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The Crystal and Molecular Structure of Bis(cyclopentamethylene)diphosphine Disulphide

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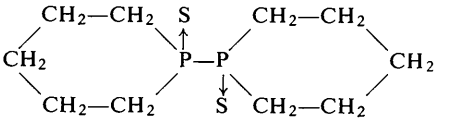
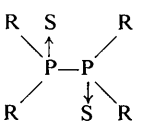
The crystal and molecular structure of bis(cyclopentamethylene)diphosphine disulphide,



has been determined by the application of Patterson and Fourier techniques, and has been refined by three-dimensional full-matrix least-squares methods. The unit cell is triclinic with space group $P\bar{1}$ (number 2), dimensions $a=9{\cdot}44$, $b=6{\cdot}85$, $c=6{\cdot}02$ Å, $\alpha=120{\cdot}1°$, $\beta=99{\cdot}0°$, $\gamma=82{\cdot}4°$, and contains one molecule. The final R index based on 783 independent observed reflexions was 10·1%. The molecule is centrosymmetric about the mid point between the two phosphorus atoms, and consequently the two sulphur atoms are *trans* to each other. The distribution of bonds round each phosphorus atom is approximately tetrahedral, but the inclusion of phosphorus in a heterocyclic ring causes some distortion and reduces the angle C–P–C from tetrahedral to 101·8°. The P–P bond length of 2·21 Å is normal for a single bond, and the P–S distances of 1·95 Å are close to the Pauling double-bond value of 1·92 Å. The ring system is saturated and puckered. The shape of this molecule is essentially similar to that of $Me_2(C_6H_5)_2P_2S_2$, $Et_4P_2S_2$ and (cyclo $C_4H_8)_2P_2S_2$. There are no structural features which would explain the reported wide melting range of 185–225 °C.

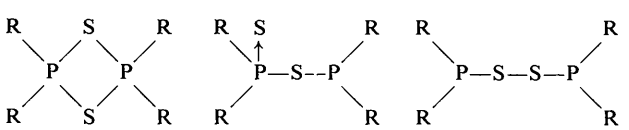
Introduction

There is considerable interest in the nature of the P–P bond (Cowley, 1965). The formulation of diphosphine disulphides as P–P bonded structures



(I)

has been questioned because proton magnetic resonance data for $(CH_3)_4P_2S_2$ reported by Harris & Hayter (1964) showed that the value of the P–P coupling constant was an order of magnitude less than in other compounds known to have a P–P bond [*i.e.* $Me_4P_2S_2$, $J_{PP}=18{\cdot}7$ c.p.s.; diphosphine, $J_{PP}=108{\cdot}2$ c.p.s. (Lynden-Bell, 1961); diphosphite anion, $J_{PP}=480$ c.p.s. (Callis, van Wazer, Shoolery & Anderson, 1957)]. Other structures containing one or more bridging sulphur atoms were therefore suggested.



(II) (III) (IV)

The analogous compound $(CH_3)_4As_2S_2$ has been found by Camerman & Trotter (1964) to have structure (III). Mass spectra, infrared and Raman spectra on $(CH_3)_4P_2S_2$ and other diphosphine disulphides (Cowley & Steinfink, 1965; Cowley & White, 1966) suggest structure (I). Accurate crystal structure determinations of 1,2-dimethyl-1,2-diphenyldiphosphine disulphide (Wheatley, 1960), tetraethyldiphosphine disulphide (Dutta & Woolfson, 1961), and bis(cyclotetramethylene)diphosphine disulphide (Lee & Goodacre, 1969) all show the P–P bonded structure (I).

The investigation of the structure of bis(pentamethylene)diphosphine disulphide was undertaken to find whether it too had a P–P bonded structure, to see if there were any special features associated with the inclusion of a phosphorus atom in a heterocyclic ring, and to see if there was any structural explanation such as disorder or *cis-trans* isomerism which would account for the large range of melting (185–225 °C) reported by Schmutzler (1964).

Experimental

Colourless crystals of bis(cyclopentamethylene)diphosphine disulphide were prepared and supplied by Dr R. Schmutzler (Technische Universität, Braunschweig, Germany). Recrystallization from chloroform gave crystals suitable for X-ray analysis, in the form of rectangular plates.

A crystal of approximate dimensions $0{\cdot}3\times0{\cdot}2\times0{\cdot}05$ mm was used to collect data along the c axis and a crystal $0{\cdot}25\times0{\cdot}25\times0{\cdot}05$ mm for $0kl$ data. The intensities of 783 independent reflexions were recorded photographically by equi-inclination Weissenberg

methods. These were measured visually and converted to $|F|$ and $|F|^2$ by applying Lorentz and polarization corrections. In view of the small crystal size and relatively low absorption coefficient, corrections for absorption were considered unnecessary. No corrections were made for extinction, and reflexions too weak to be observed were ignored.

Crystal data

$C_{10}H_{20}P_2S_2$, $M=266{\cdot}4$
Triclinic, $a=9{\cdot}44$, $b=6{\cdot}85$, $c=6{\cdot}02$ Å, $\pm 0{\cdot}02$ Å
$\alpha=120{\cdot}1$, $\beta=99{\cdot}0$ $\gamma=82{\cdot}4°$, $\pm 0{\cdot}5°$
$U=331{\cdot}5$ Å^3, $z=1$, $D_m=1{\cdot}33$ g.cm^{-3}, $D_c=1{\cdot}336$ g.cm^{-3}, $F_{000}=142$, Cu $K\alpha$, $\lambda=1{\cdot}542$ Å, $\mu=54{\cdot}5$ cm^{-1}.

No consistently absent reflexions, space group $P1$ or $P\bar{1}$. The latter is indicated from pyroelectric and statistical tests and confirmed by the structure analysis.

Structure analysis

The choice between the two possible space groups $P1$ and $P\bar{1}$ was made on the basis of a negative pyroelectric test, and also from a statistical analysis of the intensities of the $hk0$ reflexions (Howells, Phillips & Rogers, 1950; Lipson & Woolfson, 1952; Sim, 1958). Comparison of the experimental and theoretical curves pointed unequivocally to the centrosymmetric space group $P\bar{1}$. The density measured by flotation in aqueous KI solutions was found to be 1·33 g.cm^{-3} compared with the calculated value of 1·336 g.cm^{-3} based on one molecule per unit cell. Since there is only one molecule per cell, it follows that the molecule must itself be centrosymmetric.

An $hk0$ Patterson projection was difficult to interpret, but on sharpening to a system of point atoms at rest the orientations of the P and S atoms were deduced. A structure factor calculation was performed on these atoms using atomic scattering factors due to Hanson, Herman, Lea & Skillman (1964), and a computer program for the IBM 1620 written by Mr G. S. D. King (Union Carbide European Research Associates, Brussels). The initial agreement index R was 33%, and a Fourier synthesis based on these calculated phases revealed the positions of four of the five ring carbon atoms. Fourier refinement was continued, and the fifth ring carbon atom located. This gave a value of $R=18\%$. Block-diagonal least-squares refinement of individual isotropic temperature factors and positional parameters with unit weights reduced R to 12·6% after four cycles.

A sharpened Patterson projection on the $0kl$ data indicated positions for the P and S atoms, but because of the poor resolution, overlapping of peaks, and the

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

	x/a	y/b	z/c	$\sigma(x/a)$	$\sigma(y/b)$	$\sigma(z/c)$
S	0·1522	1·2604	−0·0507	0·0003	0·0004	0·0005
P	0·1118	0·9943	−0·0373	0·0002	0·0003	0·0004
C(1)	0·1398	0·7279	−0·3275	0·0009	0·0013	0·0016
C(2)	0·3002	0·6812	−0·3541	0·0010	0·0014	0·0018
C(3)	0·3843	0·6599	−0·1310	0·0011	0·0017	0·0023
C(4)	0·3754	0·8726	0·1315	0·0011	0·0018	0·0020
C(5)	0·2214	0·9450	0·2068	0·0010	0·0016	0·0018

Table 2. *Calculated positions of hydrogen atoms*

	Bonded to	x/a	y/b	z/c
H(1)	C(1)	0·0995	0·5945	−0·3146
H(11)	C(1)	0·0844	0·7370	−0·4927
H(2)	C(2)	0·3167	0·5260	−0·5303
H(12)	C(2)	0·3393	0·8179	−0·3620
H(3)	C(3)	0·3436	0·5243	−0·1230
H(13)	C(3)	0·4953	0·6195	−0·1670
H(4)	C(4)	0·4396	0·8409	0·2757
H(14)	C(4)	0·4177	1·0082	0·1258
H(5)	C(5)	0·1786	0·8135	0·2197
H(15)	C(5)	0·2216	1·0977	0·3905

Table 3. *Final temperature factor parameters*

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
S	5·16	4·82	6·43	−1·04	1·11	2·74
P	3·02	4·35	3·98	−0·66	0·49	1·91
C(1)	3·51	4·99	4·98	−0·85	0·27	2·22
C(2)	4·00	5·66	5·41	−0·46	0·75	2·27
C(3)	4·25	6·49	8·33	0·07	1·45	4·03
C(4)	4·65	8·08	5·21	−0·95	0·40	3·55
C(5)	4·05	6·86	5·37	−0·78	0·54	3·33

limited amount of data, positions of the carbon atoms were not obtained directly. However, using the y coordinates from the $hk0$ projection, coupled with bond length and bond angle calculations, carbon atom positions were deduced which were in accord with the Patterson map. The R value was 27%, but no attempt was made to refine this projection.

Subsequent refinement was performed from three-dimensional data on the SRC Chilton Atlas computer, using the *X-ray* 63 system due to Professor J. M. Stewart as adapted by Dr J. C. Baldwin. Full-matrix least-squares refinement of positional parameters, individual isotropic temperature factors and interlayer scale factors was performed using unit weights and the same atomic scattering factors as before except that those for P and S were modified for both the real and imaginary parts of anomalous dispersion (Dauben & Templeton, 1955). This reduced R to 17·0%. A weighting scheme of the type

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

was introduced. The P and S atoms were refined anisotropically and refinement of interlayer scale factors was discontinued. The form of the anisotropic temperature factors is

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

Towards the end of the refinement, hydrogen atoms were included in fixed positions at a distance of 1·075 Å from the carbon atoms to which they are bonded, and with a temperature factor of $B = 6{\cdot}5$ Å^2. The carbon atoms were then allowed to refine, and new hydrogen positions were calculated. In the final stages the carbon atoms were allowed to refine anisotropically

Table 4. *Observed and calculated structure factors*

h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc
0	-8	1	2.9	3.1	7	2	0	9.5	-10.5	-1	-6	1	3.7	3.3	-7	1	1	6.7	5.3	-4	-6	2	8.4	-7.0
0	-7	1	6.2	5.2	9	2	0	11.8	12.5	-10	-5	1	3.4	3.9	-6	1	1	8.2	-8.7	-2	-6	2	4.7	5.0
0	-4	1	18.1	20.8	10	2	0	7.1	7.6	-9	-5	1	3.0	2.5	-5	1	1	14.3	-16.7	-1	-6	2	5.5	5.2
0	-3	1	12.0	13.5	-10	3	0	3.7	2.9	-6	-5	1	3.8	-4.3	-4	1	1	19.0	-20.5	4	-6	2	2.3	-2.7
0	2	1	19.0	18.4	-8	3	0	4.0	2.8	-3	-5	1	5.9	-5.5	-3	1	1	16.1	-14.9	-10	-5	2	4.1	4.0
0	3	1	14.7	13.9	-7	3	0	4.2	2.9	0	-5	1	2.8	2.6	-2	1	1	16.5	16.7	-9	-5	2	4.7	4.1
0	4	1	10.2	10.9	-6	3	0	3.0	-3.0	1	-5	1	9.7	9.4	-1	1	1	38.7	46.9	-6	-5	2	2.7	-2.6
0	5	1	4.6	5.7	-5	3	0	2.8	-3.0	2	-5	1	7.1	7.4	0	1	1	17.6	20.1	-5	-5	2	2.8	-2.9
0	-7	2	8.7	7.2	-4	3	0	5.4	-4.8	4	-5	1	7.0	-7.0	1	1	1	14.4	-13.5	-3	-5	2	3.7	2.8
0	-6	2	5.1	5.1	-3	3	0	10.7	-9.9	5	-5	1	9.7	-9.6	2	1	1	14.8	-14.4	-2	-5	2	6.2	-6.2
0	-4	2	13.8	14.8	-2	3	0	9.3	-10.2	-7	-4	1	8.9	7.8	3	1	1	9.1	-8.1	-1	-5	2	8.3	-8.2
0	-2	2	6.2	-5.1	-1	3	0	1.4	-1.5	-6	-4	1	9.9	9.0	4	1	1	3.3	-3.4	1	-5	2	9.8	10.3
0	2	2	4.7	4.7	0	3	0	21.7	24.8	-5	-4	1	2.8	-3.4	5	1	1	1.6	2.0	2	-5	2	9.6	9.7
0	4	2	10.1	10.0	1	3	0	21.7	25.9	-4	-4	1	14.5	-14.4	-10	2	1	4.8	4.8	3	-5	2	4.7	4.2
0	5	2	5.4	4.7	2	3	0	6.9	7.1	-3	-4	1	16.6	-16.7	-9	2	1	7.8	7.0	4	-5	2	2.8	-3.0
0	-7	3	12.4	9.6	3	3	0	6.1	-5.8	-2	-4	1	11.6	-11.6	-8	2	1	7.6	6.8	5	-5	2	7.9	-9.0
0	-6	3	4.4	4.6	4	3	0	18.2	-20.4	-1	-4	1	6.3	6.2	-6	2	1	7.6	-7.4	-8	-4	2	5.5	4.9
0	-4	3	18.3	20.5	5	3	0	15.6	-18.4	1	-4	1	18.6	20.2	-5	2	1	10.2	-10.9	-7	-4	2	3.9	3.6
0	-2	3	4.8	-5.3	6	3	0	3.2	-3.3	2	-4	1	7.4	7.3	-4	2	1	10.5	-9.7	-6	-4	2	3.2	3.1
0	0	3	15.1	14.7	7	3	0	4.5	4.7	3	-4	1	7.7	-7.6	-3	2	1	4.6	4.2	-5	-4	2	2.5	2.4
0	1	3	9.6	9.5	8	3	0	7.4	7.5	4	-4	1	13.7	-13.1	-2	2	1	1.2	1.3	-4	-4	2	14.2	-14.3
0	4	3	4.5	4.8	9	3	0	7.3	7.2	5	-4	1	12.8	-13.1	-1	2	1	5.8	4.7	-3	-4	2	12.5	-12.7
0	-7	4	7.1	6.0	10	3	0	3.1	3.2	-11	-3	1	1.8	-1.9	1	2	1	5.0	-4.6	-2	-4	2	5.4	-5.9
0	-4	4	13.2	12.6	-9	4	0	3.7	2.8	-9	-3	1	9.0	7.8	3	2	1	8.3	8.7	-1	-4	2	4.0	-3.7
0	-3	4	13.1	12.8	-8	4	0	4.4	3.3	-8	-3	1	10.9	9.7	5	2	1	8.0	-8.6	1	-4	2	19.4	20.5
0	-2	4	9.5	9.4	-7	4	0	8.6	5.9	-7	-3	1	8.7	7.6	6	2	1	8.9	-11.2	2	-4	2	11.6	12.2
0	-1	4	4.1	3.8	-5	4	0	8.8	-7.3	-6	-3	1	3.8	-4.4	7	2	1	5.0	-5.1	3	-4	2	5.0	-5.0
0	1	4	6.3	6.4	-4	4	0	14.6	-12.0	-5	-3	1	16.5	-16.7	-10	3	1	1.7	1.9	4	-4	2	11.5	-13.2
0	-7	5	2.9	2.7	-3	4	0	13.5	-13.5	-4	-3	1	25.9	-26.7	-5	3	1	4.8	5.1	5	-4	2	6.8	-7.8
0	-6	5	3.4	3.5	-1	4	0	12.0	11.9	-3	-3	1	15.6	-14.6	-4	3	1	5.2	-5.4	-11	-3	2	4.3	-4.3
0	-3	5	9.8	10.7	0	4	0	17.7	18.6	-2	-3	1	21.5	24.9	-3	3	1	13.0	-13.3	-9	-3	2	5.0	4.5
0	-2	5	9.6	9.1	1	4	0	19.7	21.9	-1	-3	1	21.2	24.0	-2	3	1	9.2	-8.8	-8	-3	2	16.3	14.6
0	1	5	5.4	5.6	2	4	0	4.4	-3.9	1	-3	1	3.8	4.1	-1	3	1	9.5	-10.1	-7	-3	2	25.2	20.5
0	-7	6	2.5	2.2	3	4	0	16.2	-18.0	2	-3	1	7.6	-8.2	1	3	1	24.8	26.1	-6	-3	2	5.2	-5.9
0	-3	6	3.4	4.2	4	4	0	11.4	-12.3	3	-3	1	8.8	-9.2	2	3	1	10.3	10.8	-5	-3	2	18.5	-20.6
2	0	0	22.7	-22.0	5	4	0	7.2	-7.7	4	-3	1	4.8	-5.0	3	3	1	2.5	2.2	-4	-3	2	27.6	-26.0
3	0	0	25.9	-27.0	6	4	0	2.0	2.2	-10	-2	1	7.2	6.9	4	3	1	12.6	-12.0	-3	-3	2	25.5	-26.3
4	0	0	39.8	-41.7	7	4	0	4.9	5.8	-9	-2	1	15.6	13.7	5	3	1	15.5	-16.6	-2	-3	2	13.8	14.6
5	0	0	8.7	-9.1	8	4	0	4.2	3.7	-8	-2	1	8.4	7.6	6	3	1	8.7	-10.4	-1	-3	2	22.0	25.6
6	0	0	3.7	3.2	9	4	0	2.3	2.6	-6	-2	1	14.2	-15.3	-8	4	1	2.7	2.5	0	-3	2	18.7	22.8
7	0	0	7.9	8.8	-8	5	0	4.0	3.5	-5	-2	1	23.9	-26.5	-7	4	1	4.7	3.6	1	-3	2	11.7	13.4
8	0	0	9.9	11.0	-6	5	0	4.3	-2.8	-4	-2	1	5.0	-4.4	-4	4	1	5.5	-5.2	2	-3	2	6.6	-6.9
-11	1	0	2.7	-2.7	-5	5	0	8.5	-6.6	-3	-2	1	1.9	-2.5	-3	4	1	12.2	-13.2	3	-3	2	8.2	-9.2
-10	1	0	3.0	3.1	-4	5	0	4.8	-4.3	-2	-2	1	19.6	20.9	-2	4	1	4.3	-4.8	4	-3	2	11.2	-13.3
-9	1	0	11.2	9.4	-2	5	0	3.9	3.1	-1	-2	1	34.8	43.1	-1	4	1	8.3	8.0	5	-3	2	5.8	-5.6
-8	1	0	12.0	9.8	-1	5	0	9.0	8.0	0	-2	1	15.7	-16.6	1	4	1	13.9	13.7	-11	-2	2	2.9	-2.6
-7	1	0	3.8	3.2	0	5	0	1.9	1.4	1	-2	1	11.2	-11.7	2	4	1	2.8	2.5	-10	-2	2	3.5	3.2
-6	1	0	12.5	-11.9	3	5	0	4.1	-3.8	2	-2	1	2.8	2.9	3	4	1	7.0	-7.2	-9	-2	2	12.8	11.3
-5	1	0	10.9	-12.0	6	5	0	3.9	-3.5	3	-2	1	4.6	4.8	4	4	1	7.4	-7.9	-8	-2	2	8.6	7.8
-4	1	0	19.9	-21.8	7	5	0	3.0	-3.0	4	-2	1	3.2	3.3	5	4	1	6.2	-6.5	-7	-2	2	10.6	9.1
-3	1	0	18.7	-16.5	9	5	0	3.1	3.1	-12	-1	1	1.5	-2.7	-6	5	1	2.1	-1.8	-6	-2	2	4.4	-4.0
-2	1	0	29.3	28.0	-6	6	0	2.7	-2.2	-11	-1	1	2.2	2.5	-5	5	1	6.9	-6.0	-5	-2	2	26.4	-29.2
-1	1	0	6.9	7.4	-5	6	0	3.0	-2.2	-10	-1	1	4.0	4.6	-4	5	1	5.2	-4.7	-4	-2	2	12.5	-12.3
0	1	0	23.1	29.2	2	6	0	6.1	4.4	-9	-1	1	5.1	5.0	-1	5	1	7.8	6.7	-3	-2	2	1.8	1.4
1	1	0	26.5	30.9	3	6	0	4.6	3.5	-7	-1	1	2.6	-2.4	2	5	1	2.0	-2.9	-2	-2	2	9.1	8.8
2	1	0	28.0	-31.1	4	6	0	2.6	-2.1	-6	-1	1	12.4	11.2	3	5	1	2.4	-2.3	-1	-2	2	10.1	12.9
3	1	0	10.7	-10.7	5	6	0	5.6	-4.4	-5	-1	1	7.6	-6.2	-5	6	1	1.4	-1.4	1	-2	2	13.9	14.2
6	1	0	3.5	-3.8	6	6	0	4.5	-4.5	-4	-1	1	18.3	-14.9	1	6	1	3.2	3.0	2	-2	2	5.3	5.1
7	1	0	6.6	-7.6	-4	7	0	2.2	-2.0	-3	-1	1	4.9	-5.2	2	6	1	2.8	2.2	-11	-1	2	2.9	2.8
8	1	0	3.0	3.5	-3	7	0	2.7	-2.4	-2	-1	1	48.6	-42.4	5	6	1	2.6	-2.8	-10	-1	2	3.8	3.6
9	1	0	6.2	6.5	0	7	0	5.8	3.7	1	-1	1	16.1	17.5	-3	-8	2	2.5	-2.4	-9	-1	2	4.8	4.6
10	1	0	4.4	4.3	1	7	0	7.9	5.6	2	-1	1	34.3	37.2	-2	-8	2	3.2	-3.0	-7	-1	2	4.7	-4.6
11	1	0	4.4	4.0	2	7	0	3.4	2.3	-8	0	1	6.0	5.4	0	-8	2	2.6	2.6	-6	-1	2	4.1	3.1
-10	2	0	6.2	4.6	3	7	0	2.7	-2.0	-7	0	1	4.5	4.9	1	-8	2	3.8	4.0	-4	-1	2	3.1	-3.2
-9	2	0	8.8	7.6	4	7	0	5.0	-4.5	-6	0	1	12.4	12.0	2	-8	2	1.5	1.8	-2	-1	2	11.6	-11.9
-8	2	0	6.2	5.3	5	7	0	4.0	-4.2	-5	0	1	9.6	8.3	-7	-7	2	3.0	3.2	-8	0	2	5.1	4.9
-7	2	0	8.1	-6.4	-1	-8	1	2.0	1.1	-4	0	1	39.8	-37.7	-5	-7	2	5.7	-4.9	-7	0	2	12.0	10.4
-6	2	0	17.6	-15.0	1	-8	1	2.4	3.2	-3	0	1	33.3	-37.0	-4	-7	2	11.2	-8.7	-6	0	2	5.1	5.3
-5	2	0	6.8	-7.4	-5	-7	1	5.2	-5.2	-2	0	1	13.0	-11.6	-3	-7	2	5.7	-4.5	-5	0	2	5.0	-5.0
-4	2	0	8.8	7.4	-4	-7	1	8.3	-6.4	-1	0	1	7.5	6.5	-1	-7	2	7.4	6.3	-4	0	2	14.2	-15.5
-3	2	0	6.5	5.6	-1	-7	1	6.2	4.6	1	0	1	38.9	33.2	1	-7	2	2.9	2.8	-3	0	2	26.5	-25.5
-2	2	0	3.5	3.5	3	-7	1	3.0	-2.7	2	0	1	16.7	13.5	3	-7	2	4.5	-4.4	-2	0	2	12.2	-11.6
0	2	0	8.6	-9.5	-8	-6	1	5.9	5.4	3	0	1	12.0	-11.8	4	-7	2	3.6	-3.2	-1	0	2	20.7	18.6
1	2	0	2.1	2.3	-6	-6	1	8.9	-7.8	4	0	1	23.4	-24.0	-9	-6	2	4.6	5.2	0	0	2	19.6	18.8
2	2	0	12.1	13.2	-5	-6	1	8.7	-7.4	5	0	1	13.9	-13.6	-8	-6	2	9.1	8.1	1	0	2	21.3	19.5
3	2	0	7.5	7.8	-4	-6	1	7.5	-6.1	-10	1	1	2.8	2.5	-7	-6	2	3.3	3.4	2	0	2	19.9	17.0
5	2	0	8.2	-9.4	-3	-6	1	3.7	3.2	-9	1	1	8.6	8.5	-6	-6	2	8.2	-7.0	3	0	2	3.0	-3.5
6	2	0	9.9	-13.0	-2	-6	1	11.5	9.7	-8	1	1	12.4	11.3	-5	-6	2	12.0	-9.7	4	0	2	17.7	-20.5

Table 4 (*cont.*)

h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc
5	0	2	13.6	-13.9	-4	-6	3	6.8	-6.8	6	0	3	3.5	-3.9	3	-5	4	3.6	3.9	2	3	4	5.1	5.8
-11	1	2	2.0	-2.5	-2	-6	3	2.5	2.3	-10	1	3	2.5	-3.2	-7	-4	4	3.2	2.2	3	3	4	1.7	2.1
-9	1	2	6.3	5.9	-1	-6	3	3.7	3.9	-9	1	3	2.3	2.7	-6	-4	4	7.9	7.3	5	3	4	1.5	-2.6
-8	1	2	10.1	9.6	-10	-5	3	3.1	3.5	-8	1	3	7.7	7.5	-5	-4	4	9.3	8.3	-3	4	4	1.4	-2.5
-7	1	2	11.8	11.0	-9	-5	3	7.1	7.7	-7	1	3	8.0	7.1	-4	-4	4	4.7	-4.4	-2	4	4	2.2	-3.2
-6	1	2	5.6	6.1	-8	-5	3	5.7	5.4	-6	1	3	8.5	7.8	-3	-4	4	12.4	-11.6	1	4	4	2.0	2.9
-5	1	2	15.9	-20.7	-7	-5	3	6.8	-6.0	-5	1	3	6.6	-7.5	-2	-4	4	16.4	-16.1	2	4	4	4.1	3.8
-4	1	2	24.5	-27.6	-6	-5	3	6.5	-5.8	-4	1	3	15.3	-16.7	-1	-4	4	10.7	-10.5	-3	-8	5	1.7	-1.1
-3	1	2	11.2	-11.1	-5	-5	3	3.3	-2.6	-3	1	3	11.3	-10.6	1	-4	4	12.8	-14.8	-2	-8	5	3.1	-2.5
-2	1	2	2.4	-2.1	-3	-5	3	4.3	3.6	-2	1	3	5.7	-5.0	2	-4	4	8.1	9.1	-1	-8	5	3.1	-3.0
-1	1	2	29.6	30.1	-2	-5	3	3.4	-3.2	-1	1	3	9.4	8.2	3	-4	4	4.3	4.7	-7	-7	5	4.2	5.2
0	1	2	27.4	26.6	-1	-5	3	3.7	-3.6	1	1	3	13.6	11.4	-11	-3	4	2.9	-3.3	-6	-7	5	3.3	3.6
1	1	2	3.7	2.6	1	-5	3	4.3	4.2	2	1	3	10.6	9.4	-10	-3	4	4.1	-2.8	-4	-7	5	5.6	-4.5
2	1	2	3.2	-2.8	2	-5	3	8.6	8.7	3	1	3	7.6	-7.0	-9	-3	4	3.6	2.7	-3	-7	5	9.1	-7.9
3	1	2	10.9	-9.5	3	-5	3	2.5	2.6	4	1	3	6.1	-5.7	-8	-3	4	10.0	7.7	-2	-7	5	3.0	-2.4
4	1	2	6.8	-6.7	-8	-4	3	8.7	7.0	5	1	3	4.0	-3.6	-7	-3	4	9.9	7.7	1	-7	5	4.3	4.8
5	1	2	5.0	-5.5	-7	-4	3	7.2	6.4	6	1	3	4.1	-5.1	-6	-3	4	6.6	5.8	-8	-6	5	5.1	5.6
-10	2	2	2.0	1.9	-5	-4	3	5.1	4.2	-9	2	3	1.4	2.4	-4	-3	4	12.4	-13.1	-7	-6	5	6.5	7.8
-9	2	2	4.3	4.3	-4	-4	3	9.5	-8.2	-8	2	3	5.0	5.8	-3	-3	4	17.9	-19.2	-6	-6	5	3.2	3.2
-8	2	2	6.6	6.2	-3	-4	3	15.6	-15.8	-6	2	3	3.9	-3.4	-2	-3	4	7.6	-7.8	-5	-6	5	6.9	-6.9
-5	2	2	2.5	-3.0	-2	-4	3	15.1	-16.3	-5	2	3	4.1	-5.2	-1	-3	4	4.2	4.7	-4	-6	5	8.1	-7.8
-4	2	2	12.5	-13.5	-1	-4	3	4.8	-4.8	-4	2	3	5.0	-5.7	1	-3	4	12.2	14.0	-3	-6	5	6.5	-6.7
-2	2	2	3.4	3.4	1	-4	3	15.2	17.2	-2	2	3	3.4	2.3	2	-3	4	2.8	2.8	-1	-6	5	6.5	6.6
-1	2	2	2.1	-2.1	2	-4	3	11.5	9.8	-1	2	3	3.0	1.9	-11	-2	4	3.0	-4.0	-9	-5	5	3.0	3.8
2	2	2	8.7	8.4	4	-4	3	12.6	-13.4	1	2	3	3.1	-2.6	-9	-2	4	6.6	6.1	-8	-5	5	2.0	3.0
3	2	2	8.2	7.9	5	-4	3	7.4	-7.2	2	2	3	7.1	6.7	-8	-2	4	14.3	13.2	-5	-5	5	3.2	-2.3
5	2	2	5.3	-5.6	-11	-3	3	5.1	-6.1	3	2	3	6.8	6.6	-7	-2	4	6.7	7.0	-4	-5	5	4.5	-4.0
6	2	2	12.4	-12.1	-10	-3	3	2.3	-2.4	6	2	3	4.6	-5.1	-6	-2	4	5.9	-5.7	-2	-5	5	3.0	-2.6
7	2	2	5.4	-5.5	-9	-3	3	2.6	2.7	-4	3	3	2.3	-2.1	-5	-2	4	10.2	-9.6	-1	-5	5	2.9	-2.5
-5	3	2	3.6	3.4	-8	-3	3	10.8	9.6	-3	3	3	2.2	-2.0	-4	-2	4	12.2	-11.0	2	-5	5	5.2	5.6
-3	3	2	7.3	-7.9	-7	-3	3	20.2	17.8	-2	3	3	3.6	-3.9	-3	-2	4	5.7	-6.4	-6	-4	5	5.2	4.4
-2	3	2	5.0	-5.2	-6	-3	3	5.2	4.8	-1	3	3	2.7	-3.2	2	-2	4	2.6	-1.9	-5	-4	5	6.2	5.4
-1	3	2	4.0	-4.3	-5	-3	3	8.6	-9.5	0	3	3	2.3	1.9	3	-2	4	2.3	1.8	-3	-4	5	7.4	-7.4
0	3	2	1.6	1.8	-4	-3	3	20.5	-19.9	1	3	3	4.8	5.1	-10	-1	4	2.6	2.4	-2	-4	5	7.0	-7.9
1	3	2	8.5	9.0	-3	-3	3	21.6	-22.1	2	3	3	6.1	6.4	-9	-1	4	4.3	4.2	-1	-4	5	5.7	-4.8
2	3	2	10.7	11.6	-2	-3	3	5.6	-5.8	3	3	3	4.9	5.2	-8	-1	4	3.2	3.6	1	-4	5	6.6	5.8
3	3	2	8.3	8.8	-1	-3	3	4.7	5.0	5	3	3	5.9	-6.2	-7	-1	4	4.1	4.3	2	-4	5	8.8	9.3
4	3	2	5.4	-5.6	0	-3	3	27.1	25.4	6	3	3	4.0	-4.3	-6	-1	4	2.2	-2.4	-7	-3	5	7.1	7.6
5	3	2	11.9	-10.6	1	-3	3	30.3	26.8	-6	4	3	2.2	3.2	-3	-1	4	5.8	-5.2	-6	-3	5	7.8	8.1
6	3	2	7.8	-7.9	2	-3	3	4.9	-4.7	-4	4	3	3.6	-4.6	-2	-1	4	6.3	-5.9	-4	-3	5	11.7	-9.9
7	3	2	4.8	-4.4	3	-3	3	5.9	-7.3	-3	4	3	5.2	-5.6	-1	-1	4	10.4	-9.7	-3	-3	5	12.2	-13.0
-8	4	2	1.2	1.7	4	-3	3	7.0	-8.3	-2	4	3	3.5	-3.8	1	-1	4	13.3	13.4	-2	-3	5	6.8	-9.8
-7	4	2	3.1	3.4	-11	-2	3	2.9	-2.9	1	4	3	7.7	7.0	2	-1	4	5.8	5.1	-7	-2	5	3.0	6.4
-6	4	2	2.3	2.5	-9	-2	3	11.3	10.0	2	4	3	4.7	4.4	3	-1	4	7.1	6.6	-6	-2	5	2.5	3.4
-5	4	2	2.4	-2.3	-8	-2	3	14.2	12.2	4	4	3	3.7	-3.9	5	-1	4	6.9	-7.9	-5	-2	5	2.2	-2.4
-4	4	2	5.6	-5.7	-7	-2	3	3.7	3.7	5	4	3	3.3	-4.0	-10	0	4	1.6	-1.9	-4	-2	5	10.2	-11.9
-3	4	2	8.3	-8.0	-6	-2	3	8.0	-8.2	-3	5	3	1.6	-2.9	-7	0	4	3.6	4.0	-3	-2	5	6.9	-7.3
-2	4	2	5.0	-4.7	-5	-2	3	14.3	-14.6	0	5	3	1.3	1.9	-6	0	4	4.9	5.9	-2	-2	5	1.5	-2.0
-1	4	2	4.4	4.1	-4	-2	3	8.5	-9.5	1	5	3	1.3	1.6	-5	0	4	3.5	3.6	-1	-2	5	1.2	1.0
1	4	2	7.3	7.9	-2	-2	3	7.1	7.9	-6	-8	4	1.4	2.0	-3	0	4	14.4	-13.5	1	-2	5	3.3	3.1
3	4	2	2.4	-2.1	1	-2	3	7.7	9.6	-3	-8	4	3.3	-3.3	-2	0	4	15.4	-13.5	3	-2	5	3.0	2.9
4	4	2	5.4	-4.7	2	-2	3	7.5	7.3	-2	-8	4	3.6	-4.5	-1	0	4	5.9	-6.0	-5	-1	5	1.8	3.0
5	4	2	6.4	-5.9	-10	-1	3	4.1	4.1	0	-8	4	2.0	1.8	0	0	4	2.9	2.2	-3	-1	5	6.1	-5.3
-5	5	2	1.9	-2.2	-9	-1	3	4.4	4.6	1	-8	4	2.3	3.2	1	0	4	21.9	19.9	-2	-1	5	2.5	-2.1
-4	5	2	4.6	-5.4	-8	-1	3	6.8	6.0	2	-8	4	2.1	3.4	2	0	4	14.8	13.0	-1	-1	5	6.4	-5.7
-3	5	2	3.6	-3.7	-7	-1	3	2.9	2.7	-7	-7	4	4.1	4.9	4	0	4	3.1	-3.0	0	-1	5	2.5	-2.2
-1	5	2	3.9	3.4	-6	-1	3	8.6	-8.5	-6	-7	4	3.1	4.8	5	0	4	7.4	-7.9	1	-1	5	5.8	5.0
1	5	2	3.2	2.9	-5	-1	3	5.2	-5.2	-4	-7	4	6.0	-6.4	-8	1	4	3.8	5.4	2	-1	5	5.1	5.0
3	5	2	2.1	-1.9	-4	-1	3	3.9	3.4	-3	-7	4	7.3	-8.1	-7	1	4	5.6	5.8	3	-1	5	7.5	6.8
2	6	2	1.8	2.2	-3	-1	3	2.1	-2.1	-2	-7	4	3.6	-3.8	-6	1	4	1.5	2.4	4	-1	5	2.5	2.4
-3	-8	3	2.9	-3.7	-2	-1	3	6.1	-6.6	1	-7	4	4.0	5.5	-5	1	4	2.8	-3.7	-3	0	5	7.5	-7.1
-2	-8	3	2.5	-3.4	-1	-1	3	7.3	-8.6	-9	-6	4	5.7	6.5	-4	1	4	4.8	-5.7	-2	0	5	9.4	-8.2
1	-8	3	3.0	3.7	0	-1	3	2.2	-2.1	-8	-6	4	7.4	7.3	-3	1	4	9.4	-8.1	-1	0	5	2.8	-2.5
2	-8	3	2.1	2.7	1	-1	3	10.1	9.5	-7	-6	4	3.8	4.1	-2	1	4	7.2	-6.5	0	0	5	1.7	1.5
-8	-7	3	3.0	4.6	2	-1	3	19.6	17.8	-5	-6	4	8.1	-8.0	-1	1	4	4.7	4.3	1	0	5	6.7	5.8
-7	-7	3	4.2	5.7	3	-1	3	8.9	9.1	-4	-6	4	8.7	-8.4	1	1	4	5.4	5.6	2	0	5	6.2	5.6
-6	-7	3	2.2	3.0	4	-1	3	4.8	-5.0	-3	-6	4	5.7	-5.7	2	1	4	7.2	5.1	3	0	5	4.3	3.5
-5	-7	3	2.4	-2.6	-11	0	3	1.5	-2.2	-2	-6	4	3.6	2.7	3	1	4	2.3	-2.0	5	0	5	3.1	-3.4
-4	-7	3	8.0	-8.1	-7	0	3	12.8	11.8	-1	-6	4	8.7	8.6	4	1	4	2.8	-2.6	-4	1	5	3.7	-4.4
-3	-7	3	8.2	-8.4	-6	0	3	9.2	9.7	0	-6	4	2.5	2.4	-8	2	4	3.9	3.8	-3	1	5	6.0	-6.4
-2	-7	3	4.3	-4.1	-5	0	3	5.2	-5.7	-10	-5	4	3.0	2.6	-7	2	4	2.7	3.7	-2	1	5	6.0	-4.9
-1	-7	3	5.4	5.1	-4	0	3	8.6	-8.5	-9	-5	4	6.6	5.8	-5	2	4	3.7	-5.1	1	1	5	6.9	5.6
1	-7	3	4.1	4.5	-3	0	3	19.6	-18.5	-8	-5	4	6.3	6.0	-4	2	4	3.9	-4.5	5	1	5	1.2	-1.8
4	-7	3	3.0	-3.9	-2	0	3	18.7	-18.0	-6	-5	4	2.5	-2.0	0	2	4	2.9	2.7	-3	2	5	2.5	-3.2
-9	-6	3	5.3	6.5	1	0	3	30.7	29.5	-5	-5	4	4.8	-3.8	1	2	4	2.3	2.0	-2	2	5	1.5	-1.6
-8	-6	3	6.1	6.3	2	0	3	13.9	12.9	-4	-5	4	3.1	-2.8	-3	3	4	1.4	-1.8	1	2	5	2.6	2.7
-7	-6	3	2.5	2.9	3	0	3	4.6	-4.8	-2	-5	4	7.7	-6.2	-2	3	4	2.9	-3.2	2	2	5	2.0	2.0
-6	-6	3	3.2	-3.0	4	0	3	10.6	-11.2	0	-5	4	3.5	3.6	-1	3	4	2.5	-3.0					
-5	-6	3	10.1	-8.8	5	0	3	13.2	-15.1	2	-5	4	7.0	6.5	1	3	4	3.8	4.4					

but this only reduced R by 1%. Two reflexions, -2, -3, 5 and -7, -2,5 which consistently gave very bad agreement and large values of $w\Delta F$ were excluded from the matrix, but not from the calculation of R. The final constants used in the calculation of weights were $A=1{\cdot}28$, $B=-0{\cdot}30$ and $C=0{\cdot}077$. The introduction of a negative value for B causes the weight/F_{obs} curve to pass through a maximum, and prevents extremely weak reflexions with a large experimental error being given excessively high weights. The final value of R

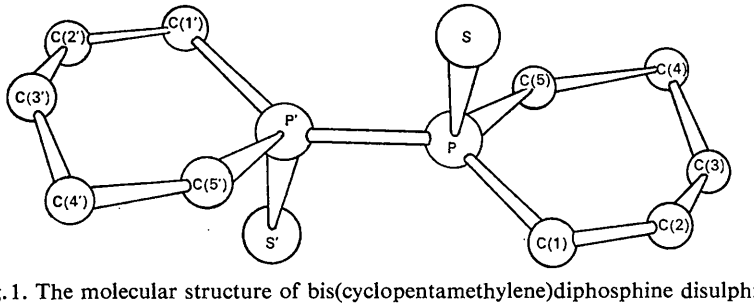


Fig. 1. The molecular structure of bis(cyclopentamethylene)diphosphine disulphide.

was 10·1%, based on 783 independent observed reflexions.

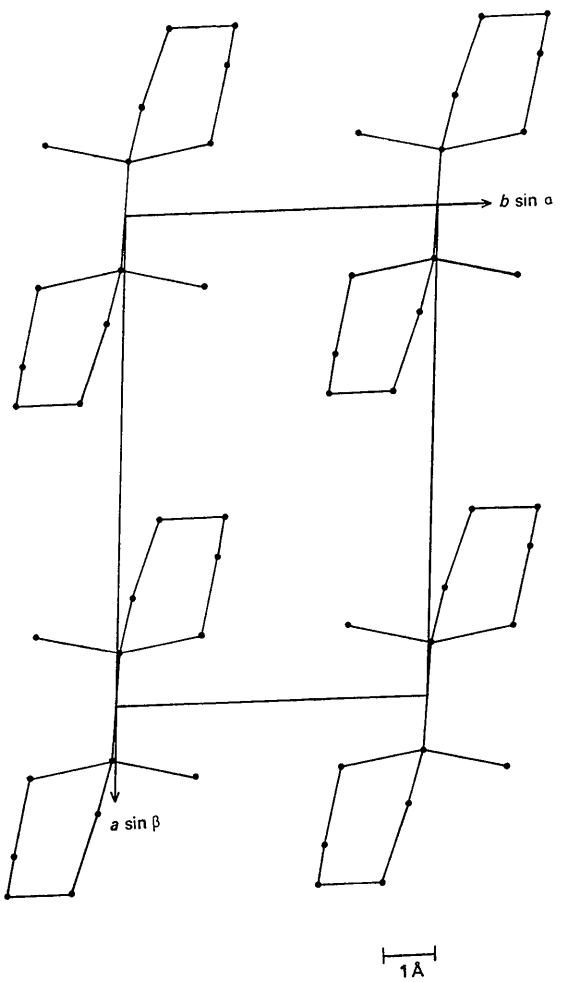


Fig. 2. A view of the structure down [001].

The final atomic coordinates are given in Table 1, the calculated positions of the hydrogen atoms are shown 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.

Discussion

A view of one molecule is given in Fig. 1, and the packing of molecules in the unit cell is shown in Fig. 2. The bond lengths and angles together with their estimated standard deviations are shown in Tables 6 and 7.

Table 6. *Bond lengths and their standard deviations*

	Distance	σ
P —P′	2·21 Å	0·004 Å
S——P	1·95	0·004
P —C(1)	1·81	0·007
P —C(5)	1·81	0·011
C(1)–C(2)	1·52	0·012
C(2)–C(3)	1·51	0·017
C(3)–C(4)	1·52	0·013
C(4)–C(5)	1·53	0·014

Table 7. *Bond angles and their standard deviations*

	Angle	σ
S —P —C(1)	114·8°	0·4°
S —P —C(5)	115·8	0·4
S —P —P′	112·7	0·2
C(1)–P —P′	105·8	0·3
C(5)–P —P′	104·7	0·4
C(1)–P —C(5)	101·8	0·4
P —C(1)–C(2)	108·7	0·5
P —C(5)–C(4)	108·9	0·8
C(1)–C(2)–C(3)	112·4	0·9
C(3)–C(4)–C(5)	113·0	0·8
C(2)–C(3)–C(4)	114·4	0·9

The molecule has the P–P bonded structure (I) and is centrosymmetrical about the mid point between the

Table 5. *Agreement analysis*

F_{obs}	Number of planes	R	sin θ	Number of planes	R	Layer	Number of planes	R
0–3	127	17·7%	0·10–0·15	1	25·0%	0*kl*	35	8·2%
3–6	263	11·3	0·15–0·20	7	12·5	*hk*0	109	11·9
6–9	163	10·0	0·20–0·25	9	10·6	*hk*1	150	9·4
9–12	80	10·7	0·25–0·30	16	9·2	*hk*2	156	8·8
12–15	62	8·0	0·30–0·35	18	8·2	*hk*3	147	9·6
15–18	24	9·2	0·35–0·40	32	9·1	*hk*4	116	11·8
18–21	26	9·3	0·40–0·45	34	6·6	*hk*5	70	13·5
21–24	11	11·4	0·45–0·50	44	7·1			
24–27	10	7·1	0·50–0·55	60	7·3			
27–30	6	7·3	0·55–0·60	56	8·1			
30–33	3	6·3	0·60–0·65	64	10·3			
33–36	3	12·9	0·65–0·70	75	10·3			
36–39	0	—	0·70–0·75	75	12·1			
39–42	4	11·4	0·75–0·80	66	12·6			
42–45	0	—	0·80–0·85	70	13·6			
45–48	0	—	0·85–0·90	48	13·3			
48–51	1	13·7	0·90–0·95	71	16·0			
			0·95–1·00	37	22·3			

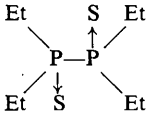
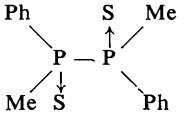
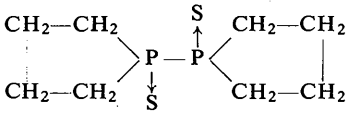
phosphorus atoms. The standard deviations of the P–P bond length and of the angles involving the P–P bond were calculated differently from the other standard deviations, to allow for the centre of symmetry at the mid point between the two phosphorus atoms (Cruickshank & Robertson, 1953). The observed P–P bond length of 2·21 Å compares closely with the values found in other diphosphine disulphides and almost all the known molecules containing P–P bonds. These are listed in Table 8. The only large deviations from this value are P_2 [where the dissociation energy corresponds to about 1·3 π-bonds per σ-bond (van Wazer, 1958)] and P_4S_7. There is no obvious explanation for the P–P bond length remaining so constant despite changes in the oxidation state of P, the size and electronegativity of the substituents, and the variation in bond angle.

The P–S bonds are shortened by back bonding from a full sulphur *p* orbital to an empty phosphorus *d* orbital. The observed length of 1·95 Å is close to the Pauling (1960) value of 1·92 Å for a double bond, and is compared with similar bonds in Table 9.

The P–C distances both of 1·81 Å are close to the values of 1·82 Å in dimethyldiphenyldiphosphine disulphide, 1·82 and 1·84 Å in tetraethyldiphosphine disulphide and 1·82 Å in bis(cyclotetramethylene)-diphosphine disulphide. The C–C bonds are all in the range 1·51–1·53 Å, and appear normal. The ring system is saturated, and is consequently puckered. The bond angles round C(1) and C(5) are slightly less than the usual tetrahedral value, whilst the angles at C(2), C(3) and C(4) are greater than tetrahedral.

The distribution of the bonds round each phosphorus atom is essentially tetrahedral, but two factors which cause a certain amount of distortion are the presence of a sulphur atom, and the inclusion of phosphorus in a heterocyclic ring. The three bond angles S–P–C(1), S–P–C(5) and S–P–P′ are all greater than tetrahedral (114·8, 115·8 and 112·7° respectively). The remaining three bond angles round the phosphorus atom C(1)–P–P′, C(5)–P–P′ and C(1)–P–C(5) are all less than tetrahedral (105·8, 104·7 and 101·8° respectively). The sulphur atom is large and because of π-bonding is rather close to the phosphorus atom, hence

Table 8. *Some* P–P *bond lengths*

Molecule	Bond length (Å)	Reference
	2·22 ± 0·006	Dutta & Woolfson (1961)
	2·21	Wheatley (1960)
	2·21 ± 0·004	Lee & Goodacre (1969)
P_2I_4	2·212 ± 0·06	Leung & Waser (1956)
P_4S_3	(average) 2·235 ± 0·005	Leung, Waser, van Houten, Vos, Weigers & Wiebenga (1957)
P_4S_5	2·20 2·21 ± 0·025	van Houten & Wiebenga (1957)
P_4S_7	2·35 ± 0·01	Vos & Wiebenga (1955, 1956)
P_4Se_3	2·25	Keulen & Vos (1959)
$P_4S_3I_2$	2·23 and 2·19 2·12 and 2·25 ± 0·04	Wright & Penfold (1959)
P_2	1·893	Douglas & Rao (1958)
P_4	2·21 ± 0·02	Maxwell, Hendricks & Mosley (1935)
Black phosphorus	2·18	Hultgren, Gingrich & Warren (1935)
$(PO_2)_6^{6-}$	(average) 2·20	Weiss (1960)
$(PCF_3)_4$	2·213 ± 0·005	Palenik & Donohue (1962)
$(PCF_3)_5$	2·223	Spencer & Lipscomb (1961, 1962)

repulsive forces between the sulphur atom and the other three atoms bonded to the phosphorus atom account for the distortion. The angle C(1)–P–C(5) is reduced more than the others, and this further distortion arises from the inclusion of two bonds from a phosphorus atom in a ring system. The strain caused in this way by a 6-membered heterocyclic ring would be expected to be less than in a 5-membered heterocyclic ring. The C–P–C angles in bis(pentamethylene)diphosphine disulphide = 101·8° and bis(tetramethylene)-diphosphine disulphide = 96·6° are in accord with this, and may be compared with the value of 107·3° in the unstrained tetraethyldiphosphine disulphide.

Ignoring contacts between hydrogen atoms, the shortest intermolecular contact is 3·63 Å, (between two carbon atoms) and all those below 4·0 Å are listed in Table 10. Disregarding the hydrogen atoms, intramolecular distances below 4·0 Å are shown in Table 11. Most of these are unavoidable distances across rings, but the distances S···C(1) = 3·17 Å and S···C(5) = 3·19 Å are particularly short, and account for bond angles S–P–C(1) and S–P–C(5) increasing from tetrahedral to 114·8 and 115·8° respectively. The distance P···S′ = 3·47 Å is of interest, and provides additional evidence that the van der Waals radius of S should be less than the Pauling (1960) value of 1·85 Å. A value of 1·72–1·73 Å has been suggested by Fava Gasparri, Nardelli & Villa (1967), Nardelli, Fava Gasparri, Giraldi Battistina & Domiano (1966), Ždanov & Zvonkova (1950), Van der Helm, Lessor & Merritt (1960), Lee & Bryant (1969*a*,*b*). Even accepting the smaller van der Waals radius of 1·72 Å for sulphur plus 1·90 Å for phosphorus, this contact is still short, and contributes to the distortion of the bonds round the phosphorus atom.

Table 10. *Intermolecular distances less than* 4·0 Å *(excluding hydrogen atoms)*

	Distance	Symmetry operation applied to second atom
S · · · · · C(1)	3·91 Å	(1)
S · · · · · C(2)	3·87	(1)
S · · · · · C(3)	3·97	(2)
C(5) · · · S	3·99	(3)
C(5) · · · C(1)	3·98	(3)
C(5) · · · C(2)	3·82	(3)
C(3) · · · C(3)	3·63	(4)
S · · · · · C(5)	3·99	(5)
C(1) · · · C(5)	3·98	(5)
C(2) · · · C(5)	3·82	(5)
S · · · · · S	3·93	(6)

Key to symmetry operations

(1)	x,	$1+y$,	$1+z$
(2)	x,	$1+y$,	z
(3)	x,	y,	$1+z$
(4)	$1-x$,	$1-y$,	$-z$
(5)	x,	y,	$z-1$
(6)	$-x$,	$3-y$,	$-z$

Table 11. *Distances of less than* 4·0 Å *between atoms in the same molecule which are not directly bonded* Hydrogen atoms are excluded.

	Distance
P · · · · · S′	3·47 Å
P · · · · · C(2)	2·71
P · · · · · C(3)	3·13

Table 9. *Some* P–S *bond lengths*

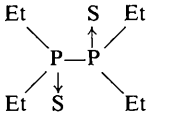
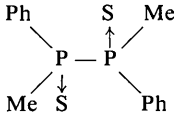
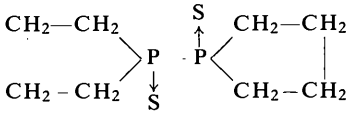
Molecule	Bond length (Å)	Reference
	1·94 ± 0·005	Dutta & Woolfson (1961)
	1·98	Wheatley (1960)
	1·95 ± 0·002	Lee & Goodacre (1969)
$P_4O_6S_4$	1·85 ± 0·02	Stosick (1939)
PSF_3	1·87 ± 0·03 1·86	Williams, Sheridan & Gordy (1952) Hawkins, Cohen & Koski (1952)
$PSCl_3$	1·85 ± 0·02	Williams, Sheridan & Gordy (1952)
$PSBr_3$ $PSBr_2F$ $PSBrF_2$	1·89 ± 0·06 1·87 ± 0·05 1·87 ± 0·05	Secrist & Brockway (1941)

Table 11 (*cont.*)

P · · · · · C(4)	2·73
P · · · · · C(1′)	3·21
P · · · · · C(5′)	3·19
S · · · · · C(1)	3·17
S · · · · · C(2)	3·62
S · · · · · C(4)	3·66
S · · · · · C(5)	3·19
S · · · · · C(1′)	3·81
S · · · · · C(5′)	3·77
C(1) · · · C(3)	2·52
C(1) · · · C(4)	3·08
C(1) · · · C(5)	2·81
C(1) · · · C(5′)	3·78
C(2) · · · C(4)	2·55
C(2) · · · C(5)	3·09
C(3) · · · C(5)	2·55
C(5) · · · C(1′)	3·78

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