Crystal and Molecular Structure of 2,*cis*-4,*trans*-6-Triphenyl-2,4,6-trithioxo-1,3,5,2,4,6-trioxatriphosphorinan

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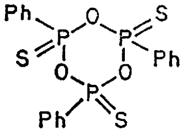
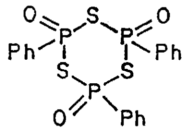
Crystals of the title compound (Ia) are monoclinic, space group $P2_1/c$ with $a = 12{\cdot}257(10)$, $b = 9{\cdot}299(7)$, $c = 21{\cdot}027(17)$ Å, $\beta = 119{\cdot}77(17)^\circ$. The structure was solved by direct methods. Diffractometer data for 3148 planes were refined by block-diagonal least-squares to R 0·043. The boat-like six-membered ring approximates closely to the symmetry m (C_s): five of the constituent atoms are coplanar to within 0·04 Å while the sixth, an oxygen atom, is displaced 0·32 Å from this plane. Two phenyl groups and one sulphur atom lie on one side of the heterocyclic ring and the other phenyl group and two sulphur atoms on the other side. The mean lengths of the chemically equivalent bonds are: P–C 1·779(4), P=S 1·896(2), P–O 1·613(3), and C$\overset{\cdots}{-}$C 1·383(7) Å.

ALTHOUGH phosphonic[1] and dithiophosphonic[2] anhydrides, $(RPO_2)_n$ and $(RPS_2)_n$, have been studied extensively, little seems to be known about the monothiophosphonic anhydrides, $(RPOS)_n$. When phenylthiophosphonic anhydride † $(PhPOS)_3$ was first synthesised[3] structures (Ia) or (Ib) were suggested. The former was taken to be the correct structure[2] and this was verified by later chemical and *X*-ray work.[4] We now report details of the *X*-ray study.



(Ia)



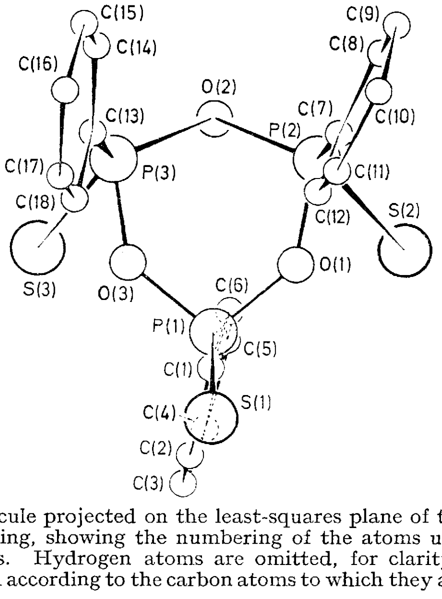
(Ib)

EXPERIMENTAL

Crystal Data.—$C_{18}H_{15}O_3P_3S_3$, $M = 468{\cdot}4$, Monoclinic, $a = 12{\cdot}257(10)$, $b = 9{\cdot}299(7)$, $c = 21{\cdot}027(17)$ Å, $\beta = 119{\cdot}77(17)$, $U = 2075{\cdot}1$ Å^3, $D_m = 1476$, $Z = 4$, $D_c = 1499$ kg m^{-3}. Space group $P2_1/c$ (C^5_{2h}, No. 14). Mo-K_α radiation, $\lambda = 0{\cdot}71069$ Å; μ(Mo-K_α) $= 540$ m^{-1}.

Unit-cell dimensions were obtained from precession photographs by a least-squares process; the standard deviations have been multiplied by 1·5 to allow for the presence of systematic errors. Intensity data were collected round b on a linear diffractometer fitted with a graphite monochromator. The maximum value of θ was 25° and 4154 independent intensities were measured, of which 3148 were judged to be significant and were used in the analysis.

Structure Determination and Refinement.—The structure was solved on a computer by direct methods.[5–8] A set of seven starting planes was used, three to determine the origin and four were assigned the symbols *a*, *b*, *c*, and *d*. Each plane was allowed up to eight different symbols, *e.g.* $+a$, $-bc$, abd, *etc.* A new sign or symbol was accepted if the sum of the contributing triple products exceeded a selected value P, which is normally just less than the product of the three smallest E values of the seven starting planes. Two attempts were made. In the first, seven starting planes with high E values were selected from the 207 planes which had $E \geqslant 1{\cdot}9$ and included three of the 47 planes with $k + l$ odd, P was 17·5. Contradictions were found between the signs of the four symbols, on one hand, and their products, on the other; however the most likely combination was chosen and used to calculate an E map which was obviously wrong. The second attempt began by preparing a list of the 207 planes in ascending order of $\Sigma|E_h E_k E_{h-k}|$ and new starting planes were selected from the most important of these. This set contained only one, origin-determining, plane with $k + l$ odd; P was 20·75. Signs or symbols were found for the 160 planes with $k + l$ even and there were no contradictions in the relations among the symbols although two were later found to have had the wrong sign. There were strong indications that $c = d = a$, so these relations were accepted and two new primary planes with $k + l$ odd were chosen; P was simultaneously reducted to 8·0. The sign-determining process was continued till signs or symbols were found for all 207 planes, no contradictions occurred and the signs for the four symbols, which were



The molecule projected on the least-squares plane of the heterocyclic ring, showing the numbering of the atoms used in the analysis. Hydrogen atoms are omitted, for clarity, but are labelled according to the carbon atoms to which they are bonded

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† Systematic name: 2,*cis*-4,*trans*-6-triphenyl-2,4,6-trithioxo-1,3,5,2,4,6-trioxatriphosphorinan.

[1] Z. E. Golubski, *Wiadomosci Chem.*, 1966, **20**, 473.

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now all correct, were used to calculate an E map which gave a refineable structure. For the refinement a least-squares method was used with a 3×3 and 1×1 or 6×6 block-diagonal approximation, the weights[9] were given by $w^{-1} = 3{\cdot}13 + |F_o| + 0{\cdot}016|F_o|^2$. Hydrogen-atom positions were found from a difference-Fourier map when R was 0·083. Further refinement led to a final R value of 0·043 for 3148 observed data. The hydrogen atoms were given an isotropic temperature factor of 0·01 units in U greater than the isotropic temperature factor of the carbon atoms to which they were bonded.

TABLE 1

Final co-ordinates and standard deviations (Å)

Atom	X	Y	Z
S(1)	1·8796(13)	6·1053(9)	2·7535(11)
S(2)	1·3850(12)	2·9968(9)	7·4869(11)
S(3)	6·9916(12)	3·2100(11)	7·8039(14)
P(1)	2·5393(10)	4·6177(7)	4·1030(8)
P(2)	2·3549(10)	4·3999(7)	7·0060(8)
P(3)	5·4170(10)	4·5131(8)	7·1780(9)
O(1)	1·7852(24)	4·5599(21)	5·1992(22)
O(2)	4·1777(24)	4·1107(23)	7·6982(23)
O(3)	4·3547(26)	4·6598(24)	5·3441(25)
C(1)	2·2318(35)	2·9980(30)	3·2662(32)
C(2)	1·8767(47)	2·8800(35)	1·7392(38)
C(3)	1·6811(53)	1·6165(41)	1·0807(45)
C(4)	1·8100(50)	0·5089(38)	1·9288(48)
C(5)	2·1635(58)	0·6095(39)	3·4369(48)
C(6)	2·3751(55)	1·8606(36)	4·1140(41)
C(7)	2·2049(35)	6·0398(30)	7·6041(33)
C(8)	2·2113(50)	6·1947(37)	9·0000(40)
C(9)	2·1171(54)	7·4601(44)	9·5077(44)
C(10)	2·0233(44)	8·5639(37)	8·6536(41)
C(11)	2·0031(49)	8·4204(37)	7·2762(44)
C(12)	2·0960(46)	7·1665(35)	6·7423(38)
C(13)	5·9531(35)	6·1943(32)	7·8136(35)
C(14)	6·5945(50)	6·4471(39)	9·3763(41)
C(15)	6·9931(59)	7·7486(45)	9·9221(52)
C(16)	6·7607(55)	8·7782(42)	8·9206(56)
C(17)	6·1309(51)	8·5184(39)	7·3619(52)
C(18)	5·7206(46)	7·2246(37)	6·8018(41)
H(2)	1·75(6)	3·71(4)	1·12(5)
H(3)	1·40(6)	1·57(5)	−0·09(4)
H(4)	1·61(6)	−0·52(5)	1·38(5)
H(5)	2·25(7)	−0·27(5)	4·18(6)
H(6)	2·50(6)	1·93(4)	5·10(5)
H(8)	2·25(5)	5·44(4)	9·55(5)
H(9)	2·19(6)	7·54(4)	10·54(5)
H(10)	1·88(5)	9·48(3)	9·03(4)
H(11)	2·08(6)	9·24(5)	6·79(6)
H(12)	2·18(4)	7·06(3)	5·78(3)
H(14)	6·80(4)	5·72(4)	10·08(4)
H(15)	7·35(5)	7·96(4)	10·91(4)
H(16)	7·04(6)	9·79(4)	9·19(6)
H(17)	5·90(6)	9·33(4)	6·47(5)
H(18)	5·36(6)	7·04(4)	5·69(6)

TABLE 2

Anisotropic temperature factors * ($Å^2 \times 10^4$)

Atom	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{13}$
S(1)	829(7)	402(4)	466(5)	107(8)	196(7)	766(10)
S(2)	613(6)	495(4)	496(5)	−233(8)	70(8)	676(9)
S(3)	478(6)	573(5)	807(7)	266(9)	4(10)	541(11)
P(1)	400(4)	344(3)	256(3)	−68(6)	−35(6)	353(6)
P(2)	379(4)	370(4)	273(3)	−65(6)	7(6)	361(6)
P(3)	338(4)	407(4)	341(4)	−31(7)	−81(6)	298(7)
O(1)	350(12)	494(12)	259(10)	−25(18)	−62(17)	308(17)
O(2)	379(12)	489(12)	342(11)	21(19)	109(19)	353(19)
O(3)	373(13)	670(15)	341(11)	−288(21)	−238(20)	381(20)
C(1)	386(17)	386(14)	254(13)	6(25)	−56(22)	263(24)
C(2)	706(25)	510(18)	352(16)	−66(35)	−114(29)	595(34)
C(3)	855(31)	603(22)	470(20)	8(41)	−328(35)	697(43)
C(4)	691(26)	487(19)	617(23)	−40(37)	−395(36)	614(41)
C(5)	1107(38)	397(18)	591(23)	−67(41)	−68(34)	853(50)
C(6)	1061(34)	414(17)	411(18)	−67(39)	−70(30)	789(43)
C(7)	365(16)	421(15)	315(14)	14(25)	−38(24)	380(25)
C(8)	791(27)	554(20)	371(17)	−164(37)	−83(30)	718(37)
C(9)	828(30)	724(25)	445(20)	69(44)	−323(37)	735(42)
C(10)	542(22)	515(19)	472(19)	71(34)	−268(32)	359(34)
C(11)	771(28)	449(18)	534(21)	216(37)	66(33)	642(41)
C(12)	665(24)	459(17)	421(18)	177(33)	110(29)	619(35)
C(13)	319(16)	463(16)	363(16)	−37(26)	−125(26)	265(26)
C(14)	688(25)	558(21)	380(18)	−152(38)	−157(32)	290(35)
C(15)	892(34)	698(26)	577(25)	−405(47)	−560(42)	613(49)
C(16)	742(30)	524(21)	883(32)	−288(41)	−475(43)	787(53)
C(17)	745(29)	472(19)	775(28)	−252(38)	−138(39)	810(47)
C(18)	589(23)	525(19)	473(19)	−142(34)	34(32)	516(36)

* In the form: $\exp -2\pi^2 (h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13})$.

RESULTS AND DISCUSSION

Tables 1—3 give the co-ordinates, thermal parameters, and the bond lengths and angles, with their corresponding standard deviations. A drawing of the molecule projected on the least-squares plane of the heterocyclic ring is shown in the Figure which also

TABLE 3

Bond lengths (Å) and angles (°), with standard deviations

(a) Bond lengths

P(1)–C(1)	1·778(3)	C(3)–C(4)	1·362(7)
P(2)–C(7)	1·777(3)	C(4)–C(5)	1·371(7)
P(3)–C(13)	1·783(4)	C(5)–C(6)	1·388(7)
Mean P–C	1·779	C(6)–C(1)	1·383(6)
P(1)–S(1)	1·894(1)	C(7)–C(8)	1·401(5)
P(2)–S(2)	1·898(1)	C(8)–C(9)	1·384(6)
P(3)–S(3)	1·895(2)	C(9)–C(10)	1·370(6)
Mean P=S	1·896	C(10)–C(11)	1·375(6)
		C(11)–C(12)	1·384(6)
P(1)–O(1)	1·611(2)	C(12)–C(7)	1·390(5)
P(1)–O(3)	1·613(3)	C(13)–C(14)	1·386(6)
P(2)–O(2)	1·623(3)	C(14)–C(15)	1·391(7)
P(2)–O(1)	1·610(2)	C(15)–C(16)	1·373(7)
P(3)–O(3)	1·606(3)	C(16)–C(17)	1·385(7)
P(3)–O(2)	1·615(3)	C(17)–C(18)	1·388(6)
Mean P–O	1·613	C(18)–C(13)	1·381(5)
		Mean C⋯C	1·383
C(1)–C(2)	1·390(5)	Mean C–H	1·02
C(2)–C(3)	1·393(6)		

(b) Bond angles

S(1)–P(1)–O(1)	113·46(10)	P(1)–C(1)–C(6)	121·30(28)
S(2)–P(2)–O(2)	111·55(10)	P(2)–C(7)–C(12)	122·22(27)
S(2)–P(2)–O(1)	114·65(10)	P(3)–C(13)–C(18)	122·07(28)
S(1)–P(1)–O(3)	112·88(11)	C(6)–C(1)–C(2)	119·7(3)
S(3)–P(3)–O(2)	111·53(10)	C(1)–C(2)–C(3)	119·7(4)
S(3)–P(3)–O(3)	114·21(1)	C(2)–C(3)–C(4)	119·7(4)
C(1)–P(1)–O(1)	104·92(14)	C(3)–C(4)–C(5)	121·2(4)
C(7)–P(2)–O(1)	104·12(14)	C(4)–C(5)–C(6)	119·8(4)
C(7)–P(2)–O(2)	106·59(14)	C(5)–C(6)–C(1)	119·9(4)
C(1)–P(1)–O(3)	104·57(14)	C(8)–C(7)–C(12)	119·2(3)
C(13)–P(3)–O(3)	103·43(1)	C(7)–C(8)–C(9)	119·9(4)
C(13)–P(3)–O(2)	105·25(15)	C(8)–C(9)–C(10)	120·3(4)
O(1)–P(1)–O(3)	101·87(13)	C(9)–C(10)–C(11)	120·2(4)
O(3)–P(3)–O(2)	102·25(13)	C(10)–C(11)–C(12)	120·7(4)
O(2)–P(2)–O(1)	101·13(12)	C(11)–C(12)–C(7)	119·7(4)
P(1)–O(3)–P(3)	136·90(17)	C(14)–C(13)–C(18)	120·4(4)
P(3)–O(2)–P(2)	134·21(16)	C(13)–C(14)–C(15)	119·7(4)
P(2)–O(1)–P(1)	137·98(15)	C(14)–C(15)–C(16)	120·2(5)
S(2)–P(2)–C(7)	117·24(12)	C(15)–C(16)–C(17)	119·9(5)
S(1)–P(1)–C(1)	117·55(12)	C(16)–C(17)–C(18)	120·5(4)
S(3)–P(3)–C(13)	118·50(13)	C(17)–C(18)–C(13)	119·4(4)
P(1)–C(1)–C(2)	118·96(27)	Mean C–C–C	120·0
P(2)–C(7)–C(8)	118·54(27)	Mean C–C–H	120
P(3)–C(13)–C(14)	117·56(28)		

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gives the labelling of the atoms used in this analysis. Final values of the structure factors are listed in Supplementary Publication No. SUP 20735 (21 pp., 1 microfiche).*

Departures from the molecular symmetry m (C_s) are caused mainly by rotations of the phenyl groups about their P–C bonds (Figure). The torsion angles in the heterocyclic ring, from P(1)–O(1) are 7·3(1), 6·1(1), –28·1(1), 28·1(1), –5·8(1), and –7·5(1)°, so that this ring is technically in the boat form. However, as the torsion angles suggest, five of the atoms are approximately coplanar (within 0·04 Å) while the sixth lies 0·32 Å from this plane. Similar rings containing five-valent phosphorus are found in a number of inorganic compounds and these are usually in the chair form[10–14] although a boat form[15] and a planar ring[16] have been described. The P–O bond lengths and O–P–O angle in the chair rings[10–14] are similar to those found for $(PhPOS)_3$ (1·613 Å and 101·8°) so that the approximate planarity of the latter does not seem to confer any additional d_π–p_π bonding. The observed boat form is achieved by an expansion of the P–O–P ring angles to 136° and a Dreiding model of the chair form of $(PhPOS)_3$ gives very unfavourable contacts between the axial substituents. An all-*cis* isomer of this compound should also exist.

The lengths of the chemically equivalent bonds are in good agreement with one another; the mean P–C bond is 1·779(4) Å (erroneously given as 1·879 Å in ref. 4). This distance is usually shorter in four- than in three-co-ordinate phosphorus compounds.[17,18] The P=S bond length [1·896(2) Å] is slightly less than for similar organo-phosphorus sulphides which are usually[17] *ca.* 1·93—1·96 Å: however, this bond is 1·86 Å in $P_4O_6S_4$.[12] The C$\overset{\cdots}{-}$C and C–H bond lengths (Table 3) are as expected. The bond angles also approximate closely to the symmetry m (C_s); the S=P–O and S=P–C angles (means 113·0 and 117·8°) are greater than the C–P–O and O–P–O angles (means 104·8 and 101·8°) as is usual in this type of compound, in accordance with the idea[19] that a double bond repels single bonds more than the latter repel each other.

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* For details see Notice to Authors No. 7 in *J.C.S. Dalton,* 1972, Index issue.

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