

## The Low Frequency Infra-red and Raman Spectra of some Diaryltellurium Dihalides

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Assignments are suggested for the low-frequency i.r. and Raman bands of the isomorphous series  $\text{Ph}_2\text{TeX}_2$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ). Resonance enhancement of the intensity of  $\nu_s(\text{TeX})$  is noted for  $\text{X} = \text{Br}, \text{I}$ . The vibrational spectra of  $\text{R}_2\text{TeX}_2$  ( $\text{R} = p\text{-tolyl}, o\text{-tolyl}, p\text{-MeOC}_6\text{H}_4, \text{C}_6\text{F}_5$ ;  $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) are also reported and assignments of  $\nu(\text{TeX})$  are suggested. It is concluded that all these compounds have  $\psi$ -trigonal bipyramidal structures with axial halogen atoms regardless of the nature of the substituents in the aryl ring. In all cases  $\nu_s(\text{TeCl})$  is assigned at higher frequency than  $\nu_{\text{as}}(\text{TeCl})$  but for the bromo- and iodo-compounds the asymmetric mode occurs at the higher frequency.

THE literature of organotellurium chemistry, whilst not negligible in quantity,<sup>1</sup> shows the need for more complete physical investigations of many of the more simple derivatives. It is only recently, for example, that studies of the vibrational spectra of the structurally intriguing organotellurium halides have been published. Fritz and Keller published i.r. spectra ( $4000\text{--}250\text{ cm}^{-1}$ ) of a variety of tellurium compounds and offered assignments for  $\nu(\text{Te-alkyl})$ ,  $\nu(\text{Te-aryl})$ , and  $\nu(\text{TeCl})$  for some organotellurium halides.<sup>2</sup> Chen and George,<sup>3</sup> using vibrational spectroscopy and other techniques, concluded that solid trimethyltellurium bromide is ionic,  $\text{Me}_3\text{Te}^+\text{Br}^-$ ; that solid dimethyltellurium dibromide consists of covalent monomers and that methyltellurium tribromide is possibly polymeric in the solid state. Hayward and Hendra<sup>4</sup> have made unambiguous assignments for  $\nu(\text{TeX})$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) for  $\text{Me}_2\text{TeX}_2$  using i.r. and laser Raman spectroscopy.

Apart from the work of Fritz and Keller,<sup>2</sup> no vibrational spectroscopic studies have been published for the aryltellurium halides. As part of a programme of

research in organotellurium chemistry we have examined the i.r. and Raman spectra of several aryltellurium halides and here we present our results for the series  $(\text{aryl})_2\text{TeX}_2$ . Although the presence of the aryl group complicates the spectrum, some crystallographic data are available to aid assignment, e.g. for  $\text{Ph}_2\text{TeBr}_2$ <sup>5</sup> and  $(p\text{-ClC}_6\text{H}_4)_2\text{TeI}_2$ <sup>6</sup> both of which are monomeric  $\psi$ -trigonal bipyramidal molecules with axial halogen atoms.

### EXPERIMENTAL

*Diphenyltellurium Dihalides and Diphenyl Telluride.*—Diphenyl telluride was synthesised by a modification of the method of Rheinboldt and Petraghani.<sup>7</sup> To an ethereal solution (100 ml) of a Grignard reagent synthesised from bromobenzene (39.3 g) and magnesium (6.1 g) was added benzene (100 ml). The temperature of the solution was lowered to  $0^\circ$  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 heated under reflux for 2 h. The cooled solution was treated with saturated ammonium chloride solution (300 ml) and the separated organic layer was

<sup>1</sup> N. Petraghani and M. De Moura Campas, *Organometallic Chem. Rev.*, 1967, **2**, 61.

<sup>2</sup> H. P. Fritz and H. Keller, *Chem. Ber.*, 1961, **94**, 1524.

<sup>3</sup> M. T. Chen and J. W. George, *J. Amer. Chem. Soc.*, 1968, **90**, 4580.

<sup>4</sup> G. C. Hayward and P. J. Hendra, *J. Chem. Soc. (A)*, 1969, 1760.

<sup>5</sup> G. D. Christofferson and J. D. McCullough, *Acta Cryst.*, 1958, **11**, 249.

<sup>6</sup> G. Y. Chao and J. D. McCullough, *Acta Cryst.*, 1962, **15**, 887.

<sup>7</sup> H. Rheinboldt and N. Petraghani, *Chem. Ber.*, 1956, **89**, 1270.

washed three times with distilled water and dried; the solvent was removed in a rotatory evaporator to afford crude diphenyl telluride (18.5 g). Our method gave no free tellurium which was reported to be a side product by Rheinboldt.<sup>7</sup>

Bromine oxidation of the crude telluride<sup>8</sup> gave diphenyltellurium dibromide (20 g). A portion (10 g) of the dibromide was reduced with sodium sulphide<sup>8</sup> to give pure diphenyl telluride, portions of which were oxidised by  $\text{SO}_2\text{Cl}_2$  to afford diphenyltellurium dichloride<sup>7</sup> and by iodine to give diphenyltellurium di-iodide.<sup>8</sup>  $\text{Ph}_2\text{TeCl}_2$ , m.p. 159° (lit. m.p. 159—161°) (Found: C, 40.1; H, 3.2. Calc. for  $\text{C}_{12}\text{H}_{10}\text{Cl}_2\text{Te}$ : C, 40.9; H, 2.8%);  $\text{Ph}_2\text{TeBr}_2$ , m.p. 197° (lit. m.p. 198—201°) (Found: C, 32.3; H, 2.3. Calc. for  $\text{C}_{12}\text{H}_{10}\text{Br}_2\text{Te}$ : C, 32.6; H, 2.7%);  $\text{Ph}_2\text{TeI}_2$ , m.p. 235—236° (lit. m.p. 237°) (Found: C, 27.1; H, 1.9. Calc. for  $\text{C}_{12}\text{H}_{10}\text{I}_2\text{Te}$ : C, 26.9; H, 1.9%).

*Di(o-tolyl)tellurium Dihalides and Di-o-tolyl Telluride.*—Two methods of preparation were employed, that due to Lederer<sup>8</sup> (substituting  $\text{TeCl}_4$  for  $\text{TeBr}_2$ ) being preferred to the more recent procedure of Taniyama *et al.*<sup>9</sup> The crude telluride was oxidised by bromine to di-o-tolyltellurium dibromide a portion of which was reduced with sodium sulphide to give the pure telluride. The dichloride and di-iodide were obtained by treatment of the telluride with  $\text{SO}_2\text{Cl}_2$ <sup>7</sup> and  $\text{I}_2$  respectively: (o-tol)<sub>2</sub> $\text{TeCl}_2$ , m.p. 185° (lit.,<sup>8</sup> 184—185°) (Found: C, 43.9; H, 3.7. Calc. for  $\text{C}_{14}\text{H}_{14}\text{Cl}_2\text{Te}$ : C, 44.1; H, 3.7%); (o-tol)<sub>2</sub> $\text{TeBr}_2$ , m.p. 182° (lit.,<sup>8</sup> 182°) (Found: C, 34.5; H, 3.0. Calc. for  $\text{C}_{14}\text{H}_{14}\text{Br}_2\text{Te}$ : C, 35.8; H, 3.0%); (o-tol)<sub>2</sub> $\text{TeI}_2$ , m.p. 175° (lit.,<sup>8</sup> 176) (Found: C, 30.5; H, 2.5. Calc. for  $\text{C}_{14}\text{H}_{14}\text{I}_2\text{Te}$ : C, 29.7; H, 2.5%).

*Di-p-tolyltellurium Dihalides and Di-p-tolyl Telluride.*—Di-p-tolyl telluride was prepared by Lederer's method<sup>10</sup> with the substitution of  $\text{TeCl}_4$  for  $\text{TeBr}_2$ . The telluride was purified and the dihalides were prepared by the method indicated above: (p-tol)<sub>2</sub> $\text{TeCl}_2$ , m.p. 160—162 (lit.,<sup>10</sup> 163—164°) (Found: C, 43.4; H, 3.9); (p-tol)<sub>2</sub> $\text{TeBr}_2$ , m.p. 197° (lit.,<sup>10</sup> 198—201°) (Found: C, 35.6; H, 3.0); (p-tol)<sub>2</sub> $\text{TeI}_2$ , m.p. 214° (lit.,<sup>10</sup> 218—219°) (Found: C, 32.4; H, 2.7); (p-tol)<sub>2</sub> $\text{Te}$ , m.p. 64° (lit.,<sup>11</sup> 63—64°; Lederer<sup>10</sup> reports m.p. 69—70°, we however agree with Zeiser's earlier determination).

*Di-p-methoxyphenyltellurium Dihalides and Di-p-methoxyphenyl Telluride.*—Di-p-methoxyphenyltellurium dichloride was prepared from the reaction of anisole and tellurium tetrachloride following the method of Morgan and Kellett.<sup>12</sup> The method for reduction of (p-MeO-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub> $\text{TeCl}_2$  is tedious,<sup>12</sup> hence the following procedure was developed. To a stirred benzene (50 ml) solution of di-p-methoxyphenyltellurium dichloride (10 g) was added a saturated aqueous solution (60 ml) of sodium metabisulphite. The mixture was stirred for 4 h after which the organic layer was separated and washed with distilled water. Removal of benzene afforded the crude telluride which was recrystallised from aqueous ethanol (yield 6.5 g, 80%; cf. lit.,<sup>12</sup> yield 37%). Oxidation of the telluride with bromine afforded (p-MeO-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub> $\text{TeBr}_2$ . (p-MeO-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub> $\text{TeCl}_2$ , m.p. 181° (lit.,<sup>12</sup> 181—182°) (Found: C, 40.7; H, 3.5. Calc. for  $\text{C}_{14}\text{H}_{14}\text{Cl}_2\text{O}_2\text{Te}$ : C, 40.7; H, 3.4%); (p-

MeO-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub> $\text{TeBr}_2$ , m.p. 190° (lit.,<sup>12</sup> 190°) (Found: C, 32.9; H, 2.8. Calc. for  $\text{C}_{14}\text{H}_{14}\text{Br}_2\text{O}_2\text{Te}$ : C, 33.5; H, 2.8%); (p-MeO-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub> $\text{Te}$ , m.p. 54° (lit.,<sup>12</sup> 53—54°) (Found: C, 47.4; H, 4.3. Calc. for  $\text{C}_{14}\text{H}_{14}\text{O}_2\text{Te}$ : C, 47.9; H, 4.0%).

*Di(perfluorophenyl)tellurium Dihalides and Di(perfluorophenyl)tellurium.*—Massey *et al.*<sup>13</sup> have recently reported a number of possible routes to di(perfluorophenyl) telluride which involve use of (a) organomercury derivatives, (b) organolithium derivatives, or (c) direct reaction of tellurium with perfluorophenyl iodide. We found it convenient to use the following Grignard route. Perfluorobromobenzene (61 g) dissolved in diethyl ether (50 ml) was added to magnesium (6.1 g) covered with diethyl ether. Reaction started easily and led to the smooth formation of a dark brown solution which was refluxed for 2 h. A procedure identical to that given for diphenyl telluride was followed to afford crude di(perfluorophenyl) telluride (25.6 g). The crude product was divided into two. One portion (12.8 g) was dissolved in carbon tetrachloride and treated with an excess of sulphuryl chloride. The solution was set aside for complete crystallisation of the product. The crude product was recrystallised from light petroleum (40—60°) to give pure di(perfluorophenyl) tellurium dichloride (10 g), m.p. 201° (Found: C, 27.2; F, 35.6.  $\text{C}_{12}\text{Cl}_2\text{F}_{10}\text{Te}$  requires C, 27.0; F, 35.7%).

The second portion of the crude telluride (12.8 g) dissolved in carbon tetrachloride was treated with an excess of a solution of bromine in carbon tetrachloride. The yellow precipitate (13.4 g) formed was recrystallised from carbon tetrachloride; it had m.p. 210° (Found: C, 24.6.  $\text{C}_{12}\text{Br}_2\text{F}_{10}\text{Te}$  requires C, 23.2).

*Dibenzyl Telluride and Dibenzyltellurium Dihalides.*—The telluride has been described once previously<sup>14</sup> as a result of a reaction between dimethylphenylbenzylammonium chloride and sodium telluride. We used the following Grignard route. Tellurium tetrachloride (10 g) in dry benzene (150 ml) was added slowly to an ice cold Grignard reagent prepared from benzyl bromide (44 g) and magnesium (6 g) in dry ether and diluted with ether (100 ml) and benzene (200 ml) prior to use. The reaction mixture was refluxed for 2 h and then cooled to room temperature and treated with a saturated solution of ammonium chloride. The organic layer was washed with distilled water and treated in a rotatory evaporator to afford yellow crude dibenzyl telluride (6.8 g). The crude product was washed with light petroleum to give a white product. As previously observed<sup>14</sup> when set aside in air, or more slowly *in vacuo*, the telluride decomposed to tellurium and an organic product which we have shown to be bibenzyl, m.p. 52° (lit.,<sup>15</sup> 52.2).

Dibenzyl telluride may be oxidised by bromine in carbon tetrachloride to the yellow and sparingly soluble dibenzyltellurium dibromide or by  $\text{SO}_2\text{Cl}_2$  to white dibenzyltellurium dichloride. Although more stable than the tellurium(II) derivative, both halides slowly deposit tellurium with time.

*Physical Measurements.*—I.r. spectra were obtained for Nujol mulls with Perkin-Elmer 457 (4000—400  $\text{cm}^{-1}$ , KBr supports) and 225 (400—200  $\text{cm}^{-1}$ , CsI supports) spectrophotometers. Spectra were also examined in the

<sup>8</sup> K. Lederer, *Ber.*, 1916, **49**, 1071.

<sup>9</sup> H. Taniyama, F. Miyoshi, E. Sakakibara, and H. Uchida, *Yakugaku Zasshi*, 1957, **77**, 191 (*Chem. Abs.*, 1957, **51**, 10,407).

<sup>10</sup> K. Lederer, *Ber.*, 1915, **48**, 2049.

<sup>11</sup> F. Zeiser, *Ber.*, 1895, **28**, 1670.

<sup>12</sup> G. T. Morgan and R. E. Kellett, *J. Chem. Soc.*, 1926, 1080.

<sup>13</sup> S. C. Cohen, M. L. N. Reddy, and A. G. Massey, *J. Organometallic Chem.*, 1968, **11**, 563.

<sup>14</sup> L. Tschugaeff and W. Chlopin, *Ber.*, 1914, **47**, 1271.

<sup>15</sup> C. R. C. Handbook of Chemistry and Physics.

region 400–60  $\text{cm}^{-1}$  with a R.I.I.C. FS 720—FS 200 interferometer spectra being computed with the ICL 1905 computer at the University. Samples were Nujol mulls in Polythene cells; the spectra were computed to a resolution of 2  $\text{cm}^{-1}$  and the instrument calibrated with water vapour. Raman spectra were obtained for microcrystalline samples with a Cary 81 instrument using laser (He–Ne) excitation.\* Some spectra were also checked with a Coderg PH 1 instrument at the University of Leicester.

X-Ray powder photographs were taken using  $\text{Cu-K}\alpha$  radiation. Conductivity measurements were made using a Henelec MRA-38 conductivity bridge.

## RESULTS

The low-frequency i.r. and Raman data for the diphenyl compounds are gathered into Table 1, similar data for the other compounds are given in Supplementary Publication No. SUP 20252 (4 pp, 1 microfiche).† No spectra for the

non-electrolytes in solvents such as methyl cyanide. The isomorphism of  $\text{Ph}_2\text{TeBr}_2$  and  $\text{Ph}_2\text{TeI}_2$  also eliminates from consideration charge transfer complex structures such as  $\text{Ph}_2\text{Te} \cdots \text{I-I}$ .

## DISCUSSION

*Diphenyltellurium Compounds.*—In Table 1 we tabulate the i.r. and Raman spectra of some simple phenyl derivatives of tellurium. The vibrations due essentially to the  $\text{Ph}_2\text{Te}$  unit may be identified with reasonable certainty. The assignments offered follow Whiffen's notation for monosubstituted benzenes.<sup>18</sup> The  $t$  and  $t'$  modes contain a considerable contribution from the stretching of the Te–phenyl bond and could be designated 'metal–phenyl stretching' modes as is common practice in organotin chemistry.<sup>19</sup> If this description is adopted here it is quite clear that these stretching modes occur

TABLE 1  
The i.r. and Raman spectra of some phenyltellurium compounds below 400  $\text{cm}^{-1}$

$\text{Ph}_2\text{TeCl}_2$		$\text{Ph}_2\text{TeBr}_2$		$\text{Ph}_2\text{TeI}_2$		$\text{Ph}_2\text{Te}$	
I.r. ( $\text{cm}^{-1}$ )	Raman ( $\Delta\nu$ )	I.r. ( $\text{cm}^{-1}$ )	Raman ( $\Delta\nu$ )	I.r. ( $\text{cm}^{-1}$ )	Raman ( $\Delta\nu$ )	I.r. ( $\text{cm}^{-1}$ )	Assignment
		393m	393w	393w		386m	Phenyl- $w$
			320w				$2 \times \nu_s(\text{TeBr})$
272s	267vs †	272m	274s	270m—s	268m	271s	$t$ } or $\nu(\text{TePh})$
249s	248m	258m—s	258m	256m	256m	261s	$t'$ }
				244sh		256sh	
230s	230m—s	243s	238s	233s	232m		Phenyl- $u$
				217w			
198vww		198m—w	200m				Phenyl- $u'$
185m	185vww	186m—s*		182m	180m—w	184m	Phenyl- $x$
				150m—w	161m	167sh	Phenyl- $x'$
262s	267vs †	186m—s*		129s ‡			$\nu_{as}(\text{TeX})$
287s	287s*	159vs	158vvs		116vvs		$\nu_s(\text{TeX})$
133m	133vw						$\delta(\text{TeX})_2$
124m	122m—w	106m	117m—w				
95w	98m	89m—w	80m	98m—w			Unassigned
	73m—w		68m				"
43w	43m		62m	54w			"
	28m		32s				"
			22s				"

\*  $\nu_{as}(\text{TeBr}) + x(\text{phenyl})$ . †  $\nu_s(\text{TeCl}) + t(\text{phenyl})$ . ‡ Asymmetric to high wavenumber.

benzyl derivatives are given since their low stability renders the data suspect. Decomposition of dibenzyl telluride to bibenzyl is not unexpected; oxidation of  $(\text{PhCH}_2)_2\text{Te}$  to  $(\text{PhCH}_2)_2\text{TeX}_2$  ( $X = \text{Cl}, \text{Br}$ ) increases the stability of the tellurium to carbon bond but even these compounds undergo colour change when set aside, the bromide more rapidly than the chloride.

The crystal structure of  $\text{Ph}_2\text{TeBr}_2$  is known<sup>5</sup> and since the shortest non-bonded distance between tellurium and bromine atoms in neighbouring molecules is 3.93 Å (*cf.* sum of van der Waals radii, 4.15 Å) we may consider the crystals to contain covalent monomers. X-Ray powder photographs for the series  $\text{Ph}_2\text{TeX}_2$  ( $X = \text{Cl}, \text{Br}, \text{I}$ ) are identical hence similar structures may be presumed for the chloride and iodide. Structures such as  $[\text{Ph}_3\text{Te}^+][\text{PhTeX}_4^-]$ , similar to that of  $\beta\text{-Me}_2\text{TeI}_2$ ,<sup>16</sup> may be further eliminated for the dichloride and di-iodide since, in agreement with Couch *et al.*,<sup>17</sup> we find these compounds to be

\* These measurements were made by courtesy of the Chemistry Department, The University of Nottingham.

† For details of Supplementary Publications, see Notice to Authors No. 7 in *J. Chem. Soc. (A)*, 1970, Issue No. 20.

<sup>16</sup> F. Einstein, J. Trotter, and C. Williston, *J. Chem. Soc. (A)*, 1967, 2018.

between 272 and 256  $\text{cm}^{-1}$  and not, as suggested in a previous report,<sup>2</sup> between 487 and 455  $\text{cm}^{-1}$ . The last region is that in which the X-sensitive  $\gamma$  mode is expected. A comparison of phenyl bands in Table 1 with the accepted phenyl band assignments for  $\text{Ph}_2\text{SnX}_2$  ( $X = \text{Cl}, \text{Br}, \text{I}$ )<sup>19–21</sup> lends support to the assignments offered in this work. In contrast to the comparable phenyl vibrations for  $\text{Ph}_2\text{SnX}_2$  and  $\text{Ph}_2\text{TeX}_2$ , the long tellurium to halogen bonds in  $\text{Ph}_2\text{TeX}_2$  lead to a dramatic lowering of the metal–halogen stretching frequencies in the tellurium series compared with the tin series.<sup>19–21</sup>

The tellurium–halogen modes in Table 1 require some comment. The Raman band at  $\Delta\nu = 267 \text{ cm}^{-1}$  is very intense and is thus a candidate for assignment as  $\nu_s(\text{TeCl})$ . However it is clearly a composite band with the phenyl  $t$  mode being coincident and contributing

<sup>17</sup> D. A. Couch, P. S. Elmes, J. E. Fergusson, M. L. Greenfield, and C. J. Wilkins, *J. Chem. Soc. (A)*, 1967, 1813.

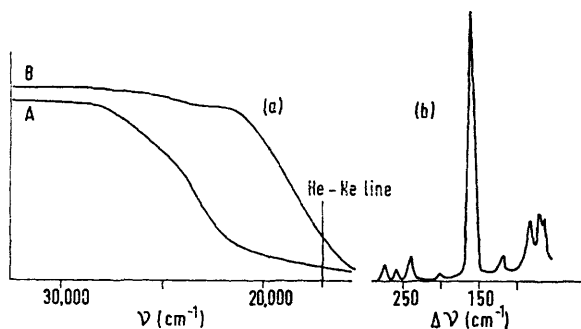
<sup>18</sup> D. H. Whiffen, *J. Chem. Soc.*, 1956, 1350.

<sup>19</sup> R. C. Poller, *Spectrochim. Acta*, 1966, 22, 935.

<sup>20</sup> A. L. Smith, *Spectrochim. Acta*, 1968, 24A, 695.

<sup>21</sup> J. R. May, W. R. McWhinnie, and R. C. Poller, *Spectrochim. Acta*, 1971, 27A, 969.

to the observed intensity. An examination of more complex diaryltellurium dihalides (see below) suggests that generally  $\nu_s(\text{TeCl}) > \nu_{as}(\text{TeCl})$  and this is in keeping with the findings of Hayward and Hendra<sup>4</sup> for  $\text{Me}_2\text{TeCl}_2$ . Thus we suggest the most probable assignments to be  $\nu_s(\text{TeCl}) = 287 \text{ cm}^{-1}$  and  $\nu_{as}(\text{TeCl}) = 262 \text{ cm}^{-1}$ . Assignments for the bromide and iodide present some difficulty.  $\nu_{as}(\text{TeBr})$  might be expected close to  $180 \text{ cm}^{-1}$  by comparison with data for  $\text{Me}_2\text{TeBr}_2$ ,<sup>3,4</sup> however the phenyl  $x$  modes are also expected in this region. The i.r. spectrum of  $\text{Ph}_2\text{TeBr}_2$  shows a band of enhanced intensity, compared with  $\text{Ph}_2\text{TeCl}_2$  and  $\text{Ph}_2\text{TeI}_2$ , at  $186 \text{ cm}^{-1}$  which we assign as  $\nu_{as}(\text{TeBr}) + x$ , however no corresponding band is seen in the Raman spectrum. Hayward and Hendra have remarked that for the series  $\text{Me}_2\text{TeX}_2$ ,  $\nu_{as}$  was of no more than medium to weak intensity in the Raman effect; this appears even more true for  $\text{Ph}_2\text{TeBr}_2$  and  $\text{Ph}_2\text{TeI}_2$ . Also the spectrum of  $\text{Ph}_2\text{TeCl}_2$



(a) Diffuse reflectance spectra of  $\text{Ph}_2\text{TeBr}_2$  (A) and  $\text{Ph}_2\text{TeI}_2$  (B).  
(b) Laser Raman spectrum of  $\text{Ph}_2\text{TeBr}_2$  (He-Ne excitation- $6328 \text{ \AA}$ )

shows the  $x$  mode to be only weakly Raman-active. By contrast the band we assign as  $\nu_s(\text{TeBr})$  is of very great intensity in the Raman effect, so great that it appears that there must be some preresonance Raman enhancement.<sup>22</sup> The Figure illustrates the diffuse reflectance spectra of the bromide and iodide together with the Raman spectrum of the former compound. The weak Raman band at  $\Delta\nu = 320 \text{ cm}^{-1}$  for  $\text{Ph}_2\text{TeBr}_2$  is assigned as  $2 \times \nu_s(\text{TeBr})$ . The Raman spectrum of  $\text{Ph}_2\text{TeI}_2$  is dominated by an extremely intense band at  $\Delta\nu = 116 \text{ cm}^{-1}$ . In this case the exciting line ( $6328 \text{ \AA}$ ,  $15,803 \text{ cm}^{-1}$ ) is coincident with the longer wavelength section of the first electronic absorption band (Figure) resulting in considerable resonance enhancement. The assignments of  $\nu_{as}$  and  $\nu_s(\text{TeI})$  are not unreasonable when compared with those accepted for  $\text{Me}_2\text{TeI}_2$ ,<sup>4</sup> however it is noted that the Raman band at  $\Delta\nu = 116 \text{ cm}^{-1}$  has no i.r. counterpart. No attempt is made to assign bands below  $100 \text{ cm}^{-1}$ .

**Other Di-organotellurium Dihalides.**—The low-frequency i.r. and Raman spectra have been measured and bands assigned to tellurium-halogen stretching vibrations are shown in Table 2. The Raman spectra of bromides and iodides again gave evidence of preresonance and resonance Raman effects with the result that  $\nu_s(\text{TeX})$  ( $X = \text{Br}, \text{I}$ ) was the dominant band in the

TABLE 2  
Tellurium halogen vibrations (i.r.)

R in $\text{R}_2\text{TeX}_2$	X = Cl	X = Br	X = I	
$\text{C}_6\text{H}_5$	287	159	116 †	$\nu_s$
	262	186	129	$\nu_{as}$
<i>p</i> - $\text{MeC}_6\text{H}_4$	264	167, 157	110 †	$\nu_s$
	248	173	149	$\nu_{as}$
<i>o</i> - $\text{MeC}_6\text{H}_4$	275	166	109 †	$\nu_s$
	255 *	172	148sh, 145	$\nu_{as}$
<i>p</i> - $\text{MeO}\cdot\text{C}_6\text{H}_4$	271	164		$\nu_s$
	247	193		$\nu_{as}$
$\text{C}_6\text{F}_5$	269	168 †		$\nu_s$
	264	184		$\nu_{as}$

\* Mixed with R modes. †  $\Delta\nu$  From Raman spectrum.

spectrum, and in the case of  $(o\text{-MeC}_6\text{H}_4)_2\text{TeI}_2$  the only band to be detected. The Raman spectra of dichlorides were generally more useful; assignments of  $\nu(\text{TeCl})$  were made by comparison of i.r. and Raman spectra with the spectra of the corresponding dibromide and di-iodide. It was found that of the two bands selected, the one at the higher frequency had the more intense Raman counterpart and was, therefore, assigned to the symmetric mode. The same difficulties encountered in the assignment of  $\nu(\text{TeBr})$  and  $\nu(\text{TeI})$  for  $\text{Ph}_2\text{TeX}_2$  arose, namely the very high intensity of  $\nu_s(\text{TeX})$  and relatively low intensity of  $\nu_{as}(\text{TeX})$  in the Raman effect. Bands between  $140$  and  $120 \text{ cm}^{-1}$  for all the dichloro-compounds may be assigned as  $\delta(\text{TeX}_2)$ .

It appears clear from Table 2 that the molecular structures of the substituted diaryltellurium dihalides considered must be similar to those of the diphenyl compounds, thus in all cases the halogen atoms occupy axial positions in a pseudo-trigonal bipyramid. The detailed tellurium halogen stretching frequencies vary slightly as a function of the substituents in the aryl-ring, but in the case of the dichlorides and dibromides the bands fall in rich regions of the spectrum and, in view of the low symmetry of the molecules, the vibrations are unlikely to be pure. Thus it would be unwise to invoke electronic effects to explain the variation of data in Table 2. In the case of the dichloro-compounds,  $\delta(\text{TeCl}_2)$  falls in an otherwise clear region of the spectrum and we note the almost complete insensitivity of these modes to R in  $\text{R}_2\text{TeCl}_2$  (see Supplementary Publication referred to earlier).

#### CONCLUSIONS

The low-frequency i.r. and Raman spectra have been assigned for  $\text{Ph}_2\text{TeX}_2$  ( $X = \text{Cl}, \text{Br}, \text{I}$ ) and surveyed for  $\text{R}_2\text{TeX}_2$  ( $\text{R} = p\text{-MeC}_6\text{H}_4, o\text{-MeC}_6\text{H}_4, p\text{-MeO}\cdot\text{C}_6\text{H}_4, \text{C}_6\text{H}_5$ ). Assignments of  $\nu(\text{TeX})$  are offered and it is concluded that the basic  $\psi$ -trigonal bipyramidal structure with axial halogen atoms is common to all compounds considered.

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<sup>22</sup> J. Behringer in 'Raman Spectroscopy, Theory and Practice', ed. H. A. Szymanski, Plenum, New York, 1967, p. 168.