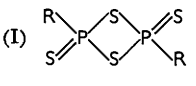
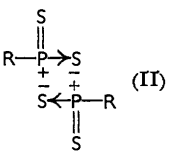
50. *An X-Ray Diffraction Determination of the Crystal and Molecular Structure of "Methyl Metadithiophosphonate,"* $[CH_3 \cdot PS_2]_2$.

By P. J. Wheatley.

A three-dimensional *X*-ray diffraction analysis of methyl metadithiophosphonate $CH_3 \cdot PS_2$ shows that the molecules are dimeric and contain a four-membered ring of two sulphur and two phosphorus atoms. The molecules have crystallographic symmetry $2/m$. The P–S distance within the ring corresponds to a single bond, and has a length 2·14 Å. The external P–S distance corresponds to a double bond, with a length 1·94 Å.

An improved method of synthesis of the so-called metadithiophosphonates or thionophosphine sulphides has recently been discovered,[1] and a study of the properties confirms the earlier conclusion [2] that the compounds are dimers $[R \cdot PS_2]_2$. Fay and Lakelma [2a] have suggested that the compounds have the structure (I), whereas Lecher *et al.*[2c] prefer an ionic formulation (II). The purpose of the present analysis was to determine the exact nature of these compounds.

(I) 

 (II)

Experimental

$[CH_3 \cdot PS_2]_2$. $M = 220{\cdot}3$. Monoclinic. $a = 6{\cdot}79_3 \pm 0{\cdot}030$, $b = 7{\cdot}04_6 \pm 0{\cdot}030$, $c = 9{\cdot}20_7 \pm 0{\cdot}040$ Å, $\beta = 92°\ 18' \pm 0{\cdot}5°$. $U = 440$ Å^3. $Z = 2$. $D_c = 1{\cdot}661$. $F(000) = 224$. Space group $I2/m$ (C_{2h}^3, No. 12). Cu-K_α radiation ($\lambda = 1{\cdot}542$ Å), single crystal rotation and Weissenberg photographs.

The crystals are very hygroscopic and had to be handled in a dry-box. They were sealed in thin-walled Pyrex capillaries for the photographic work. The crystals usually consisted of roughly spherical lumps with no definite faces, but occasionally a column could be found with the direction of elongation parallel to [*b*]. A suitable set of intensity photographs was obtained of the *h*0*l* zone, the intensities being estimated visually by means of a calibrated strip prepared from the same crystal. The crystals were small and uniform and no correction was made for absorption ($\mu = 123$ cm.$^{-1}$). The systematic absences in the *h*0*l* and *h*1*l* zones showed that the space group was $I2$, Im, or $I2/m$.

An examination of the *h*0*l* reflexions showed some very pronounced relations between the intensities. Consequently it was decided to solve the structure by an application of the Sayre relation.[3] The 26 *h*0*l* reflexions with the greatest unitary structure factors were selected, and many relations were obtained between the phases, none of which conflicted. A Fourier synthesis with these 26 planes yielded an adequate picture of the molecule in projection down the [*b*] axis. A few cycles of refinement confirmed the correctness of the structure, and it was evident that the space group was, in fact, $I2/m$, and that the molecule had crystallographic symmetry $2/m$. It was also evident that the structure could be refined three-dimensionally with little additional computation, since three of the atoms must lie in the *h*0*l* plane, and the other atom along the *y* axis.

Accordingly, intensities were collected for the layers *h*0*l*—*h*3*l* and refinement was carried out with the 254 reflexions observed to be non-zero. Although the *h* index did not run high enough to refine the only non-zero *y* co-ordinate by line syntheses along $y = 0$, there were about 20 reflexions that were very sensitive to the value of this co-ordinate. By a careful consideration of these reflexions the *y* co-ordinate of atom S_1 could be fixed within 0·001 of the cell side. The other co-ordinates were refined in the conventional way by means of Fourier and difference syntheses until the *R* factor for all 254 observed planes had dropped to 11·2%.

[1] Newallis, Chupp, and Groenweghe, *J. Org. Chem.*, 1961, **26**, in the press.

[2] (*a*) Fay and Lakelma, *J. Amer. Chem. Soc.*, 1952, **74**, 4933; (*b*) Kinnear and Perren, *J.*, 1952, 3437; (*c*) Lecher, Greenwood, Whitehouse, and Chao, *J. Amer. Chem. Soc.*, 1956. **78**, 5018.

[3] Sayre, *Acta Cryst.*, 1952, **5**, 60.

The scattering factors used were those of Tomiie and Stam [4] for the phosphorus and sulphur atoms, and that of Berghuis *et al.*[5] for the carbon atoms. Hydrogen atoms were ignored. A temperature factor of $B = 2{\cdot}0$ Å^2 proved adequate throughout. All layer lines were independently placed on an absolute scale by comparison with the calculated structure factors, the scale factor for each layer being altered, if necessary, as the refinement proceeded.

TABLE 1.

Fractional atomic co-ordinates.

Atom	x/a	y/b	z/c
S_1	0	0·225	0
S_2	0·375	0	0·202
P	0·098	0	0·142
C	−0·062	0	0·297

RESULTS

The co-ordinates of the atoms are given in Table 1, and the observed and calculated structure factors in Table 2. Fig. 1 shows the final three-dimensional Fourier section at $y = 0$, and Fig. 2 gives the labelling of the atoms, the bond lengths, and the bond angles. The P–S_2 distance agrees well with the similar bond distance found in the phosphorus sulphides (1·94—1·96 Å),[6] and is a little shorter than that found in 1,2-dimethyl-1,2-diphenyldiphosphine disulphide (1·98 Å).[7] It is estimated that the P–S distances are accurate to ±0·015 and the P–C distance to ±0·03 Å. The angles involving only

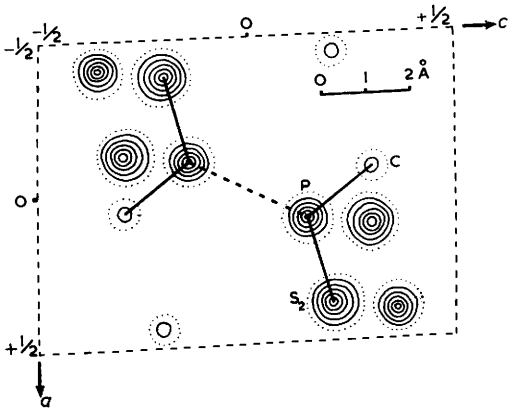


FIG. 1. Section of the molecule in the $h0l$ plane. (The contours are drawn at equal arbitrary intervals.)

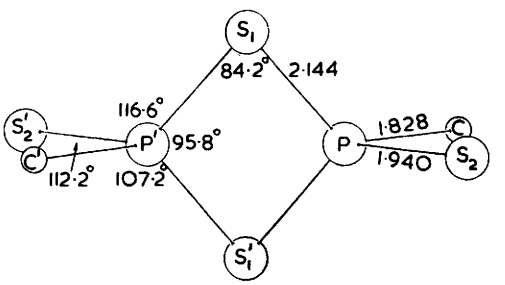


FIG. 2. The bond lengths, bond angles, and the labelling of the atoms.

phosphorus and sulphur atoms are estimated to be accurate to ±1°, and the angles involving the carbon atom to ±2°. The P–CH_3 distance is in accord with those found recently in organophosphorus compounds (1·82—1·84 Å),[7,8] provided that no fluorine atoms are attached to the carbon atom.[9] The P–S_1 distance (2·14 Å) is rather greater than the corresponding distance found in P_4S_3 (2·10 Å) [10] and in the higher phosphorus sulphides (2·08—2·085 Å),[6] but agrees exactly with that predicted from Pauling's covalent radii [11] for a single bond. It seems probable, therefore, that Fay and Lakelma's structure (I) adequately represents the bonding in the metadithiophosphonates.

[4] Tomiie and Stam, *Acta Cryst.*, 1958, **11**, 126.
[5] Berghuis, Haanappel, Potters, Loopstra, MacGillavry, and Veenendaal, *Acta Cryst.*, 1955, **8**, 478.
[6] Vos and Wiebenga, *Acta Cryst.*, 1955, **8**, 217; van Houten and Wiebenga, *ibid.*, 1957, **10**, 156.
[7] Wheatley, *J.*, 1960, 523.
[8] Dutta and Woolfson, *Acta Cryst.*, 1961, **14**, 178; Hamilton, *ibid.*, 1955, **8**, 199.
[9] Bowen, *Trans. Faraday Soc.*, 1954, **50**, 463; Spencer and Lipscomb, *Acta Cryst.*, 1961, **14**, 250.
[10] Hassel and Viervoll, *Acta Chem. Scand.*, 1947, **1**, 149.
[11] Pauling, "The Nature of the Chemical Bond," Cornell University Press, New York, 1940.

The angles within the four-membered ring are shown in Fig. 2. The S···S distance across the ring is 3·171 Å, and the P···P distance is 2·886 Å. The distance between two sulphur atoms in adjacent molecules along the [*b*] axis is 3·875 Å. The shortest contacts between the molecule at the origin and the one at the centre of the cell are: P···S_2, 3·806; C···S_2, 3·745; S_2···S_2, 4·025; S_1···S_2, 3·431; C···S_1, 4·068 Å.

TABLE 2.

Observed and calculated structure factors for one half-molecule (*i.e.*, twice the asymmetric unit).

*h*0*l*	F_o	F_c	*h*0*l*	F_o	F_c	*h*1*l*	F_o	F_c	*h*2*l*	F_o	F_c	*h*3*l*	F_o	F_c
2.0.0	18·61	18·79	$\bar{4}$.0.2	19·23	19·86	4	3·27	−2·70	4.2.2	4·03	−4·66	1.3.2	11·99	−10·97
4	5·54	−5·60	4	5·09	5·35				4	1·82	−0·78	4	3·11	−2·40
8	4·93	6·46	6	1·84	0·40	8.1.1	3·65	4·33	6	6·11	−6·64			
			8	5·15	6·48	3	1·37	−1·71	8	4·17	−3·59	1.3.6	2·09	−2·50
0.0.2	4·44	−4·3	10	4·04	2·96							10	6·07	−6·43
4	5·99	6·13				$\bar{1}$.1.2	14·71	15·82	5.2.1	2·38	−2·70			
6	13·22	13·03	$\bar{5}$.0.1	2·30	−1·43	4	15·26	−15·08	3	4·93	−4·73	2.3.3	12·86	−12·66
8	4·16	3·75	3	10·12	10·73	6	6·57	5·71	5	1·59	0·92	5	2·32	1·53
10	4·32	5·40	5	8·27	9·80	8	5·72	4·74	7	8·55	−7·69	7	2·44	3·13
			7	5·95	−4·57	10	2·21	−2·42				9	8·54	−9·21
1.0.1	3·32	2·92	9	4·90	7·50				6.2.2	2·49	−3·75			
3	13·80	13·53				$\bar{2}$.1.1	2·81	−2·66				3.3.2	16·88	−17·41
5	4·55	2·61	$\bar{6}$.0.2	6·66	7·49	3	10·78	11·29				4	8·23	8·09
7	14·87	13·60	4	3·19	3·64	5	9·43	−7·74	6.2.4	2·79	2·50	6	3·01	−2·97
			6	7·68	7·91	9	8·05	8·36	6	8·33	−10·24	8	5·73	−4·98
2.0.2	4·31	3·43	8	2·69	−1·69	11	3·39	−4·87						
4	4·14	3·47							7.2.1	1·04	0·42	4.3.1	9·32	−9·05
6	16·54	17·35	$\bar{7}$.0.1	4·57	−3·46	$\bar{3}$.1.2	10·34	8·35	5	6·33	−6·42	3	3·61	3·30
10	1·93	1·97	3	6·78	7·26	4	4·95	−4·30				5	3·16	−3·25
			5	4·26	4·80	10	4·05	5·82	8.2.2	1·72	−2·15	7	1·52	−0·77
3.0.1	1·05	−0·70										9	4·38	−4·47
3	5·15	4·93	$\bar{8}$.0.2	2·39	−1·80	$\bar{4}$.1.1	3·07	−3·03						
5	17·72	16·34	4	3·52	4·24	3	13·84	13·87	$\bar{1}$.2.1	1·81	2·06	5.3.2	2·71	−2·82
9	2·55	3·31				5	6·46	−7·34	3	9·56	−9·07	6	1·72	−1·33
			*h*1*l*			9	3·32	2·35	5	19·18	−18·87	8	5·63	−5·50
			1.1.0	6·80	7·41				7	6·15	5·30			
4.0.2	8·72	8·78	3	5·42	6·76	$\bar{5}$.1.2	2·15	−2·08	9	5·64	−6·39	6.3.1	5·73	−5·85
4	11·66	11·23	7	3·76	−4·69	4	7·55	9·02	11	5·04	−4·12	3	4·35	3·59
6	3·14	2·87				6	3·09	−3·57				5	2·63	−2·17
8	2·38	3·91	0.1.1	13·10	13·37	8	2·21	−2·02						
10	2·77	0·88	3	13·53	−13·18				$\bar{2}$.2.2	6·52	−7·37	7.3.2	5·70	5·50
			5	5·47	4·95	$\bar{6}$.1.5	3·26	4·42	4	7·71	−5·99	4	4·73	−4·26
5.0.1	8·96	9·07	7	3·71	2·94	7	2·19	−1·14	6	14·01	−13·61			
3	3·28	3·52	11	2·28	−1·73				8	2·31	1·72	$\bar{1}$.3.2	5·44	6·32
5	10·08	10·44				$\bar{7}$.1.2	1·88	−0·83	10	2·34	−2·52	4	17·19	−16·77
9	3·23	1·70	1.1.2	9·68	−8·18	4	3·44	4·02				8	2·42	1·83
			4	3·40	2·76				$\bar{3}$.2.1	2·07	1·52	10	4·12	−4·13
6.0.2	4·53	5·63				$\bar{8}$.1.3	3·83	−4·22	3	6·90	−7·75			
4	9·81	11·24	1.1.6	1·30	1·17				5	9·10	−7·19	$\bar{2}$.3.1	5·34	−6·49
6	3·39	−3·78	8	5·07	5·87	*h*2*l*			7	7·13	−7·56	3	3·32	4·20
			10	4·91	−5·07	2.2.0	4·47	−4·14	9	1·61	−0·83	5	12·21	−10·42
7.0.1	8·48	8·51				4	17·91	−18·79				7	2·43	−3·06
3	4·49	6·14	2.1.1	8·88	8·80	6	8·10	−9·42	$\bar{4}$.2.2	6·35	5·19	9	4·33	5·10
5	1·53	−0·55	3	10·41	−10·05				4	5·12	−6·58			
			5	7·28	5·94	0.2.2	22·52	−24·72	6	9·66	−9·41	$\bar{3}$.3.2	3·21	2·67
8.0.2	2·10	3·78	7	5·62	6·93	4	11·34	−11·32	8	1·84	−1·61	4	8·31	−7·35
			9	7·39	−7·88	8	5·21	−6·15				6	2·32	−1·32
$\bar{1}$.0.1	29·36	30·54	11	2·33	3·81	10	1·57	−1·99	$\bar{5}$.2.1	11·68	−12·61	8	3·72	−4·70
3	13·16	10·97							7	11·77	−11·92	10	2·56	3·31
5	8·08	−5·29	3.1.2	16·30	−16·11	1.2.1	20·36	−19·83	9	1·57	1·32			
7	17·61	17·35	4	14·48	13·77	3	8·07	−6·73				$\bar{4}$.3.1	5·81	−6·27
9	3·95	2·01	8	3·27	−2·97	5	11·04	−11·41	$\bar{6}$.2.4	3·52	−5·03	3	8·57	8·44
			10	1·54	1·94	7	1·72	1·96	8	5·52	−7·17	5	9·27	−9·58
						9	7·37	−6·08				7	3·30	−1·95
$\bar{2}$.0.2	12·45	12·59	4.1.1	6·34	−5·94	11	5·97	−6·36	$\bar{7}$.2.1	10·17	−10·94			
4	8·27	9·85	3	9·30	7·67							$\bar{5}$.3.2	4·99	−5·14
6	1·34	−1·91	9	2·23	−3·04	2.2.2	14·98	−14·74	$\bar{8}$.2.2	7·05	−7·50	4	5·04	5·07
8	11·75	11·60				4	12·50	−11·46				6	4·81	−5·61
10	4·21	4·50	5.1.4	4·29	4·26	6	4·54	4·79				8	3·01	−3·73
			8	4·07	−4·27	8	10·71	−9·59	*h*3*l*					
$\bar{3}$.0.1	18·53	19·87				10	5·47	−4·60	1.3.0	1·67	−1·08	$\bar{6}$.3.1	2·64	−2·33
3	8·53	7·44	6.1.1	3·45	−3·51				5	3·22	−4·32	5	2·03	1·61
5	3·61	5·19	3	7·99	6·87	3.2.1	15·80	−16·86	7	5·79	−6·40	7	2·75	−2·86
7	2·60	2·31	7	3·76	−3·89	3	10·20	−9·56						
9	8·05	7·01				5	4·65	3·62	0.3.1	1·52	3·19	$\bar{7}$.3.2	2·90	−2·90
11	2·79	4·16	7.1.2	7·54	8·63	7	9·85	−9·38	3	13·19	−15·24	4	1·96	1·54
						9	4·34	−3·94	9	1·74	−1·25			

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