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The Crystal Structure of Triphenyl Phosphate

BY W. O. DAVIES* AND E. STANLEY

Physics Department, College of Science and Technology, Manchester 1, *England*

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The space group of triphenyl phosphate is $P2_1/a$ and the unit-cell dimensions

$$a = 17{\cdot}24,\ b = 5{\cdot}86,\ c = 17{\cdot}24\ \text{Å};\ \beta = 104°.$$

The structure was solved by direct methods using visually estimated intensities. The three P–O bonds where the oxygen is joined to a phenyl group are found to be 1·63 Å and the remaining P–O bond is only 1·43 Å. The P–O–C angle is 122°.

Introduction

Of the phosphates examined in the past there appears to be no example of the phosphate group, PO_4, joined to three identical organic groups leaving the fourth oxygen bonded only to the phosphorus atom. Triphenyl phosphate is of this type and although the melting point is low (50 °C.) the crystals were suitable for X-ray examination.

Experimental

The sample of triphenyl phosphate was prepared using the methods described by Heim (1883) and the German Patent (1923). The material was recrystallized by slowly cooling a solution in alcohol. The crystals were colourless transparent laths.

Oscillation and Weissenberg photographs were taken about the principal axes. The Laue symmetry is $2/m$ and the unit cell dimensions are:

$$a = 17{\cdot}24 \pm 0{\cdot}15,\ b = 5{\cdot}86 \pm 0{\cdot}05,\ c = 17{\cdot}24 \pm 0{\cdot}15\ \text{Å};$$
$$\beta = 104° \pm 30'.$$

The $h0l$ reflexions are absent when h is odd and the $0k0$ reflexions are absent when k is odd. This defines the space group uniquely as $P2_1/a$. The observed density is 1·240 g.cm.$^{-3}$ (Sugden, Reed & Wilkins, 1925) and the density calculated assuming 4 molecules in the unit cell is 1·26 g.cm.$^{-3}$.

The intensities of the reflexions recorded on Weissenberg photographs were estimated visually, Lorentz and polarization corrections applied and placed on an absolute scale by the method of Wilson (1942). The crystals used were small and no correction was made for absorption.

Analysis of the structure

[010] *projection*

The Patterson synthesis is shown in Fig. 1. The highest peak is close to $\frac{1}{4}, \frac{1}{2}$ and related points. This is likely to be the position of the end of the phos-

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* Present address: Department of Chemistry, College of Technology, Sheffield, England.

phorus–phosphorus vector corresponding to a position $\frac{3}{8}, \frac{1}{4}$ in the cell projection, a position favoured by packing considerations. In this position the phosphorus atom would contribute at maximum to the structure factors of reflexions with $h+2l=4n$ and make no contribution to those with $h+2l=4n+2$. It is convenient, in this projection, to use the half-cell with $a_1=a/2$ and $h_1=h/2$.

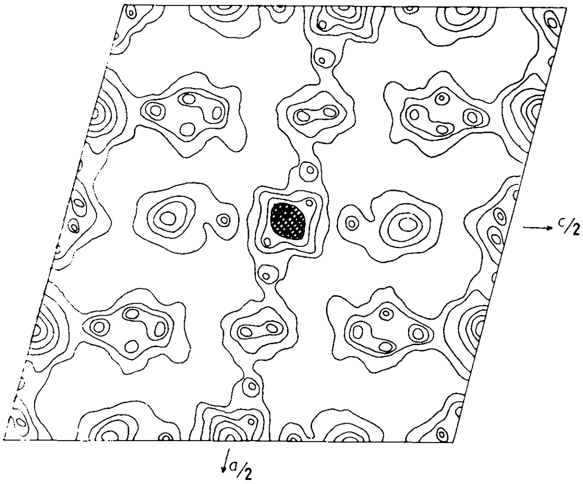

Fig. 1. Patterson synthesis projected on (010). Contours are drawn at equal, arbitrary intervals. The centre of the origin peak has been shaded.

On the basis of the half cell the reflexions were divided into four groups (Woolfson, 1957), (*a*) h_1 even, l even, (*b*) h_1 odd, l odd, (*c*) h_1 odd, l even, and (*d*) h_1 even, l odd. The twenty largest unitary structure factors from each of the groups (*a*) and (*b*) were given the same sign as the contribution from the phosphorus atom. From the relationship that

$$S(h_1, l) . S(h_1', l') . S(h_1+h_1', l+l')$$

is probably positive, the signs of other structure factors were obtained. The relationships $a_ra_sa_t$ and $b_rb_sb_t$ were used to check the consistency of the assumed signs and to obtain additional signs for members of these two groups with smaller unitary structure factors. Expressions of the type $a_rc_sc_t$ and $a_rd_sd_t$ etc., were used to determine the signs of 93 reflexions (including the 40 originally determined by the position of the phosphorus atom alone). All structure factors with a unitary value of 0·13 or more were used.

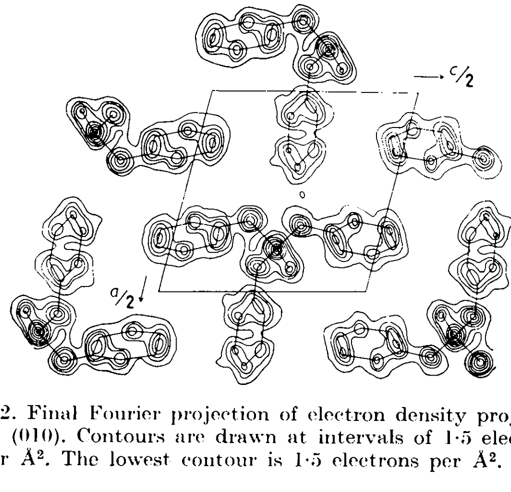

Fig. 2. Final Fourier projection of electron density projected on (010). Contours are drawn at intervals of 1·5 electrons per Å². The lowest contour is 1·5 electrons per Å².

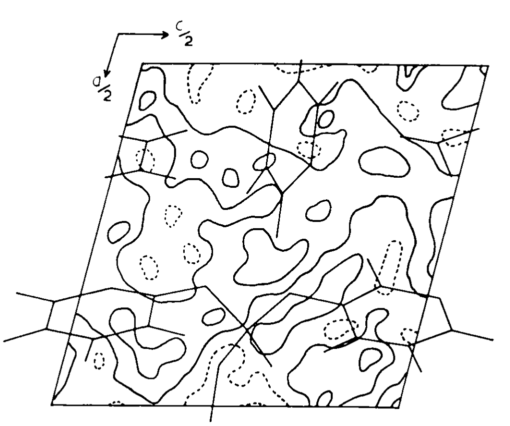

Fig. 3. Final difference electron density projected on (010). Contours are drawn at intervals of $\frac{1}{2}$ electron per Å². The negative contours are broken.

The Fourier synthesis of these terms showed sufficient detail for a model to be fitted satisfactorily. Structure factors were calculated using the analytical f values of Vand, Eiland & Pepinsky (1957). The value of $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$ at this stage was 0·32. Fourier and difference Fourier refinement (Cochran,

Table 1. *Temperature coefficients used for final structure factor calculations*

(*a*) [010] projection

Atom		B (Å²)	Atom	B (Å²)
P	max.	3·9*	C_7	5·0
	min.	1·9	C_8	5·0
O_1		4·2	C_9	5·6
O_2		3·7	C_{10}	5·6
O_3		3·7	C_{11}	5·6
O_4		5·5	C_{12}	5·6
C_1		4·6	C_{13}	5·0
C_2		4·6	C_{14}	5·8
C_3		4·6	C_{15}	5·8
C_4		4·6	C_{16}	5·8
C_5		4·6	C_{17}	5·8
C_6		4·6	C_{18}	5·8

(*b*) [100] projection

Atom	B (Å²)
P	2·6
O_1 O_2 O_3	4·0
O_5	5·0
C	4·5

* The direction of maximum vibration of the P atom is inclined at 42° to the c axis, i.e. in the direction of $50\bar{1}$.

Table 2. *Observed and calculated structure factors*

h 0 l	$\lvert F_o \rvert$	F_c
0 0 1	5	7
2	74	-102*
3	5	- 7
4	150	185*
5	4	2
6	63	- 73
7	12	6
8	29	24
9	28	- 24
10	9	10
11	9	- 15
12	4	- 6
13	11	- 13
14	20	- 23
15	25	- 23
16	4	0
17	4	- 1
18	4	- 6
19	4	2
20	3	5
2 0 0	13	22
1	61	88*
2	48	-65
3	30	29
4	52	62
5	15	- 16
6	27	- 26
7	51	- 58
8	39	40
9	3	3
10	3	6
11	21	- 21
12	4	- 2
13	26	28
14	18	15
15	11	- 15
16	11	- 15
17	4	9
18	4	0
19	3	- 6
2 0 $\bar{1}$	74	-107*
$\bar{2}$	41	- 43
$\bar{3}$	47	- 46
$\bar{4}$	26	36
$\bar{5}$	29	30
$\bar{6}$	4	- 1
$\bar{7}$	25	23
$\bar{8}$	8	- 17
$\bar{9}$	43	40
$\overline{10}$	4	- 3
$\overline{11}$	4	- 5
$\overline{12}$	8	- 9
$\overline{13}$	16	- 18
$\overline{14}$	4	- 2
$\overline{15}$	23	25
$\overline{16}$	16	12
$\overline{17}$	15	- 16
$\overline{18}$	4	1
$\overline{19}$	4	8
$\overline{20}$	3	- 5
4 0 0	135	-236*
1	11	- 9
2	40	- 45
3	48	- 58
4	23	- 25
5	39	47
6	29	30
7	29	- 30
8	34	- 40
9	35	40
10	16	20
11	11	- 4
12	16	- 16
13	18	18
14	15	19
15	4	9
16	4	- 2
17	4	8
18	3	6
4 0 $\bar{1}$	11	- 4
$\bar{2}$	19	- 22
$\bar{3}$	36	45
$\bar{4}$	60	- 74
$\bar{5}$	28	- 30
$\bar{6}$	38	29
$\bar{7}$	15	15
$\bar{8}$	11	- 6
$\bar{9}$	15	- 14
$\overline{10}$	17	- 17
$\overline{11}$	4	2
$\overline{12}$	19	22
$\overline{13}$	11	11
$\overline{14}$	26	26
$\overline{15}$	4	3
$\overline{16}$	4	- 4
$\overline{17}$	4	0
$\overline{18}$	4	8
$\overline{19}$	4	0
$\overline{20}$	4	- 7
6 0 0	33	34
1	16	- 14
2	3	- 8
3	21	21
4	25	- 21
5	18	- 16
6	15	13
7	53	66
8	10	- 15
9	27	- 30
10	13	15
11	20	23
12	15	- 15
13	17	- 16
14	4	8
15	4	2
16	4	- 9
17	3	- 3
6 0 $\bar{1}$	42	47
$\bar{2}$	14	10
$\bar{3}$	28	- 27
$\bar{4}$	29	- 34
$\bar{5}$	14	-
$\bar{6}$	13	17
$\bar{7}$	64	- 71
$\bar{8}$	32	- 32
6 0 $\bar{9}$	12	15
$\overline{10}$	4	4
$\overline{11}$	22	- 18
$\overline{12}$	4	4
$\overline{13}$	28	32
$\overline{14}$	13	- 14
$\overline{15}$	31	- 36
$\overline{16}$	4	6
$\overline{17}$	22	24
$\overline{18}$	4	- 1
$\overline{19}$	4	- 12
$\overline{20}$	4	0
8 0 0	34	- 32
1	19	- 18
2	31	29
3	39	40
4	4	2
5	35	- 39
6	29	- 31
7	15	17
8	26	30
9	14	- 18
10	21	- 24
11	4	12
12	4	9
13	4	- 10
14	4	- 5
15	4	2
8 0 $\bar{1}$	31	24
$\bar{2}$	42	44
$\bar{3}$	33	- 28
$\bar{4}$	30	- 25
$\bar{5}$	49	46
$\bar{6}$	16	- 11
$\bar{7}$	27	- 24
$\bar{8}$	37	35
$\bar{9}$	41	43
$\overline{10}$	16	- 17
$\overline{11}$	9	- 8
$\overline{12}$	3	5
$\overline{13}$	14	12
$\overline{14}$	33	- 32
$\overline{15}$	18	14
$\overline{16}$	4	7
$\overline{17}$	4	1
$\overline{18}$	4	- 9
$\overline{19}$	4	- 1
10 0 0	18	- 12
1	20	- 18
2	20	17
3	16	- 14
4	14	8
5	11	11
6	11	- 13
7	25	- 24
8	4	7
9	4	13
10	23	- 25
11	4	- 10
12	23	23
13	4	3
14	18	- 20
10 0 $\bar{1}$	18	20
$\bar{2}$	25	23
$\bar{3}$	3	- 1
10 0 $\bar{4}$	3	3
$\bar{5}$	9	13
$\bar{6}$	15	- 14
$\bar{7}$	51	53
$\bar{8}$	30	30
$\bar{9}$	30	- 26
$\overline{10}$	27	- 27
$\overline{11}$	22	18
$\overline{12}$	28	25
$\overline{13}$	29	- 27
$\overline{14}$	4	- 5
$\overline{15}$	15	15
$\overline{16}$	4	- 3
$\overline{17}$	11	- 12
$\overline{18}$	4	- 5
$\overline{19}$	4	6
$\overline{20}$	3	2
12 0 0	13	14
1	16	18
2	14	16
3	12	- 12
4	4	- 6
5	13	14
6	13	13
7	4	- 4
8	4	2
9	4	0
10	4	6
11	4	- 10
12	4	5
12 0 $\bar{1}$	20	- 19
$\bar{2}$	4	5
$\bar{3}$	11	6
$\bar{4}$	4	2
$\bar{5}$	23	- 21
$\bar{6}$	23	22
$\bar{7}$	4	- 2
$\bar{8}$	38	- 37
$\bar{9}$	23	- 18
$\overline{10}$	27	25
$\overline{11}$	12	5
$\overline{12}$	26	- 23
$\overline{13}$	17	- 16
$\overline{14}$	30	25
$\overline{15}$	15	- 10
$\overline{16}$	12	- 7
$\overline{17}$	4	- 3
$\overline{18}$	13	9
$\overline{19}$	3	1
14 0 0	21	- 23
1	12	- 6
2	4	0
3	11	8
4	4	- 7
5	4	- 2
6	4	6
7	4	- 3
8	4	1
9	4	1
14 0 $\bar{1}$	4	- 1
$\bar{2}$	10	5
$\bar{3}$	14	- 8
$\bar{4}$	20	- 15
5	4	4
14 0 $\bar{6}$	15	15
$\bar{7}$	24	- 22
$\bar{8}$	15	- 14
$\bar{9}$	15	12
$\overline{10}$	30	29
$\overline{11}$	9	- 8
$\overline{12}$	33	- 30
$\overline{13}$	11	11
$\overline{14}$	26	26
$\overline{15}$	4	4
$\overline{16}$	15	- 15
$\overline{17}$	4	- 2
$\overline{18}$	16	15
16 0 0	4	6
1	27	- 24
2	18	- 16
3	16	12
4	4	1
5	4	- 10
6	4	- 2
7	4	8
16 0 $\bar{1}$	29	29
$\bar{2}$	16	- 13
$\bar{3}$	28	- 23
$\bar{4}$	13	8
$\bar{5}$	24	20
$\bar{6}$	12	-11
$\bar{7}$	12	- 7
$\bar{8}$	4	6
$\bar{9}$	4	7
$\overline{10}$	4	- 3
$\overline{11}$	4	- 3
$\overline{12}$	4	6
$\overline{13}$	4	9
$\overline{14}$	4	- 1
$\overline{15}$	4	- 2
$\overline{16}$	3	- 4
18 0 0	14	20
1	4	5
2	4	- 6
3	4	1
4	3	8
18 0 $\bar{1}$	4	- 1
$\bar{2}$	14	- 13
$\bar{3}$	4	3
$\bar{4}$	16	12
$\bar{5}$	4	- 4
$\bar{6}$	4	- 8
$\bar{7}$	4	0
$\bar{8}$	4	1
$\bar{9}$	4	2
$\overline{10}$	4	- 6
$\overline{11}$	4	1
$\overline{12}$	4	3
$\overline{13}$	4	- 3
20 0 0	3	2
$\bar{1}$	17	- 12
$\bar{2}$	3	0
$\bar{3}$	19	16
$\bar{4}$	3	2
$\bar{5}$	3	4
$\bar{6}$	3	2
$\bar{7}$	14	12
$\bar{8}$	3	5
$\bar{9}$	3	6

Table 2 (*cont.*)

0 k l	$\lvert F_o\rvert$	F_c
0 1 1	56	-69
2	36	-44
3	23	28
4	41	34
5	19	17
0 1 6	12	12
7	7	0
8	23	19
9	21	18
10	3	3
11	12	17
12	7	-8
13	9	-9
14	9	-9
15	19	22
16	4	1
17	6	-9
18	3	1
19	8	9
20	6	-6
21	7	-7
0 2 0	17	18
1	13	-6
2	10	6
3	17	11
4	3	-6
5	14	14
6	10	-10
7	28	-24
8	7	7
9	30	35
10	3	3
11	13	-15
12	20	-22
13	25	24
14	9	4
15	7	-6
16	3	-3
17	3	2
18	3	2
19	5	-2
20	2	-2
21	2	2
0 3 1	4	2
2	35	35
3	5	-5
4	6	-12
5	19	-16

0 k l	$\lvert F_o\rvert$	F_c
0 3 6	23	25
7	3	0
8	11	-13
9	7	7
10	6	3
0 3 11	3	-3
12	7	-5
13	13	11
14	10	8
15	6	-4
16	8	-7
17	3	1
18	2	1
19	4	3
20	2	-2
0 4 0	3	7
1	4	4
2	4	-5
3	3	2
4	24	-20
5	8	-13
6	12	13
7	3	8
8	3	1
9	5	10
10	19	18
11	9	10
12	5	-7
13	3	3
14	4	2
15	5	6
16	6	-4
17	2	4
18	2	8
19	5	3
0 5 1	38	36
2	3	-3
3	29	-32
4	3	2
5	33	34
6	5	8
7	18	20
8	3	1
9	18	16
10	5	6
11	7	-7
12	3	-1

0 k l	$\lvert F_o\rvert$	F_c
0 5 13	5	4
14	3	-3
15	2	-2
16	2	2
0 6 0	8	11
1	3	4
2	8	-10
3	8	10
4	3	3
5	3	1
6	8	-12
7	3	2
8	3	6
9	4	1
10	3	-3
11	2	-3
12	2	2
13	2	1
0 7 1	3	-4
2	3	2
3	5	7
4	8	-8
5	2	-4
6	9	9
7	2	4
8	2	-3

h k 0	$\lvert F_o\rvert$	F_c
1 1 0	52	-107*
2	59	-128*
3	54	83*
4	54	72*
5	36	-35
6	8	-3
7	15	-19
8	33	-41
9	33	32
10	15	11
11	10	-9
12	12	-10
13 1 0	3	-2
14	5	5
15	6	5
16	15	17
17	8	-6
18	6	-4

h k 0	$\lvert F_o\rvert$	F_c
19 1 0	2	-2
20	7	-8
0 2 0	16	-20
1	26	20
2	4	3
3	30	-42
4	15	17
5	31	-43
6	9	7
7	10	9
8	8	8
9	13	-5
10	3	2
11	26	21
12	5	-3
13	31	23
14	3	3
15	15	-8
16	2	1
17	6	-5
18	6	-4
19	5	3
20	2	-3
1 3 0	13	14
2	11	18
3	30	-25
4	12	9
5	24	-37
6	4	1
7	7	6
8	11	12
9	29	35
10	7	-5
11	13	11
12	26	-20
13	20	-16
14	3	-5
15	8	-9
16	5	3
17	10	5
18	3	0
19	2	4
0 4 0	3	7
1	4	1
2	3	-3
3	7	-8
4	5	1
5	8	6

h k 0	$\lvert F_o\rvert$	F_c
6 4 0	9	10
7	12	31
8	5	-7
9	3	4
10	10	-9
11	5	-10
12	7	7
13	4	4
14	8	7
15	8	7
16	5	-3
17	3	2
18	2	-4
1 5 0	3	2
2	13	13
3	3	0
4	11	16
5	3	7
6	12	-13
7	3	-1
8	14	-17
9	3	-6
10	5	6
11	4	-2
12	6	9
13	2	1
14	6	-4
15	2	2
0 6 0	6	11
1	6	-4
2	3	3
3	4	-5
4	7	-10
5	5	1
6	2	-6
7	5	2
8	5	6
9	2	3
10	3	4
11	2	0
12	2	-3
1 7 0	3	-2
2	2	-2
3	5	5
4	2	-1
5	2	0
6	2	2
7	2	-2

* Reflexions which appear to be affected by extinction.

1951) including hydrogen atoms as they became resolved, adjusting the individual isotropic temperature factors of the carbon and oxygen atoms as indicated by the difference Fourier maps, and introducing an anisotropic temperature coefficient for the phosphorus atom reduced the value of R to 0·14. Some of the more intense low-order reflexions appeared to be affected by extinction; these were excluded from the later stages of refinement. The final electron-density projection is shown in Fig. 2 and the final difference map in Fig. 3. The values of the temperature coefficients are given in Table 1(*a*) and the final values of the observed and calculated structure factors are given in Table 2.

[100] *projection*

The Patterson function indicated that the y coordinate of the phosphorus atom is 0·34. The orientation of the phenyl groups could not be determined uniquely from the [010] projection. A group of low-order reflexions was selected which might be sensitive to changes in the ring orientations and each possible model was tested using this limited set of reflexions. One model gave considerably better agreement than the rest and this agreement was maintained when all the structure factors were calculated. The projection was refined using difference syntheses. There is a great deal of overlap in this projection and in many cases the shifts indicated were ambiguous.

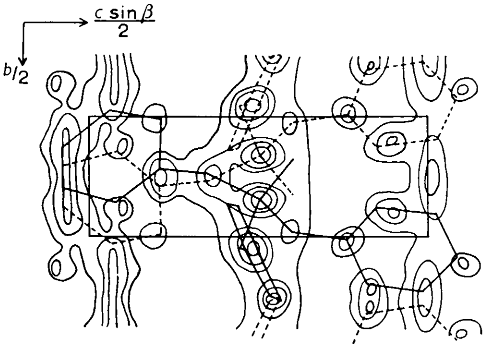

Fig. 4. Final Fourier projection of electron density projected on (100). Contours are drawn at intervals of 3 electrons per Å². The lowest contour is 3 electrons per Å².

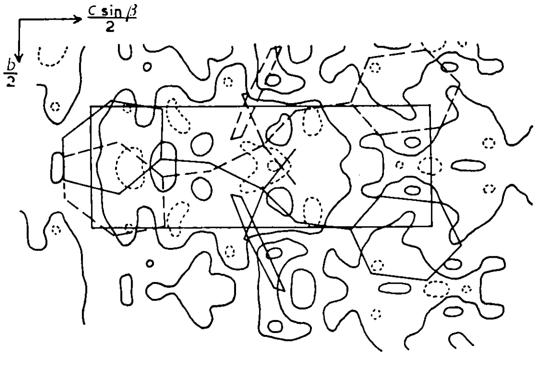

Fig. 5. Final difference electron density projected on (010). Contours are drawn at intervals of ½ electron per Å². The negative contours are broken.

The final Fourier projection of electron density on (100) is shown in Fig. 4 and the final difference map in Fig. 5. The final value of *R* was 0·19. The observed and calculated structure factors are given in Table 2.

[001] *projection*

This projection was also investigated but the overlap was even more serious than in the [100] projection. The value of *R* was reduced to 0·24 and confirms the structure determined from the other two projections. No use was made of this projection for the determination of the final values of the coordinates. The observed and calculated structure factors are given in Table 2.

Discussion of the structure

The final atomic coordinates are given in Table 3; the *x* and *z* coordinates are taken from the [010] projection and the *y* coordinate from the [100] projection. The molecule, in the aspect seen down the [010] axis is shown in Fig. 6. Details of the phosphate group alone are shown in Fig. 7.

Table 3. *Atomic parameters in fractions of unit cell edge*

Atom	x/a	y/b	z/c
P	0·389	0·340	0·253
O_1	0·436	0·546	0·223
O_2	0·323	0·238	0·175
O_3	0·332	0·480	0·298
O_4	0·441	0·170	0·299
C_1	0·522	0·550	0·231
C_2	0·563	0·360	0·206
C_3	0·648	0·370	0·220
C_4	0·688	0·563	0·252
C_5	0·644	0·758	0·283
C_6	0·559	0·745	0·269
C_7	0·340	0·210	0·104
C_8	0·381	0·010	0·108
C_9	0·401	0·970	0·032
C_{10}	0·388	0·121	0·964
C_{11}	0·347	0·295	0·965
C_{12}	0·326	0·354	0·040
C_{13}	0·353	0·511	0·382
C_{14}	0·321	0·370	0·426
C_{15}	0·340	0·403	0·514
C_{16}	0·384	0·574	0·541
C_{17}	0·411	0·721	0·494
C_{18}	0·396	0·694	0·412

Table 4. *Bond lengths and bond angles in the phosphate group with standard deviations calculated using the formula of Booth* (1947)

P–O_1	1·61 ± 0·04 Å	O_1–P–O_2	108 ± 3°
P–O_2	1·65 ± 0·04	O_2–P–O_3	101 ± 3
P–O_3	1·63 ± 0·04	O_3–P–O_1	101 ± 3
P–O_4	1·43 ± 0·04	O_4–P–O_1	114 ± 3
		O_4–P–O_2	114 ± 3
O_1–O_2	2·64 ± 0·05 Å	O_4–P–O_3	117 ± 3
O_2–O_3	2·53 ± 0·05		
O_3–O_1	2·51 ± 0·05		
O_4–O_1	2·56 ± 0·05	P–O_1–C_1	124 ± 3°
O_4–O_2	2·58 ± 0·05	P–O_2–C_7	121 ± 3
O_4–O_3	2·60 ± 0·05	P–O_3–C_{13}	122 ± 3

Details of the dimensions of the phosphate group are given in Table 4. The P–OC_6H_5 bonds are sensibly equal at 1·63 Å and the fourth bond between the phosphorus and the unshared oxygen atom is 1·43 Å. These values agree very well with other determinations. Romers, Ketelaar & McGillavry (1949) in $(NH_4)_4P_4O_{12}$ found that the P–O bonds for the unshared oxygens were 1·46 Å and for oxygen shared by two phosphorus atoms 1·62 Å. McArthur & Beevers (1957) in $Na_4P_2O_7 10H_2O$ found values of 1·45 and

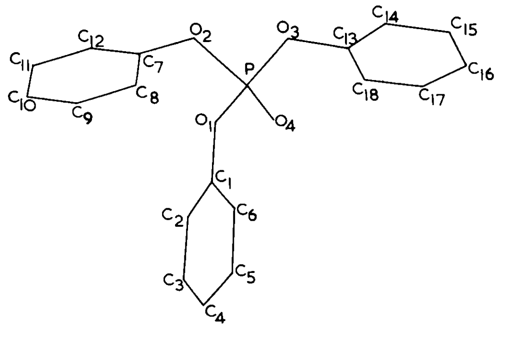

Fig. 6. Diagram of a molecule in the same orientation as Fig. 2. The atoms are labelled as in the tables.

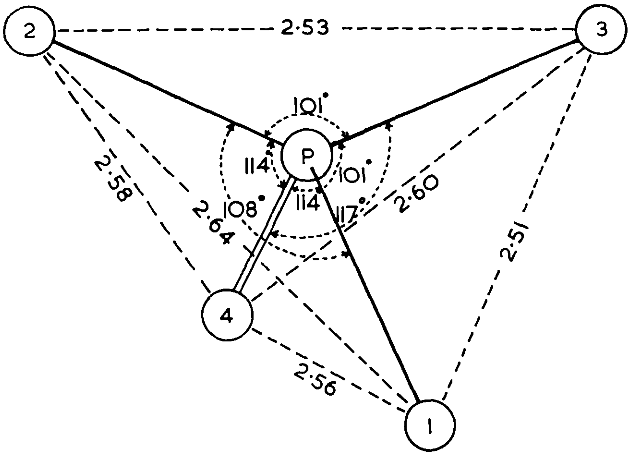

Fig. 7. Diagram of the phosphate group.

1·48 Å for the unshared oxygen atoms and 1·63 Å for the shared oxygen atoms. The value of the P–O bonds when these are equivalent as in the phosphate ion is quite different at 1·55 Å (Sundera Rao, Turley & Pepinsky, 1957; MacLennon & Beevers, 1955, 1956).

The O–P–O angles in the present structure vary between 101° and 117° which is the same range of variation found by Dunitz & Rollett (1956) in benzyl phosphoric acid and by Hampson & Stosick (1938) in P_4O_6 and P_4O_{10} using electron diffraction. The angles subtended by the unshared oxygen, O_4, and any other oxygen at the phosphorus atom are all greater than the tetrahedral angle.

The values obtained for the eighteen aromatic C–C bonds in the three phenyl groups vary between 1·28 and 1·54 Å and have a mean value of 1·40 Å. The variations in the bond lengths are consistent with the calculated standard deviation of 0·07 Å and there is no reason to suppose that they are not all equivalent.

The packing of the molecule in the unit cell is shown in Fig. 8. The structure is bound by the van der Waals attraction between the adjacent phenyl groups. There are layers of molecules in the structure parallel to the (100) face which is the lath face of the crystals.

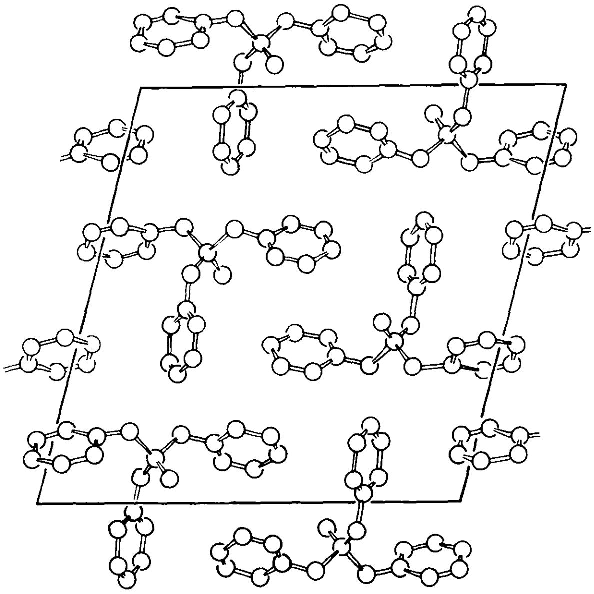

Fig. 8. Diagram of the unit cell looking along [010] showing the packing of the molecules.

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