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Structure of Bis(*p*-methoxyphenyltelluro)methane

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Abstract. $C_{15}H_{16}O_2Te_2$, $M_r = 483{\cdot}2$, orthorhombic, *Pbca*, $a = 6{\cdot}374\,(2)$, $b = 17{\cdot}069\,(2)$, $c = 28{\cdot}538\,(3)$ Å, $V = 3105\,(1)$ Å^3, $Z = 8$, $D_x = 2{\cdot}07$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 3{\cdot}763$ mm^{-1}, $F(000) = 1808$, $T = 293$ K, $R = 0{\cdot}046$, $wR = 0{\cdot}052$ for 1722 observed reflections. Each Te atom in the binuclear molecule is bonded to two different organo groups with Te—C(aliph) 2·149 (6) and 2·131 (6) Å; Te—C(arom) 2·115 (6) and 2·105 (7) Å; C—Te—C 95·2 (2), 97·8 (2)°; Te—Te distance 3·6632 (9) Å. The Te atoms exhibit different surroundings: square-planar geometry for Te1 and T-shaped for Te3.

Introduction. The importance of selenoacetals and selenium–tellurium acetals in the field of organic synthesis has been pointed out (Seebach & Beck, 1975; Krief, 1980; Kauffmann, 1982; Brandt, Comasseto, Nakamura & Petragnani, 1983). We are interested in another group of compounds closely related to these, the bis(aryltelluro)methanes, $(ArTe)_2CH_2$, also very important reagents in organic synthesis and as starting materials for the preparation of other kinds of organotellurium compounds (Otsubo, Ogura, Yamaguchi, Higuchi, Sakato & Misumi, 1981; Chikamatsu, Otsubo, Ogura & Yamaguchi, 1982; Kauffmann, 1982). The insertion reaction of carbene into the Te—Te bond of diarylditellurides described by Petragnani & Schill (1970) was utilized to prepare a series of bis(aryltelluro)methanes (Torres, 1990). The present work deals with the structural aspects of these intermediates. As far as we know this is the first structural report on the Te—CH_2—Te substructure. This study has been carried out in order to establish the precise geometry of the molecule within the tellurium surroundings.

Experimental. Crystal chosen for X-ray study with dimensions 0·45 × 0·18 × 0·18 mm, Enraf–Nonius CAD-4 diffractometer. Unit-cell parameters by least squares from 25 reflections with θ between 6 and 13°; 2277 reflections collected, 1722 considered observed with $I \geq 2{\cdot}5\sigma(I)$; ω–2θ scan mode, *hkl* range $0 \leq h \leq 7$, $0 \leq k \leq 19$, $0 \leq l \leq 31$; 2θ limit 47°. Three standard reflections monitored every 50 measurements showed no significant change in intensity. Lorentz and polarization corrections were applied, but no absorption correction was performed. The structure was solved by direct methods using *MULTAN*11/84 (Main, Germain & Woolfson, 1984). Anisotropic full-matrix least-squares refinement of non-H atoms with *SHELX*76 (Sheldrick, 1976); H-atom positions were calculated riding on the adjacent C atom assuming C—H = 0·96 Å and two different isotropic temperature factors were refined, one for methyl and one for non-methyl H atoms (final values $U = 0{\cdot}1164$ and 0·0531 Å^2, respectively); 174 parameters refined; $R = 0{\cdot}046$, $wR = 0{\cdot}052$, $w = 0{\cdot}2732/[\sigma^2(F) + 0{\cdot}01011F^2]$; $S = 1{\cdot}55$; max. $(\Delta/\sigma) = 0{\cdot}091$. Scattering factors, except tellurium, from *International Tables for X-ray Crystallography* (1974, Vol. IV); scattering factor for tellurium from Forsyth & Wells (1959). Residual electron density within −0·76 and 0·52 e Å^{-3} near the Te atoms. Drawing by *PLUTO* (Motherwell & Clegg, 1978). All calculations were performed on a Digital MicroVAX II.

Discussion. The atomic parameters are given in Table 1.† A view of the molecule with the atomic numbering scheme is shown in Fig. 1 and the packing diagram in Fig. 2. Table 2 gives bond distances and angles.

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† Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, torsion angles and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53626 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Atomic coordinates* ($\times 10^4$; Te $\times 10^5$) *with e.s.d.'s in parentheses and equivalent isotropic temperature factors* (Å^2) *for non*-H *atoms*

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	B_{eq}
Te1	71663 (8)	11946 (3)	55717 (2)	3·76
Te3	71339 (9)	10170 (3)	68509 (2)	4·52
C2	5421 (11)	1047 (3)	6210 (2)	4·01
C11	8497 (10)	59 (3)	5580 (2)	3·15
C12	10425 (10)	− 82 (4)	5769 (2)	4·18
C13	11313 (10)	− 819 (4)	5766 (2)	4·20
C14	10273 (10)	− 1437 (4)	5575 (2)	3·61
C15	8271 (9)	− 1295 (4)	5384 (2)	3·80
C16	7394 (9)	− 558 (4)	5382 (2)	3·59
O1	10956 (7)	− 2189 (3)	5550 (1)	4·69
C17	13007 (10)	− 2347 (6)	5703 (3)	5·39
C31	8417 (10)	2152 (4)	6815 (2)	3·45
C32	7367 (10)	2788 (4)	6620 (3)	4·47
C33	8243 (10)	3525 (4)	6620 (2)	3·92
C34	10091 (10)	3662 (4)	6835 (2)	3·53
C35	11181 (11)	3036 (4)	7042 (2)	4·35
C36	10298 (11)	2292 (4)	7021 (2)	4·38
O3	10822 (7)	4407 (3)	6829 (1)	4·52
C37	12709 (11)	4595 (5)	7056 (3)	5·36

Table 2. *Interatomic distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Te1—C2	2·149 (6)	C11—Te1—C2	95·2 (2)
Te1—C11	2·115 (6)	C31—Te3—C2	97·8 (2)
Te3—C2	2·131 (6)	Te3—C2—Te1	117·7 (3)
Te3—C31	2·105 (6)		
Te1···O1′	3·402 (5)	C11—Te1···O1′	167·8 (2)
Te3···O3′	3·332 (5)	C31—Te3···O3′	167·8 (2)
C12—C11	1·364 (9)	C12—C11—Te1	121·9 (5)
C16—C11	1·387 (8)	C16—C11—C12	118·9 (6)
C13—C12	1·379 (9)	C13—C12—C11	121·9 (6)
C14—C13	1·361 (9)	C14—C13—C12	120·7 (6)
C15—C14	1·409 (9)	C15—C14—C13	117·6 (6)
O1—C14	1·357 (8)	O1—C14—C13	126·8 (6)
C16—C15	1·376 (9)	O1—C14—C15	115·7 (5)
C17—O1	1·405 (8)	C16—C15—C14	121·8 (5)
		C15—C16—C11	119·2 (5)
		C17—O1—C14	117·6 (6)
C32—C31	1·392 (9)	C32—C31—Te3	123·4 (5)
C36—C31	1·356 (9)	C36—C31—C32	117·5 (5)
C33—C32	1·376 (9)	C33—C32—C31	121·2 (6)
C34—C33	1·348 (8)	C34—C33—C32	120·9 (6)
C35—C34	1·405 (8)	C35—C34—C33	119·4 (6)
O3—C34	1·355 (7)	O3—C34—C33	117·3 (5)
C36—C35	1·389 (9)	O3—C34—C35	123·3 (6)
C37—O3	1·404 (8)	C36—C35—C34	118·4 (6)
		C35—C36—C31	122·5 (6)
		C37—O3—C34	120·2 (5)

Symmetry code: for O1′: 1·5 − *x*, 0·5 + *y*, *z*; for O3′: 1·5 − *x*, −0·5 + *y*, *z*.

The distances found for Te—C(aliph) [Te1—C2 = 2·149 (6); Te3—C2 = 2·131 (6) Å] and for Te—C(arom) [Te1—C11 = 2·115 (6); Te3—C31 = 2·105 (7) Å] are within the range reported for these kinds of bonds: Te—C(aliph)$_{aver}$ = 2·14 and Te—C(arom) = 2·11–2·12 Å (Alcock & Harrison, 1982); the C—Te—C angles also lie within the expected values, C11—Te1—C2 = 95·2 (2) and C31—Te3—C2 = 97·8 (2)°. C2 maintains its original sp^3 hybridization even though slightly distorted, Te1—C2—Te3 = 117·7 (3)°. From these data, the distance Te1–Te3 is 3·6632 (9) Å [shorter than the sum of the van der Waals radii, 4·12 Å, (Bondi, 1964)].

The geometry around the tellurium is T-shaped, the third position being occupied by an O atom in a *trans* position to the aromatic C atom. These O atoms belong to neighbouring molecules (Table 2). C14′ (symmetry code 2 − *x*, −*y*, 1 − *x*) is placed *trans* to C2 at 3·680 (6) Å from Te1, slightly shorter than the sum of the van der Waals radii; this atom lies on the plane defined by the Te1, C2, C11 and O1′ [r.m.s.d. = 0·1019; $\delta_{C14'}$ = 0·138 (6) Å]. This interaction is not observed for the Te3 atom indicating that the Te atoms have different surroundings; in agreement with this, different torsion angles are

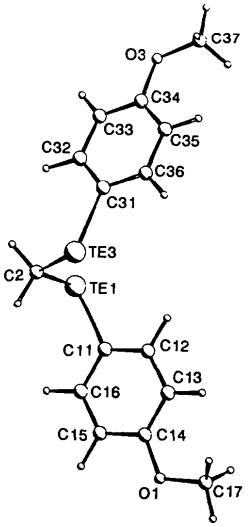

Fig. 1. A view of the molecule showing the atomic numbering.

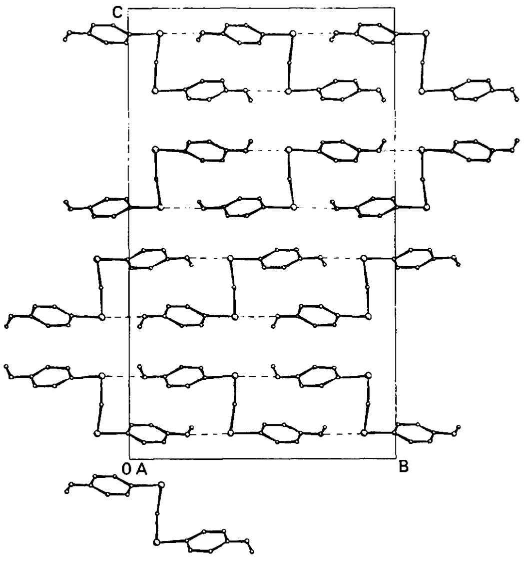

Fig. 2. Projection of the unit-cell contents down the **a** axis.

observed [C2—Te1—C11—C12 = −94·3 (5), C2—Te1—C11—C16 = 86·7 (5), C2—Te3—C31—C32 = 34·3 (6) and C2—Te3—C31—C36 = −150·6 (5)°]. Also bond lengths found for Te3 are shorter than for Te1. Taking into account the ligand distribution and following the ideas of Husebye (1983), we presume that the Te1 lone non-bonding pairs occupy octahedral positions above and below the coordination plane whereas the Te3 lone pairs occupy equatorial positions together with C2 in a trigonal bipyramidal arrangement.

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Structures of *N*-Substituted 1,2-Oxazines. II. Bicyclic Bridged Derivatives

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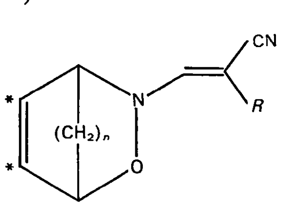
Abstract. (I) 2-(2-Oxa-3-azabicyclo[2.2.2]oct-5-en-3-yl)-1,1-ethylenedicarbonitrile, $C_{10}H_9N_3O$, $M_r = 187{\cdot}20$, orthorhombic, *Pnam*, $a = 8{\cdot}933$ (1), $b = 13{\cdot}088$ (1), $c = 8{\cdot}002$ (2) Å, $V = 935{\cdot}6$ (3) Å^3, $Z = 4$, $D_x = 1{\cdot}33$ g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 7{\cdot}5$ cm^{-1}, $F(000) = 392$, $T = 291$ K, $R = 0{\cdot}056$ for 642 observed reflections. (II) 2-(*tert*-Butylthio)-3-(2-oxa-3-azabicyclo[2.2.2]octan-3-yl)acrylonitrile, $C_{13}H_{20}N_2OS$, $M_r = 252{\cdot}38$, monoclinic, $P2_1$, $a = 12{\cdot}098$ (4), $b = 17{\cdot}770$ (5), $c = 10{\cdot}926$ (5) Å, $\beta = 112{\cdot}44$ (3)°, $V = 2171$ (1) Å^3, $Z = 6$, $D_x = 1{\cdot}16$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 2{\cdot}1$ cm^{-1}, $F(000) = 816$, $T = 291$ K, $R = 0{\cdot}064$ for 3441 observed reflections. (III) 2-(*tert*-Butylthio)-3-(6-oxa-7-azabicyclo[3.2.2]non-8-en-7-yl)acrylonitrile, $C_{14}H_{20}N_2OS$, $M_r = 264{\cdot}39$, orthorhombic, $P2_12_12_1$, $a = 9{\cdot}962$ (3), $b = 12{\cdot}576$ (3), $c = 11{\cdot}766$ (4) Å, $V = 1474{\cdot}1$ (7) Å^3, $Z = 4$, $D_x = 1{\cdot}19$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 2{\cdot}10$ cm^{-1}, $F(000) = 568$, $T = 291$ K, $R = 0{\cdot}051$ for 1259 observed reflections. The *E* configuration of the double bond is observed for both (II) and (III). Some geometrical parameters indicate clearly that the conjugation between the olefin and the ring system is less in molecule (III) than in the other two derivatives.

Introduction. A series of *N*-substituted bicyclic 1,2-oxazines has been synthetized and their thermal isomerization in epoxy-epimines has been studied (Vaerman, 1989).



$n = 0$ to 3; $R = CN$ or S^tBu; * single bond in (II)

With the aim of quantifying the effects of the bridge length (n) and that of the substituent (R) of the olefin on the geometry, we have determined the

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