Structures of Thianthrene (I), $C_{12}H_8S_2$, (Redeterminations at 163 K and 295 K) and 1-Azathianthrene (II), $C_{11}H_7NS_2$, (at 163 K)

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Abstract. (I): $M_r = 216 \cdot 32$, monoclinic, $P2_1/c$, $Z = 4$, $F(000) = 448$, $\lambda(\text{Mo } K\alpha) = 0 \cdot 71069$ Å; at 163 K $a = 11 \cdot 8672$ (17), $b = 6 \cdot 0648$ (7), $c = 14 \cdot 3856$ (16) Å, $\beta = 109 \cdot 727$ (12)°, $V = 974 \cdot 6$ (2) Å^3, $D_x = 1 \cdot 474$ g cm^{-3}, $\mu = 4 \cdot 81$ cm^{-1}, $R = 0 \cdot 034$ for 2087 reflections $(F \geq 6\sigma_F)$; at 295 K $a = 11 \cdot 9559$ (15), $b = 6 \cdot 1578$ (13), $c = 14 \cdot 4959$ (20) Å, $\beta = 109 \cdot 964$ (11)°, $V = 1003 \cdot 1$ (3) Å^3, $D_m = 1 \cdot 44$ g cm^{-3}, $D_x = 1 \cdot 432$ g cm^{-3}, $\mu = 4 \cdot 67$ cm^{-1}, $R = 0 \cdot 043$ for 1589 reflections $(F \geq 5\sigma_F)$. (II): $M_r = 217 \cdot 30$, monoclinic, $P2_1/c$, $Z = 4$, $F(000) = 448$, $\lambda(\text{Mo } K\alpha) = 0 \cdot 71069$ Å, 163 K, $a = 11 \cdot 7737$ (25), $b = 6 \cdot 0267$ (12), $c = 14 \cdot 1501$ (24) Å, $\beta = 108 \cdot 507$ (19)°, $V = 952 \cdot 1$ (3) Å^3, $D_m = 1 \cdot 47$ g cm^{-3}, $D_x = 1 \cdot 516$ g cm^{-3}, $\mu = 4 \cdot 96$ cm^{-1}, $R = 0 \cdot 034$ for 1958 reflections $(F \geq 6\sigma_F)$. The compounds were synthesized by Martin and Puig-Torres. The compounds are isomorphous and 1-azathianthrene appears to be disordered. The dihedral angles for thianthrene are 127·14 (3)° at 163 K and 128·09 (5)° at 295 K. The dihedral angle in 1-azathianthrene is 130·37 (3)°.
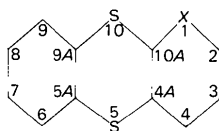
Introduction. The structures have been determined for thianthrene (I) at 163 K and 295 K (a redetermination) and for 1-azathianthrene (II) at 163 K by single-crystal X-ray diffraction analysis. Our interest lies in the effect that substitutions in or on the aromatic rings of thianthrene will have on the dihedral angle of the two planes defined by one aromatic ring and the two S atoms. The structure of (I) was redetermined to verify the values reported by Lynton & Cox (1956) and Rowe & Post (1958). X-ray data in these laboratories are collected routinely at 163 K. Therefore, data for (I)

were collected at both room temperature and 163 K in order to ascertain the effect this temperature difference would have on the dihedral angle.

Experimental. Details of data collection and structural refinement are given in Table 1. Crystals of (I) were clear, colorless prisms; crystals of (II) transparent pale-brown prisms. Densities were measured by flotation in aqueous $ZnCl_2$. The crystals were glued to glass fibers affixed in wax on a brass pin mounted on a goniometer head.

The structures were solved by *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and refined by the full-matrix least-squares method $[\sum w(F_o - F_c)^2$ minimized, $w = 1/\sigma_F^2]$. Scattering factors and anomalous-dispersion corrections for all atom types were used as programmed in *SHELX76* (Sheldrick, 1976). For each structure all atomic positional parameters were refined as well as the anisotropic thermal parameters for non-hydrogens and isotropic thermal parameters for H atoms. The H atoms were located in electron density difference maps as peaks of 0·51– 0·85 e Å^{-3}. Atomic parameters are found in Table 2.* Principal computer programs are given by Gadol & Davis (1982).

Discussion. The atom labeling, bond lengths and bond angles for the title compounds are illustrated in Figs. 1–4. We are concerned with the dihedral angles between the planes described in Table 3; each plane is defined by one aromatic ring and the two S atoms. Thianthrene has been studied and the dihedral angle calculated by various methods since 1941. The values for the dihedral angle determined in these studies

(I): $X(1) = C$
(II): $X(1) = N$

including the present study fall into two groups: (1) values in the range 127–132°, and (2) values in the range 140–144°. The first group includes four single-crystal X-ray diffraction structure determinations (Lynton & Cox, 1956; Rowe & Post, 1958; and the present study) and one gaseous-state electron diffraction study (Gallaher & Bauer, 1975).

The second group consists of dipole-moment measurements (Wood & Crackston, 1941; Aroney, LeFevre & Saxby, 1965; Davies & Swain, 1971), Kerr-constant measurements (Aroney, LeFevre & Saxby, 1965), a molecular optical anisotropy study (Canselier & Clement, 1979) and two ^{1}H NMR studies (Fronza, Ragg & Ronsisvalle, 1982; Fujiwara, Kawamura, Takagi & Sasaki, 1983). Fujiwara *et al.* (1983) after obtaining angles of 141·6 (2) and 140·2 (2)° in two different liquid-crystalline solvents concluded that the dihedral angle is dependent on the environment of the molecule. Clearly, the conformations of thianthrene in the solid and solution states are different. Some factors which could affect the dihedral angle are: (1) solvent interaction with S; (2) flapping about the S—S axis; (3) solvent interaction with the aromatic rings.

Table 1. *Summary of data collection and structure refinement*

Data collection[i,ii]

Radiation, λ(Å)		Mo $K\alpha$, 0·71069	
Mode		ω scan	
Scan range		Symmetrically over 1·0° about $K\alpha_{1,2}$ maximum	
Background		Offset 1·0 and $-1\cdot0°$ in ω from $K\alpha_{1,2}$ maximum	
	(Ib) (295 K)	(Ia) (163 K)	(II) (163 K)
2θ range[i] (°)	21–26	23–30	26–30
Scan rate (deg min^{-1})	2·0–6·0	1·5–6·0	3·0–6·0
Exposure time (h)	56·7	69·6	27·1
Stability analysis			
Computed a	0·000571	0·001308	0·000652
b	$-0·000011$	$-0·000015$	$-0·000017$
Max. correction (on I)	0·7%	2·8%	0·5%
2θ range (°)	4·0–60·0	4·0–60·0	4·0–55·0
Range hkl, min.	0,0,$\overline{19}$	$\overline{16},\overline{8},0$	0,0,$\overline{17}$
max.	16,8,19	15,0,19	15,7,17
Total reflections measd.	3185	3107	2394
Data-crystal dimensions (mm)	0·10×0·22×0·38	0·22×0·21×0·21	0·38×0·39×0·51
Data-crystal volume (mm^3)	0·009	0·010	0·069
Absorption coeff., μ(Mo $K\alpha$) (cm^{-1})	4·67	4·81	4·96
Transmission-factor range	0·904–0·959	0·894–0·916	0·819–0·852

Structure refinement

Ignorance factor p	0·04	0·04	0·04
Reflections used, $F \geq n\sigma_F$	1589 ($n = 5$)	2087 ($n = 6$)	1958 ($n = 6$)
No. of variables	159	159	155
Goodness of fit, S	1·26	1·38	2·13
R, R_w	0·043,0·045	0·034,0·041	0·034,0·051
R for all data	0·099	0·055	0·038
Max. Δ/σ	0·003	0·006	0·010
Max. peak in $\Delta\rho$ map (e Å^{-3})	0·28	0·45	0·53
Min. peak in $\Delta\rho$ map (e Å^{-3})	$-0·24$	$-0·23$	$-0·31$

Notes: (i) Unit-cell parameters were obtained by least-squares refinement of the setting angles of 45 reflections in the 2θ ranges indicated. (ii) Syntex $P2_1$ autodiffractometer with a graphite monochromator and a Syntex LT-1 inert-gas (N$_2$) low-temperature delivery system. Data reduction was carried out as described by Riley & Davis (1976). Crystal and instrument stability were monitored by re-measurement of 4 check reflections after every 96 reflections. These data were analyzed as detailed by Henslee & Davis (1975).

Table 2. *Positions in fractional coordinates and U_{eq} for non-hydrogen atoms in* (Ia) (163 K), (Ib) (295 K) *and* (II)

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

		x	y	z	U_{eq}(Å^2)
S(10)	Ia	0·23364 (4)	0·12807 (7)	0·07842 (4)	0·0242 (2)
	Ib	0·23374 (7)	0·13298 (12)	0·08035 (6)	0·0498 (3)
	II	0·23584 (4)	0·12778 (7)	0·09431 (3)	0·0267 (2)
C(10A)	Ia	0·1499 (2)	0·3149 (3)	$-0·01404$ (13)	0·0205 (6)
	Ib	0·1506 (3)	0·3164 (4)	$-0·0119$ (2)	0·0400 (10)
	II	0·1510 (2)	0·3005 (3)	$-0·00421$ (12)	0·0220 (5)
X(1)	Ia	0·0321 (2)	0·2630 (3)	$-0·07145$ (13)	0·0235 (6)
	Ib	0·0350 (3)	0·2655 (5)	$-0·0702$ (2)	0·0468 (12)
	II	0·03920 (15)	0·2295 (3)	$-0·05735$ (12)	0·0318 (5)
C(2)	Ia	$-0·0340$ (2)	0·4078 (3)	$-0·14399$ (14)	0·0259 (6)
	Ib	$-0·0299$ (3)	0·4043 (6)	$-0·1425$ (2)	0·0523 (13)
	II	$-0·0269$ (2)	0·3583 (4)	$-0·13450$ (13)	0·0302 (6)
C(3)	Ia	0·0157 (2)	0·6060 (4)	$-0·15896$ (14)	0·0269 (6)
	Ib	0·0193 (3)	0·5991 (6)	$-0·1573$ (2)	0·0543 (13)
	II	0·0163 (2)	0·5577 (4)	$-0·15715$ (13)	0·0322 (6)
C(4)	Ia	0·1327 (2)	0·6596 (3)	$-0·10198$ (14)	0·0241 (6)
	Ib	0·1341 (3)	0·6539 (6)	$-0·0998$ (2)	0·0492 (13)
	II	0·1289 (2)	0·6302 (3)	$-0·10341$ (13)	0·0260 (6)
C(4A)	Ia	0·2006 (2)	0·5129 (3)	$-0·02977$ (13)	0·0199 (5)
	Ib	0·2009 (2)	0·5115 (4)	$-0·0272$ (2)	0·0381 (10)
	II	0·19795 (15)	0·4997 (3)	$-0·02661$ (12)	0·0217 (5)
S(5)	Ia	0·35056 (4)	0·57876 (8)	0·04093 (4)	0·02197 (14)
	Ib	0·34925 (7)	0·57915 (13)	0·04420 (6)	0·0457 (3)
	II	0·34553 (4)	0·58334 (7)	0·04052 (3)	0·0229 (2)
C(5A)	Ia	0·3494 (2)	0·5112 (3)	0·16030 (13)	0·0189 (5)
	Ib	0·3481 (2)	0·5110 (4)	0·1626 (2)	0·0372 (10)
	II	0·34757 (14)	0·5258 (3)	0·16363 (11)	0·0193 (5)
C(6)	Ia	0·4009 (2)	0·6563 (3)	0·23852 (15)	0·0232 (6)
	Ib	0·3997 (3)	0·6515 (5)	0·2403 (2)	0·0462 (11)
	II	0·40044 (15)	0·6775 (3)	0·23847 (13)	0·0221 (5)
C(7)	Ia	0·4078 (2)	0·5980 (4)	0·33399 (15)	0·0274 (6)
	Ib	0·4065 (3)	0·5928 (6)	0·3342 (3)	0·0562 (13)
	II	0·4097 (2)	0·6272 (3)	0·33577 (13)	0·0274 (6)
C(8)	Ia	0·3595 (2)	0·3995 (4)	0·35093 (15)	0·0283 (6)
	Ib	0·3586 (3)	0·3986 (6)	0·3506 (3)	0·0569 (13)
	II	0·3636 (2)	0·4305 (4)	0·35844 (13)	0·0306 (6)
C(9)	Ia	0·3035 (2)	0·2590 (3)	0·27252 (14)	0·0253 (6)
	Ib	0·3031 (3)	0·2622 (6)	0·2732 (2)	0·0505 (13)
	II	0·3078 (2)	0·2830 (3)	0·28436 (13)	0·0251 (6)
C(9A)	Ia	0·2995 (2)	0·3129 (3)	0·17684 (13)	0·0198 (5)
	Ib	0·2991 (2)	0·3150 (4)	0·1784 (2)	0·0389 (10)
	II	0·30075 (14)	0·3281 (3)	0·18702 (12)	0·0212 (5)

Table 3. *Least-squares planes, deviations and dihedral angles for* (Ia) (163 K), (Ib) (295 K) *and* (II)

Plane 1: S(10), C(10A), X(1), C(2), C(3), C(4), C(4A), S(5)
(Ia): $6\cdot970x -2\cdot741y -11\cdot944z -0\cdot351 = 0$
(Ib): $7\cdot178x -2\cdot785y -11\cdot957z -0\cdot350 = 0$
(II): $7\cdot055x -2\cdot939y -11\cdot211z -0\cdot240 = 0$

Deviations (Å)

	(Ia)	(Ib)	(II)
S(10)	$-0·0103$ (5)	$-0·0029$ (8)	$-0·0091$ (5)
C(10A)	$-0·002$ (2)	$-0·007$ (3)	$-0·010$ (2)
X(1)	0·005 (2)	0·001 (3)	0·005 (2)
C(2)	0·014 (2)	0·013 (3)	0·025 (2)
C(3)	$-0·004$ (2)	0·001 (3)	$-0·002$ (2)
C(4)	$-0·016$ (2)	$-0·014$ (3)	$-0·023$ (2)
C(4A)	$-0·003$ (2)	$-0·007$ (3)	$-0·014$ (2)
S(5)	0·0169 (5)	0·0157 (8)	0·0290 (4)

Plane 2: S(10), S(5), C(5A), C(6), C(7), C(8), C(9), C(9A)
(Ia): $-10\cdot356x +2\cdot773y +1\cdot911z +1\cdot913 = 0$
(Ib): $-10\cdot441x +2\cdot807y +1\cdot977z +1\cdot902 = 0$
(II): $-10\cdot379x +2\cdot689y +1\cdot886z +1\cdot912 = 0$

Deviations (Å)

	(Ia)	(Ib)	(II)
S(10)	$-0·0015$ (5)	$-0·0064$ (9)	$-0·0147$ (5)
S(5)	$-0·0343$ (5)	$-0·0314$ (8)	$-0·0296$ (5)
C(5A)	0·018 (2)	0·023 (3)	0·027 (2)
C(6)	0·037 (2)	0·032 (3)	0·027 (2)
C(7)	$-0·014$ (2)	$-0·017$ (4)	$-0·021$ (2)
C(8)	$-0·031$ (2)	$-0·030$ (4)	$-0·028$ (2)
C(9)	0·008 (2)	0·014 (4)	0·014 (2)
C(9A)	0·017 (2)	0·016 (3)	0·025 (2)

Dihedral angles
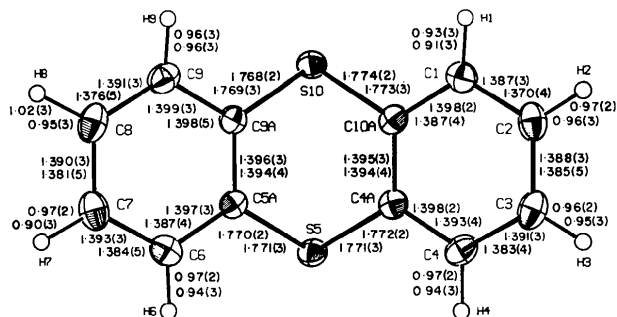(Ia): 127·14 (3)°   (Ib): 128·09 (5)°   (II): 130·37 (3)°

Fig. 1. View of (I) illustrating atom labeling and bond lengths (Å). For each bond the upper number is the length determined at 163 K and the lower number is the length determined at 295 K.
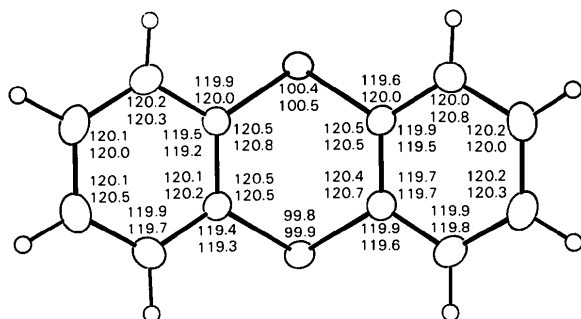

Fig. 2. Bond angles in (I) (°). The upper and lower numbers are values determined at 163 K and 295 K, respectively. E.s.d.'s at 163 K are 0·1–0·2°. At 295 K the e.s.d.'s are 0·1–0·3°.
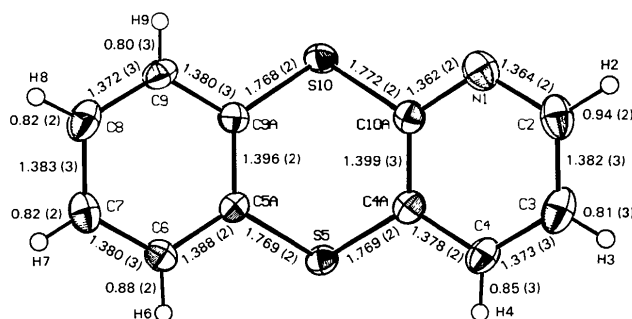

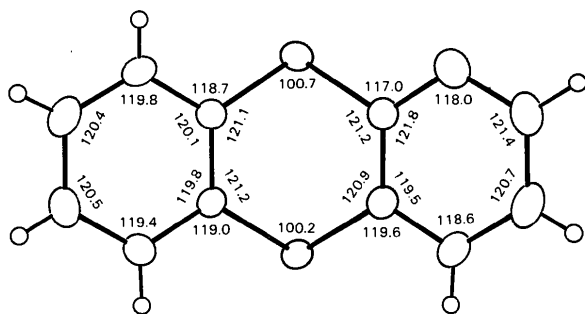Fig. 3. View of (II) illustrating atomic labeling and bond lengths (Å).

Fig. 4. Bond angles in (II) (°). E.s.d.'s are 0·1–0·2°.

Assuming the thianthrene structure to remain the same (except for the C—S—C angle) as S is coordinated, a C—S—C angle of 109·5° corresponding to a nearly tetrahedral S would result in a dihedral angle of 143°. Therefore, coordination of S would be expected to increase the dihedral angle with respect to thianthrene.

Two structures of thianthrene analogs having three-coordinate S have been reported which fit this pattern. In (thianthrene)gold(III) chloride, in which only one S is three-coordinate, a dihedral angle of 129·5° is reported (Alcock, Ang, Mok & Tan, 1978). The dihedral angle in thianthrenium bis(methoxycarbonyl)-methanide is 135·7° (Ternay, Baack, Chu, Napoleone, Martin & Alfaro, 1982). However, Hosoya (1963) in a preliminary report assigns dihedral angles of 123, 122 and 127° to the cis-dioxide, trans-dioxide and tetraoxide of thianthrene, respectively. He later reported an angle of 133·6° (Hosoya, 1966) in a complete structural paper of the trans-dioxide. However, using Hosoya's atomic coordinates, we calculate an angle of 127·7°. Studies of oxides of thianthrene are now underway.

Flapping or butterfly motion about the S—S axis is revealed in the group 1 studies. This motion would increase as the temperature changes from 163 to 295 to >428 K in the gaseous state. With this increase we see an increase in the dihedral angle from 127·14 (3) to 128·09 (5) to 130·37 (3)°. The tendency to flap even in the solid state appears to remain although it decreases with temperature. A review of the U_{eq} in Table 2 demonstrates that the thermal parameters are largest for C(2), C(3), C(7) and C(8), the atoms furthest from the pivoting axis of the flapping motion. Even at 163 K these four atoms have the largest motions. The effects of the flapping motion would be similar in the solution and gaseous states.

The third effect to be considered is solvent interactions with the aromatic rings. The effect is difficult to determine but may be similar to perturbations in the benzene rings brought about by substitutions in or on the ring systems. The dihedral angles determined by X-ray diffraction analysis for 2,7-dimethylthianthrene (Wei, 1971), perfluorothianthrene (Rainville, Zingaro & Meyers, 1980) and 1,6-dinitro-3,8-bis(trifluoromethyl)-thianthrene (Dahm, May, D'Amico, Tung & Fuhrhop, 1978) are 131·1, 132 and 137°, respectively. In an extreme effect, replacement of the benzene rings with quinoxaline rings in bis(quinoxaline) 2,2',3,3'-disulfide (Pignedoli, Peyronel & Antolini, 1977) causes the molecule to become planar.

The effect of substituting N at the 1-position in thianthrene to give 1-azathianthrene appears to be a slight flattening of the molecule to give a dihedral angle of 130·37 (3)°. The certainty in this angle is slightly diminished by a high probability of disorder for which no model was tested. This probable disorder is first

suggested by the isomorphous nature of (II) to (I) (see *Abstract*). This suggests that the N could be in any of the four possible positions with equal probability. Furthermore, placing the N at either position 1 or 6 and refining isotropically resulted in a considerably larger thermal parameter for the N *versus* the C atoms at the other three equivalent positions.

We resolved to treat the model as thianthrene until after the H atoms were located in a difference map with the hope that the N could be identified by the lack of density at the ideal H position. The electron densities corresponding to H on positions 1, 4, 6, and 9 were, respectively, 0·48, 0·56, 0·79 and 0·65 e Å^{-3}. The other four positions had densities ranging from 0·71 to 0·80 e Å^{-3}. We, therefore, assigned the N to the position of lowest density realizing that positions 4 and 9 probably contain partial N occupancy. The final ΔF map produced a peak of 0·53 e Å^{-3} 1·01 Å from N(1), most probably a combination of the lone-pair density and partial H occupancy.

The final thermal parameters (Table 2) and geometrical results (Figs. 3 and 4) when compared to thianthrene substantiate a disordered structure. The S-containing six-membered ring is essentially identical to the same ring in thianthrene. However, neither aromatic ring of (II) parallels those of (I). The C—N distances were expected to be shorter [C—N range: 1·315–1·346 Å in 1,4,9-triazaphenoxathiin and 1·333–1·340 Å in 1,3-diazaphenoxathiin (Larson & Simonsen, 1983)]. All other bond lengths except those of the S-containing six-membered ring are shorter than suggested by the thianthrene results, the effect of the unresolved disorder. The thermal parameters can be explained by approximately equal partial occupancy for N at positions 4 and 9 with very little partial occupancy for N at position 6. The decrease in the thermal parameters of C(4) and C(9) due to less electron density placed there is offset by the mislocation due to the differences in pyridine and benzene geometries.

References

ALCOCK, N. W., ANG, K. P., MOK, K. F. & TAN, S. F. (1978). *Acta Cryst.* B**34**, 3364–3366.
ARONEY, M. J., LEFEVRE, R. J. & SAXBY, J. D. (1965). *J. Chem. Soc.* pp. 571–575.
CANSELIER, J. P. & CLEMENT, C. (1979). *J. Chim. Phys. Phys.-Chim. Biol.* **76**, 699–707.
DAHM, D. J., MAY, F. L., D'AMICO, J. J., TUNG, C. C. & FUHRHOP, R. W. (1978). *Cryst. Struct. Commun.* **7**, 745–750.
DAVIES, M. & SWAIN, J. (1971). *Trans. Faraday Soc.* **67**, 1637–1653.
FRONZA, G., RAGG, E. & RONSISVALLE, G. (1982). *J. Chem. Soc. Perkin Trans.* 2, pp. 1209–1211.
FUJIWARA, H., KAWAMURA, A., TAKAGI, T. & SASAKI, Y. (1983). *J. Am. Chem. Soc.* **105**, 125–126.
GADOL, S. M. & DAVIS, R. E. (1982). *Organometallics*, **1**, 1607–1613.
GALLAHER, K. L. & BAUER, S. H. (1975). *J. Chem. Soc. Faraday Trans.* 2, pp. 1173–1182.
HENSLEE, W. H. & DAVIS, R. E. (1975). *Acta Cryst.* B**31**, 1511–1519.
HOSOYA, S. (1963). *Acta Cryst.* **16**, 310–312.
HOSOYA, S. (1966). *Acta Cryst.* **21**, 21–26.
LARSON, S. B. & SIMONSEN, S. H. (1983). In preparation.
LYNTON, H. & COX, E. G. (1956). *J. Chem. Soc.* pp. 4887–4895.
MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.
PIGNEDOLI, A., PEYRONEL, G. & ANTOLINI, L. (1977). *J. Cryst. Mol. Struct.* **7**, 173–182.
RAINVILLE, D., ZINGARO, R. A. & MEYERS, E. A. (1980). *Cryst. Struct. Commun.* **9**, 909–915.
RILEY, P. E. & DAVIS, R. E. (1976). *Acta Cryst.* B**32**, 381–386.
ROWE, I. & POST, B. (1958). *Acta Cryst.* **11**, 372–374.
SHELDRICK, G. M. (1976). *SHELX76. A crystallographic computing package.* Univ. of Cambridge, England.
TERNAY, A. L. JR, BAACK, J. C., CHU, S. S. C., NAPOLEONE, V., MARTIN, G. & ALFARO, C. (1982). *J. Heterocycl. Chem.* **19**, 833–836.
WEI, C. H. (1971). *Acta Cryst.* B**27**, 1523–1527.
WOOD, R. G. & CRACKSTON, J. E. (1941). *Philos. Mag.* **31**, 62–70.

Structure of Diphenylthiophosphinic Acid, (C6H5)2P(=S)OH, at 140 K

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Abstract. $M_r = 234\cdot3$, orthorhombic, space group *Pbca*, $a = 22\cdot62$ (1), $b = 6\cdot105$ (2), $c = 16\cdot562$ (5) Å, $V = 2287\cdot1$ Å^3, $Z = 8$, $D_m = 1\cdot34$, $D_x = 1\cdot36$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0\cdot71069$ Å, $\mu = 3\cdot9$ cm^{-1}, $F(000) = 976$, $T = 140$ K, $R = 0\cdot049$ for 2578 independent reflections. The acid hydrogen atom is attached to the oxygen atom of the POS group. The molecules form endless chains along the glide plane in the [010] direction through strong O—H···S hydrogen bonds of 3·133 (8) Å length.