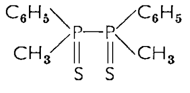
108. *An X-Ray Structural Investigation of Two Isomeric Forms of 1,2-Dimethyl-1,2-diphenyldiphosphine Disulphide.*

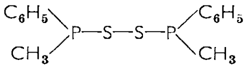
By P. J. Wheatley.

The characterization of two forms of 1,2-dimethyl-1,2-diphenyldiphosphine disulphide is described. The high-melting crystals consist of the *meso*-form, since the space group requires the molecule to have a centre of symmetry. The X-ray evidence for the structure of the low-melting crystals is inconclusive, but suggests very strongly that these crystals are the racemate. A two-dimensional X-ray structural analysis of the *meso*-form has been carried out. The bond lengths indicate that conjugation between the benzene ring and the rest of the molecule is no greater than any hyperconjugation between the methyl group and the rest of the molecule. The distribution of the bonds around the phosphorus atom departs only slightly from regular tetrahedral.

When methylthiophosphonyl dibromide, $CH_3{\cdot}PSBr_2$, reacts with an ethereal phenylmagnesium bromide solution, two isomeric products, $(C_7H_8PS)_2$, can be isolated.[1] These differ widely in their solubilities and by about 60° in their melting points. Work on similar symmetrical compounds also shows that the molecular formula is twice the empirical formula,[2] and infrared and Raman spectroscopic evidence suggests that these symmetrical compounds contain a phosphorus–phosphorus bond and not a disulphide bridge.[3] It is reasonable, therefore, to suppose that $(C_7H_8PS)_2$ should be formulated as (I) rather than (II). If (I) is the basis of the structure of the present compound, the molecule contains two asymmetric phosphorus atoms and can exist in (+)-, (—)-, and *meso*-forms. Further, crystals of the racemate, consisting of equal numbers of (+)- and (—)-molecules, may exist. The present investigation was undertaken in order to establish the structure of the two isomers that have been isolated.



(I)



(II)

The high-melting form (m. p. 207°) forms excellent lozenge-like crystals from ether–chloroform. An X-ray examination shows that the crystals are orthorhombic. The absence of reflexions $hk0$ with h odd, $0kl$ with k odd, and $h0l$ with l odd yields the space group *Pbca*. The density determined by flotation in a solution of potassium bromide shows that there are four molecules in the unit cell. Since there are eight equivalent positions in *Pbca*, the molecule must possess some symmetry, and the only possibility is a centre of symmetry. Consequently the high-melting crystals must be the *meso*-form. The crystallographic constants and a full structural analysis are described below.

The low-melting form (m. p. 145°) gives needle-like crystals from a wide variety of solvents and solvent mixtures. Rotation photographs give the length of the needle axis as 6·87 Å. Weissenberg photographs round the needle axis show that the crystals are triclinic and are invariably twinned about {010}. Measurement of the Weissenberg photographs gives 0·1185 Å^{-1}, 0·0729 Å^{-1}, and 84·5° for b^*, c^*, and α^* respectively. Thus the volume of the unit cell, calculated from the formula $V = a/b^*c^* \sin \alpha^*$, is 798 Å^3. The density determined by flotation in a solution of potassium bromide is 1·288 g.cm.$^{-3}$. The unit cell contains two molecules, and the space group is either $P1$ or $P\bar{1}$.

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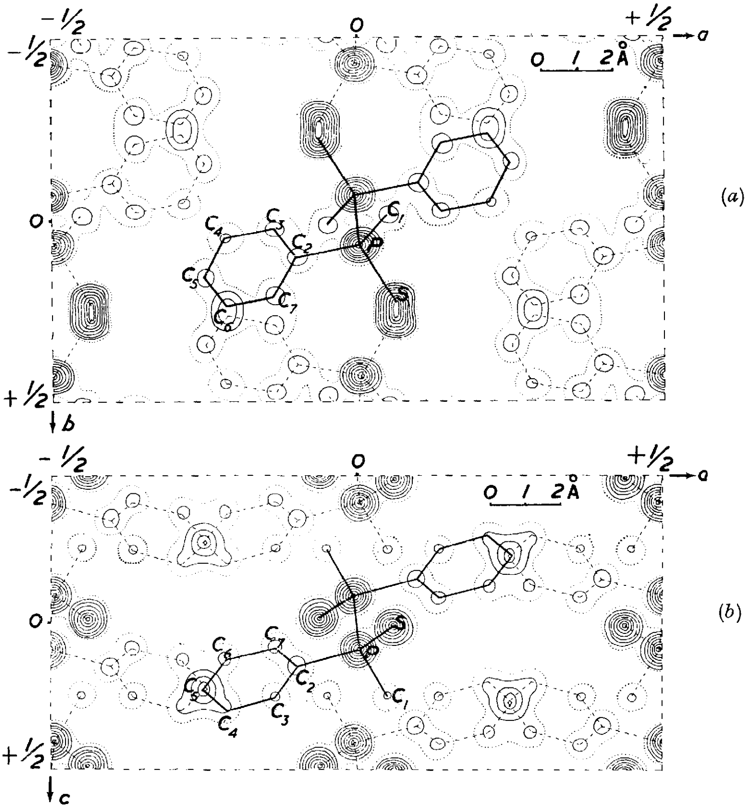
[1] Maier, *Angew. Chem.*, 1959, **71**, 575.

[2] Reinhardt, Bianchi, and Mölle, *Chem. Ber.*, 1957, **90**, 1656; Isslieb and Tzschach, *ibid.*, 1959, **92**, 704; Kuchen and Buchwald, *Angew. Chem.*, 1959, **71**, 162.

[3] Goubeau, Reinhardt, and Bianchi, *Z. phys. Chem.* (*Frankfurt*), 1957, **12**, 387; Christen, van der Linde, and Hooge, *Rec. Trav. chim.*, 1959, **78**, 161.

If the space group is $P1$, the asymmetric unit must consist of two molecules, and these may be two molecules of the (+)-form, two of the (—)-form, or one each of the (+) and the (—)-form. Each of these three possibilities is crystallographically unlikely, but nevertheless they are all possible. A solution of 0·2163 g. of the low-melting crystals in 10 c.c. of chloroform was tested in a 20 cm. cell on a Zeiss 0·01° polarimeter for optical activity. None was observed, which further reduces the possibility that these crystals consist of the pure (+)- of (—)-form. If the space group is $P\bar{1}$, the asymmetric unit consists of one molecule, and only two possibilities arise. Either the crystals are the racemate with equal numbers of (+)- and (—)-molecules centrosymmetrically related to each other, or the crystals are a second modification of the *meso*-form with the two centrosymmetric molecules in the unit cell lying in different orientations on the two types of centre of symmetry.

FIG. 1. (*a*) *Projection of the contents of the unit cell down* [*c*]. (*b*) *Projection of the contents of the unit cell down* [*b*]. *Contours are drawn at equal, arbitrary units.*



To test this last possibility, saturated solutions of the high- and low-melting crystals were made up separately in chloroform at room temperature. Each solution was seeded with a crystal of the other type but no interconversion took place. It is highly improbable therefore that the high- and the low-melting form are different crystal modifications of the same substance.

The evidence accumulated on the low-melting crystals, although not conclusive, suggests most strongly that these crystals are the racemate.

X-*Ray Structural Analysis of the* meso-*Form*.—$C_{14}H_{16}P_2S_2$. $M = 310{\cdot}4$. Orthorhombic. $a = 17{\cdot}10_4$, $b = 10{\cdot}62_9$, $c = 8{\cdot}59_2$ Å. $U = 1562$ Å^3. $D_m = 1{\cdot}329$ (by flotation),

$Z = 4$, $D_c = 1{\cdot}320$, $F(000) = 648$. Space group, *Pbca* (D_{2h}^{15}, No. 61). Cu-K_α radiation (λ 1·542 Å), single crystal rotation and Weissenberg photographs.

Multiple-film Weissenberg photographs were taken round [*b*] and [*c*] with irregular crystals, the greatest dimension of which did not exceed 0·12 mm. No correction was made for absorption ($\mu = 47{\cdot}0$ cm.$^{-1}$). Relative intensities were estimated visually by comparison with standard strips prepared from the same crystals. 102 *hk*0 and 80 *h*0*l* reflexions were observed to be non-zero.

TABLE 1. *Fractional co-ordinates.*

Atom	*x*/*a*	*y*/*b*	*z*/*c*	Atom	*x*/*a*	*y*/*b*	*z*/*c*	Atom	*x*/*a*	*y*/*b*	*z*/*c*
S	0·0625	0·222	0·019	C_2	−0·099	0·105	0·149	C_5	−0·252	0·151	0·229
P	0·005	0·072	0·092	C_3	−0·138	0·023	0·250	C_6	−0·215	0·236	0·127
C_1	0·050	−0·014	0·251	C_4	−0·215	0·046	0·298	C_7	−0·138	0·209	0·084

Each projection was solved from a sharpened Patterson synthesis. Since the molecule lies on a centre of symmetry, the P–P vector peak could readily be located about 2·2 Å from the origin of the Patterson map. Next the heavy P–S peak was found, and the co-ordinates obtained for the sulphur atom were checked against the S–S peak. A set of phases was calculated from the co-ordinates found in this manner for the sulphur and phosphorus atoms, and from the resulting Fourier map all seven carbon atoms could readily be identified. Refinement by Fourier and difference syntheses was carried out until the agreement index for each projection had dropped to $R = 13\%$. This figure includes only those reflexions that were observed. Hydrogen atoms were ignored. The scattering factors used were those of Tomiie and Stam [4] for the sulphur and phosphorus atoms, and that of Berghuis *et al.*[5] for the carbon atom. A single isotropic temperature factor, $B = 3{\cdot}4$ Å^2, proved adequate throughout.

TABLE 2. *Observed and calculated structure factors for one asymmetric unit.*

*hk*0	F_o	F_c
2.0.0	12·87	13·52
4	12·08	11·28
6	5·08	−4·00
8	4·64	3·53
10	0·65	−1·12
12	1·79	1·60
14	8·84	8·95
16	5·96	5·69
18	4·05	3·75
20	2·69	2·73
0.2.0	0·95	−0·79
4	12·91	12·01
6	9·01	−8·31
8	3·06	−1·50
10	1·32	−1·02
2.1.0	1·84	−1·51
4	15·08	16·94
6	7·96	8·21
8	4·52	3·52
10	6·46	−6·93
12	3·10	−3·19
14	1·92	−2·05
18	3·16	3·54
20	1·94	2·37
2.2.0	6·45	4·92
4	4·98	4·99
6	10·23	11·45
8	9·55	9·54
10	6·59	6·85
12	2·27	1·64
16	1·02	−1·48
18	0·60	−0·14
20	1·19	1·37
2.3.0	8·72	−8·94
4	11·20	−11·44

*hk*0	F_o	F_c
6	3·64	−3·25
8	2·63	3·13
10	5·96	6·19
12	4·70	4·66
14	3·05	3·68
16	2·29	2·24
18	0·78	0·29
2.4.0	2·52	2·60
4	3·36	−2·60
6	2·91	−2·30
8	7·45	−8·25
10	5·72	−5·98
12	5·27	−5·38
14	2·94	4·68
16.4.0	1·21	1·26
18	1·16	1·35
20	0·74	−0·74
2.5.0	0·96	−0·63
4	8·74	8·93
6	1·63	0·92
8	2·90	2·66
10	2·73	−4·06
18	1·75	2·37
20	1·12	1·42
2.6.0	9·13	−7·38
4	5·48	−4·87
6	3·50	−2·97
8	1·77	−1·03
10	5·91	−6·04
12	2·89	−2·69
14	3·31	−4·32
16	1·55	−1·48
18	2·79	−2·76
2.7.0	1·74	−2·14
6	1·28	−1·48

*hk*0	F_o	F_c
8	2·47	−2·19
10	0·72	0·09
12	2·53	2·81
14	1·64	1·73
18	0·46	−0·65
2.8.0	3·17	−3·10
4	4·08	−3·79
6	4·97	−5·22
8	4·77	−4·13
10	3·75	−3·49
12	2·79	−2·39
14	2·61	−2·01
16	1·30	−1·08
2.9.0	0·83	−1·14
6	1·18	−2·10
2.10.0	1·41	2·41
4	2·56	−3·33
6	1·37	−0·32
8	0·91	−1·11
10	0·50	−0·91
2.11.0	0·96	−1·41
4	0·46	−0·04
6	0·77	1·32
8	1·16	−1·23
10	1·89	−1·44
12	0·81	−0·65
2.12.0	1·18	0·88
4	2·01	2·00
6	2·19	1·48
8	1·76	1·58
2.13.0	1·33	−1·34
4	1·62	−1·74
*h*0*l*		
0.0.2	1·09	0·82

*h*0*l*	F_o	F_c
4	4·53	4·57
6	4·32	−4·69
8	3·39	4·04
10	1·52	1·57
1.0.2	7·41	−7·24
2	15·69	17·20
5	3·18	4·60
6	1·38	1·47
7	5·47	5·84
8	5·58	−5·32
12	2·76	3·17
13	0·99	0·70
14	4·85	3·95
15	0·94	0·58
16	4·42	3·65
17	2·37	1·75
18	3·01	2·66
19	2·71	2·25
21	1·48	1·15
1.0.4	0·91	−0·90
3	3·99	4·68
4	3·60	−2·66
5	5·78	5·86
6	8·82	−8·73
7	1·11	0·68
8	8·35	−8·43
9	0·50	−0·38
10	10·00	−10·69
11	2·22	−1·75
12	3·58	−2·56
13	2·10	1·94
14	1·06	−0·48
16	1·82	2·62
17	1·22	1·30
18	0·47	−0·49
19	1·04	1·18

*h*0*l*	F_o	F_c
20	0·71	−0·31
1.0.6	2·75	3·62
2	1·41	−1·81
3	2·67	2·67
4	4·24	−4·10
5	2·29	2·94
6	7·69	−7·59
8.0.6	7·97	−8·38
9	3·35	−3·19
10	2·50	−1·46
11	0·61	−0·36
12	1·59	−1·69
13	2·72	−3·42
14	1·99	−1·39
16	1·43	−1·25
17	0·72	−1·04
18	0·39	0·56
1.0.8	0·87	1·23
2	1·32	1·24
3	1·00	1·72
5	0·99	1·74
6	1·69	−2·20
8	1·48	−1·74
10	1·37	−1·99
11	2·53	−3·50
12	0·49	−0·50
13	1·67	−2·19
1.0.10	0·32	0·10
2	1·35	1·44
3	1·25	2·58
4	1·77	2·14
5	0·53	0·50
6	1·32	1·38
8	0·78	0·58

The co-ordinates of the atoms are given in Table 1. Figs. 1(*a*) and (*b*) show the final Fourier maps for the *hk*0 and the *h*0*l* projection respectively, and Fig. 2 the bond lengths, some of the bond angles, and the labelling of the atoms. Table 2 gives the observed and

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[4] Tomiie and Stam, *Acta Cryst.*, 1958, **11**, 126.

[5] Berghuis, Haanappel, Potters, Loopstra, MacGillavry, and Veenendaal, *ibid.*, 1955, **8**, 478.

calculated structure factors. Table 3 lists the remaining bond angles, those formed by bonds to the phosphorus atom.

TABLE 3. *The valency angles at the phosphorus atom.*

P′PS	P′PC$_1$	P′PC$_2$	SPC$_1$	SPC$_2$	C$_1$PC$_2$
111·8°	102·9°	104·0°	115·8°	113·8°	107·4°

The P–P distance is the same as that found in elementary phosphorus [6] (2·21 Å) and in P_2I_4 [7] (2·212 Å). The P–S length is a little longer than the length of formally comparable bonds found in the phosphorus sulphides [8] (1·94—1·96 Å), but is definitely longer than the P–S bond in $PSBr_3$ [9] (1·89 Å), $PSCl_3$ [10] (1·85 Å), and PSF_3 [10,11] (1·86 Å). There is no significant difference between the lengths of the two P–C bonds, and each agrees within experimental error with the corresponding length in $P(CH_3)_3$ [12] (1·87 Å). Thus there is no evidence that conjugation between the benzene ring and the rest of the molecule is greater than any hyperconjugation between the methyl group and the rest of the molecule. The bonds around the phosphorus atom are tetrahedrally disposed, but there seem to be slight departures from regular tetrahedral. The intermolecular distances are normal.

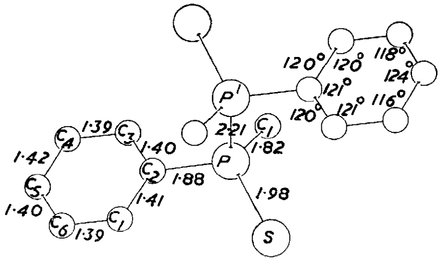

FIG. 2. *The numbering of the atoms and the molecular dimensions.*

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[6] Maxwell, Hendricks, and Mosley, *J. Chem. Phys.*, 1935, **3**, 699.

[7] Leung and Waser, *J. Phys. Chem.*, 1956, **60**, 539.

[8] Vos and Wiebenga, *Acta Cryst.*, 1955, **8**, 217; van Houten and Wiebenga, *ibid.*, 1957, **10**, 156.

[9] Secrist and Brockway, *J. Amer. Chem. Soc.*, 1944, **66**, 1941.

[10] Williams, Sheridan, and Gordy, *J. Chem. Phys.*, 1952, **20**, 164.

[11] Hawkins, Cohen, and Koski, *ibid.*, p. 528.

[12] Springall and Brockway, *J. Amer. Chem. Soc.*, 1938, **60**, 996.