te-alkyl) at 530 cm^{-1} may be compared with that of ν(TeC) at 534 cm^{-1} for Me_3TeBr.[22] The bands at 131 cm^{-1} and 177 cm^{-1} are unassigned.

Consideration of Table 19 the assignments of the infrared and Raman bands for $(p\text{-}EtO.C_6H_4)Te(O)X$ and $[(p\text{-}EtO.C_6H_4)TeO]_2O$ to the various types of vibrations i.e. "tellurium-oxygen", "tellurium-halogen" and the organic group is again a reasonably straightforward matter and some confidence may be place on the classifications of Table 19. These are done by the comparision between the parent trihalides and the hydrolysed products. The infrared spectra of three $(p\text{-}EtO.C_6H_4)Te(O)X$ (X = Cl, Br and I) are very similar implying that the structures may be similar within the series. The Raman shifts for $(p\text{-}EtO.C_6H_4)Te(O)Cl$ show virtually complete coincidence with the infrared frequencies implying a structure of low symmetry. This observation is believed to be true not only for (p-EtO.C_6H_4)Te(O)Cl but also the other RTe(O)X whose Raman data were not available owing the poor quality of the spectra or the absorption of the laser line by the compounds. The intensity of the Raman shifts of (p-EtO.C_6H_4)Te(O)Cl at 603 cm^{-1} and 425 cm^{-1} imply these to correspond to the more symmetrical (TeO) modes. Again for the ν(TeX) vibrations the assigned bands are lower than the ν(TeX) terminal in the parent trihalides as in the case of phenyl compounds in Table 18. The compound described as (p-EtO.C_6H_4)TeO(OH) in the experimental section shows a broad band centred on 3060 cm^{-1} which was assigned as ν(OH). The low frequency and the breadth of the band suggest hydrogen bonding to play an important part in this structure.

STRUCTURAL CONSIDERATIONS

One must realize that vibrational spectroscopic data alone cannot offer definite answers to the structural problems. However it is possible to make some progress towards a solution of the problems.

1. Aryltellurium oxyhalides

From the vibrational spectroscopic data of aryltellurium oxyhalides in Table 18 and 19. A structural model for the aryltellurium oxyhalides must be able to account for the rich spectrum associated with tellurium-oxygen modes and for the slight solubility of the material in water as mentioned in experimental section. The positions of tellurium-halogen modes are of interest since they are lower than those of $RTeX_3$ (in Chapter IV). This may be due to one of the three reasons; firstly, the increasing of co-ordination number of tellurium atom in RTe(O)X and secondly, the involvement of halogen atoms in bridge bonds, and finally the formation of weaker(longer) tellurium-halogen bonds in RTe(O)X. In the discussion of Chapter IV it was believed that the co-ordination number of tellurium atom in $RTeX_3$ to be five, thus to evaluate the first possibility the co-ordination number of tellurium atom must be considered to be at least six in RTeOX. It was very difficult to visualize any plausible structure involving six co-ordination number for tellurium, and if it were possible it would violate the hypothesis of Wynne and Pearson[24] who argued that there is no bonding <u>trans</u> to the organic group. This hypothesis has found to be workable in the structural analysis of $RTeCl_3$ (in Chapter IV). Therefore it led to consider the second structural possibility. The fact that tellurium-halogen modes appear to be too simple and too high frequency to convincingly imply bridging halogen atoms. So the structure involving the bridge halogen bonds is unlikely. Thus it led to consider the last structural possibility. The assignments of frequency as ν(TeX) modes in Table 18 and 19 are very closed indeed to those reported for a wide range of diorganotellurium dihalides.[30] Thus the tellurium atom may in fact exist in a distorted four co-ordinate environment such as that illustrated in Fig. 36.in which the axial bonds in the ψ-trigonal bipyramidal arrangement are longer than the equational bonds. The tellurium halogen bonds must be long and in the axial position in order to account for

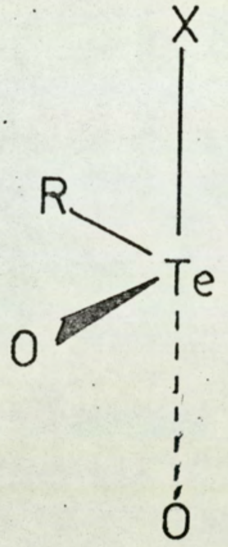


Fig.36. Suggested environment of tellurium in RTe(O)X

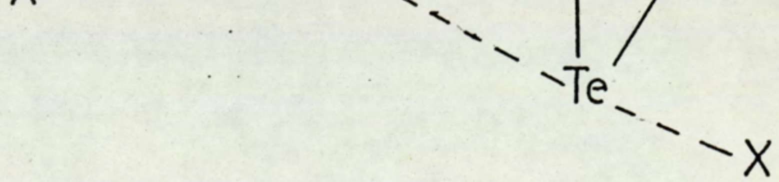


Fig. 37. Illustration of a possible ring structure for RTe(O)X

the lower frequency of ν(TeX) modes. The most probable structure of RTe(O)X is believed to be a ring structure with oxygen bridge bonds since this would account for the complexity of the tellurium-oxygen vibrations and such a structure may also account for the slight solubility of RTe(O)X in water rather than a highly polymeric model. Therefore the structural model which most reasonably accounts for the available data is one which involves four co-ordinate tellurium atom in a ring structure. The feasibility of this model is illustrated in Fig. 37.

The infrared spectroscopic data of both $(p\text{-EtO.C}_6H_4)$TeO(OH) and $[(p\text{-EtO.C}_6H_4)\text{TeO}]_2O$ are very complicated and it is not possible to discuss any further about the structure of these compounds at this stage.

2. Organotetrachlorotellurate(IV)

The compounds of interest are $(\text{PhTeCl}_4^-)(\text{PyH}^+)$, $[(p\text{-EtO.C}_6H_4)\text{TeCl}_4^-][\text{PyH}^+]$ and $(\text{PhTeCl}_4^-)(\text{Ph}_4\text{As}^+)$. The anions of these salts are analogous to the well known MeTeI_4^- which occurs in the β form of Me_2TeI_2 $(\text{Me}_2\text{Te}^-\text{MeTeI}_4^-)$[70] where the structure of MeTeI_4^- has been determined by the X-ray crystallographic technique to be a square pyramidal configuration, with iodine atoms in the base, the methyl group at the apex, and with the lone-pair completing an octahedron. Therefore a square pyramidal structure is most probable for PhTeCl_4^- anion, with chlorine atoms in the base and the phenyl group at the apex. The similar type of structure was also suggested for the molecule of MeTeCl_3(tmtu)[67] with a tmtu in addition to other three chlorine atom at the base of the square pyramidal structure. Assuming free rotation about the tellurium-carbon(phenyl) bond the symmetry of the anion is approximately C_{4v} for which two infrared active tellurium-chloride stretching vibrations are expected (A_1+E) together with three Raman bands (A_1 + B_1 + E). In Table 20 the i.r. bands and Raman shifts which are attributed to the pyridinium salt and Ph_4As^+ vibrational modes were isolated but the more complete assignment were offered in Table 18 for ($PhTeCl_4^-$)(PyH^+). Careful comparision of the spectra suggests that the complex anions have essentially the same structure in all three compounds. The band close to 280 cm^{-1} is a tellurium-chlorine stretching mode, and it is strong in Raman effect it is therefore probably the A_1 mode. The strong i.r. and weak Raman band below 230 cm^{-1} is probably the E mode. Thus the medium to strong Raman band at about $\Delta\nu$ = 250 cm^{-1} is assigned as the B_1 mode. These assignments support well the proposed square-based pyramidal structure but interpretation is complicated by the unfortunate overlap of ν(TeCl) with R modes in $RTeCl_4^-$. In conclusion it is believed that the most probable structure for these complex anions ($RTeCl_4^-$) is illustrated in Fig. 38.

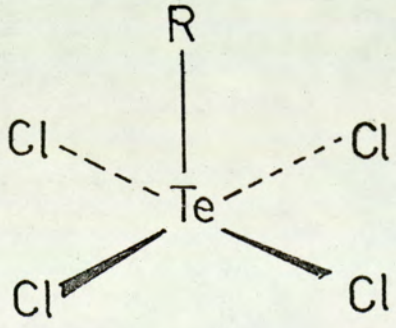


Fig. 38. Illustration of a possible structure of $RTeCl_4^-$ (R = Ph, p-EtO.C_6H_4)

CHAPTER VI

ANALYSIS OF TELLURIUM

INTRODUCTION

It became necessary to determine the tellurium content in the new organotellurium compounds, since we cannot depend only on carbon, hydrogen and nitrogen percentages in order to find out the empirical formula. So far there are only two methods available which are practical for organotellurium compounds.

Drew and Porter[41] developed a gravimetric method for the analysis of tellurium in organotellurium compounds, but it is only applicable to alkyltellurium compounds. Tsao[42] developed a new gravimetric method by fusion of organotellurium compounds with sodium peroxide in a Parr bomb the product being finally reduced to tellurium metal and weighed. This method is applicable to all types of organotellurium compounds and gives very satisfactory results. The only disadvantage of this method is that it involves a very tedious procedure. Kruse et al[43] developed a volummetric method. The sample is decomposed first by heating with 70% nitric acid and subsequently with a mixture of 30% nitric acid and 70% perchloric acid. Ferrous ammonium sulphate solution is added to the final solution and then a back-titration with standard potassium dichromate is performed. Though this method is less tedious than

Tsao's, it is more subject to errors and requires more sample for each analysis.

A new simple and reliable method is needed. By coincidence an atomic absorption spectrophotometer was installed in the Department of Geology, so the instrument was exploited for the problem. Atomic absorption spectroscopy is a very powerful and and versatile analytical tool at the present time.

The analysis of tellurium in alloys by using atomic absorption spectroscopy has been reported,[71,72] but none of these methods for the preparation of sample solutions can be used to prepare solutions of organotellurium compounds.

Various aryltellurium trihalides, $RTeX_3$ (R = Ph, $p\text{-}MeC_6H_4$, $p\text{-}MeO.C_6H_4$, $p\text{-}EtO.C_6H_4$ and $p\text{-}PhO.C_6H_4$; X = Cl, Br and I) were studied in order to evaluate the method.

Wash[73] is the first person who clearly indicated the potentiality of the atomic absorption for chemical analysis.

The concept relating to the principle of atomic absorption can be explained simply. Assume there is a cloud of atoms which is free of any molecular bonding force as shown in the outline of Fig.39[74]. If energy is applied to this atomic cloud, say in the form of heat, some of the atoms will be excited to higher energy levels. Which eventually will return to their lower energy levels by releasing the energy as the emission spectrum of atom.

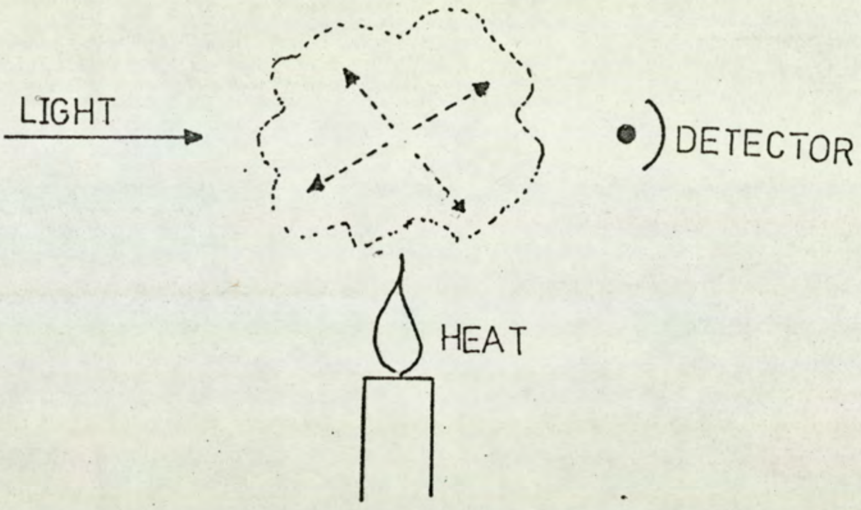


Fig. 39. The principle of atomic absorption.

Not only thermal energy that can excite atoms, but light energy whose wavelength is equivalent to the energy required to raise the atoms from their lower energy levels to higher energy levels will perform the same function. These appropriate wavelengths are absorbed by the atoms, causing excitation.

If in Fig. 39 a light beam enters from the left of the atomic clouds, the absorption of light can be monitored with a light detector at the other side of the atomic cloud. This procedure is atomic absorption spectroscopy.

The atoms excited by the absorption of light will eventually return to their lower energy levels by emission of radiation. This procedure is atomic fluorescence spectroscopy or atomic resonance spectroscopy.

To utilise atomic absorption spectroscopy, a sample must be converted into an atomic vapour. Each of the constituent elements in the vapour phase will absorb radiation at a limited wave number over a very narrow spectral region.

The number of atoms, Nj, that are excited to any energy state, j, is given by

$$Nj = No(Pj/Po)\ \exp(-Ej/kT)$$

Where No is the number of atoms in the ground state, Pj and Po are the statistical weights of the excited and ground states, and T is the absolute temperature of the vapour. The statistical weight is the probability that a particular transition will occur. Below a temperature of 3000° K only a small fraction of atoms in the atomic vapour are excited, the majority of them are unexcited.

Atoms in the ground state, un-ionized and unexcited are capable of absorbing radiation at the discrete energies(wavelengths) that are proportional to particular excited states. The change in temperatures produce an exponential change in the number of atoms that can emit light, but have not any significant effect on the number of atoms that can absorb light. So the emission methods are very sensitive to changes in temperatures, whereas the absorption methods are relatively insensitive to such changes. This freedom from the effect of changes in the vapour environment is one of the most attractive chacacteristics of atomic absorption.

The theory of atomic absorption has been developed by Wash. The term "resonance line" is usually used for lines at the end in the lowest energy state of the atom. Wash showed that the natural line width for resonance line associated with the probability distribution of each energy level is on the order of 10^{-4}A. Superimposed on this is the effect of Doppler broadening, D, which arises because the atoms will have different components of velocity along the line of observation.

This is given by:

$$D = (1.7\frac{\lambda}{C})(\frac{2RT}{M})^{\frac{1}{2}}$$

where R is the universal gas constant, M is the atomic weight, and T is the absolute temperature.

The resonance lines are affected by various factors. Pressure broadening of the resonance line occurs as a result of the concentration of foreign atoms in the environment of the emitting or absorbing atoms. The magnitude varies with the pressure of the foreign gases and their physical properties.

Resonance broadening is the same type as pressure broadening but results from the interfering effect of the same atoms that absorbing or emitting radiation. At pressure below 0.01 mmHg the effect is negligible.

Line broadening due to self-absorption and self-reversal is very important in connection with the light sources used for atomic absorption. It results from the fact that atoms of the same lines as that emitting radiation will absorb this radiation more strongly at the centre of the line than at the wings. The effect is very serious if the vapour which is absorbing radiation is considerably cooler than that which is emitting radiation. In this case it is possible to selectively remove the width of the line.

The observation of absorption is best done by illuminating the atom vapour with a lamp which emits the spectrum of the metal of interest. With the arrangement of atomic absorption, the only requirement on the monochromator is that the line used be isolated from any other lines in the spectrum of the lamp.

Any element can be determined by atomic absorption spectroscopy if its resonance line is in the portion of the spectrum that the instrument can utilise and if it can be reduced to the atomic state by the sampling technique. Most of the instruments in use operate through the visible and ultraviolet portions of the spectrum down to 1900 Å.

EXPERIMENTAL

1. The Instrument

The Perkin-Elmer Model 303 Atomic Absorption Spectrophotometer was used for the analysis of tellurium in organotellurium compound. This instrument is a double-beam ac system type. To gain an gereral understanding of the instrument system is best shown by the block diagram in Fig.40[75]

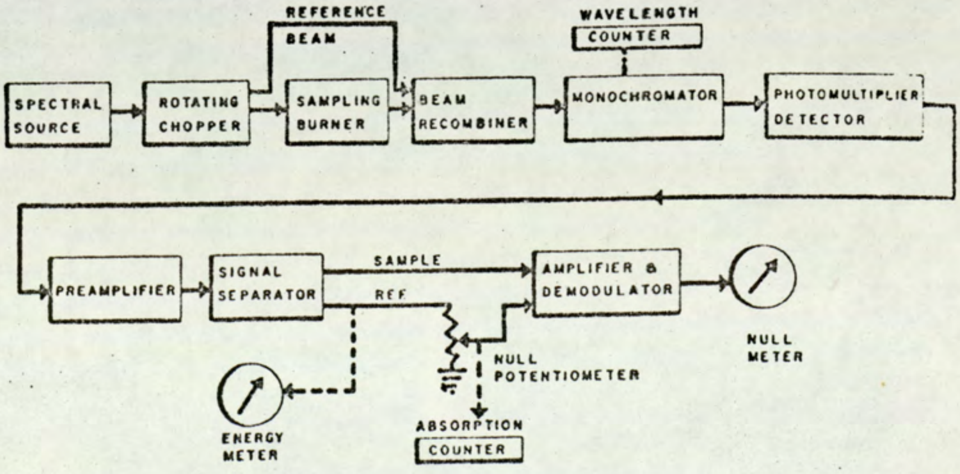


Fig. 40. Block diagram of the instrument

The emission from spectra source (a tellurium hollow-cathode lamp) is split into two beans by a rotating sector mirror. One beam is passed through the sampling flame while the other by-passes it. The two beams are then recombined by the semi-transparent mirror, and then pass through the monochromator to a photomultiplier, after which the signal is separated into sample and reference channels by a vibrating-reed chopper. The reference voltage is then attenuated by a slide-wire and recombined with the sample voltage in such a way that the difference is taken between them. This difference voltage is amplified, rectified and fed to a microammeter. The operator turns the slide-wire until the meter reads a null. A counter geared directly to the slide-wire is made to read out in percentage absorption. Alternately, this nulling process can be done automatically, by the use of a servomotor to drive the slide-wire.

2. The Procedure for the Determination of Absorbance

A full detailed of the operation method and problems encountered arising from the use of the instrument is given in the manual for the instrument. A general procedure used to run the analysed solutions will be described here.

The tellurium hollow-cathode lamp is fitted in its holder. The power is switched on and the SOURCE knob is slowly turned clock wise until the operating current of the lamp is 40 mA. After warming the lamp and the instrument for 30 minutes the wavelength of 214 nM (2143 Å), slit 3, range U.V. and appropriate filter are set according to the manual. The GAIN control is adjusted to bring the needle on the ENERGY meter to the black portion of the scale, and the fine wavelength control is adjusted to maximum defection to the right on the ENERGY meter.

The air compressor is adjusted first and then the acetylene gas; both are at a flow rate of 9 units of the flowmeter. After lighting the flame, distilled water is aspirated and the ZERO control is adjusted to bring the meter to zero deflection at 0.00 absorption reading. A scale of expansion and noise suspression are selected.

The standard and sample solutions of tellurium are run. The absorptions are obtained either from the absorption scale by bringing the needle of the ZERO meter to zero or from the chart paper of the readout unit. Distilled water is run between each sample or standard solution in order to verify base line stability. Each run of solution is 30 seconds.

The standard solutions of four different concentrations in the range of 5-20 ugTe/ml, which is the optimum concentration for tellurium, are run before and after the sample solutions. For every six samples the run of the standards is repeated.

The absorption of samples and standards are converted to absorbance using the following steps:

1. Divide all reading by the scale expansion used to converted to % absorption (%A).

2. Convert all % A obtained to absorbance using the table provided.

3. Analytical Procedure

Samples were weighed by using a "Stanton" balance capable to read to four places of dicimals.

Reagents: Telluric acid(AR), conc. nitric acid (AR,sp.gr. 1.42), conc. perchloric acid (AR, 70-72 %), conc. sulphuric acid (AR) and conc. hydrochloric acid (AR).

Preparation of Stock and Stand Solutions

The stock solution 1000 ugTe/ml was prepared by dissolving telluric acid 1.7951 g in 1 litre of volumetric flask with distilled water and conc. hydrochloric acid (10 ml). The stock solution was stored in a polythene bottle in order to avoid changing of concentration.

The standard solutions of four different concentrations were prepared by diluting the stock solution to 6-20 ugTe/ml range either by an automatic diluter or first diluting to 40 ugTe/ml and then to the range of 6-20 ugTe/ml.

Reagents for the Decomposition of Organotellurium Compounds

The organotellurium compounds were not adequately decomposed by conc. nitric acid, fuming nitric acid or conc. perchloric acid alone. Then the mixtures of acids were used and it was found that the compounds were decomposed completely either by a mixture of conc. nitric and perchloric acids or by mixtures of conc. nitric and sulphuric acids. However sulphuric acid was found to interfere in the subsequent analysis.

3. 1. Routine Procedure

Nitric and perchloric acids have low boiling points they are easily evaporated and do not present any interference. Thus this mixed acid system is suitable for the routine procedure.

A typical example for the determination of tellurium in organotellurium compounds will be described.

Determination of tellurium in p-ethoxyphenyltellurium trichloride

The sample(0.0205 g) was weighed accurately in a beaker(50 ml) and conc. nitric acid(3 ml) and conc. perchloric acid(3 ml) were added. The mixture was carefully heated on a hot plate and the acids were allowed to evaporate slowly to dryness in a very efficient fume-cupboard for 1½ hours. The white residue was dissolved in warm distilled water to which conc. hydrochloric acid (0.5 ml) was added. Then the solution was cooled and made up to an exact volume in a volumetric flask(50 ml).

The approximate tellurium concentration (154 ugTe/ml) was calculated from the assumed molecular formula. Then the calculated amount(4.0 ml) of solution was transfered into a volumetric flask(50 ml) in which the final concentration of the solution was within the optimum range (5-20 ugTe/ml). Four standard solutions (19.93, 14.54, 20.27 and 6.29 ugTe/ml) were prepared by the automatic dilutor.

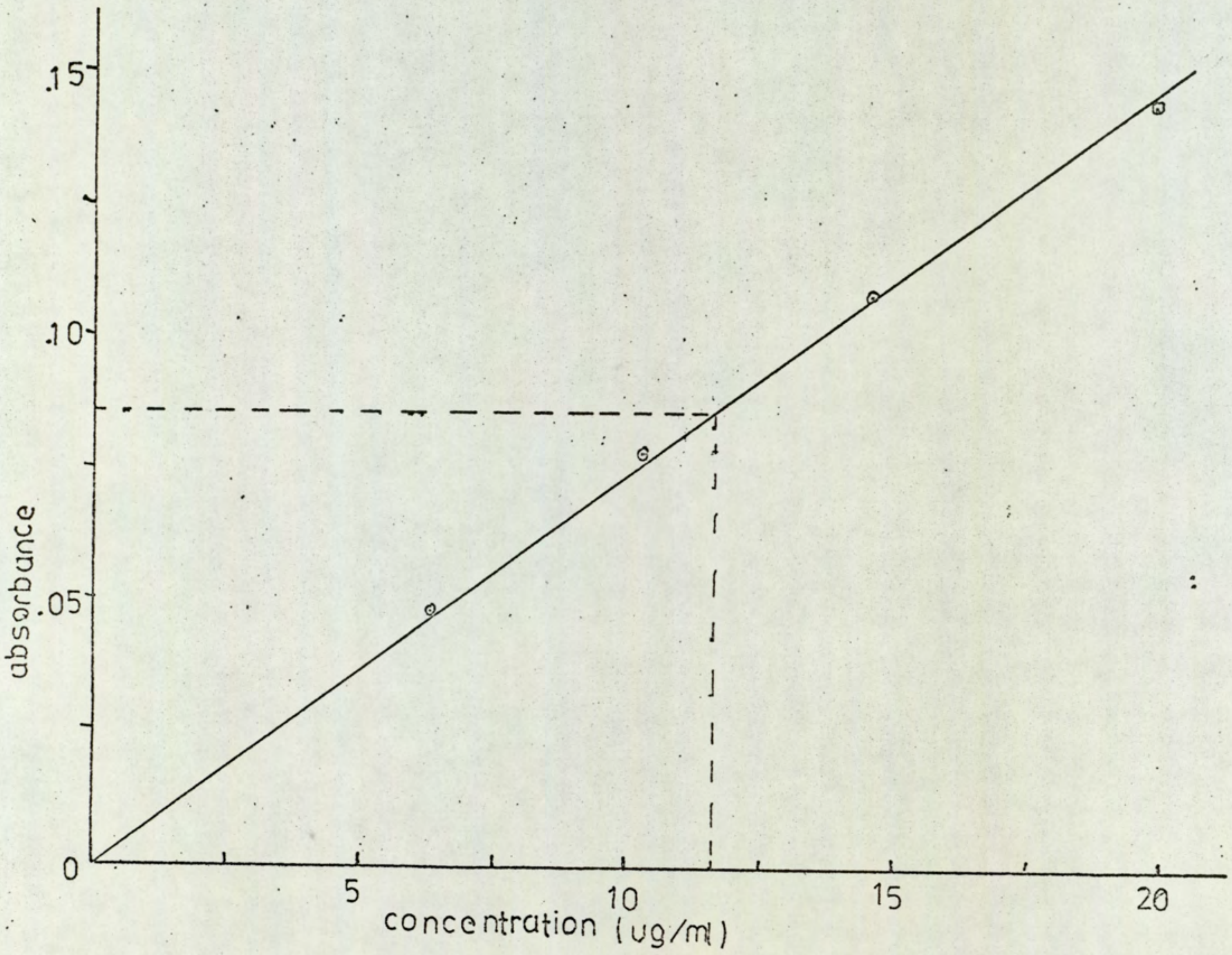


Fig. 41.

The solutions of standard and unknown were run to determine the absorption and the results were shown as following:

Solutions	% (A) S.F.x1			absorbance
	1st Reading	2nd Reading	Average	
St.19.93 ug/ml	28	28	28	0.1427
St.14.54 "	22	22	22	0.1079
St.10.27 "	17	16	16.5	0.0783
St. 6.29 "	11	10.5	10.8	0.0494
unknown			18	0.0862

A calibration graph was obtained by plotting standard concentrations versus their absorbance as shown in Fig. 41. The unknown concentration read off the graph (11.7 ug/ml).

$$\text{The Te percentage} = \frac{11.7\ \text{ug/ml} \times 50\text{ml} \times 50\text{ml} \times 100}{4\text{ml} \times 0.0205 \times 10^{6}\ \text{ug}}$$

$$= 35.67\ \%$$

The other samples were analysed by the same procedure.

3. 2. Method of Additions

Sulphuric acid is a high boiling point acid it is very difficult to evaporate all the acid from the sample so there will always some acid left. Since the salts of sulphuric acid do not dissociate readily at the temperature of the flame, errors can occur if the above routine procedure of analysis is used. The method of additions was employed to avoid such interference. A typical example of this procedure will be described.

Determination of tellurium in p-ethoxyphenyltellurium trichloride

p-Ethoxyphenyltellurium trichloride(0.0715 g) was weighed accurately in a beaker(50 ml) and conc. nitric acid (4 ml) and conc. sulphuric acid(3 ml) were added. The mixture was then carefully heated on a hot plate and the acids were allowed to evaporate slowly to dryness in an very efficient fume-cupboard. This heating and evaporation process took about 2½ hours. The white residue dissolved in warm distilled water to which conc. hydrochloric acid (0.5 ml) was added. The solution was cooled and made up to exact volume in a volumetric flask(100 ml).

The approximate tellurium content (255 ug/ml) was calculated from the assumed molecular formula. Four aliquots were transferred into four flasks(50 ml) labelled 1 to 4. The volume in the first flask was 2.0 ml and in the other three flasks was 1.5 ml. These quantities were calculated so that the final solutions contain unknown tellurium concentration in the range between 5-9 ugTe/ml except for the first flask which the concentration might be in the range between 5-20 ugTe/ml. To flasks number 3 and 4 the standard solution of 40 ugTe/ml was added with 5 and 10 ml respectively so that the final solutions contain different additions (4 and 8 ug/ml) of the tellurium. All the four flasks were made up to 50 ml with distilled water.

The first flask was for the routine procedure as a double check of the results. So this dilute solution was run after four standard solutions. Then the other three flasks were run to determine the absorption.

The results of this experiment were as following:

Solutions	Absorption(S.F.x5)		Average Absorption/5	absorbance
	1st Reading	2nd Reading		
St. 20 ug/ml	71.5	70.1	14.1	0.0662
St. 16 "	57.8	55.1	11.2	0.0518
St. 12 "	41.8	43.8	8.5	0.0385
St. 8 "	26.9	27.4	5.2	0.0234
No 1	31.3		6.2	0.0278
No 2	28.6		5.7	0.0255
No 3+4 ugTe/ml	42.3		8.5	0.0385
No 4+8 "	55.8		11.2	0.0516

The absorbance obtained was plotted versus the added concentration as in Fig. 42. The straight line was extrapolated through zero absorbance. The intercept on the concentration axis gave the concentration (7.8 ug/ml) of tellurium in the dilute solution.

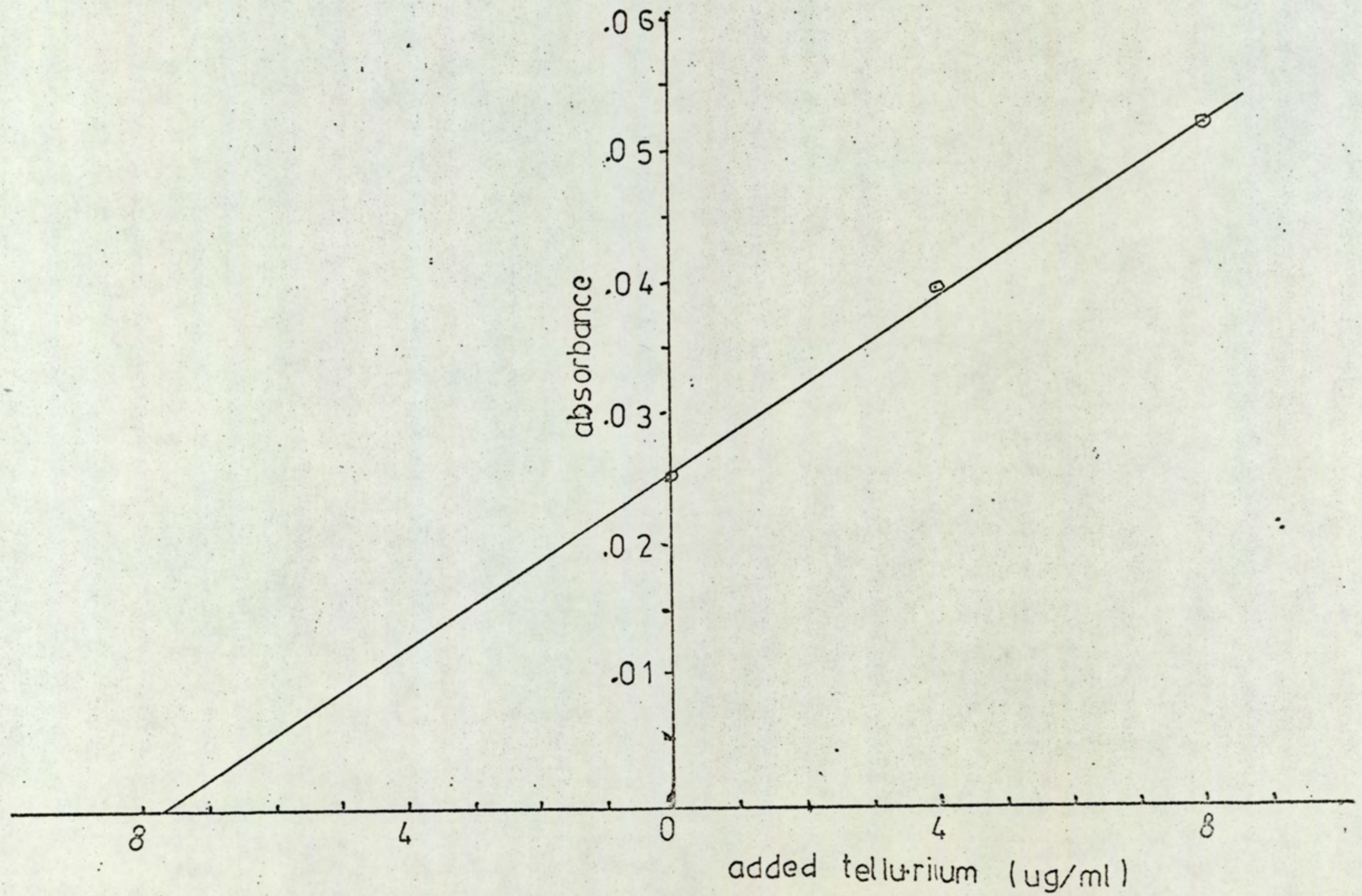


Fig. 42.

$$\text{The tellurium percentage is} = \frac{7.8 \text{ ug/ml} \times 50\text{ml} \times 100\text{ml} \times 100}{1.5 \text{ ml} \times 0.0715 \times 10^{6} \text{ ug}}$$

$$= 36.46\ \%$$

This 36.46 % could be compared to 36.60 % from the previous routine procedure, and the result was satisfactory when comparing with 36.90 % the expected percentage.

For the first flask the concentration of the dilute solution (8.6 ug/ml) read off from the calibration graph as previously described in the routine procedure.

$$\text{The tellurium percentage is} = \frac{8.6 \text{ ug/ml} \times 50\text{ml} \times 100\text{ml} \times 100}{2.0 \text{ ml} \times 0.0715 \times 10^{6} \text{ ug}}$$

$$= 31.40\ \%$$

It was clearly indicated that the percentage of 31.40 for tellurium from a routine procedure using nitric and sulphuric acids is incorrect, hence solutions of organotellurium compounds obtained by decomposition with these acids are unsuitable for the routine procedure. The above results demonstrate that the routine procedure is valid only if nitric and perchloric acids are used to prepare the sample. If sulphuric and nitric acid is used it is necessary to use the method of additions, but it is advisable to also use the routine procedure as a check on the accuracy of the addition method.

RESULTS

The results of the determination of tellurium in various aryltellurium compounds by the routine procedure are given in Table 22.

For the results of analysis of tellurium in various aryltellurium trihalides by the method of additions are given in Table 23.

TABLE 22

Determination of Tellurium in Aryltellurium compounds*

compounds	Te % obtained	Te % calculated
$(p\text{-MeC}_6H_4)TeCl_3$	39.16	39.25
$(p\text{-MeC}_6H_4)TeBr_3$	27.52	27.83
$(p\text{-MeC}_6H_4)TeI_3$	20.96	21.28
$(p\text{-EtO.C}_6H_4)TeCl$	35.60	35.90
$(p\text{-EtO.C}_6H_4)TeBr_3$	26.47	26.12
$(p\text{-EtO.C}_6H_4)TeI_3$	20.73	20.23
$PhTeBr_3$	28.30	28.70
$PhTeI_3$	21.58	21.80
$(p\text{-MeO.C}_6H_4)TeCl_3$	37.40	37.40
$(p\text{-MeO.C}_6H_4)TeBr_3$	27.37	26.89
$(p\text{-MeO.C}_6H_4)TeI_3$	20.27	20.27
$(p\text{-PhO.C}_6H_4)TeCl_3$	31.51	31.64
$(p\text{-EtO.C}_6H_4)Te(O)Cl$	42.85	42.53
$(p\text{-EtO.C}_6H_4)TeCl_4^-C_5H_6N^+$	26.73	27.20

* All the compounds gave satisfactory C and H analysis as shown in chapter IV and V.

TABLE 23

Determination of Tellurium in Aryltellurium Trihalides*

compounds	Te % obtained	Te % calculated
$(p\text{-EtO.C}_6\text{H}_4)\text{TeCl}_3$	36.11	35.90
$(p\text{-EtO.C}_6\text{H}_4)\text{TeBr}_3$	25.69	26.12
$(p\text{-EtO.C}_6\text{H}_4)\text{TeI}_3$	20.22	20.23
$(p\text{-MeO.C}_6\text{H}_4)\text{TeCl}_3$	37.84	37.40
$(p\text{-MeO.C}_6\text{H}_4)\text{TeBr}_3$	27.35	26.89

* All the compounds gave satisfactory C and H analysis as shown in chapter IV.

DISCUSSION

1. Method of Additions

The decomposition of aryltellurium compounds by a mixture of concentrated nitric and sulphuric acids was a time consuming process which usually was 2 to 3 hours. The reason that it was difficult to evaporate is that sulphuric acid has a high boiling point 338° C. If the mixture is evaporated at high temperature to increase the rate of evaporation it will cause the loss of sample. Thus it is not certain that all the sulphuric acid will be evaporated by the procedure. Since the salts of sulphuric acid are not dissociated readily at the temperature of the flame the presence of it will interfere with the absorption of the sample.

So the method of additions for analysis of tellurium was employed. This technique is suitable when it is difficult to prepare samples sufficiently similar to standards. The results of this method are shown in Table 23 which are very satisfactory, and the results of ± 0.5% error were obtained. Though it is less tedious than the previously reported methods,[42,43] and less amount of sample is required. There are two main disadvantages. The first disadvantage is that it involves many steps of transfering the solution which are subjected to error by various factors. The second is that longer time is required for the evaporation as already mentioned.

2. Routine Procedure

A more simple and general method for the routine procedure is needed. This was obtained when the organotellurium compounds were found to decompose to a water-soluble product by the action of the mixture of conc. nitric and perchloric acids. The two acids do not present any interference hence they are suitable for the routine procedure.

The sucessful application of atomic absorption spectroscopy for the determination of tellurium in organotellurium compounds is clearly indicated by the results as shown in Table 22. The modified procedure from the given procedure has been found suitable for a wide variety of compounds. This method has been found to be very reliable and less time consuming than those previously reported. It also has the great advantage as several determinations can be carried out at the same time. The further advantage of this method is that the amount of sample required is only 25-50 mg and this could be reduced further to 15 mg for compounds containing a higher percentage of tellurium. The size of the sample can be further reduced if a more sensitive balance is available, since the instrument is very sensitive.

Kruse et al[43] claimed in their method of decomposition that if the acids were allowed to evaporated to dryness it would give a lower percentage of tellurium. But according to the present method the acids were evaporated to dryness and the results were reproducible.

The preparation of the stock solution using AR telluric acid (H_6TeO_6)[76] was more convenient than the recommended method using tellurium metal.[77] As the recommended method involves the dissolving of the metal with conc. nitric acid and then expeling all nitric acid in the presence of hydrochloric acid which can easily introduce errors during the process of preparation.

The only disadvantage of the routine procedure for the analysis of tellurium is that the decomposition of compounds by a mixture of conc. nitric and perchloric acids has a danger potential due to the explosive ability of perchloric acid. But for all of the organotellurium compounds studied there has been no indication of any danger.

In general the ease of the decomposition of aryltellurium tricalides is in an order of $RTeI_3 > RTeBr_3 > RTeCl_3$ by both mixtures of acids which behave as an oxidizing agent. The fact that aryltellurium trihalides behave purely as inorganic halides with respect to the ease of oxidation ($I^- > Br^- > Cl^-$) can be explained in terms of oxidation potentials. The chloride has a higher oxidation potential than the bromide and in turn the iodide, in other word the iodide is a better reducing agent than the bromide and in turn the chloride.

3. Further suggestion for the development

The application of atomic absorption spectroscopy for the determination of tellurium by the routine procedure will be firmly established if the method of the decomposition of organotellurium compounds by Kruse et al[43] is used and studied to evaluate the procedure of analysis of tellurium compared with the developed method. Kruse and coworkers have used 70% nitric acid followed by a mixture of 30% nitric acid and 70% perchloric acid to decompose the organotellurium compounds. This method of the decomposition the acid are not allowed to evaporate to dryness which reduce the possibility of the loss of sample. But the unknown factor is how much effect will the presence of nitric acid and perchloric acid in the solutions have?

CONCLUSIONS

The assignments for diphenyl ditelluride and the identification of the tellurium-tellurium stretching modes of the vibrational spectroscopic data of some diaryl ditellurides have been made. The molecules of all ditellurides have C_2 skeletal symmetry. The tellurium-halogen vibrational modes have been assigned for five classes of aryltellurium trihalides, and the associated molecules have at least a dimeric structure with five co-ordinate tellurium atoms.

The most probable mechanisms of the hydrolysis of aryltellurium trihalides in both neutral and alkaline equeous media have been proposed, and the assignments of the tellurium-oxygen vibrational modes have been offered for the hydrolysis products. A ring structure with four co-ordinate tellurium atoms has been suggested for aryltellurium oxyhalides. For the anions of $(RTeCl_4^-)(PyH^+)$ and $(RTeCl_4^-)(Ph_4As^+)$ a configuration of C_{4v} symmetry has been suggested.

Finally, an application of atomic absorption spectroscopy for the determination of tellurium in organotellurium compounds has been developed.

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