TO MY PARENTS

FOR THEIR WARMEST AND KINDEST

ENCOURAGEMENT THROUGHOUT ALL MY STUDIES

...

"STUDIES IN TELLURIUM CHEMISTRY"

BY

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A thesis submitted for the Degree of

Doctor of Philosophy

of the

University of Aston in Birmingham

July 1980

SUMMARY

A range of hexahalotellurate (IV) salts with the formula TeX_6^{2-} where X = Cl, Br, I were prepared, with cations of different size, e.g. NH_4^+, Et_4N^+, Ph_4As^+. Thermogravimetric analysis of these salts was carried out and products identified. ^{125}Te Mössbauer data and Raman spectra were obtained and interpreted in terms of a distorted $TeCl_6^{2-}$ anion (C_{3V}) in the salt $(Ph_4As)_2(TeCl_6)$, prepared from H_2TeCl_6 and $(Ph_4As)Cl$.

The synthesis of a new class of organotelluronium carboxylates, $Ph_2MeTeOOCR$, where R = C_6H_5, $C_6H_4OCH_3$ and $C_6H_4NO_2$ is reported. These compounds decompose in solution to telluride and MeOOCR. The behaviour of these salts in solvents with different polarity was studied and it is argued that the compounds are covalent and possibly dimeric in chloroform solution, whereas in DMSO, they exist as ionic species. Physical data, including infra-red, ^1H n.mr. ^{125}Te n.m.r. spectra and vapour pressure osmometry are presented and the nature of the interaction of the Te atom with the carboxylate group is discussed.

A new class of cyclic telluronium salts $C_6H_4(CH_2)_2MeTeX$, where X = PhCOO and Cl, was synthesised. The compounds were proved to be stable (with respect to reductive elimination of MeX) in solutions such as $CHCl_3$ and DMSO. ^{125}Te n.m.r., ^1H n.m.r. and infra-red spectroscopy of these compounds in $CHCl_3$ solution indicate that they exist as dimers.

The synthesis of a new class of organotellurium (IV) species, $PhMeTeX_2$, where X = Cl, Br, and Phthalate was achieved, and their behaviour in solvents with different polarity reported. Compounds of the type PhMeTeXY where X = Cl, Y = Br and X = Cl, Y = I were also synthesised and their infra-red spectra compared with i.r. data for $PhMeTeX_2$.

KEYWORDS Tellurium Telluronium salt

Carboxylate Hexahalotellurate

ACKNOWLEDGEMENTS

The Author wishes to acknowledge with much gratitude and appreciation Professor W. R. McWhinnie, for the invaluable guidance, helpful suggestions, encouragement and support throughout the duration of the research work presented in this thesis.

Special thanks are due to Dr. E. R. Clark for his useful discussions and constant encouragement.

A debt of gratitude is owed to Dr. N. S. Dance, Department of Chemistry; Simon Fraser, University of Burnaby; B. C. Canada for his co-operation and for providing the Mössbauer data.

Thanks are also offered to the Technical Staff of the Chemistry Department, for obtaining Physical Measurements.

The work described in this thesis was carried out between 1977 and 1980 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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CHAPTER I

INTRODUCTION :

The element tellurium is found in group VIB, the oxygen group, with an electronic configuration approaching the structure of the xenon; $[Kr]\ 4d^{10},\ 5s^{2},\ 5p^{4}$, and has an electronegativity of 2.01 (Pauling Scale). It was recognised as an element in 1782 by F. J. Muller Von Reichenstein, an Austrian chemist who separated it from a mineral known as white- or gray-gold ore, which had previously been believed to be some sort of alloy of antimony and bismuth, although neither of these were in reality constituents of the mineral. The element was given its present name by M. H. Klaproth in 1798, from the Latin tellus, meaning earth.

The unusual atomic weight of tellurium which is higher than that of iodine, although it appears before, in the Periodic Table is due to the preponderace of stable heavy isotopes of tellurium. Twenty-one isotopes of tellurium have been recorded, with mass numbers between 114 and 134, eight are stable (^{120}Te, ^{122}Te, ^{123}Te, ^{125}Te, ^{126}Te, ^{128}Te and ^{130}Te).

Tellurium is located between selenium and polonium with a number of similarities to sulfur and selenium in many of its properties. Within this group the metallic nature increases as the atomic weight increases. This could be observed by looking at the insulator property of the oxygen and sulfur, semiconductivity of selenium and

tellurium and the more positively metallic nature of polonium.

Since its discovery, tellurium and its derivatives have found applications in industry: e.g.

A. In rubber technology, tellurium is employed as the element or as tellurium diethyl dithiocarbamate. Tellurium rubber is noted for its resistance to heat and abrasion. In many instances, the addition of tellurium increases the rate of vulcanisation and improves the aging and mechanical properties of the low-sulfur and sulphurless stock {1}.

B. Dialkyl tellurides are effective as oxidation inhibitors in lubricating oils {2}.

C. In metallurgy, it could be added to copper and steel for improving machinability and in glass and ceramics it can be used for colouring.

D. Alone, or in combination with other substances, tellurium, tellurium dioxide, tellurium tetrachloride, telluric acid and other compounds are very good and selective catalysts in oxidation, hydrogenation and dehydrogenation, halogenation and dehalogenation and other reactions.

1. (1). ORGANOTELLURIUM COMPOUNDS :

The synthesis of organotellurium compounds was started by Wöhler in 1840, who was successful in preparing diethyl telluride, the first organic compound of tellurium. Since 1840, several hundreds of papers have been published dealing with organic tellurium compounds however, compared to organic selenium chemistry, organic tellurium chemistry still lies in less favour. Morgan, Drew and co-workers beginning in 1920 {3} explored the chemistry of five- and six membered ring systems, concentrating on 1-tellura-3,5-cyclohexanedione and its derivatives of which some structures have recently been published {4}.

Organic tellurium compounds, and anionic species of tellurium have been investigated by Petragnani, de Moura Campos and co-workers. McWhinnie has recently studies the chemistry of diaryldditellurides and related compounds containing tellurium metal bonds (tin and copper in particular), and used ^{125}Te Mössbauer spectroscopy for characterisatation of the compounds.

Tellurium exhibits oxidation states of -II, II, IV and VI, of these IV is the most stable and co-ordination number 6 is common.

1. (i) a. Te^{-II} :

This is an example of the more non-metallic properties of this element. By accepting one pair of electrons tellurium can produce Te^{-II} to complete the inert gas configuration.

1. (i) b. Te^{II} :

In this category tellurium may show co-ordination number 2 or 4. $TeBr_2$ and cis - $Te(tu)_2Cl_2$, are examples. Electron diffraction has shown the stereochemistry of tellurium dibromide to be angular {5}.

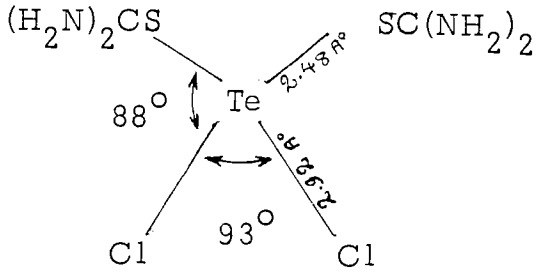


Fig. (1): The Structure of Cis-$Te(tu)_2Cl_2$ {6}

The chemistry of diorganyl tellurides has a long history back to 1840. The first organotellurium compound was diethyl telluride which was prepared by the reaction of potassium telluride with ethyl sulphate {5}. Krafft, was the first one in 1894, who prepared diphenyl telluride by the reaction of diphenyl mercury and elemental tellurium {7}.

Diorganotelluride derivatives could be either symmetrical (R_2Te) or unsymmetrical (RR'Te). Aromatic tellurides have been considered in the literature more extensively than aliphatic ones. There are several preparative methods for either symmetrical or unsymmetrical tellurides, of which a few are described below :

1. (i) b. I. SYMMETRICAL DIORGANOTELLURIDES :

Bergman {8} has reported the reduction of tetravalent diorganotellurium dihalides.

$$2\,R_2Te^{IV}X_2 \xrightarrow[MeOH]{N_2H_4} 2\,R_2Te^{II} + N_2 + 4HX$$

McWhinnie {9} synthesised diphenyl, dibenzyl and bis(pentafluorophenyl) telluride, by reacting tellurium tetrachloride with an appropriate Grignard reagent. No free elemental tellurium was observed with this modified procedure (it was reported to be a side-product by Rheinboldt) {10}.

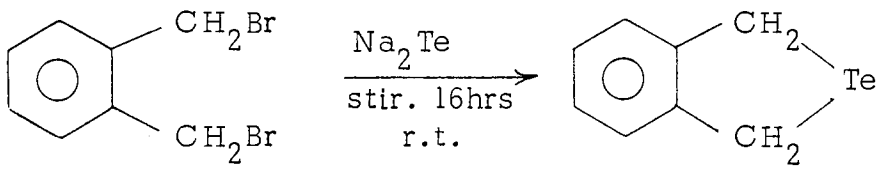
$$TeCl_4 + 4RMgX \longrightarrow R_2Te + R_2 + 4\,MgXCl$$

Diarylmercury compounds transfer the organic groups into tellurium upon heating the reactants under an inert atmosphere in a sealed tube to 230°C for several hours {11, 12, 7}.

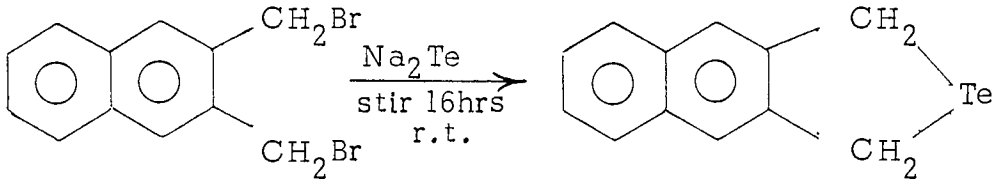
$$R_2Hg + Te \xrightarrow{\triangle} R_2Te + HgTe$$

Cuthbertson {13} has recently reported the synthesis of 1,3-dihydrobenzotellurophene (eqn. A) and 1,3-dihydronaphtho- [2,3-C] tellurophene (eqn. B) by the treatment of α,α' -dibromo-o-xylene and 2,3-bis-(bromomethyl)-naphthalene with dry sodium telluride in dry nitrogen for 16 hrs, at room temperature.

eqn. A.



eqn. B.



1. (i) b. II UNSYMMETRICAL TELLURIDES :

The chemistry of unsymmetrical tellurides has not been studied as much as that of symmetrical tellurides. Alkylaryltellurides seem to be photochemically less stable than diaryltellurides {14}. Phenyl-alkyl tellurides, C_6H_5-Te-C_nH_{2n+1}, are yellowish oils, which are

stable when stored in the dark, but decompose in light, probably to ditelluride {14}.

Irgolic has reported the synthesis of a series of alkyl aryl-tellurides, by the reaction of diaryldditelluride and lithium with appropriate alkyl halide.

$$Ar_2Te_2 + Li \xrightarrow[\text{stir}]{THF} ArTeLi$$

$$ArTeLi + RX \xrightarrow{\text{reflux}} ArRTe + LiX$$

Ar=Ph and R = CH_3, C_2H_5, C_3H_7, i-C_3H_7, C_4H_9 and $C_{14}H_{29}$

A large number of unsymmetrical diorganyl tellurides were prepared by Petragnani {15} who reacted aryltellurium bromides generated in tetrahydrofuran solution from ditellurides and bromine with Grignard reagents :

$$RTeBr + R'MgX \longrightarrow R\text{-}Te\text{-}R' + MgBrX$$

A more convenient route for the preparation of unsymmetrical di-

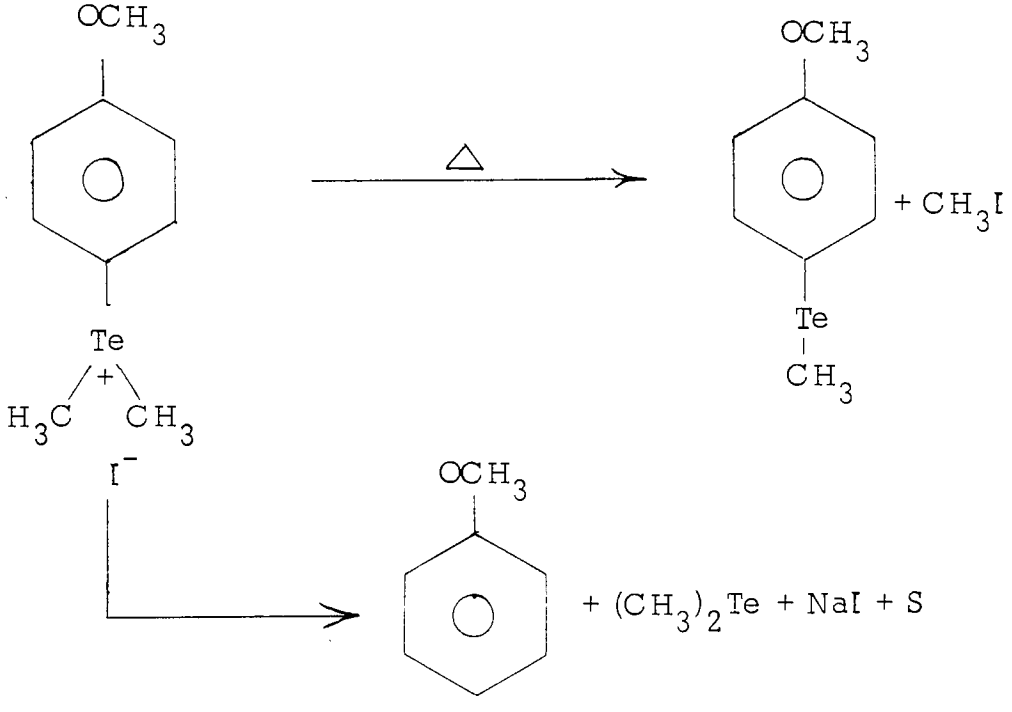
organotelluride compounds involves arytellurium trihalides {16,17} .

$$ArTeX_3 + RHgX \xrightarrow{\text{Dioxane}} \text{Dioxane } HgX_2 + ArRTeX_2$$

$$ArRTeX_2 \xrightarrow{Na_2S} ArRTe$$

R = aryl or alkyl

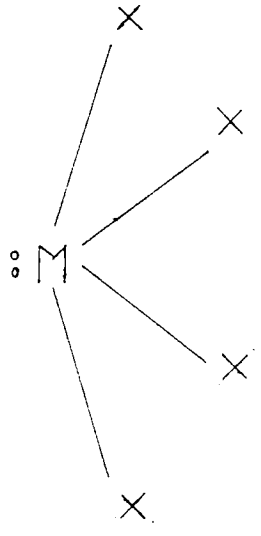
Reichel and Kirschbaum {18} found that the thermal decomposition of p-methoxy phenyl dimethyl telluronium iodide in molten Na_2S, $9H_2O$ gave rise to dimethyl telluride, the unsymmetrical telluride and p-methoxy benzene.



No explanation is given for the formation of the mixed telluride, and the formation of MeoPh by gaining a H atom from the solvent and cleavage of Te-aryl group is of considerable importance, since it is the Te-alkyl rupture in decomposition of organotelluronium salts which has so far been reported.

1. (i) c TELLURIUM IV

As was mentioned previously, this is one of the most stable oxidation states of tellurium with respect to hydrolysis and oxidation. In this state the electronic configuration becomes $[Kr]\ 4d^{10},\ 5s^{2}$, and the presence of this lone pair of electrons distorts the tetrahedral structure and generally, the structure of this type of organotellurium compound is considered to be Ψ -trigonal bipyramidal with one equatorial position occupied by an unshared pair of electrons. However, as more crystal structures become available, it is recognised that this generalisation is of increasingly limited value.



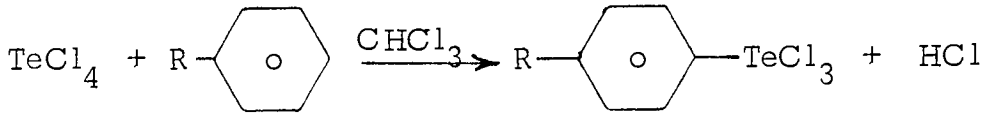
One of the basic starting materials, for the synthesis of organotellurium compounds is tellurium tetrachloride which exists as a white to yellowish solid with melting point 224°C. Greenwood {19} has studied the far-infrared and Raman spectra of tellurium tetrachloride tetrabromide and tetraiodide and interpreted the result on the basis of an ionic structure, that is $TeX_3^+ X^-$ in agreement with the literature {20, 21}, and recently Buss and Krebbs have shown that $TeCl_4$ consists of Te_4Cl_{16} units within the crystal lattice and that it could be regarded as an aggregate of 4 $TeCl_3^+$ with 4 Cl^- {22}.

Organotellurium (IV) compounds can be classified into four categories : $RTeX_3$, R_2TeX_2, R_3TeX and R_4Te.

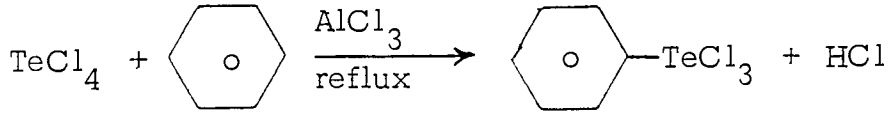
1. (i) c. I ORGANOTELLURIUM TRIHALIDES :

Organotellurium compounds of the type $RTeX_3$, where X = F, Cl, Br and I have been prepared. The aromatic derivatives possess a greater stability than the aliphatic ones.

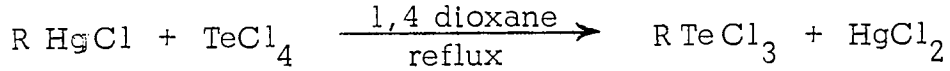
Benzene derivatives containing a ring-position activated by an alkoxy, phenoxy, hydroxy,..... condense with tellurium tetrachloride in refluxing chloroform or carbon tetrachloride, or upon heating with solvent on a water-bath, to yield organotellurium trichlorides {23}



Günther {24} has reported the synthesis of phenyl tellurium trichloride by reaction of tellurium tetrachloride with aluminium chloride in benzene.



Tellurium tetrachloride can react with aryl mercury chlorides to give the aryl tellurium trichloride {25}.

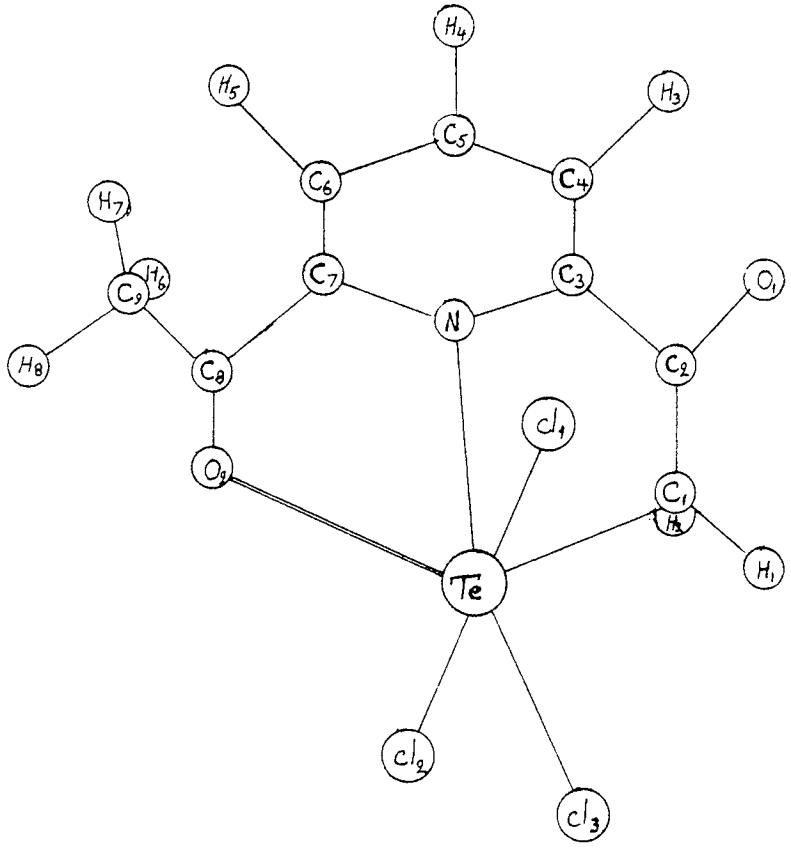


Thavornyutikarn {26} has studied the structure of phenyl tellurium trichloride by i.r. and Raman spectroscopy and has made some assignments which support the theory of Wynne and Pearson {27}. These authors postulated that for organotellurium (IV) compounds deviation from the 6-coordinate arrangement may result from replacing halogen atoms by organic groups. This produces a <u>trans</u>- effect which elongates a Te-X bond <u>trans</u> to the organic group. Thus it is expected that the tellurium atom in organotellurium trihalides will be essentially five-coordinate.

Synthesis and molecular structure of a new type of organotellurium (IV) trichloride complex has recently been reported {28}. The reaction of tellurium tetrachloride with 2,6-diacetyl pyridine in methylene chloride or tetrhydrofuran gives

$$TeCl_3(-2\text{-}CH_2Co(6\text{-}CH_3Co\text{-}C_5H_3N)$$

in which the single crystal X-ray diffraction studies indicates the organic radical bonds to the tellurium as a tridentate ligand, via a methylene carbon of one of the acetyl groups, the pyridine nitrogen, and the carbonyl oxygen of the second acetyl group.



* Stereographic View of $TeCl_3$ $(C_9H_8NO_2)$.

Thus it is certainly not true that the tellurium atom in compounds of the type "$R\,TeX_3$" need be invariably five co-ordinate.

1. (i).c.II. DIORGANOTELLURIUM DIHALIDES :

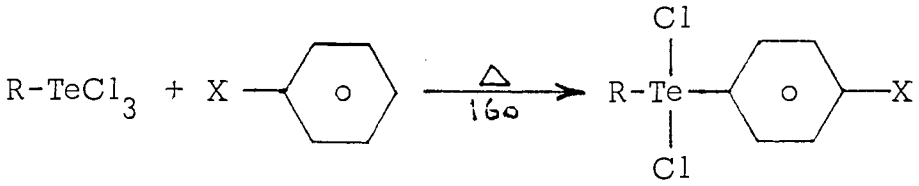
Diorganyltellurium dihalides, R_2TeX_2 (X= F, Cl, Br, I) which R_2 can be dialkyl, alkyl aryl, or diaryl, are crystalline solids, which can be easily purified by recrystallisation.

A large number of chlorides, bromides and iodides have been prepared. The reaction of diorganyl tellurides with halogens has widely been used as the synthesis of diorgano tellurium dihalides.

$$R_2Te^{II} + X_2 \underset{\text{reduction}}{\rightleftharpoons} R_2Te^{IV}X_2$$

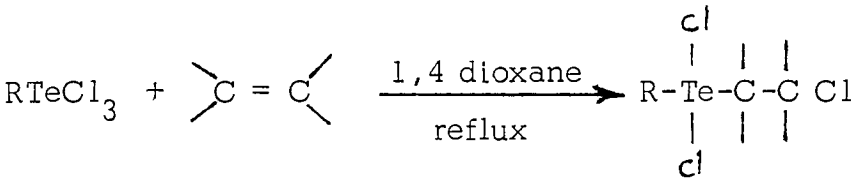
Condensation of organyl tellurium trichlorides with organic compounds.

Organyl tellurium trichlorides are intermediates in the condensations of tellurium with organic compounds, which lead to diorganyl tellurium dichloride. Drew and Morgan {23} have shown, that 4-ethoxy phenyl and 4-phenoxy phenyl tellurium trichloride when heated with the respective benzene derivative in the absence of a solvent to 160-180°C gave the dichlorides.

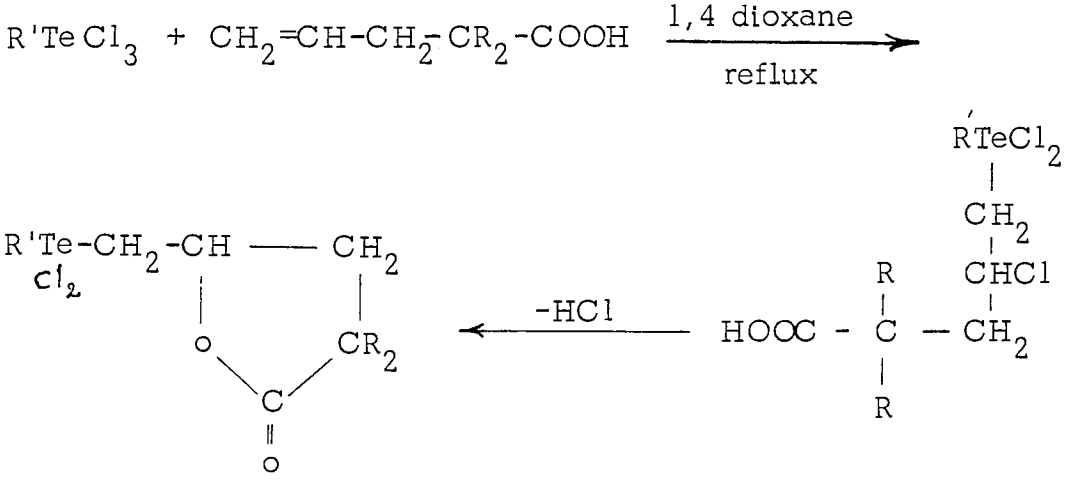


This method has an important application for the synthesis of unsymmetrical compounds.

The addition of organyltellurium trichlorides to carbon - carbon double bonds can produce unsymmetrical diorganyl tellurium dihalides, such as the addition of phenyl, 4-methoxy, 4-ethoxy and 4-phenoxy phenyl tellurium trichloride to 2,2-diphenyl-4-pentenoic acid to afford unsymmetric diorganyl tellurium dichlorides {29, 30}.



The pentenoic acids formed γ-lactones after the tellurium - carbon bond had been formed {30}.



Diorganotellurium dicarboxylates have recently been synthesised by Petragnani {31}. This method was reached by avoiding the preparation of the separate silver carboxylates. The direct treatment of the dichloride with the carboxylic acid in boiling benzene was carried out in the presence of silver oxide.

$$Ar_2TeCl_2 + 2RCO_2H \xrightarrow[\text{Benzene}]{Ag_2O} Ar_2Te\ (OOCR)_2$$

Quite recently the synthesis of compounds of the type R_2Te^{IV} (chelate), where R is an aryl group and chelate represents a di-negative anionic group which could be a dicarboxylate group became of interest {32}.

The freshly prepared sodium salts of orthophthalic acid and tetrabromo orthophthalic acid react with diaryl tellurium dichlorides in chloroform to afford new dimeric organotellurium carboxylates, R_2Te-$(C_8X_4O_4)_2$: X = H, Br [32].

Musa {33} was recently successful in synthesising diorganotellurium diisothiocyanate, and proved that the tellurium interacts more strongly with the nitrogen than with the sulfur atom of the NCS group.

$$R_2Te + (NCS)_2 \xrightarrow[0^{\circ}C]{CCl_4} R_2Te\ (NCS)_2$$

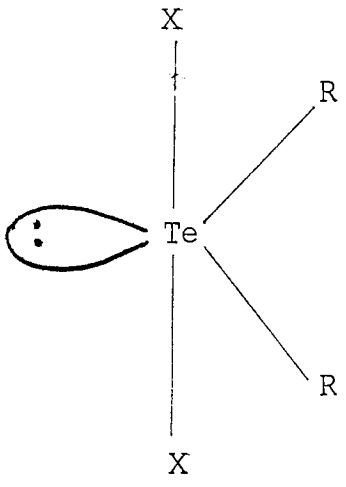
R = Ph, P-$CH_3OC_6H_4$ and P-$C_2H_5OC_6H_4$

In the light of solution studies he postulated the following equilibria :

$$R_2Te(NCS)_2 \xrightleftharpoons{CH_3NO_2} R_2Te(NCS)^+ + NCS^-$$

$$R_2Te(NCS)^- \rightleftharpoons R_2Te^{2+} + NCS^-$$

X-ray crystallography {34, 35} has determined the structure of these diorganotellurium dihalides. The groups bonded to the tellurium atom expand its electronic shell to ten electrons. With four bonding electron pair and one stereochemically active lone electron pair, these molecules possess a Ψ -trigonal bipyramidal shape with the lone pair and two organic groups occupying the equatorial position with the halogen atoms in axial positions {36}.



but inter molecular interaction may be present :

$$I \gg Br > Cl > F$$

1. (i) c. III TRIORGANOTELLURONIUM HALIDES :

A large variety of triorganotelluronium salts $\left[R_3Te\right]^+X^-$ have been synthesised. Anion X can be any sort of anionic species and R_3 may vary through trialkyl, dialkylaryl, alkyldiaryl to triaryl.

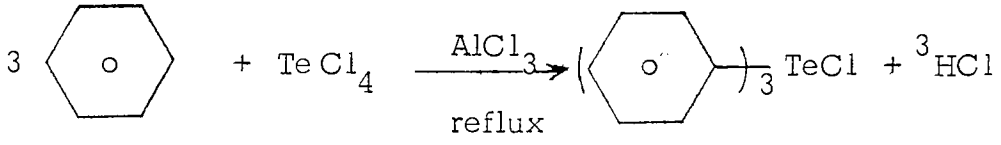
Several methods have been employed for preparation of these telluronium compounds, e.g :

Reaction of organic compounds of magnesium, lithium or zinc with tellurium tetrachloride {37, 38}.

$$TeCl_4 + 3RMgX \xrightarrow{\text{ether}} R_3TeCl + 3MgXCl$$

The above reaction has to be immediately hydrolized at 0^oC to prevent the formation of dialkyl tellurides.

Günther {24} found that the chlorotelluro group can be introduced into benzene by refluxing it with an appropriate molar mixture of tellurium tetrachloride and aluminium chloride until an amount of hydrogen chloride equivalent to the chlorine in $TeCl_4$ had been generated.



The most convenient way for synthesising the telluronium salt is the combination of diorganyl tellurides with organic halides {39} this works well for the more reactive halides.

$$Ar_2Te + RX \longrightarrow Ar_2RTeX$$

Excess of organic halide can be used as solvent. Aliphatic tellurides are more reactive than aromatic compounds. Methyl iodide, ethyl iodide, benzyl chloride and bromide and phenacyl bromide have been used as organic halides.

An ion exchange in telluronium salts.

Once a telluronium salt has been formed the anion can be exchanged easily { 39 } .

$$R_3TeI + AgX \longrightarrow R_3TeX + AgI$$

$X = Cl, Br$

The differing solubilities of the silver halides make it possible to prepare telluronium bromides from iodides and chlorides from bromides and iodides employing silver bromide and chloride respectively. The solubility of the telluronium halides in various solvents, decreases in the order of chloride $\rangle$ bromide $\rangle$ iodide. The chlorides can be converted into the bromides and iodides and the bromides into the iodides on treat-

ment of the aqueous solution of the telluronium halides with appropriate potassium halide.

Ziolo and Pritchett {40} have recently reported the synthesis of a series of triphenyl telluronium pseudohalides, Ph_3TeX, where X = CN, N_3, NCO and NCSe by the reaction of triphenyl telluronium chloride and excess amount of alkali pseudohalides. Although, there are no reported systematic investigations of the thermal decomposition of telluronium salts, it is known that triorgano telluronium halides are thermally cleaved to the organo- halides and diorganotelluride. Triorganoselenium salts also thermally decompose to form selenides {41}. The triphenyl telluronium pseudohalides decompose, in a similar manner to form diphenyl telluride and the phenyl pseudohalides as shown below :

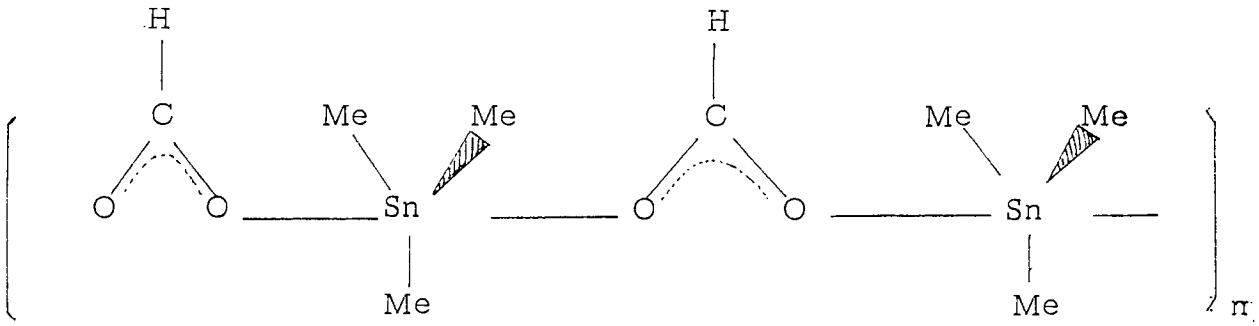
$$Ph_3TeX \longrightarrow Ph_2Te + PhX$$

which is proved by T.G.A. and mass spectral data [42] .

In the investigation of organotelluronium carboxylate compounds, many background items may be taken from organotin salts, e.g. trimethyltin formate. Trimethyltin formate was synthesised by Okawara and Webster {43} by the reaction of trimethyltin hydroxide with formic acid. On the basis of infrared studies, they advanced the novel suggestion that trimethyltin formate was an ionic compound consisting of

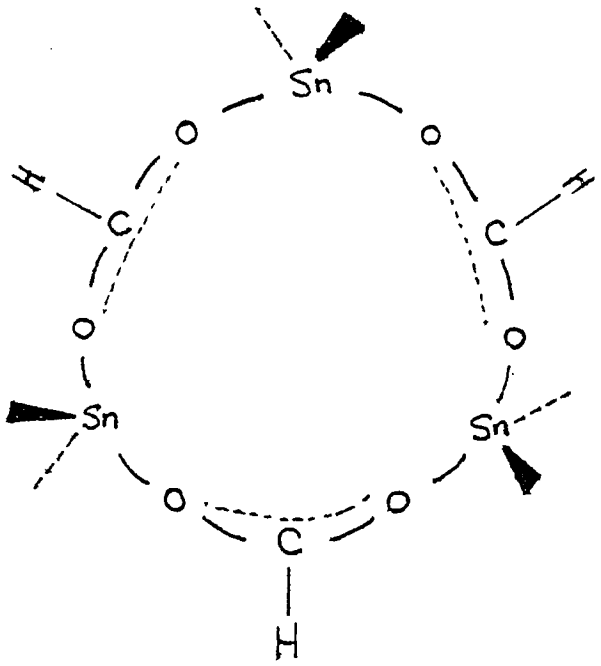
planar trimethyl tin cations and formate anions.

Poller {44} has modified this interpretation and claimed that planar trimethyltin groups are linked together by formate bridges into infinite linear chains such as (I), which account for the insolubility of the compound.



(I)

Simson and Grahams {45} succeeded to convert the classical formate to a soluble form of markedly different properties and suggest a cyclic structure of trimethyl tin formate and acetate such as (II).



(II)

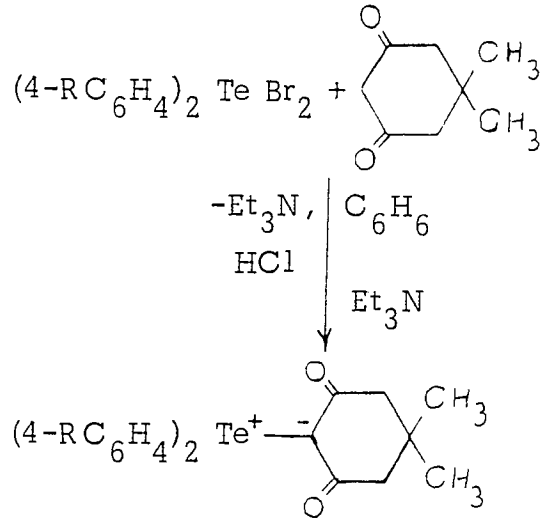
There are very few examples of selenonium or telluronium ylides compared with the large number of sulphonium ylides reported in the literature {46, 47}. The formation of an ylide requires that the carbonion should be attached to a heteroatom carrying a high degree of positive charge, which organotelluronium salts of the type $R_3Te^+\bar{X}$ are the best example. Many sulphonium ylides have been prepared by the salt method, with bases such as alkyllithium {48}, and potassium hydroxide {49}. Therefore, possibly telluronium ylides may be formed by treating telluronium salts with various bases such as potassium hydroxide and amines, e.g.

$$R_2Te^+CH_2R' \xrightarrow{\text{Base}} R_2Te^+\bar{C}HR'$$

$$X^-$$

The synthesis of two types of telluronium ylides have so far been reported :

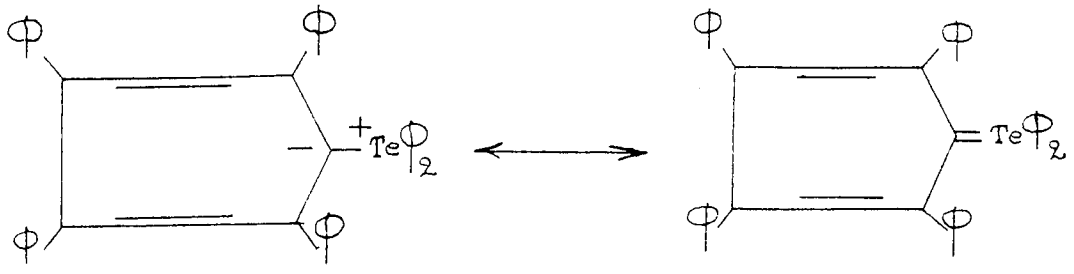
1. Sadekov {50} prepared the telluronium ylide, (A) from diaryl-tellurium dibromides and 1,1-dimethyl3,5-cyclohexadione in boiling benzene containing triethyl amine.



(A)

R = H, CH_3 and CH_3O

2. In 1970, Freeman synthesised the telluronium ylide (b), which decomposes slowly in the solid state and more rapidly in solution {51}.



(B)

Quite recently, Dance {52} investigated the behaviour of methyldiphenyl telluronium halides (Ph_2MeTeX) where X = Cl, Br, I, in chloroform and dimethyl sulfoxide (DMSO) solutions. He also measured the conductivity of these salts in DMSO and dimethylformamide (DMF) solutions and concluded that considerable ion pairing occurred in these solvents.

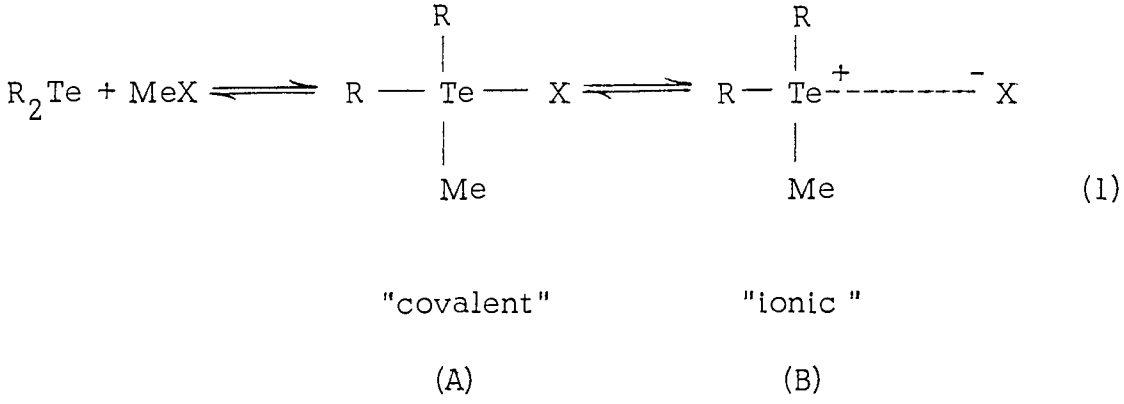
He recorded the ^1H n.m.r. spectra of those telluronium salts (Ph_2MeTeX) which are soluble in chloroform and observed the methyl singlets with satellite peaks (caused by coupling between ^1H and ^{125}Te) corresponding to the methyl group which is still attached to the tellurium atom. These resonances decayed with time to be replaced by new signals shown to arise from MeX (X = Cl, Br, I). Dance also demonstrated that the Me-Te resonance was X-dependent (table below) with the methyl proton being more shielded as the electronegativity of X increased. Thus, the methyl group and X are electronically coupled in chloroform solution of Ph_2MeTeX.

Compound	Solvent	Resonance (1) ppm	Resonance (2) ppm
Ph_2MeTeI	$CDCl_3$	3.04	2.15
$Ph_2MeTeBr$	"	2.90	2.61
$Ph_2MeTeCl$	"	2.76	2.96
Ph_2MeTeI	$DMSO(d_6)$	2.69	2.15

Methyl resonance position in ^1H n.m.r. spectra of methyl diphenyl telluronium salts (Dance thesis).

Resonance (1), is due to Me-$TePh_2X$ immediately after dissolving and resonance (2) is due to MeX.

Dance attempted to bring these observationstogether by postulating that the telluronium salts assume a covalent form in chloroform where as in DMSO, an ionic form is present. Reductive elimination of MeX then occurs via the "covalent" form :



(1)

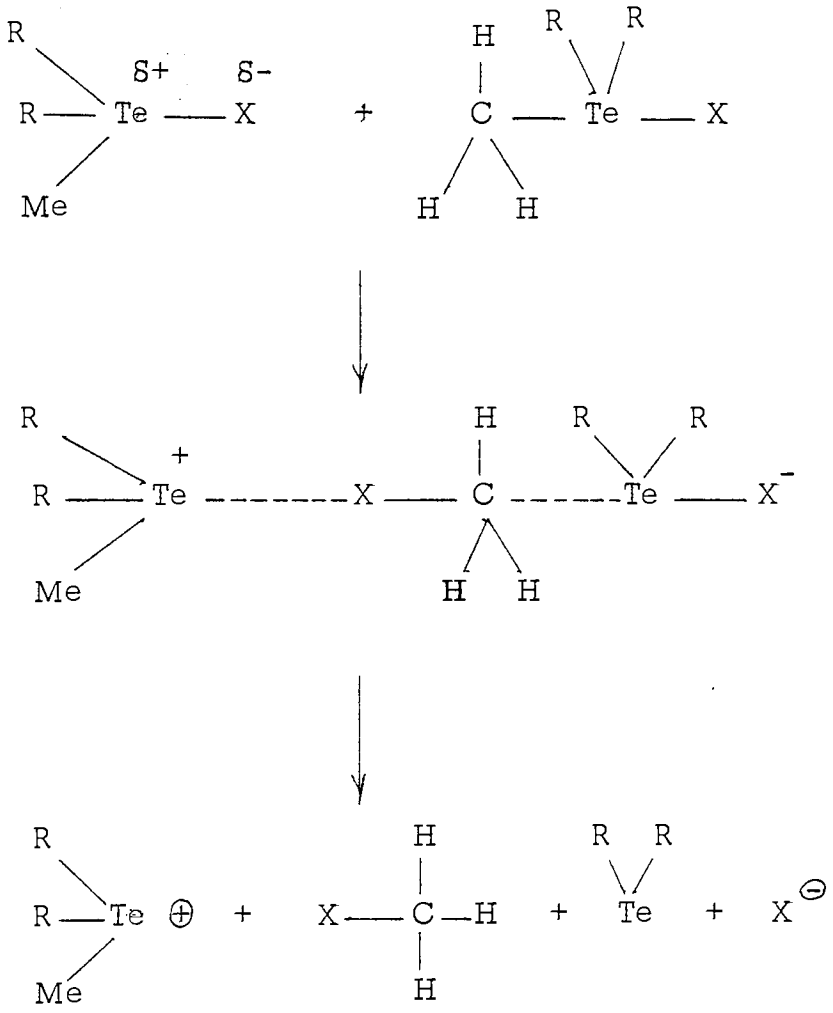
"covalent" (A) "ionic " (B)

Musa [53] synthesised methyldiphenyl telluronium isothiocyanate $Ph_2MeTe(NCS)$ and studied its behaviour in chloroform solution. He inferred that the quoted compound is ionic in solid state, but in solution ($CHCl_3$) exists as a covalent form (i.r.). The ^1H n.m.r. spectrum of this compound was recorded in $CDCl_3$ and DMSO (d_6) and a single methyl resonance was observed at $\delta = 2.70$ ppm (DMSO) and $\delta = 2.9$ ppm ($CDCl_3$) with satellite structure (^1H-^{125}Te) which vanished within 3 hrs. and was replaced by another resonance at $\delta = 2.56$ ppm due to methyl thiocyanate, i.e. :

$$Ph_2MeTe(NCS) \longrightarrow Ph_2Te + MeSCN$$

The kinetic studies of methyl diphenyl telluronium halides {52} and isothiocyanate {53} have been carried out, which provides important evidence for the mechanism of the reaction, identification of reactant species and what products are formed. Dance reacted methyl iodide and excess of diphenyltelluride which acted as solvent at 35°C within the n.m.r. spectrometer and the spectrum of the aliphatic region was recorded and integrated in time intervals until the reaction was complete. Immediately after mixing the only aliphatic resonance was that corresponding to MeI at δ = 2.15 ppm which diminished after 1 min. to be replaced first by one resonance at δ = 3.04 ppm (resonance A) eqn. (1) and this diminished slightly until an equilibrium value and more slowly by one at δ = 2.70 ppm (resonance B) eqn. (1). This indicated that in a solvent of intermediate polarity, both of the resonances observed for methyldiphenyl telluronium idodie in DMSO and $CHCl_3$ were present and that there was an equilibrium between these two species. The plot of concentration of methylated products vs time for the ionic form (B), was sigmoidal, showing that the formation has taken place from an intermediate stage, and by looking at the methyl resonances, it is clear that the covalent form (A) has been produced more rapidly initially than the ionic form, and this indicates that the product (A) is infact, the intermediate. It is apparent that decomposition of alkyl-diaryltelluronium salts generally involves cleavage of the Te-aliphatic bond rather than that of the Te- aromatic bonds. The decomp-

osition might take place via an SN_2 mechanism involving attack at the methyl group;



in which an ionic intermediate should be expected.

Musa studied methyldiphenyl telluronium isothiocyanate by monitoring the ^1H n.m.r. spectrum at time intervals over the occurrence of the reaction and found pseudo first order kinetics which was considered inconsistent with the SN_2 process. Musa suggests that the most pro-

bable mechanism for the initial stage of the reaction is one involving loss of a methyl radical : e.g.

Initiation :

$$MePh_2Te(NCS) \longrightarrow \overset{o}{Me} + Ph_2\overset{o}{Te}(NCS)$$

Propagation :

$$\overset{o}{Me} + MePh_2Te(NCS) \longrightarrow MeSCN + \overset{o}{TePh_2Me}$$

$$\overset{o}{TePh_2Me} \longrightarrow Ph_2Te + \overset{o}{Me}$$

Termination :

$$\overset{o}{Me} + Ph_2\overset{o}{Te}(NCS) \longrightarrow Ph_2Te + MeSCN$$

1. (i) C. IV. TETRAORGANOTELLURIUM :

In 1888, Marquart and Michaelis {54} failed to synthesise tetraorganyltellurium compounds. Tetraphenyltellurium was synthesised for the first time in 1952, by Wittig and Fritz {55}. They prepared this compound from tellurium tetrachloride, from triphenyl tellurium chloride and from diphenyl tellurium dichloride and an excess of phenyl lithium as yellow crystals. The chemistry of tetraorganyltellurium compounds has been relatively little studied.

1. (i). d. TELLURIUM (VI)

Tellurium in this oxidation state is common but not as stable with respect to redox process as the previous state, and the electronic configuration becomes $[Kr]\ 4d^{10},\ 5s^{o},\ 5p^{o}$. The absence of the lone pair of non-bonding electrons ensure that the structure of these tellurium VI compounds will be regular {56}. Tellurium hexafluoride is the oldest known fluoride of tellurium, a colourless gas which condenses to a volatile white solid melting at about $-38^{o}C$ and subliming at about the same temperature. It is best prepared from the element at $150^{o}C$, reaction at lower temperatures yielding mixtures containing other tellurium fluorides {57}. Infrared and Raman spectroscopy {56, 58, 59} have been studied extensively and an octahedral structure like that of selenium hexafluoride with the Te-F distance 1.84 A^{o} has been suggested. To date no organic derivatives of tellurium (VI) have been reported.

* * * * * * * * *

1. (ii). CHEMISTRY OF HEXAHALOTELLURATE (IV) SALTS :

Organotellurium compounds, have so far been synthesised employing either elemental tellurium, or tellurium tetrachloride as the main starting material. $TeCl_4$ is rather expensive (£ 6.43 per 100 gr. 1979 price) {60} and rather sensitive to the moisture, so from the economic point of view, and for the case of handling, it is worth finding out whether there is a cheaper alternative. We then became interested in

looking at tellurium dioxide (£ 4.41 per 100 gr. 1979 price) { 60} since:

$$TeO_2 + 6HX \longrightarrow H_2TeX_6 + 2H_2O$$

$$H_2TeX_6 + 2MX \longrightarrow M_2TeX_6 + 2HX$$

Where : $M = C_s$, Rb, NH_4, Me_4H, Et_4N, Ph_4AS, ...

X = Cl, Br, I

The chemistry of anionic tellurium species such as TeX_6^{2-} and TeX_5^- where X=F, Cl, Br, and I has been reported in the literature. Pentahalotellurates (IV) have a general manner of preparation in which a mixture of a solution of tellurium tetrahalide or tellurium dioxide with a solution of cation salt is treated with hydrohalic acid, also hexa-halo-tellurate (IV) salts may be prepared by dissolving tellurium dioxide in the appropriate hydrohalic acid and treating with MX.

All the penta- and hexahalotellurate (IV) salts can be recrystallised from à 40% solution of appropriate hydrohalo acid. Penta- and hexafluorotellurates are white, chlorides are yellow, bromides are orange and iodides are dark to reddish { 61, 62 } . Dipyridinium hexa-fluorotellurate (IV) is one of the few hexafluorotellurate anions which have been synthesised {62} by addition of pyridine and tellurium dioxide

in fairly concentrated hydrofluoric acid to give $(C_5H_5NH)_2TeF_6$. This compound, as well as pyridinium pentafluorotellurate, is rapidly hydrolysed by water to tellurous acid, but both are insoluble in and unchanged by, ether. Hydrochloric acid converts both fluoro forms into di-pyridinium hexahalotellurate $(C_5H_5NH)_2\,Te\,Cl_6$, hydrobromic and hydroiodic acid give the corresponding salts.

The thermal stability of the TeX_6^{2-} anion (where X=F, Cl, Br, I) increases from the fluoride to the iodide as illustrated by the ready conversion of any of the higher complex halides into a lower one by treatment with the appropriate halogen acid. This order of stability of the complex tellurium halides, i.e. :

$$\left[TeF_5\right]^- \quad \text{and} \quad \left[TeF_6\right]^{2-} < \left[TeCl_6\right]^{2-} < \left[TeBr_6\right]^{2-} < \left[TeI_6\right]^{2-}$$

is the same as that observed by Sharpe [63] for platinum (IV), e.g.

$$\left[PtF_6\right]^{2-} < \left[PtCl_6\right]^{2-} < \left[PtBr_6\right]^{2-}$$

Hexahalotellurate (IV) salts are of the general formula M_2TeX_6 where X = Cl, Br, I and M could be any sort of uni-positive cation such as PyH^+, K^+, C_s^+, Rb^+, NH_4^+, $(CH_3)_4N^+$, $(C_2H_5)_4N^+$, Ph_4As^+. In the investigation of hexahalotellurate (IV) salts, many background items can be taken from lead chemistry because $PbCl_6^{2-}$ compounds

have been used in preparative organolead chemistry. This is because of the main group element hexahalogenometallates, the $PbCl_6^{2-}$ ion most closely resembles the $TeCl_6^{2-}$ ion in size. Greenwood and co-workers [64] have studied the infra-red and Raman spectra of a series of TeF_5^- ions and suggested a square-pyramidal structure for these ions. Molecular weight and conductivity measurement of pyridinium pentafluoro tellurate (IV) in methanol and pyridine have been carried out {64} and it has been indicated that the compound is ionic and has been formulated as $(C_5H_5NH)^+ TeF_5^-$.

The tellurium atom in TeX_6^{2-} has seven electron pairs in its valency shell. X-ray crystallography examination of some hexahalo-tellurate (IV) salts, e.g. $(NH_4)_2TeBr_6$ {65}, K_2TeBr_6 {66} K_2TeI_6 {67} and $(PyH)_2 TeCl_6$ {68}, also vibrational {69} and n.q.r. {70} data gathered for these ions show that they assume octa-hedral symmetry, both in the solid and solution state. Consequently, it is cited as an exception to the valency shell electron-pair repulsion (VSEPR) advanced by Gillespie and Nyholm {71}.

Gillespie and Nyholm suggested that such species should be dis-torted from octahedral symmetry by the effect of the lone pair of electrons. However, several crystal structure determinations have failed to show any significant distortion. The seventh electron pair instead becomes stereochemically inert (in terms of an angular effect) by occupying the

a_1g MO located primarily on the tellurium atom {72, 73}. The theory of valence-shell electron-pair repulsion assumes that the stereochemistry of a molecule could be determined by the interaction between the electron pairs in the valency shell and that ligand-ligand repulsion are generally of lesser importance. For molecules in which all the valency shell electron pairs are used in importance to ligands consideration of either the repulsion between ligands or repulsion between bonding electron pairs shows the prediction of the same molecular structure. However, when there is one or more lone pairs in the valency shell of the central atom, then valence-shell electron-pair repulsion theory predicts a different shape from a consideration of ligand-ligand repulsions.

In almost every case the valence-shell electron-pair repulsion predicts a correct molecular shape, i.e. lone pairs seem to be stereochemically active. However, for high co-ordination numbers and for large ligands or small central atoms, it is clear that repulsions between ligands could be considerable for determining the molecular shape. For example, the ions $TeCl_6^{2-}$, $TeBr_6^{2-}$ and $SbBr_6^{3-}$ and some closely related molecules have regular octahedral structures {66, 74}, although they all contain seven valence shell electron pairs including one lone pair and must therefore, possess structures based on a preferred arrangement of seven electron pairs. Although, it is not possible to predict the most likely arrangement of seven electron pairs with complete certain-

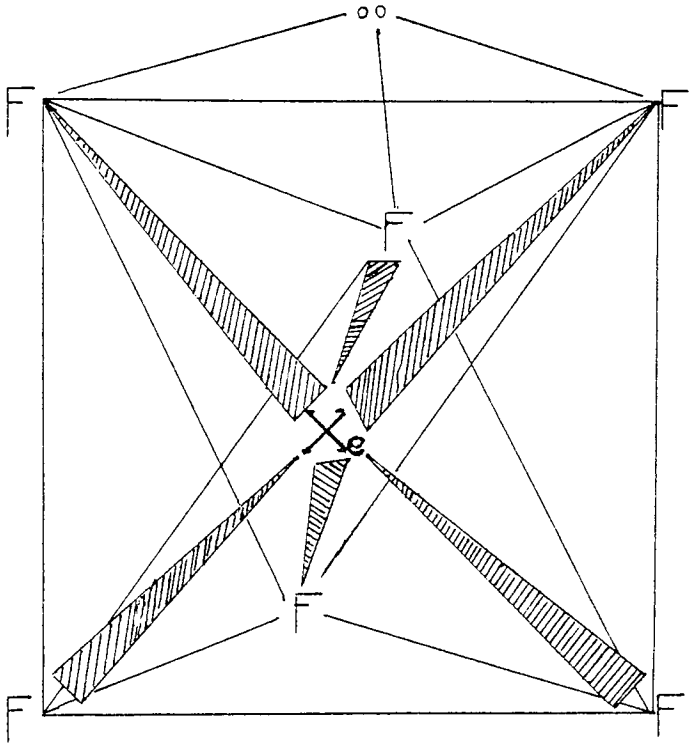
ty the six ligands would not be expected to have an octahedral arrangement. It seems reasonable to assume therefore, that the ligand-ligand repulsions determine the stereochemistry in these cases. The Br-Br distance in $TeBr_6^{2-}$ ion is 3.81 A^o which is slightly smaller than Van der Waal's distance of 3.9A^o. This probably does not mean that there is any repulsion between bromine ligands but it is clear that the ligands are essentially touching each other and therefore, there is no room for lone-pair. It would appear, therefore, that the lone pair is forced inside the valency shell into a spherical S type orbital.

Bartell [75] has shown the chlorine-chlorine distance in tellurium tetrachloride in which the lone pair is stereochemically active is only 3.3 A^o compared with the value of 3.5 A^o in $TeCl_6^{2-}$ and argues that ligand-ligand repulsion is not the only factor responsible for the octahedral structure of $TeCl_6^{2-}$.

However, as it has already been mentioned in the case of $TeBr_6^{2-}$, the chlorine-chlorine distance would be much smaller than 3.3 A^o if the lone pair were included in the valency shell.

Although, the structure of TeF_6^{2-} is not known, the related compounds IF_6^- and XeF_6 do exist and they appear to have non-octahedral structures based on an arrangement of seven electron pairs in the valency shell including the lone pair [76, 77].

The exact structure of gaseous XeF_6 has not been determined but it is known to be a slightly distorted octahedron {76} and the lone pair appears to occupy less space than the bonding pairs.



Predicted structure of XeF_6

Donaldson {78} studied the chemistry of some hexahalostannates (IV), tellurates (IV) and polomates (IV), and found out that the hexachloro-bromo stannate (IV) salts are white and in contrast the corresponding tellurates and polomates are intensely coloured. The difference between the Sn(IV), and the Te (IV) or Po (IV), is the presence of ns^2 non-bonding on the Te(IV) and Po(IV) and he concluded that the intense colour of tellurate (IV) and polomate (IV) complexes is because of the

band population by the n_s^2 non-bonding electrons.

McWhinnie et al., {79} have recently reported the Mössbauer data of a series of organotellurium compounds and found that the order of chemical isomer shifts lie as :

$$\text{Tellurides} < \text{ditellurides} < \text{dihalides} < \text{trihalides}$$

and claimed that the increasing the S electron density at the nucleus is responsible for that order. Tellurium -125 Mössbauer spectra have been reported for various tellurate anions: $TeCl_6^{2-}$, $TeBr_6^{2-}$, TeI_6^{2-} and TeF_5^- with various cations {80} and the chemical isomer shift was found to be characteristic of the anion and is rather insensitive to the nature of the cation. Shipinel et al., [81] have studied the Mössbauer spectra of a series of complex anions of formula SnX_6^{2-}, SbX_6^- and TeX_6^{2-} (where X = F, Cl, Br, I) and plotted chemical isomer shift against the electronegativity difference between metal and halogen and found the sign of the $\delta R/R$ for ^{119}Sn and ^{125}Te was the same (i.e. positive) while this was opposite to that for ^{121}Sb.

Greenwood {80} prepared a large variety of tellurate anions [table] and studied their chemical isomer shifts and disagreed with Shpinel's claim about the characterisation of TeF_6^{2-} either in solution or solid state. He then, rationalized the dependence of chemical

isomer shift on oxidation state and claimed that the tellurium IV, compounds (TeX_6^{2-}, TeF_5^-, TeX_4, TeO_2 and TeO_3^{2-}) have a positive C.I.S. whereas tellurium (VI) compounds ($Te(OH)_6$, TeO_4^{2-}, TeO_3) have a negative shift. On the basis of argument which have well been established for the neighbouring Mössbauer elements, tin, iodine and xenon {82} this implies a positive value for the sign of $\delta R/R$.

Mössbauer Parameters for Te-X complexes

Compound	Thickness mg/cm^2	δ^{*} mm/sec	Δ mm/sec
$(NH_4)_2 TeCl_6$	18	+1.95±0.05	0.0
$Rb_2 TeCl_6$	40	+1.95±0.04	0.0
$Cs_2 TeCl_6$	39	+ 1.94±0.09	0.0
$(NH_4)_2 TeBr_6$	35	+ 1.73±0.04	0.0
$(NMe_4)_2 TeBr_6$	40	+ 1.75±0.17	0.0
$Rb_2 TeBr_6$	40	+ 1.72±0.04	0.0
$Cs_2 TeBr_6$	38	+ 1.80±0.03	0.0
$(NH_4)_2 TeI_6$	32	+ 1.54±0.09	0.0
$Rb_2 TeI_6$	40	+ 1.53±0.08	0.0
$Cs_2 TeI_6$	41	+ 1.65±0.04	0.0
$NH_4 TeF_5$	20	+ 1.09±0.33	6.25±0.16
$Cs TeF_5$	42.8	+ 0.93±0.21	5.85±0.09

* : is referred to the ^{125}I-Cu source as zero.

PROSPECTS :

A. One of the aims of this project is the preparation of various hexahalotellurate (IV) salts with different size of cations, and investigation of the temperature at which these salts are decomposed, with consideration of the yields of decomposition products. The ^{125}Te Mössbauer parameters will also be determined.

B. Following the observations by Dance {52} and Musa {53} on methyl diphenyl telluronium (IV) salts (Ph_2MeTeX, where X = Cl, Br, I and NCS), We became interested in continuing this investigation to expand the chemistry of Ph_2MeTeX, where X = $C_6H_5COO^-$, CH_3COO^-, $O\text{-}CH_3OC_6H_4COO^-$ and $m\text{-}O_2N\text{-}C_6H_4COO^-$ and study their behaviour in solutions.

C. To investigate and extend the study of the solution chemistry of diorgano tellurium (IV) species such as $PhMeTeX_2$ (X = F, Cl, Br, I, NCS and $RCOO^-$), and to seek new light sensitive (or heat sensitive) organotellurium species which might have photographic applications.

CHAPTER II

2. (i) EXPERIMENTAL :

2. (i) a. CHEMICALS :

All chemicals were obtained from commercial sources and where necessary, melting points and other physical data such as infrared and ^1H n.m.r. spectra were used to assess the purity of the compounds.

Tellurium tetrachloride was supplied by British Drug Houses (B.D.H.).

2. (i) b. SOLVENTS :

Most solvents were obtained from bulk commercial sources, and were dried, and further purified, where necessary {83}.

2. (i) c. MELTING POINTS :

These were determined using a Gallenkamp electrically heated melting point apparatus.

2. (i) d. INFRA-RED SPECTRA :

Spectra in the range 4000-250 cm^{-1} were recorded on a Perkin-Elmer 457 Spectrophotometer. Solid state samples were examined as Nujol mulls supported between KBr plates. Some samples were also examined as solid discs, prepared by pressing a mixture of sample and powdered KBr.

Solution spectra were obtained from 10% solutions in chloroform using a standard liquid cell, with chloroform as reference.

2. (i) e. CONDUCTIVITY MEASUREMENTS :

Molar conductivity measurements in various solvents were carried out using a standard conductivity bridge, and a Mullard type E 7591/B cell of cell constant 1.46.

2. (i) f. NUCLEAR MAGNETIC RESONANCE :

All proton magnetic resonance spectra at 60 MH_z were recorded on a Perkin-Elmer R14 spectrometer. Appropriate solvents were chosen for each sample and T.M.S. (tetramethyl silane) was used as an internal reference.

2. (i) g. DIFFUSE REFLECTANCE SPECTRA :

The spectra in the range 55000 to 11,500 cm^{-1} were recorded on a Unicam SP800 spectrophotometer. The samples were measured on filter papers, using magnesium carbonate as reference.

2. (i) h. VISIBLE SOLUTION SPECTRA :

The visible spectra were obtained in the range 55,000 to 11,500 cm^{-1} for solutions in DMSO and DMF, using 1 cm quartz cells, and were measured with a Unicam SP800 spectrophotometer, using the rel-

evant solvent as reference.

2. (i) i X-RAY POWDER PHOTOGRAPHS :

All the X-ray photographs and diffraction traces were recorded on a Jeol JDX 75 X-ray diffractometer using Cu-K_α radiation as a source.

2. (i) j. THERMO-GRAVIMETRIC ANALYSIS DATA :

T. G. A. data were obtained on a Stanton Thermobalance (T.R, Decimilligram model), ambient to 1000^{o}C with static air.

2. (i) k. RAMAN SPECTRA :

Raman spectra in the range 400-40 cm^{-1} were obtained at Simon Fraser University, Canada, using a Cary 81 Raman instrument fitted with a He-Ne laser.

2. (i) l. MOSSBAUER DATA :

Mössbauer data were also obtained at Simon Fraser University, Canada. Specimens were cooled to 4K and measurements were duplicated. Apparatus is described in reference {79}.

2. (i) m. VAPOUR PRESSURE OSMOMETER :

All molecular weight measurements were carried out in appropriate

solvents using a Knauer Vapour Pressure Osmometer.

2. (i) n. MASS SPECTRA :

Mass spectra were obtained from an AEI-MS9 spectrometer at ionising potentials of 70 eV or 15 eV.

2. (i) o. ELEMENTAL ANALYSIS :

Microanalysis for carbon, hydrogen and halide were obtained from the Analytical Services of the Chemistry Department of Aston University.

CHAPTER III

3. (i). INTRODUCTION :

Hexahalotellurate (IV) salts of general formula TeX_6^{2-} have been studied and reported in the literature. Spectroscopic data gathered for these salts suggest an octahedral symmetry both in the solution and solid state. There they can be considered as an exception to the valency shell electron-pair repulsion (VSEPR) theory postulated by Gillespie and Nyholm {69}. These authors predicted a distorted octahedral symmetry for these compounds by the effect of lone pair of electrons.

We originally became interested in preparation of hexahalotellurate (IV) salts, since they are produced from the cheaper tellurium dioxide rather than tellurium tetrachloride, to study the direct reaction with other components for the synthesis of organotellurium compounds, this leading us to a cheaper alternative for the synthesis of organotellurium compounds.

Donaldson has studied halogen derivatives of Sn, Te and Po, and concentrating on hexabromo- and hexachlorostannate, tellurate, and polonate, and then suggested that the lack of colour and conducting property of hexabromo and chlorostannate, is because of the absence of ns^2 non-bonding lone pair orbitals {78}. In contrast, the corresponding Te (IV) and Po (IV), derivatives, which are known to be isostructural with the hexahalogenostannate, are intensely coloured. The difference

between the Sn (IV), Te (IV), and Po (IV) complexes is the presence of ns^2 non-bonding, lone pair orbitals on the group -6 elements. It was decided to attempt to obtain further data to evaluate this concept.

3. (ii) EXPERIMENTAL :

PREPARATIONS :

Bis-ammonium hexachlorotellurate (IV) :

Tellurium dioxide (5 g) was dissolved in conc. hydrochloric acid (15 ml.) and the solution evaporated in a fume cupboard to approximately 7.5 ml. A saturated solution of two molar equivalents of ammonium chloride (3.5 g. in about 12 ml. of water) was added and evaporation continued on a steam bath until a mass of glistening yellow crystals was formed. The crystals were carefully drained (unwashed, as it is shown later that Pentahalo tellurate salts are formed) on a sintered glass crucible and dried in vacuo over calcium chloride.

Bis-ammonium hexabromotellurate (IV) :

Tellurium dioxide (0.5 g) was dissolved in hydrobromic acid (5 ml. 40%). A saturated solution of two molar ammonium bromide was then added. The orange crystals appeared immediately, then the solution was evaporated on a steam bath until the crystals settled well. The crystals were collected on a sintered glass crucible and dried in vacuo over calcium chloride.

Other salts of hexabromo- and hexachlorotellurate (IV), i.e. bis-tetraethyl ammonium hexachloro, bis-tetraethyl ammonium hexabromo, bis-tetraphenyl arsonium hexachloro and bis-tetraphenyl arsonium hexabromotellurate were prepared similarly using the appropriate quantity of the cation halide. In one attempted preparation of the salts, the crystals were washed with 20 ml. of hydrohalo acids. The analysis data showed that pentahalotellurate (IV) salts were prepared. The results are tabulated in Table (4).

Reaction of bis-ammonium hexachlorotellurate (IV) with aluminium chloride and benzene

Bis-ammonium hexachlorotellurate (2 g. 0.005 mol.) and aluminium chloride (2.7 g 0.02 mol.) and dry benzene (150 ml.) were placed into a 500 ml. two-necked round-bottom flask equipped with a magnetic stirring bar, a nitrogen inlet and a condenser. The reaction mixture was heated to reflux with stirring under nitrogen for 45 min. and then poured into 400 ml. of ice water. The benzene layer was washed with water and dried over anhydrous sodium sulfate and evaporated to dryness in vacuo. No residue was left.

Reaction of bis-ammonium hexachlorotellurate (IV) with Phenetole (Phenyl ethyl ether) in the presence of solvent

A mixture of $(NH_4)_2TeCl_6$ (4.47 g., 0.011 mol.) with phenetole (1.4 ml., 0.011 mol.) and dry chloroform was heated under reflux with exclusion of moist air, during 2 hrs. No hydrogen chloride was evolved

and the solid failed to dissolve. Other experiments were carried out, using 1,4 dioxane, carbon tetrachloride or methyl cyanide as solvent, and failed.

Reaction of bis-ammonium hexachlorotellurate with Phenetole in the absence of any solvent

$(NH_4)_2TeCl_6$ (2 g.) and excess phenetole (10 ml.) were heated under reflux for 8 hrs. No hydrogen chloride was evolved.

Reaction of bis-ammonium hexachlorotellurate (IV) with DMF

Bis-ammonium hexachlorotellurate (2 g.) and DMF (15 ml.) were placed into a 250 ml. two-necked round-bottom flask and refluxed for 2 hrs. The same procedure was carried out with similar quantity of tellurium tetrachloride and in both cases elemental tellurium was released and a red solution remained. Visible spectra of both solutions showed that Te_2^{2-} was present.

Reaction of bis-ammonium hexachloro tellurate with a Grignard reagent

To an ethereal solution of a Grignard reagent synthesised from bromobenzene and magnesium, benzene (100 ml.) was added. $(NH_4)_2TeCl_6$ (9.9 g.) in 150 ml. benzene was added with vigorous stirring of the mixture at $0^{\circ}C$. The mixture was heated under reflux for 2 h. The cooled solution was treated with a saturated solution of ammonium

chloride (200 ml.) and the separated benzene layer was washed with distilled water and dried. The solvent was removed in a rotatory evaporator and the analysis of the obtained yellow crystals, indicated reformation of $(NH_4)_2TeCl_6$.

* * * * * * * *

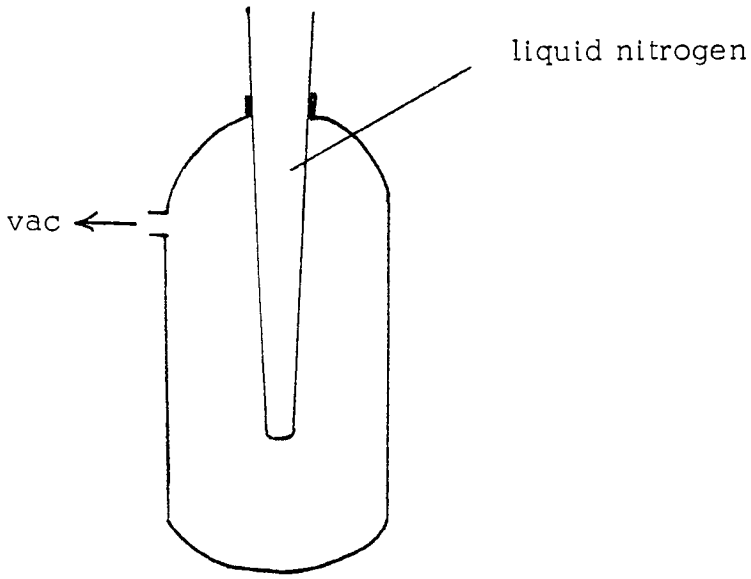
It is known (introduction p.30) that hexachloroplumbate (IV) salts may be used as the source of lead in the synthesis of organolead compounds via Grignard, organolithium and other organometallic reagents. It was therefore decided to evaluate the direct use of hexachlorotellurate (IV) in the synthesis of organotellurium compounds. So, tetraphenyltin (1.12 g, 0.002 mol.) and $(NH_4)_2TeCl_6$ (0.376 g. 0.001 mol.) were refluxed for 3 hrs. in the presence of

1. dry, distilled toluene
2. dry xylene.

In both cases the insoluble matter was removed and the volume reduced to half. A small amount of white precipitate appeared at this point, but after extraction from petrolum ether no solid was left. The analysis of the insoluble matter showed the presence of the starting material.

Sublimation of bis-ammonium hexachlorotellurate

Bis-ammonium hexachlorotellurate (2 g.) was placed into a specially made vessel, and heated in an oil bath.



At 260°C the compound started to decompose and a pale yellow sublimate deposited on the cold finger. The temperature was kept constant at this stage for half an hour and then the solid was collected and analysed and shown to be tellurium tetrachloride. The same experiment was carried out for bis-ammonium hexabromotellurate and some orangish solid was collected, and analysed. The analysis indicated impure tellurium tetrabromide. We then, became interested in doing some thermogravimetric analysis (T.G.A). The T.G.A. data for all hexahalotellurate salts prepared here are listed in Table 6.

Alternative Preparation of bis-tetraphenylarsonium hexachlorotellurate (IV)

Bis-tetraphenylarsonium hexachlorotellurate $\left[Ph_4As\right]_2 \quad TeCl_6$ was also prepared by treating a dry benzene solution of tellurium tetrachloride with the stoicheiometric amount of $\left[Ph_4As\right] Cl$. The analytical data were quite satisfactory and are given in Table 3.

3. (iii). RESULTS :

The preparation of some hexahalotellurate (IV) salts (M_2TeX_6, where: M = NH_4, Et_4N and Ph_4As and X = Cl, Br) was carried out. Bis-tetraphenyl arsonium hexachlorotellurate (IV) was also prepared by using benzene and the appropriate amount of $\left[Ph_4As\right] Cl$.

X-ray powder diffraction data proved the identity of the ammonium and tetraethylammonium salts. The results also showed lack of any other tellurium compounds such as tellurium oxide or pentahalotellurate salts, i.e. $MTeX_5$. The data for bis-tetraphenyl arsonium hexachlorotellurate (IV) prepared from TeO_2 were different from those of the specimen prepared from tellurium tetrachloride, (Table 5, Fig. 1.).

Raman spectra of all salts were recorded and tabulated in Table 1. Thermogravimetric analysis of the salts was carried out and the results are given in Table 6. Conductivity measurement of bis-ammonium hexachloro and hexabromotellurates (IV) were taken in dimethyl sulfoxide

(DMSO) solution and the results are shown in figures 2 and 3.

TABLE 1

RAMAN DATA FOR SOME HEXAHALOTELLURATE SALTS, He-Ne LASER EXCITATION, cm^{-1}

Compound	Phenyl t	ν_1 A_1g)	ν_2(Eg)	ν_3(T_2g)
$(Ph_4As)_2TeCl_6$	240	285	270	
$(Ph_4As)_2TeBr_6$	238	170	150	
$(Et_4N)_2TeCl_6$		285	245	130
$(Et_4N)_2TeBr_6$		170	152	
$(NH_4)_2TeCl_6$		300	250	145
$(NH_4)_2TeBr_6$		180	155	85

TABLE 2

MOSSBAUER DATA OF SOME HEXAHALOTELLURATE IV SALTS

COMPOUND	$^{*}\delta$ mm/sec	Δ mm/sec
$(NH_4)_2TeCl_6$	1.73	0
$(Et_4N)_2TeCl_6$	1.74	0
$(Ph_4As)_2TeCl_6$	1.43	0
$(NH_4)_2TeBr_6$	1.59	0
$(Et_4N)_2TeBr_6$	1.47	0
$(Ph_4As)_2TeBr_6$	1.57	0

* : relative to ^{125}Sb/Cu source.

TABLE 3

ANALYTICAL DATA FOR SOME HEXAHALOTELLURATE IV SALTS

Compound	Found				Calculated			
	C%	H%	X%	N%	C%	H%	X%	N%
$(NH_4)_2TeCl_6$	-	2.40	56.30	7.30	-	2.10	56.50	7.40
$(NH_4)_2TeBr_6$	-	1.60	73.50	4.10	-	1.20	74.50	4.30
$(Et_4N)_2TeCl_6$	24.80	6.10	37.40	3.90	31.90	6.65	35.40	4.60
$(Et_4N)_2TeBr_6$	23.20	4.80	54.50	3.40	22.10	4.60	55.2	3.22
$(Ph_4As)_2TeCl_6$	50.60	3.60	17.20	-	52.0	3.60	19.20	-
$(Ph_4As)_2TeBr_6$	39.90	2.80	37.80	-	41.9	2.90	34.90	-
$(Ph_4As)_2TeCl_6$*	54.50	4.20	16.90	-	52.0	3.60	19.20	-

* Prepared from benzene solution of $TeCl_4$

TABLE 4

ANALYTICAL DATA FOR SOME PENTAHALOTELLURATE IV SALTS :

Compound	Found			Calculated		
	C%	H%	X%	C%	H%	X%
$(NH_4)TeCl_5$	6.3[a]	2.9	55.40	4.30[a]	1.20	54.90
$(NH_4)TeBr_5$	2.2[a]	0.62	71.70	2.50[a]	0.73	73.30
$(Et_4N)TeCl_5$	22.0	4.8	37.50	22.0	4.6	42.10
$(Et_4N)TeBr_5$	21.9	4.8	54.30	15.0	3.04	60.80

a = N%

TABLE 5

X-RAY CRYSTALLOGRAPHY DATA OF $(Ph_4As)_2TeCl_6$
(Prepared from $TeCl_4$ and TeO_2)

2θ	d	2θ*	d*
7.9	11.32	9.8	9.0
9.6	9.27	11.1	8.1
10.8	8.19	12.1	7.7
11.2	7.93	14	6.4
12.7	7.7	15.8	5.9
13.8	6.41	17.4	5.1
15.8	5.9	17.8	5.1
16.3	5.5	18.3	4.8
17.3	5.1	19.6	4.5
17.7	5.1	20.6	4.2
18.3	4.87	25.3	3.6
19.5	4.81	27.9	3.2
20.7	4.5	29.5	3.0
22.2	4.0	31.1	2.9
22.8	3.9	32.6	2.75
25.2	3.6		
26.1	3.5		
27.5	3.34		
28.8	3.2		
30.3	2.9		
32.1	2.8		
33.7	2.75		
36.0	2.58		

* X-ray data results from $(Ph_4As)_2TeCl_6$ prepared from TeO_2

TABLE 6

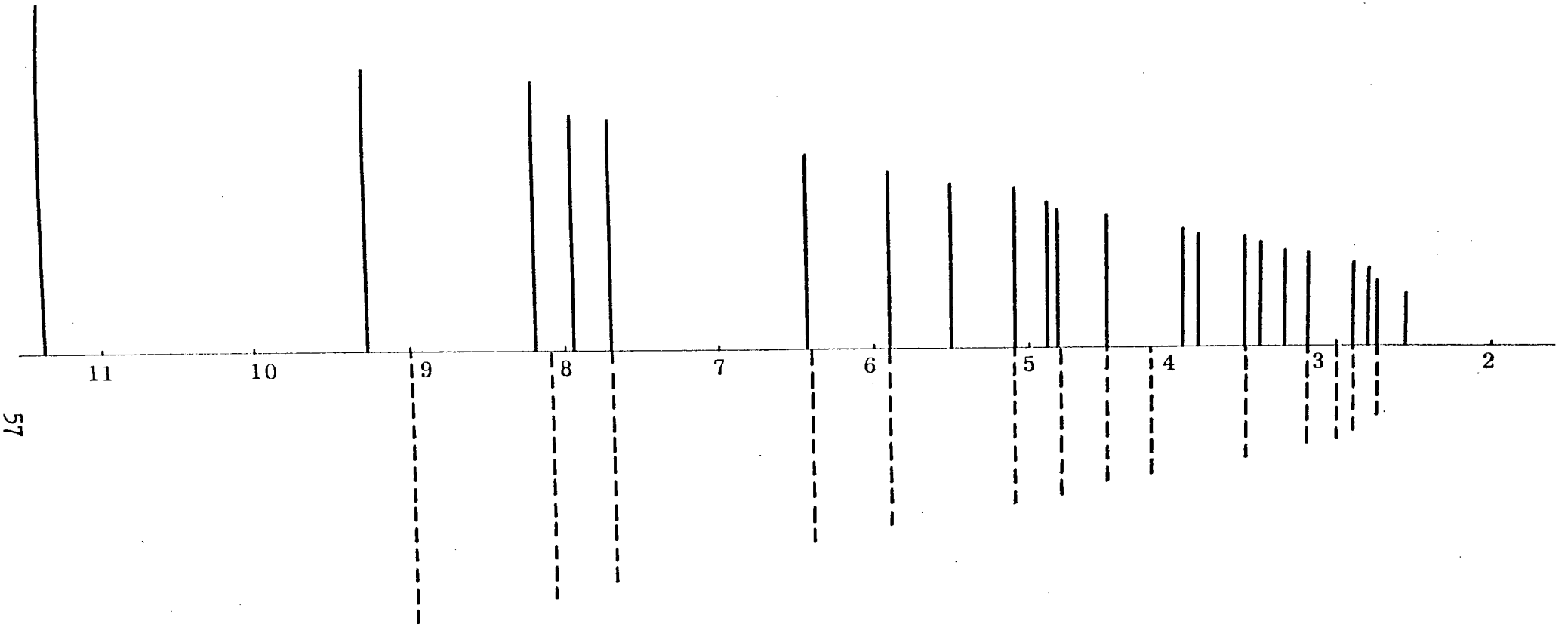
T.G.A. DATA FOR SOME HAXAHALOTELLURATE IV SALTS

Sample	Mol. Wt.	Sample Wt. mg	loss at t °C	Wt. loss at t °C	Mol. wt. of frag. lost
$(\Phi_4As)_2TeCl_6$	1106.45	50	245-335	34.7	768
$(\Phi_4As)_2TeBr_6$	1373.45	50	100-150	5.8	159
$(Et_4N)_2TeCl_6$	600.61	50	260-305	23	276
$(Et_4N)_2TeBr_6$	867.61	50	240-340	34.4	607
$(NH_4)_2TeCl_6$	376.61	50	215-350	34.3	258.4
$(NH_4)_2TeBr_6$	643.08	50	240-360	45.4	592

TABLE 7

Compound	State	Absorption mμ
$(NH_4)_2TeCl_6$	Solid	386
	Solution	390
$(Et_4N)_2TeCl_6$	Solid	384
	Solution	390
$(Ph_4As)_2TeCl_6$	Solid	378
	Solution	391
$(NH_4)_2TeBr_6$	Solid	452
	Solution	455
$(Et_4N)_2TeBr_6$	Solid	448
	Solution	454
$(Ph_4As)_2TeBr_6$	Solid	453
	Solution	454

The Visible data of some hexahalotellurate (iV) Salts



"d" values comparison of bis(tetraphenylarsonium)hexachlorotellurate (IV).

——— made from $TeCl_4$

– – – – made from TeO_2

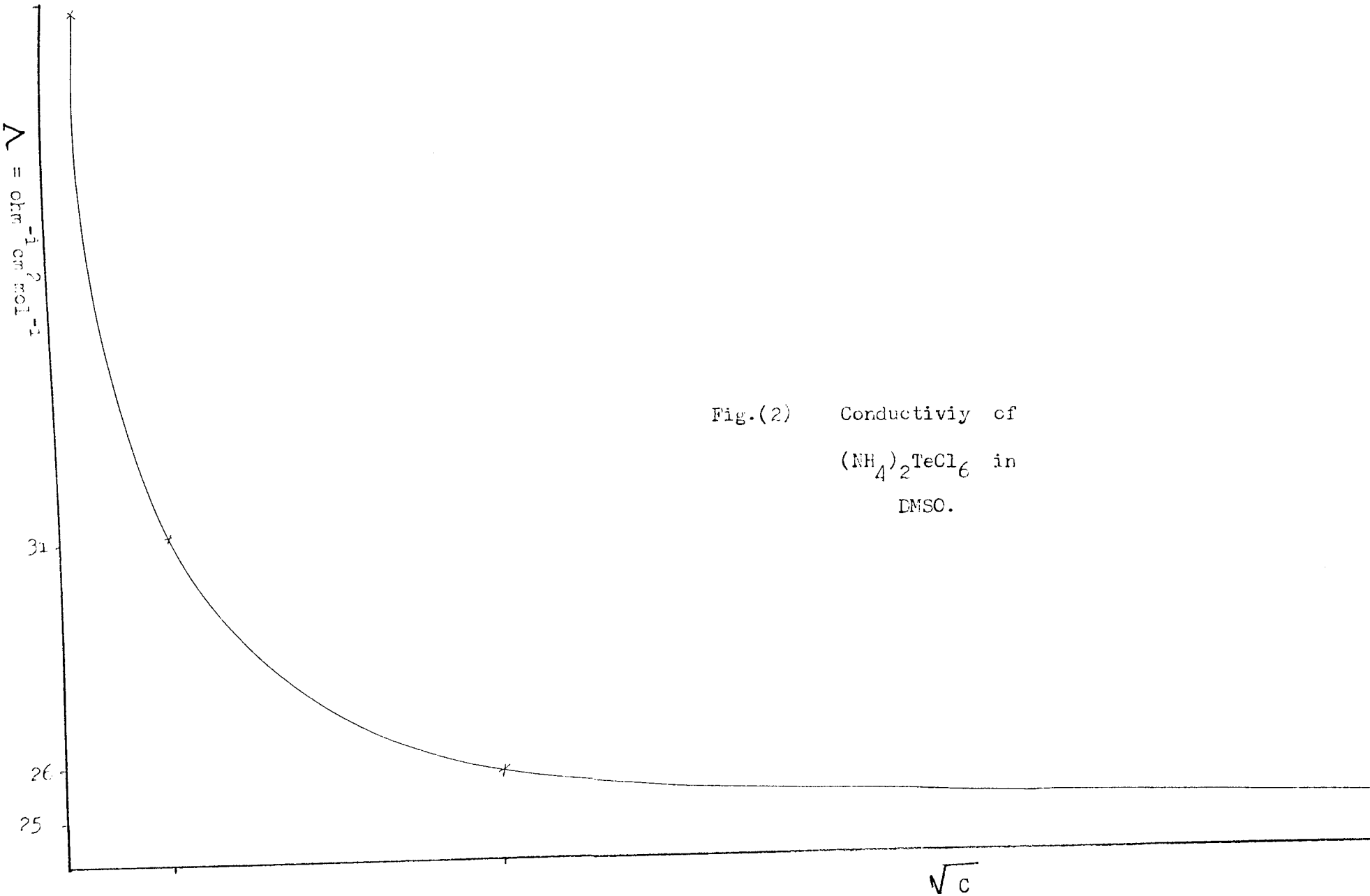


Fig.(2) Conductiviy of $(NH_4)_2TeCl_6$ in DMSO.

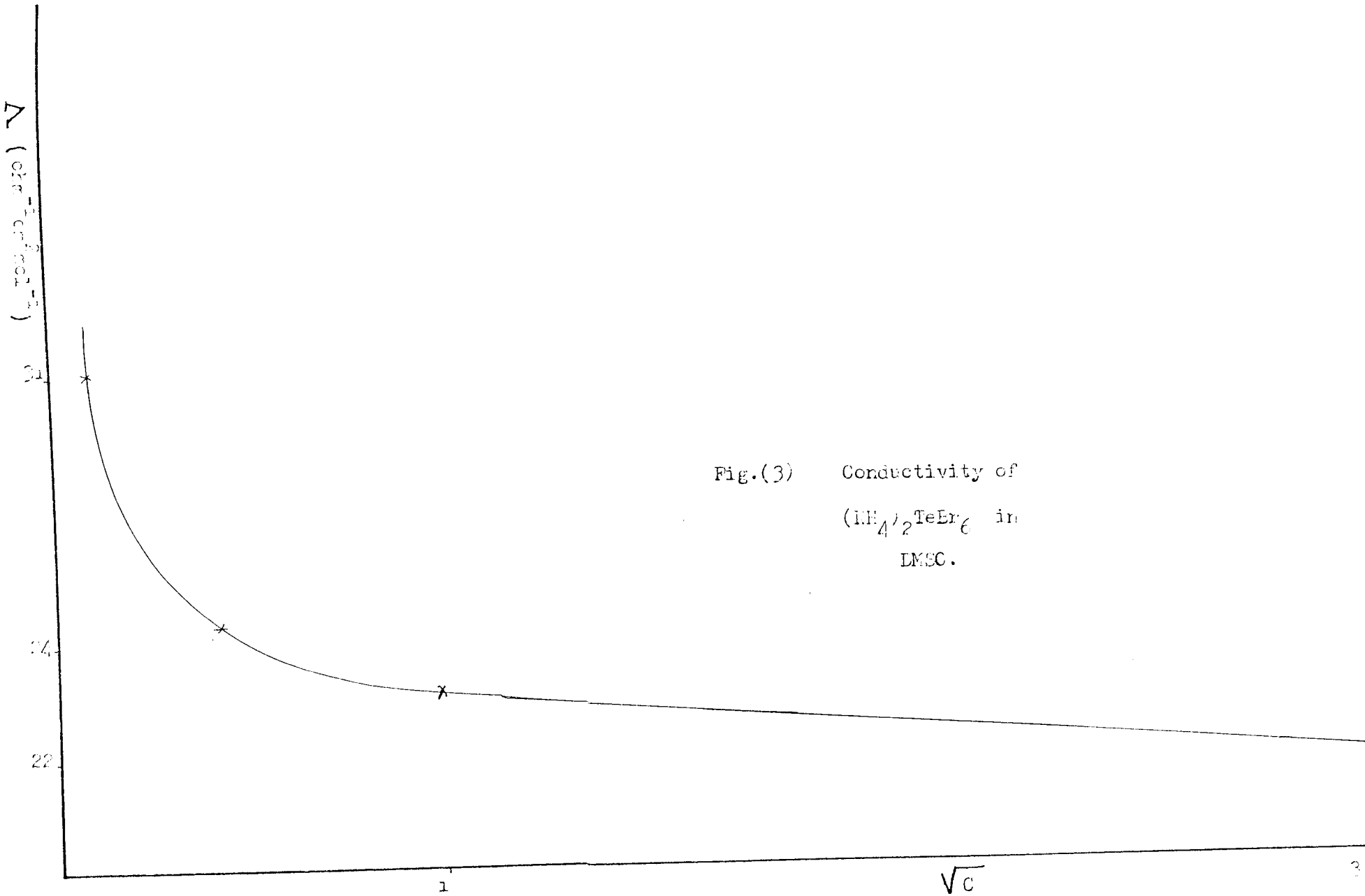


Fig.(3) Conductivity of $(Et_4N)_2TeBr_6$ in DMSO.

3. (IV) DISCUSSION :

We undertook an investigation of various hexahalotellurate (IV) species in the hopes that since they were prepared from tellurium dioxide, they might serve as a new and more economic source of organotellurium compounds. All the direct reactions of hexahalotellurate anions with phenatole, Grignard and organotin compounds failed. The only observed reaction was that of bis-ammonium hexachlorotellurate with DMF. Visible spectra of the red solution which results from treating bis-ammonium hexachlorotellurate with DMF were consistent with the presence of Te_2^{2-}, and the reaction of this red solution with n-butylbromide, gave a foul smell which was reasonably attributed to di-n-butylditelluride. Also, there was some nicely crystalline tellurium deposited, which means some reduction of tellurium (IV) had taken place. So far, the lack of data does not enable us to write any equation, but this reaction might be worth investigating further, particularly, as a possible route to ditelluride.

Unlike hexahaloplumbates in organolead chemistry, it does not appear to be possible to use hexahalotellurates directly as source of tellurium in reactions disigned to prepare organotellurium compounds. Therefore, it was decided to examine the pyrolisis of hexahalotellurate (IV) salts. There was a reasonable expectation that it would be possible to distill out the tetrahalide, then we could regard them as a cheaper source of the tellurium tetrahalide. The process will be economic if the conversion of the hexahalotellurate to tellurium tetrahalide is reasonably

quantitative. The results of the T.G.A. data presented in the previous section have been summarised and shown on page

The T.G.A. behaviour of six hexahalotellurates indicates that there was no consistent pattern of decomposition and in some cases, the decomposition went as we hoped, i.e. the ammonium systems in which telluriumtetrachloride and tetrabromide were distilled out, and as was detailed in the experimental section we went as far as designing a piece of apparatus (P. 48) and we were able to demonstrate that we could condense the tetrahalide on the cold finger, yield = 87.5%. In view of the cheapness of ammonium salts, economically speaking, it is the thermolysis of the ammonium hexahalotellurates which is the most promising. It is apparent, according to this set of data, that not all the salts break down to tetrahalide and it was interesting in the case of tetraphenyl arsonium hexachlorotellurate that, from the observed weight changes, it seemed that diphenyl tellurium dichloride is synthesised. (Proved by mass spectroscopy of the residue).

It was obviously necessary to duplicate the T.G.A. work. In synthesising fresh specimens of the salts using apparently the same method, different compounds were prepared, i.e. pentahalides. Therefore, considerable care must be taken in the synthesis of the hexahalide from tellurium dioxide and when we are confident that hexahalotellurate has been produced (C.H analysis), T.G.A. data may be reproduced.

$$[NH_4]_2[TeCl_6] \longrightarrow TeCl_4\,(g)\uparrow + 2[NH_4]Cl\,(s)$$

$$[NH_4]_2[TeBr_6] \longrightarrow TeBr_4\,(g)\uparrow + (2-n)[NH_4]Br\,(s) + n[NH_4]Br\uparrow\,(g)$$

$$[Et_4N]_2[TeCl_6] \longrightarrow TeCl_4\,(g)\uparrow + 2[Et_4N]Cl\,(s)$$

$$[Et_4N]_2[TeBr_6] \longrightarrow TeBr_4\,(g)\uparrow + (2-n)[Et_4N]Br\,(s) + n[Et_4N]Br\uparrow\,(g)$$

$$[Ph_4As]_2[TeCl_6] \longrightarrow Ph_2TeCl_2\,(s) + 2Ph_3As\,(g)\uparrow + Cl_2\uparrow$$

$$[Ph_4As]_2[TeBr_6] \longrightarrow Ph_3As\,(s) + [Ph_4As][TeBr_5] + PhBr\uparrow\,(g)$$

Pyrolysis products of some hexahalotellurate (iV) salts

All the hexahalotellurates are coloured, the chlorides are yellow and the bromides are orangish. As we change the size of the cation the colour changes. We looked at the solution spectra in DMSO, and at the solid spectra, (Table 7). In solution they all give fairly similar spectra but in the solid the maximum shifts into the U.V. as a function of size of cation. Donaldson {78} suggests that the colour of this type of compound is attributed to the s-pair of electrons of tellurium and this s-pair of electrons is effectively donated to a metallic band structure in the crystal. Since Donaldson suggests that the halogenorbital interaction is involved, if we increase the size of the cation, we might increase the separation of the anions, therefore, infact we should get less population of bands in the tetraphenyl arsonium rather than ammonium cases and this could possibly suggest an explanation of the difference in colour, i.e. $\left[Ph_4As\right]_2\ TeCl_6$ should have its absorption shifted to the U.V.

Mössbauer spectroscopy is a good way of determining this, because if the s electrons are donated to the some sort of band structure in the crystal, then the s electron density of tellurium is going to diminish and consequently, we would predict that the isomer shift should be greatest for the tetraphenyl arsonium salt, when the donation to the band structure is less, i.e. the greatest value (most positive) of chemical isomer shift for tetraphenyl arsonium, middle for tetraethyl ammonium, and lowest for the ammonium case.

Reference to our Mössbauer parameters (Table 2), shows that the Donaldson theory does not explain this mössbauer data, i.e. s electron density is less in the case of tetraphenyl arsonium and the greatest in the ammonium and tetraethyl ammonium cases, (Table 2). In agreement with the literature we found by powder photography that the ammonium and tetraethyl ammonium salts are cubic, but that the tetraphenyl arsonium salts are probably not. Raman spectra of the ammonium and tetraethyl ammonium salts are very similar, but again the tetraphenyl arsonium is some what differeent (Table 1).

Adams [84] examined the i.r. spectra of some complexes M_2TeCl_6 where M = Ph_4As and noted that the i.r. of this material was more complex than that of the others. He suggested the complexity was due to the Raman active modes coming through, and he therefore made certain assignments of frequencies on which basis he postulated a C_{3V} site symmetry for the complex ion. The extra bands agree virtually exactly what those we observe in our Raman spectra (Table 1). (Adams stated that he could not obtain a Raman spectrum). He then, suggested that the symmetry of the hexahalotellurate anions was less in the tetraphenyl arsonium salt than in the others, this means that the lone pair of electrons is in an orbital of more directional character, i.e. the s electron density at tellurium is reduced.

The nature of the bis-tetraphenyl arsonium hexahalotellurate (IV)

prepared via tellurium tetrachloride and benzene was different to the one prepared from tellurium dioxide. X-ray crystallographic data (powder) show differences, as do the different chemical isome shifts produced by the two specimens. At this point in time, it appears that the anion in the tetraphenyl arsonium salts synthesised from tellurium dioxide is more distorted than the other two, this distortion is apparently dominant in determining the difference in Mössbauer behaviour, therefore, the Donaldson theory may well apply to the ammonium and tetraethyl ammonium salts, and it will apply to any cubic salt, but it need not apply to any non-cubic lattice.

So, as we increase the size of the cation, we infact increase the separation of the anions, this makes the Donaldson picture less favourable, and it now becomes energitically preferable for the lone pair to occupy an orbital with some directional character, which distorts the anion, which reduces the isomer shift in the Mössbauer and complicates the Raman spectrum and also infrared spectrum as demonstrated by Adams.

The influence on the hexabromotellurate is less, a fact which probably reflects the large size of the hexabromotellurate ion (the chemical isomer shift of M_2TeBr_6 is independent of M within experimental error).

It would appear that for the $TeCl_6^{2-}$ series Ph_4As^+ is of the critical size when cubic and non-cubic lattices are of comparable energy.

CHAPTER IV

4. (i). INTRODUCTION :

The organotellurium carboxylates have recently become of interest as synthetic intermediates in organotellurium chemistry. Carboxylate groups may interact in a number of ways with metal centres, they may act as unidentate ligands, symmetrical (or unsymmetrical) bidentate ligands, and they may be bridging groups or even be present as free ions.

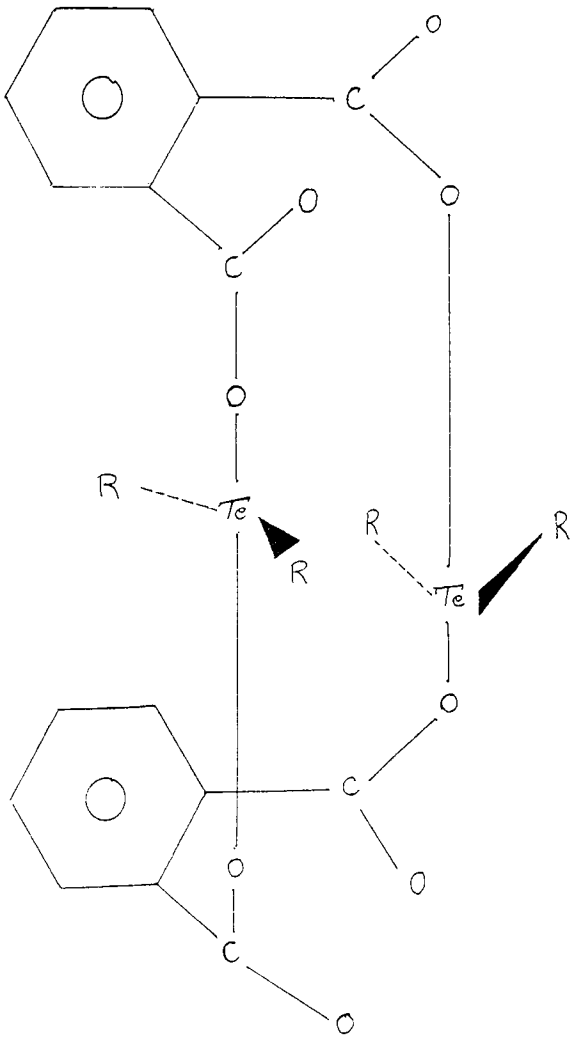
Curtis [85] has given a useful and concise survey of the possibilities for the acetate group in the presence of transition metal compounds and has also discussed the relationship between the mode of interaction and the infrared spectrum.

In the recent years a lot of work has been made about the preparation of organotellurium carboxylate and dicarboxylates. Diaryltellurium dicarboxylates are a well established, though not yet large, class of organotellurium compounds. The carboxylate groups may be introduced by the reaction of diaryltellurium dichloride with the silver carboxylate [86] or by the more recent reported reaction of diaryltellurides with lead ^{IV} tetraacetate [87] .

$$Ar_2TeCl_2 + 2\,Ag\,OOCR \xrightarrow[\text{ref. 4 h.}]{\text{dioxane}} Ar_2Te(OOCR)_2 + 2\,AgCl$$

$$Ar_2Te + Pb(OAC)_4 \xrightarrow[\text{stirr. 4 h}]{\text{Benzene}} Ar_2Te(OAC)_2 + Pb(OAC)_2$$

McWhinnie et. al., [88] have suggested that the structure of diaryltellurium dicarboxylates are based on a four co-ordinate Ψ-trigonal bipyramidal arrangement of groups about the central tellurium atom. Dance [32] has recently synthesised a new type of organo-tellurium carboxylate by reaction of freshly prepared sodium salts of orthophthalic acid and tetrabromo orthophthalatic acid with diaryl-tellurium dichlorides in chloroform. He claimed that these compounds, of the general formula of $R_2Te\ (C_8X_4O_4)$ where X = H, Br, exist as dimers and suggested their structures to be :

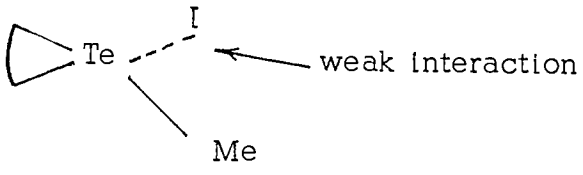


Possible dimeric structure of $R_2Te(C_8H_4O_4)$

Quite recently, Tamagaki [94] has reported the synthesis of a series of diphenyltellurium dicarboxylates by treating diphenyl telluroxide with carboxylic acids or anhydrides in chloroform. It is of considerable interest that he has reported the synthesis of monomeric diphenyltellurium phthalate by the described method.

The synthesis of a new class of organotelluronium compound was carried out in our group. 1-iodo-1-methyl-3,4-benzo-1-telluracyclopentane was prepared by reaction of 3,4-benzo-1-telluracyclopentane with methyl iodide. The conductivity measurements of this compound in DMF and DMSO gave the values of molar conductivity indicating that they are less than 1:1 electrolytes.

The presence of ion-pairing in this compound has been postulated, indicating the possible structure of this telluronium salt to be :



An infra-red spectroscopic study of 1-iodo-1-methyl-3,4-benzo 1-telluracyclopentane showed the presence of the ν (Te-alkyl) frequency at 525 cm^{-1}. The ^1H n.m.r. spectrum of this compound was recorded in deuterated chloroform and the methyl group showed a sharp singlet resonance at $\delta = 2.4$ ppm, with satellite peaks (caused by ^{125}Te-^1H coupling).

Once this type of stable cyclic telluronium iodide has been synthesised, we became interested in converting it to other cyclic telluronium salts and investigate their behaviour in solutions with different polarity.

4. (ii) EXPERIMENTAL :

4. (ii). a. UNSTABLE CARBOXYLATE SALTS

In the following experiments, reactions were carried out in the dark under an inert nitrogen atmosphere, and dry solvents were used.

Reaction of tellurium tetrachloride with benzoic acid

A slight excess of benzoic acid (1.5 g, 0.012 mol.) was added to a solution of tellurium tetrachloride (1.g., 0.003 mol.) in benzene (30 ml.). The mixture was shaken well, and heated to 60-70^{o}C for 4 hrs. after which a condenser was fitted and the temperature was then slowly raised to 10^{o}C higher than the melting point of the acid (121^{o}C) until hydrochloric acid was released. The mixture was then cooled, but no solid was obtained.

Reaction of tellurium tetrachloride with silver benzoate in 1,4 dioxane

Silver benzoate (3.4 g., 0.012 mol.) was added in small portions to a stirred solution of tellurium tetrachloride (lg. 0.003 mol.) in 1,4 dioxane (100 ml.). An exothermic reaction took place and the mixture was refluxed for 4 hrs. Filtration was followed by evaporation of the filtrate and recrystallisation of the crude product gave yellow-whitish solid which was dried over vacuo in P_2O_5 m.p. = 114^{o}C compound (A).

Found : C = 66.7% H = 5.0%

Benzoic acid exp : C = 68.8% H = 4.9%

Reaction of silver benzoate with tellurium tetrachloride in benzene.

Tellurium tetrachloride (1 g., 0.003 moles) was dissolved in benzene (50 ml), and silver benzoate (3.4 g., 0.012 moles) was added in small portions. An exothermic reaction occurred, the mixture, then refluxed for 4 hrs. Filtration followed by evaporation of the filtrate and recrystallization from benzene gave a white crystal which dried in vacuo. m.p = 115°C.

	Found:	C = 66.4%	H = 4.7%
Benzoic acid exp. :		C = 68.8%	H = 4.9%

Reaction of silver acetate with tellurium tetrachloride.

A 1:4 molar ratio mixture of tellurium tetrachloride and silver acetate in benzene was refluxed for 4 hrs. The mixture was cooled and filtered, evaporation of the filtrate gave a white solid which was dried in vacuo.

Reaction of lead tetraacetate with tellurium tetrachloride.

Tellurium tetrachloride (0.5 g., 0.001 moles) in benzene (25 ml.) was added to a well stirred freshly prepared solution of lead tetraacetate in benzene (30 ml.). The mixture was stirred for an additional 4 hrs. Filtration followed by evaporation of the yellow solution. The solid was dried under vacuo. The infra-red data were not informative.

Reaction of tellurium tetrachloride with silver-benzoate in the absence of solvent.

In a glove box fitted with a great amount of P_2O_5, tellurium tetrachloride (0.003 moles. 1.g), and silver benzoate (0.012 moles, 3.4 g) were mixed and well ground. The mixture, then was heated until it melted and dry benzene (50 ml.) was added and the mixture was stirred for 10 min. Filtration followed by evaporation of the solvent, gave a white solid which was collected and dried over P_2O_5 in vacuo. m.p = 112°C, i.r. spectrum was obtained.

Reaction of bis-p-ethoxyphenyltellurium trichloride with silver benzoate in the absence of solvent

A 1:3 molar ratio of bis-p-ethoxyphenyl tellurium trichloride and silver benzoate was mixed and ground well. The mixture, then was heated to melting and dry benzene was added and stirred for 10 min. After filtration and evaporation of the solvent, the resulting solid was collected and dried in vacuo. m.p. = 116°C, the i.r. spectrum was recorded.

Methyldiphenyltelluronium carboxylate :

PREPARATION OF DIPHENYLTELLURIDE

McWhinnie, [9] has recently reported the synthesis of diphenyl-telluride by a modification of the method of Rheinboldt and Petragnani [10].

To an ethereal solution (100 ml.) of a Grignard reagent synthesised from bromobenzene (26.3 ml.) and magnesium (6.1 g.) was added benzene (100 ml.). The temperature of the solution was lowered to 0^{o} and vigorous stirring was commenced. Tellurium tetrachloride (13.5 g.) in benzene (200 ml.) was added slowly to the stirred solution after which the reaction mixture was refluxed for 2 hrs.

The cooled solution was added to a saturated ammonium chloride solution (300 ml.) and the organic layer was separated and washed with distilled water and dried. The solvent was removed and treated with bromine in carbon tetrachloride. The diphenyl tellurium dibromide was reduced employing hydrazine and pure diphenyl telluride was obtained.

No free tellurium was produced by this method while it was reported as side product by Rheinboldt. [10] .

PREPARATION OF METHYL DIPHENYL TELLURONIUM IODIDE

Dry diphenyl telluride (4 g.) and dry methyl iodide (10-12 ml) were mixed and left for 2 hrs. in a flask, previously nitrogen flushed.

The yellow crystals were filtered and dried over P_2O_5. The solid was placed in a conical flask with some distilled water and heated at $60^{o}C$ for half an hour.

Recrystallisation from water gave white crystals of methyl diphenyltelluronium iodide which melted at 116°C (lit: 124°).

Found : C% = 36.9 H% = 4.1

$C_{13}H_{13}ITe$ requires : C% = 36.9 H% = 3.1

* * * * * * * *

Reaction of diphenyl methyl telluronium iodide with silver benzoate

Methyl diphenyl telluronium iodide (1g., 0.002 mole), silver benzoate (0.458 g, 0.002 mole) and distilled water (50 ml) were placed into a round-bottom flask fitted with a condenser and magnet bar. The mixture was stirred for 30 min. at room temperature which was followed by four hrs. refluxing.

The yellow precipitate was filtered hot and the filtrate concentrated and cooled to give a white solid which was collected and dried over P_2O_5 in vacuo. m.p. = 105°C. The results have been tabulated in Table (4).

Reaction of methyl diphenyl telluronium iodide with silver acetate.

a. Methyl diphenyltelluronium iodide (0.96 g., 0.002 moles), silver acetate (0.37 g., 0.002 moles) and 50 ml. of distilled water were placed in a flask fitted with a condenser and magnet bar. The

mixture was stirred for 4 hrs. at room temperature in which time an exothermic reaction took place. The yellow precipitate of silver iodide was collected as the solution was hot. The filtrate was concentrated and on a further standing no solid was observed. The water was evaporated using rotary evaporator in which an oily residue was left. The infra-red spectrum of this material was recorded and shown to be similar to that of diphenyl-telluride.

b. The same quantity of methyldiphenyl telluronium iodide, silver acetate and distilled water were placed in a flask fitted with a consenser and magnet bar, and the mixture was refluxed for 4 hrs. in which the precipitate of silver iodide was collected and the evaporation of the filtrate left an oily residue, shown by the infra-red spectrum to be diphenyl telluride.

SYNTHESIS OF METHYL DIPHENYL TELLURONIUM (o-METHOXY BENZOATE)

A. Methyl diphenyl telluroinium iodide (0.5 g., 0.001 mol.), freshly prepared o-methoxy silver benzoate (0.259 g., 0.001 mol.) and distilled water (50 ml.) were placed into a round-bottom flask, equipped with magnet bar and condenser. The mixture was refluxed for 2 hrs. after which the yellow precipitate of silver iodide was filtered and the filtrate was evaporated using high vacuum in low temperature. A pale yellow liquid was obtained, the i.r. spectrum was recorded.

B. An equimolar mixture of methyl diphenyl telluronium iodide and o-methoxy silver benzoate were placed into a flask, distilled water (50 ml.) was added and the mixture was stirred for 3 hrs. at room temperature. The yellow precipitate of silver iodide was collected and the filtrate was placed into a large vessel and left in a non-vacuum desiccator containing a large quantity of P_2O_5. A white solid was collected after a few weeks, m.p = 98°C. The results are tabulated in Table (4).

SYNTHESIS OF METHYL DIPHENYL TELLURONIUM (m-NITRO BENZOATE)

Methyl diphenyl telluronium iodide (0.4 g., 0.001 mol.), freshly prepared m-nitro silver benzoate (0.33 g., 0.001 mol.) and distilled water (50 ml.) were placed into a round-bottom flask. The mixture was stirred for 2 hrs. at room temperature, after which the yellow precipitate of silver iodide was filtered and the filtrate was left in a non-vacuum desiccator containing P_2O_5.

The off-white solids of methyl diphenyl telluronium m-nitro benzoate was collected after 2 weeks. m.p. = 110°C. (Table 4).

4. (ii). b. STABLE CARBOXYLATE SALTS

PREPARATION OF 1-IODO-1-METHYL-3,4-BENZO-1-TELLURACYCLOPENTANE

3,4-benzo-1-telluracyclopentane (prepared according to the literature

13) (2 g., 0.004 mol.) and dry methyl iodide (10 ml.) were placed into a flask flushed with nitrogen. An exothermic reaction took place and the precipitates of cyclic telluronium iodide were collected after 2 hrs. and recrystallised from a mixture solution of water and ethanol (3:1). The white glistening crystals of 1-iodo-1-methyl-3,4 benzo-1-telluracyclopentane were collected and dried in vacuum over P_2O_5, m.p. = 192°C.

SYNTHESIS OF 1-METHYL-3,4-BENZO-1-TELLURACYCLOPENTANE BENZOATE

$C_9H_{11}TeI$ (1 g., 0.002 mol.) silver benzoate (0.458 g., 0.002 mol.) in distilled water (50 ml.) were stirred for 30 min. at room temperature and then heated under reflux for 2 hrs, after which the hot solution was filtered and the yellow precipitate of silver iodide was collected. The solution was evaporated at low temperature. The white solids of 1-methyl 3,4-benzo-1-telluracyclopentane benzoate were collected and dried in vacuum. m.p. = 155°C.

SYNTHESIS OF 1-METHYL-3,4-BENZO-1-TELLURACYCLOPENTANE CHLORIDE

This compound was prepared by an ion exchange reaction employing silver chloride. IRA 400 resin (2 g.), exchanged with Cl^-, was added to an aqueous solution (50 ml.) of 1-iodo-1-methyl-3,4 benzo-1-telluracyclopentane. The mixture was stirred for 6 hrs. after which

the resin was removed the solution was evaporated in high vacuum to afford white crystals of m.p. = 220°C.

SYNTHESIS OF BIS-TRIPHENYLTELLURONIUM o-PHTHALATE

Triphenyltelluronium chloride (5.5g., 0.014 mol.) in chloroform (50 ml.) was treated with a freshly prepared sodium salt of ortho-phthalic (1.5 g., 0.007 mol.). The reaction mixture was shaken for 48 hrs. at room temperature after which filtered to remove the sodium chloride and unreacted sodium phthalate. The solution was washed with water and dried. The organotellurium carboxylate was recovered from the filtrate and recrystallised from petroleum ether/benzene, m.p. = 199-200°C.

Attempts to extend the above method to other acids (iso- and terephthalic) failed and triphenyltelluronium chloride was obtained.

* * * * * * * *

4. (ii). c. ARYL TELLURONIUM FLUORIDE COMPOUNDS :

PREPARATION OF TRIPHENYLTELLURONIUM FLUORIDE :

Two different methods were used to prepare this compound.

A. Conversion of aryltelluronium chloride to fluoride by ion exchange using silver fluoride.

B. Neutralisation of telluronium hydroxide by hydrofluoric acid.

PREPARATION OF SILVER FLUORIDE :

Silver carbonate (2.5 g.) and distilled water (25 ml.) were placed into a platinum vessel and hydrofluoric acid (10 ml.) was added dropwise until no yellow precipitate was formed. This solution was neutralised by addition of silver carbonate in small portions, and the colourless filtrate was evaporated at low temperature. The yellow precipitate of silver fluoride was collected and dried in vacuo.

A: Ion exchange method :

Ion exchange resin (1 g.) in chloride form was treated with an aqueous solution of silver fluoride. The mixture was stirred for 6 hrs. at room temperature, after which the resin was treated with an aqueous solution of triphenyltelluronium chloride. The mixture was stirred for 6 hrs. and the filtrate was evaporated to afford white solid of triphenyltelluronium fluoride, m.p. = 178 - 180^{o}C. The results have been tabulated in Table (4).

B. Reaction of triphenyltelluronium chloride with silver oxide:

Triphenyl telluronium chloride (3.3g., 0.0086 mol.), silver oxide (1.0g., 0.0043 mol.) and distilled water were placed into a conical flask and stirred for 2 hrs. at room temperature after which the

chloride was converted into the base. The base solution was neutralised with hydrofluoric acid and the white solid of triphenyl-telluronium fluoride was collected after evaporation of the solution, m.p. = 180°C (Table 4).

The extension of the above experiments to afford the synthesis of methyldiphenyl telluronium fluoride yielded the hydrolysed product (i.r.).

4. (iii). RESULTS :

1. SOLUBILITY :

The tellurium carboxylate compounds are soluble in DMSO and DMF , and with the exception of methyl diphenyl telluronium (m-nitro benzoate), they are soluble in methanol, ethanol and chloroform. All the telluronium carboxylate salts were found to be insoluble in carbon tetrachloride and benzene.

2. CONDUCTIVITY MEASUREMENTS :

The molar conductivity of each tellurium carboxylate was determined in dimethyl sulfoxide and dimethylformamide. Conductivities were also measured as a function of concentration (p .85, 86).

3. INFRARED SPECTRA :

The infra-red spectra of all tellurium carboxylate salts in the range of 4000-250 cm^{-1} in KBr disc and 4000 - 200 cm^{-1} in NuJol mull were recorded and presented on pages 98, 106, 109, 111, 116.

The infra-red solution spectra of the compounds in chloroform were obtained in the range of 4000-200 cm^{-1} and shown on pages 100, 108. The initial spectra of telluronium salts indicate a sharp band at 1600 cm^{-1} due to the ν_{as} (CO) frequency in which decays and replaced by another band at 1710 cm^{-1}.

1-methyl-3,4-benzo-1-telluracyclopentane benzoate spectrum showed two sharp bands at 1600 and 1365 cm^{-1} which remained constant. The infra-red spectrum of this compound in chloroform solution was obtained and observed frequencies were similar to the data obtained from the solid state.

4. ^1H n.m.r. SPECTRA

The ^1H n.m.r spectrum of each tellurium carboxylate compound was recorded in a suitable solvent and the results are as follows :

A. Methyl diphenyl telluronium benzoate :

The ^1H n.m.r. spectrum of this compound was obtained in both deuterated chloroform and dimethyl sulfoxide (d_6). In chloroform, the initial spectrum consisted of a singlet methyl resonance at δ = 2.96 ppm (relative to TMS) with satellites corresponding to ^1H - ^{125}Te coupling (J = 24 HZ), this singlet was diminished and replaced by another resonance at δ = 3.85 ppm.

In dimethyl sulfoxide (d_6) this methyl resonance was observed at δ = 2.86 ppm with satellites which vanished and replaced by another resonance at δ = 3.85 ppm.

B. Methyl diphenyl telluronium (o-methoxy benzoate).

The initial spectrum of this compound in deuterated chloroform showed a methyl resonance at δ = 2.98 ppm with satellites which was substituted by another resonance at δ = 3.85 ppm.

C. Methyl diphenyl telluronium (m-nitro benzoate).

The ^{1}H n.m.r. spectrum of this compound in DMSO (d_6) initially consisted of a methyl resonance at δ = 2.8 ppm with satellites which was replaced by another resonance at δ = 3.9 ppm.

D. 1-methyl-3,4-benzo-1-telluracyclopentane benzoate.

This is a new class of stable organotelluronium carboxylate compound which was proved by n.m.r. spectroscopy. The ^{1}H n.mr. spectra of this compound were obtained in deuterated chloroform and dimethyl sulfoxide (d_6). There are two types of aliphatic resonances in this compound, one is due to the methyl group and the other due to the presence of two methylene groups. The position of the methyl resonance both in chloroform and dimethyl sulfoxide remained unchanged. The spectrum of this compound in $CDCl_3$ indicated a singlet resonance at δ = 2.12 ppm with satellites due to methyl group and four resonances at δ = 3.7, 3.95, 4.4 and 4.65 ppm due to the methylene groups. In DMSO (d_6), the spectrum showed a resonance at δ = 2.0 ppm due to the methyl group and resonances at δ = 3.8, 4.05, 4.2 and 4.45 are due to the methylene groups.

5. Molecular weight measurements :

The molecular weight measurement of each telluronium salt was carried out in chloroform and the results are shown on page 92.

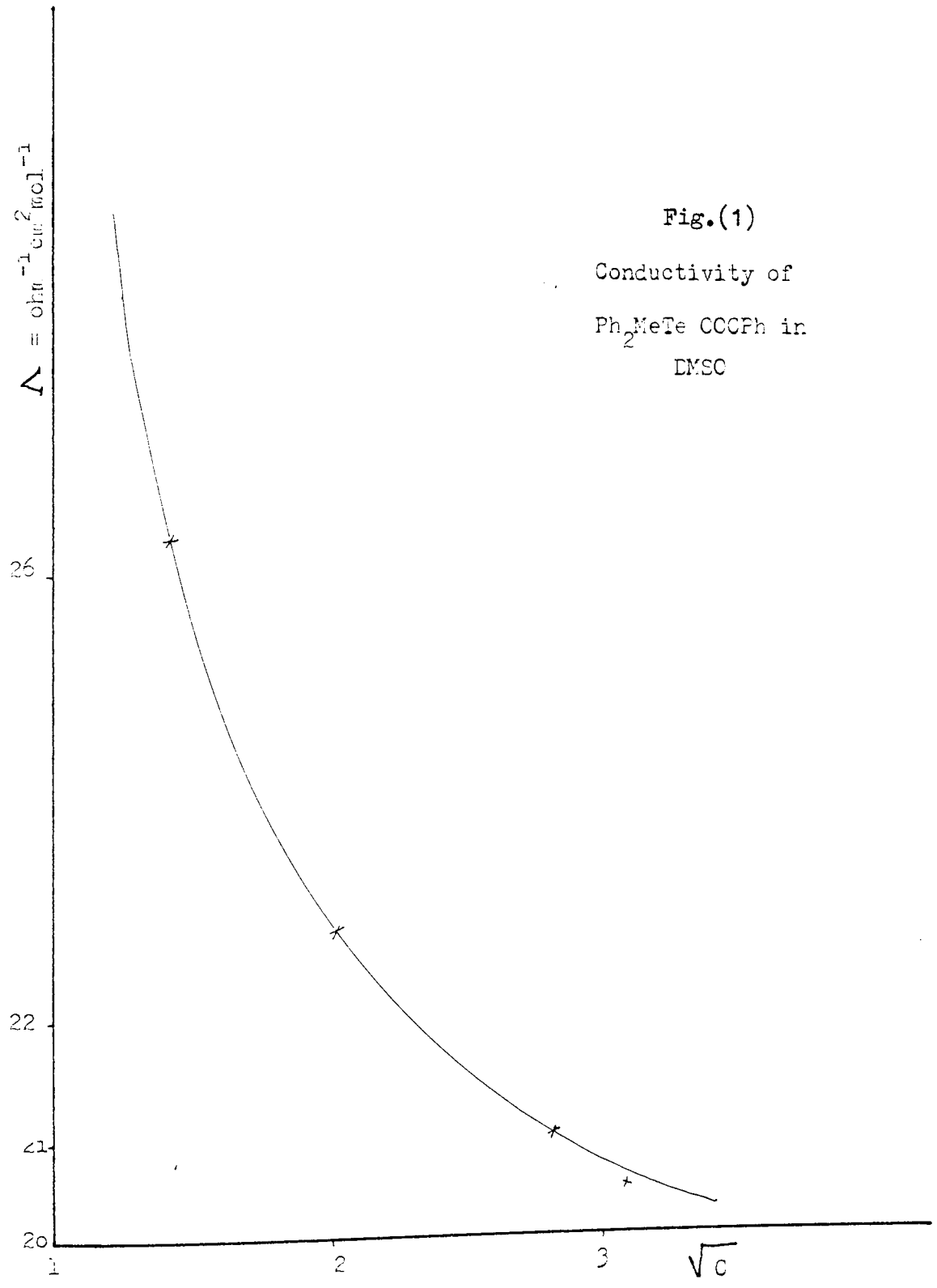


Fig.(1)

Conductivity of

$Ph_2MeTe\ CCCPh$ in

DMSO

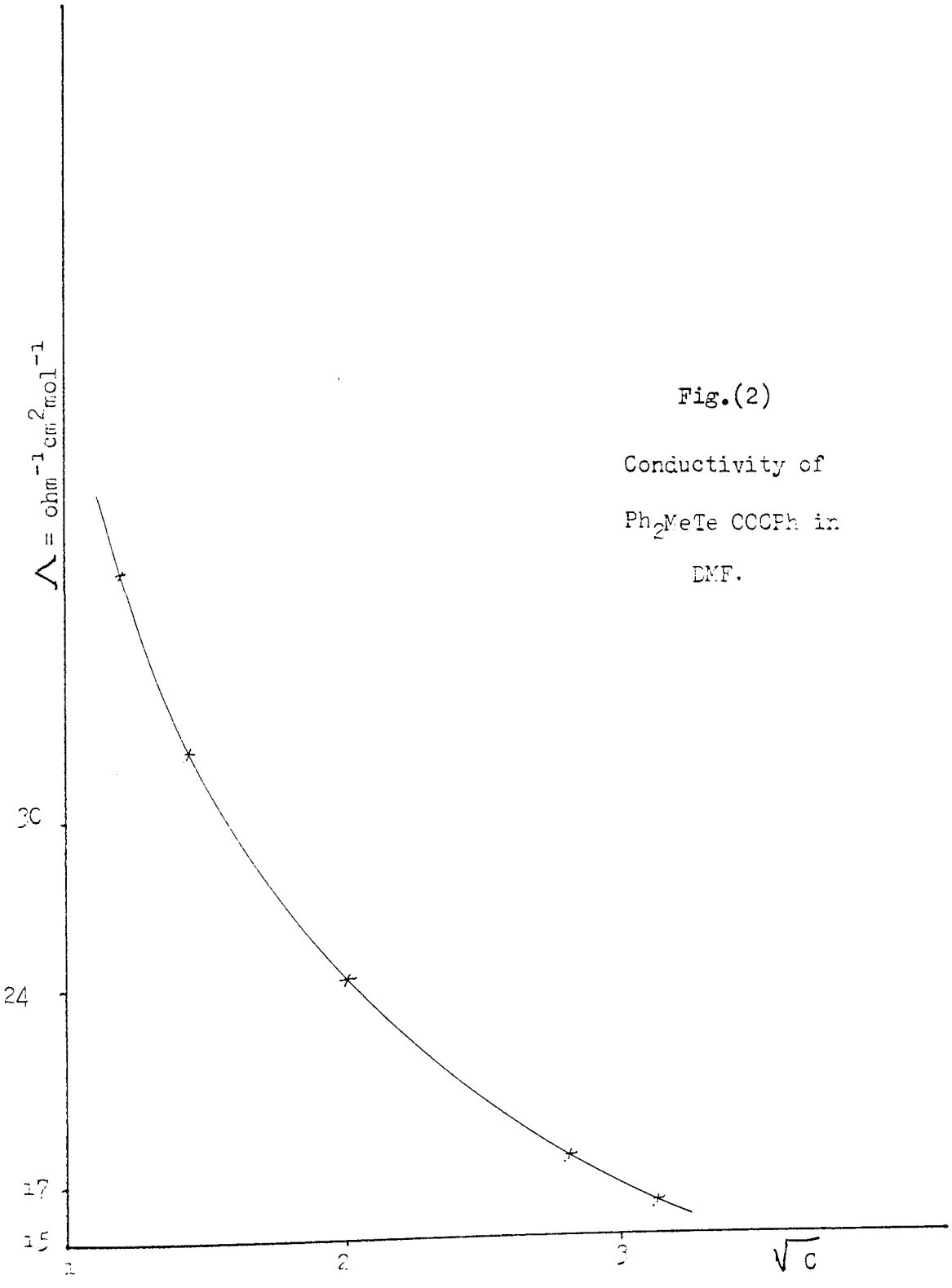


Fig.(2)

Conductivity of

Ph_2MeTe CCCPh in

DMF.

TABLE (1) Solubility of some organotellurium compounds.

COMPOUND	SOLVENT	
	Chloroform	DMSO
Ph_2Me Te $OOCC_6H_4OCH_3$	Very soluble	Soluble
Ph_2 Me Te $OOC C_6H_5$	Very soluble	Soluble
Ph_2 Me Te $OOC C_6H_4NO_2$	Insoluble	Soluble
$C_6H_4(CH_2)_2$ Me Te $OOC C_6H_5$	Soluble	Soluble
$C_6H_4(CH_2)_2$ Me Te I	Slightly soluble	Soluble
$C_6H_4(CH_2)_2$ Me Te Cl	Insoluble	Soluble

TABLE (2)

Conductivity measurements on solutions of some organotellurium carboxylate salts.

COMPOUND	Solvent/ molar conductivity ($ohm^{-1}\ cm^{2}\ mol^{-1}$)	
	DMSO	DMF
$Ph_2\ Me\ Te\ OOC\ C_6H_4\ OCH_3$	25.1	38.2
$Ph_2\ Me\ Te\ OOC\ C_6H_5$	20.1	15.7
$Ph_2\ Me\ Te\ OOC\ C_6H_4\ NO_2$	23.3	32.1
$C_6H_4\ (CH_2)_2\ Me\ Te\ OOC\ C_6H_5$	21.9	17.5

Solutions were 10^{-3} molar.

TABLE (3) Infra-red data of some new organotellurium compounds.

Solution spectra were obtained in chloroform.

Compound	ν (Co) as cm^{-1}	ν (Co) as cm^{-1}	Δ cm^{-1}	(Te - Me) solid cm^{-1}
$Ph_2MeTeOOCC_6H_4OCH_3$	1600	1385	215	520
	1600	1385	215	
$Ph_2MeTeOOCC_6H_5$	1600	1390	210	-
	1600	1380	220	
$Ph_2MeTeOOCC_6H_4NO_2$	1605	1345	260	515
	-	-	-	
$C_6H_4(CH_2)_2MeTeOOCC_6H_5$	1600	1365	235	530
	1600	1385	215	

TABLE (4)

COMPOUND	FOUND			CALCULATED		
	C%	H%	X%	C%	H%	X%
$Ph_2MeTeOOC\,C_6H_4OCH_3$	56.30	4.70	-	56.20	4.70	-
$Ph_2MeTeOOC\,C_6H_5$	57.60	4.40	-	57.50	4.3	-
$Ph_2MeTeOOC\,C_6H_4NO_2$	50.00	3.50	4.3*	51.80	3.60	3.0
$C_6H_4(CH_2)_2MeTeOOCC_6H_5$	51.60	4.60	-	52.30	4.30	-
$C_6H_4(CH_2)_2MeTeCl$	36.00	3.0	14.50	38.40	3.9	12.61
Ph_3TeF	55.90	3.80	-	57.20	4.00	-

Analytical data for some new organotellurium salts.

* = N%

TABLE 5

The positions of the methyl resonances of some organo tellurium salts in ^1H n.m.r. spectra.

COMPOUND	Solvent	Resonance (1) ppm	Resonance (2) ppm
Ph_2 Me Te OOC C_6H_4 OCH_3	$CDCl_3$	2.98	3.85
Ph_2 Me Te OOC C_6H_5	$CDCl_3$	2.96	3.85
Ph_2 Me Te OOC C_6H_4 NO_2	DMSO (d_6)	2.8	3.9
C_6H_4 $(CH_2)_2$ Me Te OOC C_6H_5	$CDCl_3$	2.12	-
C_6H_4 $(CH_2)_2$ Me Te I	$CDCl_3$	2.42	-
C_6H_4 $(CH_2)_2$ Me Te Cl	DMSO (d_6)	1.9	-
Me OOC C_6H_5	$CDCl_3$	3.85	-

P.s. Resonance (1) is due to the peak immediately after dissolving. Resonance (2) corresponds to the peak which eventually replaced the first peak.

TABLE (6)

Molecular weight of some organotelluronium compounds

Compound	M (monomer)	M(dimer)	M(obs)
$Ph_2MeTeOOCC_6H_5$	417	834	622
$C_6H_4(CH_2)_2$ MeTe I	372	744	741
$C_6H_4(CH_2)_2MeTeOOCC_6H_5$	367	734	731

TABLE 7

Species	m/e	Relative intensity
$Ph_2MeTeO_2CPh^+$	420	4
Ph_2TeMe^+	299	6.5
Ph_2Te^+	284	100
$PhTeMe^+$	222	20
$PhTe^+$	207	100
Ph_2^+	154	100
$C_6H_5CO_2Me^+$	136	100
$PhCO_2^+$	121	21
Ph^+	77	100
$C_4H_3^+$	51	8

151 metastable for :

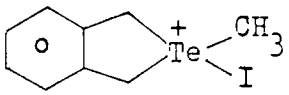
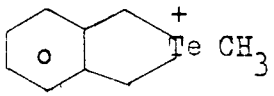
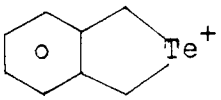
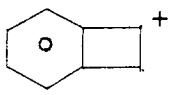
$$Ph_2Te^+ \longrightarrow PhTe^+$$

83.5 metastable for:

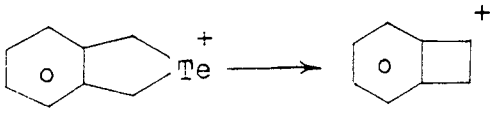
$$Ph_2Te^+ \longrightarrow \emptyset_2^+$$

Mass spectral data for methyl diphenyl telluronium benzoate relative to ^{130}Te, ^{16}O, ^{12}C, ^{1}H.

TABLE (8)

SPECIES	m/e	Relative Intensity
$C_{17}H_{19}ITe^+$	480	3
	376	10
	249	57
	234	100
Ph Te^+	207	100
	104	100
Ph^+	77	50
Me I^+	142	100
I^+	127	60

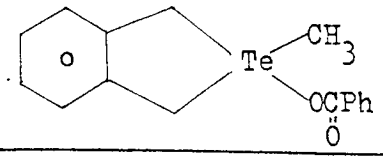
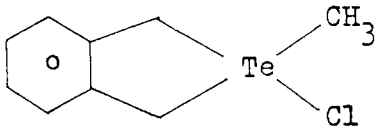
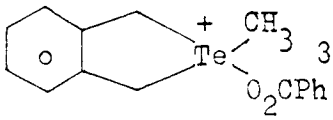
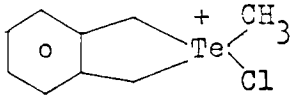
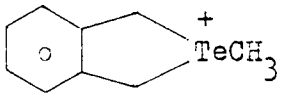
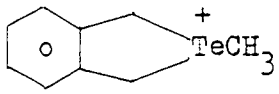
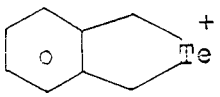
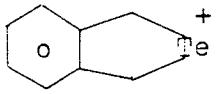
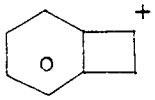
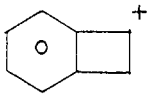
46.2 metastable for



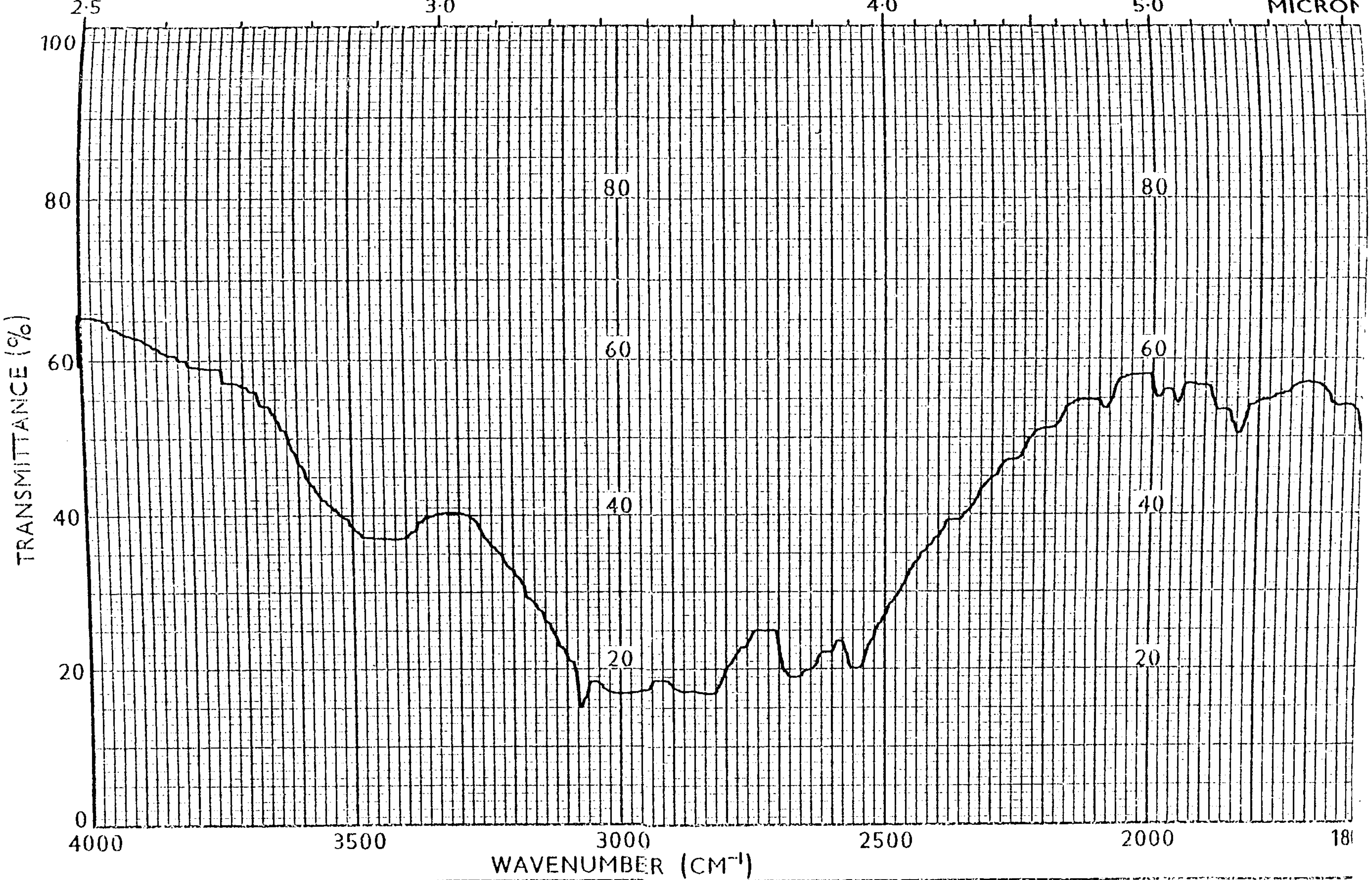
57 metastable for

Mass spectra data for cyclic-telluronium iodide.

TABLE (9)

					
Species	m/e	Rel.Int.	Species	m/e	Rel.Int.
$C_{24}H_{24}O_2Te^+$	470	83	$C_{17}H_{19}Cl\ Te^+$	388	4
	370	58		284	29
	249	8		249	30
	234	100		234	100
$Ph\ Te^+$	207	38	$Ph\ Te^+$	207	33
	104	100		104	100
Ph^+	77	3	Ph^+	77	55
Me OCPh (O)	136	17	Me Cl	50	33
$PhCO_2^+$	121				

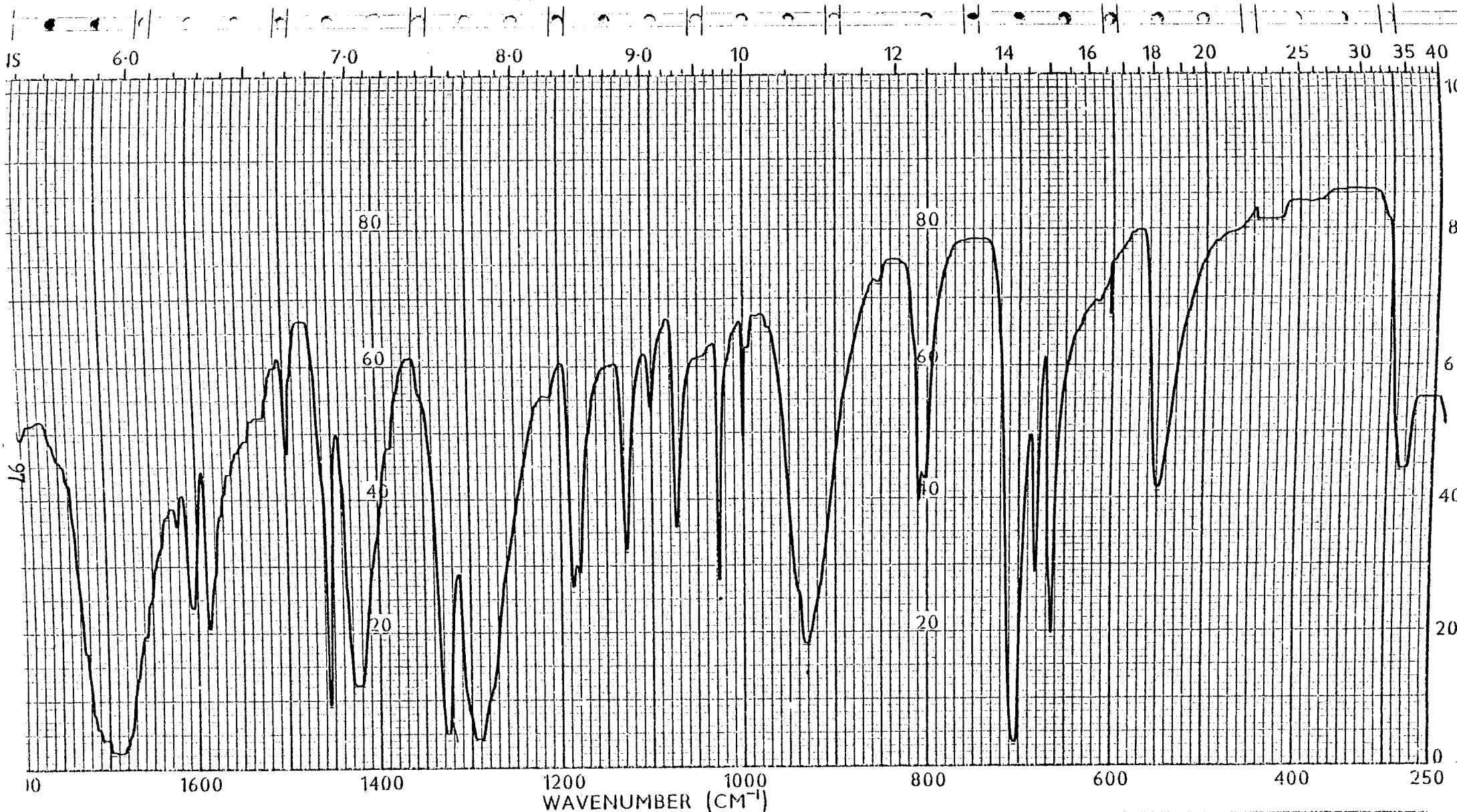
Mass spectra data for two telluronium salts.



Te Cl_4+ Ph COOAg
in
Benzene

Fig.(3)

SOLVENT
CONCENTRATION
CELL PATH
REFERENCE

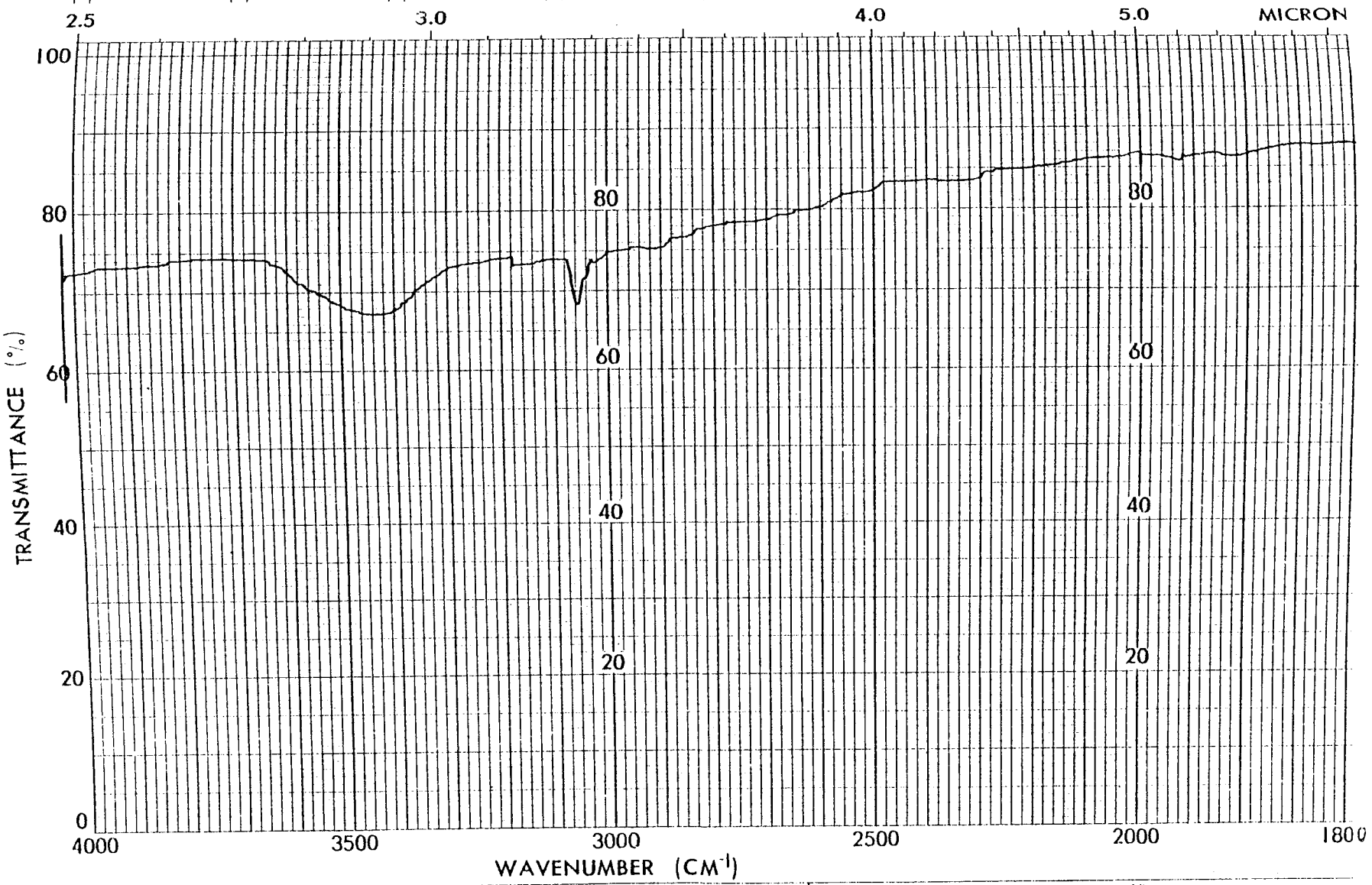


REMARKS

$Te Cl_4$ + Ph COOAg
in
Benzene (cont.)

SCAN SPEED Medium.
SLIT Standard.
RPK/219/1002 457-5001
Intek

OPERATOR V.H. Cheetham.
DATE 15th Jan 1968
REF. No 1/553.



SAMPLE I.R. spectrum of $Ph_2MeTeOOCPh$

Fig.(4)

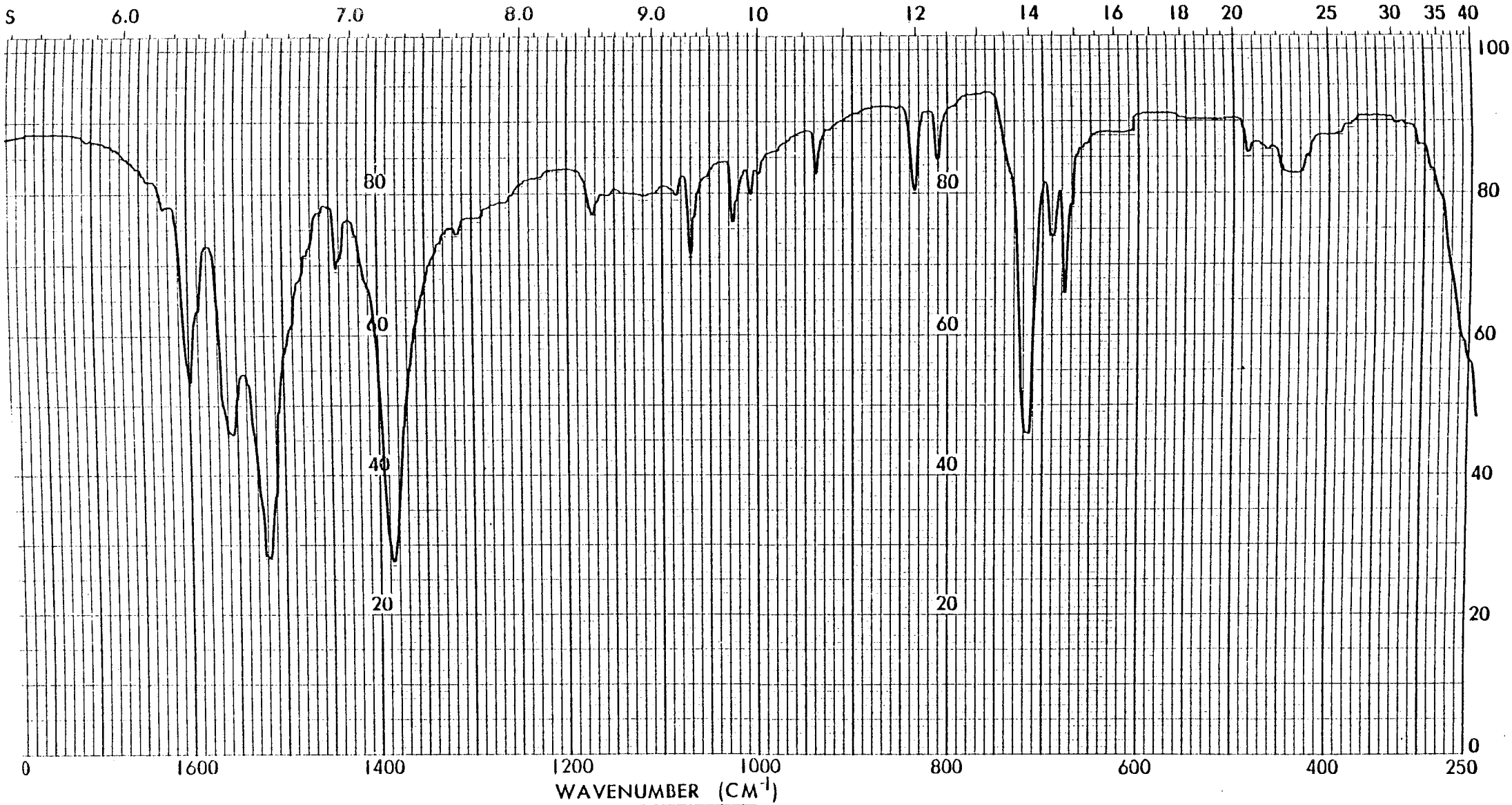
ORIGIN J. Mallaki.

SOLVENT KBr.

CONCENTRATION less than 1.0%

CELL PATH 13 s"/m. dia. disc

REFERENCE Air.



REMARKS

I.R. spectrum of

$Ph_2Me\ Te\ OOCPh$ (cont.)

SCAN SPEED Medium

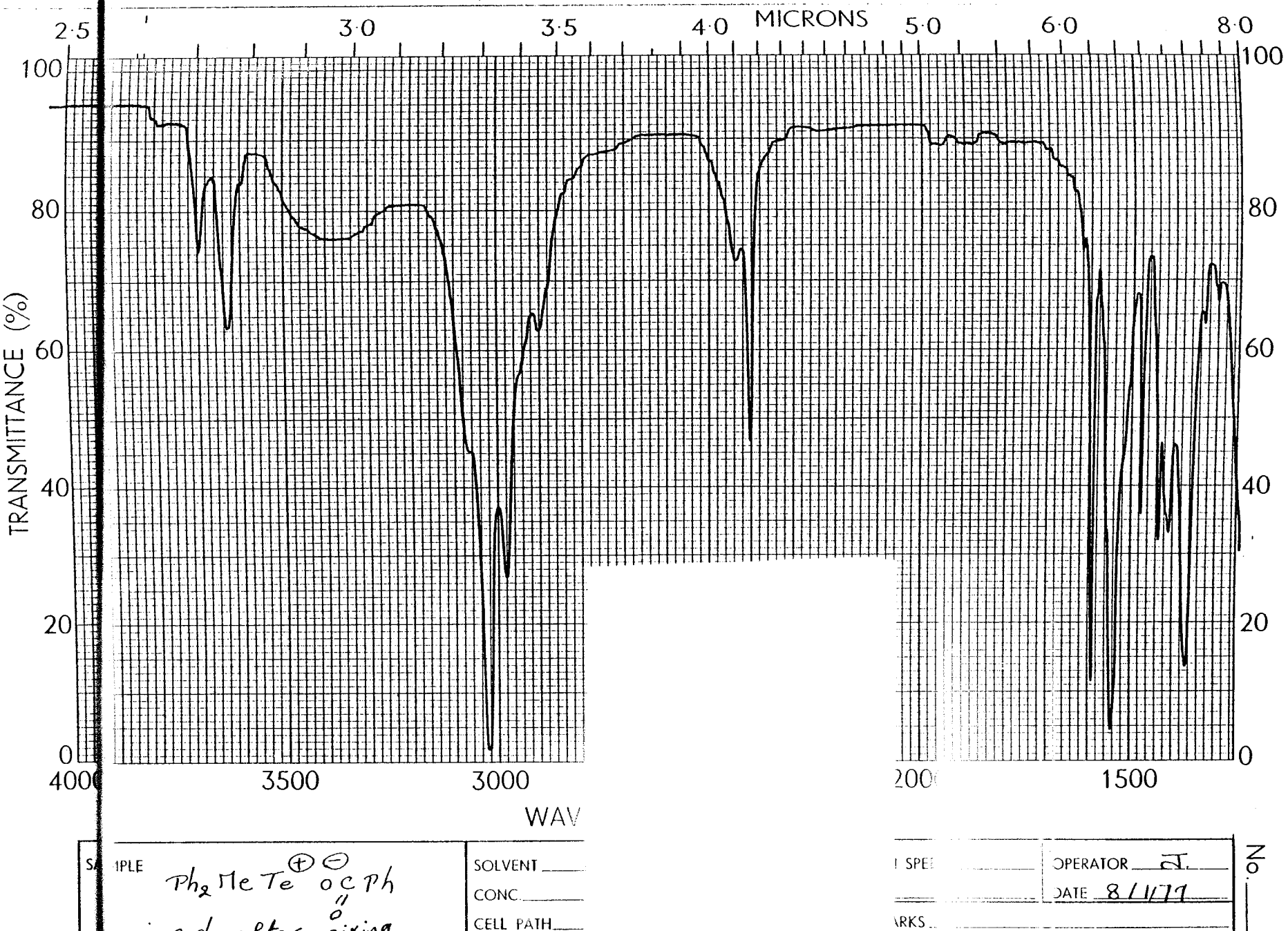
SLIT Standard.

No 457-5001

OPERATOR V.M. Clinton.

DATE 30th November 1978

REF. No 1/1086



SAMPLE $Ph_2MeTe^{\oplus}\,^{\ominus}OC(=O)Ph$ imm'd. after mixing. Fig.(5)

SOLVENT

CONC.

CELL PATH

REFERENCE

ORIGIN

OPERATOR J.

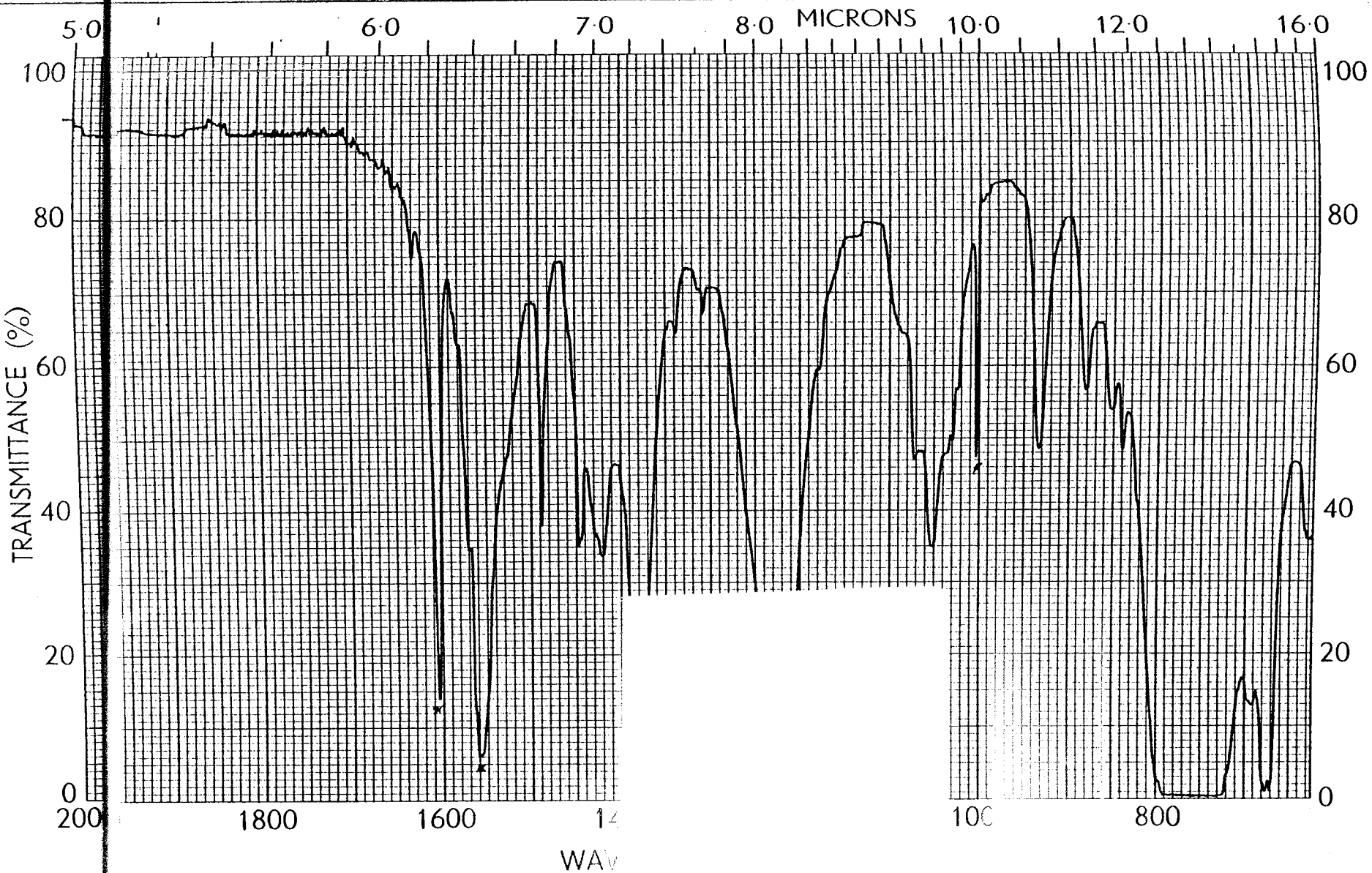
DATE 8/1/79

MARKS

No.

PA No. 237E - 1034/C2

ENSITI COATINGS LTD., COULSDON, SURREY 4782



SAMPLE $Ph_2Me\,Te^{\oplus}\,O\,C_7H_{15}$ after mixing immed. (Cont.)

SOLVENT

CONC.

CELL PATH

REFERENCE

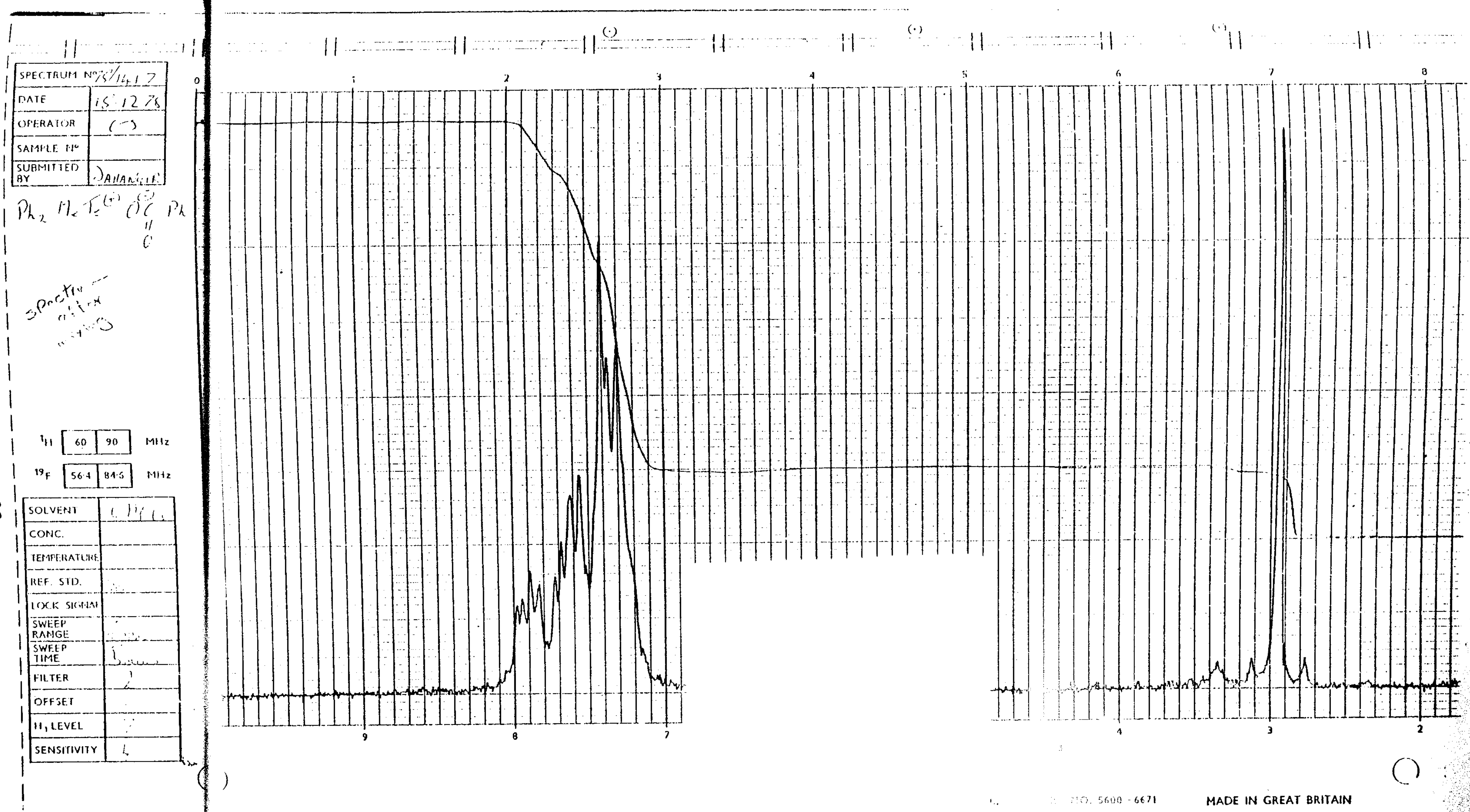
OPERATOR J.

DATE 8/1/79

No.

PART No. 237E - 1035/C2

SENSITIVE COATINGS LTD., COULSDON, SURREY 4783



ig.(6) The ^{1}H n.m.r. spectrum of Ph_2Me TeOOCPh in $CDCl_3$ immed. after dissolving.

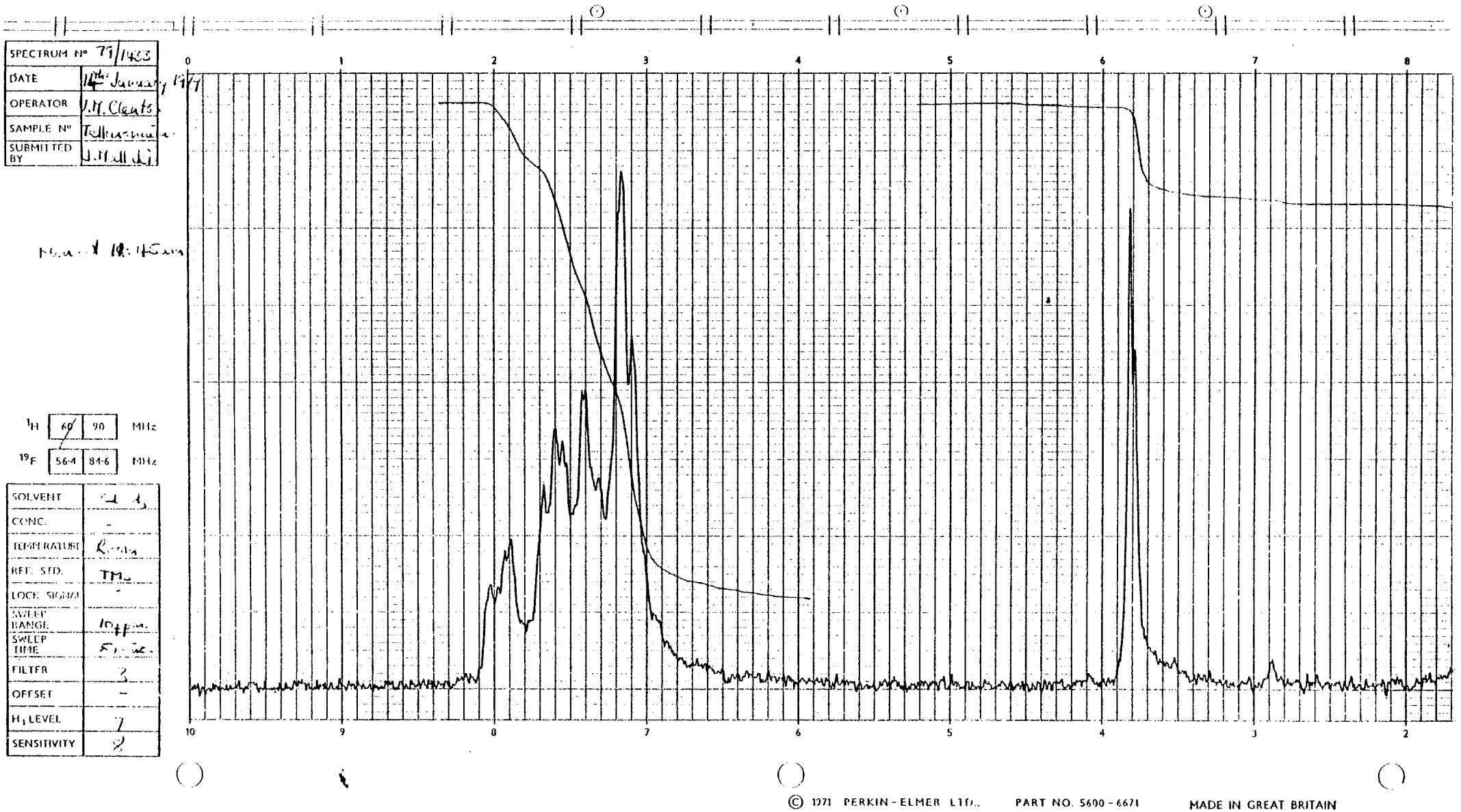


Fig.(7) The ^{1}H n.m.r. spectrum of $Ph_2MeTe\ OOCPh$ in $CDCl_3$ after 5 days.

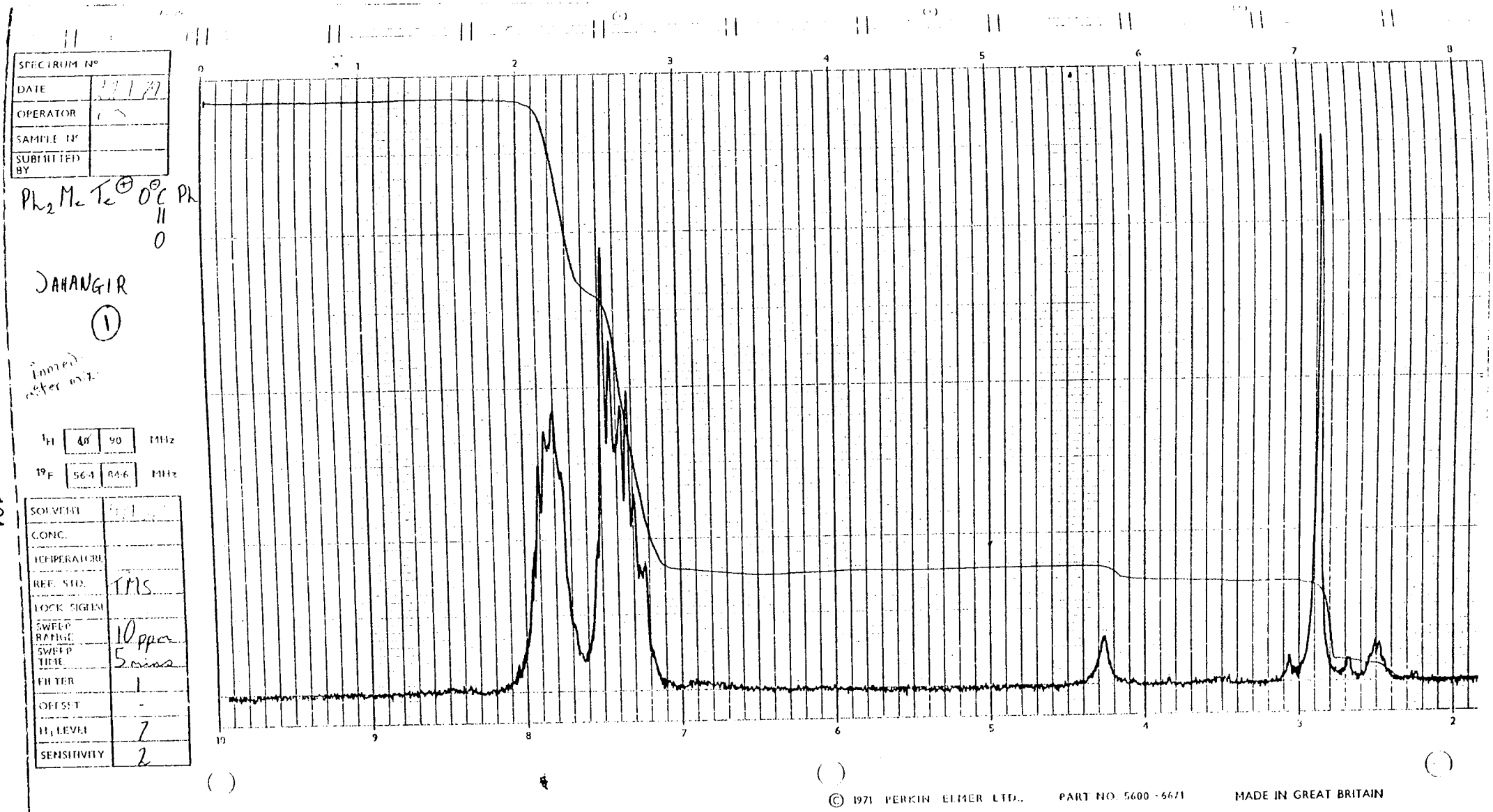


Fig.(8) The ^1H n.m.r. spectrum of $Ph_2MeTe\ OOCPh$ in DMSO (d_6) immed. after dissolving.

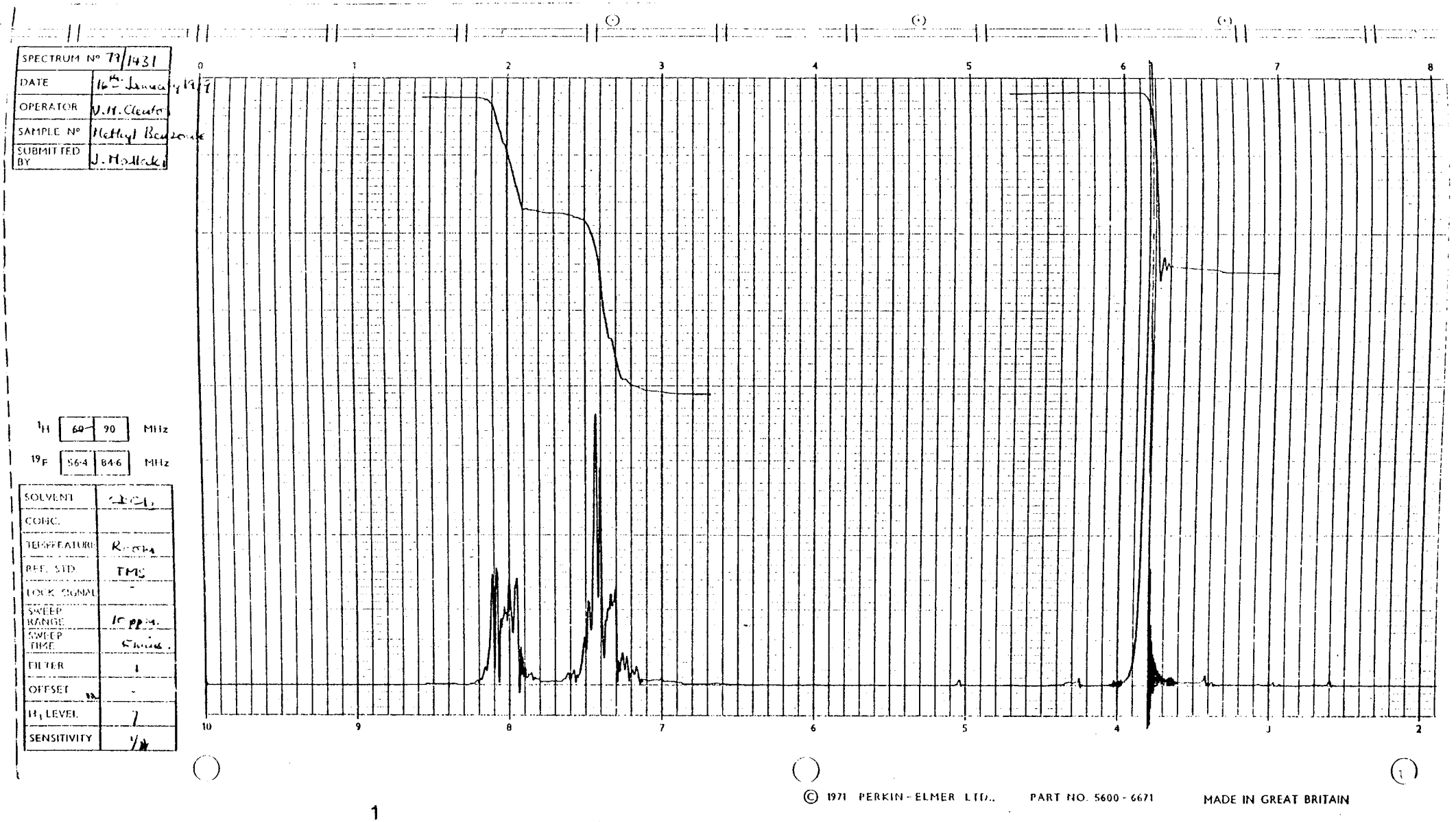
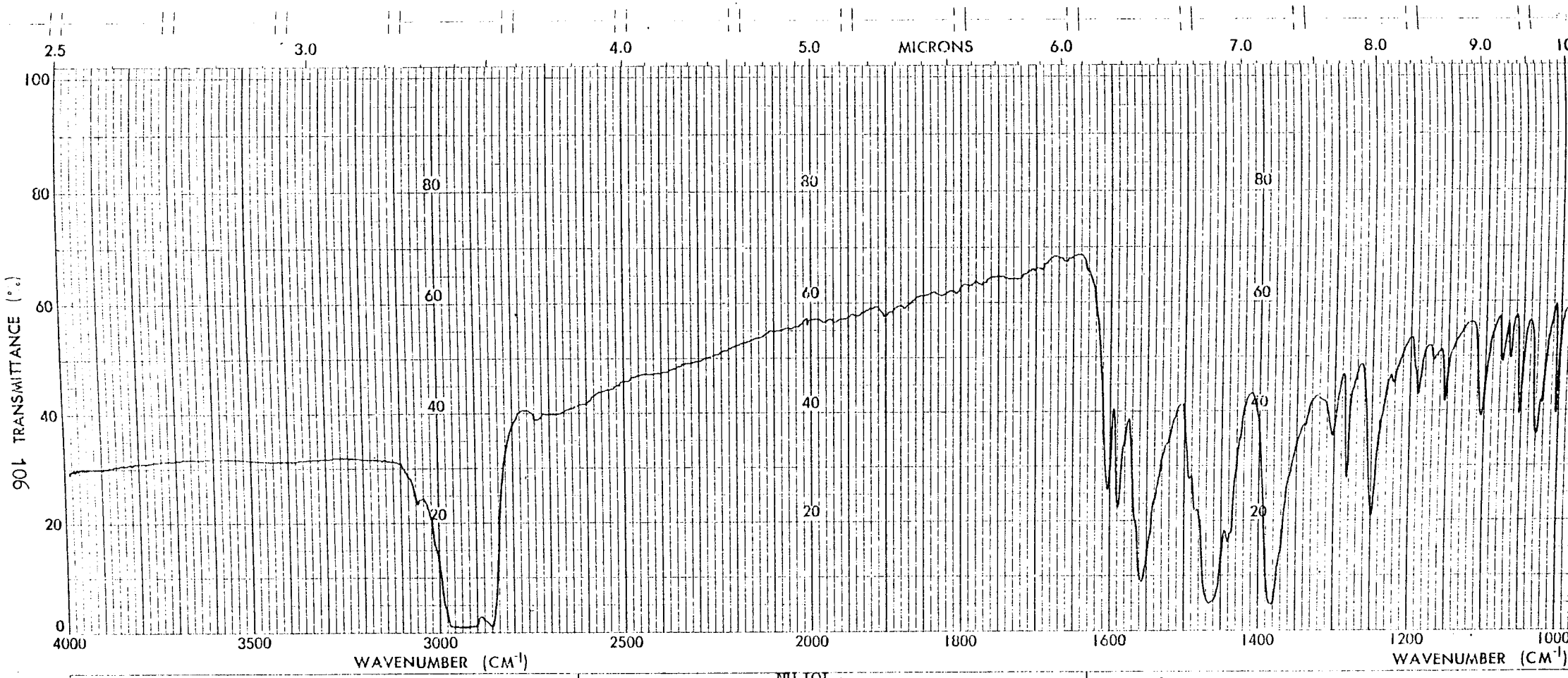
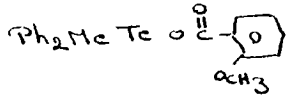


Fig.(9) The ^{1}H n.m.r. spectrum of methyl benzoate in $CDCl_3$



SAMPLE Ph_2MeTe  Fig.(10)

ORIGIN

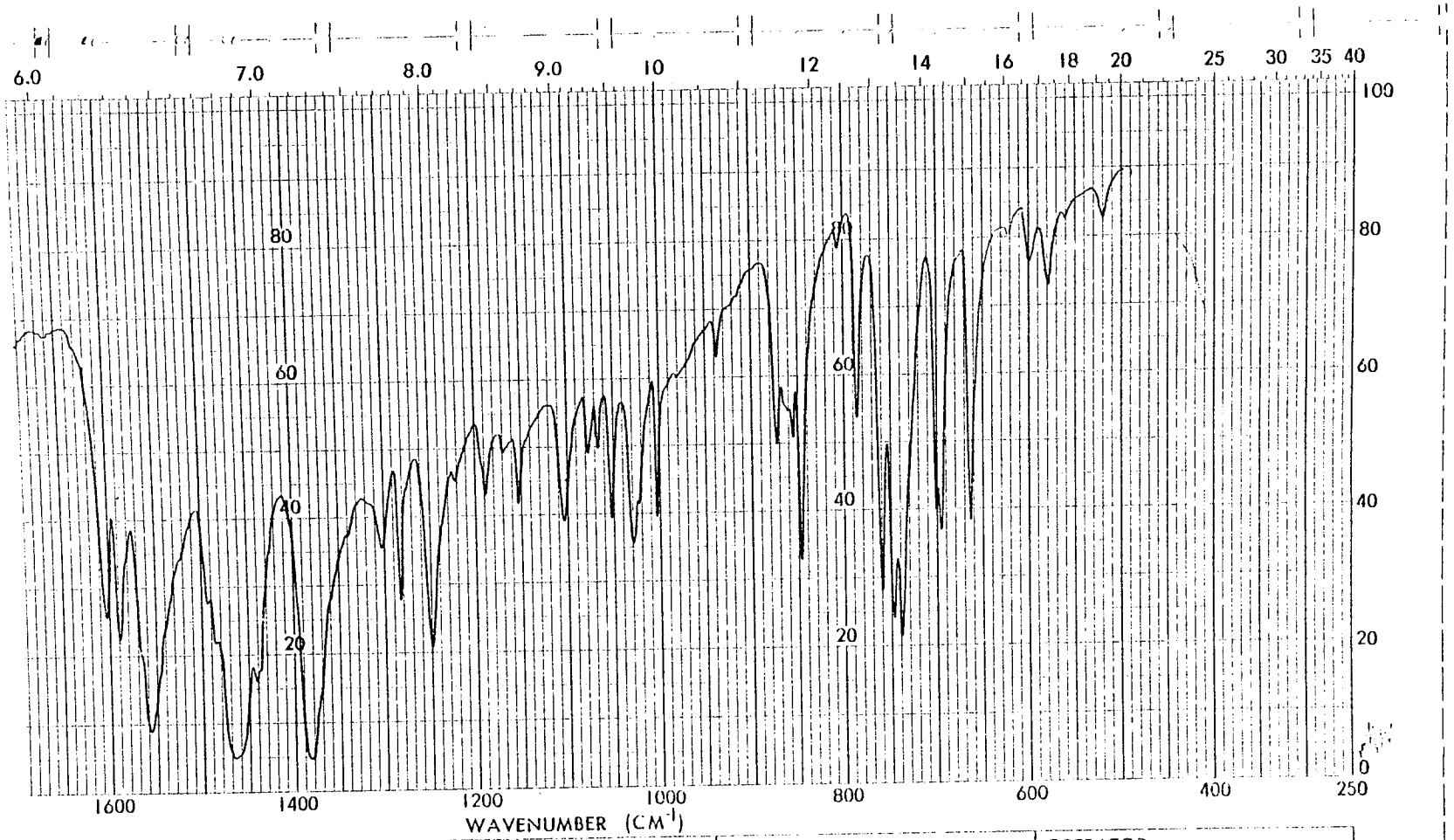
SOLVENT NUJOL

CONCENTRATION

CELL PATH

REFERENCE

REMARKS



REMARKS

I.R. spectrum of

$Ph_2MeTe\ OOCC_6H_4OCH_3$ in NUJOL (cont.)

SCAN SPEED

SLIT

No 457-5001

OPERATOR

DATE

REF. No

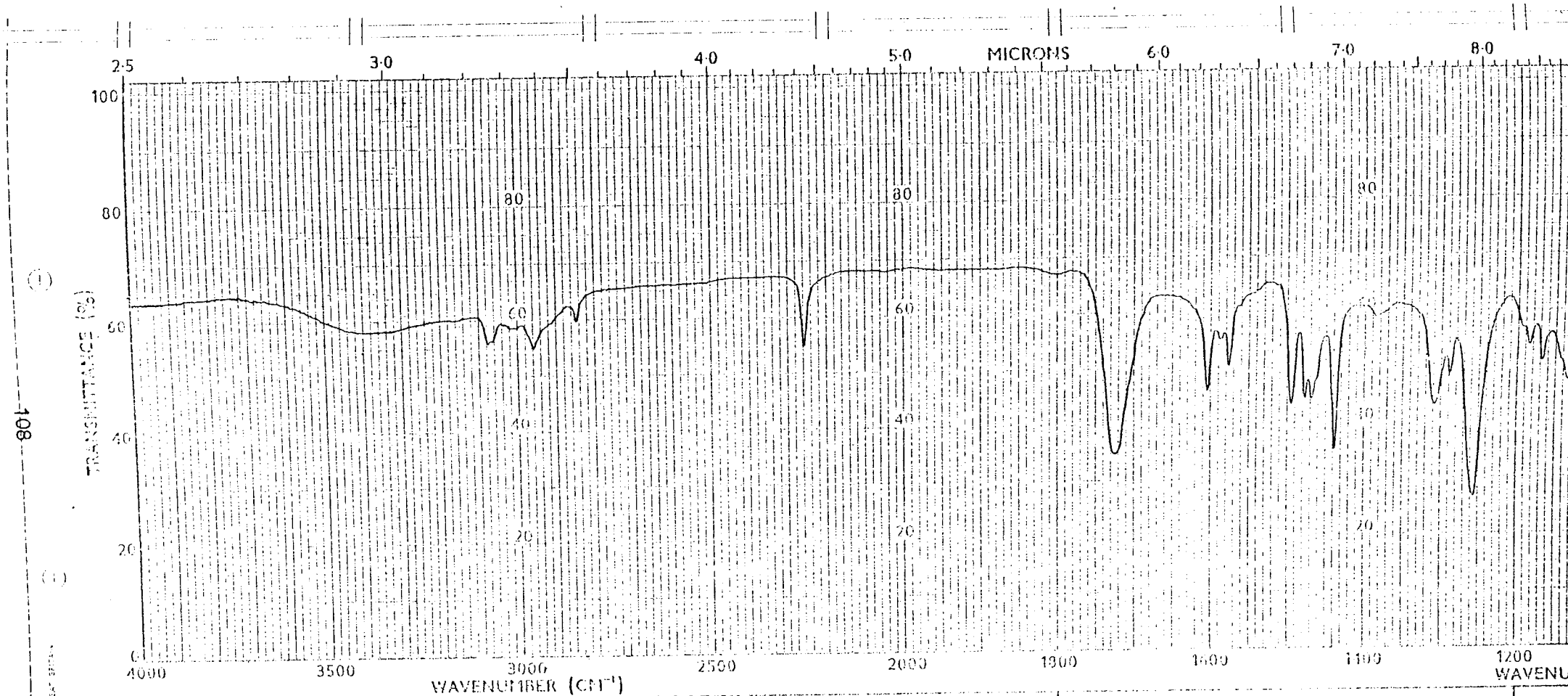

2·5
3·0
4·0
5·0
MICRONS
6·0
7·0
8·0
100
80
60
40
20
0
TRANSMITTANCE (%)
4000
3500
3000
2500
2000
1900
1600
1100
1200
WAVENUMBER (CM⁻¹)
SAMPLE
I.R. spectrum of $Ph_2MeTe\ OOCC_6H_4OCH_3$ in $CDCl_3$ after 3 days.
ORIGIN
SOLVENT
CONCENTRATION
CELL PATH
REFERENCE
REMARKS
SCAN
SLIT
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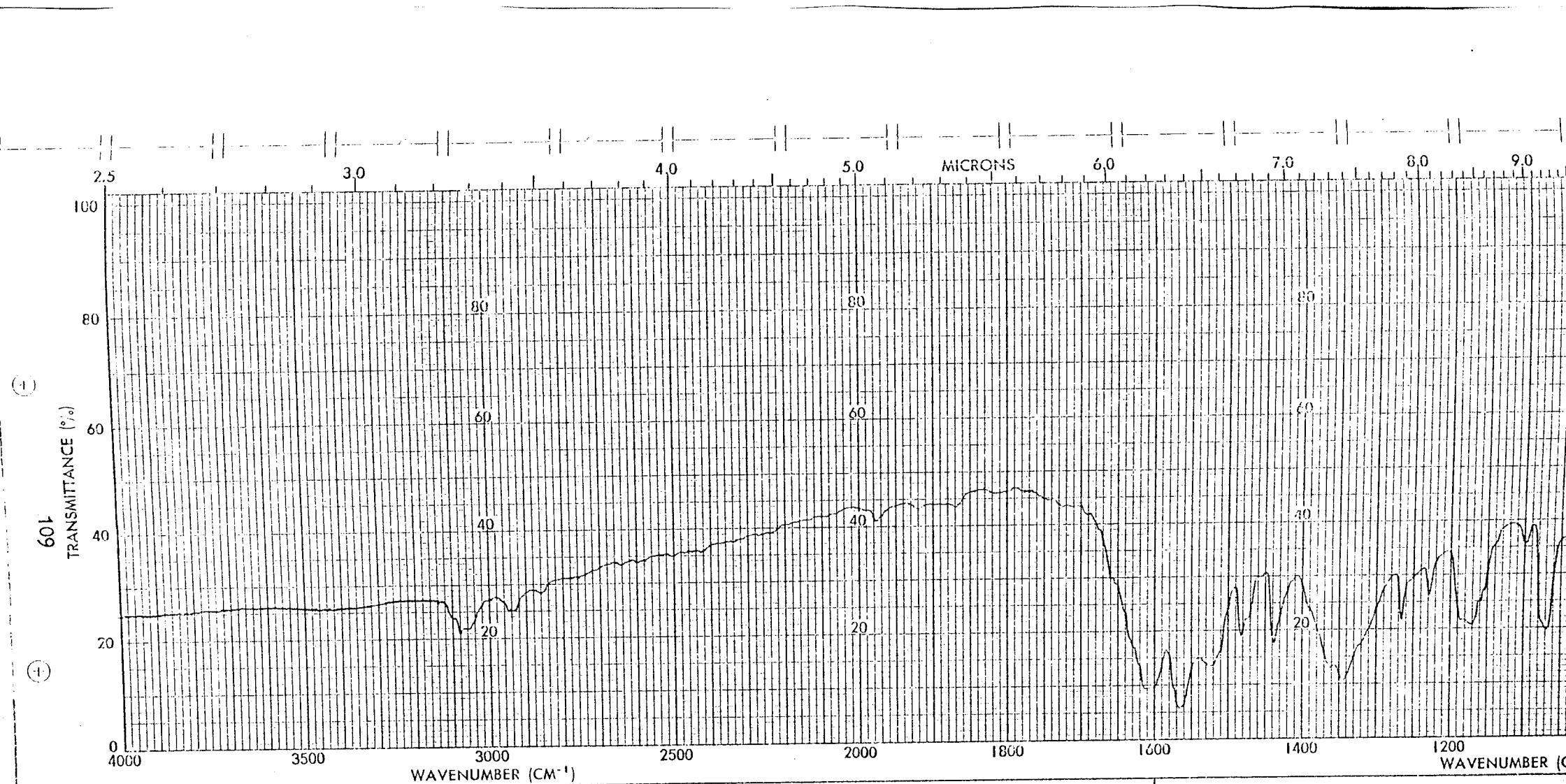
Fig.(11)



109

SAMPLE $Ph_2MeTc\,O\,C(=O)\,C_6H_4\,NO_2$ Fig.(12)

ORIGIN

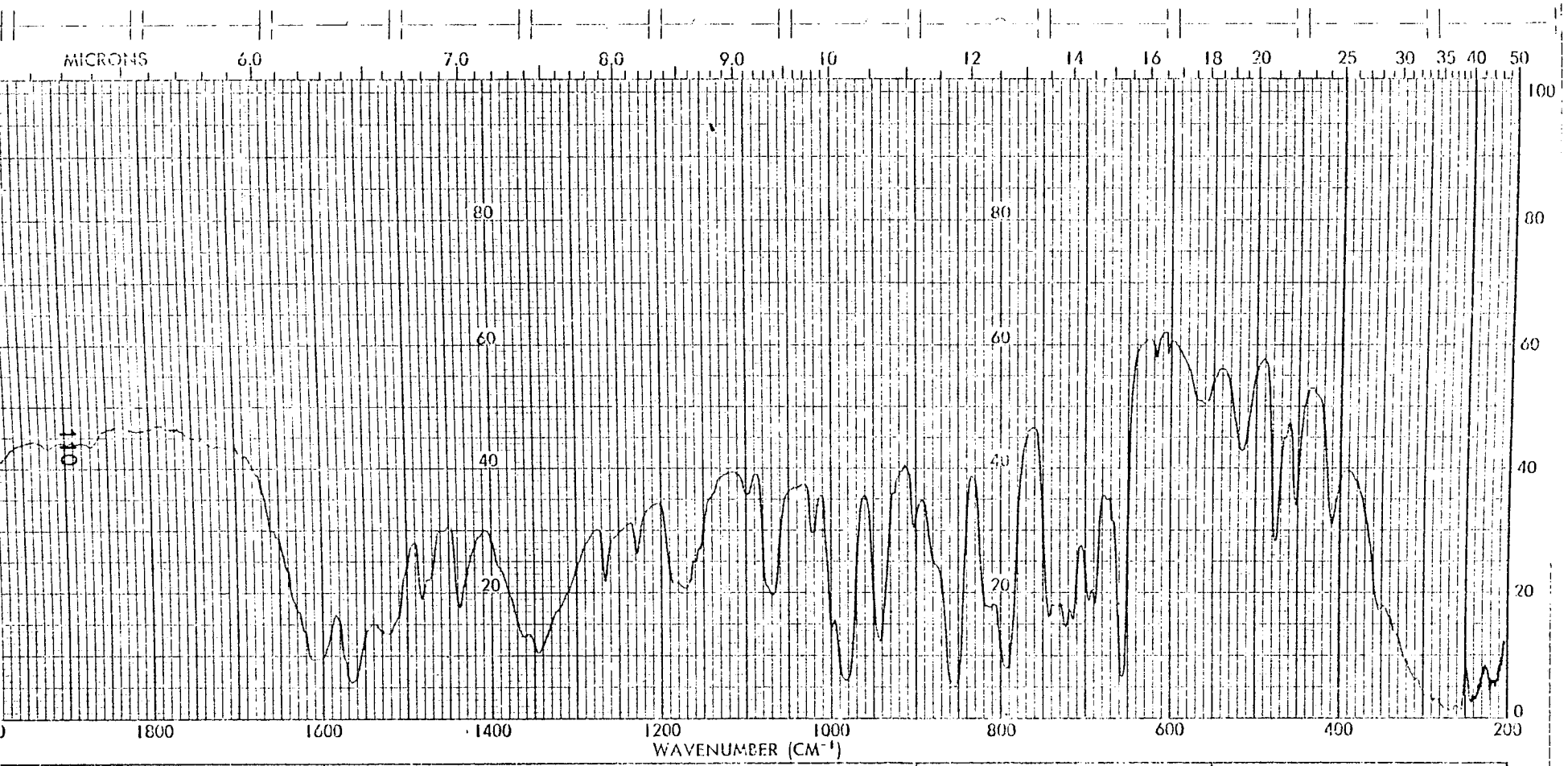
SOLVENT Hexachlorobutadiene

CONCENTRATION

CELL PATH

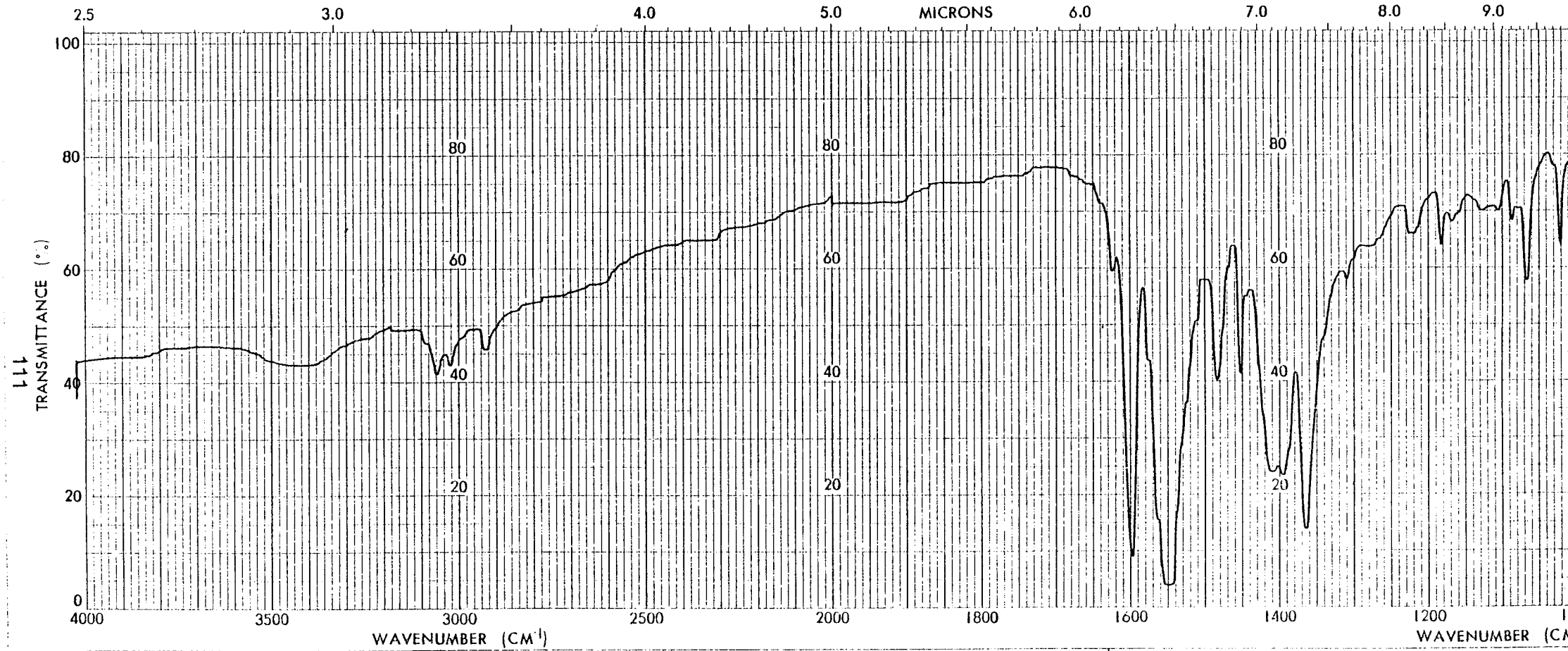
REFERENCE

REMARKS

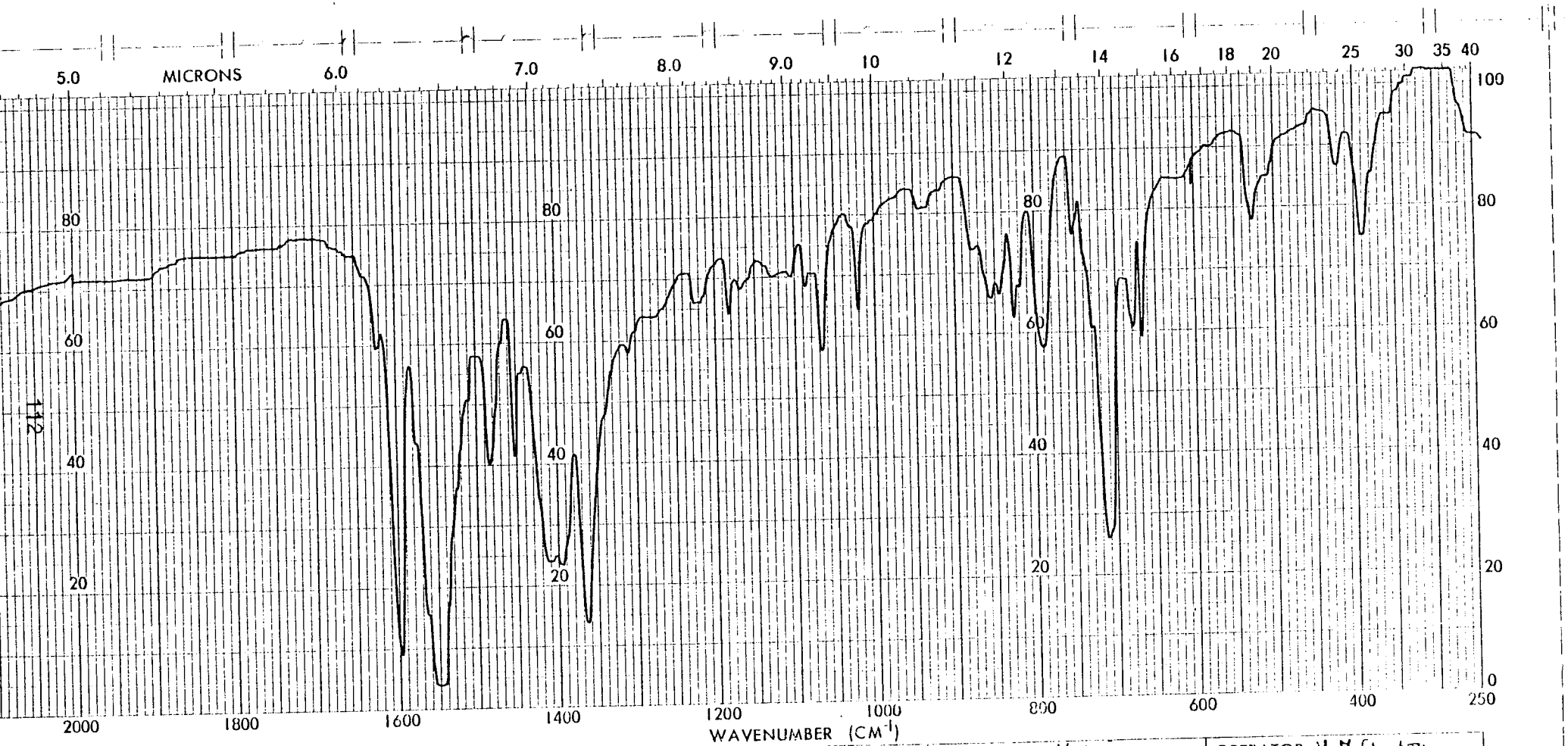


butadiene	REMARKS I.R. spectrum of $Ph_2MeTe\ OOCC_6H_4NO_2$ in Hexachlorobutadiene (cont.)	SCAN MODE SLIT TIME CONSTANT PART No. 457 - 5133	OPERATOR DATE REF. No

Infra



SAMPLE Infra-red spectrum of Cyclic telluronium benzoate.	SOLVENT KBr.	REMARKS
ORIGIN J. Hallaki. Fig.(13)	CONCENTRATION approx. 1.0%	
	CELL PATH 13.0 mm. dia. disc	
	REFERENCE Air.	



KBr.
approx. 1:200.
13.0 mm. dia. disc
Air.

REMARKS Infra-red spectrum of
Cyclic telluronium benzoate (cont.)

SCAN SPEED Medium
SLIT Standard.

No 457 - 5001

OPERATOR V.M. Clinton.
DATE 30th October 1971

REF. No 1/2197

SPECTRUM N°	79/1664
DATE	29-10-79
OPERATOR	CJ
SAMPLE N°	[illegible]
SUBMITTED BY	✓

CYC

DAY 1.

113

^1H	60	90	MHz
^{19}F	56.4	84.6	MHz

SOLVENT	$CDCl_3$
CONC.	-
TEMPERATURE	-
REF. STD.	TMS
LOCK SIGNAL	-
SWEEP RANGE	10 ppm
SWEEP TIME	5 mins
FILTER	1
OFFSET	-
H_1 LEVEL	7
SENSITIVITY	4

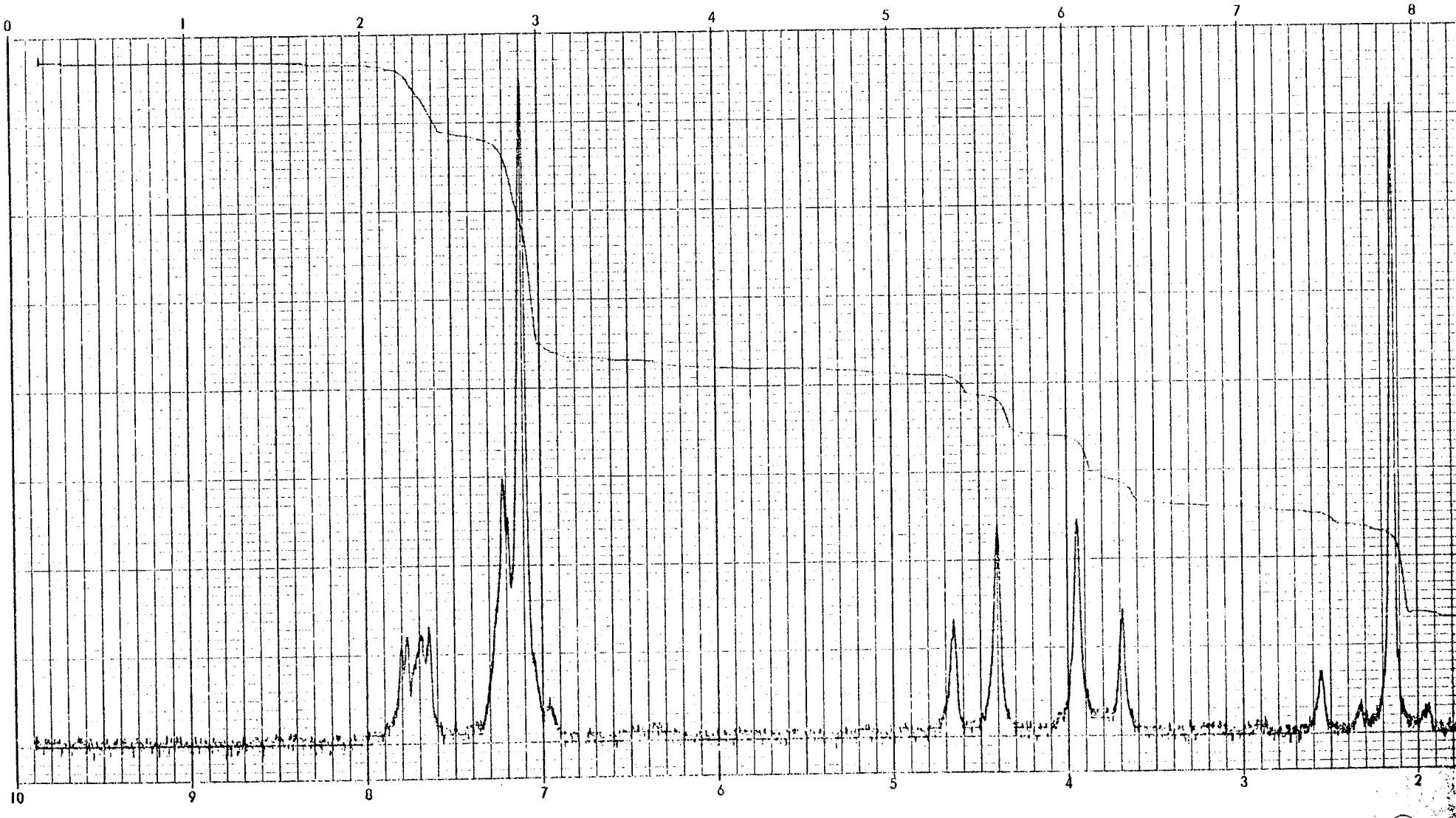


Fig.(14) The ^1H n.m.r. spectrum of Cyclic telluronium benzoate in $CDCl_3$.

No. 5600-6671

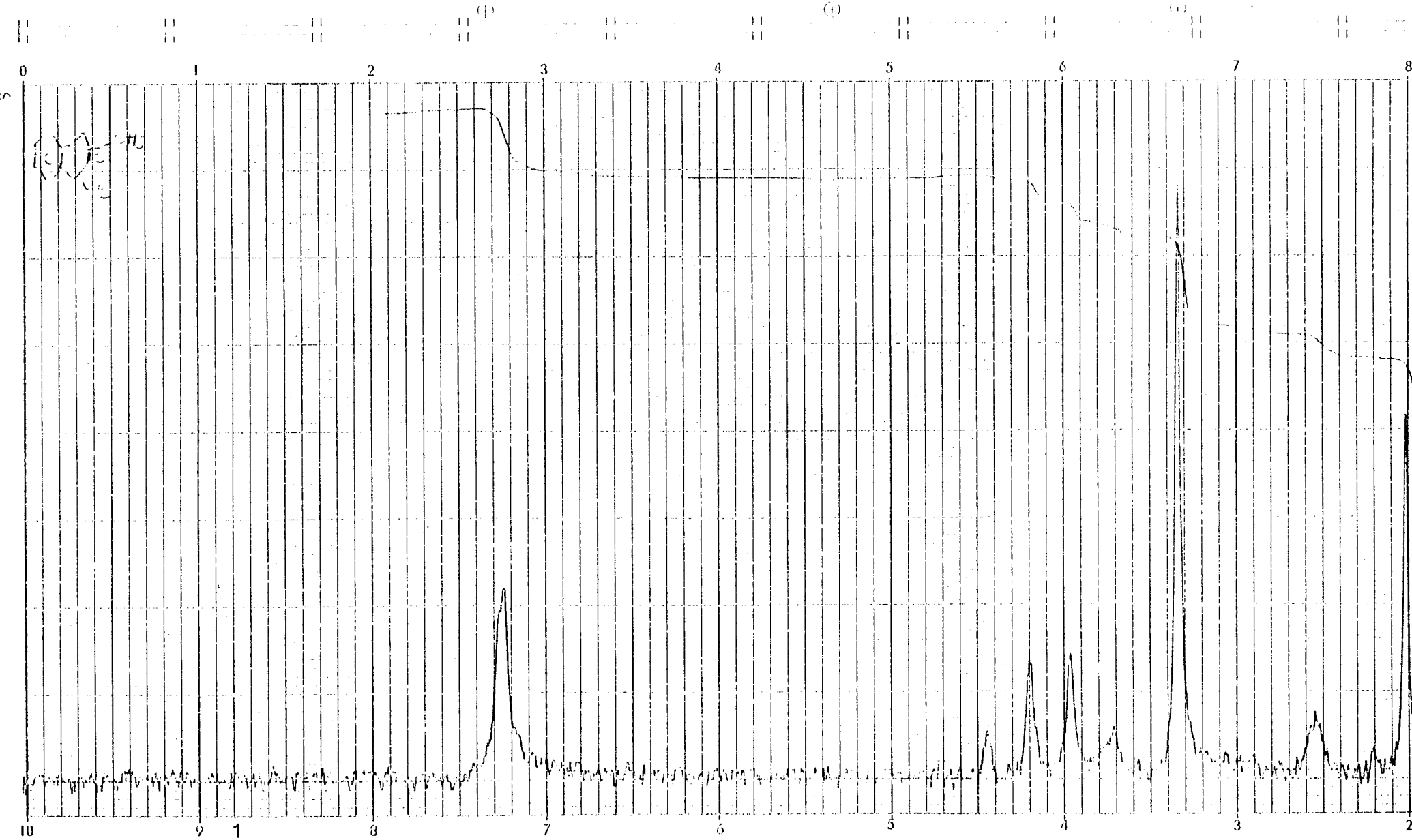
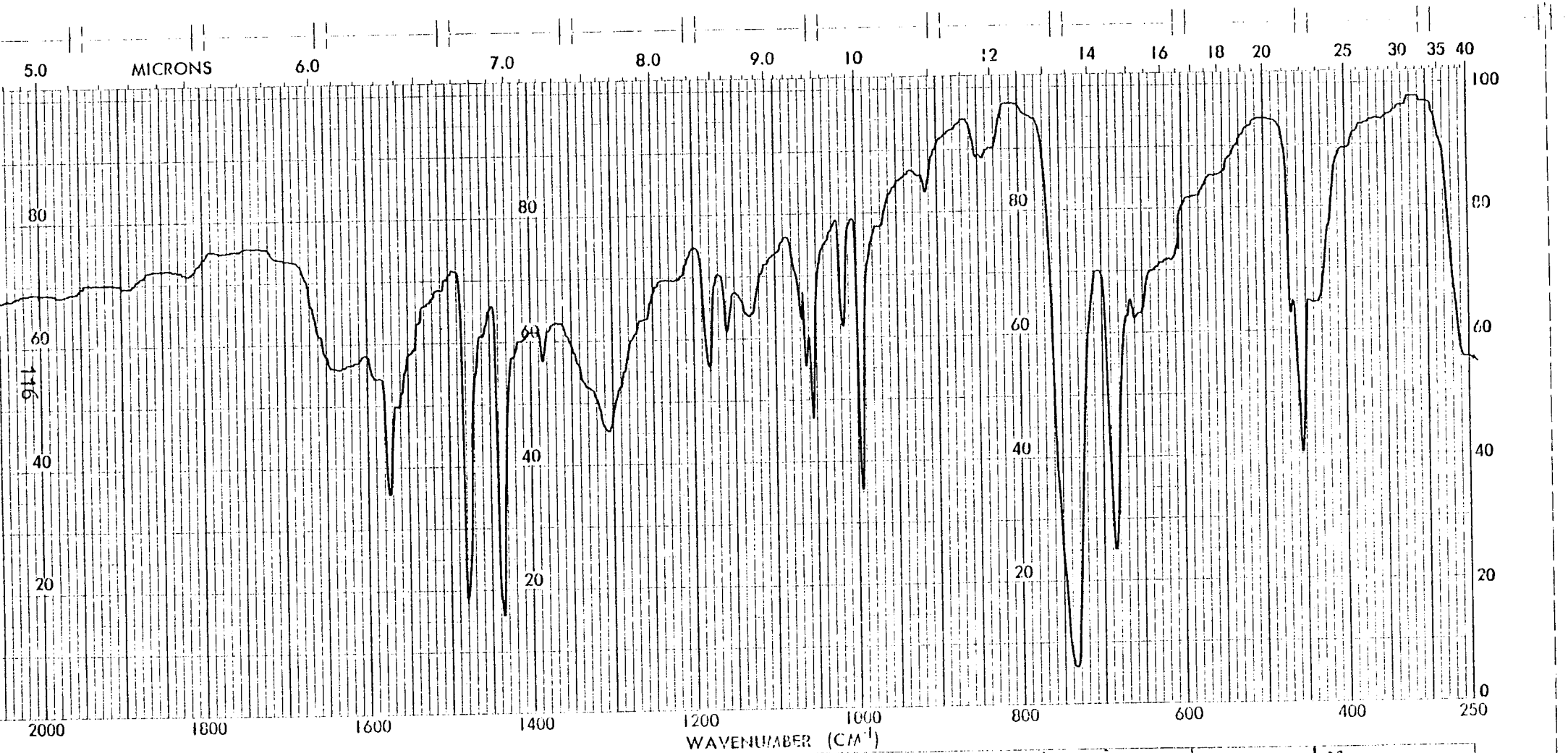


Fig.(15) · The H n.m.r. spectrum of

Cyclic telluronium chloride in DMSO (d_6)



REMARKS

Infra-red spectrum of

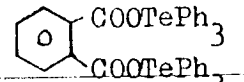


Fig.(16)

SCAN SPEED

SLIT

No 457-5001

OPERATOR

DATE

REF. No

4. (vi). DISCUSSION :

4. (iv).a. CHEMISTRY OF UNSTABLE ORGANOTELLURONIUM CARBOXYLATES :

We originally started the investigation of tellurium carboxylate compounds by attempting to repeat the reported preparation of tellurium tetracarboxylate [89] . This is apparently the only claim for the synthesis of tellurium tetracarboxylate. In spite of following the exact procedure of the quoted report, in our hands the reaction of tellurium tetrachloride with carboxylic acids failed to afford tellurium tetracarboxylate $Te(OOCR)_4$, where R = alkyl, aryl. Infact, hydrogen chloride was evolved, but the product that we obtained was not a tellurium tetracarboxylate.

A series of reactions were attempted using silver benzoate and acetate reacted with tellurium tetrachloride for the preparation of $Te(OOCR)_4$. Silver chloride was precipitated and a white solid which melted in the range 114-118^{o}C was obtained by evaporation of the benzene solution. Subsequent investigation (i.r., mass spectroscopy) showed this material to be benzoic acid. To judge from the release of silver chloride, there is a possibility that the tellurium tetracarboxylate might have been formed but it was undoubtedly a very moisture sensitive compound in that what we observe is the acid which is a hydrolysis product. e.g.

$$Te(OOCR)_4 + 2\ H_2O \longrightarrow TeO_2 + 4\ RCOOH$$

(TeO_2 was doubtless mixed with AgCl)

The synthesis of organotellurium tricarboxylates has been attempted by Pant [88] . He was successful in synthesising phenyl tellurium triacetate by reacting diphenyl ditelluride with lead tetra-acetate in benzene. The product was identified by ^1H n.m.r. spectroscopy [87] . All his attempts to isolate the solid compound failed due to hydrolysis which yielded a white material smelling of acetic acid. Therefore, it seems that tellurium tetracarboxylate and organotellurium tricarboxylate compounds are very moisture sensitive. Knowing this fact, we considered other tellurium carboxylate compounds for two reasons. First to get a stable carboxylate to look at, and secondly to place it in the context of work carried out within our group, initiated by Dance [52] . There are also some comparisons with triorganotin carboxylates which often have different structures in the solid state and in solution, e.g., five-co-ordinate tin (IV) with bridging carboxylate in the solid and four-co-ordinate with monodeviate carboxylate in solution. It is possible that similar differences exist for tellurium in the series $R_3Te(OOCR')$.

The synthesis of a series of telluronium carboxylates was then attempted: methyl diphenyl telluronium benzoate, o-methoxy benzoate and m-nitro benzoate were prepared and their behaviour in solutions with different polarity was characterised.

A. METHYL DIPHENYL TELLURONIUM BENZOATE :

This compound was synthesised by the treatment of methyl diphenyl telluronium iodide with silver benzoate and the white solid, methyldiphenyl telluronium benzoate, was collected, m.p. = 105°C.

The infra-red spectra of this compound in chloroform solution and in the solid state are shown on pages 98 - 101. The infra-red spectrum in chloroform is different from that of the solid state. In the solid state the bands at 1600 and 1390 cm^{-1} are due to $\nu_{as}(CO)$ and $\nu_{s}(CO)$, respectively. In solution the initial spectrum gave a sharp band at 1600 cm^{-1} corresponding to $\nu_{as}(CO)$ which decays with time to be replaced by another peak growing at 1720 cm^{-1}. The infra-red spectrum of authentic methyl benzoate was recorded and a sharp band at 1720 cm^{-1} due to the ester group was observed. Thus, there is a good evidence that over a period of time the telluronium benzoate is decomposing to methyl benzoate and, presumably, diphenyl telluride is reformed (eventually confirmed by ^{1}H n.m.r.), so we can write:

$$Ph_2MeTeOOCPh \longrightarrow Ph_2Te + PhC(=O)OMe$$

The infra-red spectrum of methyl diphenyl telluronium benzoate in DMSO was obtained at time intervals and the sharp peak observed at 1600 cm^{-1} diminished and replaced by another peak at 1715 cm^{-1}.

Two solutions of the salt in chloroform were prepared and kept one in the dark and the other in presence of light. The infra-red spectra of these two solutions were obtained at time intervals and the rate of decomposition was observed in both cases to be slow and identical. The spectra of both solutions after leaving in the n.m.r. compartment for one day, indicated the decomposition of the compound. This might lead us to deduce that the decomposition, is thermochemical rather than photochemical.

The chemistry of methyl diphenyl telluronium salts (Ph_2MeTeX, where X = Cl, Br, I), in solution was studied by Dance [90] . We decided to investigate the reductive elimination of alkyl carboxylate from methyldiphenyl telluronium carboxylate employing 'H n.m.r. spectroscopy and study the spectrum in solvents with different polarity.

The 'H n.m.r. spectrum of a solution of methyl diphenyl telluronium benzoate in deuterated DMSO was recorded and shown on page The initial spectrum consisted of a singlet methyl resonance at δ= 2.86 ppm. This singlet has satellite peaks caused by coupling between 'H and ^{125}Te, and must therefore be due to the methyl group which is still attached to the tellurium atom. The 'H n.m.r. spectrum of this compound dissolved in deuterated chloroform also contains a singlet methyl resonance at δ= 2.96 ppm with satellite peaks. The value of the resonance indicates that the methyl group is attached to an electropositive atom, as would be expected for a telluronium salt. This

resonance had vanished within five days and was replaced by another singlet at δ= 3.85 ppm without any satellite peaks.

Two other related telluronium carboxylates, i.e. methyl diphenyl telluronium (o-methoxy benzoate) and methyl diphenyl telluronium (m-nitro benzoate) were synthesised and the rate of reductive elimination of the alkyl carboxylate and the difference in the positions of the methyl resonances were studied.

B METHYLDIPHENYL TELLURONIUM (o-METHOXY BENZOATE) :

The reaction of methyldiphenyl telluronium iodide with silver o-methoxybenzoate at room temperature afforded methyl diphenyl telluronium (o-methoxybenzoate). m.p. = 98°C. Attempts to isolate this compound by thermal evaporation of the solvent yielded the corresponding telluride, hence the solution of the compound was kept in a dry atmosphere at room temperature for two weeks to crystallise.

The infra-red spectrum of methyl diphenyl telluronium (o-methoxybenzoate) in solution ($CHCl_3$) is different to that of the solid state and both are shown on pages 106 - 108. In the solid state the bands at 1600 and 1380 cm^{-1} are due to ν_{as} (CO) and ν_s (CO), respectively. In solution, the initial spectrum indicated a sharp band at 1600 cm^{-1} which decays with time to be replaced by another peak at 1725 cm^{-1}.

The ^1H n.m.r. spectrum of this compound in deuterated chloroform was obtained and the initial spectrum consisted a singlet methyl resonance at δ = 2.98 ppm with satellite peaks which vanished within 3 days and was replaced by another resonance at δ = 3.85 ppm. This final resonance did not possess any satellite peaks, therefore, this means that the methyl group is no longer bonded to tellurium atom. This implies that decomposition of this compound in chloroform solution has taken place and this parallels decomposition of the telluronium benzoate in chloroform.

$$Ph_2MeTeOOC\,C_6H_4OCH_3 \longrightarrow Ph_2Te + MeOOC\,C_6H_4OCH_3$$

C. METHYL DIPHENYL TELLURONIUM (m-NITROBENZOATE)

This compound was also obtained as an off-white solid with m.p. = 110°C, by the reaction of silver-nitrobenzoate with methyl diphenyl telluronium iodide at room temperature. The behaviour of this compound is parallel the above two telluronium carboxylate salts. The infra-red spectra of solution and solid states are different. In the solid state peaks at 1610 and 1345 cm^{-1} are due to ν_{as} (CO) and ν_s (CO) respectively. This compound was insoluble in chloroform and the ^1H n.m.r. spectrum was recorded in dimethyl sulfoxide (d_6). The singlet methyl resonance was initially observed at δ = 2.8 ppm and was

eventually replaced by another peak at δ = 3.9 ppm.

Following the observations by Dance [90] and Musa [53] on Ph_2MeTeX (where X = Cl, Br, I and NCS) and considering the infra-red and 'H n.m.r. data for the telluronium carboxylates, we can postulate that, in solution, methyl diphenyl telluronium carboxylates decompose to diphenyl telluride and the methyl carboxylate. This was parallelled by their T.G.A. behaviour.

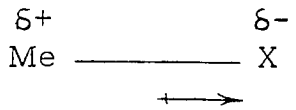
$$Ph_2MeTeOOCR \longrightarrow Ph_2Te + RCOOMe$$

$R = C_6H_5$, $C_6H_4OCH_3$ and $C_6H_4NO_2$

** * * * * * * *

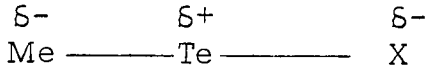
As was mentioned before, Dance studied 'H n.m.r. spectra of Ph_2MeTeX (X = Cl, Br, I) in chloroform. The iodide gave a singelt with satellite at δ = 3.04 ppm which was replaced by another peak at δ = 2.15 ppm. The bromide gave a resonance at δ = 2.90 ppm which vanished and replaced by another peak at δ = 2.61 ppm, and finally the chloride at δ = 2.76 ppm which was substituted by another resonance at δ = 2.96 ppm. He, therefore, made a plot of the chemical shift for the methyl singlet against the electronegativity of halogen (Page 125) and it is apparent that the effect follows a trend that is opposite to that observed for the methyl

halides, as the electronegativity of the halogen increases the electron density at the methyl group decreases for the halides, but for the telluronium salts, if the electronegativity of the halogen increases, the electron density of the methyl group increases. This is because the effect is being transmitted through the tellurium atom, presumably involving a three centre, 4 electron orbital.



Low electron density at the

methyl group



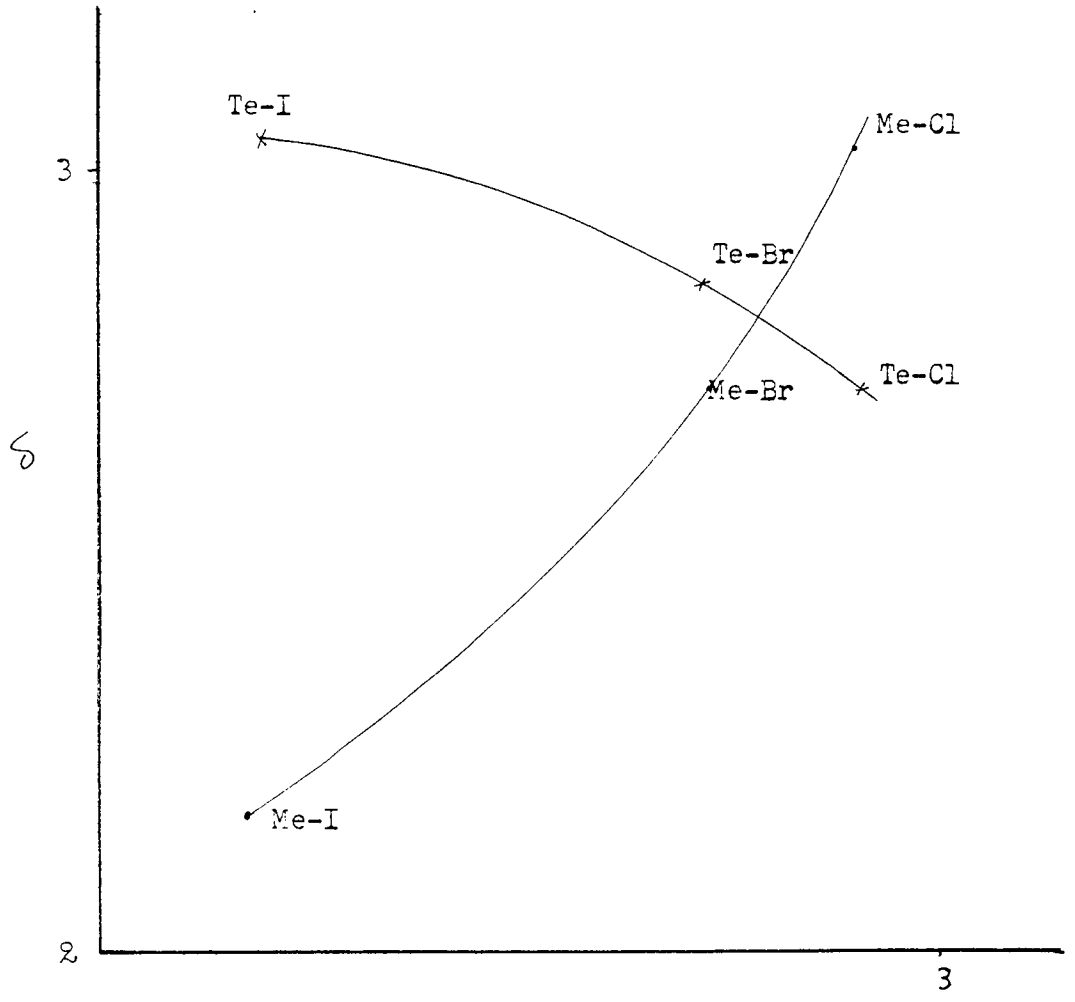
High electron density at the methyl

group

To judge from the curve (page 125), we can predict that the chemical shift for the methyl group in telluronium benzoate will be $\delta = 2.4$ ppm taking the electronegativity of oxygen, the ligand atom to be 3.5, but what we actually observe is $\delta = 2.9$. This trend must be due to the lower effective electronegativity of O in the benzoate group, therefore, other factors must also be responsible for the stability of

covalent form.

Pauling =	O	Cl	Br	I
electronegativity	3.5	2.83	2.74	2.21

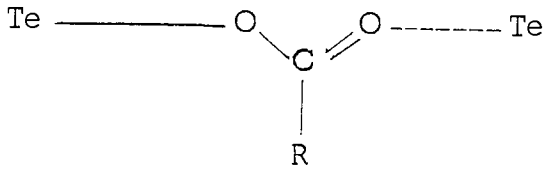


δ for the CH_3 singlet in the ^1H n.m.r. spectra of Ph_2MeTe X and Me-X.

We took the infra-red spectra of the methyldiphenyl telluronium carboxylates in chloroform solution and in solid state and we looked at the separation between the symmetric and antisymmetric vibrations and from that it seems the compounds are more covalent in chloroform solution (more "ester-like") [85] . Infra-red spectroscopy provides very useful information on the type of interaction between the carboxylate groups and the tellurium atom. Carboxylate groups may act as (a) unidentate ligands, (b) symmetrical or unsymmetrical bidentate ligands or, (c) they may be ionic and there are distinct relationships between the type of interaction with a metal centre and the infra-red spectra observed.

McWhinnie et. al., [88] , have studied the structure and vibrational frequencies of a series of diorganotellurium dicarboxylates and have shown that they are non-electrolytes in nitromethane solution and observed no evidence for acetate ions in the i.r. spectrum, so ionic structures such as $(-R_2TeO\diagdown\!\!\diagup C\diagdown\!\!\diagup O)^{n+}$ $-(OOC\,CH_3)_n^-$ were eliminated. The spectrum of the two infra-red active carboxylate stretching frequencies, ν_{as} (CO) and ν_s (CO) has previously been used to measure the degree of ester-like character for organotin carboxylates [91] , and organotellurium carboxylates [88] . For instance, the separation of the unsymmetrical and symmetrical frequencies (Δ) for tricyclohexyltin acetate [91] is 361 cm^{-1}, which is known to possess a unidentate acetate group and for dimethyltin diacetate, Δ = 227 cm^{-1}, [92] for which unsymmetrical bidentate acetate groups are proposed.

Values of $\triangle$ for all the telluronium carboxylates fall within the range 210-260 cm^{-1} and it is therefore, reasonable to postulate that these compounds contain unsymmetrical bidentate carboxylate groups, so, it can be suggested that the type of interaction between the carboxylate group and tellurium atom is as :



At this time, we decided to determine some molecular weights of telluronium salts. Considering the problem of dissociation of Ph_2MeTeX in chloroform, the slowly decomposing methyldiphenyl telluronium benzoate seemed the only possible choice for study. It was interesting that in-spite of some dissociation the molecular weight obtained was much higher than expected for a monomeric Ph_2MeTeO_2CPh. This suggests that probably the dissociation of methyl halide or methyl benzoate from telluronium halides and benzoate in chloroform could take place from a dimer rather than a monomer. Mass spectra showed that even in the gas phase the peak of highest m/e ishigher than that what we expected for the parent ion of the monomer. ^{125}Te n.m.r. of methyl diphenyl telluronium benzoate showed the presence of only one environment for tellurium, therefore, all these data lead us to the idea that we are probably dealing with a dimeric bridged system. So, we can conclude that the stabil-

ity of the covalent form is not only a function of electronegativity of the ligand, but it is also a function of the size of the anion (since we must minimize solvation energy) and it is also a function of its capacity to bridge, so ideally we want a relatively large, relatively high electronegative and effective bridging group, and in fact, benzoate is not a bad approximation to those three requirements.

At this time, it was necessary to try to firm up on those views and therefore, we decided to find some carboxylates of telluronium salts which were stable with respect to decomposition.

4. (iv).b. CHEMISTRY OF STABLE ORGANOTELLURONIUM CARBOXYLATES

1-methyl-3,4-benzo-1-telluracyclopentane benzoate was synthesized by reaction of 1-iodo-1-methyl-3,4-benzo-1-telluracyclopentane with silver benzoate, as a white solid with m.p. = 155°C. The infra-red spectra of this compound in solid and solution state were recorded and shown on page 111. The bands at 1600 and 1365 cm^{-1} corresponding to ν_{as} (CO) and ν_{s} (CO) and peak at 525 cm^{-1} due to Te-Me vibration were observed in the solid state which were similar to those obtained in solution state spectrum recorded in chloroform. The infra-red spectrum of this compound in chloroform solution was recorded at time intervals and the frequencies remained constant. The separation of the two unsymmetrical and symmetrical frequencies ($\triangle$) is

235 cm^{-1}, indicating that this compound contains bidentate carboxylate group, so the type of interaction between the carboxylate group and tellurium atom parallels the previous suggestion (page 127).

The ^1H n.m.r. spectrum of this compound in deuterated chloroform consisted of several peaks. In the aliphatic region, the singlet resonance appearing at $\delta = 2.12$ ppm is due to the methyl group which contains satellite peaks due to ^{125}Te-^1H coupling (J = 24 Hz) and furthermore, there are two doublets appearing at $\delta = 3.7$, 3.95, 4.4 and 4.65 ppm corresponding to the splitting of the two inequivalent methylene protons. The spectrum of this compound in chloroform (d) was recorded at time intervals and the position of the methyl group remained constant.

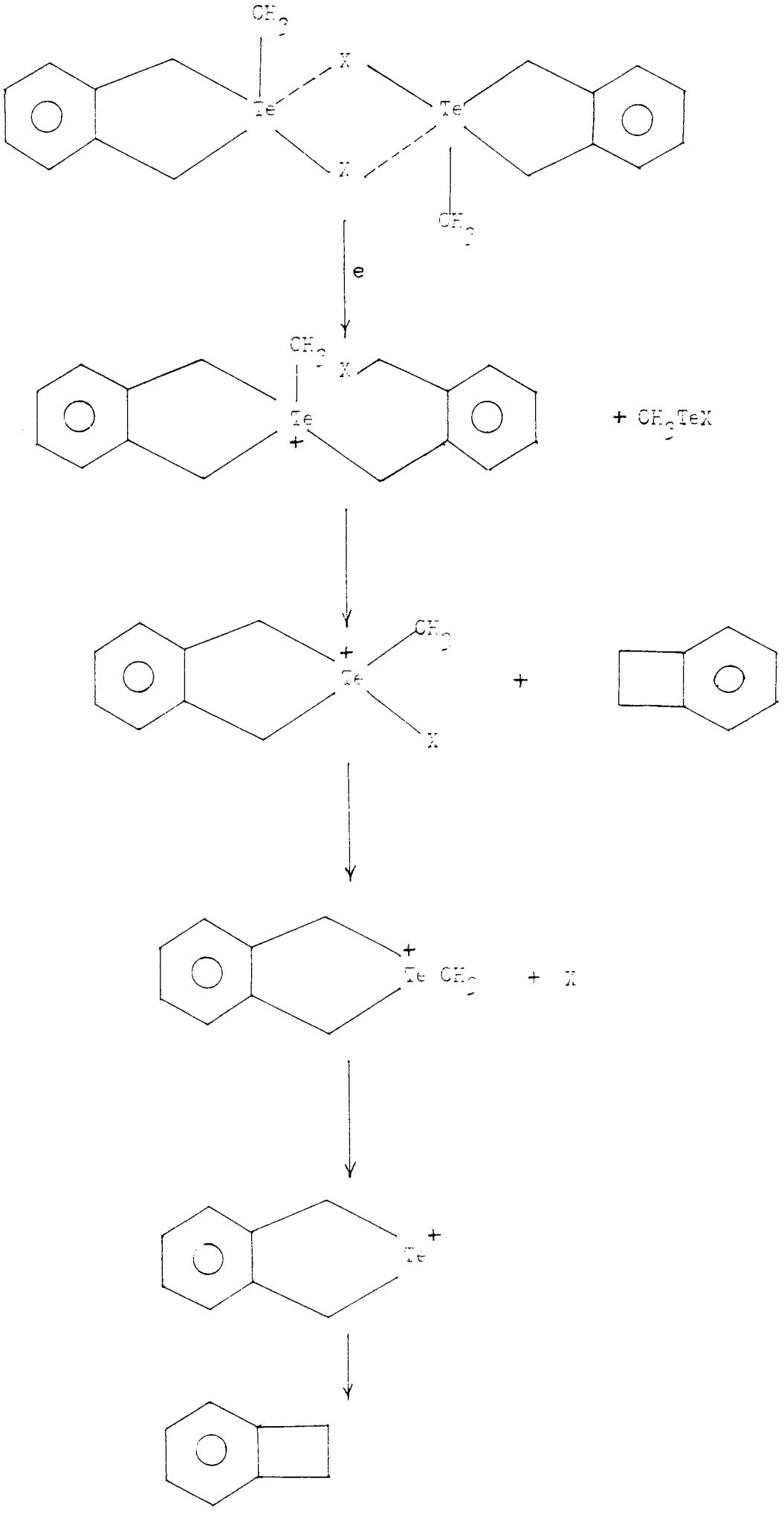
1-iodo-1-methyl-3,4-benzo-1-telluracyclopentane was found to be partially soluble in chloroform (yellow solid). Molecular weight measurement of the yellow form of $C_9H_{11}ITe$ and of $C_{16}H_{16}O_2Te$ was carried out in chloroform and the values (Table 6) indicate that these compounds exist as dimers.

Mass spectroscopy has previously been used for the characterisation of a series of Ph_2MeTeX (X = Cl, Br, I and NCS) and in all cases the decomposition involved thermolysis to give diphenyl telluride and MeX. Mass spectra of a series of cyclic telluronium salts have been tabulated in tables (7,8,9). The most important features of the mass

spectra of these salts is that the peaks of the highest m/e are fragments of much greater molecular weight than the parent ion of the monomer. For instance, in the cyclic telluronium benzoate, the highest m/e = 470 due to P^+ of the monomer.

As was mentioned before, molecular weight data showed that cyclic telluronium benzoate exists as dimer (M.W. of dimer = 740). The lost fragment from a supposed dimer does match with the molecular weight of methyl tellurium benzoate thus it is quite reasonable to predict that, methyl tellurium benzoate has been lost and the peak which we observe at 470, corresponds to $C_{24}H_{23}O_2Te^+$. The above prediction may well indeed apply to cyclictelluronium chloride and iodide, since for the cyclic telluronium chloride the highest observed peak is m/e = 388 compared with m/e = 284 for the parent ion of the monomer, and if methyl tellurium chloride is lost from the dimer, the species left would be $C_{17}H_{19}ClTe^+$. (M.W. 388). Loss of methyl tellurium iodide from dimeric cyclic telluronium iodide, would leave us $C_{17}H_{19}ITe^+$ (M.W.480) with m/e = 480 compared with m/e = 376 due to the P^+ of the monomer.

The results indicate definite association of the so called anion and the so called cation in the gas phase.


CH3
X
Te
Te
X
CH3
e
CH3
X
Te
+
+ CH3TeX
+
CH3
Te
X
+
+
Te CH3
+ X
+
Te

We may conclude that the idea of association is now firmly established, and is supported by mass spectral and molecular weight data.

4. (iv).c. ORGANOTELLURONIUM FLUORIDES :

Fluorine the most electronegative of the halogens and if the Dance [90] electronegativity arguments are followed through, this one ought to give the most stable of the covalent form of Ph_2MeTeX. All our attempts to synthesise methyl diphenyl telluronium fluoride failed due to hydrolysis which yielded a white material. At this time, we decided to synthesise triphenyl telluronium fluoride and here we were successful and we obtained a solid which analysed satisfactorily.

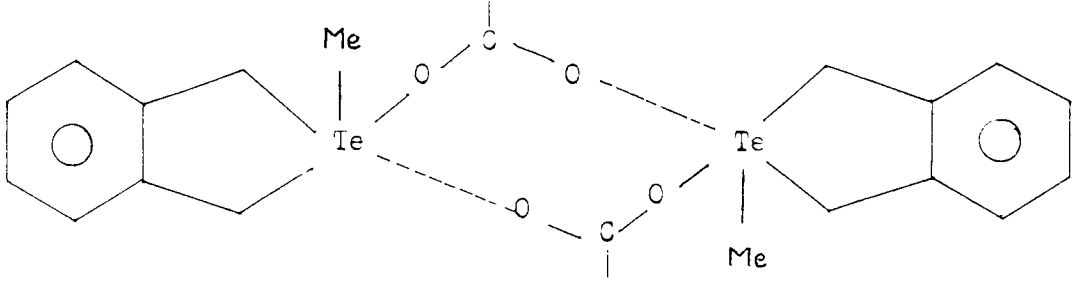
The ^{19}F n.m.r. spectrum showed resonance with no evidence for satellites due to ^{125}Te- ^{19}F and also ^{125}Te n.m.r. showed a single signal with no ^{19}F coupling. Therefore, the only explanation for these data is that this compound isionic. This requires that we consider the solvation energy of the anion because although fluorine is the most electronegative of the halogens, it also happens to be the smallest. Consequently, F^- is the smallest of the halogen anions, and therefore, will have the greatest solvation energy.

So, once again our data confirm that the stability of the covalent form of the covalent form of the telluronium salt is very much a function

of the (1) solvation energy of the supposed anion, which in turn is the function of the size of that anion. (2) It is a function of the ability of that anion to bridge between two tellurium atoms, and it is also a function of the (3) electronegativity of that anion.

As far as the structures of these telluronium compounds are concerned, the telluronium fluorides are being neglected since they were proved to be ionic, but in the case of carboxylates, we have two lines of evidence: we observe no doubling of the infra-red CO stretching frequencies, these appear to be single, therefore, if we are looking for dimers, this must mean that two-benzoate groups in the dimer are equivalent, also ^{125}Te n.m.r. spectra have been obtained [93] , in which single signals are observed, again this must mean that the two Te atoms within the dimer are equivalent and therefore, any proposed structure must be consistent with the equivalence of the bridging groups and equivalence of the Te atoms, so it can be concluded that they are symmetric dimers, possibly centro-symmetric as illustrated.

N.B. : Bridge probably has one short and one long bond.



4. (iv).d. CHEMISTRY OF ORGANOTELLURONIUM PHTHALATE SALTS :

Attempts to prepare bis-methyldiphenyl telluronium phthalate by reacting methyldiphenyl telluronium iodide with the silver salt of phthalic acid were unsuccessful, probably due to decomposition and release of methyl iodide. Therefore, we decided to employ a more stable telluronium salt and triphenyltelluronium chloride was selected. Bis-triphenyl telluronium o-phthalate was obtained by the reaction of sodium salt of o-phthalic acid with triphenyltelluronium chloride in chloroform as white solid with m.p. = 199-200°C.

The infra-red spectrum of this compound in the solid state is quite similar to that of the solution state and peaks at 1645 and 1305 cm^{-1} due to ν_{as} (CO) and ν_{s} (CO) are observed. This compound showed stability with respect to decomposition in chloroform solution. Molecular weight measurements of the compound in chloroform was carried out and the result clearly indicated that the compound must be formulated as monomer.

CHAPTER V

5. (i). INTRODUCTION :

Diorganotellurium (IV) species (R_2TeX_2) include a large variety of compounds, $(R)_2$ can be diaryl, arylalkyl and dialkyl and X may be any sort of anionic species such as, F^-, Cl^-, Br^-, I^-, NCS^-, $RCOO^-$, ... The synthesis of a large number of different chlorides, bromides and iodides has been reported. The reaction of diorganotellurides with elemental halogens has widely been used as the synthesis of diorganotellurium dihalides.

$$R_2Te^{(II)} + X_2 \longrightarrow R_2Te^{(IV)}X_2$$

The difluorides can be prepared by exchanging halogen with silver fluoride [95] . The methyl, phenyl [95] and 4-methoxy-phenyl [96] derivatives are the only known difluorides.

Shestha and Thayer [97] found that dimethyl tellurium diiodide decomposes readily at room temperature in acetone and similar solvents, producing methyl iodide and in addition, always displaying the faint odour of dimethyl telluride. They have postulated the first step to be:

$$(CH_3)_2TeI_2 \longrightarrow CH_3TeI + CH_3I$$

Plus to a slight extent :

$$(CH_3)_2\ Te\ I_2 \longrightarrow (CH_3)_2\ Te + I_2$$

Although the synthesis of a large variety of unsymmetrical diorganotellurium dihalide compounds, $RR'TeX_2$ where R = aryl and R' = aryl, alkyl, has been reported in the literature, little is known about the chemistry of this type of compound, especially if R' = methyl.

Following the observation by Shestha and Thayer [97] on the behaviour of dimethyltellurium diiodide in acetone and chloroform solutions, the synthesis of a various methyl phenyl tellurium dihalides were attempted in the hope to characterise the behaviour of this new class of unsymmetrical diorganotellurium dihalides in solution. There is a possibility that :

$$R_2Te\ X_2 \xrightarrow{h\nu} RTeX + RX$$

$$\downarrow$$

$$Te$$

If this was so, such compounds might be useful for image formation.

5. (ii) EXPERIMENTAL :

PREPARATION OF METHYL PHENYL TELLURIDE :

Two different procedures were carried out for preparation of this compound:

A. Diphenyl ditelluride (5 gr. 0.01 mol.) was dissolved in dry-distilled tetrahydrofuran (150 ml.) and placed in a 250 ml. three-necked round-bottom flask fitted with a high-speed wire stirrer and nitrogen inlet. Freshly cut, small pieces of lithium metal (1.7 gr. 0.02 mol.) were added through the third neck. The mixture was then stirred at room temperature for 8 hours. After this time, the initial dark red solution became yellowish. Under the nitrogen atmosphere the mixture was filtered and to this solution (phenyl lithium telluride), dry methyl iodide (0.02 mol.) was added drop-wise with stirring. The reaction mixture was then stirred for $\frac{1}{2}$ hr. at room temperature, which was followed by another 30 min. refluxing to complete the reaction. The solvent was distilled off, water (15 ml.) and ether (30 ml.) were added to the residue. The etherial layer was dried and distilled and the light yellow oily residue of methyl phenyl telluride was collected.

B. Diphenyl ditelluride (5 gr.) and dry methyl iodide (35 ml.) were

placed in a flask and heated under reflux for $1\frac{1}{2}$ hrs. after which the yellow precipitate of dimethyl phenyl telluronium iodide was filtered. The mother-liquer contained methyl phenyl tellurium diiodide which was obtained as red-glistening crystals. This was reduced by potassium metabisulfate at $0^{\circ}C$, and the light-yellow oily residue of methyl phenyl telluride was collected.

PREPARATION OF METHYL PHENYL TELLURIUM DIIODIDE

Methyl phenyl tellurium diiodie was synthesized as described above (Section B) as red-glistening crystals with m.p. = $142^{\circ}C$.

SYNTHESIS OF METHYL PHENYL TELLURIUM DIBROMIDE

To a freshly prepared solution of methyl phenyl telluride (0.02 mol) in carbon tetrachloride (25 ml.), bromine (0.02 mol.) in carbon tetrachloride (20 ml.) was added drop-wise with stirring. The mixture was stirred at room temperature for another 2 hrs, after which, the yellow precipitate of methyl phenyl tellurium dibromide was filtered and dried at room temperature, m.p. = $140^{\circ}C$.

SYNTHESIS OF METHYL PHENYL TELLURIUM DICHLORIDE

To a freshly prepared solution of methyl phenyl telluride (0.02 mol) in dry benzene (30 ml.) was added a solution of thionyl chloride (0.02 mol.) drop-wise with stirring during 30 min. under the nitrogen

atmosphere. The mixture was further stirred for 3 hrs. at room temperature, after which the white precipitate of dichloride was collected and recrystallised from hot glacial acetic acid. Methyl phenyl tellurium dichloride, as white-glistening crystals, has a m.p. = 138 - 140°C.

REACTION OF METHYL PHENYL TELLURIDE WITH LEAD TETRA-ACETATE

To a solution of methyl phenyl telluride in dry-distilled tetrahydrofuran (25 ml.) an equimolar quantity of freshly prepared lead tetracetate in the same solvent (20 ml.) was added. The mixture was stirred at room temperature for 4 hrs. under a nitrogen atmosphere, filtration followed by evaporation of the solvent left no residue.

REACTION OF METHYL PHENYL TELLURIUM DIBROMIDE WITH SILVER BENZOATE

Methyl phenyl tellurium dibromide (1 gr, 0.002 mol.), silver benzoate (1.2 gr. 0.004 mol.) and distilled water (50 ml.) were placed into a round-bottom flask fitted with a condenser and magnet bar. The mixture was heated under reflux for 2 hrs. with stirring, after which the hot solution was filtered and pale yellow precipitate of silver bromide was collected on further concentration and cooling the filtrate, the white solid product appeared which was dried in vacuum over P_2O_5. m.p. = 145°C. The infra-red spectrum of the solid was obtained.

ATTEMPT TO PREPARE METHYL PHENYL TELLURIUM DI-ISOTHIOCYANATE

An aqueous solution of silver nitrate (1 gr. in 20 ml. distilled water) was added to an aqueous solution of potassium thiocyanate (1 gr. in 20 ml. water) until a curdy white precipitate of silver thiocyanate was formed. Methyl phenyl tellurium dibromide (0.5 gr. in 100 ml. water) was added to the above mixture. The mixture was stirred for 1 hr. at room temperature and then refluxed for another 3 hrs. The yellow precipitate of the silver bromide was filtered and the solution was concentrated. The oily red to yellowish residue was obtained, an i.r. spectrum was recorded.

PREPARATION OF METHYL PHENYL TELLURIUM BROMIDE CHLORIDE

A mixture of methyl phenyl tellurium dichloride (1 g., 0.003 mol) in dry chloroform (25 ml.) and potassium bromide (0.357g., 0.003 mol) in the same solvent (10 ml.) was heated under reflux for 2 hrs. Filtration followed by evaporation of the solution to afford white crystals of methyl phenyl tellurium bromide chloride with m.p. = 154^{o}C. The infra-red spectrum was obtained.

SYNTHESIS OF METHYL PHENYL TELLURIUM O-PHTHALATE

To a solution of o-phthalic acid (2 g.) in distilled water (50 ml.) an aqueous solution of sodium hydroxide was added unlit neutralisation.

The solution was evaporated and the white precipitate of the sodium salt was finely ground and treated with a chloroform solution (50 ml.) of methyl phenyl tellurium dichloride (1.74 g.). The reaction mixture was shaken for 48 hrs. at room temperature after which was filtered to remove sodium chloride and unreacted sodium phthalate. The solution was washed with water and dried over sodium sulphate. The white precipitate of methyl phenyl tellurium o-phthalate was recovered from the filtrate and recrystallised from a solution mixture of benzene/pet. ether, m.p. = 102°C.

The extension of the reaction to other carboxylic acids, i.e. iso-phthalic, terephthalic acids failed in both cases to produce isolable products.

5. (iii) RESULTS :

Analytical data for tellurium salts, i.e. $PhMeTeX_2$ (X = Cl, Br, I) are listed in Table 3.

SOLUBILITY :

Methyl phenyl tellurium dihalides are all soluble in DMSO, DMF, acetone and chloroform, but insoluble in carbontetrachloride.

CONDUCTIVITY MEASUREMENTS:

The molar conductivity of each tellurium dihalide was determined in DMSO and DMF, conductivities were also measured as a function of concentration. Two examples have been shown on pages 152, and 153. The results are given in Table (1).

INFRA-RED SPECTRA:

The infra-red spectra as K Br and polythene discs of all methyl phenyl tellurium dihalides in the range of 4000-200 cm^{-1} were recorded and a typical example has been shown on page 146.

^{1}H n.m.r. SPECTRA:

The ^{1}H n.m.r. spectra of methyl phenyl tellurium dichloride, dibromide anddiiodide were recorded in deuterated chloroform and are shown on pages 147-9. Methyl phenyl tellurium diiodide was the only compound among these three in which some dissociation was observed after 24 hrs. In chloroform, the initial spectrum consisted of a singlet methyl resonance at δ = 3.5 ppm (relative to TMS) with satellites corresponding to ^{125}Te-^{1}H coupling ($J = 25\ H_z$). After 24 h. this singlet was accompanied by another singlet at δ = 2.15 ppm. The initial spectrum of methyl phenyl tellurium dichloride and dibromide contained a singlet methyl resonance at δ = 3.25 ppm and δ = 3.42 ppm respectively with satellite and remained constant over 48 hrs, nor were new resonances noted.

The ^1H n.m.r. spectrum of methyl phenyl tellurium phthalate in deuterated chloroform was obtained and the initial spectrum consisted of a single methyl resonance at δ = 3.28 ppm with satellite peaks which remained constant after 48 hrs.

TABLE (1)

Conductivity measurements on solutions of some methyl phenyl tellurium dihalides.

COMPOUND	Solvent/ molar conductivity ($ohm^{-1}\ cm^2\ md^{-1}$)	
	DMSO	DMF
PhMeTe I_2	52.5	54.0
PhMeTe Br_2	21.9	17.5
PhMeTe Cl_2	25.4	21.2

Solutions were 10^{-3} molar.

TABLE (2)

The positions of the methyl resonances of some methyl-phenyl tellurium (IV) species.

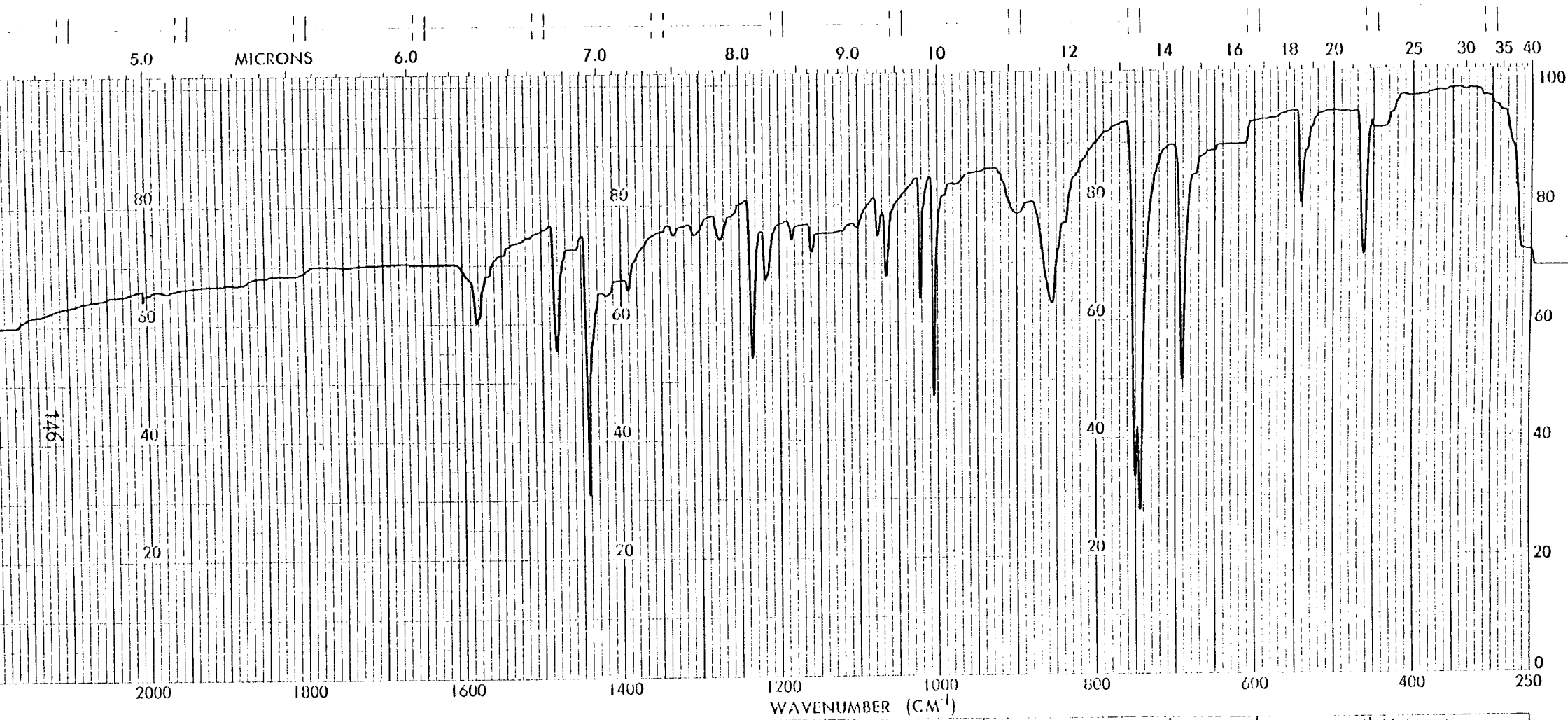
Compound	Solvent	Resonance (1) ppm	Resonance (2) ppm	J_{Hz}
Ph Me Te I_2	$CDCl_3$	3.5	2.15	25
Ph Me Te Br_2	$CDCl_3$	3.42	-	"
Ph Me Te Cl_2	$CDCl_3$	3.25	-	"
Ph Me Te $(C_8H_4O_4)$	$CDCl_3$	3.28	-	"

Resonance (1) is due to the peak appeared, immediately after dissolving, and Resonance (2), is the peak which subsequently replaced the first peak.

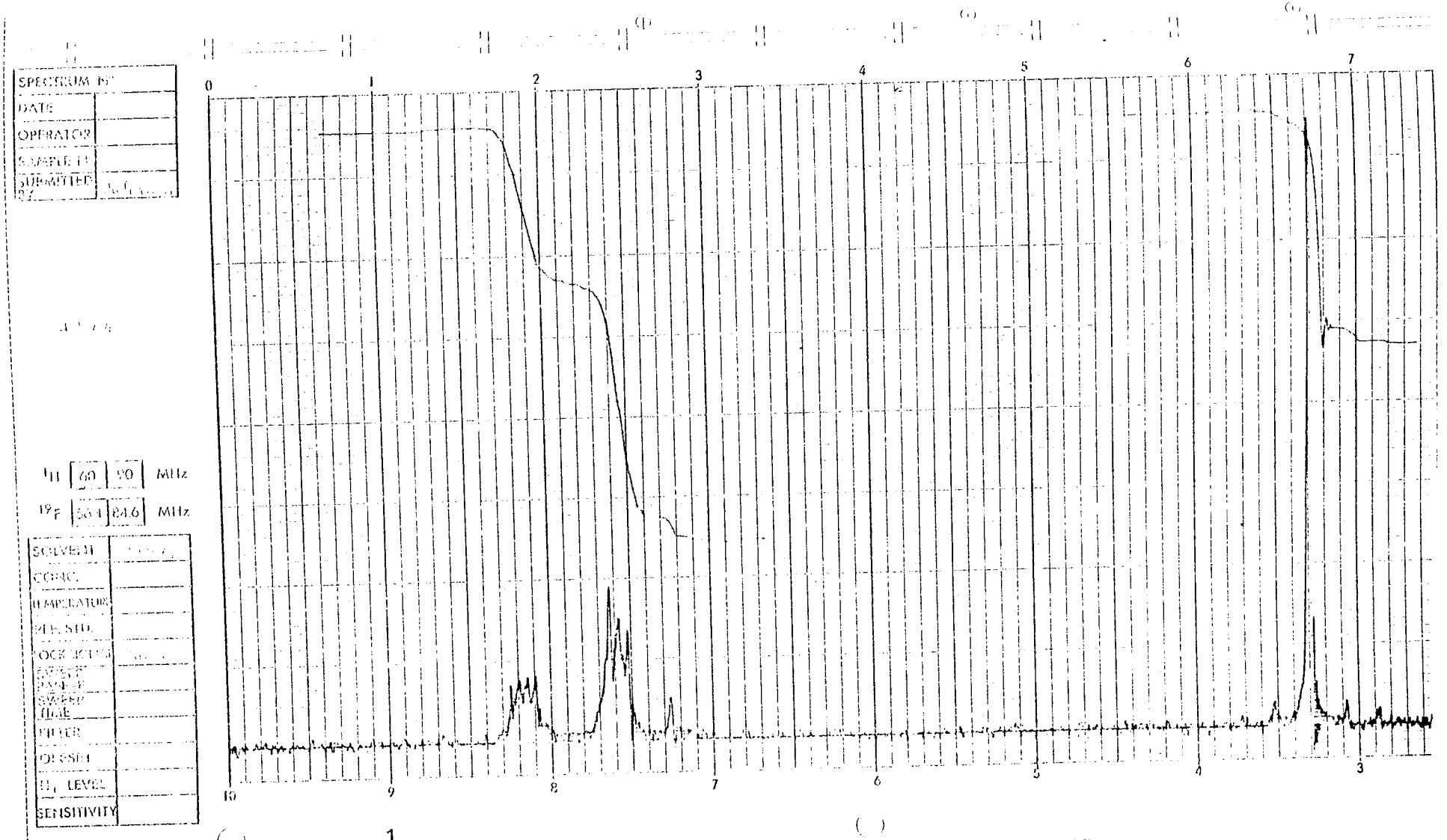
TABLE (3)

COMPOUND	FOUND			CALCULATED		
	C%	H%	X%	C%	H%	X%
Ph Me Te I_2	16.90	1.50	-	17.80	1.69	-
Ph Me Te Br_2	22.30	2.20	39.1	22.20	2.10	42.2
Ph Me Te Cl_2	28.90	2.60	23.0	28.90	2.70	24.4
Ph Me Te ($C_8H_4O_4$)	45.30	2.80	-	46.90	3.13	-

Analytical data for some new organotellurium compounds.



KBr.	REMARKS Infra-red spectrum of $PhMeTeBr_2$ Fig.(3)	SCAN SPEED Medium	OPERATOR V. H. Gordon.
RATION approx. 1.0%		SLIT Standard	DATE 11th January 1957
H 13.2% in. dia. disc		No 457-5001	REF. No 42821
E 11th.			



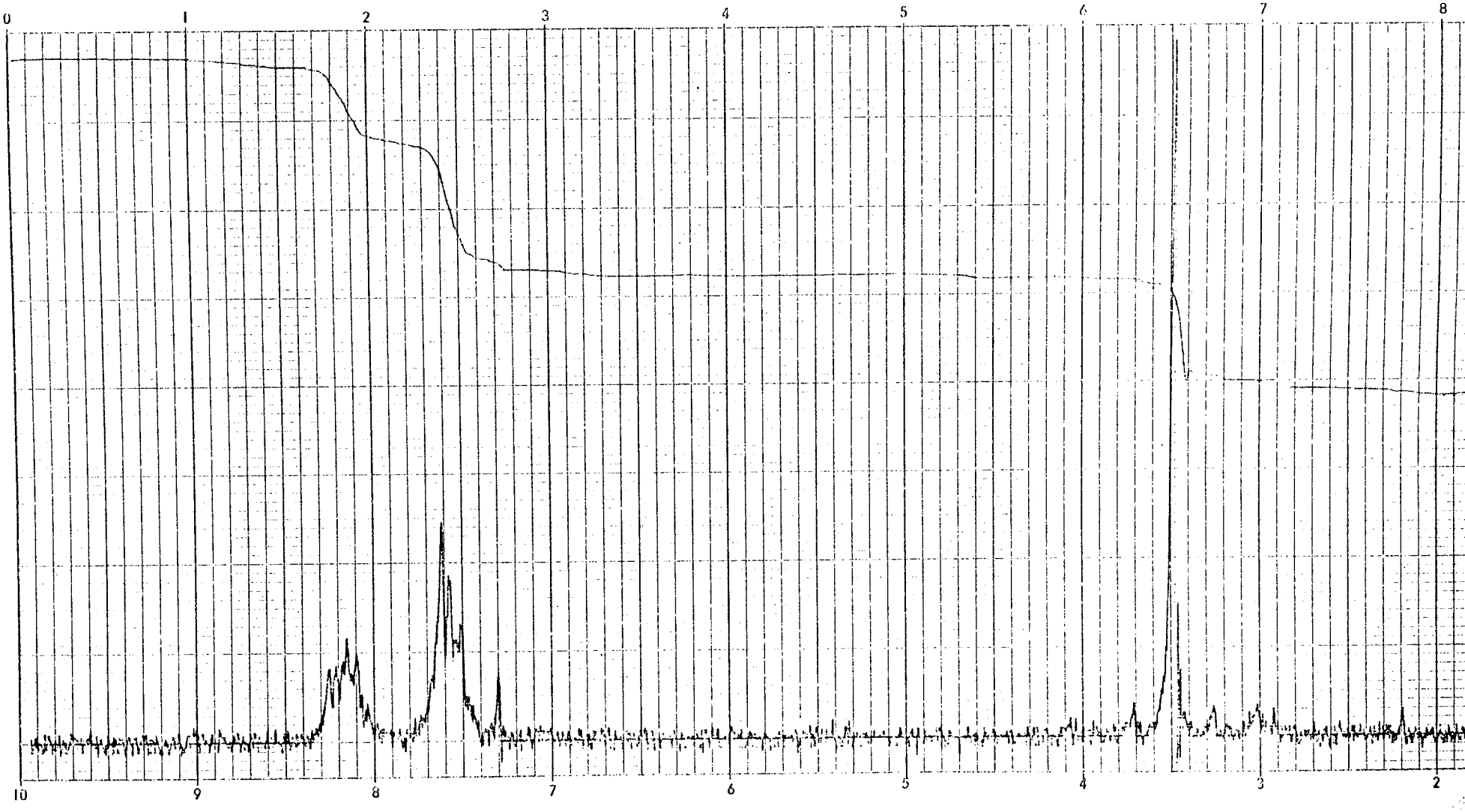
^{1}H n.m.r. spectrum of $PhMeTeCl_2$ in $CDCl_3$ Fig.(4)

SPECTRUM N°	
DATE	
OPERATOR	
SAMPLE N°	
SUBMITTED BY	

148

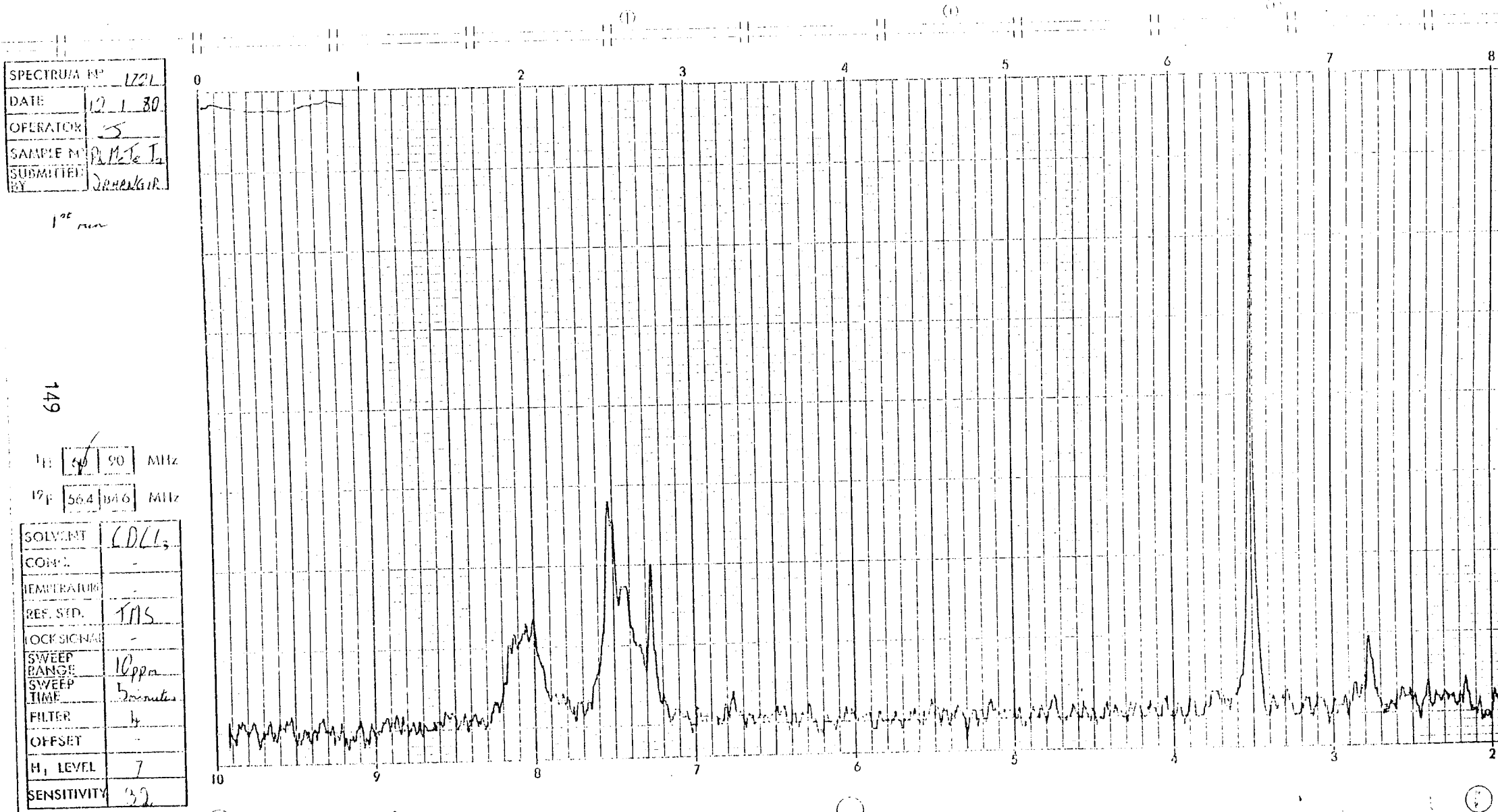
^{1}H	60	90	MHz
^{19}F	56.4	84.6	MHz

SOLVENT	$CDCl_3$
CONC.	-
TEMPERATURE	-
REF. STD.	TMS
LOCK SIGNAL	-
SWEEP RANGE	Upper
SWEEP TIME	Smooth
FILTER	1
OFFSET	-
H_1 LEVEL	7
SENSITIVITY	2



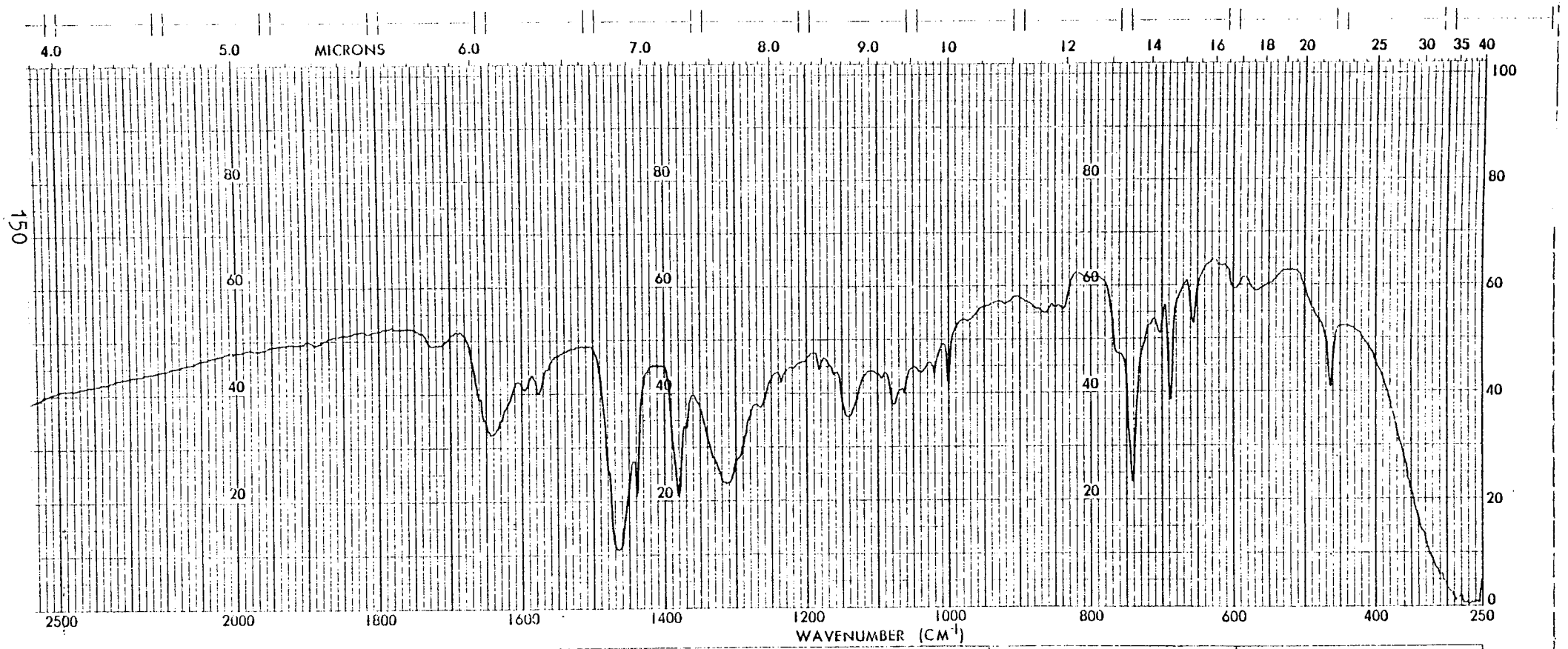
^{1}H n.m.r. spectrum of $PhMeTeBr_2$ in $CDCl_3$ Fig.(5)

No. 5600-6671



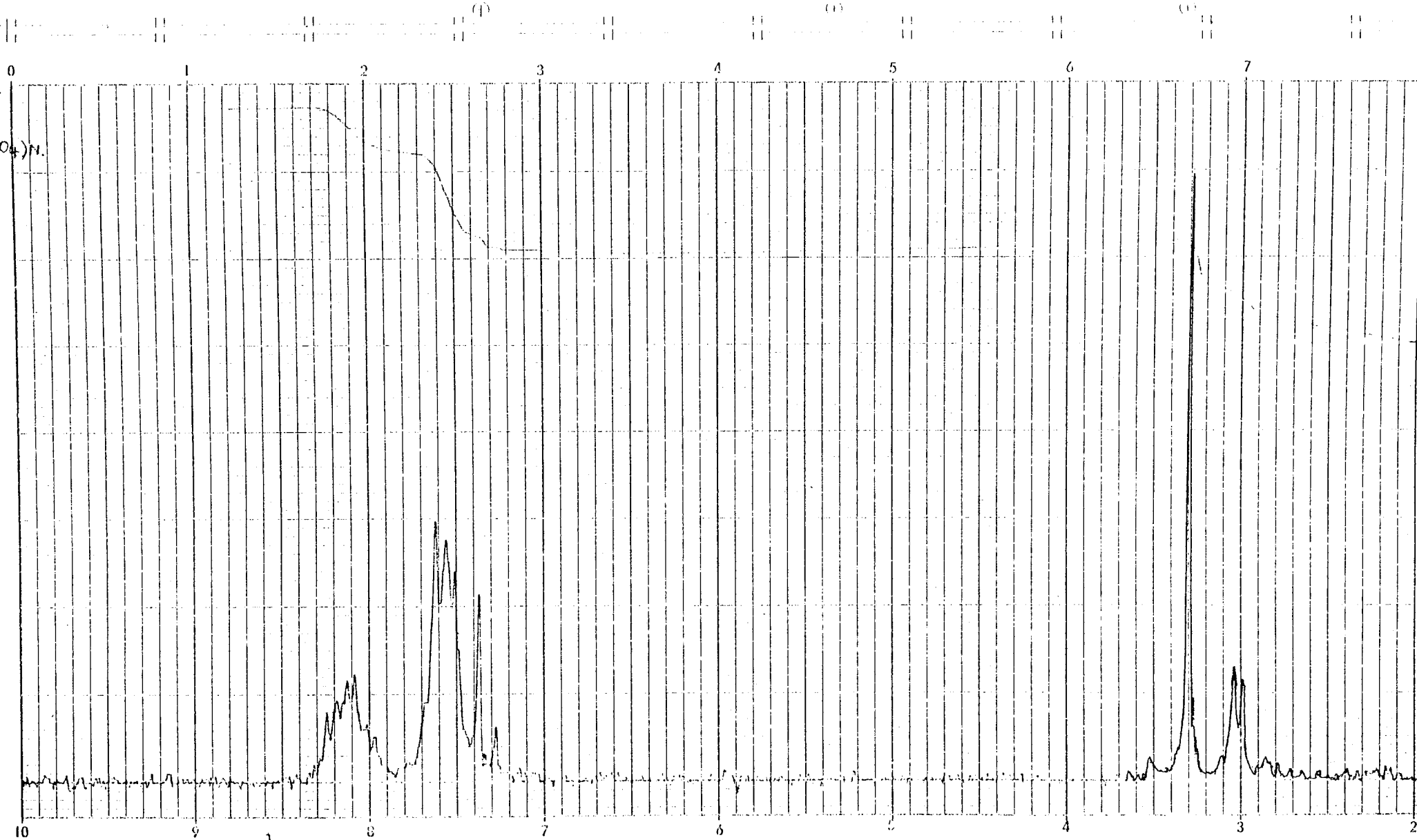
^{1}H n.m.r. spectrum of

$PhMeTeI_2$ in $CDCl_3$ Fig.(6)



150

SOLVENT	REMARKS Infra-red spectrum of PhMeTe ($C_8H_4O_4$) Fig.(7)	SCAN SPEED	OPERATOR
CONCENTRATION		SLIT	DATE
CELL PATH		No 457-5001	REF. No
REFERENCE			



The ^{1}H n.m.r. spect. of $PhMeTe(C_8H_4O_4)$.

Fig.(8)

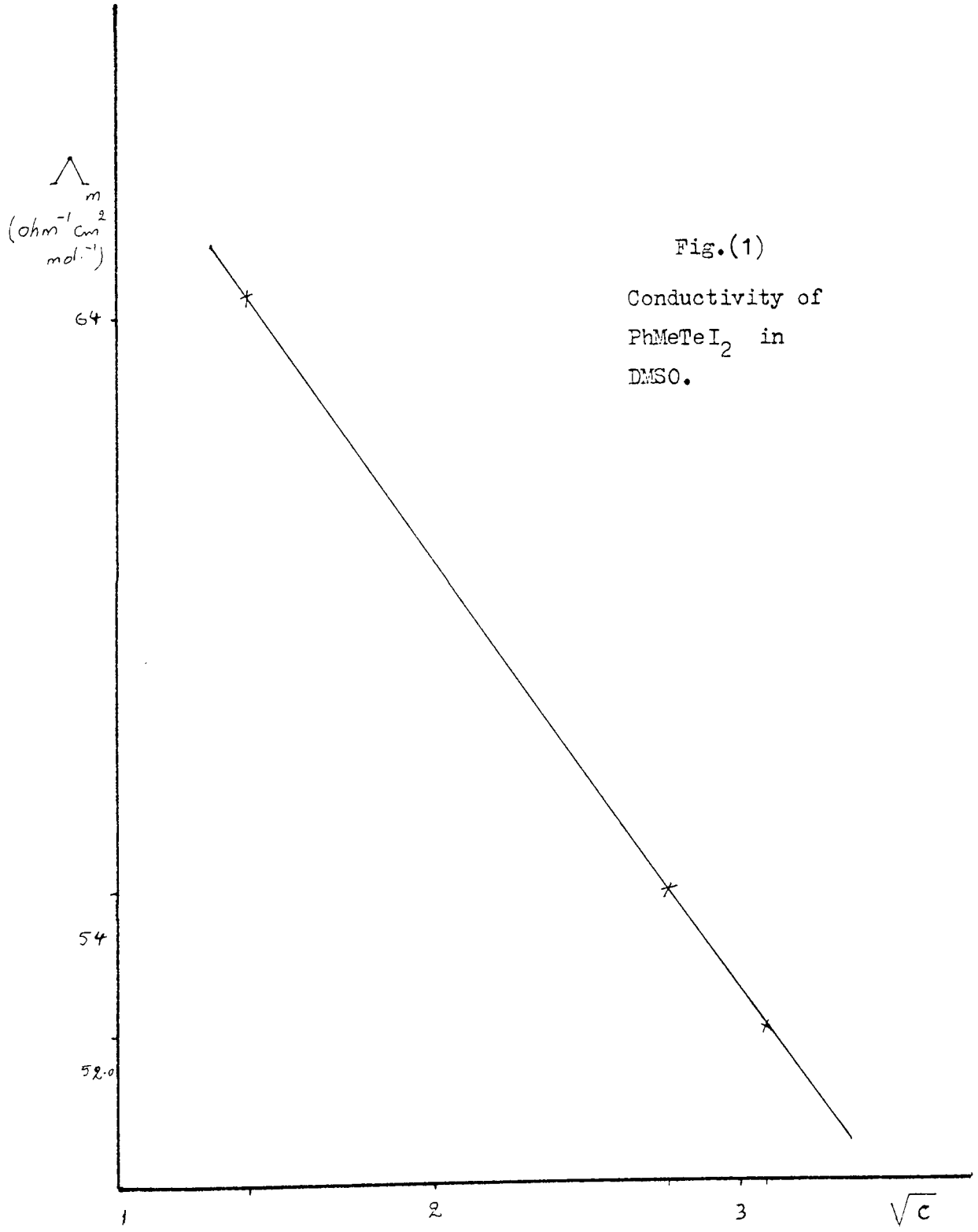


Fig.(1)

Conductivity of $PhMeTeI_2$ in DMSO.

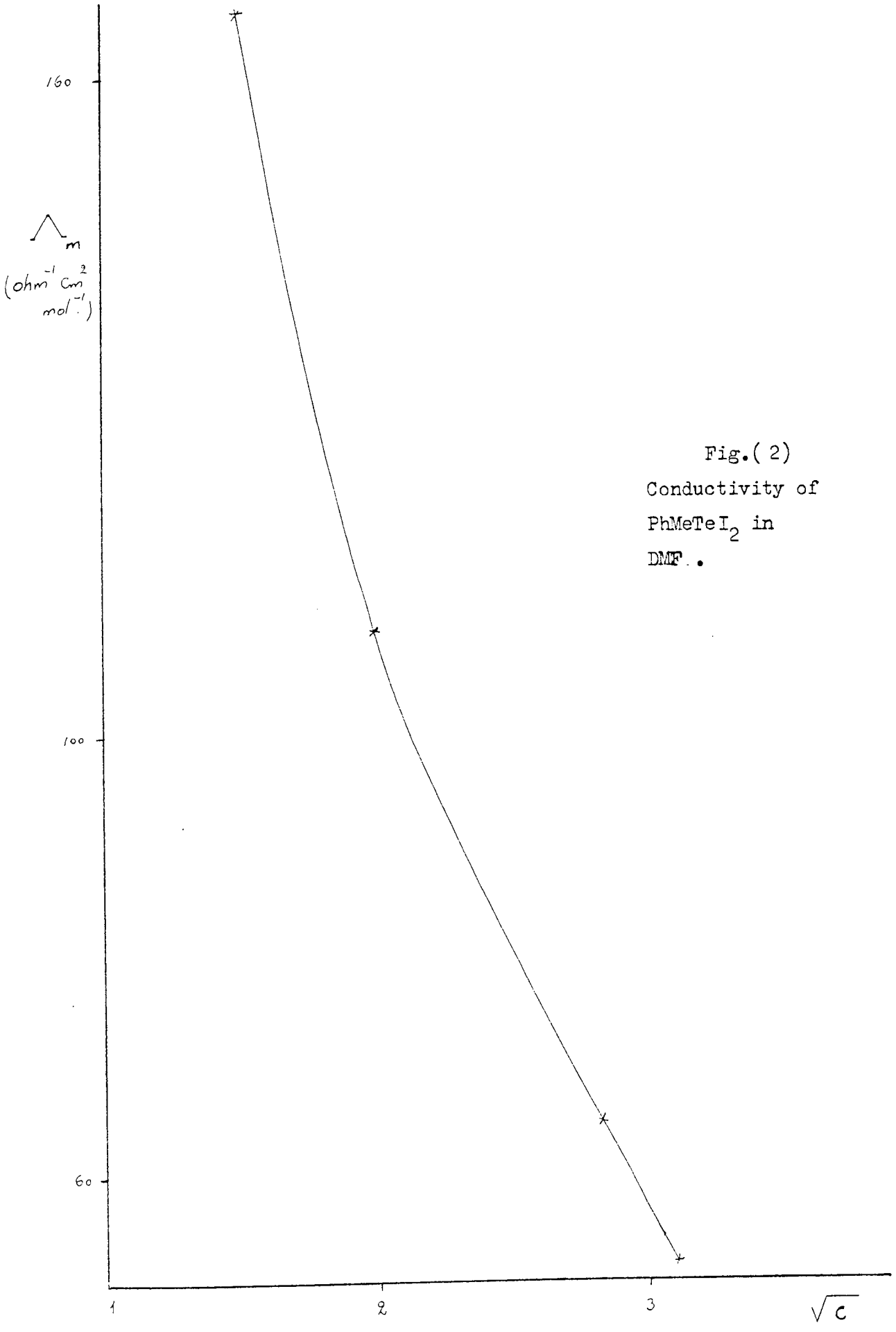


Fig.(2)
Conductivity of
$PhMeTeI_2$ in
DMF.

5. (iv). DISCUSSION :

The chemistry of methyl phenyl tellurium (IV) species ($PhMeTeX_2$), where X = I, Br, Cl, NCS, RCOO, has not been reported in the literature. A new class of unsymmetrical diorganotellurium (IV) species such as methyl phenyl tellurium dibromide, dichloride and o-phthalate was synthesised and their behaviour and stability in solvents with different polarity was investigated. Furthermore, some compounds of the type PhMeTeXY, where X = Cl, Y = Br and X = Cl, Y = I were synthesised and Te-X vibrations were compared with the vibrations in $PhMeTeX_2$.

A large number of organic tellurium compounds have been investigated in the literature with infra-red and Raman techniques. The tellurium-carbon (alkyl) stretching frequencies are located in the region 530-450 cm^{-1} {98} . The corresponding tellurium-carbon (phenyl) modes { 9, 99, 100 } occur between 200-260 cm^{-1} and not in the region 555-487 cm^{-1} as suggested by Keller {101} . A region of 700-300 cm^{-1} has been suggested for Te-O vibrations in tellurinic acid halides {102} whereas in diaryltellurium diacetate a band at 280 cm^{-1} was assigned to this mode {88} . McWhinnie et al., {103} have investigated the low frequency infra-red and Raman spectra of a large number of diaryltellurium dihalides and concluded that all these compounds have Ψ-trigonal bipyramidal structures with axial halogen atoms regardless of the nature of the substituents in the aryl ring. The tellurium-

halogen stretching vibrations were found in the region 287-262 cm^{-1} (Cl), 186-159 cm^{-1} (Br) and 153-109 cm^{-1} (I).

Infra-red spectra of methyl phenyl tellurium dichloride, bromide chloride and iodide chloride in the solid state in polythene discs were recorded and tellurium-chlorine vibrations in all three compounds were assigned, and despite the fact that analysis indicate that we are dealing with the right compounds, infra-red examination revealed some similarity of vibration frequencies. There can be no doubt, that methyl phenyl tellurium dichloride is pure and following previous Ph_2TeCl_2 reference { 9 }, the two Te-Cl frequencies are 278 and 260 cm^{-1} due to ν_s and ν_{as} respectively, furthermore, Te-Me frequency is located as ν= 540 cm^{-1}. When we consider the structure of PhMeTeBrCl and PhMeTeICl, it is clear that strong bands at ν = 277 and ν = 260 cm^{-1} persist, thus despite good analysis, we must accept these materials as mixtures. In the case of PhMeTeBrCl a definite shoulder is observed at 282 cm^{-1}. This is possibly the Te-Cl stretching of the desired compound. Hence the mixture may be complex, in addition to the presence of $PhMeTeCl_2$ we may also have PhMeTeBrCl and $PhMeTeBr_2$, in such proportions as to give a C, H analysis. Unfortunately, therefore, this discussion must be terminated since we can no longer be confident that pure compounds are under consideration.

The synthesis of a new class of organotellurium derivatives of dicarboxylic acids has been recently reported { 32 }. These compounds

of the general formula $R_2Te(C_8X_4O_4)$ where X = H and Br; were found to be dimer in benzene solution. Following the synthesis of methyl phenyl tellurium dichloride, we became interested to extend the series of organotellurium carboxylate compounds by attempting to synthesise methyl phenyl tellurium phthalate. Therefore, the reaction of freshly prepared sodium salts of ortho- phthalic acid with methyl phenyl tellurium dichloride in chloroform yielded a white solid with mp = 102°C.

The infra-red spectrum of this compound in the solid state is shown on page 150. The bands at 1645 and 1310 cm^{-1} correspond to ν_{as} (CO) and ν_s (CO) and the peak at 565 cm^{-1} is due to Te-Me vibration, similar to data were obtained in chloroform solution. The infra-red spectrum of the compound in chloroform solution was recorded at time intervals and the frequencies remained constant. The separation of the unsymmetrical and symmetrical frequencies (Δ) is 335 cm^{-1}, this separation which can be taken as a measure of "ester-like" character of the carboxylate group coupled with the fact that the COO^- groups are equivalent (no doubling of (COO)) lead us to postulate that the phthalate group acts as a bidentate ligand, with one oxygen atom of each carboxylate acting as donor.

Molecular weight measurement of methyl phenyl tellurium phthalate in chloroform was carried out and the results clearly indicate that the compound must be formulated as a monomer. The synthesis and

molecular weight measurement of diphenyl tellurium phthalate has been carried out within our group and the compound has been reported to be a dimer in benzene solution, therefore, the recent report of Tamagaki {94} on the monomer nature of Ph_2Te (Phthalate) could be considered surprising, however, Tamagaki did use a different method of synthesis.

The ^1H n.m.r. spectrum of methyl phenyl tellurium phthalate in deuterated chloroform was obtained and the initial spectrum consisted of a single methyl resonance at $\delta = 3.28$ ppm with satellite peaks due to ^{125}Te-^1H coupling ($J = 25$ H_z) which remained constant after 48 hrs.

The different observations on the nature of R_2Te (Phthalate) compounds by Dance (R = P-EtO and -MeO) and Tamagaki (R = Ph) and with what we observed on PhMeTe ($C_8H_4O_4$), could be explained by considering an equilibrium such as (1). The Dance model {32} for the dimer invokes strain free interaction between phthalate and tellurium, whereas (see below) strain may be involved in the monomer. The solvation energy of a given monomer is likely to be greater than that of the corresponding dimer,

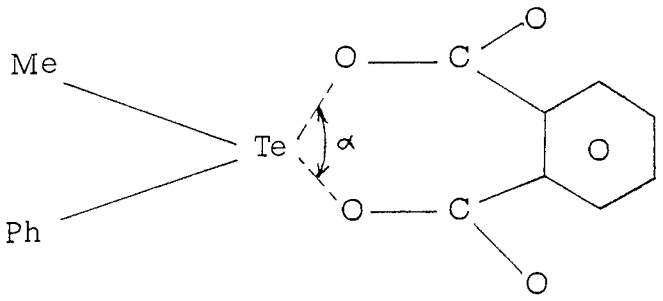
$$\text{Dimer} \rightleftharpoons 2\ \text{Monomer} \qquad (1)$$

however, if large para-substituents are located on the phenyl rings, the difference in solvation energy between that monomer-dimer pair may

become dominant. Thus, we propose that the difference in behaviour observed between Dance and Tamagaki and ourselves may be interpreted in terms of the fine balance between loss of solvation energy (monomer ⟶ dimer) and gain in Te-O bond strength (monomer ⟶ dimer). It should be noted that repulsion between Te atoms may occur in the dimer, however, this is likely to be consistent and independent of para-substituent.

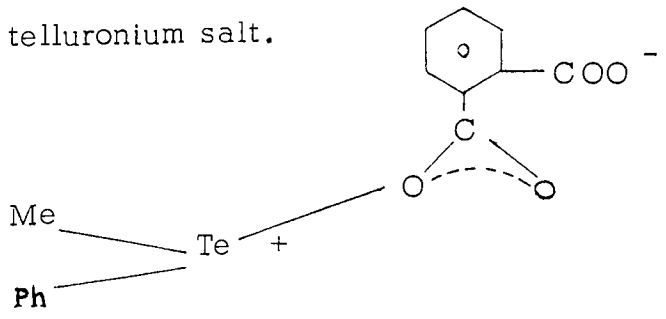
As far as the structure of methyl phenyl tellurium phthalate is concerned, two structural forms could be suggested :

(A) : Since we have postulated that one oxygen atom of each carboxylate acts as donor.



Where α must be considerably less than 180°.

(B) or an internal telluronium salt.



and since it is suggested that the two carboxylate groups are equivalent, on the infra-red time-scale, this means that they have to fluctuate within less than 10^{-13} sec. for differences to be undetected in the infra-red, which is very unlikely, i.e. structure B is ruled out, therefore, structure A becomes the only possibility for the arrangements of the groups round the Te atom.

Since the character of this compound does not vary between the solution and the solid state, it is probable that a rich solid state chemistry awaits examination and elucidation in this area, and it is hoped that these results will form a useful basis for future X-ray crystallographic studies.

* * * * * * * * * *

Among methyl phenyl tellurium dihalides, diiodide was the only one which showed some dissocation in chloroform solution over 24 hrs. The ^{1}H n.m.r. spectrum of methyl phenyl tellurium diiodide in $CDCl_3$, initially consisted of a singlet methyl resonance at δ = 3.5 ppm (relative to TMS) with satellite peaks which after 24 hrs. was accompanied by another singlet at δ = 2.15 ppm due to MeI. Conductivity measurements of this compound in DMSO and DMF, also showed a high value for Λ_M. The conductivity was studied as a function of concentration (Λ_M versus $\sqrt{C}$), and straight lines were observed for $PhMeTeI_2$, thus strong

electrolytes are indicated.

Vernon {104} has reported the existence of two forms of dimethyl tellurium dihalides which he originally formulated as cis - trans isomers {105}, designated as α- and β- forms. Conductivity and spectral studies by Lowry and co-workers {106} strongly support the Vernon's suggestion that β- compounds are $\{R_3Te\}^+ \{RTeX_4\}^-$ and α- derivatives show behaviour which support a structure of the type $\{R_2TeX\}^+X^-$ at least in solution.

Therefore, loss of MeI from methyl phenyl tellurium diiodide, high Λ_M and with the background of Vernon's suggestion on dimethyl tellurium dihalides we can postulate:

$$Ph_2MeTe^+ \quad MeTeI_4^-$$

$$\downarrow$$

Covalent form

$$\downarrow$$

$$PhMeTe + "PhMeTeI_4"$$

$$\downarrow$$

$$PhTeI + I_2 + MeI$$

Evidence for PhTeI was obatined by introducing the thiurea group into the Te^{II} compound and PhITe $\{SC(NH_2)_2\}$ was obtained (i.r. and C,H analysis). Dissociation of methyl phenyl tellurium diiodide in the form of

$$PhMeTeI_2 \longrightarrow\!\!\!\!\!\!\times \quad PhTeI + MeI$$

is ruled out because of high molar conductivity of this compound.

The extension of the series of methyl phenyl tellurium (IV) species to acetate, benzoate and thiocyanate failed to produce isolable products (in the case of acetate and thiocyanate), but in the case of benzoate, the analysis (i.r., C, H analysis) of the white solid obtained showed that hydrolysis had taken place.

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