Crystal and Molecular Structure of Tetraphenylcyclotetraphosphine Monosulphide

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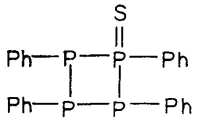
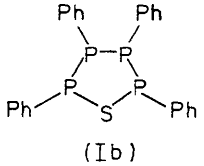
Crystals of $[C_6H_5P]_4S$ are orthorhombic, a = 24·700(6), b = 13·508(3), c = 13·410(2) Å, Z = 8, space group *Pbca*. The structure was solved from diffractometer data by direct methods, and refined by full-matrix least-squares methods to R 0·083 for 1475 observed reflexions. The phosphorus and sulphur atoms form a five-membered ring which has a puckered conformation, with the sulphur atom nearly in the mean plane through the ring atoms and the phosphorus atoms alternately above and below it. Mean bond lengths are: P–P 2·190(5), P–S 2·116(5), P–C 1·831(22), and C–C 1·382(16) Å. The angle at sulphur is 110·4(2)° and the endocyclic angles at phosphorus range from 104·2(2)—105·9(2)°, mean 105·2°. The phenyl rings are nearly perpendicular to the mean plane through the five-membered P_4S ring. Pairs of phenyl rings on the same side of the P_4S ring are close to being parallel to each other and perpendicular to the pair on the other side.

THE structure of tetraphenylcyclotetraphosphine monosulphide has previously been postulated[1] as either a four- (Ia) or five-membered (Ib) ring. The compound can be prepared by a variety of methods[2] and appears to be quite stable, as indicated by the difficulty of removing the sulphur with tributylphosphine.[2] The preparative reactions are structurally uninformative, however, and a crystal structure analysis was thus undertaken.



(Ia)



(Ib)

EXPERIMENTAL

Crystals are yellow needles elongated along b. A crystal of dimensions *ca.* 0·20 × 0·40 × 0·15 mm was placed in a sealed glass capillary.

Crystal Data.—$C_{24}H_{20}P_4S$, M = 464·38, Orthorhombic, a = 24·700(6), b = 13·508(3), c = 13·410(2) Å, U = 4474 Å^3, D_c = 1·379 g cm^{-3}, Z = 8, $F(000)$ = 1920. Space group *Pbca* (No. 61) from absent reflexions: $0kl$, $k \neq 2n$, $h0l$, $l \neq 2n$, $hk0$, $h \neq 2n$. Mo-K_α radiation, λ = 0·71069 Å; μ(Mo-K_α) = 4·37 cm^{-1}.

Unit-cell parameters were obtained by least-squares refinement of $\sin^2\theta$ values for 28 reflexions measured on a General Electric XRD 6 diffractometer. Intensity data were collected on a Datex-automated General Electric XRD 6 diffractometer with a scintillation counter, Mo-K_α radiation (zirconium filter and pulse-height analyser) and a θ—2θ scan. The scanwidth in 2θ was $(1·80 + 0·86 \tan\theta)°$ with 20 s background counts taken on either side of every scan. All reflexions with 2θ(Mo-K_α) $\leq 45°$ were measured. A check reflexion was monitored every 30 reflexions throughout data collection and its intensity had decreased by *ca.* 18% of its starting value at the end. The intensity of this reflexion was used to put the data on the same relative scale. Lorentz and polarization corrections were applied and structure amplitudes derived. Correction for absorption was considered unnecessary because of the

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[1] L. Maier, in 'Organic Phosphorus Compounds,' eds. G. M. Kosolapoff and L. Maier, Wiley–Interscience, New York, 1972, vol. 1, p. 12.

[2] H. P. Calhoun, M. R. LeGeyt, N. L. Paddock, and J. Trotter, *J.C.S. Chem. Comm.*, 1973, 623.

small value of μ. Of 2934 reflexions measured, 1475 (50·3%) were considered observed, having intensities $>2\sigma(I)$ above background, where $\sigma^2(I) = S + B + (0{\cdot}03S)^2$, with S = scan count and B = background count.

Structure Analysis.—The structure was solved by direct methods. Sixteen sets of signs for 300 reflexions with $|E| \geq 1{\cdot}84$ were determined by a computer program which uses Sayre relationships in an iterative procedure.[3] The starting set of reflexions is given in Table 1. One set of signs converged in 7 cycles and had the highest consistency index [3] (0·93) with 152 positive signs and 148 negative signs. An E map was computed by use of the 300 signed values of E from this set, and the five-membered P_4S ring was located from the map. Carbon atoms were then located from three-dimensional difference maps. The structure was refined by full-matrix least-squares methods, initially with isotropic temperature factors and finally with anisotropic temperature factors for all non-hydrogen atoms. The hydrogen atoms could not all be located from a difference map, but were included in calculated positions with isotropic temperature factors (B 10·0 Å^2); the parameters for these atoms were not refined. Convergence was reached at R 0·083 for 1475 observed reflexions. On the last cycle of refinement no parameter shift was $>0{\cdot}3\sigma$.

TABLE 1

Starting set of reflexions

h	k	l	E	
1	10	8	5·79	Origin-determining
16	5	3	3·49	
15	7	4	3·13	
1	2	8	3·87	
3	6	4	4·15	
3	10	8	−5·23	
1	6	4	−2·87	

Least-squares refinement was based on the minimization of $\Sigma w(|F_o| - |F_c|)^2$. Anisotropic thermal parameters are U_{ij} in the expression $f = f_o \exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)]$. Scattering factors, f_o, were obtained from ref. 4 for all non-hydrogen atoms, and for the hydrogen atoms from ref. 5. Approximately constant average values of $w(|F_o| - |F_c|)^2$ over ranges of $|F_o|$ were obtained by use of a standard errors weighting scheme of the form $w = 1/\sigma^2(F_o)$. Unobserved reflexions were not included in the least-squares refinement.

Final positional and thermal parameters are given in Table 2. Measured and calculated structure factors are listed in Supplementary Publication No. SUP 20890 (15 pp., 1 microfiche).*

DISCUSSION

Bond lengths and angles with estimated standard deviations are given in Table 3, and a general view of the molecule in Figure 1. Equations of mean planes through the molecule are given in Table 4, and dihedral angles in the five-membered P_4S ring in Table 5.

The phosphorus and sulphur atoms form a five-membered ring, as in (Ib). The P_4S ring assumes a puckered conformation with S nearly in the mean plane through the ring atoms; deviations of atoms

TABLE 2

Final positional parameters (fractional $\times 10^4$) and thermal parameters (anisotropic U_{ij}, Å$^2 \times 10^4$ for P and S; $\times 10^3$ for C), with standard deviations in parentheses

Atom	x	y	z
P(1)	2290(1)	959(3)	2117(2)
P(2)	2462(1)	30(2)	818(2)
P(3)	2352(1)	1025(2)	−458(2)
P(4)	2563(1)	2499(3)	102(2)
S	2457(1)	2428(3)	1667(2)
C(1)	1539(5)	883(10)	2072(9)
C(2)	1209(6)	1695(10)	1965(10)
C(3)	662(7)	1568(12)	2023(10)
C(4)	431(6)	666(16)	2185(12)
C(5)	763(8)	−146(13)	2298(13)
C(6)	1323(7)	−39(11)	2264(11)
C(7)	3188(5)	−107(8)	859(10)
C(8)	3480(5)	−191(10)	−34(10)
C(9)	4034(6)	−377(9)	−2(11)
C(10)	4296(5)	−481(10)	886(15)
C(11)	4013(7)	−397(13)	1780(13)
C(12)	3466(6)	−226(11)	1733(10)
C(13)	1612(4)	1078(9)	−493(8)
C(14)	1341(5)	1969(9)	−677(9)
C(15)	777(6)	1973(10)	−778(11)
C(16)	482(5)	1106(11)	−689(10)
C(17)	758(5)	231(10)	−526(9)
C(18)	1309(5)	217(8)	−407(9)
C(19)	3299(4)	2408(9)	−56(9)
C(20)	3487(6)	2552(10)	−1027(9)
C(21)	4039(6)	2516(12)	−1226(11)
C(22)	4399(5)	2376(11)	−461(14)
C(23)	4214(6)	2263(11)	497(12)
C(24)	3669(5)	2282(9)	712(9)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P(1)	661(25)	597(25)	509(22)	−27(19)	−63(18)	−18(20)
P(2)	561(18)	428(18)	526(17)	19(17)	−112(22)	−22(19)
P(3)	532(21)	425(21)	540(20)	−4(17)	−59(17)	44(18)
P(4)	580(21)	421(19)	647(21)	56(21)	−106(18)	37(18)
S	735(21)	531(21)	744(20)	−62(26)	12(22)	−185(18)
C(1)	60(9)	62(10)	45(8)	−10(8)	3(7)	−11(8)
C(2)	68(11)	71(10)	68(10)	6(9)	(8)	−3(8)
C(3)	60(11)	103(14)	73(11)	−(9)	−4(9)	−14(10)
C(4)	73(12)	136(18)	74(12)	−26(12)	−8(9)	−9(12)
C(5)	109(17)	86(13)	99(14)	−38(11)	17(12)	7(12)
C(6)	92(13)	72(11)	91(12)	−12(10)	7(10)	19(10)
C(7)	70(8)	39(7)	47(7)	−4(6)	4(8)	−1(8)
C(8)	39(8)	70(10)	81(11)	7(7)	−7(7)	−4(9)
C(9)	77(11)	55(9)	74(11)	10(8)	5(9)	5(8)
C(10)	63(10)	73(10)	113(14)	18(7)	−28(12)	7(12)
C(11)	71(13)	133(16)	91(14)	3(11)	−26(11)	17(11)
C(12)	70(11)	88(12)	58(10)	9(9)	−9(8)	6(9)
C(13)	51(7)	44(8)	40(7)	−16(7)	−12(6)	5(7)
C(14)	54(8)	54(8)	52(9)	6(7)	−10(7)	2(7)
C(15)	79(11)	67(10)	69(10)	4(8)	−18(9)	1(9)
C(16)	54(8)	81(11)	63(9)	−15(8)	(8)	−4(9)
C(17)	55(9)	68(11)	69(11)	−16(8)	−8(7)	−2(8)
C(18)	49(9)	43(9)	73(10)	7(7)	−16(7)	5(7)
C(19)	67(9)	42(8)	62(9)	−10(8)	−5(7)	−7(8)
C(20)	84(11)	74(11)	56(10)	−18(9)	−13(8)	13(9)
C(21)	70(11)	122(15)	80(11)	−4(13)	17(9)	−20(11)
C(22)	63(10)	74(11)	118(14)	−20(9)	18(10)	−24(11)
C(23)	59(10)	90(12)	87(12)	−12(8)	−7(9)	−6(9)
C(24)	53(8)	72(10)	70(10)	−17(7)	−6(8)	2(9)

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* See notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue.

[3] R. E. Long, Ph.D. Thesis, University of California at Los Angeles, 1965.

[4] 'International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

[5] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

from the mean plane are in Table 4(*b*). The conformation of the ring appears to be closer to the half-chair[6] than to the envelope conformation.[6] In the related compound $[PhP]_5$[7] the five-membered P_5 ring is in the envelope conformation, with four phosphorus atoms nearly in a plane and the fifth 1·26 Å from the plane. There is, however, a closer approach to planarity of the five-membered ring in $[PhP]_4S$, as seen in the smaller deviations of the atoms from the mean plane through all five ring atoms [for $[PhP]_5$ these deviations † are: P(2) −0·061, P(3) 0·483, P(4) −0·617, P(5) 0·382, and P(1) −0·188 Å] and in the smaller dihedral angles in the five-membered ring (for $[PhP]_5$ these angles are: −60·6, 36·5, −2·2, −33·3, and 58·1°).

TABLE 3

Bond lengths (Å) and angles (deg.), with standard deviations in parentheses (σ for the mean values is the larger of the least-squares value and the root-mean-square deviation from the mean)

(*a*) Distances

P(1)–S	2·114(5)	C(6)–C(1)	1·380(16)
P(4)–S	2·118(4)	C(7)–C(8)	1·403(15)
Mean P–S	2·116(5)	C(8)–C(9)	1·392(16)
		C(9)–C(10)	1·363(18)
P(1)–P(2)	2·188(5)	C(10)–C(11)	1·392(19)
P(2)–P(3)	2·193(4)	C(11)–C(12)	1·373(17)
P(3)–P(4)	2·190(5)	C(12)–C(7)	1·370(15)
Mean P–P	2·190(5)	C(13)–C(14)	1·400(14)
		C(14)–C(15)	1·400(15)
P(1)–C(1)	1·857(12)	C(15)–C(16)	1·384(16)
P(2)–C(7)	1·803(11)	C(16)–C(17)	1·381(15)
P(3)–C(13)	1·829(11)	C(17)–C(18)	1·371(14)
P(4)–C(19)	1·836(11)	C(18)–C(13)	1·389(14)
Mean P–C	1·831(22)	C(19)–C(20)	1·397(15)
		C(20)–C(21)	1·389(16)
C(1)–C(2)	1·373(15)	C(21)–C(22)	1·372(18)
C(2)–C(3)	1·366(18)	C(22)–C(23)	1·372(17)
C(3)–C(4)	1·363(19)	C(23)–C(24)	1·376(15)
C(4)–C(5)	1·380(19)	C(24)–C(19)	1·387(14)
C(5)–C(6)	1·390(18)	Mean C–C	1·382(16)

(*b*) Angles

P(1)–S–P(4)	110·4(2)	C(2)–C(1)–C(6)	120·7(12)
		C(1)–C(2)–C(3)	118·8(13)
S–P(1)–P(2)	105·9(2)	C(2)–C(3)–C(4)	122·4(15)
P(1)–P(2)–P(3)	104·2(2)	C(3)–C(4)–C(5)	118·6(16)
P(2)–P(3)–P(4)	105·1(2)	C(4)–C(5)–C(6)	120·4(16)
P(3)–P(4)–S	105·6(2)	C(5)–C(6)–C(1)	119·1(14)
Mean endocyclic P	105·2	C(8)–C(7)–C(12)	117·5(11)
		C(7)–C(8)–C(9)	119·7(12)
S–P(1)–C(1)	103·7(5)	C(8)–C(9)–C(10)	120·9(14)
P(2)–P(1)–C(1)	97·9(4)	C(9)–C(10)–C(11)	120·4(13)
P(1)–P(2)–C(7)	103·2(4)	C(10)–C(11)–C(12)	117·9(14)
P(3)–P(2)–C(7)	102·1(4)	C(11)–C(12)–C(7)	123·6(13)
P(2)–P(3)–C(13)	99·6(4)	C(14)–C(13)–C(18)	118·4(10)
P(4)–P(3)–C(13)	102·2(4)	C(13)–C(14)–C(15)	119·8(11)
P(3)–P(4)–C(19)	97·8(4)	C(14)–C(15)–C(16)	120·7(12)
S–P(4)–C(19)	103·5(4)	C(15)–C(16)–C(17)	118·7(11)
		C(16)–C(17)–C(18)	121·2(11)
P(1)–C(1)–C(2)	123·5(11)	C(17)–C(18)–C(13)	121·0(11)
P(1)–C(1)–C(6)	115·5(12)	C(20)–C(19)–C(24)	119·4(11)
P(2)–C(7)–C(8)	119·6(10)	C(19)–C(20)–C(21)	120·0(11)
P(2)–C(7)–C(12)	122·5(11)	C(20)–C(21)–C(22)	119·9(13)
P(3)–C(13)–C(14)	121·1(9)	C(21)–C(22)–C(23)	119·9(12)
P(3)–C(13)–C(18)	120·3(9)	C(22)–C(23)–C(24)	121·4(13)
P(4)–C(19)–C(24)	125·1(10)	C(23)–C(24)–C(19)	119·4(12)
P(4)–C(19)–C(20)	115·3(10)	Mean C–C–C	120·0(14)

TABLE 4

Mean planes through the molecule

(*a*) Equations of planes in the form $lX + mY + nZ = p$, where *X*, *Y*, *Z* are orthogonal co-ordinates (Å) with respect to ***a***, ***b***, ***c***

Plane	Atoms	*l*	*m*	*n*	*p*
(1):	P(1)—(4), S	−0·9947	0·0860	−0·0557	−5·8616
(2):	C(1)—(6)	−0·0343	−0·1668	−0·9854	−3·0782
(3):	C(7)—(12)	−0·1796	−0·9836	−0·0193	−1·2903
(4):	C(13)—(18)	0·0949	−0·1489	−0·9843	0·8105
(5):	C(19)—(24)	−0·0467	−0·9888	−0·1416	−3·5997

(*b*) Distances (Å) of atoms from the mean planes (σ in parentheses; *d*/σ in square brackets)

Plane (1): P(1) 0·189(3) [59·0], P(2) −0·244(3) [82·5], P(3) 0·237(3) [79·8], P(4) −0·152(3) [51·2], S −0·016(4) [4·7]

Plane (2): C(1) 0·010(12) [0·8], C(2) −0·003(13) [0·3], C(3) −0·005(14) [0·3], C(4) 0·004(16) [0·3], C(5) 0·010(17) [0·6], C(6) −0·017(15) [1·1]

Plane (3): C(7) −0·004(10) [0·4], C(8) 0·001(13) [0·1], C(9) 0·002(12) [0·1], C(10) 0·000(13) [0·0], C(11) −0·008(17) [0·5], C(12) 0·008(14) [0·6]

Plane (4): C(13) 0·002(10) [0·2], C(14) 0·002(12) [0·2], C(15) 0·002(14) [0·1], C(16) −0·011(13) [0·8], C(17) 0·016(13) [1·2], C(18) −0·010(12) [0·8]

Plane (5): C(19) 0·014(12) [1·2], C(20) −0·016(13) [1·2], C(21) 0·007(16) [0·4], C(22) 0·007(15) [0·4], C(23) −0·004(14) [0·2], C(24) −0·007(12) [0·6]

(*c*) Angles (deg.) between the planes

(1)–(2)	85·72	(2)–(4)	7·48
(1)–(3)	84·54	(2)–(5)	72·18
(1)–(4)	93·01	(3)–(4)	81·47
(1)–(5)	91·76	(3)–(5)	10·37
(2)–(3)	79·10	(4)–(5)	73·61

TABLE 5

Dihedral angles (deg.) in the P_4S ring

P(1)–P(2)–P(3)–P(4)	−29·9	P(4)–S–P(1)–P(2)	−11·7
P(2)–P(3)–P(4)–S	23·0	S–P(1)–P(2)–P(3)	25·6
P(3)–P(4)–S–P(1)	−7·1		

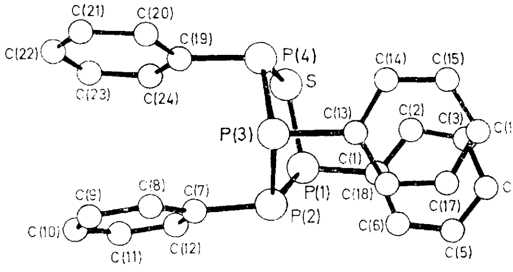

FIGURE 1 General view of the molecule

The phenyl rings are all nearly perpendicular to the mean plane through the five-membered P_4S ring (Table 4). The angles between planes also show that pairs of phenyl rings on the same side of the P_4S ring are close to being mutually parallel, being roughly perpendicular to the other pair. This orientation (of the phenyl rings) is not possible in $[PhP]_5$ because of the additional phenyl ring. The phenyl rings are

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† The unweighted mean plane through all ring atoms in the P_5 ring in $[PhP]_5$ was calculated by use of the atomic co-ordinates and unit-cell parameters given in ref. 7. The equation for the plane is: $0{\cdot}6335X - 0{\cdot}7737Y + 0{\cdot}0080Z = -0{\cdot}8891$, where *X*, *Y*, *Z* are orthogonal co-ordinates with respect to ***a***, ***b***, ***c****.

[6] C. Romers, C. Altona, H. R. Buys, and E. Havinga, in ' Topics in Stereochemistry,' eds. E. L. Eliel and N. L. Allinger, Wiley–Interscience, New York, 1969, vol. 4, p. 39.

[7] J. J. Daly, *J. Chem. Soc.*, 1964, 6147.

all statistically planar, the largest deviation of a carbon atom from the mean plane through the ring being 0·017(15) Å.

The P–P bonds are all equal, mean 2·190(5) Å. The endocyclic angle at phosphorus ranges from 104·2(2) to 105·9(2)°, mean 105·2°. In $[PhP]_5$ the P–P bond length [2·217(6) Å] is 0·027 Å (*ca.* 5σ) longer, and the endocyclic angles at phosphorus range from 94·1(2) to 107·2(2)°, mean 100·0°. The wider range of endocyclic angles and greater depature from planarity indicate greater strain in the five-membered ring in $[PhP]_5$. The larger and more regular endocyclic angles at phosphorus in $[PhP]_4S$, presumably a result of reduced steric repulsion of the phenyl groups, allow better overlap of phosphorus σ bonding orbitals and explain the slightly shorter P–P bond length. The length is in agreement with twice the covalent radius of phosphorus (2·20 Å) indicating that the P–P bonds are single bonds.

The P–S bonds are equal, mean 2·116(5) Å. This length is smaller than the sum of the covalent radii (2·14 Å), but close to the sum of the covalent radii after correction for the difference in electronegativity, one estimate being $2{\cdot}10_6$ (ref. 8) and another 2·12 Å.[9] The P–S bonds are thus single bonds. The length can be compared with the P–S(bridge) bond lengths found in other phosphorus sulphides, typical values being in the range 2·079 to 2·114 Å.[10] An exact comparison is difficult since the P–S(bridge) bond length seems to be sensitive to the angle at sulphur and phosphorus, to the oxidation state of phosphorus, and also to the other groups attached to phosphorus.

The angle at sulphur, 110·4(2)°, is 5·2° larger than the average endocyclic angle at phosphorus. The P–S–P angle in other phosphorus sulphides typically ranges from 99 to 110°,[10] unless the ring or cage is unusually strained. The value in the present compound is thus not unusually large, but it is not fully understood why it is so much larger than the endocyclic angle at phosphorus. Perhaps it is a result of steric effects due to the particular orientation of the phenyl rings, which in turn could be due to more favourable crystal-packing considerations.

The P–C bond lengths range from 1·803(11) to 1·857(12) Å, mean 1·831(22) Å. Although there are some rather large differences among the observed lengths, the mean is in good agreement with the values for Ph_3P [11] 1·828(5) and $[PhP]_5$ 1·843(14) Å.

The C–C bond lengths range from 1·363(19) to 1·403(15) Å, mean 1·382(16) Å, which is close to the standard value [12] (1·395 Å). The C–C–C angles range from 117·5(11) to 123·6(13)°, mean 120·0(14)°.

The P–P–C and S–P–C angles range from 97·8(4) to 103·7(5)°, mean 101·3°. The largest deviations from the mean occur at P(1) and P(4), the S–P–C angle at both atoms being larger than the P–P–C angle. A large spread in the P–P–C angles has also been observed in $[PhP]_5$, the value ranging from 96·4(4) to 109·8(4)°, mean 102·0°.

The P–C–C angles also show a large spread, ranging from 115·3(10) to 125·1(10)°, mean 120·4°. The largest deviations from the mean occur at C(1) and C(19), the angle closest to the sulphur atom being larger at both atoms. A large spread in the P–C–C angles has also been observed in $[PhP]_5$ [114·5(10)—125·5(10), mean 120·2°] and in Ph_3P [115·8(4)—124·9(4), mean 120·0°].

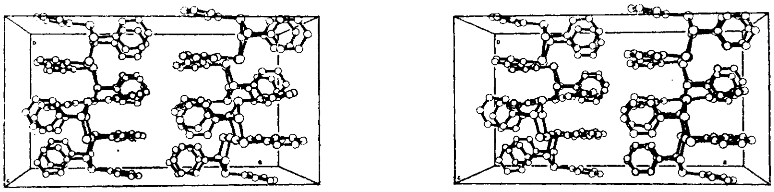
FIGURE 2 Stereoview of the unit-cell contents

The arrangement of the molecules in the unit cell is shown in Figure 2. The molecules are held together by normal van der Waals forces. The shortest intermolecular distances of each type are C · · · C 3·56, P · · · P 3·55, and P · · · S 3·70 Å. There are no intermolecular P · · · C or S · · · C contacts <3·8 Å. The P · · · P distance of 3·55 Å is considerably shorter (0·25 Å) than the sum of Pauling's [13] van der Waals radii, but such shortening is not unusual, *e.g.* in β-$P_4S_3I_2$ [14] P · · · S 3·34(1) Å (0·4 Å less than the sum of the van der Waals radii) is found. Therefore no special significance is given to this short distance.

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