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THE LOW FREQUENCY VIBRATIONAL SPECTRA OF SOME DIARYL DITELLURIDES

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SUMMARY

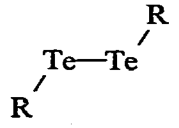
The IR and Raman spectra of a series of diaryl ditellurides, R_2Te_2 (R = Ph, p-$CH_3C_6H_4$, 2-naphthyl, p-$MeOC_6H_4$, p$EtOC_6H_4$ and p-$PhOC_6H_4$), are presented. Detailed assignments of the spectra below 400 cm^{-1} are offered for Ph_2Te_2 and the tellurium–tellurium stretching frequency is identified in all cases between 187 and 167 cm^{-1}. No supporting evidence for an earlier claim that Ph_2Te_2 is substantially dissociated into radicals in solution was found. All the compounds appear to have structures of C_2 skeletal symmetry.

INTRODUCTION

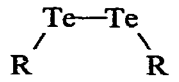
As part of a wider programme of work in the area of organotellurium chemistry, we are subjecting some of the stoichiometrically more simple aryl tellurium compounds to analysis by vibrational spectroscopy. The ditellurides are useful intermediates in the synthesis of some classes of organotellurium compounds and since the diarylditellurides are relatively stable crystalline solids and simple examples of compounds containing a metal to metal bond, we decided to examine their vibrational spectra with the particular object of identifying ν(Te–Te).

Apart from a limited investigation by Fritz and Keller[1] in which the IR spectrum of Ph_2Te_2 was examined to 250 cm^{-1}, the only examinations of a ditelluride to be reported are those of Chen and George[2] and of Sink and Harvey[3] of the recently reported dimethyl ditelluride. Chen and George suggested that a weak IR band at 122 cm^{-1} was ν(TeTe) but the complete study of Sink and Harvey showed unambiguously that the strongest Raman band at $\Delta\nu = 188$ cm^{-1} was the correct assignment.

A linear structure is improbable for a ditelluride, thus the most probable configuration is one of approximately C_2 symmetry between the limiting planar cases of C_{2h} and C_{2v} symmetry shown below. Such a structure was found



C_{2h}



C_{2v}

for bis(*p*-chlorophenyl) ditelluride[4] which is isomorphous with the analogous diselenide for which the dihedral angle between the planes containing the selenium to carbon bonds was 74.5°. The tellurium–tellurium bond length (2.70Å) was less then the covalent single bond length (2.74 Å). Also the vibrational analysis of Me_2Te_2 was consistent with a structure of C_2 symmetry with a dihedral angle in the region of 82°.

EXPERIMENTAL

The compounds considered in this paper were prepared by the literature methods indicated in Table 1 which also includes analytical and physical data. It was confirmed that (p-$MeOC_6H_4)_2Te_2$ was unstable unless ampouled and stored in the dark and that (p-$PhOC_6H_4)_2Te_2$ decomposed slowly in petroleum ether solution to afford a small quantity of yellow insoluble material. Di-2-naphthyl ditelluride also became yellowish on storing for one year but purification was achieved by recrystallisation. The nature of these decomposition reactions is under investigation.

TABLE 1

ANALYTICAL AND PHYSICAL DATA FOR DIARYL DITELLURIDES[a]

Compound	Ref.	Found		Calcd.		Found m.p. (°C)	Literature m.p. (°C)
		C (%)	H (%)	C (%)	H (%)		
$(C_6H_5)_2Te_2$	5	36.0	2.4	35.2	2.5	65–66	66–67[6]
(p-$CH_3C_6H_4)_2Te_2$	5	39.2	3.0	38.4	3.2	51–52	52.5[6]
(p-$CH_3OC_6H_4)_2Te_2$	7,8	36.3	3.1	35.8	3.0	56.5–58	60
(p-$C_2H_5OC_6H_4)_2Te_2$	5,8	39.4	3.6	38.6	3.6	104–106	107–108
(p-$C_6H_5OC_6H_4)_2Te_2$	9	49.2	3.0	48.7	3.1	84—86	87–88
(2-$C_{10}H_7)_2Te_2$	10	47.0	2.8	47.1	2.7	120–121	123.5–124.5

[a] Mass spectral analysis confirmed the purity of the materials.

Since the mass spectra of the diaryl ditellurides, R_2Te_2, contained RTe^+ as a prominent feature we argued that examination of the appearance potentials of RTe^+ and $R'Te^+$ derived from R_2Te_2, R'_2Te_2 and RTe_2R' would enable a series of ditellurides to be arranged in order of increasing Te–Te bond strength. Unsymmetrical ditellurides are unknown. The fact that relevant compounds RTeH and RTeX (X = halogen) are either unknown or of limited stability precludes a route similar to that used to synthesise unsymmetrical diselenides[11].

$$RSeX + R'SeH \rightarrow RSe_2R' + HX$$

It has been suggested that some decomposition of diaryl ditellurides to free radicals occurs in solution[6] and this observation has been used, amongst others, to support the postulate of a radical mechanism to account for the formation of both Ph_2Te and Ph_2Te_2 when phenylmagnesium bromide reacts with elemental tellurium[12]. Thus on the assumption that free radicals may be produced we irradiated a benzene solution containing both Ph_2Te_2 and (p-$EtOC_6H_4)_2Te_2$ with UV radiation over 6 h. Thin layer chromatography of the solution showed only the presence of the two symmetrical starting materials. The reduction of mixtures of $RTeX_3$ and $R'TeX_3$ with a variety of reducing agents afforded in each case only symmetrical products.

We then attempted to evaluate Farrar's claim[6] that dissociation to radicals occurs in solution. We find Ph_2Te_2 to be sparingly soluble in ethanol ($< 10^{-3}$ M) but find that the visible absorption maximum of the ditelluride (24,600 cm^{-1}) agrees well with that reported by Farrar (24,570 cm^{-1}) for a chloroform solution. Also substitution of the less polar carbon tetrachloride for chloroform gives solutions which obey Beer's law and for which $\lambda_{max} = 24{,}600$ cm^{-1} and $\varepsilon_{max} = 937$ which agrees very well with Farrar's data for chloroform ($\varepsilon_{max} = 930$). Furthermore, although resolution is much poorer, it is clear from Fig. 1 that the diffuse reflectance spectrum of solid diphenyl ditelluride is very similar indeed to the solution spectra. Farrar suggests that the fact that Beer's law is obeyed by dilute chloroform solutions of diphenyl ditelluride implies that dissociation is largely complete; our data would suggest that dissociation in the solid state and in ethanolic, chloroform or carbon tetrachloride solution is largely incomplete. We did however also examine the ESR spectra of the solutions and were unable to detect the presence of any paramagnetic species. Thus it seems very unlikely that the ditellurides will readily dissociate into radicals as required in one step of the mechanism proposed to account for the reaction of PhMgBr with tellurium[12].

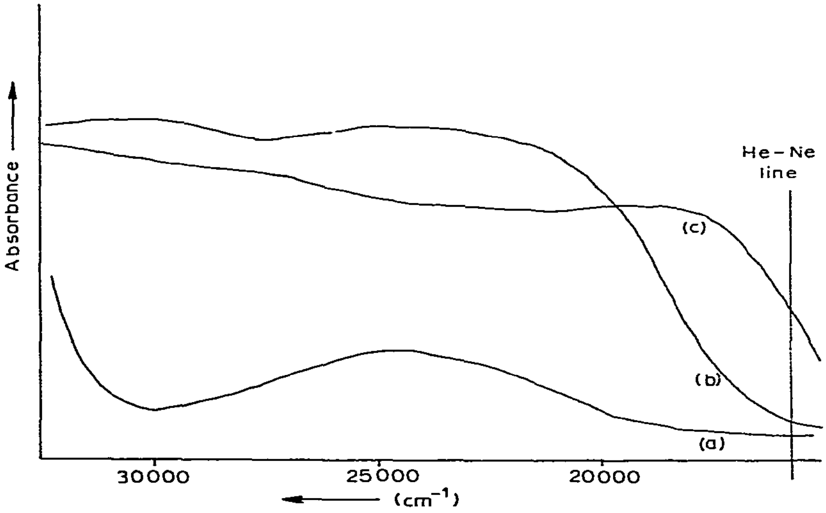


Fig. 1. (a): Spectrum of Ph_2Te_2 in carbon tetrachloride (2×10^{-4} M). (b): Diffuse reflectance spectrum of Ph_2Te_2. (c): Diffuse reflectance spectrum of $(p\text{-}PhOC_6H_4)_2Te_2$ (dilute with MgO).

Spectroscopic measurements

IR spectra were determined for nujol mulls with the following instruments: 4000–400 cm^{-1}, Perkin–Elmer 457; 400–200 cm^{-1}, Perkin–Elmer 225; 400–40 cm^{-1} R11C FS720/FS200. The output from the interferometer was computed to a resolution of 2 cm^{-1} on the University ICL 1905 computer. The interferometer was calibrated with water vapour. It was difficult to find suitable solvents for solution work but one compound, $(p\text{-}MeOC_6H_4)_2Te_2$, was sufficiently souble in n-heptane for the spectrum of a dilute solution to be obtained.

Raman spectra were obtained with a Coderg PH1 instrument using He-Ne laser excitation (6328 Å). Two compounds, $(p\text{-}MeOC_6H_4)_2Te_2$ and $(p\text{-}PhOC_6H_4)_2Te_2$, decomposed immediately to elemental tellurium when placed in the laser beam. These were the only two compounds of the six investigated that absorbed appreciably at 15,803 cm^{-1} (6328 Å), see Fig. 1.

Diffuse reflectance spectra (*vs.* $MgCO_3$) and solution spectra were determined with a Unicam SP 800 instrument. Mass spectra were recorded using the AEI MS 9 spectrometer and ESR measurements were attempted using a Hilger and Watts microspin instrument operating on the X-band frequency.

RESULTS

The vibrational spectra below 400 cm^{-1} are tabulated in Tables 2 and 3. The diffuse reflectance spectra of the ditellurides are illustrated in Fig. 1.

TABLE 2

THE LOW FREQUENCY ($< 400\ cm^{-1}$) VIBRATIONAL SPECTRA OF CRYSTALLINE DIPHENYL DITELLURIDE

Infrared (cm^{-1})	Raman $\Delta\nu(cm^{-1})$	Assignment
398 w		Phenyl *w*
350 w		Phenyl *w′*
274 w		Phenyl *u*
255 s	253 w–m	ν_{as}(TePh) or phenyl *t*
202 (sh)	204 vs	ν_s (TePh) or phenyl *t′*
188 s	183 w, (sh)	Phenyl *x*
169 (sh)	167 vs	ν(TeTe)
146 w		Phenyl *x′*
94 w	92 s	Unassigned
	51 s	Unassigned

TABLE 3

LOW FREQUENCY VIBRATIONAL SPECTRA OF SOME DIARYL DITELLURIDES

$(p\text{-}MeOC_6H_4)_2Te_2$ IR (cm^{-1})	$(p\text{-}PhOC_6H_4)_2Te_2$ IR (cm^{-1})	$(p\text{-}MeC_6H_4)_2Te_2$		$(p\text{-}EtOC_6H_4)_2Te_2$		$(Naphthyl)_2Te_2$	
		IR (cm^{-1})	Raman($\Delta\nu$)	IR (cm^{-1})	Raman ($\Delta\nu$)	IR (cm^{-1})	Raman ($\Delta\nu$)
375 m	400 m			380 m			
316 m–s	348 w			313 vs		274 w	
310 (sh)	287 m–s			232 w	226 (sh)	258 w	
223 s^a	275 m–s	275 w		204 s	206 w	240 s	238 w
213 s^a	192 s	232 s	231 w	186 m^b	186 vvs^b	234 s	233 w
178 s^b	185 s^b	197 (sh)	197 m	166 (sh)	165 w	184 s^b	187 vs^b
140 w	145 w	184 s		140 (w)			135 w
		156 (sh)	169 vs^b			126 w	
			65 w				64 m
			51 w				

[a] In n-heptane solution these bands appear at 217 cm^{-1} and 205 cm^{-1}. [b] Bands to which stretching of the Te–Te bond is considered to contribute.

DISCUSSION

The IR spectra of phenyl compounds have been extensively discussed and may now be considered to be reasonably well understood. We therefore consider first the data for diphenyl ditelluride (Table 2). The low frequency vibrations may either be described as vibrations of a monosubstituted benzene, PhX, in which case the vibrations are conveniently labelled following Whiffen[13]. Alternatively some low frequency modes may be described as skeletal vibrations, in the present case as stretching or deformation of the C–Te–Te–C skeleton. The last approach has been used with success in discussing the spectra of phenyltin compounds[14], but the description is an approximate one. However, in the case of diphenyl ditelluride description of some low frequency modes as skeletal vibrations of the C–Te–Te–C unit gives a more satisfactory interpretation.

The fact that many coincidences are observed between Raman and IR data eliminates a skeletal structure of C_{2h} symmetry. The strong IR band at 188 cm^{-1} has only a very weak Raman counterpart. A recent study of the diphenyltellurium dihalides[15] suggests that this is characteristic of the Whiffen x mode in phenyl–tellurium compounds. A skeletal structure of C_{2v} symmetry should result in comparable IR intensity for ν_{as}(Te–C) and ν_s(Te–C) whereas a structure intermediate between C_{2v} and C_{2h} (C_2 symmetry) would probably result in a more intense ν_{as}(TeC) and a less intense ν_s(TeC) in the IR and the reversal of this intensity relationship in the Raman effect. Thus, accepting the arguments of this paragraph, the assignments of Table 2 completely support a skeletal structure of C_2 symmetry with a relatively large dihedral angle.

The assignment of ν(TeTe) at 167 cm^{-1} requires some comment. We expect ν(TeTe) to be the strongest Raman band below $\Delta\nu = 200$ cm^{-1}. Simple mass considerations, and the fact that from the crystal structure of $(p\text{-ClC}_6H_4)_2Te_2$[4] we have no cause to assume that the Te–Te bond is abnormally weak, lead us to believe that ν(SnSn) in Me_6Sn_2 and Ph_2Sn_2 may be comparable to ν(TeTe) in Me_2Te_2 and Ph_2Te_2. Bulliner *et al.*[16] have reliably assigned ν(SnSn) at 140 cm^{-1} in Ph_6Sn_2 and Brown *et al.*[17]. suggest ν(SnSn) to occur at 190 cm^{-1} in Me_6Sn_2. Thus the fact that we assign ν(TeTe) for Ph_2Te_2 in a region comparable with ν(SnSn) and the fact that the frequency is slightly lower for the diphenyl as opposed to the dimethyl compound[3] appears consistent. We also note that for $F_5Te–TeF_5$, ν(TeTe) has been assigned at 168 cm^{-1} [18]. Since we deal with crystalline materials, we do not attempt to assign bands below 100 cm^{-1} since lattice vibrations will occur together with low frequency skeletal modes.

We have not attempted a detailed analysis of the spectra of the more complex ditellurides, however it does appear very reasonable to assign the strongest Raman band below $\Delta\nu = 200$ cm^{-1} as ν(TeTe) (*vide supra*). In two cases we must rely on IR data alone and the bands indicated in Table 3 for these compounds (R = p-MeOC$_6$H$_4$ and p-PhOC$_6$H$_4$) certainly contain contributions from aromatic ring modes.

It is observed that ν(TeTe) is sensitive to some extent to R in R_2Te_2. It would however be injudicious to attribute this to an electronic effect of R since shifts of ν(TeTe) could equally well arise from crystal effects. In one case for which solution IR data was obtained considerable shifts of some bands on change of phase were noted (Table 3). Our attempts to establish more positively the existence or non-existence of a relationship between ν(TeTe) and the Te–Te bond strength was frustrated by our failure to synthesise unsymmetrical ditellurides.

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