Journal of Organometallic Chemistry, 152 (1978) 305—310

THE CRYSTAL AND MOLECULAR STRUCTURE OF 1,2-DIPHENYL-1,2-DIPHOSPHOLANE-1,2-DISULPHIDE

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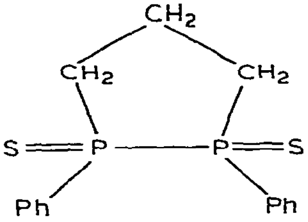
(Received December 16th, 1977)

Summary

The crystal and molecular structure of 1,2-diphenyl-1,2-diphospholane-1,2-disulphide has been determined from three dimensional X-ray diffraction data by Patterson and Fourier techniques. The structure has been refined by full matrix least squares methods to a final *R* value of 0.055 based on 1733 observed reflexions. The unit cell is orthorhombic, space group $P2_12_12_1$, with dimensions a = 13.867 Å, b = 12.379 Å and c = 9.312 Å (all ±0.003 Å), and contains 4 molecules. The P—P bond length of 2.253 ± 0.002 Å is similar to that in several diphosphine disulphides and phosphorus sulphides, and indicates the absence of any π bonding in the P—P bond.



Experimental

A pale yellow crystal of approximate dimensions 0.2 × 0.2 × 0.15 mm was used to collect equi-inclination Weissenberg intensity data for the layers $hk0$ to $hk9$ using an $\omega/2\theta$ scan on a Stöe diffractometer. Of 1778 reflexions measured, 1733 had intensities greater than 3σ and were treated as observed reflexions. Lorentz and polarization corrections were applied, but corrections for absorption and extinction were considered unnecessary.

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Crystal data

$C_{15}H_{16}P_2S_2$, mol. wt. 322.38. Orthorhombic, $a = 13.867$, $b = 12.379$, $c = 9.312$ Å ± 0.003 Å; $U = 1598.5$ Å^3; $Z = 4$; $D_m = 1.32$, $D_c = 1.339$ g cm^{-3}; $F(000) = 672$, Cu-K_α, $\lambda = 1.5418$ Å. Space group $P2_12_12_1$ (absences $h00$ when $h = 2n + 1$, $0k0$ when $k = 2n + 1$, $00l$ when $l = 2n + 1$).

Structure analysis

The position and orientation of the sulphur and phosphorus atoms were eventually derived from a three dimensional Patterson map. A structure factor calculation was performed using atomic scattering factors [1] corrected for the real part of anomalous dispersion [2], and gave an initial R value of 0.54. The structure was gradually refined by full matrix least squares methods, and the carbon atoms were located on Fourier maps. Using unit weights and isotropic temperature factors, refinement continued until $R = 0.16$ and then using a weighting scheme [3] $w = 1/(A + B|F_0| + C|F_0|^2)$ with $A = 1.3421$, $B = -0.10363$ and $C = 0.00732$ and refining anisotropic temperature factors for P and S, R fell to 0.079. Finally hydrogen atoms were included in calculated positions and the carbon atoms were allowed to refine anisotropically giving a final value of $R = 0.055$. The final atomic coordinates are shown in Table 1, the calculated hydrogen positions in Table 2, the temperature factors in Table 3, and an agreement analysis in Table 4. A table of structure factors is given in the M.Sc. Thesis of one of us (AHB), and may be referred to in the library at Loughborough University.

The form of the anisotropic temperature factors used is

$$TF = \exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2\,hk\beta_{12} + 2\,hl\beta_{13} + 2\,kl\beta_{23})]$$

TABLE 1

FINAL POSITIONAL PARAMETERS AND e.s.d.'s

Atom	x/a	y/b	z/c
S(1)	0.2186(2)	0.2731(1)	0.2605(2)
S(2)	0.1320(2)	0.3123(1)	−0.2703(2)
P(1)	0.2173(1)	0.3570(1)	0.0842(2)
P(2)	0.2136(1)	0.2567(1)	−0.1176(2)
C(1)	0.1243(4)	0.4583(4)	0.0746(6)
C(2)	0.1273(5)	0.5389(5)	−0.0307(8)
C(3)	0.0535(5)	0.6160(5)	−0.0365(8)
C(4)	−0.0201(5)	0.6132(6)	0.0590(9)
C(5)	−0.0227(5)	0.5339(7)	0.1625(10)
C(6)	0.0477(5)	0.4572(6)	0.1710(8)
C(11)	0.1882(4)	0.1179(4)	−0.0666(6)
C(12)	0.2531(4)	0.0598(5)	0.0194(8)
C(13)	0.2359(5)	−0.0466(6)	0.0499(8)
C(14)	0.1550(6)	−0.0963(5)	−0.0050(8)
C(15)	0.0916(5)	−0.0411(5)	−0.0870(9)
C(16)	0.1088(4)	0.0666(5)	−0.1240(7)
C(21)	0.3342(4)	0.4159(5)	0.0358(7)
C(22)	0.3949(5)	0.3232(6)	−0.0256(9)
C(23)	0.3440(4)	0.2688(5)	−0.1495(8)

TABLE 2

CALCULATED HYDROGEN POSITIONS

Atom	Bonded to	x/a	y/b	z/c
H(2)	C(2)	0.1844	0.5426	−0.1055
H(3)	C(3)	0.0558	0.6775	−0.1170
H(4)	C(4)	−0.0761	0.6730	0.0527
H(5)	C(5)	−0.0817	0.5309	0.2346
H(6)	C(6)	0.0440	0.3949	0.2510
H(12)	C(12)	0.3158	0.0986	0.0613
H(13)	C(13)	0.2847	−0.0913	0.1167
H(14)	C(14)	0.1435	−0.1802	0.0146
H(15)	C(15)	0.0267	−0.0808	−0.1195
H(16)	C(16)	0.0603	0.1092	−0.1954
H(21)	C(21)	0.3249	0.4789	−0.0410
H(21*)	C(21)	0.3684	0.4483	0.1313
H(22)	C(22)	0.4621	0.3552	−0.0634
H(22*)	C(22)	0.4079	0.2645	0.0570
H(23)	C(23)	0.3734	0.1892	−0.1633
H(23*)	C(23)	0.3552	0.3153	−0.2451

TABLE 3

FINAL TEMPERATURE FACTOR PARAMETERS AND STANDARD DEVIATIONS

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S(1)	0.0103(1)	0.0096(1)	0.0115(2)	−0.0013(1)	−0.0027(2)	0.0026(1)
S(2)	0.0108(1)	0.0078(1)	0.0156(3)	0.0014(1)	−0.0061(2)	0.0000(2)
P(1)	0.0057(1)	0.0061(1)	0.0101(2)	−0.0008(1)	−0.0006(1)	0.0000(1)
P(2)	0.0053(1)	0.0058(1)	0.0104(2)	−0.0002(1)	−0.0016(1)	0.0000(1)
C(1)	0.0056(3)	0.0066(3)	0.0118(7)	−0.0006(3)	−0.0007(4)	−0.0013(4)
C(2)	0.0082(4)	0.0062(4)	0.0147(9)	−0.0001(3)	0.0001(5)	−0.0001(5)
C(3)	0.0081(4)	0.0081(4)	0.0144(9)	0.0004(4)	−0.0022(5)	−0.0007(5)
C(4)	0.0072(4)	0.0093(5)	0.0196(12)	0.0003(4)	−0.0011(6)	−0.0017(7)
C(5)	0.0066(4)	0.0114(6)	0.0222(14)	−0.0002(4)	0.0019(6)	−0.0014(8)
C(6)	0.0063(3)	0.0107(6)	0.0158(11)	−0.0020(4)	0.0009(5)	−0.0001(6)
C(11)	0.0046(2)	0.0067(3)	0.0124(7)	0.0001(2)	−0.0009(4)	−0.0004(4)
C(12)	0.0066(3)	0.0078(4)	0.0151(9)	0.0003(3)	−0.0011(4)	0.0011(5)
C(13)	0.0085(4)	0.0081(5)	0.0157(10)	0.0006(4)	0.0004(5)	0.0016(6)
C(14)	0.0107(5)	0.0071(4)	0.0146(10)	−0.0005(4)	0.0041(6)	0.0002(5)
C(15)	0.0073(4)	0.0080(4)	0.0205(11)	−0.0027(4)	0.0009(6)	−0.0018(7)
C(16)	0.0058(3)	0.0077(4)	0.0152(9)	−0.0003(3)	−0.0001(4)	−0.0014(5)
C(21)	0.0063(3)	0.0082(4)	0.0140(8)	−0.0017(3)	0.0004(4)	−0.0013(5)
C(22)	0.0060(3)	0.0104(5)	0.0191(10)	−0.0007(4)	−0.0004(5)	−0.0011(7)
C(23)	0.0060(3)	0.0086(5)	0.0153(9)	−0.0011(3)	0.0007(4)	0.0002(5)

Discussion

A view of the molecule is given in Fig. 1, and the bond lengths and angles are given in Tables 5 and 6.

The P—P bond length of 2.253 Å is compared [4] with the values in a number of diphosphine disulphides, and also with a number of phosphorus sulphides and P_4.

In the present compound, the dihedral angle between the plane through atoms S(1), P(1) and P(2) and the plane through P(1), P(2) and S(2) is 39.1°, compared

TABLE 4

AGREEMENT ANALYSIS

F_{obs}	Number of reflexions	R	sin θ/λ	Number of reflexions	R	Zone	Number of reflexions	R
0—5	427	0.177	0.0—0.1	10	0.054	*hk*0	191	0.051
5—10	538	0.081	0.1—0.2	62	0.043	*hk*1	221	0.048
10—15	313	0.046	0.2—0.3	153	0.041	*hk*2	214	0.054
15—20	140	0.044	0.3—0.4	285	0.045	*hk*3	206	0.046
20—25	102	0.039	0.4—0.5	462	0.058	*hk*4	195	0.049
25—30	68	0.045	0.5—0.6	597	0.078	*hk*5	182	0.054
30—35	32	0.033	0.6—0.7	164	0.106	*hk*6	164	0.068
35—40	26	0.041				*hk*7	145	0.078
40—45	23	0.039				*hk*8	122	0.078
45—50	17	0.047				*hk*9	93	0.085
50—55	10	0.027						
>55	37	0.029						

with 180° in the diphosphine disulphides. The P_4 molecule is tetrahedral and the phosphorus sulphides are based on a distorted tetrahedron. It would seem that the P—P bond length does not change significantly if rotation occurs about this bond, and hence there can be no double bond character in the P—P bond in any of these compounds.

The P=S bond lengths of 1.943 Å and 1.944 Å are in close agreement with the values 1.94—1.98 Å found in the diphosphine disulphides [4]. The distribution of the four bonds round phosphorus is roughly tetrahedral, but the large size and short bond length P=S causes some distortion, and the bond angles S—P—P, S—P—C are all increased from tetrahedral to 114—115°.

The heterocyclic ring of two P and three C atoms also causes some distortion at P. The angles P(2)—P(1)—C(21) and P(1)—P(2)—C(23) are reduced from the tetrahedral value to 92.2 and 93.9° respectively. The heterocyclic P—C distances are 1.832 and 1.838 Å.

The bond lengths in the benzene rings are all in the range 1.35—1.40 Å. The maximum deviation from planarity in the ring comprising atoms C(1)—C(6) is 0.0027 Å, and in the ring comprising atoms C(11)—C(16) is 0.02 Å. The planes through the benzene rings make an angle of 66.2° with each other.

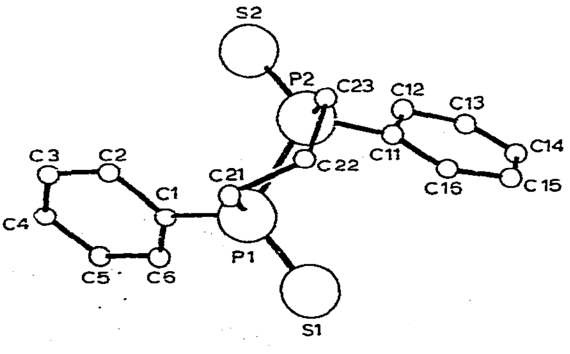

Fig. 1. A view of the molecule.

TABLE 5

BOND LENGTHS (Å) AND THEIR ESTIMATED STANDARD DEVIATIONS

Bond	Distance	Bond	Distance	Bond	Distance
P(1)—P(2)	2.253(2)	C(1)—C(2)	1.40(1)	C(11)—C(16)	1.38(1)
P(1)—S(1)	1.943(2)	C(1)—C(6)	1.39(1)	C(12)—C(13)	1.37(1)
P(2)—S(2)	1.944(2)	C(2)—C(3)	1.40(1)	C(13)—C(14)	1.38(1)
P(1)—C(1)	1.802(6)	C(3)—C(4)	1.35(1)	C(14)—C(15)	1.35(1)
P(2)—C(11)	1.817(6)	C(4)—C(5)	1.38(1)	C(15)—C(16)	1.40(1)
P(1)—C(21)	1.832(6)	C(5)—C(6)	1.36(1)	C(21)—C(22)	1.54(1)
P(2)—C(23)	1.838(6)	C(11)—C(12)	1.40(1)	C(22)—C(23)	1.51(1)

A number of short non-bonded intra molecular and intermolecular distances exist, and these are listed in Table 7. Many of the intramolecular contacts are unavoidable, but the possibility of hydrogen bonding between S(1)···H(6) and S(2)···H(16) was examined and rejected because the angles S(1)···H(6)—C(6) and S(2)···H(16)—C(16) are 111.1° and 111.7° respectively. The intermolecular contacts S(1)···H(4) of 2.91 Å are shorter than the sum of the van der Waals radii of 1.85 Å for S and 1.2 Å for H quoted by Pauling [5], but many workers now feel the value for S should be 1.72 Å, and these contacts are not thought to be hydrogen bonds. However, the contacts S(2)···H(15) of 2.77 Å are significantly

TABLE 6

BOND ANGLES (DEGREES) AND THEIR ESTIMATED STANDARD DEVIATIONS

S(1)—P(1)—P(2)	114.2(1)
S(1)—P(1)—C(1)	114.9(2)
S(1)—P(1)—C(21)	114.2(2)
P(2)—P(1)—C(21)	92.2(2)
P(2)—P(1)—C(1)	109.0(2)
C(21)—P(1)—C(1)	110.2(3)
S(2)—P(2)—P(1)	115.4(1)
S(2)—P(2)—C(11)	114.4(2)
S(2)—P(2)—C(23)	115.2(2)
P(1)—P(2)—C(23)	93.9(2)
P(1)—P(2)—C(11)	107.9(2)
C(23)—P(2)—C(11)	108.1(3)
P(1)—C(1)—C(2)	120.7(4)
P(1)—C(1)—C(6)	120.5(5)
C(2)—C(1)—C(6)	118.8(6)
C(1)—C(2)—C(3)	119.5(6)
C(2)—C(3)—C(4)	120.5(6)
C(3)—C(4)—C(5)	119.8(7)
C(4)—C(5)—C(6)	121.2(7)
C(5)—C(6)—C(1)	120.1(7)
P(2)—C(11)—C(12)	120.6(4)
P(2)—C(11)—C(16)	119.3(4)
C(12)—C(11)—C(16)	119.9(5)
C(11)—C(12)—C(13)	120.0(6)
C(12)—C(13)—C(14)	119.7(7)
C(13)—C(14)—C(15)	120.9(7)
C(14)—C(15)—C(16)	120.7(7)
C(15)—C(16)—C(11)	118.7(6)

TABLE 7

SHORT NON BONDED INTERATOMIC DISTANCES INVOLVING SULPHUR

(a) Intramolecular distances (Å)

S(1)···C(1)	3.16
S(1)···C(6)	3.39
S(1)···C(21)	3.17
S(1)···H(6)	2.85
S(2)···C(11)	3.16
S(2)···C(16)	3.35
S(2)···C(23)	3.19
S(2)···H(16)	2.79

(b) Intermolecular distances (Å) with the symmetry related molecule at $-x, \frac{1}{2}+y, \frac{1}{2}-z$

Atom in symmetry related molecule	
S(1)···H(4)	2.91
H(4)···S(1)	2.91
S(2)···H(15)	2.77
H(15)···S(2)	2.77

short and the angle S(1)···H(4)—C(4) is 174°. This indicates intermolecular hydrogen bonding between pairs of molecules in such a way that H(15) on the first molecule is bonded to S(2) on the second, and S(2) on the first molecule receives a hydrogen bond from H(15) on the second molecule.

Acknowledgements

The authors are grateful to Professors K. Issleib and R. Schmutzler for providing the compound, and to the staff of the Loughborough University Computer Centre. One of us (AHB) is grateful to the National Iranian Oil Company for a period of study leave.

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