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Structure of α-Tetrachlorothiophene 1,1-Dioxide at 150 K

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(*Received* 5 *October* 1992; *accepted* 7 *January* 1993)

Abstract

Tetrachlorothiophene 1,1-dioxide is polymorphic, crystallizing either in space group *C*2/*c* (α-form) or in *P*2$_1$/*c* (β-form). Crystals of the α-form at 150 K are built from molecules with approximate C_s (*m*) symmetry; the thiophene ring is non-planar, the C—S—C plane being folded by 4.1° out of the plane of the butadiene unit. The C—Cl distances are 1.682 (3)-1.696 (3) Å.

Comment

The title compound was first synthesized in 1980; it has been used as a Diels-Alder reagent because it readily loses sulfur dioxide when attacked by dienophiles (Raasch, 1980). In the course of charge-density studies of cyclic sulfones we have found that two crystalline forms of the title compound exist; both are monoclinic but the α-form has space group *C*2/*c* whereas the β-form has space group *P*2$_1$/*c*. The structure of the α-form, based on data collected to conventional resolution limits, is presented here. The structure was determined to supplement a study of the β-form, based on high-resolution data measured at 123 K, which will be described elsewhere (Frampton, Laidig & Muir, 1992).

The tetrachlorothiophene 1,1-dioxide molecule (Fig. 1) has approximate C_s (*m*) symmetry; the non-crystallographic mirror plane is defined by S, O(1), O(2) and the midpoint of the C(2)—C(3) bond. The conformation of the thiophene ring is that of a shallow envelope: the atoms of the *cis*-diene unit, defined by C(1)-C(4), are coplanar to within 0.007 (2) Å, but the S atom is displaced by 0.087 (1) Å from the mean plane defined by C(1)-C(4). The rather irregular displacements of the four Cl atoms from the diene plane [−0.127 (1), −0.088 (1), 0.074 (1) and 0.042 (1) Å] represent the most significant departure from C_s symmetry. Corresponding bond lengths agree to within 0.009 (4) Å and corresponding valence angles to within 1.9 (2) ° (see Table 2). The bond lengths also agree well with the mean values proposed by Allen, Kennard, Watson, Brammer, Orpen & Taylor (1987), though the C(sp^2)—Cl distance of 1.713 (11) Å given by these authors is slightly longer than the values of 1.682 (3)-1.696 (3) Å found here.

All intermolecular contacts shorter than the sum of the van der Waals radii [S 1.85, Cl 1.80, O 1.40, C 1.70 Å (Pauling, 1960)] are listed in Table 2. Each molecule is

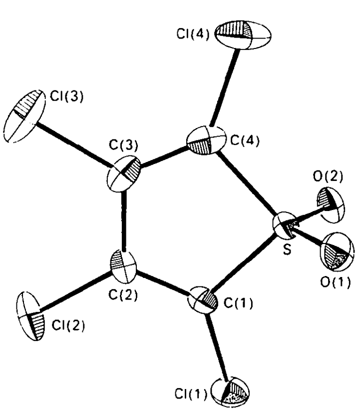

Fig. 1. A view of the molecule showing the atom labels and 50% probability ellipsoids.

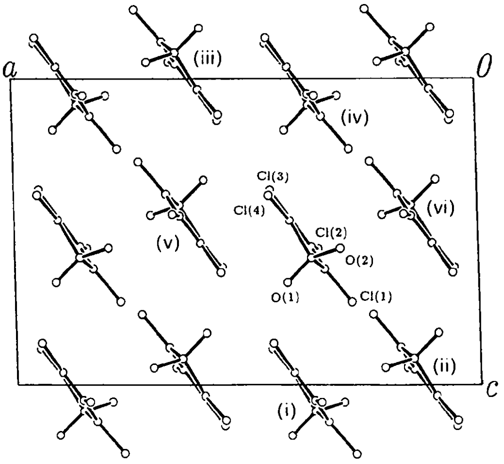

Fig. 2. The molecular packing viewed in projection down the *b* axis. Atom labels are attached to the reference molecule defined by the coordinates in Table 1. Roman numerals (see also Table 2) refer to the following symmetry operations: (i) $x, 1 - y, \frac{1}{2} + z$; (ii) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$; (iii) $1 - x, y, \frac{1}{2} - z$; (iv) $x, 1 - y, z - \frac{1}{2}$; (v) $1 - x, 1 - y, 1 - z$; (vi) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$.

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in contact with eight neighbouring molecules and, of the exocyclic Cl and O atoms, only O(1) and Cl(4) are not involved in such contacts. The molecular packing (Fig. 2) is based on sheets of molecules lying parallel to the (201) planes. Within a sheet, each molecule is in contact with four neighbouring molecules; thus the reference molecule defined by the coordinates of Table 1 is in contact with screw- and diad-related molecules [(ii) and (iii) in Fig. 2] and also with molecules related by translations of +1 or −1 along *b*. Inter-sheet contacts of the reference molecule involve *c*-glide-related molecules (i) and (iv) and centrosymmetrically related molecules (v) and (vi). At 295 K the contacts within each sheet [Cl(1)···O(2^{ii}) 3.162 (3), Cl(3)···Cl(3^{iii}) 3.439 (2), Cl(2)···O(2^{vii}) 3.067 (3) Å] are still significantly shorter than the sum of the van der Waals radii, but this is no longer true of the inter-sheet contacts, except for Cl(1)···Cl(3^{i}) which is 3.552 (2) Å.

Experimental

Crystal data

$C_4Cl_4O_2S$
$M_r = 253.9$
Monoclinic
$C2/c$
$a = 18.204$ (4) Å
$b = 7.855$ (1) Å
$c = 11.751$ (2) Å
$\beta = 91.77$ (2)°
$V = 1679.5$ (6) Å^3
$Z = 8$
$D_x = 2.008$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 23 reflections
$\theta = 12.4$–16.7°
$\mu = 16.0$ cm^{-1}
$T = 150$ K
Prism
0.76 × 0.68 × 0.34 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω-2θ scans
Absorption correction: by integration from crystal shape
$T_{min} = 0.37$, $T_{max} = 0.58$
3152 measured reflections
3078 independent reflections
2721 observed reflections [$I > 3.0\sigma(I)$]

$R_{int} = 0.040$
$\theta_{max} = 35°$
$h = 0 \rightarrow 29$
$k = 0 \rightarrow 12$
$l = -19 \rightarrow 19$
2 standard reflections
frequency: 60 min
intensity variation: 8.0%

Refinement

Refinement on F
Final $R = 0.043$
$wR = 0.080$
$S = 3.3$
2721 reflections
101 parameters
Weighting scheme based on measured e.s.d.'s: $w = 1/[\sigma^2(F)]$
$(\Delta/\sigma)_{max} = 0.01$
$\Delta\rho_{max} = 1.2$ e Å^{-3}
$\Delta\rho_{min} = -1.0$ e Å^{-3}

Extinction correction: Larson (1967)
Extinction coefficient: 0.0034 (5)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2B and 2.3.1)

Data collection: CAD-4 (Enraf-Nonius). Cell refinement: CAD-4 (Enraf-Nonius). Data reduction: *DREAM* (Blessing, 1987). Program(s) used to solve structure: *MITHRIL* (Gilmore, 1984). Program(s) used to refine structure: *GX* (Mallinson & Muir, 1985). Molecular graphics: *ORTEP* (Johnson, 1971; Mallinson & Muir, 1985). Software used to prepare material for publication: *GX* (Mallinson & Muir, 1985).

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Cl(1)	0.27236 (3)	0.43417 (7)	0.72966 (4)	0.031
Cl(2)	0.34378 (4)	0.72891 (7)	0.55617 (7)	0.041
Cl(3)	0.44528 (3)	0.56237 (11)	0.36506 (5)	0.044
Cl(4)	0.44822 (4)	0.12835 (10)	0.38269 (5)	0.048
S	0.35837 (2)	0.19584 (6)	0.58590 (3)	0.019
O(1)	0.41166 (9)	0.13183 (21)	0.66767 (13)	0.030
O(2)	0.29570 (9)	0.09306 (19)	0.55521 (14)	0.029
C(1)	0.33035 (10)	0.40449 (23)	0.62179 (15)	0.021
C(2)	0.35816 (10)	0.51668 (25)	0.55064 (16)	0.023
C(3)	0.40177 (10)	0.43896 (29)	0.46038 (15)	0.026
C(4)	0.40437 (11)	0.26929 (29)	0.46424 (16)	0.026

Table 2. *Geometric parameters* (Å, °)

Cl(1)—C(1)	1.691 (2)	S—C(1)	1.771 (2)
Cl(2)—C(2)	1.689 (3)	S—C(4)	1.775 (2)
Cl(3)—C(3)	1.696 (3)	C(1)—C(2)	1.326 (3)
Cl(4)—C(4)	1.682 (3)	C(2)—C(3)	1.476 (3)
S—O(1)	1.435 (2)	C(3)—C(4)	1.334 (4)
S—O(2)	1.435 (2)		
Cl(1)···Cl(3^{i})	3.483 (1)	Cl(3)···C(3^{v})	3.407 (2)
Cl(1)···O(2^{ii})	3.111 (2)	O(2)···C(1^{vi})	3.049 (2)
Cl(3)···Cl(3^{iii})	3.408 (1)	Cl(2)···O(2^{vii})	2.991 (2)
Cl(3)···C(1^{iv})	3.500 (2)		
O(1)—S—O(2)	119.1 (1)	Cl(2)—C(2)—C(1)	124.7 (2)
O(1)—S—C(1)	111.0 (1)	Cl(2)—C(2)—C(3)	121.5 (2)
O(1)—S—C(4)	109.1 (1)	C(1)—C(2)—C(3)	113.7 (2)
O(2)—S—C(1)	110.4 (1)	Cl(3)—C(3)—C(2)	120.7 (2)
O(2)—S—C(4)	111.8 (1)	Cl(3)—C(3)—C(4)	125.2 (2)
C(1)—S—C(4)	92.1 (1)	C(2)—C(3)—C(4)	114.1 (2)
Cl(1)—C(1)—S	119.8 (2)	Cl(4)—C(4)—S	119.3 (2)
Cl(1)—C(1)—C(2)	129.8 (2)	Cl(4)—C(4)—C(3)	130.9 (2)
S—C(1)—C(2)	110.3 (2)	S—C(4)—C(3)	109.6 (2)
C(4)—S—C(1)—C(2)	−3.6 (2)	Cl(2)—C(2)—C(3)—Cl(3)	5.3 (2)
C(1)—S—C(4)—C(3)	4.4 (2)	C(1)—C(2)—C(3)—C(4)	1.4 (2)
Cl(1)—C(1)—C(2)—Cl(2)	3.0 (2)	Cl(3)—C(3)—C(4)—Cl(4)	0.1 (2)
S—C(1)—C(2)—C(3)	2.0 (2)	C(2)—C(3)—C(4)—S	−4.1 (2)

Symmetry code: (i) $x, 1-y, \frac{1}{2}+z$; (ii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z$; (iii) $1-x, y, \frac{1}{2}-z$; (iv) $x, 1-y, z-\frac{1}{2}$; (v) $1-x, 1-y, 1-z$; (vi) $\frac{1}{2}-x, \frac{1}{2}-y, 1-z$; (vii) $x, 1+y, z$.

A preliminary room-temperature analysis was first performed. At 295 K the cell dimensions are: $a = 18.424$ (4), $b = 7.915$ (1), $c = 11.927$ (5) Å, $\beta = 90.48$ (3)°, $V = 1739.2$ (8) Å^3. Coordinates derived from the 295 K analysis were used as a starting point for refinement of the 150 K data. Cooling the crystal from 295 to 150 K produced only expected changes in the structural results: the atomic displacement parameters decreased by rather more than 50% on average and intermolecular contact distances shortened. Accordingly, only the more precise results obtained at 150 K are fully presented here.

We thank SERC for the financial support of CSF and GD, Dr K. Mackenzie, Chemistry Department, University of Bristol, for gifts of crystals and Dr P. R. Mallinson for helpful discussions.

Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55998 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA1035]

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Acta Cryst. (1993). C**49**, 1199–1201

Structure of a Chiral Monocyclic Phosphonamide

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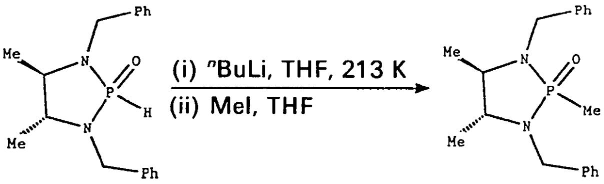
(*Received* 24 *August* 1992; *accepted* 9 *December* 1992)

Abstract

The crystal structure of a chiral racemic monocyclic phosphonamide, 1,3-dibenzyl-2,4,5-trimethyl-2,3,4,5-tetrahydro-1*H*-1,3,2-diazaphosphole 2-oxide, $C_{19}H_{25}N_2OP$, m.p. 412.6–414 K, has been determined by X-ray diffraction. The title molecule consists of a five-membered ring with a tetrahedrally coordinated P^{V} atom and *trans* methyl substituents at C atoms. In addition to two N atoms of the five-membered ring, the P atom is bonded to an O atom and a methyl.

Comment

We recently reported the synthesis of chiral phosphonamides by the alkylation of phosphorous acid diamides (Koeller & Spilling, 1991). Treatment of phosphorous acid diamide (1) with *n*-butyllithium in THF solution followed by alkylation of the resulting anion with methyl iodide gave the monocyclic phosphonamide (2).



(1) (2)

Recently, several publications have described the use of chiral phosphonamides as auxiliaries in asymmetric reactions. Related phosphonamides have shown useful diastereofacial biases upon further reaction of the organic chain. Alkylation of the *α* anions of bicyclic phosphonamides proceeds with high diastereoselectivity (Hanessian, Delorme, Beaudoin & Leblanc, 1984; Hanessian & Bennani, 1990; Hanessian, Bennani & Delorme, 1990). The stereoselectivity and rate of the carbanion accelerated Claisen rearrangement (CACR) of 2-allyloxy-allyl phosphonamides (Denmark, Stadler, Dorow & Kim, 1991) was shown to be dependent on the nature of the phosphonamide. The crystal structures of four bicyclic phosphonamides have been reported (Bélanger-Gariépy, Delorme, Hanessian & Brisse, 1986; Bélanger-Gariépy, Bennani, Hanessian & Brisse, 1989; Bennani, Bélanger-Gariépy & Hanessian, 1990). The most striking contrast between the monocyclic compound (2) and the bicyclic compounds is the environment of the N atoms. The N atoms in the monocyclic compound (2) are close to planar, as indicated by the sum of the three N-atom bond angles ($\sum N$). $\sum N(1) = 358.9$ (2) and $\sum N(2) = 355.4$ (2)° for compound (2), whereas in the bicyclic compounds the N atoms, are approximately midway between tetrahedral ($\sum N = 328.5°$) and planar ($\sum N = 360°$) geometry, as indicated by $\sum N(1) = 344.3$ and $\sum N(2) = 345.5°$ (Bennani *et al.*, 1990).

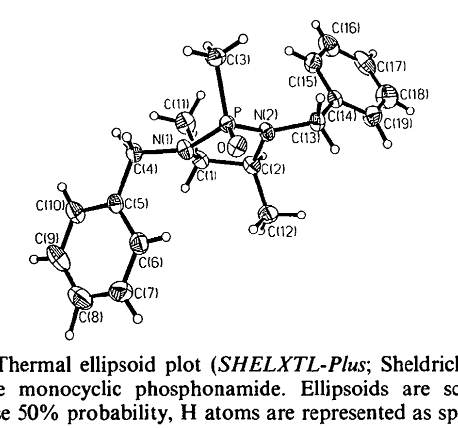


Fig. 1. Thermal ellipsoid plot (*SHELXTL-Plus*; Sheldrick, 1991) of the monocyclic phosphonamide. Ellipsoids are scaled to enclose 50% probability, H atoms are represented as spheres of arbitrary radii.

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