to nearby naphthyl groups. Van der Waals distances between carbons in neighboring naphthyl groups are between 3·620 and 3·719 Å.

Conclusions

The significant features of the structure can be summarized in the following manner. The calcium ion is coordinated to seven oxygen atoms, all almost equidistant from the calcium, arranged in a distorted pentagonal bipyramid. Phosphate and other bond distances and angles appear normal except that the C–O(PO_3) bond distances are significantly shorter and the C–O–P bond angles are significantly larger in calcium 1-naphthyl phosphate than in other organic phosphates for which the structures are known. The organic phosphates with which this is compared involve non-aromatic carbon atoms.

Since hardly any data are available on hydrolysis rates of the organic phosphates discussed here, no conclusions regarding hydrolysis rates can be made at this time. However, the short C–O bond distances and the longer P–OR bond distances suggest hydrolysis attack at P–O rather than C–O in aromatic organic phosphates.

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Refinement of the Crystal Structure of Triphenyl Phosphate

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The structure of triphenyl phosphate has been refined by full-matrix least-squares computations to a final R of 0·109 for 762 reflections with measurable intensities. The space group is $P2_1/a$ with unit-cell dimensions of $a=17·124$, $b=5·833$, $c=16·970$ Å and $\beta=105°21'$. The P–O bond distances are 1·599, 1·554, 1·549 and 1·432 Å. O–P–O bond angles range from 119·1° to 96·6°. The remaining bond distances and angles are in agreement with previously determined structures.

Introduction

We are interested in the structures of organic phosphates as part of a program to correlate the structural data with hydrolysis rate studies. Such a correlation requires accurate structural details for a variety of organic phosphates including monosubstituted, disubstituted and trisubstituted phosphates.

Accurate structures are known for calcium thymidylate as determined by Trueblood, Horn & Luzzati (1961), 2-aminoethanol phosphate as determined by Kraut (1961), adenosine-5′ -phosphate, determined by Kraut & Jensen (1963) and calcium 1-naphthyl phosphate, determined by Li & Caughlan (1965), all of which are monosubstituted organic phosphates. The

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only disubstituted organic phosphate for which a structure is known is dibenzyl phosphate determined by Dunitz & Rollett (1956). The structure of triphenyl phosphate was determined by Davies & Stanley (1962), but since it was determined in projections, and since there was considerable overlap in two of the projections, bond lengths and angles of sufficient accuracy for meaningful comparison were not obtained. Since we had collected three-dimensional data at the time of their publication, we decided to proceed with the refinement in order to determine the precise bond lengths and angles required for our study.

Experimental

Commercial triphenyl phosphate (Eastman Distillation Products Co.) was recrystallized by slow evaporation of an ether solution to produce long thin needles. X-ray examination indicated monoclinic symmetry. Unit-cell parameters were measured on Weissenberg and precession films obtained with Cu $K\alpha$ radiation. Sodium chloride data were obtained on the same film for calibration. The lattice parameter $a=5{\cdot}6402$ Å (Swanson & Fuyat, 1953) was used for the sodium chloride and a wavelength of 1·5418 Å was taken for the mean of $K\alpha_1$, and $K\alpha_2$. The cell parameters of triphenyl phosphate determined in this manner are:

$$a=17{\cdot}124\pm0{\cdot}048\text{ Å}$$
$$b=\ 5{\cdot}833\pm0{\cdot}036$$
$$c=16{\cdot}970\pm0{\cdot}042$$
$$\beta=105°21'\pm15'$$

Within experimental error these agree with those of Davies & Stanley (1962). The uncertainties indicated are estimated standard deviations. The needle axis of the crystal habit was parallel to the b axis.

The density of triphenyl phosphate is $1{\cdot}302\pm0{\cdot}001$ g.cm^{-3} (*Handbook of Chemistry and Physics*, 1952). The computed density is 1·331 g.cm^{-3} with four molecules per unit cell. Systematic absence of $h0l$ reflections with h odd and $0k0$ with k odd fixes the space group as $P2_1/a$.

Unidimensionally integrated Weissenberg photographs of levels from $k=0$ to $k=3$ were taken with

Table 1. *Atomic parameters for triphenyl phosphate*

Atom	x/a	$\sigma(x/a)$	y/b	$\sigma(y/b)$	z/c	$\sigma(z/c)$
P(1)	0·3888	0·0002	0·3454	0·0007	0·2539	0·0002
O(2)	0·4388	0·0005	0·5459	0·0016	0·2253	0·0005
O(3)	0·3229	0·0005	0·2812	0·0018	0·1752	0·0006
O(4)	0·3317	0·0005	0·4742	0·0018	0·2966	0·0005
O(5)	0·4396	0·0005	0·1687	0·0017	0·2989	0·0005
C(6)	0·5246	0·0007	0·5460	0·0030	0·2358	0·0008
C(7)	0·5652	0·0007	0·3702	0·0024	0·2114	0·0008
C(8)	0·6479	0·0009	0·3800	0·0033	0·2189	0·0009
C(9)	0·6902	0·0009	0·5835	0·0034	0·2557	0·0009
C(10)	0·6444	0·0009	0·7644	0·0025	0·2789	0·0009
C(11)	0·5622	0·0009	0·7391	0·0031	0·2689	0·0009
C(12)	0·3420	0·0008	0·2102	0·0027	0·1022	0·0008
C(13)	0·3794	0·0009	0·0086	0·0025	0·1017	0·0009
C(14)	0·4013	0·0009	0·9551	0·0034	0·0289	0·0012
C(15)	0·3846	0·0014	0·0917	0·0055	0·9629	0·0012
C(16)	0·3453	0·0014	0·2890	0·0048	0·9694	0·0012
C(17)	0·3244	0·0008	0·3680	0·0028	0·0411	0·0009
C(18)	0·3516	0·0007	0·5172	0·0029	0·3794	0·0008
C(19)	0·3234	0·0010	0·3638	0·0034	0·4261	0·0009
C(20)	0·3383	0·0010	0·4037	0·0047	0·5062	0·0011
C(21)	0·3840	0·0011	0·5970	0·0042	0·5453	0·0011
C(22)	0·4105	0·0010	0·7457	0·0030	0·4944	0·0013
C(23)	0·3954	0·0009	0·7099	0·0031	0·4133	0·0011
			Calculated hydrogen coordinates			
H(24)	0·5300		0·2210		0·1825	
H(25)	0·6818		0·2394		0·2004	
H(26)	0·7572		0·6020		0·2680	
H(27)	0·6754		0·9210		0·3031	
H(28)	0·5259		0·8763		0·2852	
H(29)	0·3899		−0·1083		0·1530	
H(30)	0·4359		−0·2076		0·0281	
H(31)	0·4031		0·0528		−0·0923	
H(32)	0·3266		0·3914		−0·0850	
H(33)	0·2958		0·5384		0·0449	
H(34)	0·2872		0·2129		0·3982	
H(35)	0·3171		0·2870		0·5474	
H(36)	0·3977		0·6210		0·6087	
H(37)	0·4434		0·8980		0·5211	
H(38)	0·4177		0·8289		0·3746	

An isotropic B of 4·500 was assigned to all the hydrogens.

Cu $K\alpha$ radiation. In addition, unidimensionally integrated precession photographs of the zero levels $hk0$ and $0kl$ were taken with Mo $K\alpha$ radiation. The intensities of the reflections were estimated visually by comparison with a standard intensity scale. No correction was made for absorption effects since the crystal was small ($0{\cdot}05\times0{\cdot}05\times3$ mm); the linear absorption coefficient was 14·11 cm^{-1} for Cu $K\alpha$ radiation.

Of the total of approximately 3642 unique reflections within the Cu $K\alpha$ limit, intensity data were obtained for 762, which is 21%.

The refinement

Atomic scattering factors used in the refinement were: hydrogen of McWeeny (1951), carbon and oxygen of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955), phosphorus of Viervoll & Øgrim (1949).

The coordinates of Davies & Stanley (1962) were used to begin the refinement. The initial R was 0·21. One cycle of refinement with the program of Busing & Levy (1959) reduced R to 0·15. Coordinates, isotropic temperature factors, and an overall scale factor were adjusted in the first cycle. The weighting scheme weighted all reflections as $1/F_o$.

Two cycles of least-squares refinement with anisotropic temperature factors reduced R to 0·13. Weighting for these two cycles was again $1/F_o$.

For the final three cycles of least-squares computations, the weighting scheme of Hughes (1941) was employed. The weighting was:

$$\sqrt{w}=4F_{o\ \min}/F_o,\quad F_o>4F_{o\ \min}$$
$$\sqrt{w}=1{\cdot}0\qquad,\quad F_o\leq 4F_{o\ \min}.$$

Table 2. *Thermal parameters for triphenyl phosphate*

Standard deviations are below each entry

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
P(1)	0·00283	0·02910	0·00363	0·00069	0·00072	0·00170
	0·00012	0·00207	0·00015	0·00036	0·00011	0·00041
O(2)	0·00415	0·01747	0·00531	−0·00167	0·00138	0·00233
	0·00041	0·00438	0·00046	0·00097	0·00035	0·00102
O(3)	0·00449	0·04330	0·00603	−0·00180	0·00287	0·00094
	0·00043	0·00520	0·00057	0·00110	0·00041	0·00125
O(4)	0·00411	0·03988	0·00470	0·00120	0·00155	0·00041
	0·00039	0·00526	0·00064	0·00104	0·00035	0·00106
O(5)	0·00482	0·04043	0·00330	0·00217	0·00083	0·00091
	0·00041	0·00504	0·00038	0·00122	0·00033	0·00115
C(6)	0·00344	0·01730	0·00480	−0·00159	0·00169	0·00718
	0·00062	0·00840	0·00071	0·00191	0·00056	0·00178
C(7)	0·00418	0·00740	0·00545	0·00196	0·00255	−0·00367
	0·00060	0·00663	0·00070	0·00156	0·00053	0·00165
C(8)	0·00556	0·03816	0·00524	−0·00163	0·00344	−0·00464
	0·00075	0·00972	0·00076	0·00207	0·00062	0·00215
C(9)	0·00589	0·01796	0·00611	−0·00178	0·00226	0·00173
	0·00072	0·00923	0·00086	0·00219	0·00067	0·00190
C(10)	0·00622	0·00308	0·00605	0·00036	0·00121	−0·00180
	0·00083	0·00779	0·00083	0·00189	0·00065	0·00168
C(11)	0·00376	0·03199	0·00508	−0·00395	0·00144	−0·00189
	0·00069	0·00881	0·00071	0·00162	0·00056	0·00179
C(12)	0·00581	0·03897	0·00244	0·00071	0·00158	0·00001
	0·00066	0·00767	0·00056	0·00178	0·00051	0·00163
C(13)	0·00772	0·01689	0·00557	−0·00290	0·00240	0·00137
	0·00080	0·00742	0·00077	0·00173	0·00062	0·00177
C(14)	0·00601	0·04860	0·00665	−0·00236	0·00223	−0·00693
	0·00085	0·01019	0·00113	0·00214	0·00080	0·00254
C(15)	0·01252	0·05992	0·00327	0·00080	0·00072	−0·00230
	0·00141	0·01479	0·00089	0·00357	0·00083	0·00298
C(16)	0·01094	0·04730	0·00656	−0·00758	0·00089	0·00956
	0·00126	0·01510	0·00115	0·00302	0·00095	0·00293
C(17)	0·00658	0·03612	0·00420	0·00065	0·00173	0·00169
	0·00075	0·00818	0·00069	0·00174	0·00060	0·00182
C(18)	0·00380	0·03920	0·00319	0·00677	0·00165	0·00011
	0·00060	0·00858	0·00062	0·00173	0·00051	0·00181
C(19)	0·00833	0·05818	0·00312	−0·00577	0·00194	−0·00086
	0·00090	0·00968	0·00071	0·00253	0·00067	0·00231
C(20)	0·00710	0·09971	0·00482	−0·00545	0·00222	0·00504
	0·00091	0·01442	0·00099	0·00308	0·00077	0·00303
C(21)	0·00672	0·04985	0·00716	0·00120	0·00291	−0·00119
	0·00091	0·01132	0·00097	0·00258	0·00080	0·00285
C(22)	0·00827	0·02289	0·00736	−0·00714	0·00298	−0·00361
	0·00096	0·00822	0·00107	0·00217	0·00087	0·00227
C(23)	0·00689	0·03246	0·00517	−0·00665	0·00030	−0·00406
	0·00082	0·00942	0·00089	0·00206	0·00074	0·00215

In the final two cycles of least-squares refinement, hydrogen atoms were included in their computed positions. The isotropic temperature factors of the hydrogen atoms were arbitrarily assigned the value $B = 4{\cdot}5$ Å^2. The mean final adjustment in each type of parameter, in terms of their standard deviations, was $0{\cdot}3\sigma$. The greatest final adjustment was $1{\cdot}0\sigma$, which occurred for two parameters.

A concluding round of structure factor calculations resulted in an R value of 0·109 for the 762 observed reflections with measurable intensities. The refined atomic parameters are given in Tables 1 and 2. Observed and calculated structure factors are listed in Table 3.

Discussion

Fig. 1 and Table 4 contain the bond distances and angles calculated from the parameters of Table 1.

Several noteworthy facts may be pointed out. For the P–OR bonds, the lengths are comparable to although slightly shorter than those reported by Davies & Stanley (1962), and about the same as those reported for dibenzyl phosphate. The short P–O bond length of 1·432 Å is shorter than any yet reported in organic phosphates. However, P–O bond lengths as low as 1·40 Å have been reported (Cruickshank, 1961) for inorganic phosphates. The length of this bond in triphenyl phosphate suggests that it is very nearly a double bond, as one would expect. The mean P–OR distance is 1·567 Å with an r.m.s. deviation of 0·023 Å. This agrees well with a reported mean P–OR distance of 1·565 (Kraut & Jensen, 1963) and 1·555 Å in dibenzyl phosphate (Dunitz & Rollett, 1956).

There appears to be some slight difference in the bond distance for the three P–OR bonds, since P–O(2) appear longer than P–O(3) or P–O(4). At first sight

Table 3. *Observed and calculated structure factors*

Within each group the columns reading from left to right contain the values of l, $10F_o$ and $10F_c$.

Table 4. *Bond angles in triphenyl phosphate*

Atoms	Angle	Standard deviation
O(2)–P(1)–O(3)	104·0°	0·54°
O(2)–P(1)–O(4)	104·0	0·66
O(2)–P(1)–O(5)	112·9	0·60
O(3)–P(1)–O(4)	96·6	0·54
O(3)–P(1)–O(5)	119·1	0·65
O(4)–P(1)–O(5)	117·8	0·58
P(1)–O(2)–C(6)	125·3	0·91
P(1)–O(3)–C(12)	122·6	0·82
P(1)–O(4)–C(18)	123·1	0·80
O(2)–C(6)–C(7)	123·4	1·28
O(2)–C(6)–C(11)	114·4	1·38
C(7)–C(6)–C(11)	122·1	1·28
C(6)–C(7)–C(8)	122·0	1·36
C(7)–C(8)–C(9)	117·1	1·55
C(8)–C(9)–C(10)	118·5	1·40
C(9)–C(10)–C(11)	120·2	1·42
C(6)–C(11)–C(10)	120·0	1·54
O(3)–C(12)–C(13)	118·7	1·27
O(3)–C(12)–C(17)	114·2	1·37
C(13)–C(12)–C(17)	126·9	1·51
C(12)–C(13)–C(14)	115·8	1·43
C(13)–C(14)–C(15)	123·3	1·95
C(14)–C(15)–C(16)	116·0	2·15
C(15)–C(16)–C(17)	125·8	1·99
C(12)–C(17)–C(16)	112·0	1·66
O(4)–C(18)–C(19)	116·3	1·33
O(4)–C(18)–C(23)	122·0	1·45
C(19)–C(18)–C(23)	121·7	1·45
C(18)–C(19)–C(20)	118·4	1·82
C(19)–C(20)–C(21)	121·5	2·07
C(20)–C(21)–C(22)	118·0	1·75
C(21)–C(22)–C(23)	121·4	1·70
C(18)–C(23)–C(22)	119·0	1·68

this appears significant; however, examination of the thermal parameters suggests that corrections for thermal motion for P–O(3) and P–O(4) would lengthen these bonds more than the P–O(2) bond. With this in mind we estimated the effects, according to Busing & Levy (1964). It seems that either a riding motion of the oxygen atom on the phosphorus or some correlated parallel motion would most likely describe the effect. Accordingly the calculations show the following results:

	Uncorrected	Riding	Upper bound	Lower bound
P–O(2)	1·599 Å	1·599 Å	1·719 Å	1·599 Å
P–O(3)	1·549	1·571	1·709	1·552
P–O(4)	1·554	1·569	1·704	1·556
P–O(5)	1·432	1·467	1·592	1·434

In the light of these effects, we feel any differences in the P–OR bond lengths are accounted for by thermal motion. Further consideration of these effects is speculative without more accurate knowledge of the rigid body motion of the phenyl groups.

The phosphate tetrahedron appears more distorted in triphenyl phosphate than in any yet reported in organic phosphates. The bond angles for O–P–O bonds range from 96·6° to 119·1°. As one would expect, the bond angles between the oxygen atom with the short bond and the other three oxygen atoms are the largest, ranging from 112·9° to 119·1°, indicating maximum repulsion of these oxygen atoms due to the very short P–O bond distance. The angles between the other oxygen atoms, involved in longer bonds, are considerably less, ranging from 96·6° to 104·0°.

The dihedral angles between the P–O–C planes are given in Table 5. The dihedral angles between the phenoxy groups and the P–O–C planes of which the phen-

Table 5. *Dihedral angles between* P–O–C *planes in triphenyl phosphate*

Planes	Angle
P(1)–O(2)–C(6) and P(1)–O(3)–C(12)	84° 1′
P(1)–O(2)–C(6) and P(1)–O(4)–C(18)	78 13
P(1)–O(3)–C(12) and P(1)–O(4)–C(18)	26 26

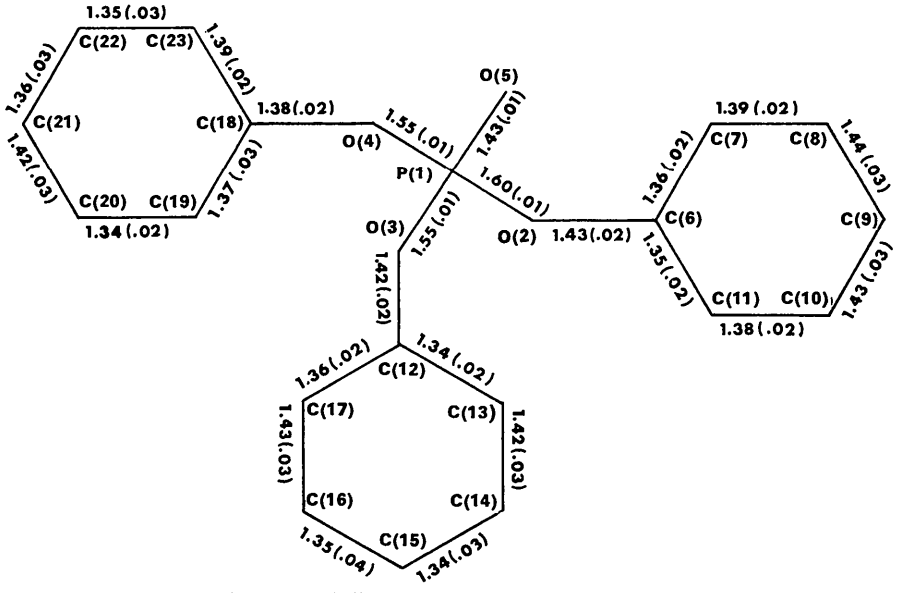

Fig. 1. Bond distances for triphenyl phosphate.

oxy groups are part are given in Table 6. The equations of the planes are presented in Table 7. The mean deviation of the atoms from the planes is 0·016 Å. For the above calculations, an orthogonal cell was chosen where the X axis of the orthogonal cell is coincident with the x axis of the monoclinic cell.

Table 6. *Dihedral angles between* P-O-C *planes and benzene rings in triphenyl phosphate*

Planes	Angle
P(1)–O(2)–C(6) and O(2)–C(6) –C(11)	50°41′
P(1)–O(3)–C(12) and O(3)–C(12)–C(17)	69 5
P(1)–O(4)–C(18) and O(4)–C(18)–C(23)	94 52

Table 7. *Equations of planes in triphenyl phosphate referred to orthogonal coordinates*

Where $X=x+z\cos\beta$ and $Z=z\sin\beta$; $Y=y$

P(1)–O(2)–C(6)	$-0{\cdot}1075X+0{\cdot}4461Y+0{\cdot}8885Z=3{\cdot}9971$
P(1)–O(3)–C(12)	$0{\cdot}04625X+0{\cdot}9514Y-0{\cdot}3044Z=0{\cdot}9069$
P(1)–O(4)–C(18)	$0{\cdot}4692X+0{\cdot}8702Y-0{\cdot}1503Z=3{\cdot}7175$
O(2)–C(6)–C(11)	$-0{\cdot}0815X-0{\cdot}4092Y+0{\cdot}9088Z=1{\cdot}5380$
O(3)–C(12)–C(17)	$0{\cdot}8290X+0{\cdot}4438Y+0{\cdot}3403Z=5{\cdot}6154$
O(4)–C(18)–C(23)	$0{\cdot}8391X-0{\cdot}5253Y+0{\cdot}1414Z=2{\cdot}8987$

Dunitz & Rollett (1956) found that the dihedral angles between P–O–C planes and P–O–H planes were near 90°. The values for two pairs of planes in triphenyl phosphate are near 80°, for the other pair, about 30°. The difference may be attributed to packing considerations.

The mean C–O bond length in triphenyl phosphate is 1·412 Å. This bond length lies between the single bond length of 1·43 Å and the shortened partial double bond length of 1·36 Å (*International Tables for X-ray Crystallography*, 1962).

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