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# References

- BELL, R. N. (1950). Inorganic Synthesis, Vol. 3, p. 99. New York: McGraw-Hill.
- BENEDICT, W. S., GAILAR, N. & PLYLER, E. K. (1956). J. Chem. Phys. 24, 1139.
- CALVO, C. (1967). Acta Cryst. 23, 289.
- Corbridge, D. E. C. (1957). Acta Cryst. 10, 85. CRUICKSHANK, D. W. J. (1964). Acta Cryst. 17, 674.
- HUGHES, E. W. (1941). J. Amer. Chem. Soc. 63, 1737.
- International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
- KARLE, J. & KARLE, I. L. (1966). Acta Cryst. 21, 849.
- LEININGER, E. & CHULSKI, T. (1949). J. Amer. Chem. Soc. 71, 2385.
- McDonald, W. S & CRUICKSHANK, D. W. J. (1967). Acta Cryst. 22, 43.
- MOOTZ, D. & ALTENBURG, H. (1969). Acta Cryst. B25, 1077.
- ROBERTSON, B.E. & CALVO, C. (1968). Canad. J. Chem. 46,605.



Fig.2. Projection of parts of the  $Na_2H_2P_2O_7.6H_2O$  (heavy lines) and Na<sub>2</sub>H<sub>2</sub>P<sub>2</sub>O<sub>6</sub>.6H<sub>2</sub>O (light lines) structures down the b axis. The large circles represent oxygen atoms and the small circles hydrogen atoms. Dashed lines represent hydrogen bonds.

- WAZER, J. R. VAN (1958). Phosphorus and its Compounds. Vol. 1, p. 622. New York: Interscience.
- WEBB, N. C. (1966). Acta Cryst. 21, 942.
- WILSON, A. J. C. (1942). Nature Lond, 150, 152.
- WILSON, A. & MCGEACHIN, H. MCD. (1964). Acta Cryst. 17, 1352.

Acta Cryst. (1971). B27, 302

# A Redetermination of the Crystal Structure of Tetramethyldiphosphine Disulphide

BY J. D. LEE AND G. W. GOODACRE

Department of Chemistry, University of Technology, Loughborough, Leicestershire, England

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The crystal structure of tetramethyldiphosphine disulphide



has been determined from three-dimensional X-ray diffraction data. The unit cell is monoclinic with space group C2/m (number 12), dimensions a = 18.882, b = 10.703, c = 6.984 Å;  $\beta = 94^{\circ}42'$ , and contains six molecules, which occupy two different sets of special positions. The structure was refined by fullmatrix least-squares methods on 916 independent observed reflexions to R = 8.9%. The molecules adopt a non-eclipsed ethane-like conformation. There are appreciable differences in bond lengths between the two sets of molecules (P-P, 2.245 and 2.161 Å; P-S, 1.951, 1.970 and 1.965 Å; P-C, 1.80, 1.82 and 1.82 Å). Apart from some molecular crowding round the sulphur atoms of one set, there is no obvious reason for these differences.

### Introduction

The structure of tetramethyldiphosphine disulphide was originally assigned by Christen, van der Linde & Hooge (1959), as containing a P-P linkage (I)



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based on infrared and Raman data. The nuclear magnetic resonance work of Harris & Hayter (1964) suggested a sulphur-bridged structure with no direct P–P bond (II).



A preliminary X-ray structure reported by Pedone & Sirigu (1967) based on 168 observed reflexions confirmed structure (I) as correct.

The X-ray structures of 1,2-dimethyl-1,2-diphenyldiphosphine disulphide (Wheatley, 1960), tetraethyldiphosphine disulphide (Dutta & Woolfson, 1961), bis(cyclotetramethylene)diphosphine disulphide (Lee & Goodacre, 1969) and bis(cyclopentamethylene)diphosphine disulphide (Lee & Goodacre, 1970) all show structures similar to (I). As part of a series of detailed structure investigations on compounds containing P–P and P–S bonds, an accurate crystal structure determination was performed on tetramethyldiphosphine disulphide.

# Experimental

A sample of tetramethyldiphosphine disulphide was kindly provided by Prof. R. Schmutzler (Technical University, Braunschweig, Germany). This was recrystallized from 3:1 toluene-ethanol and gave colourless acicular crystals elongated along c, which frequently clumped together to form a hollow cylinder. Most of the crystals were twinned, but eventually a single crystal of dimensions  $0.08 \times 0.08 \times 0.19$  mm was used firstly to obtain oscillation, zero- and first-layer equi-inclination Weissenberg photographs rotating about the c axis, then to collect three-dimensional intensity data using a Stöe diffractometer. The layers hk0-hk7 were collected, and of 1493 independent reflexions measured, 916 were considered significantly above background and were treated as observed. Lorentz and polarization corrections were applied, but no corrections were made for absorption or extinction.

# Crystal data

C<sub>4</sub>H<sub>12</sub>P<sub>2</sub>S<sub>2</sub>,  $M = 186 \cdot 22$ Monoclinic,  $a = 18 \cdot 882$ ,  $b = 10 \cdot 703$ ,  $c = 6 \cdot 984$ , all  $\pm 0.005$  Å;  $\beta = 94^{\circ} 42' \pm 30'$ ,  $U = 1406 \cdot 7$  Å<sup>3</sup>, Z = 6,  $D_m =$  $1 \cdot 31$  g.cm<sup>-3</sup>,  $D_c = 1 \cdot 319$  g.cm<sup>-3</sup>,  $\mu = 74 \cdot 6$  cm<sup>-1</sup>. F(000) =588, Cu K $\alpha$ ,  $\lambda = 1 \cdot 54051$  Å ( $\alpha_1$ ) and  $1 \cdot 54433$  Å ( $\alpha_2$ ).

# Structure analysis

An N(z) test (Howells, Phillips & Rogers, 1950; Sim, 1958) performed on the three-dimensional data indicated a centrosymmetric structure. The space group is therefore C2/m rather than C2 or Cm. The density

measured by flotation in aqueous potassium bromide solutions was found to be 1.31 compared with the calculated value of 1.319 g.cm<sup>-3</sup> based on 6 molecules per unit cell, occupying different sets of special positions. A three-dimensional Patterson map was interpreted and showed the two phosphorus atoms almost exactly vertically above each other up the *c* axis, with the centre of one molecule occupying the special position 2(a)(*International Tables for X-ray Crystallography*, 1965) with symmetry 2/m, and positions 0 0 0 and  $\frac{1}{2}$   $\frac{1}{2}$  0 and the centre of the other molecule occupying the special position 4(i) with symmetry *m*, and positions x 0 z;  $\bar{x} 0 \bar{z}$ ;  $\frac{1}{2} + x$ ,  $\frac{1}{2}$ , z; and  $\frac{1}{2} - x$ ,  $\frac{1}{2}$ ,  $\bar{z}$ . This was in close agreement with the approximate structure found by Pedone & Sirigu (1967).

A structure-factor calculation was performed on the P, S and C atoms, using the atomic scattering factors due to Hanson, Herman, Lea & Skillman (1964), with real and anomalous dispersion corrections (Dauben & Templeton, 1955) applied to P and S atoms, and gave an initial R index of 24.4%. Refinement was carried out using the full-matrix least-squares program in the X-ray 63 System due to Professor J. M. Stewart as adapted by Dr J. C. Baldwin for the SRC Chilton Atlas computer. Positional parameters and isotropic temperature factors were refined using unit weights, then a Hughes (1941) type of weighting scheme, and interlayer scale factors were introduced based on the sum of  $F_0$ and  $F_c$ . Then the P and S atoms were allowed to refine anisotropically, refinement of interlayer scale factors was discontinued, and a Cruickshank type of weighting scheme

$$w = 1/(A + B|F_o| + C|F_o|^2)$$

was introduced. When R had fallen to 13.9%, the positions of hydrogen atoms were calculated at a distance of 1.075 Å from the carbon atoms to which they are bonded. The methyl hydrogen atom positions were calculated assuming that one hydrogen atom occupied a position in the same vector sense as a specified bond in the chain of three heavier atoms required by the calculation. The positions of the remaining two hydrogen atoms were then calculated using the positions of two heavier atoms and the hydrogen atom just calculated, and assuming a tetrahedral distribution. In this particular case the three heavier atoms required to define the chain may be C, P, C'; C, P, S; or C, P, P. Three possible sets of hydrogen atom positions were calculated assuming that the first C-H bond was in the same vector sense as the P-C', P-S and P-P bonds respectively. Structure factor and bond length calculations on all three possibilities indicated that the P-C' vector should be used to locate the first hydrogen atom. This choice was confirmed by a difference Fourier synthesis. The positions chosen have two hydrogen atoms on one methyl group pointing roughly towards two hydrogen atoms from the other methyl group attached to the same phosphorus atom. Models show that this arrangement minimizes close approaches with other atoms.

	x/a	у/b	z/c	$\sigma(x a)$	$\sigma(y/b)$	$\sigma(z/c)$
S(1)	0.0875	0.0000	0.3035	0.0001	0.0000	0.0005
P(1)	-0.0054	0.0000	0.1589	0.0001	0.0000	0.0004
C(1)	-0.0608	0.1321	0.2024	0.0004	0.0007	0.0013
S(2)	0.2607	0.5000	0.3236	0.0001	0.0000	0.0005
S(3)	0.0742	0.5000	0.8215	0.0001	0.0000	0.0005
P(2)	0.1652	0.2000	0.4181	0.0001	0.0000	0.0004
P(3)	0.1696	0.2000	0.7282	0.0001	0.0000	0.0004
C(2)	0.1120	0.6365	0.3454	0.0004	0.0008	0.0016
C(3)	0.2252	0.6337	0.7976	0.0003	0.0006	0.0011

Table 1. Final coordinates and their estimated standard deviations

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Isotropic temperature factors of B = 6.0 Å<sup>2</sup> were chosen for the hydrogen atoms (1 Å<sup>2</sup> greater than the average isotropic value for the carbon atoms). The hydrogen atom parameters were not refined. The carbon atoms were then allowed to refine anisotropically, and new hydrogen atom positions were calculated. The final value of R was 8.9 % based on 916 observed reflexions.

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The final weight constants used were A = 0.382, B = 0.609 and C = 0.0086. The form of the anisotropic temperature factors used was

$$TF = \exp[-\frac{1}{4}(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + l^2c^{*2}B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23})]$$

The final atomic coordinates are given in Table 1, the calculated positions of the hydrogen atoms are given in Table 2, and the final temperature factors are listed in Table 3. The observed and calculated structure factors are tabulated in Table 4, and an agreement analysis is shown in Table 5.

# Table 2. Calculated positions of hydrogen atoms

Atom	Bonded to	x/a	y/b	z/c
H(1)	C(1)	-0.0277	0.2109	0.1764
H(11)	C(1)	-0.1080	0.1321	0.1054
H(21)	C(1)	-0.0754	0.1321	0.3481
H(2)	C(2)	0.1434	0.7170	0.3883
H(12)	C(2)	0.1010	0.6207	0.1938
H(22)	C(2)	0.0645	0.6206	0.4120
H(3)	C(3)	0.1923	0.7128	0.7565
H(13)	C(3)	0.2381	0.6174	0.9482
H(23)	C(3)	0.2713	0.6174	0.7206

# Discussion

Two independent types of molecules are contained in the unit cell. Fig. 1 shows the packing of molecules in



a sin β Fig. 1. Packing of the molecules in one unit-cell viewed down [001].

# Table 3. Final temperature factor parameters

	<i>B</i> <sub>11</sub>	B <sub>22</sub>	$B_{33}$	$B_{12}$	B <sub>13</sub>	$B_{23}$
S(1)	3.09	5.04	5.55	0.00	-0.08	0.00
P(1)	2.37	2.63	5.05	0.00	0.60	0.00
C(1)	4.56	4.11	6.57	0.65	1.14	-0.90
S(2)	2.93	5.71	6.80	0.00	1.32	0.00
S(3)	2.94	4.41	7.66	0.00	0.73	0.00
P(2)	2.23	3.18	4.44	0.00	0.30	0.00
P(3)	1.97	3.10	4.34	0.00	0.26	0.00
C(2)	4.24	4.54	9.24	1.21	-0.50	1.15
C(3)	3.91	3.95	3.87	-1.17	-0.76	-0.48

The H atoms were assigned an isotropic temperature factor of B = 6.00 Å<sup>2</sup>.



Fig.2. A view of one molecule.

the unit cell in the [001] projection, and a view of one molecule is given in Fig. 2. The two P atoms are almost vertically above each other up the c axis. The two methyl groups and one S atom attached to each P atom are roughly tetrahedrally distributed, and the whole molecule has a non-eclipsed ethane-like structure. There is nearly a threefold axis and nearly a sixfold inversion axis in the molecule, and it is probable that the tendency to twinning of the crystals is due to the molecule adopting a different but related position in the lattice.

Table 4. Observed and calculated structure factors

					-		64 F4		To Fr
<b>h k t</b>	Fo Fc	h k t	<b>Γυ FC</b>	nkt	Fo 10		10 10		
				-12 3 3	2011 - 18 1	4 10 4	30.1 -31.4	11 3 5	8.5 -7.8
-12 6 2	42.8 -41.0	8 6 3	32.1 -21.1			N 10 4	3 8 4.1	13 5 5	15.0 -15.1
-14 6 2	22.4 -18.6	10 6 J	8.3 6.3	-15 5 5	19.4 - 11.5		12 8 -15 5	2 6 5	4.9 5.2
-16 6 2	27.5 -23.3	14 6 3	14.1 -40.4	-19 5 3	45.0 -41.4	1 11 4	12.8 -15.5		
- 20 6 2	77 -08	18 6 3	14.0 -11.4	-2 6 3	12.0 -11.1	-4 0 4	64.7 65.5		5.1 -5.5
			21 4 31 5	-1 6 3	48.3 -33.8	-604	9.1 9.2	14 6 5	2.4 3.2
-1 / 2	27.1 21.3	1 1 1			12.2 -17.6	-8 0 4	76.3 -77.5	175	13,7 -15.0
-372	40.1 -34.1	373	14.0 -7.1	-0 0 5	36 0 33 0	-10 0 4	17.5 -11.4	775	16.0 13.7
-5 7 2	4.0 4.3	573	41.5 -47.4	18 6 J	36.0 34.9	-10 0 4	11.3 -13.4		9.4 -10.6
-7 7 2	14.3 -13.2	1 1 3	19.3 -24.3	-10 6 3	45.3 -41.1	-14 0 4	23.3 -23.1		
	26 9 -21 8	973	12.3 -10.4	-12 6 3	4.7 -5.4	-16 0 4	31.9 32.7	0 8 9	4.4 5.0
			12 9 -28 8	-14 6 3	18.2 -16.2	-514	82.1 -82.8	195	7.1 -8.0
-13 / 2	6.1 -0.9		30 0 34 3	-16 6 3	41 8 +38 4	-7 1 4	24.5 27.0	0 10 5	3.2 -3.2
-282	46.8 -40.1	13 / 3	38.8 34.2	-10 0 0	12 4 12 6	-9 1 4	25.8 -26.2	2 10 5	2.1 2.5
-4 8 2	23.4 -23.3	17 7 3	25.4 -27.0	-20 0 3			16 0 15 2	-2 0 5	6.2 7.7
-6 8 2	16.0 15.4	283	49.7 -52.5	-1 7 3	15.0 41.0	-13 1 4	10.0 10.1		14 2 -15 7
-8 8 2	5.7 5.6	483	6.1 6.8	-373	16.8 -21.1	-15 1 4	15.6 15.2	-803	14.2 -10.1
-10 8 3	10 4 11 5	6 8 3	16.0 -19.5	-773	63,2 -66,2	-17 1 4	39.1 -37.0	-17 1 5	8.9 8.2
-10 6 4	10.0 13.3		22.4 -20.7	-9 7 1	10.3 7.1	-19 1 4	8.2 7.1	-2 2 5	16.4 16.7
-12 8 2	33.1 -27.9		22.3 -20.1		12 1 -12 2	-21 1 4	2.1 -2.0	-6 2 5	29.5 29.0
-14 8 2	17.3 -17.3	10 S J	10.7 9.8	-13 7 3	12.1 -12.2		10.0 -11.1	-10 2 5	11.3 8.3
-16 8 2	17.6 -15.8	12 8 3	8.5 5.7	-15 7 3	20.5 -19.3		10.0 -11.0		17.1 -17.2
-1 9 2	15.8 10.5	14 8 3	36,2 -34.6	-17 7 3	1.7 1.3	-4 2 4	42.5 41.6	-1 3 5	17.1 -17.2
-1 0 1	21.6 -19.6	16 8 3	8.9 6.9	-19 7 3	38.5 -36.3	-624	6.8 -5.0	-3 3 5	14.0 -15.7
-3 9 4	23.0 -19.0		16 7 21 4	-4 8 1	37 0 -44.0	-8 2 4	54.7 -56.8	-445	2.7 1.4
-9 9 2	19.4 -13.6		10.7			-10 2 4	11.9 -15.3	-14 4 5	14.6 16.0
-11 9 2	19.9 -20.7	2 9 2	4.5 -4.5	-0 0 5	24 4 23 2	-14 2 4	22 8 =25.0	-13 5 5	2.5 -3.2
-13 9 2	8.0 -6.3	5 9 3	33.7 -40.8	-8 6 3	24.5 25.2				7 7 4 4
-2 10 2	23.3 -18.3	793	12.6 -10.9	-10 8 3	27.6 -29.6	-16 2 4	37.8 36.4	-17 3 3	
-4 10 3	82 -83	11 9 3	28.5 -24.6	-14 8 3	15.8 -14.2	-20 2 4	9.6 -13.3	-265	7.0 0.4
10 10 1		11 9 1	22 6 21 2	-16 8 3	31.0 -31.4	-1 3 4	6.2 4.7	-16 6 5	10.3 8.0
-10 10 2	13.3 9.6	1.5 . 5 . 5			19 9 -25 9	-5 3 4	66.5 -69.5	-175	1.2 -0.5
-12 10 2	29.8 -23.6	2 10 3	29.6 -34.7		12 2 -14 3		13.6 -15.9	-7 7 5	11.9 13.7
-14 10 2	14.0 -11.6	4 10 3	10.3 13.1	-3 - 3 - 3	13.7 -13.3				8 2 7 8
-3 11 2	5.2 -5.8	6 10 3	14.8 -11.2	-793	41.8 -48.9	-13 3 4	20.3 24.2		
-9 11 3	18 1 - 18 8	8 10 3	22.9 -25.6	-11 9 3	8.1 6.1	-15 3 4	16.6 16.2	-195	2.2 -2.4
-11 11 1	14 7 -16 2	10 10 1	7.3 5.7	-13 9 3	12.2 -14.3	-17 3 4	46.1 -43.0	-395	1.5 -1.4
-11 11 4	14.7 -10.2	10 10 3	10.7 15.5	-15 0 1	8.8 -10.9	-6 4 4	8.4 -9.3	-11 9 5	2.7 2.8
-2 12 2	10.2 -11.0	1 11 3	10.7 13.3	2 10 3	9 7 -7 9	-8 4 4	35 4 -39.4	-2 10 5	6.0 5.9
-4 12 2	4.0 -4.1	511 3	10.1 -11.0	-2 10 3	3.5			2 0 6	25 2 26 1
-8 12 2	5.8 -4.6	911 3	10.8 -10.0	-4 10 3	22.3 -25.1	-10 4 4	11.0 -10.5		13.0 15.4
2 0 3	118.4-126.2	2 12 3	17.9 -23.5	-6 10 3	8.5 -11.7	-12 4 4	9.5 12.1	14 0 6	13.0 13.4
	120 149	4 12 3	9.5 9.4	-10 10 3	27,2 -28.4	-14 1 4	23.1 -25.4	3 1 6	4.3 4.4
	44.4.40.7	-2 0 1	6 2 -9 3	-12 10 3	3.4 -3.8	-15 4 4	39.0 34.8	716	18.6 22.0
	44.5 -30.5		00.0 -07.5	-1 -1 - 3	12 0 -12.4	-18 4 4	5.4 -5.2	11 1 6	7.2 8.2
80.	28.6 -27.4		30.3 -91.3			-10 4 4	13 2 -13 8	13 1 6	18.6 21.6
10 0 3	3 15.8 16.7	-6 0 3	9.4 -11.4	-5 11 3	10.4 -10.1		10.1 -60.0		18 9 18 6
12 0 3	3 21.2 18.9	-8 O 3	60.2 64.8	-7 11 3	27.5 -34.8	-5 5 4	38.1 -39.0		22.6 27.4
14 0 3	71.6 -64.9	-10 0 3	49.3 -52.5	-11 11 3	6.5 7.8	-13 5 4	18'4 18'1	0 4 0	21.5 -21.4
14 0	160 147	-12 0 3	16.6 -13.8	-4 12 3	13.9 -18.0	-15 5 4	10.5 11.2	826	2.7 2.5
		-14 0 3	10 0 -11 7	204	37 8 -41.9	-17 5 4	37.9 -34.8	10 2 6	10.3 9.9
18 0	3 21.4 -21.0	-14 0 5	48 0 47 1		78 8 -80 2	-2 6 4	10.6 -10.0	14 2 6	9.7 12.3
20 0	18,5-18.8	-16 0 3	30.5 -31.1		10.0 00.0		20 5 22 4	7 1 6	20 1 16 4
1 1 1	3 66.9 70.0	-18 0 3	6.1 -5.4	604	13.7 -13.7		20.0 02.4		10.0 -7.4
5 1 3	3 90.3 -87.5	-20 0 3	27.8 23.3	804	25.0 23.4	-8 6 4	41.1 -43.0	3 3 6	10.0 -7.4
1 1 3	3 41.6 -47.1	-22 0 3	16.5 -14.8	10 0 4	15.2 -13.1	-14 6 4	17.3 -18.8	9 2 6	9.1 -0.2
	22 0 -17 6	-1 1 3	67.1 -70.7	16 0 4	36.9 -38.8	-16 6 4	24.7 22.5	376	3.7 3.6
	40.0 44.7		40 5 +41 9	3 1 4	40.5 -36.9	-574	44.5 -47.1	-4 0 6	5.7 5.3
11 1 3	49.8 -45.7		40.5 -45.5			-11 7 4	11.8 -11.4	-12 0 6	10.7 10.8
13 1	3 69.1 59.4	-2 1 3	0.4 -3.5						16 1 17 6
15 1	3 3.5 -3.3	-713	124.9-122.9	7 1 4	52.8 -55.0	-15 / 4	9.0 0.4	-14 0 0	
17 1	3 37,9 -38,3	-9 1 3	17.2 18.8	914	9.4 7.3	-17 7 4	22.1 -20.9	-5 1 6	34.8 33.3
19 1	3 8.6 -9.4	-11 1 3	11.4 13.2	13 1 4	34.2 -34,2	-484	23.1 25.6	-17 1 6	19.8 21.6
		-15 1 3	12 9 -12 4	2 2 4	13.1 -14.7	-884	34.8 -37.2	-10 2 6	20.7 17.4
		-17 1 3	0 0 1 2	4 2 4	86 4 +88.8	-14 8 4	14.8 -12.0	-14 2 6	18.8 17.5
02	3 9.4 11.1				14 4 17 7	-16 8 4	14 9 15.8	-1 3 6	9.2 8.3
2 2	3 99.3-100.2	-19 1 3	65.7 58.7				21 1 - 22 2	-15 7 6	16 5 -21.0
4 2	3 41.7 43.8	-21 1 3	11.4 9.6	16 2 4	34.5 -40.8	-3 5 4		-15 0 0	
6 2	3 38.9 -40.0	-2 2 3	28.3 -31.4	134	36.2 -37.4	-794	5.9 6.7	-2 4 6	14.9 19.4
8 2	3 51.4 -48.8	-4 2 3	64.8 -63.2	334	10.5 -13.2	-994	10.9 -8.7	-14 4 5	15.0 16.3
10 2	1 11 0 11 5	-6 2 3	32.1 -34.8	5 3 4	20.5 23.3	-11 9 4	8.7 -7.3	-356	22.7 27.6
			54 7 48 6	7 3 4	34.5 -37.7	-13 9 4	8.7 8.5	-756	14.0 13.5
12 2		-10 2 7	70 2 .65 2	11 1 4	20.0 -15.3	-2 10 4	12.3 -10.1	-8 6 6	27.8 25.1
14 2	3 57.0 -51.2	-10 - 3	20.4 -10.4		23 5 -25 8	-4 10 4	11.4 10.6	-12 6 6	3.6 3.5
18 2	3 18.2 -15.8	-14 2 3	23.4 -13.4				10 2 10 4	-1 7 6	10.1 10.0
20 2	3 17.6 -18.8	-16 2 3	55.2 -52.8	12 2 4	14.8 -13.8	-0 10 4	19.1 -19.9		no 7 00 0
1 3	3 71.6 68.7	-18 2 3	8.1 -4.2	044	10.6 -10.7	-10 10 4	3.3 -3.2		
3 3	3 14.9 18.8	-20 2 3	19.5 17.8	4 4 4	77.9 -81.4	-1 11 4	2.2 2.5	-1 7 6	
• •	1 105 0-108 8	-22 2 3	10.8 -13.0	10 4 4	7.8 9.7	-5 11 4	21.4 -19.8	-585	18.3 -16.2
	7 73 8 -19 1		15.4 -14.4	12 4 4	19.6 -16.8	10 0 5	13.4 -12.1	-886	17.3 21.2
	20.0 -10.1		51.9 -50.3	15 4 4	40.4 -40.1	14 0 5	9.3 7.1	-396	12.8 -9.2
9 3	3 29.1 -29.0	-3 3 3	31.9 -30.3		40.4		24 5 -20 0	4 0 7	2 1 -7 6
11 3	3 50.1 -43.8	-5 3 3	37.6 -40.7	1 5 4	23.0 -28.4	1 1 3	24.3 -23.5		26 0 27 7
13 3	3 45.6 37.3	-733	126.8-117.0	3 5 4	15.4 -14.8	313	23.9 28.0		20.0 27.7
17 3	3 24.7 -24.8	-933	8.1 6.1	554	16.1 12.5	515	15.6 13.7	8 2 7	1.0 -2.9
19 2	3 68 -66	-11 3 3	25.8 27.2	754	32.4 - 30.9	715	26.0 24.2	737	1.5 -0.9
	2 12 7 15 0	-11 2 2	24.8 -23 6	11 5 4	9.4 -9.7	9 1 5	19.5 -16.7	247	2.6 -3.2
	5 13.7 15.0		10.0 -10.0		10 4 +21 9	13 1 4	28.0 -29.7	1 5 7	7.3 4.5
24	3 76.6 -86.6	-15 3 3	19.6 -16.6	13 3 4	0.1 - 23.8	2 2 4	7 8 6 9		1.3 -1.3
4 4	3 48.7 54.7	-19 3 3	51.8 -47.6	15 5 4	3.3 -3.6	4 4 3	1.0 0.0		
64	3 26.2 - 30.1	-21 3 3	2.0 2.7	17 5 4	4.2 4.2	4 2 5	12.9 -8.9	-0 0 7	10.1 12.0
8 4	3 59.1 -55 A	-243	31.0 -34.4	264	13.0 -16.5	625	13.0 14.7	-8 0 7	1.4 -1.5
14 6	3 41 0 -16 4	-4 4 3	43.0 -51.8	4 6 4	56.8 -55.1	12 2 5	1.5 1.4	-12 0 7	30.1 29.9
			40.0 -44	16 6 4	11.8 -30 2	3 3 5	17.3 19.2	-14 0 7	7.5 -6.7
10 4	3 11.6 -10.2		30.0 36.5		10 1 -10 0		22.2 22.7	-1 1 7	1.5 0.7
20 4	3 17.5 -18.8	-8 4 3	39.2 36.0		10.1 -13.9				4 8 -6 0
15	3 46.8 52.9	-10 4 3	74.8 -66.1	774	37.0 -33.2	11 3 5	3.1 -3.0	- 2 2	2 2 2 2 2
35	3 11.1 10.1	-12 4 3	4.4 3.7	13 7 4	26.1 -23.7	13 3 5	22.2 -18.5	-937	2.3 2.3
5.5	3 76.4 -84 4	-14 4 3	12.C -8.0	284	16.6 -15.3	17 3 5	6.3 4,6	-8 4 7	5.5 -4.3
	1 22 7 -19 6	-16 4 3	45.7 -43.7	4 8 4	38.3 -40.4	045	17.8 -18.8	-10 4 7	4.9 -3.3
	3 34 3 -37 6	-18 4 3	43 -7 4	8 6 4	15.9 11.4	2 4 5	8.7 6.2	-12 4 7	14.5 18.7
9 3	3 24.2 -23.6	-10 4 7	12 7 11 6	14 8 4	3	4 4 5	14.9 -16.8	-267	1.5 1.2
11 5	3 39.9 - 33.9	-20 3	12.7 11.6	1 0 4	11.2 -1.8		21.6 21.5	-8 6 7	2.4 -2.1
-35	3 39.9 32.2	-153	29.0 -31.5	3 9 4	11.2 -9.9				
17 5	3 22.3 -25.5	-353	36.2 - 39.3	594	4.5 4.9	10 4 5	8.0 -9.2		
26	3 68,6 -71.4	-5 5 3	25.4 -23.9	794	27.3 -24.8	3 5 5	17.3 17.2		
4 6	3 17.0 20.6	-7 5 3	101.0 -95.7	0 10 4	2.7 -3.2	5 5 5	13.2 17.1		
6 6	1 21 6 -26 1	-11 5 3	22.5 20.9	2 10 4	1.8 -1.7	7 5 5	10.1 9.0		

n x t	Fo Fc	hĸt	tu tr	h k (	to Fe	n . (	FO FC		70 PC
					(0) 1 -18 1	4 10 4	30.1.+31.4	11 5 5	8.5 -7.8
-12 6 2	42.8 -41.0	8 6 1	32.4 -21.1	-13 - 1	10.1 -10.1	# 10 A	1 8 4 1	13 5 5	15.0 -15.1
-14 6 2	22.4 -18.6	10 6 3	8.3 6.5	-13 3 3	10.4		17 8 -15 5	2 6 5	4.9 5.2
-16 6 2	27.5 -23.3	14 6 3	44.1 -40.4	-19 3 3	44.0 -41.4	-4 0 4	64 7 65 5	4 6 5	5.7 -5.9
-20 6 2	7.7 -8.8	18 6 3	14.0 -11.4	-2 6 3	12.0 -11.1		01 02	14 6 5	24 3.2
-172	27.1 21.3	1 7 3	21.4 31.5	-163	48.3 -33.6		76 2 -22 5		13 2 -15 0
-372	40.1 -34.1	373	14.0 -7.1	-6 6 3	13.2 -17.6		17.5 -12.4	1 1 5	16 0 13 7
-572	4.0 4.3	573	41.5 -47.4	18 6 3	36.0 32.9	-10 0 4	17.5 -15.4		8.4 -10.6
-772	14.3 -13.2	773	19.7 -24.3	-10 6 3	45.3 -41.1	-14 0 4	23.3 -23.1	575	5.4 -10.0
-11 7 2	26.9 -23.8	973	12.5 -10.4	-12 6 3	4.7 -3.4	-16 0 4	31.9 32.7		
-13 7 2	6.1 -6.9	11 7 3	32.9 -28.8	-14 6 3	18.2 -16.2	-5 1 4	82.1 -82.8	1 9 5	7.1 -0.0
-2 6 2	46.8 -40.1	13 7 3	38.8 34.2	-16 6 3	41.8 -38.4	-7 1 4	24.5 27.0	0 10 5	3.2 -3.2
-4 8 2	23.4 -23.3	1773	25.4 -27.0	-20 6 3	12.4 12.6	-9 1 4	25.8 -26.2	2 10 5	2.1 2.3
-682	16.0 15.4	283	49.7 -52.5	-1 7 3	35.0 -43.0	-13 1 4	16.0 15.2	-2 0 3	10.2 -15 1
-8 6 2	5.7 5.6	483	6.1 6.8	-373	16.8 -21.1	-15 1 4	15.6 15.2		14.2 -13.3
-10 8 2	18.6 13.5	683	16.0 -19.5	-7 7 3	63.2 -66.2	-17 1 4	J9.1 -57.0	-17 1 3	16 4 16 7
-12 8 2	33.1 -27.9	683	22.5 -20.7	-973	10.3 7.1	-19 1 4	8.2 7.1		10.4 10.4
-14 8 2	17.3 -17.3	10 8 J	10.7 9.8	-13 7 5	12.1 -12.2	-21 1 4	2.1 -2.0	-0 2 3	29.5 29.0
-16 8 2	17.6 -15.8	12 8 3	8.5 5.7	-15 7 3	20.5 -19.5		10.9 -11.5	-10 2 3	17.1 -17.3
-192	15.8 10.5	14 8 3	36.2 -34.6	-17 7 3	1.7 1.3		42.5 41.0	-1 -2 -3	14.0 -15.1
-392	25.6 -19.6	16 8 3	8.9 6.9	-19 7 3	38.5 - 36.3	-0 2 4	0.0 -3.0		2 7
-992	19.4 -13.6	193	16.7 21.4	-4 8 3	37.0 -44.0	-8 2 4	54.7 -56.0		
-11 9 2	19.9 -20.7	393	4.5 -4.3	-6 8 3	7.5 -5.8	-10 2 4	11.9 -15.5		14.0 10.0
-13 9 2	8.0 -6.3	593	33,7 -40.8	-8 8 3	24,5 23.2	-14 2 4	22.8 -25.0	-13 5 5	2.0 -0.4
-2 10 2	23.3 -18.3	793	12.6 -10.9	-10 8 J	27.6 -29.6	-16 2 4	37.8 30.4	-17 3 3	7.5 0.1
-4 10 2	8.2 -8.3	11 9 3	28.5 -24.6	-14 8 3	15.8 -14.2	-20 2 4	3.6 -13.3	-16 6 -	10.1
-10 10 2	13.9 9.8	13 9 3	22.6 21.2	-10 8 3	31.0 -31.4		66 A .69 F	-10 0 3	12 -0.5
-12 10 2	29.8 -23.6	2 10 3	29.6 -34.7	-1 a 3	19.9 -25.9	-0 3 4	13 6 -15 0		11 9 17 7
-14 10 2	14.0 -11.6	4 10 3	10.3 13.1	-0 9 3	13.7 -15.3	-9 3 4	10.0 -10.9		87 74
-2 11 2	5.2 -5.8	6 10 3	14.8 -11.2	-7 9 3	41.8 -48.9	-13 3 4	20.3 24.2	-1 0 5	2.2
-9112	18.3 -18.8	8 10 3	22.9 -25.6	-11 9 3	8.1 6.1	-15 3 4	10.0 10.2	-1	
-11 11 2	14.7 -16.2	10 10 3	7.3 5.7	-13 9 3	12.2 -14.3	-17 3 4	40.1 -43.0	-11 0 5	2 7 2 6
-2 12 2	10.2 -11.0	1 11 3	10.7 15.5	-15 9 3	8.8 -10.9	-6 4 4	8.4 -9.3	-11	
-4 12 2	4.0 -4.1	5 11 3	30.3 -33.8	-2 10 3	9.3 -7.8	-8 4 4	36.4 -39.4	-2 10 5	0.0 0.0
-8 12 2	5.8 -4.6	911 3	10.8 -10.0	-4 10 3	22.3 -25.1	-10 4 4	11.0 -10.3		12 0 15
203	118.4-126.2	2 12 3	17.9 -23.5	-6 10 3	8.5 -11.7	-12 4 4	9.5 12.1	14 0 6	13.0 13.
4 0 3	12.0 14.9	4 12 3	9.5 9.4	-10 10 3	27,2 -28,4	-14 4 4	23.1 -23.4	3 1 6	1.5 1.4
603	44.5 -50.3	-203	6.2 -9.3	-12 10 3	3.4 -3.8	-16 4 4	10.0 14.8		18.0 22.0
8 O 3	28.6 -27.4	-4 0 3	90.9 -97.5	-1 11 3	12.0 -12.4	-18 4 4	5.4 -5.2	11 1 6	1.2 0.4
10 0 3	15.8 16.7	-6 0 3	9.4 -11.4	-5 11 3	10.4 -10.1	-20 4 4	13.2 -13.8	13 1 0	10.0 21.0
12 0 3	21.2 18.9	-803	60,2 64.8	-7 11 3	27.5 - 34.8	-5 5 4	58.1 -59.0		38.5 38.6
14 O J	71.6 -64.9	-10 0 3	49.3 -52.5	-11 11 3	6.5 7.8	-13 5 4	19.7 19.1	0 2 0	21.3 -21.
16 O J	16.0 14.7	-12 0 3	16.6 -13.8	-4 12 3	13.9 +18.0	-13 5 4	10.5 11.2	10 2 6	10.1 0.0
18 O J	21.4 -21.0	-14 0 3	30.9 -33.7	204	37.8 -41.9	-17 5 4	37.5 -34.8	10 1 0	0.7 12
20 0 3	18.5 -18.8	-16 0 3	58.9 -57.1	4 0 4	78.6 -8/).2	-2 6 4	10.6 -10.0	7 7 6	20 1 16
1 1 3	66.9 70.0	-18 0 0	6.1 -5.4	604	13.7 -13.7	-4 6 4	29.5 32.4	0 3 6	20.1 16.4
5 1 3	90.3 -87.5	-20 0 3	27.8 23.3	804	25.0 23.4		41.1 -45.6		0.0 -1.
7 1 3	41.6 -47.1	-22 0 3	16.5 -14.8	10 0 4	15.2 -13.1	-14 6 4	17.3 -10.8	2 2 4	
913	22.0 -17.6	-1 1 3	67.1 -70.7	15 0 4	36.9 - 38.8	-16 6 4	24.7 22.3		
11 1 3	49.8 -45.7	-3 1 3	4C.5 -43.9	3 1 4	40.5 - 36.9	-5 / 4	44.5 -47.1	-12 0 6	10.7 10.1
13 1 3	69.1 59.4	-5 1 3	6.4 -5.5	214	8.7 7.4	-11 7 4	0.0 6.4	-14 0 6	16 1 17 1
15 1 3	3.5 -3.3	-7 1 3	124.9-122.9	1 1 1	52.8 -55.0		12.1 -20.9	-1 1 6	14 8 15
17 1 3	37,9 -38.3	-9 1 3	17.2 18.8	9 1 4	9.4 7.3		22.1 -20.5	-12 1 6	10 8 21 4
19 1 3	8.6 -9.4	-11 1 3	11,4 13.2	13 1 4	34.2 - 34.2	- 4 0 4	23.1 23.0	-10 2 6	20 7 17
21 1 3	7.4 -5.1	-15 1 3	32.9 - 32.4		13.1 -14.7		14 8 -12 6	-14 2 4	10 0 17
023	9.4 11.1	-17 1 3	9,9 5,2		80.4 -60.0	-14 6 4	14.8 -12.0	-1 1 6	
223	99.3-100.2	-19 1 3	65.7 -58.7	8 2 4	15.4 17.7	-10 8 4	14.5 15.6		16.6 - 21.4
4 2 3	41.7 43.8	-21 1 3	11.4 9.6	10 2 4	34,3 -44,8		5 9 6 7		14 9 19
623	38,9 -40.0	-2 2 3	28.3 -31.4	1 3 4	30.2 -37.4			-14 4 4	14.0 16
8 2 J	51.4 -48.8	-4 2 3	64.8 +6J.2	3 3 4	10.5 -13.2		10.3 -0.1		22.7 22.1
10 2 3	11.0 11.5	-6 2 3	32.1 -34.8		20.5 23.5	-12 0 4		-7 5 6	14 0 11
12 2 3	10.7 9.0	-8 2 3	54.7 48.6		39.3 -37.7	-2 10 4	12 3 -10 1	-8 6 6	27.8 25.1
14 2 3	57.0 -51.2	-10 2 3	70.2 -05.2		21 6 - 25 8	-4 10 4	11 4 10 6	-12 6 6	16 1
18 2 3	18.2 -15.8	-14 2 3	25.4 -19.4	15 3 4	14 8 -13 8	-5 10 4	19 7 -19 5	-1 7 6	10.1 10.0
20 2 3	17.6 -18.8	-10 2 3	JJ.2 - J2.8		10 6 -10 7	+10 10 4	3.3 -3 2	-5 7 6	22.7 22.3
1 3 3	71.6 68.7	-18 2 3	0.1		77 9 -91 4	-1 11 4	2 2 2 5	-7 7 6	7.9 7.
3 3 3	14.9 18.8	-20 2 3	19.3 17.8		7 8 9 7		21 4 - 19 8	-6 8 6	18.3 -16.3
5 3 3	105.0-108.8	-22 2 3	10.8 -13.0	12 4 4	19.6 -16.8	10 0 5	17.4 -12.1	-8 8 6	17.3 21.3
7 3 3	2J.8 -18.1		51 9 50 7	16 4 4	40.4 -40 1	14 0 4	9.3 7.1	-3 9 6	12.8 -9.
9 3 3	29.1 -29.0		31.5 -30.5		22 0 -29 4		24 5 - 29 9	4 0 7	7.1 +7.4
11 3 3	50.1 -43.8	-5 3 3	37.0 .40.7		15 4 -14 9		25 9 28 6	9 1 7	28 0 27
13 3 3	45.6 37.3	-7 3 3	120.0-117.0		16 1 12 5		15.6 13.7	8 2 7	1.8 -2.
17 3 3	24.7 -24.8	-9 3 3	3.1 0.1		12 4 - 10 9	7 1 5	26 0 24.2	7 3 7	1.5 -0.5
18 2 3	6.8 -6.8	-12 3 3	23.0 27.2		9.4 -9.7	915	19.5 -16.7	2 4 7	2.6 -3.
043	13.7 13.0	-15 3 3	19 6 -16 6	13 5 4	30.4 -25 8	13 1 5	28.0 -29.2	1 5 7	7.3 4.
2 4 3	76.8 -86.6	-10 3 3	19.0 -10.0	15 5 4	9 3 -9 6	2 2 5	7.8 6.8	7 5 7	1.3 -1.
	26.2 - 10	-21 3 3	20 27	1, 5 4	4.2 4.2	4 2 5	12.9 -8.9	-6 0 7	13,1 12.1
	10.2 - 30.1	-7 4 7	31.0 -34 4	2 6 4	13.0 -16.5	6 2 5	13.0 14.7	-807	1.4 -1.
14 4 7	41 0 -36 4	-4 4 1	43.0 -51 8	4 6 4	56.8 -55.1	12 2 5	1.5 1.4	-12 0 7	30.1 29.1
18 4 3	11.6 -10.2	-6 4 3	40.0 -44.5	16 6 4	33.8 -30.2	3 3 5	17.3 19.2	-14 0 7	7.5 -6.
20 4 3	17.5 =18.8	-8 4 3	39.2 36.0	3 7 4	18.1 -19.9	5 3 5	22.2 22.7	-1 1 7	1.5 0.
1 . 1	46.8 52 9	-10 4 3	74.8 -66.1	7 7 4	37.0 -33.2	11 3 5	9.1 -9.0	-7 1 7	4.8 -6.
	11 1 10 1	-12 4 3	4.4 3.7	13 7 4	26.1 -23.7	13 3 5	22.2 -18.5	-937	2.3 2.
5 5 7	76.4 -84 4	-14 4 3	12.0 -8.0	2 8 4	16.6 -15.3	17 3 5	6,3 4,6	-847	5.5 -4.
7 5 1	22.7 -19.8	-16 4 3	45.7 -43.7	4 8 4	38.3 -40.4	0 4 5	17.8 -18.8	-10 4 7	4.9 -3.
953	24.2 -23.6	-18 4 3	4.3 -3.8	8 8 4	15.9 11.4	245	8.7 6.2	-12 4 7	14.5 18.
11 5 3	39,9 -33.9	-20 4 3	12.7 11.6	14 8 4	3.5 -3.8	445	14.9 -16.8	-267	1.5 1.3
-3 5 3	39.9 32.2	-1 5 3	29.0 -31.5	394	11.2 -9.9	645	21.6 21.5	-867	2.4 -2.
17 5 3	22.3 -25.5	-353	36.2 -39.3	594	4.5 4.9	10 4 5	8.0 -9.2		
2 6 3	68.6 -71.4	-5 5 3	25.4 -23.9	794	27.3 -24.8	3 5 5	17.3 17.2		
4 6 3	17.0 20.6	-7 5 3	101.0 -95.7	0 10 4	2.7 -3.2	5 5 5	13.2 17.1		

Table 4 (cont.)

The bond lengths and angles, together with their standard deviations, are shown in Tables 6 and 7. The standard deviations of the P–P bond length in molecule I, the bond angles involving the P–P bond in molecule I, and the C–P–C bond angles in molecules I and II were calculated differently from the other standard deviations, to allow for the centre of symmetry between the two P atoms in molecule I, and the mirror plane relating the two C atoms respectively (Cruickshank & Robertson, 1953).

The observed P–P distances of 2.245 Å in molecule I and 2.161 Å in molecule II differ significantly from one another, and from the values of 2.22 Å in tetraethyldiphosphine disulphide (Dutta & Woolfson, 1961), 2.21 Å in 1,2-dimethyl-1,2-diphenyldiphosphine disulphide (Wheatley, 1960), bis(cyclotetramethylene)diphosphine disulphide (Lee & Goodacre, 1969) and bis(cyclopentamethylene)diphosphine disulphide (Lee & Goodacre, 1970).

The lengths of the P-S bonds differ significantly and are 1.951 Å in molecule I and 1.970 Å in molecule II. These bonds are shortened by back bonding from a full 60-65

65-70

70-75

75--80

80-85

85-90

90-95

>95

	Number of			Number of			Number of	
$F_{\rm obs}$	planes	R	$\sin \theta$	planes	R	Layer	planes	R
05	67	15.8%	0.0-0.1	2	6.4%	hk0	77	7.7%
5-10	141	18.6	0.1 - 0.5	12	8.7	hk1	225	8.8
10-15	149	13.5	0.2-0.3	30	8.2	hk2	192	8.9
15-20	110	11.8	0.3-0.4	61	7.9	hk3	192	10.5
2025	92	10.1	0.4-0.2	87	7.6	hk4	117	7.2
25-30	66	10.5	0.2-0.6	130	7.7	hk5	58	11.0
30-35	54	$7 \cdot 2$	0.6-0.2	138	10.4	hk6	36	11.3
35-40	47	7.7	0.7-0.8	152	10.2	hk7	19	12.7
40-45	44	8.7	0.8-0.9	194	10.4			
4550	21	10.4	0.9-1.0	110	11.7			
50-55	22	7.1						
55-60	17	6.8						

#### Table 5. Agreement analysis

Table 6. Bond lengths and their standard deviations

5.1

3.8

7.5

3.7

6.3

7.0

6.8

10.0

9

14

15

5

4

3

6

30

	Distance	$\sigma$	
P(1) - P(1')	2·245 Å	0·006 Å	
P(2) - P(3)	2.161	0.004	
P(1) - S(1)	1.951	0.003	
P(2)-S(2)	1.970	0.004	
P(3) - S(3)	1.965	0.004	
P(1)-C(1)	1.80	0.008	
P(2) - C(2)	1.82	0.008	
P(3) - C(3)	1.82	0.007	

Table 7. Bond angles and their standard deviations

	Angle	σ
S(1) - P(1) - C(1)	115·0°	0·3 °
S(2) - P(2) - C(2)	114.0	0.3
S(3) - P(3) - C(3)	115.9	0.2
S(1) - P(1) - P(1')	111.2	0.2
S(2) - P(2) - P(3)	112.1	0.5
S(3) - P(3) - P(2)	111.9	0.5
C(1)-P(1)-P(1')	105.6	0.3
C(2)-P(2)-P(3)	104.7	0.4
C(3)-P(3)-P(2)	103-9	0.3
C(1)-P(1)-C(1')	103.5	0.4
C(2)-P(2)-C(2')	106.6	0.4
C(3)-P(3)-C(3')	103.9	0.3

sulphur p orbital to an empty phosphorus d orbital. These values may be compared with the values of 1.94 Å in tetraethyldiphosphine sulphide, 1.98 Å in 1,2-dimethyl-1,2-diphenyldiphosphine disulphide, 1.95 Å in bis(cvclotetramethylene)diphosphine disulphide and 1.95 Å in bis(cyclopentamethylene)diphosphine disulphide. The sum of Pauling's (1960) double-bond radii for P and S is 1.94 Å, which when corrected for the difference in electronegativity (Schomaker & Stevenson, 1941) gives a distance of 1.92 Å for this bond.

The P-C distances of 1.80 Å in molecule I and 1.82 and 1.82 Å in molecule II differ by two standard deviations, but are close to the values of 1.82 and 1.84 Å in tetraethyldiphosphine disulphide, 1.82 Å in 1,2-dimethyl-1,2-diphenyldiphosphine disulphide, 1.82 Å in bis(cyclotetramethylene)diphosphine disulphide and 1.81 Å in bis(cyclopentamethylene)diphosphine disulphide. The sum of the Pauling single-bond radii for P and C is 1.872 Å, which when corrected for the difference in electronegativity (Schomaker & Stevenson, 1941) gives a bond length of 1.84 Å.

The distribution of bonds round each P atom is essentially tetrahedral. The S atom is large, and because of  $\pi$  bonding is rather close to the P atom and causes some distortion. Because of repulsion between S and the other three atoms bonded to P, the three bond angles S-P-C, S-P-C' and S-P-P' are all greater than tetrahedral [115.0, 115.0 and 111.0° round P(1); 114.0, 114.0 and 112.1° round P(2); and 115.9, 115.9 and 111.9 round P(3)]. The remaining three bond angles round each P atom are consequently smaller than tetrahedral.

The observation that the P(1)-S(1) bond in molecule I is shorter than the comparable bonds P(2)-S(2) and P(3)-S(3) in molecule II may be partly due to molecular crowding of S(1) by non-bonded H atoms. The distances between S(1) of the central molecule and H(21) repeated at -x, -y, 1-z and -x, y, 1-z are both 2.84 Å. These cannot be considered to be hydrogen bonded since they involve an  $S \cdots H - C$  angle of 67°, but the distances are significantly short. Taking the Pauling (1960) values for van der Waals radii of S = 1.85and H = 1.20 Å, the minimum non-bonded S  $\cdots$  H contact would be 3.05 Å. It has been suggested by several workers that the van der Waals radius for S should be 1.72-1.73 Å (Fava Gasparri, Nardelli & Villa, 1967; Nardelli, Fava Gasparri, Giraldi Battistini & Domiano, 1966; Ždanov & Zvonkova, 1950; van der Helm, Lessor & Merritt, 1960; Lee & Bryant, 1969). Even using the smaller radius for S, these  $S \cdots H$  contacts are still short. The structure contains numerous nonbonded S...H contacts of 2.91 Å, in agreement with the smaller van der Waals radius.

There is no simple explanation for the differences in the observed lengths of P-P and P-C bonds in molecules I and II.

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#### References

- CHRISTEN, P. J., VAN DER LINDE, L. M. & HOOGE, F. N. (1959). Rec. Trav. Chim. Pays-Bas, 78, 161.
- CRUICKSHANK, D. W. J. & ROBERTSON, A. P. (1953). Acta Cryst. 6, 698.
- DAUBEN, C. H. & TEMPLETON, D. H. (1955). Acta Cryst. 8,841.
- DUTTA, S. N. & WOOLFSON, M. M. (1961). Acta Cryst. 14, 178.
- FAVA GASPARRI, G., NARDELLI, M. & VILLA, A. (1967). Acta Cryst. 23, 384.

- HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). Acta Cryst. 17, 1040.
- HARRIS, R. K. & HAYTER, R. G. (1964). Canad. J. Chem. 42, 2282.
- Howells, E. R., Phillips, D. C. & Rogers, D. (1950). Acta Cryst. 3, 210.
- HUGHES, E. W. (1941). J. Amer. Chem. Soc. 63, 1737.
- International Tables for X-ray Crystallography (1965). Vol. I. Birmingham: Kynoch Press.
- LEE, J. D. & BRYANT, M. W. R. (1969). Acta Cryst. B25, 2094, 2497.
- LEE, J. D. & GOODACRE, G. W. (1969). Acta Cryst. B25, 2127.
- LEE, J. D. & GOODACRE, G. W. (1970). Acta Cryst. B26, 507.
- NARDELLI, M., FAVA GASPARRI, G., GIRALDI BATTISTINI, G. & DOMIANO, P. (1966). Acta Cryst. 20, 349.
- PAULING, L. (1960). The Nature of the Chemical Bond, 3rd Ed. Ithaca: Cornell Univ. Press.
- PEDONE, C. & SIRIGU, A. (1967). J. Chem. Phys. 47, 339.
- SCHOMAKER, V. & STEVENSON, D. P. (1941). J. Chem. Amer. Soc. 63, 37.
- SIM, G. A. (1958). Acta Cryst. 11, 123.
- VAN DER HELM, D., LESSOR, A. E. JR & MERRITT, L. L. JR (1960). Acta Cryst. 13, 1050.
- WHEATLEY, P. J. (1960). J. Chem. Soc. p. 523.
- ŽDANOV, G. S. & ZVONKOVA, Z. V. (1950). Zh. Fiz. Khim. 24, 1339.

Acta Cryst. (1971). B27, 307

# The Crystal Structure of Glucitol–Pyridine

BY H.S. KIM, G.A. JEFFREY AND R.D. ROSENSTEIN

Department of Crystallography, University of Pittsburgh, Pittsburgh, Pennsylvania 15213, U.S.A.

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The crystal structure of a 1:1 glucitol-pyridine complex,  $C_6H_{14}O_6.C_5H_5N$ , has been determined by the application of the symbolic addition and tangent formulas to diffractometer Cu K $\alpha$  data. The anisotropic refinement terminated at R = 0.04. The space group is  $P2_1$  with two molecules in a unit cell of dimensions a = 4.652 (3), b = 10.207 (4), c = 13.439 (5) Å,  $\beta = 90.3$  (3)°. The structure consists of layers of hydrogen-bonded glucitol molecules separated by layers of pyridine molecules stacked in a herringbone arrangement. The two layers are linked by  $O-H\cdots N$  hydrogen bonds of 2.814 Å. The glucitol molecule has a non-planar carbon chain such that the parallel alignment of C(1)-OH to C(3)-OH and C(2)-OH to C(4)-OH is avoided.

# Introduction

Glucitol forms a 1:1 solvent complex on crystallization from pyridine, which has been used for purification (Strain, 1934, 1937). A similar derivative has been reported for 2-deoxyglucitol (Wolfrom, Konigsberg, Moody & Goepp, 1946). In addition to the intrinsic interest in the structure of the complex, this compound provides an opportunity to examine the conformation of the glucitol molecule in a crystal-field environment different from that in the crystal structure of Dglucitol itself, which has also been determined (Jeffrey & Park, 1970).

# **Crystal data**

Large, transparent monoclinic crystals of  $C_6H_{14}O_6$ .  $C_5H_5N$ ,

m.p. 76°C, which decomposed on exposure to air, were obtained by slowly cooling a saturated solution of D-glucitol in pyridine. They gave the following data:

Space group  $P2_1$ , from systematic absences 0k0 absent for k odd

$$\begin{array}{ll} a = \ 4.652 \ (3) \ \text{\AA} & V = 638 \cdot 15 \ \text{\AA}^3 \\ b = 10.207 \ (4) & Z = 2 \\ c = 13.439 \ (5) & D_m = 1.365 \ \text{g.cm}^{-3} \ \text{at} \ 23 \ ^\circ\text{C} \end{array}$$