

The authors wish to thank Mr James Voytas for his help with the data collection and the computations on $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7 \cdot 6\text{H}_2\text{O}$.

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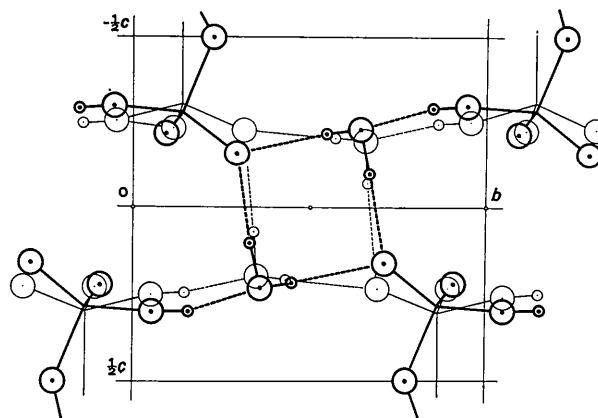


Fig. 2. Projection of parts of the $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7 \cdot 6\text{H}_2\text{O}$ (heavy lines) and $\text{Na}_2\text{H}_2\text{P}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$ (light lines) structures down the b axis. The large circles represent oxygen atoms and the small circles hydrogen atoms. Dashed lines represent hydrogen bonds.

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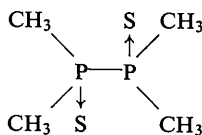
A Redetermination of the Crystal Structure of Tetramethyldiphosphine Disulphide

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

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

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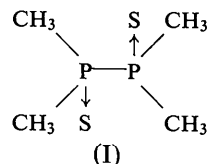
The crystal structure of tetramethyldiphosphine disulphide



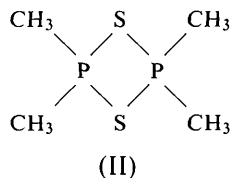
has been determined from three-dimensional X-ray diffraction data. The unit cell is monoclinic with space group $C2/m$ (number 12), dimensions $a = 18.882$, $b = 10.703$, $c = 6.984 \text{ \AA}$; $\beta = 94^\circ 42'$, and contains six molecules, which occupy two different sets of special positions. The structure was refined by full-matrix 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 \AA ; P-S, 1.951, 1.970 and 1.965 \AA ; P-C, 1.80, 1.82 and 1.82 \AA). 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)



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 × 0.08 × 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

$C_4H_{12}P_2S_2$, $M = 186.22$

Monoclinic, $a = 18.882$, $b = 10.703$, $c = 6.984$, all ± 0.005 Å; $\beta = 94^\circ 42' \pm 30'$, $U = 1406.7$ Å³, $Z = 6$, $D_m = 1.31$ g.cm⁻³, $D_c = 1.319$ g.cm⁻³, $\mu = 74.6$ cm⁻¹. $F(000) = 588$, $Cu K\alpha$, $\lambda = 1.54051$ Å (α_1) and 1.54433 Å (α_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⁻³ 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_o 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.

Table 1. *Final coordinates and their estimated standard deviations*

	x/a	y/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	0.5000	0.4181	0.0001	0.0000	0.0004
P(3)	0.1696	0.5000	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

Isotropic temperature factors of $B=6.0 \text{ \AA}^2$ were chosen for the hydrogen atoms (1 \AA^2 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.

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

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

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

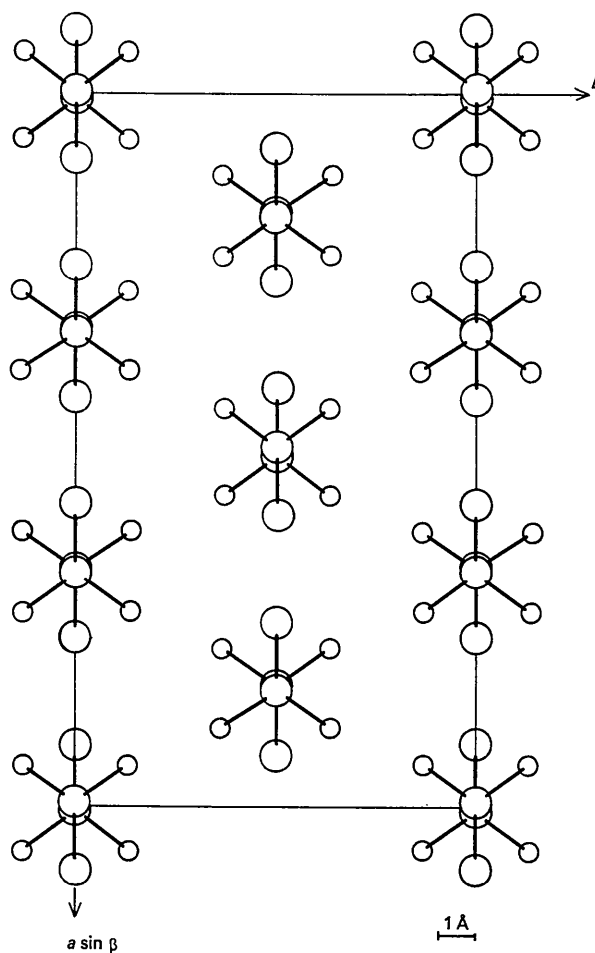


Fig. 1. Packing of the molecules in one unit-cell viewed down [001].

Table 3. *Final temperature factor parameters*

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	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 $B=6.00 \text{ \AA}^2$.

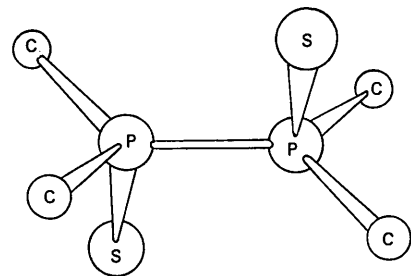


Fig. 2. A view of one molecule.

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

h k l	F _o	F _c	h k l	F _o	F _c	h k l	F _o	F _c	h k l	F _o	F _c
-12 6 2	42.8	-41.0	8 6 3	22.4	-27.7	-13 5 3	20.1	-18.1	4 10 4	20.1	-21.4
-14 6 2	27.2	-18.0	10 6 3	8.3	6.3	-15 5 3	19.4	-11.3	8 10 4	3.8	4.1
-16 6 2	22.5	-23.3	14 6 3	14.1	-6.4	-19 5 3	49.1	-40.4	11 5 3	15.4	-15.7
-17 2 2	27.1	21.3	1 7 3	21.4	31.3	-1 6 3	48.5	-23.8	-4 0 4	64.7	50.2
-17 2 2	40.3	-31.7	5 7 3	15.7	-11.4	-2 6 3	47.9	-17.6	-6 0 4	9.1	9.2
-17 2 2	4.0	4.3	7 7 3	41.5	-47.4	-8 6 3	36.0	-42.9	-10 0 4	17.5	-13.4
-17 2 2	14.3	-13.2	7 7 3	19.3	-24.3	-10 6 3	45.3	-31.1	-10 0 4	31.9	-32.7
-17 2 2	23.2	-23.3	11 7 3	32.9	-28.8	-14 6 3	47.7	-25.4	-10 0 4	41.8	-38.4
-17 2 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
-17 2 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
-17 2 2	23.2	-23.3	17 7 3	25.4	-27.0	-20 6 3	12.4	12.6	-9 1 4	25.8	-26.2
-17 2 2	16.8	15.8	17 7 3	25.4	-27.0	-20 6 3	35.0	-43.0	-13 1 4	36.1	-35.2
-17 2 2	5.7	-5.8	18 6 3	16.0	-19.5	-7 7 3	6.2	-6.2	-17 1 4	19.1	-17.0
-17 2 2	18.6	15.8	6 8 3	16.0	-19.5	-7 7 3	10.3	-7.1	-19 1 4	8.2	7.1
-17 2 2	23.1	-27.9	6 8 3	22.7	-20.7	-9 7 3	10.3	-7.1	-19 1 4	8.2	7.1
-17 2 2	17.3	-17.3	10 8 3	10.7	9.8	-13 7 3	12.9	-12.2	-21 1 4	2.1	-2.0
-17 2 2	17.6	-15.8	12 8 3	8.5	5.7	-15 7 3	20.5	-19.3	-22 2 4	10.9	-11.3
-19 2	15.8	-10.5	14 8 3	36.2	-34.6	-17 7 3	38.5	-36.3	-6 2 4	6.8	-5.0
-19 2	19.4	-10.6	1 9 3	16.7	21.4	-8 8 3	37.0	-44.0	-6 2 4	54.7	-46.0
-19 2	19.9	-20.9	5 9 3	45.5	-42.0	-6 8 3	17.5	-15.8	-10 2 4	9.6	-9.3
-19 2	8.0	-6.2	5 9 3	33.7	-40.8	-8 8 3	24.5	-23.2	-14 2 4	22.8	-25.0
-20 2	23.1	-18.3	7 9 3	12.6	-10.9	-10 8 3	27.6	-29.6	-18 2 4	37.8	-36.4
-20 2	3.2	-4.3	11 9 3	28.8	-24.6	-12 8 3	13.7	-12.3	-2 4 4	66.5	-69.5
-20 2	13.9	9.8	13 9 3	22.6	21.2	-16 8 3	31.9	-25.4	-3 4 4	12.6	-15.9
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-20 2	14.0	-10.4	4 10 3	10.3	13.3	-12 9 3	15.5	-14.1	-6 4 4	26.3	-24.2
-20 2	5.2	-5.8	6 10 3	14.8	-11.2	-7 9 3	41.8	-48.9	-13 4 4	26.3	-24.2
-20 2	13.1	-18.8	8 10 3	32.9	-27.1	-11 9 3	41.8	-48.9	-13 4 4	26.3	-24.2
-20 2	14.7	-12.6	10 10 3	7.3	5.7	-13 9 3	12.2	-14.3	-17 3 4	4.0	-4.0
-20 2	10.2	-11.0	1 11 3	10.7	15.5	-15 9 3	6.8	-10.9	-6 4 4	8.4	-9.3
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2 0 3	118.4	-126.2	2 12 3	17.9	-23.5	-6 10 3	8.5	-11.7	-12 4 4	39.0	-34.8
-4 0 3	12.6	-12.6	4 12 3	12.6	-12.6	-12 10 3	27.4	-27.4	-12 4 4	11.0	-11.0
6 0 3	44.5	-30.3	-2 13 3	6.2	-9.3	-12 10 3	3.4	-3.8	-16 4 4	23.1	-25.4
8 0 3	28.6	-27.4	-4 0 3	90.9	-93.7	-10 10 3	10.5	-10.5	-16 4 4	39.0	-34.8
8 0 3	28.6	-27.4	-4 0 3	90.9	-93.7	-10 10 3	10.5	-10.5	-16 4 4	39.0	-34.8
12 0 3	21.2	18.9	-8 0 3	66.2	64.8	-7 11 3	27.5	-34.8	-5 5 4	18.1	-19.0
14 0 3	18.0	-18.0	8 10 3	22.3	-24.8	-5 3 4	15.2	-15.1	-2 6 4	41.1	-43.6
14 0 3	18.0	-18.0	8 10 3	22.3	-24.8	-5 3 4	15.2	-15.1	-2 6 4	41.1	-43.6
18 0 3	21.4	-21.4	-14 0 3	30.8	-33.7	-4 12 3	13.9	-13.8	-15 5 4	10.5	-11.0
18 0 3	21.4	-21.4	-14 0 3	30.8	-33.7	-4 12 3	13.9	-13.8	-15 5 4	10.5	-11.0
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5 1 3	90.0	-67.5	-20 0 3	27.8	23.3	8 0 4	25.0	23.4	-6 6 4	17.3	-18.8
5 1 3	90.0	-67.5	-20 0 3	27.8	23.3	8 0 4	25.0	23.4	-6 6 4	17.3	-18.8
9 1 3	22.0	-17.6	-1 1 3	67.1	-70.7	16 0 4	36.9	-38.6	-11 6 4	24.7	-22.5
11 1 3	49.8	-45.7	-3 1 3	40.5	-43.9	8 0 4	36.9	-38.6	-11 6 4	24.7	-22.5
11 1 3	49.8	-45.7	-3 1 3	40.5	-43.9	8 0 4	36.9	-38.6	-11 6 4	24.7	-22.5
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15 1 3	3.5	-3.3	-7 1 3	124.9	-122.9	7 1 4	52.8	-55.0	-15 7 4	9.0	9.4
19 1 3	8.6	-9.4	-11 1 3	11.4	13.2	13 1 4	34.2	-34.2	-4 8 4	23.1	-25.6
21 1 3	7.4	-5.1	-15 1 3	32.9	-32.4	2 2 4	13.1	-14.7	-8 8 4	34.8	-34.8
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8 2 3	51.4	-48.8	-4 2 3	64.8	-63.2	3 3 4	10.5	-13.2	-9 9 4	16.9	-18.7
8 2 3	51.4	-48.8	-4 2 3	64.8	-63.2	3 3 4	10.5	-13.2	-9 9 4	16.9	-18.7
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18 2 3	9.1	-13.8	-14 2 3	25.4	-25.8	-6 4 4	18.2	-18.2	-20 10 4	12.3	-13.1
20 2 3	17.6	-18.8	-16 2 3	55.2	-52.8	15 3 4	14.8	-13.8	-8 10 4	15.7	-15.5
20 2 3	17.6	-18.8	-16 2 3	55.2	-52.8	15 3 4	14.8	-13.8	-8 10 4	15.7	-15.5
1 3 3	71.6	68.7	-18 0 3	8.1	-4.2	0 4 4	10.6	-10.7	-10 10 4	3.3	-3.2
1 3 3	71.6	68.7	-18 0 3	8.1	-4.2	0 4 4	10.6	-10.7	-10 10 4	3.3	-3.2
5 3 3	105.0	-108.8	-22 2 3	10.4	-13.0	10 4 4	7.8	9.7	-5 11 4	21.4	-19.8
5 3 3	105.0	-108.8	-22 2 3	10.4	-13.0	10 4 4	7.8	9.7	-5 11 4	21.4	-19.8
7 3 3	23.8	-18.1	-1 3 3	15.4	-14.4	13 4 4	4.6	-4.6	-14 0 4	15.5	-15.5
7 3 3	23.8	-18.1	-1 3 3	15.4	-14.4	13 4 4	4.6	-4.6	-14 0 4	15.5	-15.5
11 3 3	50.1	-43.9	-5 3 3	37.6	-40.7	1 5 4	23.0	-24.7	1 1 5	24.5	-29.9
11 3 3	50.1	-43.9	-5 3 3	37.6	-40.7	1 5 4	23.0	-24.7	1 1 5	24.5	-29.9
17 3 3	45.6	-37.3	-9 3 3	25.9	-25.8	5 6 4	16.5	-16.8	5 6 4	19.5	-18.1
17 3 3	45.6	-37.3	-9 3 3	25.9	-25.8	5 6 4	16.5	-16.8	5 6 4	19.5	-18.1
19 3 3	6.8	-6.6	-11 3 3	25.8	-27.2	7 5 4	30.4	-30.9	7 5 4	26.0	-24.2
19 3 3	6.8	-6.6	-11 3 3	25.8	-27.2	7 5 4	30.4	-30.9	7 5 4	26.0	-24.2
2 4 3	76.6	-66.6	-15 3 3	19.6	-16.6	13 5 4	30.4	-25.8	13 5 4	28.0	-29.2
2 4 3	76.6	-66.6	-15 3 3	19.6	-16.6	13 5 4	30.4	-25.8	13 5 4	28.0	-29.2
4 4 3	48.7	-54.7	-19 3 3	31.6	-47.6	15 5 4	9.1	-9.6	2 5 4	15.8	-16.8
4 4 3	48.7	-54.7	-19 3 3	31.6	-47.6	15 5 4	9.1	-9.6	2 5 4	15.8	-16.8
8 4 3	59.1	-55.8	-2 4 3	21.0	-24.4	2 6 4	13.0	-16.5	6 2 5	13.0	-14.7
8 4 3	59.1	-55.8	-2 4 3	21.0	-24.4	2 6 4	13.0	-16.5	6 2 5	13.0	-14.7
14 4 3	41.0	-36.6	-6 4 3	40.0	-44.5	16 6 4	33.8	-30.2	3 3 5	15.7	-15.2
14 4 3	41.0	-36.6	-6 4 3	40.0	-44.5	16 6 4	33.8	-30.2	3 3 5	15.7	-15.2
20 4 3	17.5	-18.8	-8 4 3	39.2	-36.0	3 7 4	18.1	-19.9	5 3 5	23.2	-22.7
20 4 3	17.5	-18.8	-8 4 3	39.2	-36.0	3 7 4	18.1	-19.9	5 3 5	23.2	-22.7
2 5 3	12.0	-14.8	-12 5 3	30.5	-32.8	4 8 4	29.5	-26.8	0 4 5	15.9	-16.8
2 5 3	12.0	-14.8	-12 5 3	30.5	-32.8	4 8 4	29.5	-26.8	0 4 5	15.9	-16.8
3 5 3	11.1	-10.1	-14 5 3	12.2	-14.3	-17 3 4	13.7	-14.7	13 3 5	22.2	-18.5
3 5 3	11.1	-10.1	-14 5 3	12.2	-14.3	-17 3 4	13.7	-14.7	13 3 5	22.2	-18.5
5 5 3	76.4	-68.4	-14 4 3	12.0	-8.0	2 8 4	16.6	-15.3	17 3 5	8.3	-8.3
5 5 3	76.4	-68.4	-14 4 3	12.0	-8.0	2 8 4	16.6	-15.3	17 3 5	8.3	-8.3
11 5 3	39.9	-33.9	-20 4 3	12.1	-11.6	4 8 4	39.5	-40.0	4 8 4	15.9	-16.6
11 5 3	39.9	-33.9	-20 4 3	12.1	-11.6	4 8 4	39.5	-40.0	4 8 4	15.9	-16.6
9 5 3	24.2	-23.6	-18 4 3	4.4	-3.8	8 4 4	15.9	-11.4	2 4 5	8.7	8.2
9 5 3	24.2	-23.6	-18 4 3	4.4	-						

Table 5. Agreement analysis

F_{obs}	Number of planes	R	$\sin \theta$	Number of planes	R	Layer	Number of planes	R
0-5	67	15.8%	0.0-0.1	2	6.4%	hk0	77	7.7%
5-10	141	18.6	0.1-0.2	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
20-25	92	10.1	0.4-0.5	87	7.6	hk4	117	7.2
25-30	66	10.5	0.5-0.6	130	7.7	hk5	58	11.0
30-35	54	7.2	0.6-0.7	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			
45-50	21	10.4	0.9-1.0	110	11.7			
50-55	22	7.1						
55-60	17	6.8						
60-65	9	5.1						
65-70	14	3.8						
70-75	15	7.5						
75-80	5	10.0						
80-85	4	3.7						
85-90	3	6.3						
90-95	6	7.0						
>95	30	6.8						

Table 6. Bond lengths and their standard deviations

	Distance	σ
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	0.2
S(3)-P(3)-P(2)	111.9	0.2
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(cyclo-tetramethylene)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(cyclo-tetramethylene)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 π 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...H-C angle of 67°, but the distances are significantly short. Taking the Pauling (1960) values for van der Waals radii of S=1.85 and H=1.20 Å, the minimum non-bonded S...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...H contacts are still short. The structure contains numerous non-

bonded 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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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, $C_6H_{14}O_6 \cdot C_5H_5N$, 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...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 & Goepf, 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 D-glucitol itself, which has also been determined (Jeffrey & Park, 1970).

Crystal data

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

$$\begin{array}{ll} a = 4.652 \text{ (3) \AA} & V = 638.15 \text{ \AA}^3 \\ b = 10.207 \text{ (4)} & Z = 2 \\ c = 13.439 \text{ (5)} & D_m = 1.365 \text{ g.cm}^{-3} \text{ at } 23^\circ\text{C} \end{array}$$