The Crystal and Molecular Structure of Tetraethyl Diphosphine Disulphide

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The crystal and molecular structure of tetraethyl diphosphine disulphide, $(C_2H_5)_4P_2S_2$, has been determined by the application of direct methods and refined by a three-dimensional least-squares treatment. The unit cell is triclinic with

$$a = 8\cdot98 \pm 0\cdot03, \quad b = 6\cdot45 \pm 0\cdot02, \quad c = 6\cdot15 \pm 0\cdot02 \text{ Å}; \quad \alpha = 113\cdot0 \pm 0\cdot5, \quad \beta = 85\cdot2 \pm 0\cdot3, \quad \gamma = 102\cdot5° \pm 0\cdot3°.$$

The space group is $P\bar{1}$ and the unit cell contains one molecule.

By far the most striking feature of the analysis is the establishment, for the first time, of an accurate P–P bond length (2·22 ± 0·01 Å) in an organo-phosphorus compound. In view of the lack of structural investigations in this field a searching analysis of the results has been made.

Introduction

In recent years the chemistry of organo-phosphorus compounds has attracted considerable attention. Of special interest are the tetra-alkyl diphosphine disulphides which are formed as unexpected products during the course of organomagnesium synthesis (see, for instance, Kabachnik & Shepheleva, 1949; Fox, 1957). The nature of such compounds is not clear (Kosolapoff, 1950).

Since the precise nature of the chemical bonding, especially the nature of P–P bond, is likely to be of great import to research workers in this field it seemed to be of interest to undertake the structural investigation of the methyl and ethyl derivatives. In this paper we shall be concerned with the crystal and molecular structure of tetraethyl diphosphine disulphide; since, so far as the authors are aware, no crystallographic studies on compounds of this type have been made, it was considered worthwhile to carry out a three-dimensional analysis to establish accurate bond lengths and bond angles.

Experimental

Crystals of tetraethyl diphosphine disulphide, $(C_2H_5)_4P_2S_2$, suitable for X-ray analysis, were supplied by Dr P. C. Crofts, of the Chemistry Department, College of Science and Technology, Manchester, and prepared by Fox (1957). The crystals (m.p. 76 °C.) were colourless, well-defined plates parallel to (001).

Crystal data

Oscillation and Weissenberg photographs taken about the three axes with Cu $K\alpha$ radiation showed the unit cell to be triclinic with the following dimensions:

$$a = 8\cdot98 \pm 0\cdot03, \quad b = 6\cdot45 \pm 0\cdot02, \quad c = 6\cdot15 \pm 0\cdot02 \text{ Å};$$
$$\alpha = 113\cdot0 \pm 0\cdot5, \quad \beta = 85\cdot2 \pm 0\cdot3, \quad \gamma = 102\cdot5 \pm 0\cdot3°.$$

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The density as measured by flotation was found to be 1·25 g.cm.$^{-3}$ which required 1 molecule per unit cell (calculated density = 1·27 g.cm.$^{-3}$).
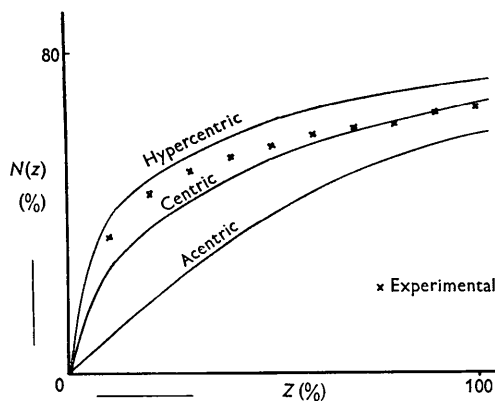

Fig. 1. Intensity distribution curve for $(C_2H_5)_4P_2S_2$: (001) projection.

The choice between the two possible space groups $P1$ and $P\bar{1}$ was made from a statistical analysis of the intensities of the $hk0$ reflexions (Howells, Phillips & Rogers, 1950; Lipson & Woolfson, 1952). Comparison of the experimental and theoretical distribution curves, as shown in Fig. 1, pointed unequivocally to the centrosymmetric space group $P\bar{1}$. Since there is only one molecule in the unit cell, this demands that the molecule itself should be centrosymmetric.

Intensity data

Multiple-film equi-inclination Weissenberg photographs around the two short axes were used to record the intensities. Using Ni-filtered Cu $K\alpha$ radiation all the layer lines with equi-inclination angles less than 40° $(hk0)$, $(hk1)$ ... $(hk5)$ and $(h0l)$ ... $(h5l)$ were surveyed. Thus, about 86% (1216) of the total (1415)

observable reflexions were explored. Of these, however, only 864 were observed.

The dimensions of the crystal specimens used were

$$0{\cdot}02 \text{ mm.} \times 0{\cdot}14 \text{ mm.} \times 0{\cdot}25 \text{ mm.}$$
and
$$0{\cdot}03 \text{ mm.} \times 0{\cdot}25 \text{ mm.} \times 0{\cdot}34 \text{ mm.}$$

for the c and b axis photographs respectively.

The intensities were measured visually by comparison with an intensity scale of calibrated spots of known relative exposures developed under identical conditions. Of the 864 unique reflexions observed, the intensities of 203 were estimated once, 509 twice (i.e. on separate photographs taken around different axes) and 152 three times. For each layer line the film ratios were determined by independent measurement of the common reflexions of medium intensity.

The L–P, spot-shape and absorption factors were calculated on the Manchester University Mercury computer. The procedure adopted for correcting absorption was essentially a machine adaptation of Albrecht's (1939) method. As for spot-shapes, Phillips' (1954, 1956) method was applied first; later on, however, it turned out that Phillips' formula did not adequately correct for such variations; the intensities were therefore normalised to the absolute scale by comparing independently, separately for each layer, the observed and calculated values for the extended and contracted reflexions.

The preliminary structure

The preliminary structure of $(C_2H_5)_4P_2S_2$ was determined by two-dimensional Fourier projection studies. Owing to the relative shortness of the c and b axes, the (001) and (010) projections were selected for this purpose. Direct sign-determining methods were used exclusively in solving both these projections.

The (001) projection

Harker–Kasper inequalities were used first to relate the signs of as many structure factors as possible. They yielded information about thirty-six structure factors; of these six were proved to be positive, two could be assumed to be positive and three of the others were obtained in terms of two letter symbols a and b.

The sign relationship

$$S_H \approx S\left\{\sum_{H'} S_{H'} S_{H+H'}\right\}$$

(Zachariasen, 1952) was used next to establish signs for thirteen relatively large structure factors ($0{\cdot}27 \leq |U_H| \leq 0{\cdot}30$).

Thus, eventually, signs of 49 of the 99 observed reflexions were determined. With the signs of about 50% of the larger structure factors (fairly distributed among the various parity groups) known it was certain that the Fourier synthesis would give a recognizable

representation of the structure. However, the presence of the two letter symbols a and b meant that there were four possible sets of signs.
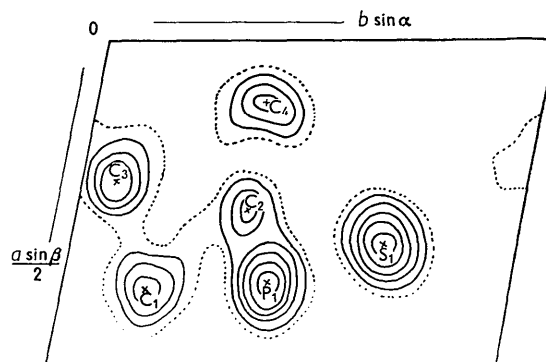

Fig. 2. The (001) Fourier projection. Contour scale, arbitrary; the starting (zero) contours are dashed.

However, the further application of the sum and difference inequalities

$$(U_H \pm U_{H'}) \leq (1 \pm U_{H+H'})(1 \pm U_{H-H'})$$

pointed strongly to the conclusion that $a = -1$. This eliminated two possibilities; the Fourier syntheses corresponding to the remaining two sign-combinations were computed on the Manchester University Mark I computer. On inspection, the synthesis corresponding to $a = -1$ and $b = +1$ gave a map which clearly showed the molecule. The projection was partially refined by conventional Fourier methods; Fig. 2 shows the electron-density distribution after two stages of normal Fourier refinement.

At this stage the conventional reliability index was 19% (excluding the accidental absences).

The (010) projection

Direct methods were used once again for determining the signs of the $h0l$ reflexions; the technique adopted was very similar to that followed for the $hk0$-zone.
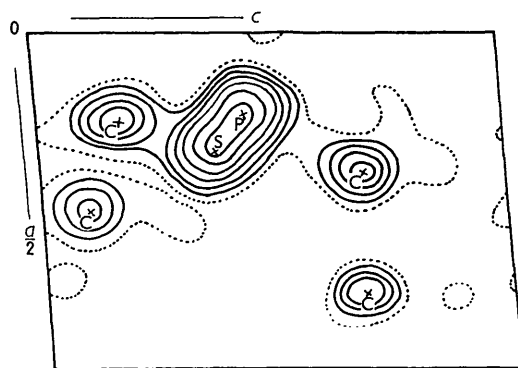

Fig. 3. The (010) Fourier projection. Contour scale, arbitrary; the starting (zero) contours are dashed.

Eventually signs of 38% of the observed reflexions were established with reasonable certainty in terms of two arbitrary symbols a and b and a final check for self-consistency of the signs indicated strongly that $a=b$. As a consequence, although $a=b$ was not definitely accepted, it seemed reasonable to assign priority to such sets of signs; however, $a = b = +1$ was not possible since a large 'origin-peak' would be inconsistent with the (001) projection so that the set corresponding to $a=b=-1$ was given the highest priority. The Fourier synthesis corresponding to these signs gave peaks which agreed very well with the projection of the model constructed on the basis of the (001) projection. The Fourier map after two stages of normal Fourier refinement is shown in Fig. 3. The agreement residual at this stage was 26%.

Three-dimensional refinement

The structure was refined by successive applications of the method of least squares as adapted by Hughes (1941) to the problem of multi-parameter refinement in crystal-structure analyses. The computations were carried out on the Manchester University Mercury computer. The authors are indebted to Mr O. S. Mills, of the Department of Chemistry, University of Manchester, for providing the programme for this purpose.

The logic involved in the design of the programme consisted essentially of three basic stages, namely:

(i) the calculation of the structure factors,
(ii) evaluation, formation and accumulation of the relevant derivatives and appropriate 'product commands' for each atom,
(iii) solution of the resulting normal equations for positional parameter shifts and for the changes in the temperature and scale-factors.

For the calculation of the structure factors the atomic scattering factors given by Berghuis *et al.* (1955) for carbon and those by Tomiie & Stam (1958) for phosphorus and sulphur were used.

The refinement was carried out essentially in two parts; the first stage was used to assign individual isotropic temperature factors to each atom, while the second part consisted of six stages of isotropic refinement. Convergence was indicated after three successive stages; nevertheless the refinement was carried out for three more stages just to follow up the 'mood' of convergence somewhat further. In the final refinement stage the average shifts in positional parameters was about 0.001 Å, the maximum shift being less than 0.003 Å.

The final values of the atomic parameters are listed in Table 1.

The resulting agreement between the observed and calculated structure factors is shown in Table 2.

It would appear that the final structure-factor agreement is very satisfactory considering that the contributions of hydrogen atoms have not been in-

Table 1. *Atomic parameters*

	x/a	y/b	z/c	B_i (Å^2)
P_1	0·1197	0·0484	0·0614	1·59
S_1	0·1832	−0·1916	0·1257	3·21
C_1	0·1193	0·3168	0·3217	5·75
C_2	0·2221	0·1267	−0·1725	5·28
C_3	0·2768	0·4399	0·4197	6·94
C_4	0·3915	0·1312	0·1734	6·23

cluded and reflexions showing pronounced extinction have not been excluded in the calculation of R-factors.

The values of R are given in Table 3 as a function of l.

The overall R factor is 14·9% with accidental absences excluded and 17·4% if they are included. Undoubtedly (and conventionally) this value could be reduced somewhat by omitting reflexions suspected of extinction and by including the hydrogen scattering.

As a check on the least-squares refinement a final three-dimensional Fourier synthesis was calculated using all the observed reflexions. A general Fourier synthesis programme designed by Mr Mills for the Mercury computer was used for this purpose. The speed of computation was extremely fast; each section
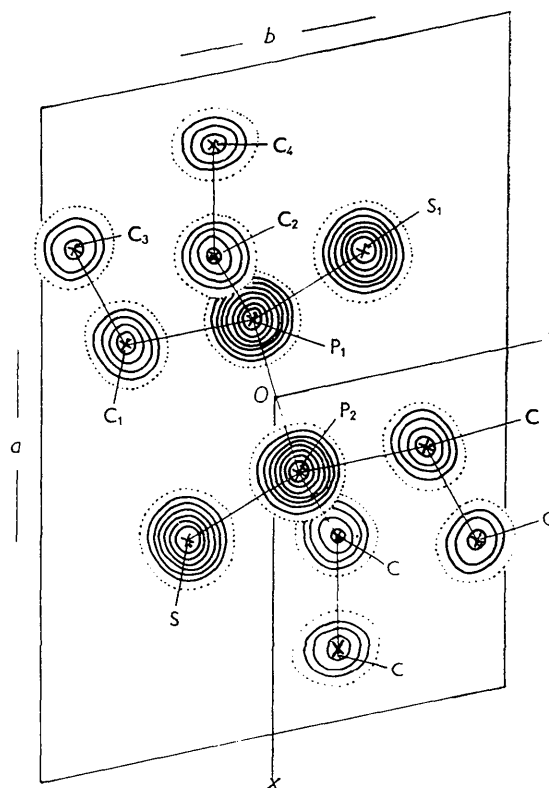

Fig. 4. Composite map of sections through (or near) the atomic sites in the three-dimensional Fourier synthesis shown projected on the c-plane.

Contour intervals are 1 e.Å^{-3} for carbon and 2·5 e.Å^{-3} for phosphorus and sulphur; the starting contours 2 e.Å^{-3} (in the case of C) and 2·5 e.Å^{-3} (in the case of P and S) are dotted.

Table 2. *Comparison of observed and calculated structure factors*

h	k	l	$10F_o$	$10F_c$
1	0	0	256	297
2			291	-270
3			292	-266
4			190	-168
5			29	6
6			17	9
7			48	39
8			39	32
9			23	22
10			38	23
11			10	1
-11	1	0	10	3
-10			44	54
-9			69	71
-8			20	21
-7			116	-106
-6			76	-73
-5			69	47
-4			42	-45
-3			57	-55
-2			65	-57
-1			182	191
0			247	303
1			56	55
2			44	54
3			289	-245
4			227	-235
5			10	-18
6			70	65
7			128	100
8			49	48
9			10	1
10			10	-15
-11	2	0	10	-5
-10			30	35
-9			66	66
-8			58	51
-7			58	-39
-6			73	-85
-5			107	-127
-4			10	-17
-3			161	149
-2			10	-20
-1			23	7
0			10	10
1			40	15
2			78	82
3			20	-31
4			71	-72
5			128	-115
6			20	-29
7			112	94
8			72	70
9			10	10
10			20	-24
-11	3	0	10	2
-10			10	9
-9			53	49
-8			69	66
-7			17	13
-6			67	-75
-5			195	-193
-4			132	-128
-3			44	41
-2			207	216
-1			280	253
0			60	-66
1			124	-114
2			14	1
3			10	-4
4			43	-36
5			85	-73
6			10	-7
7			57	48
8			40	46
9			20	23
-10	4	0	14	16
-9			10	5
-8			10	-7
-7			17	14
-6			17	-20
-5			142	-131
-4			116	-94
-3			33	50
-2			220	201
-1			139	172
0			10	-6
1			95	-86
2			151	-141
3			80	-71
4			17	24
5			29	30
6			20	30
7			14	18
8			17	10
-10	5	0	17	20
-9			20	-5
-8			40	-30
-7			17	-21
-6			10	-19
-5			10	-4
-4			10	13
-3			10	-9
-2			36	42
-1			66	67
0			44	31
1			44	-26
2			101	-86
3			57	-55
4			10	-5
5			34	38
6			52	48
7			14	13
-8	6	0	35	-22
-7			61	-41
-6			43	-36
-5			10	8
-4			52	35
-3			14	27
-2			10	13
-1			10	-12
0			10	13
1			10	15
2			10	-29
3			49	-42
4			30	-20
5			35	22
-6	7	0	68	-44
-5			10	-2
-4			74	40
-3			82	49
-2			10	19
-1			10	-15
0			10	-16
1			10	-18
2			10	-14
-3	-7	1	10	-6
-2			10	-13
-1			32	-27
0			35	-17
1			10	5
2			53	41
3			78	51
-5	-6	1	14	8
-4			10	-28
-3			10	-29
-2			10	-17
-1			10	-5
0			10	10
1			10	-12
2			10	11
-7	-5	1	20	28
-6			45	54
-5			35	34
-4			43	-50
-3			123	-109
-2			96	-90
-1			46	43
0			97	98
1			35	30
2			17	30
3			17	18
4			10	13
5			10	-14
6			52	-59
7			54	-46
8			29	-21
9			20	25
10			32	44
-8	-4	1	10	6
-7			14	13
-6			49	50
-5			10	23
-4			53	-56
-3			104	-110
-2			122	-118
-1			10	24
0			143	134
1			203	188
2			100	100
3			116	-111
4			151	-110
5			71	-69
6			10	-21
7			56	26
8			10	12
9			10	16
10			17	18
11			10	18
-9	-3	1	20	27
-8			29	31
-7			14	10
-6			10	-15
-5			38	-39
-4			20	21
-3			10	-14
-2			108	-96
-1			54	-21
0			10	-5
1			189	147
2			172	175
3			10	8
4			144	-144
5			200	-206
6			14	-8
7			100	95
8			52	46
9			10	12
10			10	-5
11			10	2
-10	-2	1	14	-11
-9			58	39
-8			52	69
-7			69	62
-6			17	-22
-5			149	-136
-4			101	-92
-3			10	-9
-2			101	109
-1			52	-55
0			250	-231
1			237	230
2			348	297
3			111	81
4			121	-132
5			238	-218
6			78	-77
7			20	18
8			73	85
9			65	68
10			14	5
11			10	-15
-10	-1	1	10	-9
-9			25	24
-8			83	83
-7			157	122
-6			46	-45
-5			263	-236
-4			182	-194
-3			61	-67
-2			218	182
-1			216	202
0			247	249
1			160	151
2			221	-185
3			23	-26
4			81	-67
5			169	-130
6			65	-56
7			10	-2
8			80	76
9			81	72
10			20	27
11			10	-15
-11	0	1	10	7
-10			25	16
-9			29	18
-8			36	24
-7			39	28
-6			38	-31
-5			42	-47
-4			151	-163
-3			218	-166
-2			235	222
-1			309	313
0			270	332
1			10	-3
2			279	-299
3			238	-227
4			130	-118
5			120	110
6			110	89
7			17	-17
8			23	11
9			46	31
10			32	21
11			14	-11
-11	1	1	10	15
-10			42	49
-9			25	27
-8			10	-11
-7			40	-39
-6			32	-37
-5			49	38
-4			23	-21
-3			97	-64
-2			132	-149
-1			45	-49
0			396	444
1			192	182
2			183	-191
3			218	-232
4			87	-109
5			61	73
6			72	68
7			51	44
8			10	18
9			14	-11
10			10	-4
-11	2	1	10	8
-10			46	53
-9			63	70
-8			23	33
-7			99	-101
-6			143	-131
-5			10	-5
-4			25	15
-3			25	8
-2			23	-32
-1			98	103
0			225	192
1			56	33
2			27	12
3			109	-132
4			160	-173
5			29	-33
6			55	56
7			88	89
8			40	44
9			10	-6
10			10	-23
-11	3	1	10	9
-10			40	35
-9			55	50
-8			20	19
-7			71	-69
-6			105	-108
-5			101	-114
-4			10	-8
-3			206	192
-2			162	161
-1			48	63
0			69	-57
1			104	-100
2			43	-38
3			51	-46
4			14	-17
5			10	-14
6			10	8
7			53	60
8			43	42
9			10	-1
-10	4	1	10	5
-9			10	2
-8			10	5
-7			27	-12
-6			39	-37
-5			83	-75
-4			17	-20
-3			95	76
-2			131	127
-1			96	111
0			63	-73
1			148	-146
2			61	-60
3			39	18
4			39	44
5			10	9
6			10	7
7			10	17
8			10	8
-9			10	-10
-8			25	-25
-7			10	-8
-6			10	8
-5			20	-28
-4			40	-31
-3			10	11
-2			80	77
-1			86	74
0			10	-14
1			54	-52
2			60	-64
3			27	-31
4			17	24
5			27	33
6			10	23
-7	6	1	35	-27
-6			10	-13
-5			10	9
-4			42	32
-3			10	19
-2			10	17
-1			10	13
0			10	-1
1			17	-19
2			49	-42
3			10	-25
4			20	6
-4	7	1	53	40
-3			35	28
-2			10	3
-1			20	-25
0			20	-22
-4	-7	2	10	6
-3			10	-2
-2			10	-23
-1			53	-49
0			20	-18
1			44	44
2			75	56
3			43	36
-6	-6	2	10	9
-5			10	-8
-4			14	-25
-3			20	-30
-2			10	-18
-1			10	-16
0			10	9
1			10	22
2			69	54
3			114	75
-7	-5	2	23	36
-6			20	30
-5			39	-11
-4			106	-87
-3			68	-82
-2			10	-7
-1			67	63
0			114	109
1			14	34
2			32	-18
3			10	-18
4			10	-3
5			10	-3
6			61	-75
7			64	-53
8			35	23
9			53	52
10			38	40
-8	-4	2	10	9
-7			17	16
-6			23	35
-5			10	22
-4			64	-65
-3			128	-119
-2			91	-98
-1			101	106
0			222	221
1			75	39
2			75	-59
3			119	-86
4			44	-39
5			10	1
6			23	-16
7			10	6
8			10	2
9			10	16
10			36	31
11			10	10
-9	-3	2	25	28
-8			10	15
-7			10	-12
-6			29	25
-5			14	22
-4			65	-53
-3			118	-109
-2			133	-124
-1			20	35
0			159	121
1			229	109
2			120	171
3			125	-124
4			136	-174
5			98	-93
6			10	-2
7			74	66
8			38	35
9			10	15
10			10	2
11			10	0
-10	-2	2	14	18
-9			55	52
-8			59	53
-7			10	0
-6			51	-60
-5			141	-143
-4			43	-51
-3			29	41
-2			10	-2
-1			83	85
0			61	72
1			176	168
2			139	131
3			48	-69
4			180	-177
5			245	-244
6			32	-30
7			137	141
8			113	102
9			25	28
10			25	-22
11			10	-22
-10	-1	2	10	3
-9			47	45
-8			59	61
-7			27	26
-6			71	-84
-5			222	-201
-4			105	-99
-3			79	78
-2			346	316
-1			269	223
0			300	-236
1			105	-93
2			39	36
3			10	-8
4			90	-89
5			157	-124
6			10	13
7			63	64
8			87	73
9			51	47
10			14	-15
11			10	-34
-10	0	2	20	3
-9			17	7
-8			27	25
-7			103	71
-6			36	-17
-5			196	171
-4			147	-132
-3			23	8
-2			240	205
-1			125	109
0			32	29
1			10	25
2			196	-200
3			58	-67
4			56	58
5			10	15
6			10	12
7			10	-6
8			40	27
9			42	29
10			10	4
-10	1	2	20	28
-9			14	15
-8			10	0
-7			10	-6
-6			52	-50
-5			32	-33
-4			74	-71
-3			127	-127
-2			69	82
-1			206	213
0			210	250
1			27	39
2			177	-209
3			158	-184
4			90	-102
5			69	70
6			104	106
7			20	20
8			10	-3
9			10	-1
10			10	1
-10	2	2	47	52
-9			32	31
-8			20	-32
-7			83	-90
-6			78	-89
-5			10	15
-4			55	52
-3			63	69
-2			49	40
-1			17	-4
0			100	137
1			40	51
2			132	-144
3			183	-185
4			69	-82
5			69	79
6			95	55
7			47	50
8			10	9
9			20	-25
-10	3	2	23	31
-9			17	28
-8			10	-3
-7			91	-80
-6			110	-101
-5			10	10
-4			108	96
-3			131	110
-2			17	11
-1			34	-35
0			20	-12
1			51	-53
2			14	-18
3			10	-17
4			10	-28
5			10	12
6			32	35
7			38	42
8			10	12
-9	4	2	23	34
-8			10	3
-7			32	-57
-6			53	-46
-5			42	-36
-4			10	3
-3			92	91
-2			101	85
-1			10	18
0			50	-61
1			63	-78
2			10	-15
3			10	7
4			10	18
5			10	11
6			10	1
7			10	15
-8	5	2	10	-16
-7			17	-14
-6			10	-10
-5			25	-21
-4			10	1
-3			51	45
-2			74	60
-1			71	45
0			23	-34
1			86	-83
2			56	-48
3			10	6
4			29	38
5			20	15
-6	6	2	20	13
-5			20	18
-4			20	13
-3			10	9
-2			10	16
-1			10	11
0			23	-22
1			38	-33
2			10	-24
-4	-7	3	10	1
-3			10	-21
-2			30	-38
-1			30	-30
0			10	8
1			86	67
2			120	64
3			10	15
-6	-6	3	10	-5
-5			10	-20
-4			10	-24
-3			10	-10
-2			10	5
-1			10	-20
0			10	-1
1			98	71
2			141	67
3			46	18
4			87	-55
-7	-5	3	23	35
-6			10	-6
-5			44	-43
-4			46	-51
-3			35	-27
-2			29	28
-1			63	41
0			48	52
1			10	2
2			25	-26
3			39	29
4			17	-5
5			43	-42
6			55	-52
7			39	-23
8			52	36
9			47	46
10			17	26
-8	-4	3	23	21
-7			34	29
-6			27	23
-5			10	-7
-4			94	-103
-3			110	-113
-2			10	-2
-1			113	103
0			180	164
1			43	43
2			55	-55
3			70	-70
4			30	-39
5			20	28
6			14	-28
7			54	-43
8			10	17
9			58	45
10			56	35
-9	-3	3	14	21
-8			10	17
-7			10	-5
-6			10	-1
-5			10	-7
-4			73	-76
-3			105	-102
-2			94	-81
-1			141	128
0			363	323
1			143	114
2			126	-104
3			258	-197
4			116	-123
5			10	-5
6			44	21
7			68	59
8			39	36
9			10	9
10			10	8
11			10	-6
-9	-2	3	42	44
-8			20	14
-7			65	-59
-6			53	-59
-5			25	-15
-4			17	-5
-3			10	11
-2			10	2
-1			93	111
0			78	82
1			53	15
2			55	40
3			118	-149
4			165	-176
5			49	-53
6			61	65
7			113	119
8			46	50
-10	-1	3	17	21
-9			46	41
-8			29	30
-7			20	-19
-6			56	-65
-5			135	-125
-4			14	-22
-3			126	134
-2			98	94
-1			43	27
0			81	-87
1			10	-7
2			53	61
3			10	-19
4			51	-43
5			127	-108
6			23	-19
7			103	95
8			76	71
9			10	11
10			10	-33
-10	0	3	10	6
-9			44	25
-8			49	38
-7			27	26
-6			73	-65
-5			207	-162
-4			105	-89
-3			92	50
-2			272	223
-1			232	233
0			47	-74
1			111	-132
2			64	-57
3			10	-5
4			14	-15
5			44	-57
6			23	15
7			68	47
8			58	39
9			35	22
10			17	-14
-10	1	3	10	16
-9			10	-2
-8			20	-21
-7			10	-1
-6			25	-23
-5			111	-90
-4			72	-62
-3			49	48
-2			250	237
-1			156	152
0			10	-8
1			74	-84
2			187	-198
3			122	-111
4			27	34
5			85	60
6			65	66
7			10	13
8			10	-2
9			10	-4
-10	2	3	10	22
-9			10	-7
-8			32	-38
-7			29	-36
-6			23	-32
-5			17	24
-4			59	56
-3			10	4
-2			10	16
-1			32	17
0			43	53
1			25	-22
2			121	-120
3			63	-75
4			10	-6
5			62	69
6			78	79
7			14	14
8			17	-22
-9	3	3	10	13
-8			17	-25
-7			38	-59
-6			59	-49
-5			17	28
-4			57	63
-3			47	49
-2			10	8
-1			25	-44
0			10	6
1			10	19
2			10	-27
3			29	-52
4			42	-30
5			40	36
6			49	47
7			10	20
-8	4	3	10	-10
-7			45	-42
-6			54	-53
-5			10	1
-4			71	60
-3			109	81
-2			25	26
-1			20	-32
0			30	-37
1			40	-43
2			14	-17
3			10	7
4			10	9
5			10	16
-6	5	3	10	-10
-5			10	6
-4			27	23
-3			39	41
-2			30	29
-1			10	-8
0			60	-47
1			59	-52
2			10	-8
3			10	22
-3	-7	4	10	-29
-2			14	-26
-1			10	4
0			29	15
1			61	61
2			39	35
3			43	-31
-5	-6	4	10	-24
-4			10	-6
-3			10	-1
-2			10	-11
-1			27	-9
0			10	8
1			57	59
2			78	50
3			10	-5
4			83	-61
-7	-5	4	10	22
-6			10	-17
-5			63	-51
-4			42	-39
-3			10	-5
-2			59	43
-1			17	16
0			17	-13
1			44	42
2			87	50
3			34	16
4			63	-54
5			77	-75
6			58	-28
7			10	7
-8	-4	4	17	28
-7			35	32
-6			23	-18
-5			61	-77
-4			56	-80
-3			17	-29
-2			62	71
-1			84	99
0			100	105
1			20	15
2			140	-97
3			52	-52
4			10	-26
5			14	-18
6			10	-17
7			10	-2
8			51	43

Table 3. *Discrepancy factor R as a function of l*

l	No. of observed reflexions	R (%)
0	101	13·0
1	191	15·6
2	175	14·7
3	161	16·3
4	118	17·9
5	95	17·4
6 and 7	23	17·5
hkl	864	14·9

took about 5 min. (including output time) and provision was made for computing successive sections in a continous sequence. On examination of the various sections the atoms appeared as well-defined maxima at positions very close to those expected from the final stage of the least-squares refinement. To show the structure clearly a composite map through (or near) the atomic sites and projected down the c-axis is shown in Fig. 4.

All the atoms (excluding hydrogens) are clearly resolved. The peak-shapes too were very satisfactory including the 'smudged' peaks for the carbon atoms C_3 and C_4, which is to be expected in view of their fairly obvious degree of vibrational freedom. Nevertheless, there were some spurious fluctuations in the background electron density, none of which was large enough to be significantly disturbing, being of the order of 1 e.Å^{-3}. Unfortunately, this meant that the synthesis could not be expected to reveal the hydrogen atoms unambiguously since the hydrogen peaks would be of the same order of magnitude as the spurious detail. Although some plausible guess could have been made regarding the hydrogen positions, such a course seemed unnecessary since the molecular structure of the compound had been well established.

Molecular dimensions

The intramolecular bond lengths and bond angles were calculated using the final atomic coordinates; these are listed in Table 4.

Table 4. *Bond lengths and bond angles*

Bond	d	Angle	
$P_1–P_2$	2·22 Å	$P_2–P_1–S_1$	112·8°
$P_1–S_1$	1·94	$P_2–P_1–C_1$	102·2
$P_1–C_1$	1·84	$P_2–P_1–C_2$	102·2
$P_1–C_2$	1·82	$S_1–P_1–C_1$	114·5
$C_1–C_3$	1·51	$S_1–P_1–C_2$	116·3
$C_2–C_4$	1·51	$C_1–P_1–C_2$	107·3
		$P_1–C_1–C_3$	113·2
		$P_1–C_2–C_4$	113·2

The schematic structure is shown in Fig. 5.

Accuracy of the structure

The standard deviations of the atomic positional parameters were calculated using the weighted resid-
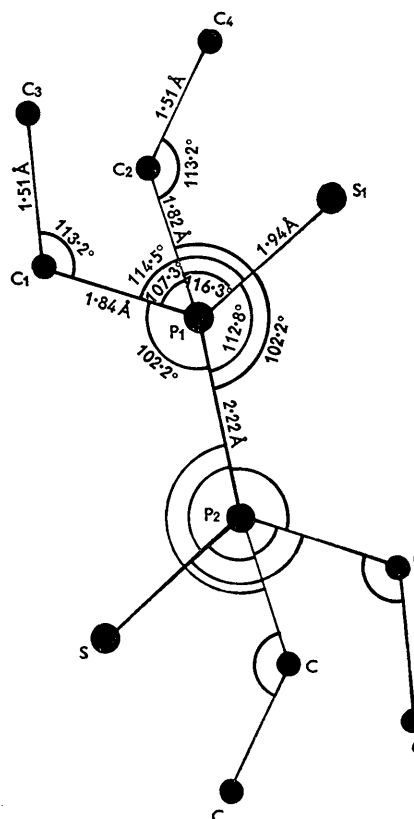
Fig. 5. The schematic structure.

uals from the least-squares treatment. The results of these calculations are set out in Table 5.

The corresponding standard deviations for bond lengths are given in Table 6.

Table 5. *Standard deviations of atomic positions*

	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
P_1	0·0027 Å	0·0026 Å	0·0031 Å
S_1	0·0036	0·0033	0·0037
C_1	0·0126	0·0135	0·0141
C_2	0·0117	0·0129	0·0129
C_3	0·0144	0·0148	0·0154
C_4	0·0135	0·0148	0·0141

Table 6. *Standard deviations for bond lengths*

Bond	Standard deviation $\sigma(l)$	
$P_1–P_2$	0·006 Å	
$P_1=S_1$	0·005	
$P_1–C_1$	0·014	$\sigma(\text{P–C}) = 0·01$
$P_1–C_2$	0·013	
$C_1–C_3$	0·018	$\sigma(\text{C–C}) = 0·014$
$C_2–C_4$	0·020	

In view of the non-orthogonal nature of the crystal, no accurate assessment of the standard deviations for bond angles was attempted; however, using the equation of Ahmed & Cruickshank (1953) it was estimated

Table 7. P–P *bond lengths in some inorgano-phosphorus compounds*

Substance	State*	P–P	Method*	Reference
P_4S_3	c	$2 \cdot 235 \pm 0 \cdot 005$ Å	XRD	Leung et al. (1957)
P_4S_5	c	$2 \cdot 21 \pm 0 \cdot 025$	XRD	Houten & Wiebenga (1957)
P_2I_4	c	$2 \cdot 21 \pm 0 \cdot 06$	XRD	Leung & Waser (1957)
P_4S_7	c	$2 \cdot 35 \pm 0 \cdot 01$	XRD	Vos & Wiebenga (1955, 1956)
P_4 (black)	c	$2 \cdot 18$	XRD	Hultgren & Warren (1935)
P_4 (black)	a	$2 \cdot 27$	XRD	Thomas & Gingrich (1938)
P_4 (red)	a	$2 \cdot 29$	XRD	Thomas & Gingrich (1938)
P_4 (yellow)	l	$2 \cdot 25$	XRD	Thomas & Gingrich (1938)
P_4 (red)	c	$2 \cdot 28$	XRD	Gingrich & Hultgren (1935)
P_4	g	$2 \cdot 21 \pm 0 \cdot 02$	ED	Maxwell et al. (1935)

* *XRD* = X-ray diffraction; *ED* = electron diffraction; c = crystalline; l = liquid; g = gaseous; a = amorphous.

approximately that the standard deviations of bond angles are unlikely to exceed $0 \cdot 5°$.

Discussion of the results

In the light of the foregoing estimation of accuracy of the analysis and the consistency of similar molecular dimensions, it is perhaps reasonable to conclude that the accuracy* of the bond-length determination should be at least as high as $\pm 0 \cdot 01$ Å for P–P and P–S, $\pm 0 \cdot 015$ Å for P–C and $\pm 0 \cdot 02$ Å for C–C and the bond angles should be accurate to within 1°.

By far the most striking feature of the analysis is the first establishment of an accurate P–P bond length $(2 \cdot 22 \pm 0 \cdot 01$ Å$)$ for an organic structure; what is more, this value agrees precisely with the value $(2 \cdot 22$ Å$)$ predicted by the covalent-radii table (see Pauling, 1940).

Comparison with the values of some of the inorgano-phosphorus compounds so far investigated, set out in Table 7, shows that the P–P bond length for the organo-phosphorus compound studied is, keeping in view the limits of error in various investigations, not significantly different from the rest (with the singular exception of that from P_4S_7); however, we believe that our determination is likely to be more reliable than the others in view of the use of three-dimensional analysis.

The mean value for the P–C bond length fits exactly with the expected value $(1 \cdot 83$ Å$)$ according to the

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* A somewhat higher deviation has been assumed in view of the possible inaccuracies in the dimensions of *the unit cell*.

revised covalent radii and additivity rule for partially ionic bonds formulated by Schomaker & Stevenson (1941). It is evident from Table 8 that the value found is not significantly different from the values reported for other organo-phosphorus compounds subjected to structural investigation; indeed it is encouraging to find a close resemblance between the two X-ray values based on careful three-dimensional analysis.

In so far as the P=S bond length is concerned, our value $(1 \cdot 94 \pm 0 \cdot 01$ Å$)$ agrees precisely with the value $(1 \cdot 94$ Å$)$ predicted by the covalent radii table (Pauling, 1940) for a true double bond. A comparison with some of the bond lengths for inorganic compounds (shown in Table 9) reveals that the length of P=S bond for the organo-phosphorus compound investigated is not significantly different from the reported true P=S bond lengths in organic compounds.

Nevertheless, it is interesting to note that the present value is significantly different from those reported for the molecular structures of the halogen derivatives (such as PSF_3, $PSBr_3$, $PSFBr_2$, PSF_2Br) investigated by electron diffraction in the gaseous phase. For these latter, systematic reductions from the predicted covalent bond radii have been observed (see, for example, Secrist & Brockway, 1944; Stevenson & Russell, 1939) and the interest lies mainly in the fact that these divergences have been generally attributed to the presence of semi-polar linkages. In view of the great controversy regarding the precise nature of bonding between phosphorus and sulphur atoms in organo-phosphorus compounds (see Kosolapoff, 1950), the findings of the present investigation could, in conjunction with other structural studies,

Table 8. P–C *bond lengths in some organo-phosphorus compounds*

Substance	State	P–C	Method	Reference
$[(CH_3)_2PBH_2]_3$	c	$1 \cdot 837 \pm 0 \cdot 007$ Å	XRD	Hamilton (1955)
$P(CH_3)_3$	g	$1 \cdot 87 \pm 0 \cdot 02$	ED	Springal & Brockway (1938)
$(C_2H_5)_4P_2S_2$	c	$1 \cdot 83 \pm 0 \cdot 015$	XRD	Present investigation

Table 9. P=S *bond lengths in some inorganic compounds*

Substance	State	P=S	Method	Reference
P_4S_5	c	$1 \cdot 94 \pm 0 \cdot 02$ Å	XRD	Houten & Wiebenga (1957)
P_4S_7	c	$1 \cdot 95 \pm 0 \cdot 02$	XRD	Vos & Wiebenga (1955, 1956)
P_4S_{10}	c	$1 \cdot 955 \pm 0 \cdot 015$	XRD	Vos & Wiebenga (1955)

Table 10. *Some C–C bond lengths and C–C–C bond angles*

Substance	Nature of analysis*	C–C	C–C–C	Reference
L-Threonine	3-*D*	1·52 Å	113°	Shoemaker *et al.* (1950)
DL-Alanine	3-*D*	1·52	111	Donohue (1950)
L-Glutamine	2-*D*	1·51	114	Cochran & Penfold (1952)
Hexamethylene diamine	2-*D*	1·52	115·5	Binnie & Robertson (1950)
α-Pimelic acid	3-*D*	1·52	113	Kay & Katz (1958)

* 3-*D* = three-dimensional X-ray analysis; 2-*D* = two-dimensional X-ray analysis.

throw some interesting new light on this perplexing problem.

The average C–C distance of $(1\cdot51 \pm 0\cdot02$ Å), though not significantly different from the normal single-bond distance, is perhaps rather low compared with the diamond value of 1·54 Å. Although in the absence of any X-ray study on a related organo-phosphorus compound any plausible explanation for this shortening is likely to be speculative in nature, it is perhaps true to say that, in the light of some careful X-ray studies on some aliphatic compounds in recent years, this is hardly surprising. To give a few examples, some of the reported values are given in Table 10.

It is therefore probable that the 'slightly short' value for the C–C bond length is genuine.

As regards the angle P–C–C the divergence from the tetrahedral C–C–C angle is probably 'just significant'. Here again, in the absence of any related studies, no precise comparison can be made; nevertheless, it would appear that our value compares favourably with some of the C–C–C values reported in Table 10. The slight increase in the P–C–C angle from the conventional C–C–C value may be attributed to the possibility of strain arising from the non-bonding interaction between various atoms especially since some of them lie within the Van der Waals radii of one another. Some of the relevant non-bonding intramolecular distances are shown in Table 11.

Table 11. *Some relevant intramolecular interatomic (non-bonding) distances*

Non-bonded atoms	Distance	Non-bonded atoms	Distance
P_1–C_3	2·80 Å	C_2–C_3	3·42 Å
P_1–C_4	2·79	C_3–C_4	3·59
S_1–C_1	3·19	P_2–S_1	3·47
S_1–C_2	3·20	P_2–C_1	3·17
S_1–C_3	3·69	P_2–C_2	3·15
S_1–C_4	3·46	P_2–C_3	4·58
C_1–C_2	2·95	P_2–C_4	4·55
C_1–C_4	3·72		

Examination* of the distances between molecules indicates that, in general, all the intermolecular con-

* The authors are grateful to Dr D. Rogers, Department of Physics, University College of South Wales and Monmouthshire, Cardiff, for designing a suitable programme on the Newport computer ZEBRA and for checking the various intermolecular contact distances arising out of the possible translational modes.

tacts correspond within reasonable limits, to normal Van der Waals interactions.

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On the Least-Squares Plane Through a Set of Points*

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A recent discussion by Schomaker *et al.* of the eigenvalue equation determining the best least-squares plane through a set of points is extended. A non-diagonal weight matrix is introduced, the errors associated with the coefficients of the plane are discussed, a criterion for the rejection of a given set as co-planar is given, and a more general form of the equations, valid for the case where certain restrictions are placed on the plane, is presented.

Introduction

In a recent paper, Schomaker, Waser, Marsh & Bergman (1959, hereinafter referred to as SWMB) have presented a derivation of the eigenvalue equation which leads to the best least-squares plane through a set of points. A footnote points out that the weight for an individual point should be chosen inversely proportional to the variance of the perpendicular distance of the point to the plane. It is becoming common practice in the least-squares refinement of atomic positions in crystal structures to invert the complete matrix of coefficients of the normal equations to obtain a variance–covariance matrix (matrix of second moments) which gives not only the errors in the coordinates but their correlations as well. These correlations may well be important in determining the best plane and, in particular, assessing its significance, and it would thus seem desirable to introduce a non-diagonal weight matrix into the scheme of SWMB. It is the main purpose of this paper to present the equations for such an extended treatment and to discuss as well the statistical significance of the results thus obtained.

Notation and mathematical formulation

It is desirable for compactness to use matrix notation throughout.† The following symbols will be used throughout.

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† See Hamilton (1954).

$\mathbf{B}_{m,n}$ $\equiv \{b_{ij}\}$, a matrix of m rows and n columns. The subscripts may be omitted after a particular matrix is defined.

B_{ij} or b_{ij}, the element in the ith row and jth column of $\mathbf{B}$.

$\mathbf{B}'_{n,m}$, the transpose of the matrix $\mathbf{B}_{m,n}$.

$\hat{\mathbf{B}}_{n,n}$, the adjoint of a square matrix $\mathbf{B}_{n,n}$.

$\mathbf{B}^{-1}_{n,n}$, the inverse of a square matrix $\mathbf{B}_{n,n}$.

$|\mathbf{B}_{n,n}|$, the determinant of $\mathbf{B}$.

$\mathbf{I}_{n,n}$, a unit matrix.

$\mathbf{O}_{m,n}$, a matrix composed entirely of zeroes.

$\mathbf{a}_j, j = 1, 2, \ldots, n$, a linearly independent set of vectors forming the basis for an n-dimensional space.

$\mathbf{G}^{-1}_{n,n} \equiv \{\mathbf{a}_i \cdot \mathbf{a}_j\}$, the metric for this space.

$\mathbf{x}^i_{n,1} \equiv \{x^i_j\}$, a point in this space.

x^i_j, the coordinate of the point $\mathbf{x}^i$ referred to $\mathbf{a}_j$.

$\mathbf{X}_{n,p} \equiv (\mathbf{x}^1 \, \mathbf{x}^2 \ldots \mathbf{x}^p)$, a set of p points.

$\mathbf{m}_{1,n}$, a vector of coefficients describing the plane

$$\mathbf{mx} - d = 0 . \tag{1}$$

D^i, the distance of the point $\mathbf{x}^i$ to the plane described by $\mathbf{m}$ and d:

$$D^i = (\mathbf{mx}^i - d)/(\mathbf{mGm}')^{\frac{1}{2}} . \tag{2}$$

$\mathbf{D}_{1,p} \equiv (D^1 D^2 \ldots D^p)$, the set of p such distances for the points $\mathbf{X}$.

At this point it becomes convenient to introduce the augmented matrices