Bonding and Structure of Diphenyltellurium(IV) Difluoride

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The structure analysis of the title compound reveals a ψ-trigonal-bipyramidal arrangement of ligands around tellurium with only very weak interactions between tellurium and fluorine atoms in adjacent molecules. The ^{125}Te Mössbauer parameters indicate different bonding properties in the difluoride as compared with other diaryltellurium(IV) dihalides. The crystal structure has been determined by the heavy-atom method from *X*-ray diffractometer data and refined by full-matrix least-squares methods to R = 0.024 for 1 184 reflections. Crystals are monoclinic, space group $C2/c$, with a = 14.67(1), b = 9.61(1), c = 7.97(1) Å, β = 101.3(2)°, and Z = 4.

DIORGANOTELLURIUM(IV) dihalides of the type TeR_2X_2 (X = Cl, Br, or I) have been known for many years and have been shown to adopt similar molecular structures [1-4] with some intermolecular association between tellurium and the halogen atoms. The ^{125}Te Mössbauer parameters for these compounds have been shown to be consistent with their molecular structures.[5] However, the preparations of diaryltellurium(IV) difluorides have only recently been reported [6] and their ^{125}Te Mössbauer parameters found [5] to be different from those of the heavier congeners. In this respect it is interesting to note that TeF_4 [7] has a different structure from $TeCl_4$ [8] or TeI_4,[9] polymeric SbF_3 differs in structure [10] and Mössbauer parameters [11] from the other molecular antimony(III) halides, and diphenylantimony(III) fluoride [12] forms a chain polymer whilst the related chloride and bromide appear to be molecular solids.

EXPERIMENTAL

Crystals of $TePh_2F_2$ [6] were obtained from a solution of the compound in toluene–light petroleum (b.p. 60—80 °C). Unit-cell and space-group data were obtained photographically and intensity data were recorded on a diffractometer.

Crystal Data.—$C_{12}H_{10}F_2Te$, M = 319.6, Monoclinic, a = 14.67(1), b = 9.61(1), c = 7.97(1) Å, β = 101.3(2)°, U = 1 102 Å^3, Z = 4, D_c = 1.93 g cm^{-3}, $F(000)$ = 608, space group $C2/c$ (C^6_{2h}, no. 15) or Cc (C^4_s, no. 9) from systematic absences hkl when $h + k \neq 2n$, $h0l$ when $l \neq 2n$, and $0k0$ when $k \neq 2n$. The centrosymmetric space group $C2/c$ was confirmed by the subsequent successful refinement of the structure. Mo-K_α radiation, λ 0.710 7 Å, μ 25 cm^{-1}.

Structure Determination.—Intensity data were collected about the b axis (layers $h0$—$10l$) with a Stoe two-circle computer-controlled diffractometer as described previously.[13] Within the range $0.1 < (\sin\theta)/\lambda < 0.65$, 1 184 independent reflections having $I > 3\sigma(I)$ were observed. Data were corrected for Lorentz and polarization factors but not for absorption.

The structure was solved by standard Patterson–Fourier techniques. Scattering factors used were those for neutral atoms,[14] with corrections for anomalous dispersion.[15] Refinement was initially by full-matrix least-squares methods, with layer scale factors refined separately, all atoms vibrating isotropically, and with unit weights. This resulted in R 0.062. Refinement was continued with layer scale factors held constant and with the introduction of anisotropic thermal parameters, for all atoms, of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c + 2U_{12}hka^*b^*)]$, to produce R 0.029. At this stage a difference-Fourier map showed the positions of the five hydrogen atoms, and the inclusion of these parameters with the isotropic temperature parameters for the hydrogen atoms in the refinement resulted in final values of R and R' $\{= [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$ of 0.024, with final parameter shift $< 0.1\sigma$. In the final stages of refinement, weights derived from the counting statistics were found to give a satisfactory analysis of the variation of $w\Delta^2$ with increasing $(\sin\theta)/\lambda$ and with increasing fractions of $|F_o|$. The calculations were carried out on the ICL 1906A computer at the University of Birmingham Computer Centre using the program [16] SHELX-76. Observed and calculated structure factors and thermal parameters are listed in Supplementary Publication No. SUP 22860 (9 pp.),† and the final positional parameters are in Table 1. Interatomic distances and angles are given in Table 2.

TABLE 1

Final atomic positional parameters with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
Te	0	0.082 52(3)	$\frac{1}{4}$
F	−0.086 4(1)	0.095 0(2)	0.021 9(3)
C(1)	−0.175 9(2)	0.251 8(4)	0.251 2(4)
C(2)	−0.231 8(2)	0.349 3(4)	0.311 9(5)
C(3)	−0.198 6(3)	0.422 1(4)	0.459 8(5)
C(4)	−0.109 5(3)	0.399 2(4)	0.549 4(6)
C(5)	−0.052 9(2)	0.302 5(4)	0.491 0(5)
C(6)	−0.086 4(2)	0.228 6(3)	0.341 7(3)
H(1)	−0.201 6(27)	0.198 6(45)	0.149 8(54)
H(2)	−0.305 2(37)	0.355 8(60)	0.258 9(71)
H(3)	−0.246 2(37)	0.485 9(67)	0.500 8(78)
H(4)	−0.089 0(37)	0.444 4(50)	0.660 7(71)
H(5)	0.012 1(31)	0.294 1(42)	0.547 2(61)

DISCUSSION

The structure analysis shows that $TePh_2F_2$ adopts a distorted ψ-trigonal-bipyramidal arrangement (Figure 1)

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† For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

in which the fluorine atoms occupy axial positions with the F–Te–F bond angle (173°) close to the theoretical value of 180°. The angle between the equatorial phenyl groups of 96.9° (theoretical, 120°) may be correlated with the repulsion of the aromatic groups by the tellurium lone pair according to simple valence-shell electron-pair repulsion (VSEPR) theory.

TABLE 2

Bond distances (Å) and angles (°) with estimated standard deviations in parentheses

(*a*) Distances

Te–F	2.006(2)	Te · · · F	3.208(2)
Te–C(6)	2.115(3)	Te · · · Te	4.289(1)
C(6)–C(1)	1.387(4)	C(6)–C(5)	1.390(4)
C(1)–C(2)	1.393(5)	C(5)–C(4)	1.386(5)
C(2)–C(3)	1.376(6)	C(4)–C(3)	1.380(6)
C(1)–H(1)	0.97(4)	C(2)–H(2)	1.08(5)
C(3)–H(3)	1.03(6)	C(4)–H(4)	0.98(5)
C(5)–H(5)	0.97(5)		

(*b*) Angles

F–Te–C(6)	87.6(1)	F–Te–F^{I}	173.1(1)
C(6)–Te–C(6^{I})	96.9(1)	C(5)–C(6)–C(1)	120.2(3)
C(6)–C(1)–C(2)	119.3(3)	C(1)–C(2)–C(3)	120.5(3)
C(2)–C(3)–C(4)	120.2(3)	C(3)–C(4)–C(5)	120.2(4)
C(4)–C(5)–C(6)	119.8(3)		

Roman numeral superscript I refers to an atom in the position $-x, y, \frac{1}{2} - z$.

The Te–F distance of 2.006 Å is significantly longer than the average terminal Te–F distance[7] in TeF_4 of 1.86 Å; the difference in geometry between these compounds is unlikely to be a significant factor. The lower electron-withdrawing power of the phenyl groups as compared with the fluorine atoms may be the major contributory factor as has recently been suggested for the Sb–F bond length in $SbPh_2F$.[12] However, a direct comparison is complicated by the activity of fluorine as a strong bridging ligand in the antimony compound. The Te–C distance of 2.115 Å is very similar to that in other diorganotellurium(IV) dihalides[1-4] and to the Sb–C distance[12] of 2.13 Å in $SbPh_2F$.

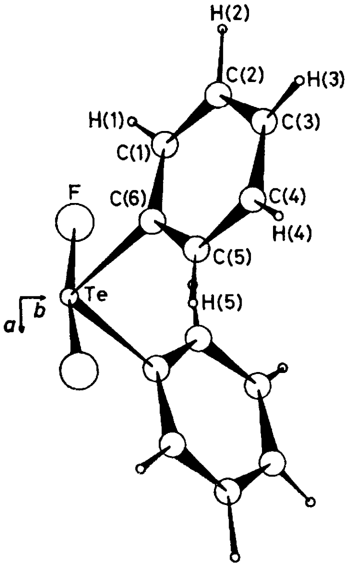

FIGURE 1 Projection down [001] showing the atom numbering

The overall co-ordination about tellurium in $TePh_2F_2$ is almost identical to that in $SbPh_2F$ despite the extensive bridging by fluorine atoms in the latter compound. The F–Sb–F and C–Sb–C bond angles of 165.0 and 99.9° respectively are similar to those found in $TePh_2F_2$. This arrangement of ligands around the central atom therefore seems to be so favourable that the antimony compound develops the strong fluorine-bridge bond to attain this degree of co-ordination. It is interesting that the tellurium compound shows no propensity for similarly strong intermolecular bridging whereby the ψ-octahedral arrangement found[7] in TeF_4 could be achieved. There are, however, two long bridging contacts from tellurium to fluorine (Te · · · F 3.208 Å) which lie either side of the Te lone pair. These weak contacts effectively link the units into chains parallel to *c* (Figure 2). Such long weak bonds, grouped around the lone pair, are a feature of the structure of a number of fluorine compounds.[17] The ratio Te-F(terminal): Te–F(bridge) of 1.60 : 1 is very large and the intermolecular interaction is therefore minimal.

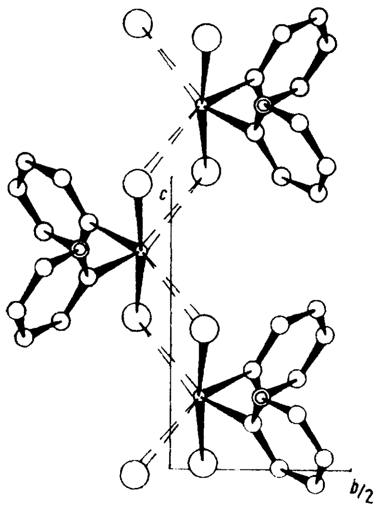

FIGURE 2 Projection of part of the structure down [100] showing the weak intermolecular interactions (hydrogen atoms are not shown, for clarity)

The structures of other diorganotellurium(IV) dihalides[1-4] have been described as distorted trigonal bipyramidal, distorted tetrahedral, and distorted octahedral according to the significance which has been attributed to intermolecular associations through bridging halogens and the mixing of *s* with *p* electrons. The description of $TePh_2F_2$ as a ψ-trigonal bipyramid implies that there is no marked deviation of the structure from that of the other dihalides.

The ^{125}Te Mössbauer parameters of the diaryltellurium(IV) dihalides have been found to be independent of the nature of the organic group for any specific halide.[5] These parameters for the difluorides are characterized by low chemical isomer shifts and large quadrupole splittings and are indicative of compounds which, although adopting essentially similar structures to those of the heavier halides, have subtle differences in bonding and structure.

The relatively small C–Te–C bond angles for the diaryltellurium(IV) dihalides [1,3] and the positive chemical isomer shifts suggest that the lone pair has predominantly $5s^2$ character and that bonding to the halogens is primarily $5p$ in nature. The magnitude of the quadrupole splitting in organotellurium compounds is mainly determined by the $5p$ orbital population and the observed order $I < Br < Cl < F$ reflects the increasing removal of p electron density along the X–Te–X axis and concomitant p orbital imbalance with increasing electronegativity of the halogen. The larger quadrupole splitting of the difluoride is indicative of the dominating effect of electronic, rather than ligand, asymmetry in these compounds. It is also reasonable that the lower degree of intermolecular association in the difluoride as compared with the other dihalides is reflected in this larger quadrupole splitting.

Since removal of $5p$ electrons would lead to a deshielding of Te $5s$ electrons and hence an increase in the s-electron density at the Te nucleus, and since $\Delta R/R$ is positive for the ^{125}Te transition,[18] the chemical isomer shifts of the difluorides might be expected to be more positive than those of the other dihalides. In fact all the dihalides have similar isomer shifts [5] with those for the difluorides falling at the lower end of the velocity range, indicating a greater stereochemical activity of the $5s$ electrons in the difluorides. However, the bond angles are essentially the same as those in the other dihalides.[1,3]

The ^{125}Te Mössbauer parameters of these compounds may be considered, however, in terms of the extent of intermolecular association as measured by the ratio of the crystallographically determined tellurium–halogen intermolecular distance to that of the intramolecular distance, with values of 1.60 : 1 for $TePh_2F_2$, 1.39 : 1 for $TeMe_2Cl_2$, 1.47 : 1 for $TePh_2Br_2$, 1.41 : 1 for $Te(C_6H_4Cl\text{-}p)_2I_2$, and 1.34 : 1 for $TeMe_2I_2$.

The difluoride is clearly the dihalide with least intermolecular association. It is also clear that intermolecular association is more significant in alkyl than the corresponding aryl compounds, presumably a reflection of the closer packing in the former species due to the smaller size of the alkyl group. In this respect it is interesting that the isomer shifts for TeX_4 (X = Cl, Br, or I) [19] and SbX_3 (X = F, Cl, Br, or I) [11] are, like those for the diaryltellurium(IV) dihalides reported here, similar within each series. This relative constancy of s-electron density at Sb or Te nuclei within a given series of compounds suggests that the stereochemical activity of the lone pair and the degree of intermolecular association vary in a complex way with changes in the electronegativity of the halogen and in the co-ordination about the Sb or Te atom.

[0/110 *Received*, 21*st January*, 1980]

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