A Spectroscopic Examination of Phenyltellurium Trihalides

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The far-i.r. spectra, and where possible the Raman spectra, of $RTeX_3$ are presented and assignments of tellurium–halogen modes are made (R = Ph, *p*-$Me{\cdot}C_6H_4$, *p*-$MeO{\cdot}C_6H_4$, *p*-$EtO{\cdot}C_6H_4$, *p*-$PhO{\cdot}C_6H_4$; X = Cl, Br, or I). Consideration of the low-frequency vibrational data and other physical evidence suggests the compounds are associated to some degree with dimeric structures involving five-co-ordinate tellurium atoms the most probable for chlorides and iodides. There is evidence to suggest that some bromides notably $PhTeBr_3$, (*p*-$Me{\cdot}C_6H_4$)$TeBr_3$, and (*p*-$PhO{\cdot}C_6H_4$)$TeBr_3$ are more associated. It is suggested that the variety of structural possibilities are best understood in terms of donor–acceptor interactions between X^- and $RTeX_2^+$.

THE organotellurium halides provide a challenging area for structural investigations. Vibrational spectroscopy is, in principle, a powerful tool for these investigations but the possibility that ambiguous conclusions may be drawn from attempts to interpret the i.r. and Raman spectra of complex molecules is well illustrated by the recent literature of $TeCl_4$.[1,2] Thus both covalent structures based on the ψ-trigonal bipyramid ($TeCl_4$) [1a] and ionic structures ($TeCl_3^+Cl^-$) [2] were proposed. Despite a number of earlier attempts [3] the structure of the tetrachloride was only recently shown by *X*-ray methods [4] to be based on the tetrameric unit Te_4Cl_{16} with the co-ordination number of each tellurium atom being six by virtue of three normal covalent bonds (2·3 Å) and three much longer bonds (2·9 Å).

We recently considered a series of diaryltellurium dihalides,[5] R_2TeX_2, and concluded that the ψ-bipyramidal structure with axial halogen atoms held for a considerable variety of groups R. In this paper we consider the more difficult problem of the aryltellurium trihalides. Although the presence of an aryl group complicates the low-frequency vibrational spectra, the greater ease of preparation and handling and the possibility of examining a wide range of compounds offers some compensation. Understandably, the methyltellurium trihalides have been the subject of some investigations. Of particular relevance to this work are the investigations of Chen and George [6] with $MeTeBr_3$ and of Wynne and George with some selenium analogues [7]. Wynne and Pearson [8,9] have recently published two papers which will be relevant to our discussion. An early investigation of the i.r. spectra of some phenyltellurium compounds including $PhTeCl_3$ is also noted.[10]

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[1] (*a*) G. C. Hayward and P. J. Hendra, *J. Chem. Soc.* (*A*), 1967, 643; (*b*) N. Katsaros and J. W. George, *Inorg. Chim. Acta*, 1969, **3**, 165.

[2] (*a*) N. N. Greenwood, B. P. Straughan, and A. E. Wilson, *J. Chem. Soc.* (*A*), 1966, 1479; 1968, 2209; (*b*) D. M. Adams and P. J. Lock, *ibid.*, 1967, 145; (*c*) I. R. Beattie and H. Chudzynska, *ibid.*, 1967, 984.

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[6] M. T. Chen and J. W. George, *J. Amer. Chem. Soc.*, 1968, **90**, 4580.

[7] K. J. Wynne and J. W. George, *J. Amer. Chem. Soc.*, 1969, **91**, 1649.

[8] K. J. Wynne and P. S. Pearson, *Inorg. Chem.*, 1969, **9**, 106.

[9] K. J. Wynne and P. S. Pearson, *Chem. Comm.*, 1970, 556.

[10] H. P. Fritz and H. Keller, *Chem. Ber.*, 1961, **94**, 1524.

EXPERIMENTAL

Synthesis of the Compounds.—The majority of the compounds we consider have previously been reported in the literature (see Table 1 for references) but limited details of $PhTeBr_3$ have been given [11] and $PhTeI_3$, (p-MeC_6H_4)$TeBr_3$, and (p-MeC_6H_4)TeI_3 appear to be new compounds. The trichlorides $RTeCl_3$ (where R = p-$MeO{\cdot}C_6H_4$, p-$EtO{\cdot}C_6H_4$, and p-$PhO{\cdot}C_6H_4$) were prepared by the direct reaction of tellurium tetrachloride and the appropriate ether. The corresponding bromides and iodides were obtained *via* the diaryl ditellurides by oxidation with either bromine or iodine.[12] When R = Ph or p-MeC_6H_4– it is possible to synthesise the aryltellurium trichloride by reaction of tellurium tetrachloride with the appropriate organomercuric halide,[13] however despite purification of all starting materials we found both $PhTeCl_3$ and (p-MeC_6H_4)$TeCl_3$ prepared by this method to be contaminated with small amounts of a greyish material which was difficult to remove by recrystallisation. We therefore found it convenient to reduce the crude trichlorides to the ditelluride [13] and reoxidise the purified ditelluride with chlorine to pure $RTeCl_3$ (R = Ph or p-MeC_6H_4). The ditellurides were also required for the preparation of the bromides and iodides.

TABLE 1

Analytical and physical data for aryltellurium trihalides

Compound	Found (%)		Calc. (%)				
	C	H	C	H	M.p. (°C)	Lit. m.p.	Ref.
(C_6H_5)$TeCl_3$	22·5	1·55	23·2	1·6	214—217	215—218	13
(C_6H_5)$TeBr_3$	16·2	1·15	16·2	1·15	227—229		11 and this work
(C_6H_5)TeI_3	12·5	0·85	12·3	0·85	180—181		This work
(p-MeC_6H_4)$TeCl_3$	25·9	2·1	25·9	2·15	187—188	181—182	13
(p-MeC_6H_4)$TeBr_3$	18·8	1·65	18·3	1·55	215—216		This work
(p-MeC_6H_4)TeI_3	14·6	1·5	14·0	1·15	175—176		This work
(p-$MeO{\cdot}C_6H_4$)$TeCl_3$	24·2	2·05	24·6	2·05	196—197	190	*a*
(p-$MeO{\cdot}C_6H_4$)$TeBr_3$	17·6	1·4	17·7	1·5	189—190	188—189	*b*
(p-$MeO{\cdot}C_6H_4$)TeI_3	13·7	1·1	13·7	1·15	131—133	131—133	*b*
(p-$EtO{\cdot}C_6H_4$)$TeCl_3$	26·8	2·55	27·1	2·55	184—187	182—183	*c*
(p-$EtO{\cdot}C_6H_4$)$TeBr_3$	19·3	1·9	19·7	1·85	197—206	195—205	*b*
(p-$EtO{\cdot}C_6H_4$)TeI_3	15·7	1·45	15·3	1·45	133—134	133—134	*b*
(p-$PhO{\cdot}C_6H_4$)$TeCl_3$	36·1	2·15	35·8	2·25	155—156	156—157	*d*
(p-$PhO{\cdot}C_6H_4$)$TeBr_3$	26·5	1·65	26·9	1·7	204—205	206·5—207	*b*
(p-$PhO{\cdot}C_6H_4$)TeI_3	22·2	1·45	21·3	1·35	161—162	160·5—161	*b*

[a] G. T. Morgan and R. E. Kellet, *J. Chem. Soc.*, 1926, 1080. [b] N. Petragnani, *Tetrahedron*, 1960, **11**, 11. [c] G. T. Morgan and H. D. K. Drew, *J. Chem. Soc.*, 1925, 2307. [d] H. D. K. Drew, *J. Chem. Soc.*, 1926, 227.

Phenyl- and (p-*Tolyl*)*tellurium Tribromide.*—Bromine in carbon tetrachloride was slowly added with stirring to a carbon tetrachloride solution of the diaryl ditelluride (2 mmol) at 10 °C. The brown ditelluride became yellow and yellow crystals were deposited. Addition of bromine was continued until an excess was present. The mixture was stirred for a further 30 min after which the precipitate was filtered off and dried. The product was recrystallised from glacial acetic acid to afford yellow *crystals* of $RTeBr_3$ (0·79 g, R = Ph; 0·61 g, R = p-MeC_6H_4).

Phenyl- and (p-*Tolyl*)*tellurium Tri-iodide.*—The appropriate diaryl ditelluride (1 mmol) in carbon tetrachloride was maintained at 3—5 °C whilst iodine (0·72 g) in carbon tetrachloride was added. The solution was then stirred for 30 min after which the red-brown precipitate was collected and dried. The crude tri-iodide was recrystallised from benzene–light petroleum ($PhTeI_3$, yield 0·31 g *brown crystals*) or benzene [(p-MeC_6H_4)TeI_3, yield 0·65 g *red-brown needles*].

It was noted that if iodine was added to diphenyl ditelluride at 10—15 °C a black, benzene-soluble material was obtained. Careful inspection showed this to be a mixture of $PhTeI_3$ and a second substance. We found no suitable solvent for the separation of the two substances. It is suggested that the black material may be the intermediate phenyltellurenyl iodide, PhTeI. Very few tellurenyl compounds are known and only one organotellurenyl halide, (2-naphthyl)TeI, has been reported.[14] Analytical and physical data are given in Table 1.

Physical Measurements.—I.r. spectra were recorded on the following instruments: 4000—400 cm^{-1}, Perkin-Elmer 457 (Nujol mulls or KBr discs); 400—200 cm^{-1}, Perkin-Elmer 225 (Nujol mulls, Polythene supports); 400—40 cm^{-1}, R.I.I.C. FS 720—FS 200 Fourier spectrometer, spectra were computed to a resolution of 2 cm^{-1} with the University ICL 1905 computer. Samples were Nujol mulls in Polythene cells and the instrument was calibrated with water vapour. Raman spectra were determined for crystalline specimens by He–Ne laser excitation using a Cary 81 instrument. These measurements were made by courtesy of the Chemistry Department, University of Nottingham.

X-Ray powder photographs were taken with Cu-K_α radiation. The results were disappointing in some cases despite replication of the measurements with various exposure times.

Conductivity measurements were made with a Henelec bridge.

RESULTS

The low-frequency i.r. and Raman spectra are tabulated in Tables 2 (phenyl-compounds) and 3. The tri-iodides absorbed strongly at 6328 Å and showed signs of decomposition in the laser beam, therefore only limited data are reported. The *X*-ray powder data were of poor quality, particularly for the bromides, however the following isomorphous systems may be noted: $PhTeCl_3$ and $PhTeI_3$; (p-MeC_6H_4)$TeCl_3$ and (p-MeC_6H_4)TeI_3; (p-$EtO{\cdot}C_6H_4$)$TeCl_3$

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[11] N. Petragnani and G. Vicenti, *Univ. São Paulo, Fre. Filosoff. Cienc. Letres. Bol. Comm.*, 1959, **5**, 75.

[12] N. Petragnani, *Tetrahedron*, 1960, **11**, 15.

[13] W. V. Farrar, *Research*, 1951, **4**, 177.

[14] G. Vicenti, E. Giesbrecht, and L. R. M. Pitombo, *Chem. Ber.*, 1959, **92**, 40.

and (p-EtO·C_6H_4)$TeBr_3$. In other cases the data do not enable definite conclusions to be drawn. However careful examination of the i.r. spectra (4000—400 cm^{-1}) showed considerable differences between $PhTeBr_3$ and $PhTeX_3$ (X = Cl or I); the spectra of all three p-methoxyphenyl-compounds differed in detail and (p-PhO·C_6H_4)TeI_3 differed from the other two members of the group. By contrast the i.r. spectra (4000—400 cm^{-1}) of the p-tolyl-series were identical and this was the case for the p-ethoxyphenyl-series. Thus there is correlation between observed spectral differences and the more positive conclusions from the X-ray measurements.

The solubilities of the phenyl-compounds in benzene were qualitatively investigated, and the order of solubility was $PhTeCl_3 \gg PhTeI_3 > PhTeBr_3$. This is in contrast to the behaviour of the methyl series where the order of solubilities was $MeTeCl_3 > MeTeBr_3 > MeTeI_3$(insoluble).[8] We found that, in general, the iodide was more soluble than the bromide within a given group. Evidence for complex conductivity behaviour in polar solvents was found but the need to seriously consider ionic structures for the solid state does not arise.

A further point of interest from Table 1, which does not seem to have previously drawn comment, is that, with the exception of the group $RTeX_3$ for which R = p-MeO·C_6H_4, the bromide has a higher melting point than the other two members.

TABLE 2

The low-frequency vibrational spectra of phenyltellurium trihalides

$PhTeCl_3$		$PhTeI_3$		$PhTeBr_3$		
I.r. (cm^{-1})	Raman	I.r. (cm^{-1})	Raman	I.r. (cm^{-1})	Raman	
337s	342s	169s	168s	220sh		ν(Te–X) terminal
317sh	318m			213s	210sh	
306s	303m	158s	153s	198m	198vs	
178s	174w	97m	94m	134m	132w	ν(Te–X) bridge + δ(TeX_2)
153sh	143m	86m		123m 113sh	120vw	
260 255 m 250	263 256 m	250sh 247 m 241	241 238m	260m—s	234m	ν(Te–Ph) *i.e.* phenyl *t* and *t′* modes
206m			205			
		196m		185m		Phenyl *x* and *u* modes
	100m			93w		Unassigned

TABLE 3

Tellurium–halogen vibrations of aryltellurium trihalides, $RTeX_3$

	X = Cl		X = Br		X = I
R	I.r. (cm^{-1})	Raman	I.r. (cm^{-1})	Raman	I.r. (cm^{-1})
p-MeC_6H_4	336s	341s	220ms	219m	178s
	318sh	316w	204vs	199vs	155s
	304s	303w	126ms	131mw	
	180s	179m	113ms		
	152m				
p-MeO·C_6H_4	323s	329s	213s	209m	164s
	295s	301m, 298m	192ms		154vs
	180s	186w	136m		91ms
	148s	139m	115ms		
p-EtO·C_6H_4	334s	330s	218s	216s	174s
	326s	327s	206vs		154ms
	318s		194vs	192wm	94m
	298s	305m	126s	135m	
	179s		104vs	105mw	
	146s				
p-PhO·C_6H_4	334s	339s	224m	224s	162s
	320s	315m—s	211s	204vs	154s
	311s		194s	190s	94m—s
	172s	179w	136m	133m	
			120m—s		

DISCUSSION

Our data for $PhTeCl_3$ do not agree exactly with those of Fritz and Keller [10] who fail to report a band at 337 cm^{-1}, however Wynne and Pearson [8] report bands at 338 cm^{-1} and 315 cm^{-1} for $MeTeCl_3$. The positions of the three tellurium–bromide modes reported by Chen and George [6] for $MeTeBr_3$ are in good agreement with those we assign for $PhTeBr_3$ in Table 2. Assignments of bands below 200 cm^{-1} to tellurium–halogen modes, must be made with caution since both lattice modes and low-frequency vibrations of complex organic groups R in $RTeX_3$ complicate the spectra. Also, given the possibility that both long and short tellurium–halogen bonds may be present, as in $TeCl_4$, stretching vibrations associated with the long bonds and deformation modes associated with the short bonds may occur in similar regions. Thus, particularly in the case of the trichlorides, when two vibrations below 200 cm^{-1} are assigned as tellurium–halogen modes (Tables 2 and 3), it is probable that one is a deformation mode.

Phenyltellurium Trihalides.—It is convenient to discuss the phenyl compounds separately since the ring vibrations may be identified with more certainty in these cases.[15] Both the high frequency i.r. data (*vide supra*) and the X-ray data indicate that $PhTeBr_3$ may differ structurally from the other two members of the group. The higher melting point and reduced solubility in benzene indicate a greater molecular complexity in this case. This is in contrast to the methyltellurium trihalides where the tri-iodide was considered to have the higher degree of association.[8] We therefore take the view that the chloride and iodide are iso-structural and note the relatively simple i.r. spectrum of the iodide which would be compatible with a structure based on ' $PhTeI_2^+$ units ' associated *via* iodide bridges to give a five co-ordinate tellurium atom in agreement with the theory of Wynne and Pearson.[8] Thus the higher frequency bands at 169 cm^{-1} and 158 cm^{-1} are assigned to the stretching of the short tellurium–iodine bonds of ' $PhTeI_2^+$ ' and the lower frequency bands at 97 cm^{-1} and 86 cm^{-1} to both stretching vibrations involving the bridge bonds and also, possibly, deformation vibrations of ' $PhTeI_2^+$ '. We do not imply the structure to be ionic, but that we may conveniently regard the structure as being built up from $RTeX_2^+$ and X^- units to give the molecular types illustrated in the Figure. The appearance of three bands in the 340—300 cm^{-1} region for $PhTeCl_3$ probably reflects coupling of vibrations of ' $PhTeCl_2^+$ ' groups within a molecular unit or between chromophores within the unit cell, since the isomorphism of $PhTeCl_3$ and $PhTeI_3$ does not enable us to interpret the greater band multiplicity for ν(TeCl) than for ν(TeI) in terms of structural differences. The phenyl *t* modes are also affected by coupling in the case of the chloride and iodide. For a substituent of the mass of tellurium, it is the phenyl *t* and *t′* modes [15] which are most reasonably termed tellurium–phenyl stretching vibrations, but, as calculations on simple monohalogeno-benzenes [16] demonstrate, such a description is approximate.

Although there are many coincidences between the i.r. and Raman frequencies for $PhTeCl_3$ and $PhTeI_3$, some differences of the order of 5—10 cm^{-1} are noted and in this respect data for $TeCl_4$ and $TeBr_4$ are similar. Thus whilst it is not apparent from the available data that a centrosymmetric structure exists, final judgement must be reserved until more detailed *X*-ray data are available since as implied in the above discussion of coupling of ν(TeX), the observed spectra more properly reflect the symmetry, of the unit cell. Several structures may be built up from donor–acceptor interactions of X^- and $PhTeX_2^+$ which, in accordance with the theory of Wynne and Pearson [8] have five-co-ordinate tellurium atoms and the absence of bonds to halogen in positions *trans* to phenyl. Also differing degrees of association may be readily accounted for, thus if $PhTeCl_3$ and $PhTeI_3$ are at least dimers, $PhTeBr_3$ may be a trimer as illustrated in the Figure.

Other Aryltellurium Trihalides.—Allowing for the greater complexity of the spectra due to the more complex aryl groups, it may be concluded that a pattern very similar to that for the phenyl compounds emerges. Thus, in general, there is more evidence of vibrational coupling for the chlorides than for the bromides and iodides and also agreement between i.r. and Raman tellurium–halogen frequencies is less precise for the chlorides than for the bromides. The relative simplicity of the i.r. data for the iodides is again noted, although it now becomes difficult to assign confidently tellurium–halogen modes below 100 cm^{-1} due to the presence of the more complex aryl groups. Again structures built from $RTeI_2^+$ and I^- may be proposed with dimeric molecules being the most probable. We believe that the structures of the chlorides and bromides may be understood in similar terms.

We suggest that the conclusions that may be legitimately drawn from this study are as follows. There is good evidence to suggest that $PhTeBr_3$ is more associated than $PhTeCl_3$ and $PhTeI_3$, and that similar conclusions are valid for $(p\text{-}MeC_6H_4)TeBr_3$ and $(p\text{-}PhO{\cdot}C_6H_4)TeBr_3$. However it is not generally true that the bromide is the most complex member of any series $RTeX_3$, the structure being a function of both R and X. We believe that the most probable structure for the chlorides and iodides is the dimer represented in the Figure; this is in agreement with the theory of Wynn and Pearson.[8] However, more complex structures are possible in which the co-ordination number of the tellurium remains five and in which no halogen atom *trans* to the organic groups is present. The structural variety possible for the compounds is best understood if we consider each structure to arise from donor–acceptor interaction between X^- and $RTeX_2^+$.

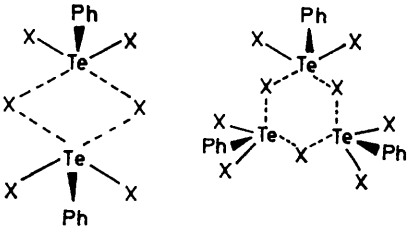

Illustration of typical structures resulting from donor–acceptor interaction of X^- and $PhTeX_2^+$

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