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The Crystal Structure of Bis(Cyclotetramethylene)diphosphine Disulphide

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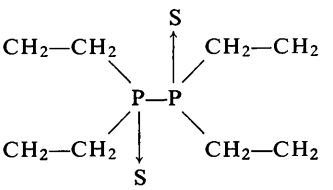
The crystal structure of bis(cyclotetramethylene)diphosphine disulphide,



has been determined from three-dimensional X-ray diffraction data. The unit cell is triclinic with space group $P\bar{1}$ (number 2), dimensions $a=7{\cdot}65$, $b=6{\cdot}90$, $c=5{\cdot}88$ Å; $\alpha=75°30'$, $\beta=104°15'$, $\gamma=92°36'$, and contains one molecule. The structure was refined by Fourier and full-matrix least-squares methods on 771 independent observed reflexions to $R=10{\cdot}4\%$. The molecule possesses a centre of symmetry at the mid-point between the two phosphorus atoms and the two sulphur atoms are *trans* to each other. The environment of each phosphorus atom is that of a distorted tetrahedron; the inclusion of phosphorus in a ring system reduces the angle C–P–C from tetrahedral to 96·6°. The ring system is saturated and consequently puckered.

Experimental

A sample of bis(cyclotetramethylene)diphosphine disulphide prepared by Dr R. Schmutzler (see Schmutzler 1964) was recrystallized from toluene–ethanol (3:1). Crystals were in the form of colourless needles elongated along **c**. Crystals of dimensions $0{\cdot}31\times0{\cdot}14\times0{\cdot}09$ mm and $0{\cdot}22\times0{\cdot}11\times0{\cdot}08$ mm were used to collect data along the *c* and *a* axes respectively. Three-dimensional equi-inclination Weissenberg data were collected photographically, allowing the observation of 771 independent reflexions. Intensities were measured visually and converted to $|F|$ and $|F|^2$ by applying Lorentz and polarization corrections. No corrections were made for absorption or extinction, and reflexions too weak to be observed were ignored.

Crystal data

$C_8H_{16}P_2S_2$, $M=238{\cdot}3$.
Triclinic $a=7{\cdot}65$, $b=6{\cdot}90$, $c=5{\cdot}88$, all $\pm0{\cdot}02$ Å;
$\alpha=75°30'$, $\beta=104°15'$, $\gamma=92°36''$ all $\pm30'$.
$U=291{\cdot}2$ Å^3, $Z=1$, $D_m=1{\cdot}32$ g.cm^{-3},
$D_c=1{\cdot}359$ g.cm^{-3}. $F_{000}=126$, Cu $K\alpha$, $\lambda=1{\cdot}542$ Å, $\mu=61{\cdot}4$ cm^{-1}. No consistently absent reflexions, space group $P1$ or $P\bar{1}$ (assumed to be $P\bar{1}$).

Structure analysis

The orientation of the P and S atoms was found from an *hk*0 Patterson summation, and two possible orientations of the ring carbon atoms were suggested. Both trial structures were centrosymmetric. A negative pyroelectric test indicated a centre of symmetry, although the statistical test (Howells, Phillips & Rogers, 1950; Sim, 1958) on the *hk*0 data was inconclusive. The space group was assumed initially to be $P\bar{1}$, and this choice was justified by the subsequent refinement. The unit cell contains one molecule, and the mid point of the P–P bond was placed on the centre of symmetry at the origin. Structure-factor calculations were performed by the use of scattering factors due to Hanson, Herman, Lea & Skillman (1964) and these indicated the correct trial structure. All the atoms in this projection were well resolved, and the positional and isotropic temperature factors were refined by Fourier and block-diagonal least-squares methods by computer programs written

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

	x/a	*y/b*	*z/c*	σ *x/a*	σ *y/b*	σ *z/c*
S	0·1812	1·2129	−0·2832	0·0003	0·0003	0·0004
P	0·1338	0·9851	−0·0333	0·0002	0·0002	0·0003
C(1)	0·1422	0·7341	−0·0780	0·0011	0·0009	0·0014
C(2)	0·3073	0·6350	0·1119	0·0013	0·0012	0·0018
C(3)	0·3259	0·7130	0·3367	0·0012	0·0012	0·0017
C(4)	0·2962	0·9376	0·2598	0·0011	0·0010	0·0014

by Mr G.S.D. King (Union Carbide European Research Associates) on an IBM 1620 computer. By the use of unit weights the reliability index, R, was reduced to 10·8%. By a similar process the $0kl$ data were refined, to $R=25·6\%$, though the atoms were much less clearly resolved. Full three-dimensional data were then used, first with unit weights, then with a weighting scheme

$$w=0·5+\frac{0·4}{|F_o|}+\frac{0·02}{|F_o|^2}.$$

Convergence occured at $R=16·1\%$.

Refinement was continued by the use of the *X-ray* 63 full-matrix least-squares method on the SRC Chilton Atlas computer. The same atomic scattering factors were used as before, but those for P and S were modified for both the real and imaginary parts of anomalous dispersion (Dauben & Templeton, 1955). The P and S atoms were refined anisotropically, and the final weighting scheme used was

$$w=\frac{1}{A+B|F_o|+C|F_o|^2},$$

with chosen values of $A=13$, $B=1$ and $C=1·2$. At $R=13·8\%$, the positions of hydrogen atoms were calculated assuming a C–H bond length of 1·075 Å. The $1\bar{7}2$ reflexion, which consistently gave very bad agreement and a large value of $w\Delta F$, was excluded from the least-squares matrix, but not from the calculation of R. Hydrogen atoms were included in the structure factor calculations, with isotropic temperature factors of $B=5·0$ Å^2. The hydrogen parameters were not refined, but after each cycle of refinement of the P, S and C atoms, new H positions were calculated. The final value of R was 10·4%, based on 771 independent observed reflexions.

The final atomic coordinates and their estimated standard deviations are given in Table 1, the calculated hydrogen positions are given in Table 2, and the final temperature factors are shown in Table 3. The observed and calculated structure factors are listed in Table 4, and agreement analysis is given in Table 5.

Table 2. *Calculated positions of hydrogen atoms*

	x/a	*y/b*	*z/c*
H(1)	0·0223	0·6539	−0·0506
H(11)	0·1565	0·7406	−0·2571
H(2)	0·2915	0·4754	0·1566
H(12)	0·4257	0·6709	0·0429
H(3)	0·2270	0·6446	0·4323
H(13)	0·4587	0·6778	0·4527
H(4)	0·2428	0·9877	0·3885
H(14)	0·4205	1·0124	0·2434

Discussion

A representation of one molecule is shown in Fig. 1 and the packing of molecules is shown in Fig. 2. Bond lengths and bond angles together with their estimated standard deviations are given in Tables 6 and 7. The structure is centrosymmetric about the mid point between the phosphorus atoms, which are separated by 2·21 Å. This distance is in close agreement with the value of 2·20 Å for a single bond (Pauling, 1960), 2·21 Å in 1,2-dimethyl 1,2-diphenyl diphosphine disulphide

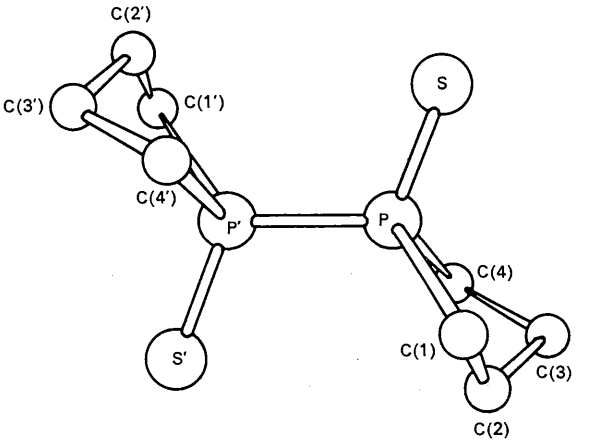


Fig. 1. The molecular structure of bis(cyclotetramethylene)-diphosphine disulphide.

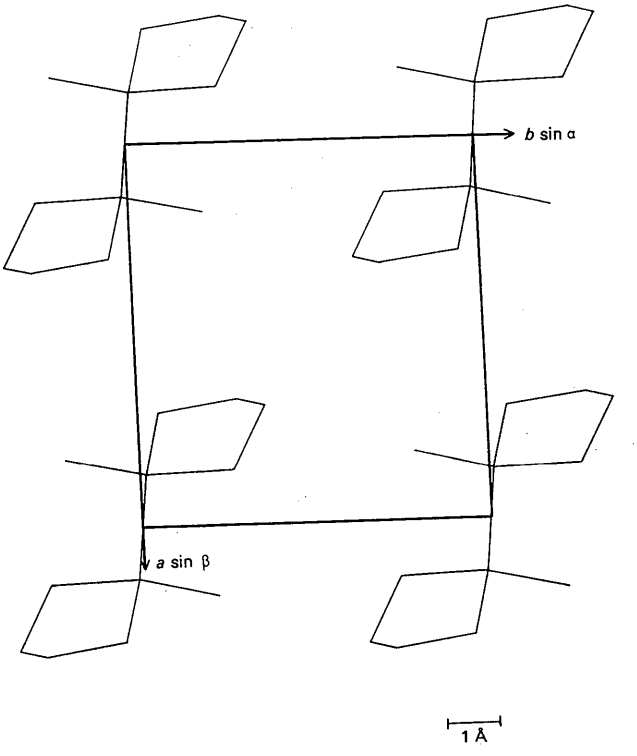


Fig. 2. A view of the structure down [001].

(Wheatley, 1960), and 2·22 Å in tetraethyl diphosphine disulphide (Dutta & Woolfson, 1961). The two sulphur atoms are *trans* to each other, and the P–S bonds are shortened by back bonding from a full *p* orbital on the sulphur to an empty *d* orbital on the phosphorus. The observed bond length of 1·95 Å is close to the Pauling (1960) value of 1·92 Å for a double bond, and compares with 1·98 Å in dimethyl diphenyl diphosphine di-

Table 3. *Final temperature factor parameters*

All the hydrogen atoms were assumed to have isotropic temperature factors of $B = 5{\cdot}00$ Å^2.

For anisotropic vibration the smearing function is given by

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

	B (Å^2)	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
S		3·90	3·04	3·48	−0·38	1·11	0·19
P		1·77	2·02	2·42	0·06	0·22	−0·51
C(1)	2·96						
C(2)	4·31						
C(3)	4·19						
C(4)	3·23						

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	1	0	28.3	31.5	6	0	0	17.1	15.5	0	4	2	3.2	3.1	1	1	-2	29.4	26.5	2	-6	-5	10.8	-10.8
0	2	0	11.0	-9.3	6	1	0	6.7	-5.5	0	4	3	15.2	16.3	1	1	-1	25.3	20.9	2	-6	-4	4.7	-4.2
0	3	0	21.1	20.6	6	2	0	8.9	-8.7	0	4	4	3.3	3.4	1	1	1	30.0	32.3	2	-6	-3	3.5	-3.6
0	4	0	23.9	24.7	6	4	0	4.1	3.8	0	4	5	3.6	-3.8	1	1	2	28.3	29.1	2	-6	-2	12.4	-13.9
0	5	0	17.8	16.8	6	6	0	5.7	-5.2	0	5	1	13.2	12.7	1	1	3	7.5	5.9	2	-6	-1	8.8	-9.7
0	6	0	4.3	4.3	7	-5	0	5.5	6.2	0	5	2	6.1	-5.8	1	1	4	4.9	3.8	2	-6	0	4.0	2.9
0	8	0	2.3	3.1	7	-3	0	5.3	5.9	0	5	4	5.9	6.5	1	1	5	8.9	9.0	2	-6	2	6.0	-6.9
1	-8	0	4.9	-4.3	7	-2	0	13.6	12.0	0	6	1	15.4	15.7	1	1	6	2.8	3.3	2	-5	-7	2.8	-3.2
1	-6	0	8.8	6.6	7	-1	0	12.9	12.6	0	6	2	8.5	8.2	1	2	-3	10.9	-10.2	2	-5	-5	7.8	-8.0
1	-5	0	9.6	7.8	7	0	0	12.4	12.1	0	6	4	3.8	3.7	1	2	-2	19.2	14.7	2	-5	-4	7.9	-9.7
1	-4	0	9.5	-7.8	7	1	0	6.0	5.2	0	6	5	4.6	4.5	1	2	-1	24.6	21.7	2	-5	-3	1.2	1.1
1	-3	0	12.4	-11.8	7	3	0	12.9	12.2	0	6	6	2.5	-2.6	1	2	1	2.8	-2.5	2	-5	-2	6.4	-6.9
1	-2	0	17.1	15.3	7	4	0	11.1	10.5	0	7	1	8.5	7.1	1	2	2	22.7	24.0	2	-5	-1	17.4	-19.8
1	-1	0	10.5	11.6	8	-3	0	4.0	4.8	0	7	2	10.4	9.8	1	2	3	18.0	19.8	2	-5	2	6.7	-5.9
1	0	0	22.2	23.7	8	-2	0	8.0	8.3	0	7	5	2.8	2.4	1	2	4	6.1	6.3	2	-5	3	5.4	-5.8
1	1	0	26.3	27.0	8	-1	0	5.9	5.7	0	8	2	4.7	4.8	1	2	5	7.0	8.5	2	-4	-7	4.9	-5.5
1	2	0	13.6	-11.9	8	1	0	5.2	5.6	0	8	4	4.2	-4.0	1	2	6	9.6	9.4	2	-4	-6	6.2	-5.5
1	3	0	17.8	18.5	8	2	0	9.8	9.6	1	-8	-3	4.5	-5.0	1	2	7	2.2	3.0	2	-4	-5	5.5	-5.5
1	4	0	33.2	37.2	8	3	0	8.6	9.0	1	-8	-1	2.5	-2.3	1	3	-4	12.9	11.4	2	-4	-4	15.5	-18.1
1	5	0	15.5	14.2	8	4	0	6.0	6.1	1	-8	1	2.7	3.5	1	3	-3	5.9	-5.1	2	-4	-3	13.4	-16.1
1	7	0	4.4	4.5	9	2	0	4.3	4.6	1	-7	-4	4.8	-3.7	1	3	-2	7.1	-6.0	2	-4	-1	13.5	-13.1
1	8	0	9.5	10.3	0	-8	1	8.3	9.5	1	-7	-3	10.4	-8.2	1	3	-1	31.1	29.8	2	-4	1	3.1	2.8
2	-8	0	6.0	-6.2	0	-7	1	6.1	5.8	1	-7	-2	4.2	-3.1	1	3	1	6.0	-4.7	2	-4	2	5.6	5.1
2	-5	0	11.4	-9.2	0	-7	2	9.8	10.8	1	-7	-1	6.9	5.5	1	3	2	13.7	14.2	2	-4	3	4.2	-3.2
2	-4	0	12.6	-15.2	0	-6	2	10.0	9.2	1	-7	2	3.3	7.7	1	3	3	19.0	22.9	2	-3	-7	4.2	-4.1
2	-3	0	9.0	-8.3	0	-6	3	9.9	8.9	1	-6	-3	2.1	1.7	1	3	4	9.8	10.6	2	-3	-6	12.5	-11.7
2	-2	0	8.7	9.1	0	-5	1	5.1	4.6	1	-6	-2	9.3	-7.9	1	3	5	3.6	4.1	2	-3	-5	8.4	-7.4
2	-1	0	11.1	11.1	0	-5	2	9.3	7.5	1	-6	1	4.4	-3.6	1	3	6	8.0	7.4	2	-3	-4	6.3	-6.2
2	0	0	35.1	-39.4	0	-5	3	16.4	15.7	1	-6	3	7.2	7.9	1	3	7	4.9	5.5	2	-3	-3	24.1	-25.7
2	1	0	25.6	-26.0	0	-5	4	9.7	7.7	1	-5	-4	10.3	-8.3	1	4	-4	7.2	5.5	2	-3	-2	15.0	-16.8
2	2	0	8.8	8.9	0	-4	1	16.5	15.9	1	-5	-3	5.6	4.8	1	4	-3	12.7	9.6	2	-3	-1	2.8	2.7
2	3	0	7.9	7.7	0	-4	2	4.3	3.7	1	-5	-1	10.2	-11.6	1	4	-2	8.4	-8.0	2	-3	1	2.7	-3.0
2	4	0	3.2	3.2	0	-4	3	12.8	10.0	1	-5	1	9.0	10.7	1	4	-1	9.7	8.9	2	-3	2	13.1	11.2
2	7	0	7.4	6.8	0	-4	4	13.9	12.8	1	-5	2	4.3	-3.6	1	4	1	16.5	15.7	2	-3	3	8.3	7.6
2	8	0	6.7	7.7	0	-4	5	3.5	3.1	1	-5	3	3.6	3.0	1	4	2	7.6	6.9	2	-2	-7	2.0	-2.0
3	-8	0	4.0	-4.6	0	-3	1	28.6	27.2	1	-5	4	8.4	9.9	1	4	3	17.8	19.7	2	-2	-6	11.1	-9.7
3	-6	0	7.7	-6.9	0	-3	2	11.8	10.5	1	-4	-4	14.3	-16.4	1	4	4	12.8	14.3	2	-2	-5	15.6	-15.7
3	-5	0	19.7	-19.0	0	-3	4	6.1	5.8	1	-4	-3	6.9	-7.1	1	5	-3	16.0	13.8	2	-2	-4	4.7	3.8
3	-4	0	15.4	-17.1	0	-3	5	7.4	6.3	1	-4	-2	7.6	7.5	1	5	-2	13.0	10.1	2	-2	-3	5.1	4.6
3	-3	0	6.5	5.9	0	-2	1	15.2	11.9	1	-4	-1	10.0	-9.6	1	5	-1	3.3	-2.9	2	-2	-2	21.4	-24.4
3	-1	0	22.3	-24.5	0	-2	2	29.1	28.7	1	-4	1	21.7	24.8	1	5	1	18.7	19.8	2	-2	-1	1.4	-1.7
3	0	0	21.7	-24.5	0	-2	3	12.2	11.2	1	-4	2	13.6	16.3	1	5	2	1.7	1.2	2	-2	1	16.2	-15.2
3	1	0	13.1	-14.5	0	-2	4	2.7	2.6	1	-4	4	8.2	9.0	1	5	3	4.5	4.8	2	-2	2	11.8	-9.7
3	2	0	7.4	6.9	0	-2	5	8.4	7.7	1	-4	5	8.4	9.7	1	5	4	11.5	13.1	2	-2	3	6.6	6.5
3	3	0	4.3	-3.6	0	-2	6	4.9	5.0	1	-3	-4	8.0	-7.6	1	5	5	5.0	5.7	2	-1	-7	1.4	-1.3
3	4	0	20.1	-20.8	0	-1	1	20.5	-18.1	1	-3	-3	6.3	-6.0	1	6	-3	1.8	2.0	2	-1	-5	15.7	-16.6
3	5	0	15.3	-12.3	0	-1	2	22.0	20.6	1	-3	-2	16.6	16.7	1	6	-2	14.7	12.9	2	-1	-4	17.7	-17.8
4	-7	0	6.4	-5.4	0	-1	3	28.6	28.7	1	-3	-1	24.8	22.7	1	6	-1	6.6	6.3	2	-1	-3	9.3	8.5
4	-6	0	10.9	-10.6	0	-1	4	6.0	6.4	1	-3	1	2.8	3.2	1	6	1	11.8	13.5	2	-1	-2	12.1	-12.7
4	-5	0	9.1	-9.9	0	-1	5	2.2	2.5	1	-3	2	23.4	26.5	1	6	2	9.1	10.3	2	-1	-1	35.3	-42.3
4	-4	0	9.7	-9.7	0	-1	6	5.8	6.3	1	-3	3	5.1	5.3	1	6	4	5.4	5.8	2	-1	1	19.4	16.6
4	-3	0	7.2	-6.1	0	0	1	27.1	30.7	1	-3	5	8.9	9.9	1	6	5	7.2	7.5	2	-1	2	13.7	-13.3
4	-2	0	8.5	-9.9	0	0	2	6.0	-5.0	1	-2	-3	9.6	-8.9	1	6	6	2.1	2.4	2	0	-7	6.0	-5.6
4	-1	0	28.9	-32.5	0	0	3	22.9	24.4	1	-2	-2	10.0	8.7	1	7	-2	2.4	2.4	2	0	-5	5.5	-5.3
4	0	0	20.3	-20.3	0	0	4	12.6	13.0	1	-2	-1	35.3	34.8	1	7	-1	11.1	10.2	2	0	-4	23.0	-25.0
4	1	0	5.9	4.7	0	0	5	5.8	-6.0	1	-2	1	12.9	-13.1	1	7	1	5.7	4.9	2	0	-3	13.1	-11.9
4	3	0	16.3	-17.1	0	0	7	2.4	2.6	1	-2	2	12.0	15.0	1	7	2	13.2	13.6	2	0	-2	10.0	9.7
4	4	0	18.8	-18.7	0	1	1	44.4	53.0	1	-2	3	16.1	19.1	1	7	3	9.5	8.9	2	0	-1	39.1	-43.8
4	5	0	6.8	-5.8	0	1	2	12.8	-11.9	1	-2	5	2.4	1.4	1	7	4	3.7	3.6	2	0	1	35.3	36.4
4	7	0	5.9	-5.3	0	1	4	19.5	21.0	1	-2	6	8.6	9.8	1	7	5	4.5	4.8	2	1	-7	6.8	-8.1
5	-4	0	8.2	6.6	0	1	5	3.6	4.2	1	-1	-2	19.3	-20.2	1	8	-1	5.8	6.6	2	1	-6	7.5	-7.8
5	-3	0	11.8	-9.9	0	1	6	6.0	-5.2	1	-1	1	9.0	8.0	1	8	1	3.5	3.4	2	1	-4	11.3	-11.7
5	-2	0	12.7	-14.6	0	2	1	25.3	28.2	1	-1	2	8.8	8.8	1	8	2	3.4	3.6	2	1	-3	19.0	-20.3
5	-1	0	4.9	-4.4	0	2	2	16.8	18.6	1	-1	3	24.0	27.3	1	8	3	6.0	7.5	2	1	-2	13.2	14.1
5	0	0	6.1	-5.6	0	2	3	11.7	-11.5	1	-1	4	16.5	18.2	1	8	4	2.8	3.6	2	1	-1	22.8	26.0
5	1	0	4.9	-4.8	0	2	4	6.8	7.5	1	-1	5	2.3	2.3	2	-8	-4	3.0	-3.7	2	1	1	0.9	0.8
5	2	0	11.5	-10.8	0	2	5	12.9	14.5	1	-1	6	5.4	5.7	2	-8	-3	8.0	-8.7	2	2	-6	8.2	-7.8
5	3	0	14.2	-16.3	0	2	7	1.6	-1.7	1	0	-2	5.4	6.0	2	-8	-2	8.1	-7.5	2	2	-5	3.9	-3.6
5	4	0	8.6	-8.2	0	3	1	15.7	14.1	1	0	-1	17.3	14.2	2	-8	-1	4.6	-3.4	2	2	-3	12.7	-12.8
5	7	0	6.0	-6.4	0	3	2	30.4	34.3	1	0	1	26.3	26.0	2	-7	-5	7.4	-6.8	2	2	-2	12.1	-13.2
6	-6	0	5.6	5.6	0	3	3	13.0	14.5	1	0	2	14.6	12.1	2	-7	-4	4.3	-3.5	2	2	-1	16.5	19.8
6	-5	0	9.4	9.6	0	3	4	3.6	-3.4	1	0	3	10.9	9.7	2	-7	-3	10.4	-8.9	2	2	1	15.7	-15.6
6	-4	0	9.8	9.3	0	3	5	4.9	4.7	1	0	4	19.4	19.4	2	-7	-2	11.1	-11.2	2	2	2	14.7	13.9
6	-3	0	2.2	1.9	0	3	6	2.6	2.4	1	0	5	8.6	9.6	2	-7	-1	2.7	-2.5	2	3	-6	3.9	-3.4
6	-2	0	2.3	-1.8	0	3	7	3.8	-4.1	1	0	6	1.8	1.6	2	-7	1	5.7	-5.9	2	3	-5	8.3	-6.8
6	-1	0	13.4	13.5	0	4	1	6.4	6.0	1	1	-3	4.7	3.6	2	-6	-6	5.3	-5.5	2	3	-3	0.9	0.8

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
2	3	-2	12.5	-13.8	3	-2	2	21.7	-18.4	4	-5	-1	3.4	2.7	4	6	0	1.9	1.2	5	5	-1	6.1	-6.0
2	3	-1	11.0	-11.3	3	-1	-7	3.6	-3.3	4	-5	1	9.4	-9.3	4	6	1	4.2	-3.5	5	5	1	12.1	-12.3
2	3	1	2.1	-1.9	3	-1	-5	10.8	-8.8	4	-5	2	3.2	-2.5	4	6	2	9.9	-9.8	5	5	2	10.9	-10.1
2	3	2	5.1	-4.7	3	-1	-4	15.4	-11.9	4	-4	-7	3.5	4.0	4	6	3	3.8	-3.9	5	6	-3	2.2	2.7
2	3	3	18.6	17.5	3	-1	-3	1.3	-0.9	4	-4	-5	3.0	3.1	4	7	-2	3.5	-4.1	5	6	-2	4.0	-3.8
2	4	-5	7.5	-7.6	3	-1	-2	4.9	-4.6	4	-4	-4	6.6	6.4	4	7	-1	9.3	-10.8	5	6	-1	8.8	-9.6
2	4	-4	9.6	-9.6	3	-1	-1	22.8	-26.4	4	-4	-3	8.0	-7.4	4	7	2	5.5	-5.9	5	6	0	2.0	-1.5
2	4	-3	0.8	1.0	3	-1	1	9.9	-9.0	4	-4	-2	13.3	-12.6	5	-7	-5	4.7	5.3	5	6	1	3.6	-3.0
2	4	-2	2.3	2.4	3	-1	2	19.2	-14.6	4	-4	-1	3.5	-2.8	5	-7	-4	2.3	2.9	5	6	2	9.4	-10.1
2	4	-1	7.9	-6.7	3	0	-7	5.1	-4.5	4	-4	1	16.1	-17.6	5	-7	-3	3.5	4.3	5	7	-1	3.7	-4.5
2	4	1	19.8	17.8	3	0	-6	4.4	-3.2	4	-4	2	7.7	-8.8	5	-7	-2	5.2	6.4	5	7	1	1.5	-1.7
2	4	2	6.1	5.4	3	0	-5	2.5	-2.3	4	-3	-7	4.1	3.7	5	-6	-6	2.9	3.3	6	-7	-4	4.8	5.5
2	4	3	3.9	3.1	3	0	-4	18.3	-18.1	4	-3	-6	4.0	3.2	5	-6	-5	4.6	5.8	6	-7	-3	3.3	4.1
2	5	-4	8.1	-8.2	3	0	-3	21.2	-23.9	4	-3	-5	6.2	-5.4	5	-6	-4	4.4	5.3	6	-7	-2	5.9	6.9
2	5	-3	5.7	-4.8	3	0	-2	13.1	-14.2	4	-3	-4	1.4	-1.0	5	-6	-1	3.3	3.7	6	-7	-1	6.0	7.0
2	5	-2	7.6	7.0	3	1	-7	2.3	-2.7	4	-3	-3	2.4	2.3	5	-6	0	3.7	-2.7	6	-6	-5	5.0	5.7
2	5	-1	4.1	4.1	3	1	-6	9.8	-10.7	4	-3	-2	15.3	-15.4	5	-5	-5	2.4	2.1	6	-6	-4	7.3	7.8
2	5	0	2.4	-2.0	3	1	-5	4.5	-4.5	4	-3	-1	18.6	-17.2	5	-5	-4	8.5	9.2	6	-6	-2	4.0	3.2
2	5	1	13.0	11.3	3	1	-4	4.2	-3.8	4	-3	1	15.6	-14.3	5	-5	-3	6.9	6.5	6	-6	-1	7.7	8.4
2	5	2	18.9	17.3	3	1	-3	19.2	-23.2	4	-3	2	13.6	-15.7	5	-5	-1	4.7	4.9	6	-5	-6	2.2	2.2
2	5	3	6.1	4.8	3	1	-2	19.7	-22.5	4	-2	-6	5.4	4.2	5	-5	0	5.7	5.0	6	-5	-4	9.1	9.2
2	6	-3	6.4	-5.6	3	1	-1	8.1	-10.7	4	-2	-5	3.5	-3.1	5	-5	1	6.4	-5.4	6	-5	-3	7.9	7.1
2	6	-2	3.0	2.8	3	1	1	12.3	-15.3	4	-2	-4	18.0	-17.7	5	-4	-7	4.8	5.6	6	-5	-1	5.9	5.6
2	6	-1	10.1	9.0	3	2	-6	7.5	-8.7	4	-2	-3	3.7	-4.2	5	-4	-6	4.3	5.1	6	-5	1	4.1	3.6
2	6	0	1.4	-1.2	3	2	-5	12.7	-14.9	4	-2	-1	20.8	-19.3	5	-4	-4	6.6	5.8	6	-4	-6	5.5	5.1
2	6	1	4.1	-3.7	3	2	-3	3.8	-2.9	4	-2	1	2.1	1.3	5	-4	-3	13.2	12.9	6	-4	-5	2.9	2.4
2	6	2	10.9	8.7	3	2	-2	17.3	-20.8	4	-2	2	10.7	-10.2	5	-4	-1	4.5	-3.9	6	-4	-4	6.9	6.8
2	6	3	11.3	9.5	3	2	-1	7.1	-6.8	4	-1	-7	3.7	-3.5	5	-4	2	10.5	-10.5	6	-4	-3	14.0	15.5
2	7	-2	4.8	-4.4	3	2	1	9.6	-9.8	4	-1	-5	9.7	9.4	5	-3	-7	5.1	5.9	6	-4	-2	10.4	9.5
2	7	-1	6.5	6.0	3	2	2	15.4	-15.9	4	-1	-4	9.2	-6.3	5	-3	-6	9.2	10.3	6	-4	-1	4.6	4.0
2	7	2	3.5	3.4	3	3	-5	10.3	-11.7	4	-1	-3	18.0	-17.4	5	-3	-5	5.6	5.2	6	-4	1	6.0	6.6
2	7	3	11.7	10.2	3	3	-4	10.1	-11.3	4	-1	-2	5.5	4.7	5	-3	-3	10.9	8.9	6	-3	-6	6.7	6.7
2	8	1	5.7	5.4	3	3	-3	3.4	3.7	4	-1	-1	5.3	-6.3	5	-3	-2	5.4	5.4	6	-3	-5	11.5	9.7
2	8	2	4.0	3.0	3	3	-2	11.1	-13.1	4	-1	1	15.4	-14.1	5	-3	-1	13.7	-13.2	6	-3	-4	4.6	3.8
3	-8	-3	6.0	-6.1	3	3	-1	22.2	-27.4	4	-1	2	2.2	-2.8	5	-3	1	2.9	3.3	6	-3	-3	8.3	8.2
3	-8	-2	7.6	-7.9	3	3	1	4.2	3.7	4	0	-6	6.3	-5.6	5	-3	2	5.9	-5.9	6	-3	-2	14.7	14.5
3	-8	-1	2.2	-2.4	3	3	2	10.8	-10.8	4	0	-5	3.5	3.4	5	-2	-6	7.5	6.8	6	-3	-1	6.0	5.0
3	-7	-5	3.8	-3.9	3	3	3	7.2	-5.9	4	0	-4	6.9	6.4	5	-2	-5	8.3	5.9	6	-3	1	6.8	6.7
3	-7	-4	3.7	-3.7	3	4	-5	2.7	-2.5	4	0	-3	22.2	-19.7	5	-2	-4	3.8	-2.8	6	-2	-7	3.2	3.7
3	-7	-3	3.7	-3.3	3	4	-4	14.7	-15.6	4	0	-2	15.6	-15.8	5	-2	-2	10.7	10.8	6	-2	-6	4.1	2.8
3	-7	-2	11.2	-10.9	3	4	-3	7.0	-6.4	4	1	-6	4.1	-3.9	5	-2	1	3.2	-3.6	6	-2	-5	14.1	11.7
3	-7	-1	12.1	-10.3	3	4	-2	2.1	2.2	4	1	-5	8.3	-7.9	5	-2	2	2.8	1.8	6	-2	-4	13.1	11.7
3	-7	0	4.0	-3.3	3	4	-1	18.6	-21.4	4	1	-4	2.0	0.7	5	-1	-5	8.1	7.4	6	-2	-2	7.3	5.9
3	-7	1	7.1	-6.7	3	4	1	5.0	4.3	4	1	-3	8.5	-9.8	5	-1	-4	2.8	1.4	6	-2	-1	9.8	9.7
3	-6	-6	2.0	-1.7	3	4	2	2.4	1.7	4	1	-2	31.4	-36.4	5	-1	-3	6.9	-6.2	6	-1	-4	16.8	14.4
3	-6	-5	5.5	-4.5	3	4	3	6.5	-5.0	4	1	-1	12.7	-14.7	5	-1	-2	3.0	2.4	6	-1	-3	10.5	9.3
3	-6	-4	11.1	-10.4	3	5	-4	6.3	-7.8	4	1	1	17.6	-21.9	5	-1	-1	8.1	9.1	6	-1	-1	11.3	13.4
3	-6	-3	5.5	-5.2	3	5	-3	15.1	-14.8	4	2	-5	9.1	-8.3	5	-1	1	9.3	-9.6	6	-1	1	2.1	-2.0
3	-6	-2	2.2	-2.2	3	5	-1	3.2	2.9	4	2	-4	6.9	-6.5	5	0	-7	4.2	4.8	6	0	-6	6.7	6.4
3	-6	-1	11.5	-11.1	3	5	1	1.3	-1.5	4	2	-3	2.8	2.5	5	0	-5	6.4	5.4	6	0	-4	9.6	7.4
3	-6	2	8.0	-7.0	3	5	2	10.7	9.3	4	2	-2	11.8	-13.7	5	0	-4	16.3	12.1	6	0	-3	19.1	19.0
3	-5	-7	2.5	-2.7	3	6	-3	6.7	-7.1	4	2	-1	23.9	-27.5	5	0	-3	2.9	2.8	6	1	-6	8.2	9.6
3	-5	-4	6.9	-7.0	3	6	-2	9.4	-9.0	4	2	0	2.2	-2.3	5	1	-6	4.5	5.4	6	1	-5	5.3	6.5
3	-5	-3	13.7	-14.7	3	6	-1	3.7	2.8	4	2	1	4.0	-3.3	5	1	-5	3.5	-2.7	6	1	-3	11.7	14.5
3	-5	-2	4.2	-3.6	3	6	1	9.7	-7.8	4	2	2	19.7	-22.2	5	1	-4	2.8	2.0	6	1	-2	12.5	14.9
3	-5	-1	6.8	-6.1	3	6	2	3.3	2.9	4	3	-6	1.0	0.7	5	1	-3	7.4	6.9	6	1	-1	6.8	-8.3
3	-5	1	8.4	-8.0	3	6	3	6.0	5.4	4	3	-5	2.6	-2.4	5	1	-2	4.9	-5.3	6	1	1	7.5	7.5
3	-4	-7	2.5	-2.4	3	7	-2	5.7	-6.6	4	3	-4	9.2	-9.5	5	1	-1	8.9	-10.4	6	2	-5	7.2	7.5
3	-4	-6	6.0	-5.2	3	7	-1	6.7	-5.9	4	3	-3	3.7	-4.2	5	1	1	7.7	-8.8	6	2	-2	10.8	12.4
3	-4	-3	15.3	-17.8	3	7	1	4.2	-3.4	4	3	-2	1.7	1.7	5	2	-6	6.1	7.2	6	2	-1	5.7	5.8
3	-4	-2	16.7	-18.4	3	7	2	5.3	-4.4	4	3	-1	13.1	-13.8	5	2	-4	8.4	-9.9	6	3	-5	5.3	5.4
3	-4	-1	4.0	-3.1	3	7	3	3.2	3.4	4	3	1	3.5	-3.6	5	2	-2	1.9	1.3	6	3	-4	6.7	5.9
3	-4	1	27.5	-25.9	3	8	0	1.7	-1.5	4	3	2	11.3	-11.5	5	2	-1	10.6	-12.9	6	3	-1	9.7	9.5
3	-4	2	5.3	-4.8	3	8	1	3.3	4.1	4	4	-5	1.8	1.9	5	2	2	4.9	-3.8	6	3	1	5.3	-4.8
3	-3	-6	10.7	-9.3	4	-8	-3	2.7	3.0	4	4	-4	5.0	-5.1	5	3	-5	6.5	8.4	6	3	2	4.0	3.4
3	-3	-5	12.3	-10.8	4	-8	-1	2.5	-2.9	4	4	-3	12.6	-13.8	5	3	-4	2.7	-2.4	6	4	-4	6.6	8.0
3	-3	-4	5.3	-5.5	4	-7	-4	1.4	-1.6	4	4	-2	7.8	-9.2	5	3	-3	6.6	-7.2	6	4	-3	6.0	7.2
3	-3	-3	17.5	-15.9	4	-7	-2	2.1	-2.1	4	4	-1	6.3	-7.5	5	3	-2	7.0	7.4	6	4	-1	2.0	2.1
3	-3	-2	26.0	-29.8	4	-7	-1	8.9	-8.4	4	4	1	12.5	-14.4	5	3	1	12.1	-10.8	6	4	1	5.5	-5.5
3	-3	-1	12.2	-10.3	4	-6	-6	3.6	4.1	4	4	2	3.1	-2.2	5	3	2	4.4	-3.8	6	4	2	7.9	-7.7
3	-3	1	17.2	-15.7	4	-6	-5	2.3	2.1	4	4	3	7.5	-6.1	5	4	-5	3.5	4.1	6	5	-3	6.0	6.1
3	-3	2	15.7	-14.8	4	-6	-4	5.5	-5.2	4	5	-3	9.4	-9.1	5	4	-4	5.3	5.9	6	5	-1	5.1	-4.1
3	-3	3	4.8	4.6	4	-6	-2	2.8	2.6	4	5	-2	13.0	-13.6	5	4	-3	7.5	-8.8	6	5	2	5.8	-5.9
3	-2	-6	6.6	-5.3	4	-6	-1	7.6	-6.4	4	5	-1	5.9	-5.5	5	4	-2	6.6	-5.7	6	6	-2	3.1	3.6
3	-2	-5	14.7	-12.9	4	-6	1	4.5	-3.2	4	5	1	16.5	-14.2	5	4	-1	6.8	6.2	6	6	-1	2.8	-2.8
3	-2	-4	8.1	-6.3	4	-5	-5	4.8	4.5	4	5	2	8.4	-7.6	5	4	1	18.3	-18.0					
3	-2	-3	6.7	-5.0	4	-5	-4	2.4	-2.1	4	6	-3	1.7	-1.3	5	4	2	9.0	-7.7					
3	-2	-2	21.6	-23.9	4	-5	-3	7.4	-7.6	4	6	-2	9.5	-10.0	5	5	-4	3.4	3.8					
3	-2	-1	23.9	-27.5	4	-5	-2	3.3	2.8	4	6	-1	7.9	-7.4	5	5	-2	12.5	-14.2					

Table 5. *Agreement analysis*

F_{obs}	Number of planes	Agreement factor R	Sin θ	Number of planes	Agreement factor R
0–3	84	15·6%	0·10–0·15	3	8·9%
3–6	197	12·9	0·15–0·20	5	9·9
6–9	175	11·3	0·20–0·25	12	9·7
9–12	107	10·2	0·25–0·30	12	9·6
12–15	75	10·5	0·30–0·35	25	9·1
15–18	47	10·0	0·35–0·40	16	9·4
18–21	34	8·9	0·40–0·45	36	8·2
21–24	18	9·5	0·45–0·50	39	10·9
24–27	13	8·9	0·50–0·55	46	9·6
27–30	8	6·7	0·55–0·60	59	10·3
30–33	6	8·7	0·60–0·65	58	11·5
33–36	5	8·7	0·65–0·70	71	12·1
36–39	0	–	0·70–0·75	67	12·3
39–42	1	10·6	0·75–0·80	58	11·0
42–45	0	–	0·80–0·85	69	10·9
45–48	1	17·3	0·85–0·90	64	11·0
			0·90–0·95	80	10·4
			0·95–1·00	51	11·7

sulphide and 1·94 Å in tetraethyl diphosphine disulphide. The bond angle S–P–P′ of 111·1° compares with 112° in dimethyl diphenyl diphosphine disulphide and 113° in tetraethyl diphosphine disulphide.

Table 6. *Bond lengths and their standard deviations*

Bond	Distance	σ
P —P′	2·21 Å	0·004 Å
S —P	1·95	0·002
P —C(1)	1·82	0·007
P —C(4)	1·82	0·007
C(1)–C(2)	1·52	0·011
C(3)–C(4)	1·51	0·010
C(2)–C(3)	1·52	0·015

Table 7. *Bond angles and their standard deviations*

	Angle	σ
S —P —C(1)	118·7°	0·3°
S —P —C(4)	116·5	0·3
S —P —P′	111·1	0·1
C(1)–P —P′	105·5	0·1
C(4)–P —P′	107·0	0·1
C(1)–P —C(4)	96·6	0·3
P —C(1)–C(2)	104·6	0·5
P —C(4)–C(3)	105·1	0·6
C(1)–C(2)–C(3)	108·5	0·8
C(2)–C(3)–C(4)	108·8	0·7

The bond lengths and angles in the ring show a regular arrangement. The P–C distances, both of 1·82 Å, are close to the values of 1·82 Å in dimethyl diphenyl diphosphine disulphide and of 1·82 and 1·84 Å in tetraethyl diphosphine disulphide. These values are in close agreement with the value of 1·84 Å obtained from the sum of Pauling's (1960) single bond covalent radii. The ring system is saturated and is consequently puckered, and the bond angles round the carbon atoms are slightly less than the usual tetrahedral value. The inclusion of phosphorus in a heterocyclic ring causes considerable distortion of the tetrahedral environment round the phosphorus, and the bond angle C(1)–P–C(4) is 96·6°. It is surprising that this has no observable effect on the bond order of the P–P and P=S bonds. A large number of intermolecular contacts occur in the range 3·85–4·0 Å, but there are no intermolecular contacts below 3·85 Å except those involving hydrogen atoms.

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The Crystal Structure and Absolute Configuration of the *N*(*b*)-Methiodide of (−)-Kopsanone

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Crystals of the *N*(*b*)-methiodide of the indole alkaloid (−)-kopsanone, $[C_{21}H_{25}N_2O]^+I^-$, are orthorhombic with lattice translations $a=13{\cdot}98$, $b=17{\cdot}20$, $c=7{\cdot}67$ Å, space group $P2_12_12_1$, four formula units per unit cell. The crystal structure has been determined from 1800 three-dimensional X-ray intensity data, collected with an automatic four-circle diffractometer, the absolute configuration being established from the Cu $K\alpha$ anomalous scattering of the iodide ion. Refinement of positional and isotropic temperature factors was by full-matrix least-squares, giving convergence at $R=0{\cdot}08$. Hydrogen atom positions were not determined. The results confirm the molecular structure previously proposed on the basis of chemical and spectral data. The heptacyclic molecular structure has a cage-like aliphatic portion, with the piperidine ring *D* in the chair form. The conformation of the remainder of the molecule and of (−)-kopsanone itself follows from the interlocking nature of the ring fusions.

Introduction

Several families of indole alkaloids with similar molecular structures have been isolated from *Aspidosperma*, *Pleiocarpa*, *Kopsia* and other genera. The chemistry of these alkaloids has been reviewed by Gilbert (1965). In considering their structural and biosynthetic relationships, (−)-kopsanone is important since it has been