Secondary Bonding. Part 12.* Aryltellurium Iodides: Crystal and Molecular Structures† of *cis*- and *trans*-Phenyltellurium(IV) Tri-iodide and Two Modifications of Diphenyltellurium(IV) Di-iodide

Nathaniel W. Alcock and W. David Harrison
Department of Chemistry and Molecular Sciences, University of Warwick, Coventry CV4 7AL

The crystal and molecular structures of *cis*- and *trans*-phenyltellurium(IV) tri-iodide and two polymorphs of diphenyltellurium(IV) di-iodide have been determined from diffractometer data: *cis*-$(PhTeI_3)_2$, orthorhombic, space group $Cmc2_1$, a = 19.915(5), b = 12.617(2), c = 8.867(2) Å, Z = 4, 1 267 reflections, R = 0.044; *trans*-$(PhTeI_3)_2$, orthorhombic, space group $Pnnm$, a = 8.911(2), b = 11.559(2), c = 13.506(2) Å, Z = 2, 1 201 reflections, R = 0.048; α-Ph_2TeI_2, tetragonal, space group $I4_1$, a = 11.684(3), c = 10.196(2) Å, Z = 4, 575 reflections, R = 0.030; and β-Ph_2TeI_2, monoclinic, $P2_1/c$, a = 9.722(1), b = 15.627(2), c = 19.338(7) Å, β = 107.08(2), Z = 8, 3 303 reflections, R = 0.034. Both tri-iodides form iodine-bridged dimers with square-based pyramidal geometry at the tellurium. The phenyl rings are both on one side of this plane (*cis*), or on opposite sides (*trans*). No Te ··· I secondary bonds occur but they contain I ··· I interactions. Both polymorphs of the di-iodide have pseudo-trigonal bipyramidal geometry (with one vacant position), and have either one or two Te ··· I secondary bonds occupying the fifth and sixth positions of distorted octahedra. Te–I distances are: 2.775(2)—2.792(2) and 3.152(2)—3.285(1) Å (tri-iodide, terminal and bridge, respectively); 2.883(1)—2.959(1) Å (di-iodide).

Three series of organotellurium halides exist with formulae R_3TeX, R_2TeX_2, and $RTeX_3$. Examples of the first series have been found to occur essentially as ionic species, $R_3Te^+X^-$.[1] The structures of the phenyl dihalides (X = F, Cl, or Br)[2–4] have previously been reported, and these are present as monomers, linked by secondary Te ··· X bonds. By contrast, the isomorphous $PhTeCl_3$ and $PhTeBr_3$[3,5] form infinite chains, with bridging halides but no Te ··· X secondary bonds. In this paper we add the iodides to these series. Both of the compounds concerned occur in two forms. $PhTeI_3$ occurs as dimers, in contrast to the polymeric chlorides and bromides, and these dimers have either *cis*,(1), or *trans*,(2), oriented phenyl groups. α-Ph_2TeI_2 (3) and β-Ph_2TeI_2 (4) differ only in packing and the arrangement of secondary bonds.

Experimental

β-Ph_2TeI_2 was prepared by reacting Ph_2TeO [6] (3.0 g, 0.01 mol) with a slight excess of aqueous HI in methanol (20 cm³); the reaction mixture was warmed to complete the reaction and on cooling deposited an orange solid. Recrystallization from C_6H_6 or $CHCl_3$ gave deep orange-red crystals of β-Ph_2TeI_2 (m.p. 241—242 °C; lit.,[7] 237 °C). Recrystallization from hot toluene gave a mixture (recognised microscopically) of these crystals and deep carmine-red crystals of α-Ph_2TeI_2.

The complex *cis*-$(PhTeI_3)_2$ was prepared by treating Ph_2Te_2 (4.1 g, 0.01 mol, obtained as in ref. 3) with a 5% excess over the stoicheiometric amount of I_2 in $CHCl_3$ (50 cm³) at 50 °C. A heavy deep red-brown precipitate is formed, which can be recrystallised with some difficulty from MeOH–C_6H_6, to give red-black needles.

The remaining compounds were obtained in the course of reactions intended to produce $PhTeI_3$. The complex Ph_2Te_2 (4.1 g, 0.01 mol) was reacted with a slight deficit of I_2 (1.5 g, 0.0045 mol) in $CHCl_3$ (20 cm³) at 0 °C to give a deep brown precipitate (supposedly crude PhTeI). On allowing the supernatant liquid to stand for 24 h, shiny black plates of ' PhTeI ' were produced. These are crystalline and have been examined by *X*-ray methods, but have been found to be twinned; they have not been further identified. Attempted recrystallization of the precipitate from hot toluene gave deep carmine-red crystals, identified as α-Ph_2TeI_2 (m.p. 194—196 °C); a very fine precipitate of elemental Te was also formed, presumably the result of the disproportionation $2PhTeI \longrightarrow Ph_2TeI_2 + Te$. Recrystallization was then attempted from toluene at room temperature. The precipitate was suspended in toluene, and slowly dissolved slightly to give a deep blue-black solution. This was filtered and allowed to evaporate; after a couple of days, deep red crystals were formed, identified by *X*-ray analysis as *trans*-$(PhTeI_3)_2$. The formation of this product suggests that the crude precipitate may contain iodine, possibly in a charge-transfer complex with PhTeI.

Crystallographic Study.—Crystal data are given in Table 1. Unit-cell constants were determined by least-squares fit to the positions of 15 high-angle reflections using the standard programs of a Syntex $P2_1$ four-circle diffractometer. For (1), the temperature was held at 173 K with the Syntex LT-1 attachment. For all compounds, data were collected with variable scan rates of 2—29° min⁻¹ depending on the intensity of a two-second prescan; background counts of a quarter of the scan time were taken before and after each scan. The intensities of three check reflections were monitored regularly during data collection and showed no significant deterioration for any of the crystals. Lorentz, polarization, and absorption corrections were applied (the latter with ABSCOR) [8] and refinement carried out on the observed reflections [$I/\sigma(I) \geqslant 3.0$].

Structure Solution and Refinement.—For (3), the structure was refined from the atomic positions of the isomorphous dibromide.[4] The molecule has site symmetry 2, with the Te atom in position 4*a* of space group $I4_1$ (z = 0, arbitrarily). For (2), a Patterson synthesis was interpreted in terms of one heavy atom in a general position and one in special position 4*g* of *Pnnm*; this space group was chosen initially in preference to *Pnn*2, and shown to be correct by the satisfactory refine-

---

* Part 11 is ref. 5.

† *Supplementary data available* (No. SUP 23841, 45 pp.): structure factors and thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Table 1. Crystal data

	(1)	(2)	(3)	(4)
Compound	$C_6H_5TeI_3$ (*cis*)	$C_6H_5TeI_3$ (*trans*)	$(C_6H_5)_2TeI_2$ (α)	$(C_6H_5)_2TeI_2$ (β)
T/K	173	289	289	289
System	Orthorhombic	Orthorhombic	Tetragonal	Monoclinic
Space group	$Cmc2_1$	$Pnnm$	$I4_1$	$P2_1/c$
Absences	hkl, $h + k \neq 2n$ $h0l$, $l \neq 2n$	$0kl$, $k + l \neq 2n$ $h0l$, $h + l \neq 2n$	hkl, $h + k + l \neq 2n$ $00l$, $l \neq 4n$	$h0l$, $l = 2n$ $0k0$, $k \neq 2n$
a/Å	19.915(5)	8.911(2)	11.684(3)	9.722(1)
b/Å	12.617(2)	11.559(2)	11.684	15.627(2)
c/Å	8.867(2)	13.506(2)	10.196(2)	19.338(7)
β/°	90	90	90	107.08(2)
U/Å^3	2 227.9(8)	1 391.0(4)	1 391.9(5)	2 808(1)
M	585.41	585.41	535.61	535.61
D_c/g cm^{-3}	3.50	2.80	2.56	2.54
D_m/g cm^{-3}	*ca.* 3.3	2.82	2.61	2.48
Z	4 (dimer)	2 (dimer)	4	8
μ(Mo-K_α)/cm^{-1}	108.48	86.88	65.06	64.46
F(000)	2 016	1 008	960	1 920
Reflections: total	1 461	1 865	669 unique 2 482 total	*
$I/\sigma(I) \geqslant 3.0$	1 267	1 201	575	3 303
$2\theta_{max.}$/°	55	55	50	50
Range (2θ) about $K_{\alpha_1} - K_{\alpha_2}$/°	−1.05, + 1.15	±1.0	−1.0, + 1.1	±1.0
Final R	0.044	0.048	0.030	0.034
Crystal dimensions/mm	0.3 × 0.1 × 0.2	0.2 × 0.2 × 0.3	0.1 × 0.3 × 0.3	*
Transmission factor range	0.54—0.78	0.29—0.46	0.28—0.59	*

* Output listing accidentally destroyed.

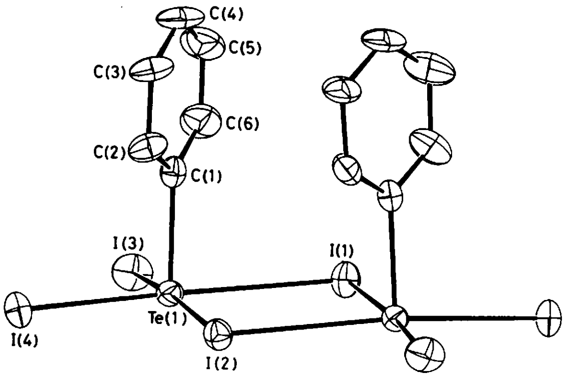


Figure 1. Molecular structure and atomic numbering for *cis*-$(PhTeI_3)_2$ (1)

ment. A Fourier synthesis with I (general) and Te (special) revealed a further iodine atom (position 4*e*), and the six carbon atoms (four peaks, two in general positions and two in positions 4*g*). This showed that the compound was dimeric with molecular symmetry 2/*m*. For (1), the systematic absences allowed a choice between three space groups, *Cmcm*, *Cmc*2₁, and *Cmc*2 (non-standard setting of *Ama*2). The three-dimensional and zonal intensity distributions calculated by MULTAN-80 [9] strongly suggested a non-centrosymmetric space group, with *Cmc*2₁ more likely than *Cmc*2; the solution with highest figure of merit in this space group contained five large peaks, and the structure was satisfactorily refined from this starting point, being revealed as a dimer lying on a crystallographic mirror plane. For (4), the Patterson synthesis was not readily interpretable for six heavy atoms, and MULTAN-80 was used. The solution with highest figure of merit provided a satisfactory starting point for refinement. For all compounds, hydrogen atoms were inserted at calculated positions with fixed isotropic temperature factors, and were not refined.

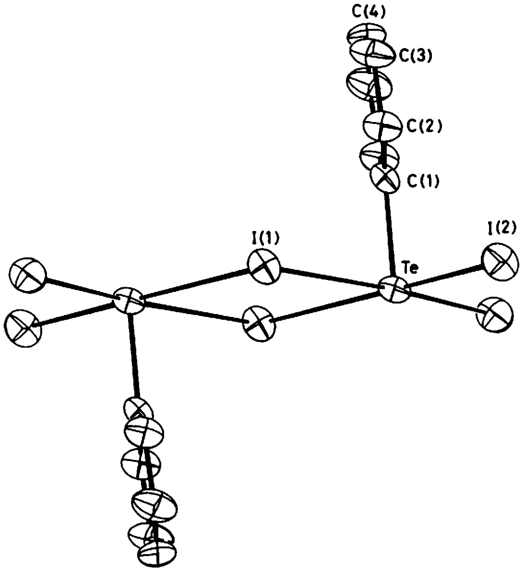


Figure 2. Molecular structure and atomic numbering for *trans*-$(PhTeI_3)_2$ (2)

Final refinement was by least-squares methods in large blocks, with an analytical weighting scheme giving reduced weight to reflections with low sinθ/λ and high *F*. This was shown to be satisfactory by weight analyses. For all compounds, final difference-Fourier syntheses showed only slight residual electron density, in the neighbourhood of the heavy atoms. For (1) and (3), it was necessary to check the hand of the particular crystal examined. For (1), this was achieved by refining Δ*f*″, which did not shift appreciably from its input literature value; the original hand was therefore accepted. For (3), a full refinement with the original hand gave $R =$

Table 2. Atomic co-ordinates ($\times 10^4$) with standard deviations in parentheses

Atom	x	y	z	Atom	x	y	z
(*a*) *cis*-$(PhTeI_3)_2$ (1)							
Te(1)	3 866.6(5)	3 505.1(9)	5 000.0	C(4)	3 978(12)	1 291(21)	507(27)
I(1)	5 000	2 034(1)	6 333(3)	C(5)	3 860(15)	833(18)	1 884(33)
I(2)	5 000	5 014(2)	3 671(3)	C(6)	3 844(14)	1 464(18)	3 135(34)
I(3)	2 903.8(6)	2 272.4(11)	6 429.4(26)	H(2)	3 985	3 766	1 546
I(4)	2 953.4(6)	4 928.7(13)	3 734.4(25)	H(3)	4 101	2 662	−720
C(1)	3 909(9)	2 537(14)	2 996(23)	H(4)	4 042	795	−315
C(2)	3 997(9)	3 012(18)	1 636(24)	H(5)	3 807	63	1 959
C(3)	4 043(13)	2 399(21)	332(24)	H(6)	3 787	1 151	4 145
(*b*) *trans*-$(PhTeI_3)_2$ (2)							
Te	3 355.6(13)	3 286.4(9)	0.0	C(3)	7 318(19)	1 295(13)	889(12)
I(1)	5 000.0	5 000.0	1 608.5(9)	C(4)	7 914(23)	1 013(19)	0
I(2)	2 020.2(12)	1 987.5(8)	1 491.8(7)	H(2)	5 506	2 133	1 497
C(1)	5 320(21)	2 249(14)	0	H(3)	7 774	1 065	1 499
C(2)	5 972(16)	1 923(12)	885(9)	H(4)	8 826	586	0
(*c*) α-Ph_2TeI_2 (3)							
Te	5 000	0	0	C(6)	4 154(13)	2 224(12)	1 314(17)
I	7 500.7(8)	127.3(10)	−111.9(17)	H(2)	6 314	778	2 475
C(1)	4 929(11)	1 348(11)	1 409(14)	H(3)	6 267	2 307	4 057
C(2)	5 751(11)	1 370(10)	2 415(16)	H(4)	4 979	3 770	3 816
C(3)	5 739(16)	2 297(15)	3 344(18)	H(5)	3 564	3 714	2 146
C(4)	4 958(15)	3 131(14)	3 213(18)	H(6)	3 611	2 218	601
C(5)	4 140(14)	3 130(12)	2 208(18)				
(*d*) β-Ph_2TeI_2 (4)							
Te(1)	−64.4(9)	4 761.5(5)	1 294.5(5)	C(28)	4 512(12)	2 918(8)	423(7)
Te(2)	3 967.2(7)	1 364.7(4)	−613.1(4)	C(29)	4 947(13)	3 337(8)	1 067(6)
I(11)	2 464(1)	4 857(1)	2 594(1)	C(210)	5 516(11)	2 895(6)	1 701(6)
I(12)	−2 386(1)	4 778(1)	−45(1)	C(211)	5 683(9)	2 004(6)	1 678(6)
I(21)	2 536(1)	39(1)	9(1)	C(212)	5 236(10)	1 570(6)	1 029(6)
I(22)	5 584(1)	2 536(1)	−1 225(1)	H(12)	2 300	3 398	1 472
C(11)	151(12)	3 401(7)	1 266(6)	H(13)	2 501	1 882	1 449
C(12)	1 450(13)	3 043(8)	1 374(7)	H(14)	468	1 041	1 185
C(13)	1 566(16)	2 145(9)	1 352(8)	H(15)	−1 812	1 665	952
C(14)	378(15)	1 653(8)	1 201(8)	H(16)	−1 096	3 093	655
C(15)	−962(14)	2 020(8)	1 072(8)	H(18)	−324	3 923	2 696
C(16)	−1 101(12)	2 904(8)	1 122(8)	H(19)	−1 831	4 031	3 463
C(17)	−1 448(13)	4 784(7)	1 963(7)	H(110)	−3 848	4 935	3 144
C(18)	−1 145(13)	4 302(8)	2 575(8)	H(111)	−4 336	5 728	2 107
C(19)	−2 040(14)	4 365(9)	3 017(8)	H(112)	−2 883	5 669	1 331
C(110)	−3 228(16)	4 895(10)	2 837(8)	H(22)	2 271	2 384	−1 995
C(111)	−3 493(17)	5 356(9)	2 232(9)	H(23)	15	3 124	−2 386
C(112)	−2 665(16)	5 326(8)	1 769(8)	H(24)	−1 469	3 274	−1 629
C(21)	2 009(9)	2 092(6)	−997(6)	H(25)	−707	2 707	−471
C(22)	1 632(9)	2 439(6)	−1 682(6)	H(26)	1 444	1 928	−54
C(23)	333(12)	2 879(7)	−1 904(7)	H(28)	4 139	3 235	−23
C(24)	−525(14)	2 971(7)	−1 464(7)	H(29)	4 858	3 952	1 079
C(25)	−124(14)	2 627(8)	−790(7)	H(210)	5 782	3 194	2 161
C(26)	1 160(13)	2 180(8)	−539(7)	H(211)	6 145	1 694	2 121
C(27)	4 661(10)	2 018(6)	406(6)	H(212)	5 320	955	1 014

0.032, but refinement on the enantiomorph (co-ordinates $x + \frac{1}{2}, y, -z$) gave $R = 0.030$, which was therefore accepted.

Computing was with the *X*-RAY 76 system,[10] on a Burroughs B6700 computer. Scattering factors in the analytical form and anomalous dispersion factors were taken from ref. 11. Final atomic co-ordinates for all compounds are given in Table 2, and bond lengths and angles in Table 3.

Discussion

Compounds (1) and (2) have been identified by crystal-structure determination as dimers of $PhTeI_3$, having the phenyl groups respectively on the same side of the Te_2I_6 plane [complex (1)] or on opposite sides [complex (2)] (Figures 1 and 2). The existence of these isomers demonstrates a stability in the Te^{IV}–halide bonds against dissociation in solution that is at first sight surprising. To some extent however, the previous non-observance of isomers for Te^{IV} has resulted from the character of the compounds; thus the monomeric R_2TeX_2 and polymeric $RTeX_3$ species do not have possible isomers. The isolation of mixed halogeno-anions, $[RTeX_3Y]^-$ *etc.*,[12] suggests some stability in the Te–X bonds, as does the existence of β-Me_2TeI_2, structurally $[Me_3Te]^+[MeTeI_4]^-$, in contrast to the monomeric α-Me_2TeI_2.[13] It should be possible to synthesise further Te^{IV} isomers.

In both (1) and (2), the geometry at Te is square pyramidal, *i.e.* octahedral with one vacant position (occupied by a lone pair) as predicted for six electron pairs, with apical phenyl

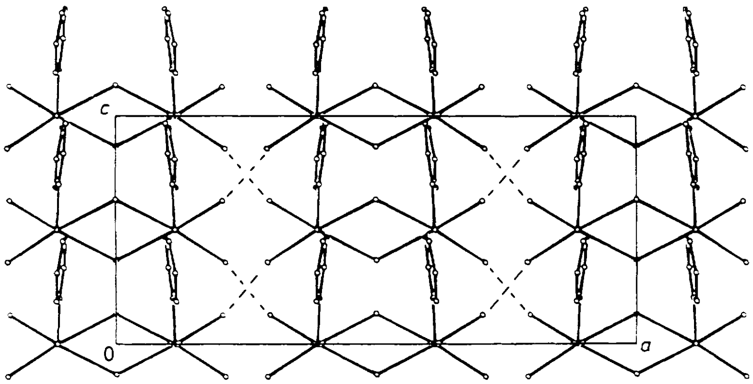


Figure 3. Packing for *cis*-$(PhTeI_3)_2$ (1) viewed down *b*. Secondary bonds are dashed

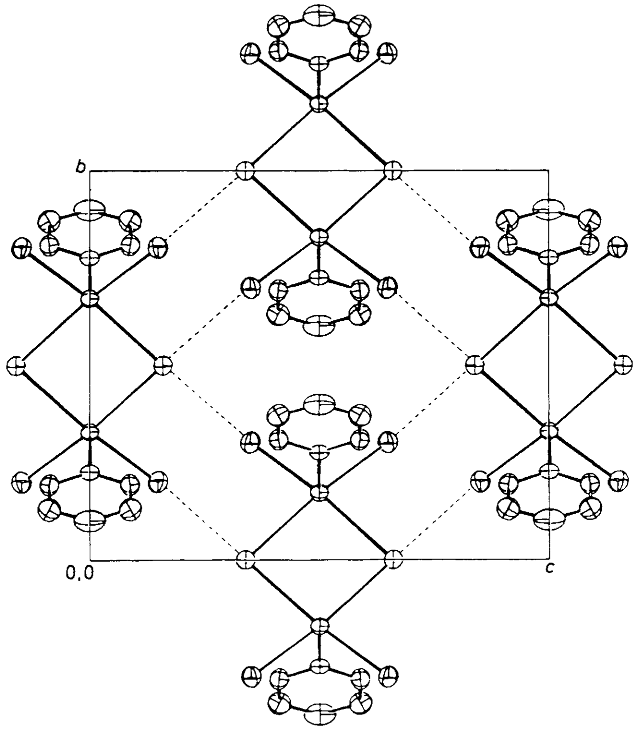


Figure 4. Packing for *trans*-$(PhTeI_3)_2$ (2) viewed down *a*. Secondary bonds are dashed

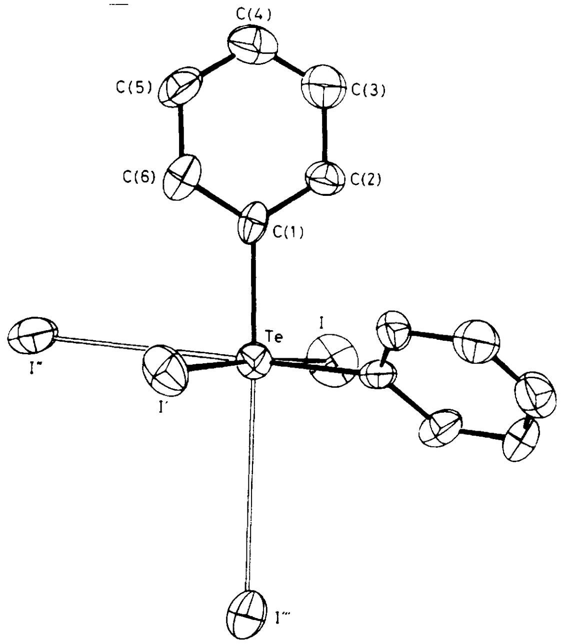


Figure 5. Molecular structure and atomic numbering for α-Ph_2TeI_2 (3). In Figures 5 and 6, primary bonds are shown solid, secondary bonds open. Primed atoms are symmetry-related to the corresponding unprimed atoms; I′ and I‴ are equivalent to I^{I} and I^{II} respectively in Table 3(*c*)

groups. Unexpectedly, both Te atoms are slightly *above* the I_4 plane, towards the C atom [by 0.08 and 0.04 Å in (1) and (2) respectively]; this difference from the normal behaviour may be caused by the bulk of the iodine atoms. The same co-ordination is adopted by $PhTeCl_3$ and $PhTeBr_3$ but both form infinite polymeric chains $(PhTeX_3)_n$ rather than discrete dimers. We have previously noted [5] this tendency among $RTeX_3$ compounds for the chlorides to be polymeric, the bromides either polymeric or dimeric, and the iodides dimeric [*e.g.* $(4\text{-}MeOC_6H_4)TeI_3$]; [14] however if R is particularly bulky (*e.g.* R = 2-biphenylyl, X = Br or I) monomeric structures are the rule. Presumably the size of the halogen is the other determining factor, with dimeric structures preferred as halogen size increases.

Square-pyramidal, pseudo-octahedral geometry [as in (1) and (2)] normally prohibits the formation of secondary bonding from the *central* atom because the vacant position, where the secondary bond should form, is already occupied by the lone pair. This is confirmed in the present examples, whose packing diagrams (Figures 3 and 4) show no such bonding. However, both compounds show I · · · I secondary bonds. In (1) the most significant I · · · I interaction [3.848(2) Å] links the terminal iodine atoms of two molecules, while (2) contains an interaction [3.886(1) Å] between bridge and terminal atoms; both form nearly linear Te–I · · · I systems. Complex (1) also contains a number of weaker interactions not in linear systems; but in (2) the only further I · · · I distances <4.5 Å are intramolecular.

The packing differences are probably responsible for the significant differences in Te–I bond lengths between (1) and (2). The formation of a secondary bond by donation of a lone pair into a σ* orbital (here of a primary Te–I bond) [15] involves also an increase in antibonding electron density in the primary bond. It is usually very difficult to detect any effect on this bond, because of the lack of valid comparisons, but the *cis*

Table 3. Principal bond lengths (Å) and angles (°) with standard deviations in parentheses; C–C distances and C–C–C angles have normal values

(*a*) *cis*-$(PhTeI_3)_2$ (1) [a]			
Te–I(1)	3.152(2)	I(1)–Te–I(2)	89.04(5)
Te–I(2)	3.179(2)	I(1)–Te–I(3)	89.63(5)
Te–I(3)	2.775(2)	I(1)–Te–I(4)	174.91(6)
Te–I(4)	2.792(2)	I(1)–Te–C(1)	86.9(5)
Te–C(1)	2.16(2)	I(2)–Te–I(3)	174.49(7)
		I(2)–Te–I(4)	85.88(5)
I(1) ··· I(2$^{\mathrm{I}}$)	4.263(3)	I(2)–Te–C(1)	90.34(5)
I(1) ··· I(3$^{\mathrm{II}}$)	4.186(2)	I(3)–Te–I(4)	95.40(6)
I(2) ··· I(4$^{\mathrm{II}}$)	4.078(2)	I(3)–Te–C(1)	94.9(5)
I(3) ··· I(4$^{\mathrm{III}}$)	4.081(3)	I(4)–Te–C(1)	93.4(5)
I(3) ··· I(4$^{\mathrm{IV}}$)	3.848(2)		
		Te–I(1)–Te$^{\mathrm{II}}$	91.46(6)
		Te–I(2)–Te$^{\mathrm{II}}$	90.47(6)
		Te–I(3) ··· I(4$^{\mathrm{IV}}$)	162.48(6)
(*b*) *trans*-$(PhTeI_3)_2$ (2) [b]			
Te–I(1)	3.285(1)	I(1)–Te–I(2)	92.14(3)
Te–I(2)	2.780(1)	I(1)–Te–C(1)	88.4(3)
Te–C(1)	2.12(2)	I(1)–Te–I(1$^{\mathrm{I}}$)	82.81(4)
		I(2)–Te–C(1)	92.7(3)
I(2) ··· I(1$^{\mathrm{II}}$)	3.886(1)	I(2)–Te–I(1$^{\mathrm{I}}$)	174.78(4)
		I(2)–Te–I(2$^{\mathrm{I}}$)	92.88(5)
		Te–I(1)–Te$^{\mathrm{I}}$	97.19(4)
		Te–I(2) ··· I(1$^{\mathrm{II}}$)	174.87(4)
(*c*) α-Ph_2TeI_2 (3) [c]			
Te–I	2.928(1)	I–Te–C(1)	91.5(3)
Te–C(1)	2.133(13)	I–Te–I$^{\mathrm{I}}$	175.53(5)
Te ··· I$^{\mathrm{II}}$	3.955(1)	I–Te ··· I$^{\mathrm{II}}$	92.80(3)
		I$^{\mathrm{I}}$–Te ··· I$^{\mathrm{II}}$	84.19(3)
		I–Te–C(1)	91.4(3)
		C(1)–Te–C(1$^{\mathrm{I}}$)	95.3(5)
		C(1)–Te ··· I$^{\mathrm{II}}$	175.6(3)
(*d*) β-Ph_2TeI_2 (4)			
Te(1)–I(11)	2.959(1)	I(11)–Te(1)–I(12)	174.40(5)
Te(1)–I(12)	2.893(1)	I(11)–Te(1)–C(11)	90.5(3)
Te(1)–C(11)	2.139(11)	I(11)–Te(1)–C(17)	89.9(3)
Te(1)–C(17)	2.122(15)	I(12)–Te(1)–C(11)	92.5(3)
Te(2)–I(21)	2.942(1)	I(12)–Te(1)–C(17)	94.5(3)
Te(2)–I(22)	2.883(1)	C(11)–Te(1)–C(17)	96.7(5)
Te(2)–C(21)	2.153(8)	I(21)–Te(2)–I(22)	174.23(4)
Te(2)–C(27)	2.146(10)	I(21)–Te(2)–C(21)	92.1(3)
Te(1) ··· I(12$^{\mathrm{I}}$)	3.926(1)	I(21)–Te(2)–C(27)	91.1(3)
Te(2) ··· I(21$^{\mathrm{II}}$)	3.924(1)	I(22)–Te(2)–C(21)	93.3(3)
Te(2) ··· I(11$^{\mathrm{III}}$)	3.850(1)	I(22)–Te(2)–C(27)	90.7(3)
		C(21)–Te(2)–C(27)	94.2(4)
		I(12$^{\mathrm{I}}$) ··· Te(1)–C(17)	168.4(3)
		I(21$^{\mathrm{II}}$) ··· Te(2)–C(21)	176.8(3)
		I(11$^{\mathrm{III}}$) ··· Te(2)–C(27)	175.7(3)

[a] I = $1-x$, $1-y$, $\frac{1}{2}+z$; II = $1-x$, y, z; III = x, $1-y$, $\frac{1}{2}+z$; IV = $\frac{1}{2}-x$, $\frac{1}{2}-y$, $\frac{1}{2}+z$. [b] I = $1-x$, $1-y$, $-z$; II = $x-\frac{1}{2}$, $\frac{1}{2}-y$, $\frac{1}{2}-z$. [c] I = $1-x$, y, z; II = $\frac{1}{2}-y$, $x-1$, $z-\frac{1}{4}$. [d] I = $-x$, $1-y$, $-z$; II = $1-x$, $-y$, $-z$; III = x, $\frac{1}{2}-y$, $z-\frac{1}{2}$.

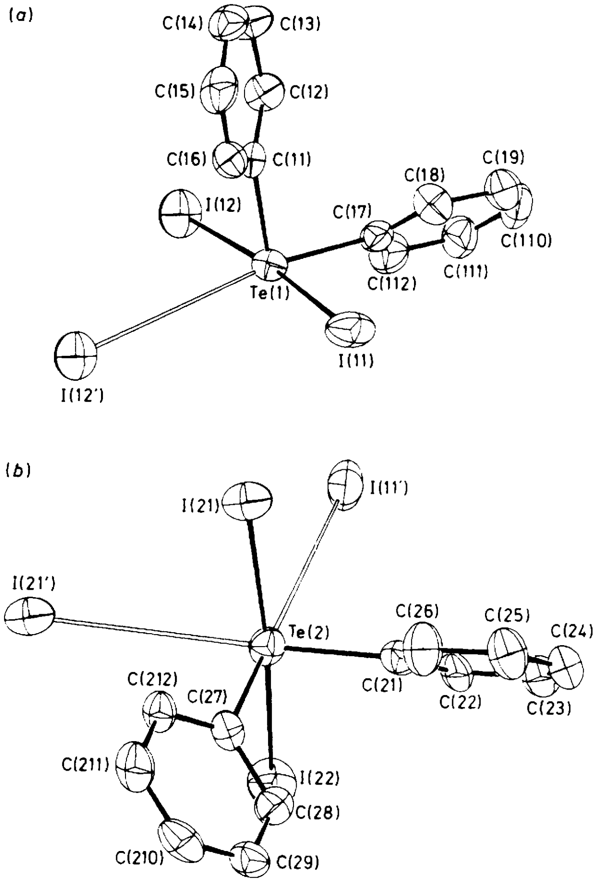


Figure 6. Molecular structure and atomic numbering for β-Ph_2TeI_2 (4): (*a*) molecule (1); (*b*) molecule (2). The atoms I(12′), I(11′), and I(21′) are equivalent to atoms I(12$^{\mathrm{I}}$), I(11$^{\mathrm{III}}$), and I(21$^{\mathrm{II}}$) respectively in Table 3(*d*)

and *trans* forms of $(PhTeI_3)_2$ should be identical as isolated molecules. The difference between the bridge Te–I distances of 3.285(1) Å for the *trans* and 3.165 Å (av.) for the *cis* can be directly attributed to the lengthening associated with the secondary bonding present in the *trans* and absent in the *cis* form.

The molecular structures and packing diagrams for α- and β-Ph_2TeI_2 are shown in Figures 5—7. In both, the primary geometry is pseudo-trigonal bipyramidal, with axial iodine atoms (I–Te–I, 174.2—175.5°). In the β form, the Te–I bonds are rather variable, with the two independent molecules each having one longer and one shorter bond (2.883—2.959 Å), while the value in the α form falls in the middle of this range; the shortest bond of all is to the only iodine atom [I(22)] not involved in secondary bonding. These bonds fall between the terminal and bridge bond lengths in $(PhTeI_3)_2$, while the Te–C distances in the two sets of compounds are indistinguishable.

The difference between α- and β-Ph_2TeI_2 lies in the packing and secondary bonding pattern. In the former, two secondary bonds complete an irregular octahedron about each Te, and link the molecules into a three-dimensional network (Figure 7). In the latter, Te(2) also has two secondary bonds, but in Te(1), an octahedron with one vacant position is produced. Again, a three-dimensional network is produced, although the corresponding packing diagram is too complex to be informative.

Seven other structures of diorganotellurium di-iodides have been reported, all of which exhibit secondary bonding (summarised in Table 4). With the exception of 4,4-di-iodo-1-thia-$4\lambda^4$-telluracyclohexane, $\overline{S(CH_2)_2TeI_2(CH_2)_2}$, which contains Te atoms with distorted pentagonal bipyramidal geometry, and Te(1) of β-Ph_2TeI_2, all the compounds contain tellurium atoms with four primary and two secondary bonds giving rise to distorted octahedral geometry at the tellurium atoms; however, in $(p\text{-}ClC_6H_4)_2TeI_2$ the Te ··· I secondary bonds are very weak (>4.10 Å) and I ··· I bonds are of more

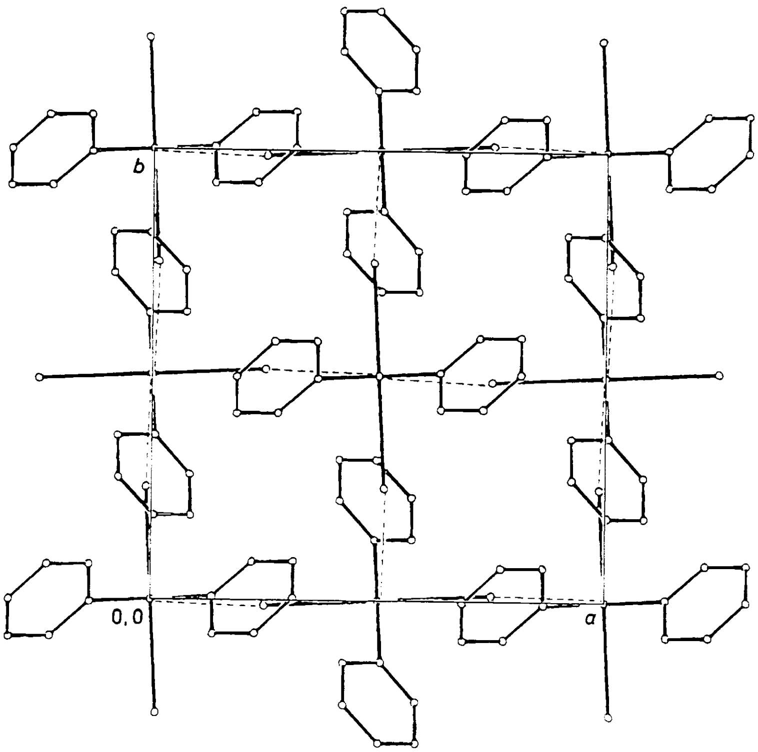
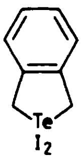
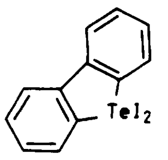


Figure 7. Packing for α-Ph_2TeI_2 (3), viewed down *c*. Secondary bonds are dashed

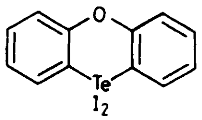
Table 4. Comparative structural data for R_2TeI_2 compounds



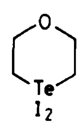
(5)



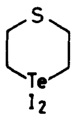
(6)



(7)



(8)



(9)

	Ph_2TeI_2								
Compound	α	β	$(p\text{-ClC}_6H_4)_2$-TeI_2	Me_2TeI_2	(5)	(6)	(7)	(8)	(9)
Te–C/Å	2.133(13)	2.122(15)—2.153(8)	2.13(2), 2.10(2)	2.10(3)—2.16(3)	2.139(12), 2.145(12)	2.111(4), 2.113(4)	2.11(2), 2.09(2)	2.17(1), 2.15(1)	2.13(2)—2.18(2)
Te–I/Å	2.928(1)	2.883(1)—2.959(1)	2.922(2), 2.947(2)	2.854(3)—2.994(3)	2.900(1), 2.928(1)	2.944(1), 2.928(1)	2.945(2)	2.886(1), 2.938(1)	2.884(2)—2.985(2)
I–Te–I/°	175.53(5)	174.40(5), 174.23(4)	173.5(1)	177.3(2)—178.0(2)	176.53(4)	178.47(1)	176.44(6)	177.08(4)	174.9(1) 178.1(1)
C–Te–C/°	95.3(5)	96.7(5), 94.2(4)	101.1(10)	91(2)—97(2)	86.0(5)	81.8(2)	91.5(6)	94.1(4)	100(1)
Te · · · I/Å	3.955(1)	3.926(1), 3.924(1), 3.850(1)	4.13, 4.46	3.659(3)—4.030(3)	3.653(1), 3.878(1)	3.696(1), 3.717(1)	3.739(2), 3.788(2)	3.814(1), 3.692(1)	3.76—4.16
I · · · I/Å	—	—	3.85	3.948—4.250	—	—	—	—	3.66, 3.90
Ref.	This work	This work	*a*	*b*	*c*	*d*	*e*	*f*	*g*

[a] G. Y. Chao and J. D. McCullough, *Acta Crystallogr.*, 1962, **15**, 887. [b] L. Y. Y. Chan and F. W. B. Einstein, *J. Chem. Soc., Dalton Trans.*, 1972, 316. [c] C. Knobler and R. F. Ziolo, *J. Organomet. Chem.*, 1979, **178**, 423. [d] J. D. McCullough, *Inorg. Chem.*, 1975, **14**, 1143. [e] J. D. McCullough, *Inorg. Chem.*, 1973, **12**, 2669. [f] J. D. McCullough, *Inorg. Chem.*, 1973, **12**, 2665. [g] C. Knobler, J. D. McCullough, and H. Hope, *Inorg. Chem.*, 1970, **9**, 797.

Table 5. Comparative structural data for Ph_2TeX_2

				I[d]		
X =	F[a]	Cl[b]	Br[c]	α	β	
Te–X/Å	2.006(2)	2.528(5), 2.483(4)	2.682(3)	2.928(1)	2.959(1), 2.893(1)	2.942(1), 2.883(1)
Te–C/Å	2.115(3)	2.12(1), 2.10(2)	2.14(3)	2.133(13)	2.122(15)—2.153(8)	
X–Te–X/°	173.1(1)	175.5(1)	178.0(2)	175.53(5)	174.40(5)	174.23(4)
C–Te–C/°	96.9(1)	98.9(1)	96.3(12)	95.3(5)	96.7(5)	94.2(4)
Te · · · X/Å	3.208(2)	3.680(4)	3.93	3.955(1)	3.926(1)	3.924(1), 3.850(1)
(Te · · · X) – (Te–X)/Å	1.20	1.15—1.20	1.25	1.03	0.97, 1.03	0.91—1.04

[a] Ref. 2. [b] Ref. 3. [c] Ref. 4. [d] This work.

importance. The chlorine substituents in the *para* positions of the benzene ring in this compound produce a very significant change of structure as compared to the unsubstituted compound; it has one notably short I · · · I interaction (3.85 Å) and two longer ones (4.14 and 4.32 Å). Quite why this change should occur is not clear but an inductive effect by the chlorine atoms, withdrawing electron density from the TeI_2 system may be ultimately responsible. The significantly shorter secondary bonds in R_2TeX_2 when R = alkyl rather than R = aryl may also be connected to electron-inductive effects.

The structures for the complete series Ph_2TeX_2 (X = F, Cl, Br, or I) are now known, and comparative data are presented in Table 5. All the compounds show very similar primary geometry, in each case supplemented by secondary bonds, producing either octahedral or square-pyramidal coordination (in Ph_2TeCl_2 and one molecule of β-Ph_2TeI_2). The strength of these bonds is best measured by the difference between corresponding primary and secondary Te–X bonds.[16] This parameter shows a general decrease from X = F to X = I, interrupted by the values for Ph_2TeBr_2; however, there must be a suspicion about the accuracy of this relatively early film-based determination. Leaving this aside, the increasingly strong interactions correlate with the greater overlap possible for the heavier halogens, and confirm the trends found in other systems.[16]

Acknowledgements

We thank the S.E.R.C. for research support.

References

1 See, for example, R. F. Ziolo and J. M. Troup, *Inorg. Chem.*, 1979, **18**, 2271.
2 F. J. Berry and A. J. Edwards, *J. Chem. Soc., Dalton Trans.*, 1980, 2306.
3 N. W. Alcock and W. D. Harrison, *J. Chem. Soc., Dalton Trans.*, 1982, 251.
4 G. D. Christofferson and J. D. McCullough, *Acta Crystallogr.*, 1958, **11**, 249.
5 N. W. Alcock and W. D. Harrison, *Acta Crystallogr., Sect. B*, 1982, **38**, 2677.
6 N. W. Alcock and W. D. Harrison, *J. Chem. Soc., Dalton Trans.*, 1982, 709.
7 K. Lederer, *Chem. Ber.*, 1916, **49**, 1071.
8 N. W. Alcock, in ' Crystallographic Computing,' ed. F. Ahmed, Munksgard, Copenhagen, 1970.
9 P. Main, MULTAN-80, University of York, 1980.
10 J. M. Stewart, Technical Report TR-446, Computer Science Centre, University of Maryland, 1976.
11 ' International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.
12 N. Petragnani, L. T. Castellanos, K. J. Wynne, and W. Maxwell, *J. Organomet. Chem.*, 1973, **55**, 295.
13 F. Einstein, J. Trotter, and C. Williston, *J. Chem. Soc. A*, 1967, 2018.
14 P. H. Bird, V. Kumar, and B. C. Pant, *Inorg. Chem.*, 1980, **19**, 2497.
15 N. W. Alcock, *Adv. Inorg. Chem. Radiochem.*, 1972, **15**, 1.

Received 18*th July* 1983; *Paper* 3/1232