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Bond Length and Reactivity: Structures of Five Dialkyl Aryl Phosphates: 2-Phenoxy-1,3,2-dioxaphosphorinane 2-Oxide, $C_9H_{11}O_4P$, (2*a*); 2-(3-Nitrophenoxy)-1,3,2-dioxaphosphorinane 2-Oxide, $C_9H_{10}NO_6P$, (2*b*); 2-(2-Nitrophenoxy)-1,3,2-dioxaphosphorinane 2-Oxide, $C_9H_{10}NO_6P$, (2*c*); 2-(4-Chloro-2-nitrophenoxy)-1,3,2-dioxaphosphorinane 2-Oxide, $C_9H_9ClNO_6P$, (2*d*); and 2-(2,4-Dinitrophenoxy)-1,3,2-dioxaphosphorinane 2-Oxide, $C_9H_9N_2O_8P$, (2*e*)

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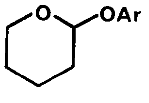
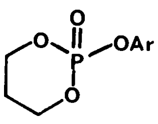
Abstract. Structures have been determined for a homogeneous series of five phosphate triesters (2*a*)–(2*e*). Mo $K\alpha$, $\lambda = 0{\cdot}71093$ Å, 293 K. (2*a*): $M_r = 214{\cdot}16$, orthorhombic, $Pna2_1$, $a = 15{\cdot}453\ (3)$, $b = 11{\cdot}005\ (2)$, $c = 5{\cdot}925\ (2)$ Å, $V = 1007{\cdot}6\ (7)$ Å^3, $Z = 4$, $D_x = 1{\cdot}41$ Mg m^{-3}, $\mu = 0{\cdot}25$ mm^{-1}, $F(000) = 448$, $R = 0{\cdot}045$ for 2146 unique observed reflections; (2*b*): $M_r = 259{\cdot}16$, orthorhombic, $P2_12_12_1$, $a = 5{\cdot}710\ (2)$, $b = 9{\cdot}042\ (2)$, $c = 21{\cdot}409\ (4)$ Å, $V = 1105{\cdot}3\ (6)$ Å^3, $Z = 4$, $D_x = 1{\cdot}56$ Mg m^{-3}, $\mu = 0{\cdot}26$ mm^{-1}, $F(000) = 536$, $R = 0{\cdot}037$ for 2434 reflections; (2*c*): $M_r = 259{\cdot}16$, triclinic, $P\bar{1}$, $a = 7{\cdot}394\ (2)$, $b = 7{\cdot}970\ (2)$, $c = 9{\cdot}966\ (3)$ Å, $\alpha = 86{\cdot}68\ (2)$, $\beta = 70{\cdot}73\ (2)$, $\gamma = 85{\cdot}06\ (2)°$, $V = 552{\cdot}1\ (6)$ Å^3, $Z = 2$, $D_x = 1{\cdot}56$ Mg m^{-3}, $\mu = 0{\cdot}26$ mm^{-1}, $F(000) = 268$, $R = 0{\cdot}047$ for 2250 reflections; (2*d*): $M_r = 293{\cdot}61$, triclinic, $P\bar{1}$, $a = 6{\cdot}226\ (2)$, $b = 9{\cdot}586\ (2)$, $c = 10{\cdot}148\ (2)$ Å, $\alpha = 93{\cdot}77\ (2)$, $\beta = 92{\cdot}51\ (2)$, $\gamma = 100{\cdot}96\ (2)°$, $V = 592{\cdot}3\ (6)$ Å^3, $Z = 2$, $D_x = 1{\cdot}65$ Mg m^{-3}, $\mu = 0{\cdot}47$ mm^{-1}, $F(000) = 300$, $R = 0{\cdot}046$ for 2110 reflections; (2*e*): $M_r = 304{\cdot}16$, triclinic, $P\bar{1}$, $a = 5{\cdot}547\ (2)$, $b = 10{\cdot}382\ (2)$, $c = 10{\cdot}696\ (2)$ Å, $\alpha = 87{\cdot}01\ (2)$, $\beta = 89{\cdot}63\ (2)$, $\gamma = 79{\cdot}90\ (2)°$, $V = 605{\cdot}6\ (6)$ Å^3, $Z = 2$, $D_x = 1{\cdot}67$ Mg m^{-3}, $\mu = 0{\cdot}26$ mm^{-1}, $F(000) = 312$, $R = 0{\cdot}044$ for 2425 reflections. All five compounds are in the expected chair conformation with the aryloxy group axial and significant flattening at phosphorus. The P—OAr bond length increases to a limiting value of 1·600 Å as the aryl group becomes more electron withdrawing. (2*a*)–(2*d*) show a linear relationship between P—OAr bond length and reactivity; (2*e*) shows a negative deviation from this linearity. Further trends are (i) a shortening of the O—Ar bond and (ii) a change of the torsion angle about O—Ar from synclinal towards coplanar.

Introduction. We wish to test the generality of the linear relationship (Jones & Kirby, 1979) between the length of a bond in the crystal and the free energy of activation for its heterolytic cleavage in solution. We have looked so far at four series of acetals; axial and equatorial aryl tetrahydropyranyl acetals (1) and α- and β-glucopyranosides. Of these four series, three showed C—OAr bond lengths strongly dependent on the nature of the Ar group, and approximately proportional to log $k_{\rm hyd}$ (Briggs, Glenn, Jones, Kirby & Ramaswamy, 1984). A survey of another four broad classes of compounds containing C—O bonds (methyl, primary, secondary and tertiary alkyl ethers and esters), using the Cambridge Database, showed evidence of similar behaviour (Allen & Kirby, 1984). We have further shown, in preliminary studies (Jones, Sheldrick, Kirby & Abell, 1984*a*,*b*) that phosphate monoester dianions may behave in the same way.

This paper reports crystal structures for a homogeneous series of phosphate triesters (2). Triesters are of interest because they react quite differently from monoesters. In particular, their reactions in solution are exclusively associative (Khan & Kirby, 1970), and heterolytic cleavage of the P—OAr bond, in the sense P$^+$ $^-$OAr, is expected to be energetically highly unfavourable. The series of cyclic esters (2) is convenient because all the compounds form good crystals, and because extensive kinetic data are available (Khan & Kirby, 1970). Their preparation and physical properties are described by Khan & Kirby (1970).



(1)



(2)

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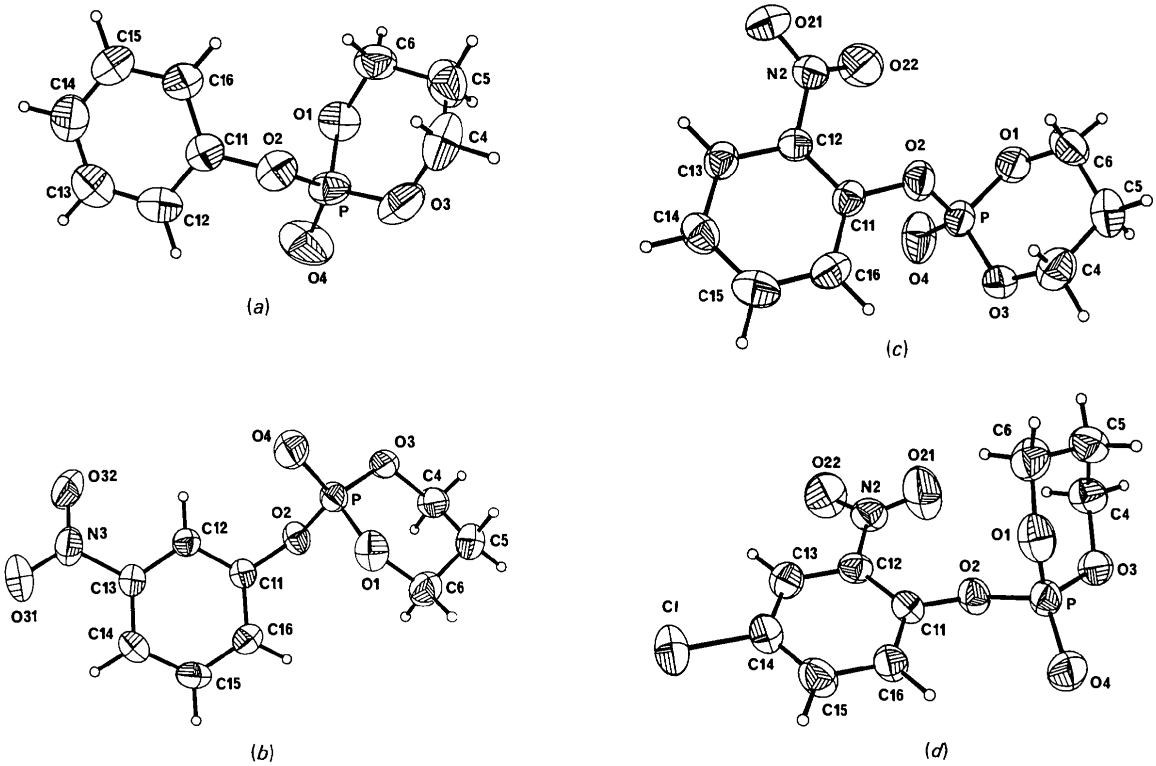

Fig. 1. (*a*)–(*e*) Thermal ellipsoid plots (50% probability) for (2*a*)–(2*e*), respectively, showing the atom numbering schemes.

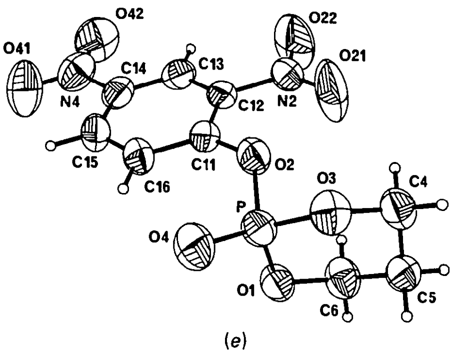

Fig. 1 (*cont.*)

Experimental. The following features of crystal growth, data collection, structure solution and refinement are common to all five structures: crystals obtained by liquid diffusion, monochromated Mo $K\alpha$ radiation, no variation of standard reflection intensity, solution by automatic direct methods, refinement on F with all non-H atoms anisotropic, isotropic H atoms included with a riding model [C—H 0·96 Å, H—C—H 109·5°, $U(\mathrm{H}) = 1{\cdot}2\ U_{\mathrm{eq}}(\mathrm{C})$], weighting scheme $w^{-1} = \sigma^2(F) + gF^2$, cell constants refined from 2θ values of strong reflections in the range 20–24° (measured on a Stoe–Siemens four-circle diffractometer). All calculations were performed with the *SHELXTL* program system written by GMS. For other information, see Table 1.†

Discussion. Final atomic coordinates are given in Table 2; thermal ellipsoid plots are presented in Figs. 1(*a*)–(*e*). Phosphate oxygen atoms are consistently numbered as follows: O(1) and O(3), ring oxygens; O(2) bonded to aromatic ring; O(4) forms double bond to phosphorus. Since the discussion largely centres on the geometry of the phosphate group, Table 3 presents only selected bond lengths, bond angles and torsion angles.†

Compounds (2*a*)–(2*e*) form a homogeneous series. All five exist in the expected chair conformation, with the aryloxy group axial and significant flattening at phosphorus. This is characteristic of systems exhibiting the generalized anomeric effect (Kirby, 1983), which involves n–σ^* overlap between the non-bonding

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† Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and bond lengths, bond angles and torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39231 (95 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Details of crystal growth, data collection, structure solution and refinement for* (2*a*)–(2*e*)

Compound	(2*a*)*	(2*b*)	(2*c*)	(2*d*)	(2*e*)
Ar	Phenyl	3-Nitrophenyl	2-Nitrophenyl	4-Chloro-2-nitrophenyl	2,4-Dinitrophenyl
Solvent	9:1 $CCl_4/CHCl_3$	CH_2Cl_2	CH_2Cl_2	CH_2Cl_2	CH_2Cl_2
Precipitant	Hexane	Hexane	Hexane	Diethyl ether	Ethyl acetate
Habit	Colourless prisms	Colourless prisms	Pale yellow, equidimensional	Pale yellow prisms	Pale yellow, equidimensional
Reflections for cell-constant refinement	32	40	30	40	38
Diffractometer	Stoe 2-circle	Stoe 2-circle	Stoe 4-circle†	Stoe 4-circle†	Stoe 4-circle†
$2\theta_{max}$(°)	55	55	55	55	55
Crystal size (mm)	0·6×0·15×0·1‡ 0·7×0·35×0·35§	0·55×0·3×0·2¶ 0·38×0·3×0·2¶ 0·45×0·35×0·25§	0·4×0·4×0·35	0·55×0·25×0·1	0·6×0·6×0·6
Reflections measured	5923‡ (layers −4 to +6) 3939§** (layers 0–12)	252¶ (layer 0) 4277¶ (layers 0–6) 2729§ (layers 0–7)	2536	2827	3798
Unique reflections††	2444‡‡¶¶	2683‡‡§§	2536	2705	2773
Observed reflections ($F > 4\sigma$)	2146	2434	2250	2110	2425
R_{int}	0·025	0·017	—	0·029	0·029
R	0·045	0·037	0·047	0·046	0·044
R_w	0·042	0·035	0·055	0·048	0·054
g	0·00025	0·0004	0·0003	0·00025	0·0002
S	1·86	1·40	2·23	1·96	2·80
Number of parameters	126	154	155	163	182
Max. Δ/σ	0·01	0·01	0·004	0·002	0·08
Max. and min. in final $\Delta\rho$ synthesis (e Å^{-3})	+0·2, −0·7	+0·3, −0·7	+0·3, −0·3	+0·35, −0·4	+0·3, −0·2
Secondary extinction parameter x***	—	—	0·044 (3)	—	0·014 (2)
Anomalous dispersion parameter η†††	+1·1 (2)	+1·1 (2)	—	—	—

* Redetermination; the original structure (Geise, 1967) was not precise enough for our purposes.

† Intensities by on-line profile fitting (Clegg, 1981).

‡ Crystal mounted parallel to **c**.

§ Crystal mounted parallel to **b**.

¶ Crystal mounted parallel to **a**.

** Absorption correction based on indexed faces; transmissions 0·87–0·96.

†† Friedel opposites not merged for (2*a*), (2*b*).

‡‡ Interlayer scale factors derived from least-squares analysis of common reflections.

§§ 'Handedness' problem on merging overcome by using different fragments of the same large crystal.

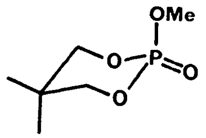
¶¶ 'Handedness' problem on merging; the handedness of each crystal was determined by η refinements (Rogers, 1981) on the two separate data sets.

*** The calculated structure factor becomes $F = F_c/(1 + 0{\cdot}002xF_c^2/\sin 2\theta)^{0{\cdot}25}$.

††† Rogers (1981).

electron pairs on the ring-oxygen atoms and the antibonding orbital of the P—OAr bond. The effect has been noted previously in a cyclic phosphate by van Nuffel, Lenstra & Geise (1980) who determined the structure of the methyl ester (3).

The ring torsion angles for compounds (2*a*)–(2*e*) and (3)* are compared in Table 3*A*, which shows that the flattening of the ring is somewhat greater for the aryl esters, but shows no systematic increase with increasing electron withdrawal in the Ar group.



(3)

Bond angles around phosphorus show no systematic variations over the whole set of six compounds, and the only obvious trend in torsion angles (Table 3*B*) is from synclinal towards coplanarity about O(2)—C(11) as the aromatic ring becomes more strongly electron withdrawing. A weak trend is, however, discernible in the lengths of the bonds to O(2); O(2)—C(11) is shorter for the phenol derivatives, as expected (though the angle at oxygen is in no case less than 120°), and becomes shorter still as more electron-withdrawing substituents are added to the aromatic ring. The P—OAr bond, by

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* Compound (3) is the only simple phosphate ester available for comparison. Other compounds containing the 2-aryloxy- or 2-alkyloxy-1,3,2-dioxaphosphorinane 2-oxide unit are unsuitable because of distortions induced by either additional fused rings or electron-withdrawing groups such as chlorine on the phosphorinane ring. However, the 5-*tert*-butyl methyl ester analogous to (3), despite disorder, shows a P—OMe bond length very similar to (3) [1·567 (6) Å, *cf.* 1·565 (4) Å; Warrent, Caughlan, Hargis, Yee & Bentrude (1978)].

contrast, lengthens over this series, until it reaches a limiting value of 1·600 Å.

The length of this bond, P—O(2), is plotted against the pK_a of the conjugate acid of the leaving group (itself linearly related to log k_{hyd}, as shown by Khan & Kirby, 1970) in Fig. 2. The points for four of the aryl esters (2*a*)–(2*d*) fall on a good line, which also passes through the point for the methyl ester (3), defining another linear relationship between bond length and reactivity. The point for the 2,4-dinitrophenyl compound (2*e*) shows an appreciable negative deviation from this line. We need data for more compounds with strongly electron-withdrawing groups before we speculate on the significance of this negative deviation. It is clearly important that the slope of the line of Fig. 2 is some three times smaller than the corresponding plot for phosphate monoester dianions (Jones, Sheldrick, Kirby & Abell, 1984*b*). It appears, not unexpectedly, that the easier it is to break the bond P—O*R* chemically, the more sensitive is the length of the bond to the effective electronegativity of the O*R* group oxygen atom.

Table 2. *Atomic coordinates* ($\times 10^4$) *and isotropic thermal parameters* (Å^2 $\times 10^3$) *for* (2*a*), (2*b*), (2*c*), (2*d*), (2*e*)

	x	*y*	*z*	U_{eq}*
(2*a*)				
P	383 (1)	2324 (1)	5000	54 (1)
O(1)	−245 (1)	1341 (1)	5901 (3)	60 (1)
O(2)	1242 (1)	2228 (1)	6459 (3)	53 (1)
O(3)	28 (1)	3564 (1)	5809 (4)	75 (1)
O(4)	526 (2)	2231 (3)	2573 (4)	103 (1)
C(4)	−310 (2)	3665 (3)	8106 (6)	78 (1)
C(5)	−963 (2)	2698 (3)	8555 (6)	75 (1)
C(6)	−587 (2)	1448 (2)	8177 (4)	64 (1)
C(11)	1780 (1)	1201 (2)	6287 (4)	47 (1)
C(12)	2291 (1)	1043 (2)	4403 (4)	60 (1)
C(13)	2839 (1)	51 (3)	4332 (5)	70 (1)
C(14)	2878 (1)	−743 (2)	6076 (5)	71 (1)
C(15)	2369 (2)	−574 (3)	7937 (6)	75 (1)
C(16)	1816 (1)	417 (2)	8077 (5)	62 (1)
(2*b*)				
P	4038 (1)	432 (1)	3272 (1)	38 (1)
O(1)	3233 (3)	−661 (2)	3792 (1)	50 (1)
O(2)	2183 (2)	1749 (1)	3283 (1)	40 (1)
O(3)	3474 (2)	−300 (2)	2630 (1)	48 (1)
O(4)	6460 (2)	912 (2)	3344 (1)	65 (1)
C(4)	1295 (4)	−1133 (2)	2561 (1)	50 (1)
C(5)	1045 (4)	−2230 (2)	3076 (1)	54 (1)
C(6)	1054 (4)	−1494 (2)	3704 (1)	51 (1)
C(11)	2179 (3)	2773 (2)	3774 (1)	34 (1)
C(12)	3872 (3)	3848 (2)	3792 (1)	37 (1)
C(13)	3779 (3)	4846 (2)	4280 (1)	38 (1)
C(14)	2084 (4)	4817 (2)	4738 (1)	43 (1)
C(15)	384 (4)	3727 (2)	4696 (1)	50 (1)
C(16)	414 (3)	2699 (2)	4215 (1)	44 (1)
N(3)	5597 (3)	5995 (2)	4305 (1)	54 (1)
O(31)	5779 (4)	6732 (2)	4771 (1)	88 (1)
O(32)	6862 (4)	6150 (2)	3858 (1)	96 (1)
(2*c*)				
P	4141 (1)	7577 (1)	1632 (1)	46 (1)
O(1)	4926 (2)	9321 (2)	1626 (2)	55 (1)
O(2)	4395 (2)	6734 (2)	3059 (1)	54 (1)
O(4)	2214 (2)	7625 (2)	1562 (2)	77 (1)
O(3)	5652 (2)	6606 (2)	403 (1)	52 (1)
C(4)	7665 (3)	6624 (3)	285 (3)	59 (1)
C(5)	8223 (3)	8396 (3)	227 (3)	62 (1)
C(6)	6962 (3)	9376 (3)	1473 (3)	63 (1)
C(11)	3427 (3)	5377 (2)	3790 (2)	40 (1)
C(12)	2367 (2)	5484 (2)	5219 (2)	38 (1)
C(13)	1464 (3)	4105 (2)	5984 (2)	44 (1)
C(14)	1632 (3)	2607 (2)	5313 (2)	51 (1)
C(15)	2712 (3)	2490 (3)	3898 (3)	60 (1)
C(16)	3608 (3)	3862 (3)	3128 (2)	54 (1)
N(2)	2116 (2)	7038 (2)	5996 (2)	50 (1)
O(21)	1694 (3)	6916 (2)	7284 (2)	76 (1)
O(22)	2291 (3)	8375 (2)	5342 (2)	91 (1)
(2*d*)				
P	183 (1)	2072 (1)	1818 (1)	45 (1)
Cl	7158 (1)	1629 (1)	7231 (1)	81 (1)
O(1)	1474 (3)	994 (2)	1202 (2)	54 (1)
O(2)	1924 (3)	3155 (2)	2784 (1)	47 (1)
O(3)	−293 (3)	3053 (2)	732 (2)	51 (1)
O(4)	−1754 (3)	1396 (2)	2444 (2)	75 (1)
C(4)	1439 (4)	3551 (3)	−158 (2)	54 (1)
C(5)	2344 (4)	2333 (3)	−735 (3)	57 (1)
C(6)	3197 (4)	1490 (3)	292 (3)	61 (1)
C(11)	3159 (4)	2762 (2)	3802 (2)	40 (1)
C(12)	5333 (4)	3429 (2)	4065 (2)	43 (1)
C(13)	6557 (4)	3102 (3)	5125 (2)	50 (1)
C(14)	5620 (4)	2079 (3)	5918 (2)	51 (1)
C(15)	3471 (4)	1388 (3)	5684 (2)	53 (1)
C(16)	2247 (4)	1739 (3)	4638 (2)	49 (1)
N(2)	6448 (4)	4502 (2)	3226 (2)	53 (1)
O(21)	5660 (4)	4604 (3)	2146 (2)	108 (1)
O(22)	8173 (3)	5220 (2)	3631 (2)	85 (1)
(2*e*)				
P	−43 (1)	1919 (1)	1497 (1)	49 (1)
O(1)	1972 (2)	982 (1)	825 (1)	55 (1)
O(2)	1318 (3)	2461 (1)	2619 (1)	62 (1)
O(3)	−1616 (2)	1063 (1)	2271 (1)	59 (1)
O(4)	−1431 (3)	2924 (1)	674 (1)	70 (1)
C(4)	−363 (4)	−142 (2)	2940 (2)	58 (1)
C(5)	1265 (4)	−962 (2)	2057 (2)	55 (1)
C(6)	3148 (4)	−245 (2)	1487 (2)	62 (1)
C(11)	2839 (3)	3366 (1)	2573 (2)	47 (1)
C(12)	4558 (3)	3328 (2)	3530 (1)	48 (1)
C(13)	6033 (4)	4258 (2)	3569 (2)	55 (1)
C(14)	5776 (3)	5243 (2)	2637 (2)	55 (1)
C(15)	4128 (4)	5305 (2)	1673 (2)	59 (1)
C(16)	2660 (4)	4366 (2)	1642 (2)	56 (1)
N(2)	4908 (3)	2290 (1)	4531 (1)	62 (1)
O(21)	3759 (5)	1445 (2)	4556 (2)	134 (1)
O(22)	6397 (5)	2336 (2)	5306 (2)	121 (1)
N(4)	7362 (3)	6237 (2)	2679 (2)	75 (1)
O(41)	7145 (4)	7083 (2)	1838 (2)	112 (1)
O(42)	8798 (4)	6161 (2)	3550 (2)	101 (1)

* Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

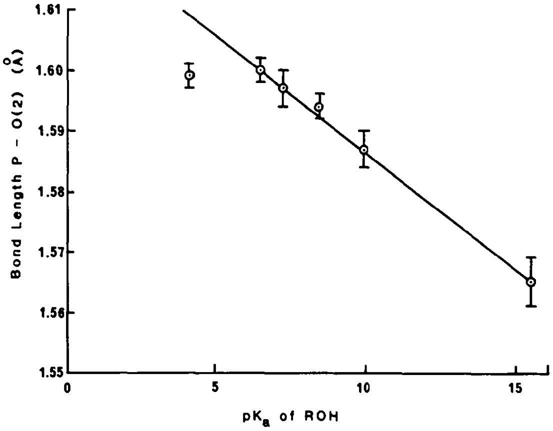

Fig. 2. Plot of bond length P–O(2) against pK_a of *R*OH for (2*a*)–(2*e*) and (3). The least-squares line through the five points for (2*a*)–(2*d*) and (3) has a correlation coefficient *r* of 0·992.

Table 3. *Selected structural parameters for the phosphate esters* (3), (2*a*)–(2*e*)

	(3)*	(2*a*)	(2*b*)	(2*c*)	(2*d*)	(2*e*)
A. Ring torsion angles (°, absolute values)						
C(6)–O(1)–P–O(3)	45·2 (6)	41·1 (3)	38·7 (2)	44·7 (3)	40·4 (3)	38·5 (3)
O(1)–P–O(3)–O(4)	44·0 (6)	41·3 (3)	38·9 (2)	46·6 (3)	41·0 (3)	40·2 (3)
P–O(3)–C(4)–C(5)	53·4 (6)	52·0 (4)	50·7 (3)	54·3 (3)	50·6 (3)	52·1 (3)
O(3)–C(4)–C(5)–C(6)	56·5 (6)	57·1 (4)	58·9 (3)	55·4 (4)	56·4 (4)	59·1 (3)
C(4)–C(5)–C(6)–O(1)	57·6 (6)	56·5 (4)	58·6 (3)	53·9 (4)	55·5 (4)	57·6 (3)
C(5)–C(6)–O(1)–P	55·1 (6)	50·7 (3)	50·2 (3)	50·9 (3)	49·1 (3)	48·9 (3)
B. Bond and torsion angles at phosphorus (°)						
C(6)–O(1)–P	118·0 (3)	119·4 (2)	118·9 (2)	118·2 (2)	119·0 (3)	119·3 (2)
O(1)–P–O(3)	105·7 (2)	106·7 (2)	107·5 (2)	105·9 (2)	107·7 (2)	107·6 (2)
P–O(3)–C(4)	118·0 (3)	118·8 (3)	118·0 (2)	117·9 (2)	118·6 (3)	118·5 (2)
O(1)–P–O(2)	101·7 (3)	106·8 (2)	105·5 (2)	100·7 (2)	105·4 (2)	105·5 (2)
O(3)–P–O(4)	111·1 (2)	114·9 (2)	114·6 (2)	113·2 (2)	113·8 (2)	114·6 (2)
O(2)–P–O(4)	116·0 (2)	113·9 (2)	114·0 (2)	115·0 (2)	114·6 (2)	114·6 (2)
P–O(2)–C(11)	122·5 (4)	120·6 (2)	120·4 (2)	124·3 (2)	124·7 (2)	129·0 (2)
O(1)–P–O(2)–C(11)		67·7 (3)	72·3 (2)	160·4 (2)	−56·4 (3)	74·5 (2)
O(3)–P–O(2)–C(11)		179·0 (3)	−175·9 (2)	−89·6 (2)	−168·6 (3)	−174·1 (2)
O(4)–P–O(2)–C(11)		−57·4 (3)	−52·4 (2)	35·9 (3)	68·5 (3)	−51·5 (3)
P–O(2)–C(11)–C(12)		73·8 (3)	75·7 (3)	−125·3 (3)	140·9 (3)	−154·7 (2)
C. Bond lengths (Å)						
P–O(2)	1·565 (4)	1·587 (3)	1·594 (2)	1·597 (3)	1·600 (2)	1·599 (2)
P–O(1)	1·567 (4)	1·549 (3)	1·559 (2)	1·550 (3)	1·542 (3)	1·547 (2)
P–O(3)	1·565 (4)	1·547 (3)	1·559 (2)	1·551 (2)	1·550 (3)	1·557 (2)
P–O(4)	1·444 (4)	1·458 (3)	1·458 (2)	1·447 (3)	1·449 (3)	1·445 (2)
C(6)–O(1)	1·450 (6)	1·453 (4)	1·467 (4)	1·467 (4)	1·476 (4)	1·473 (3)
C(4)–O(3)	1·472 (6)	1·462 (5)	1·461 (3)	1·455 (4)	1·468 (4)	1·472 (3)
C(11)–O(2)	1·428 (6)	1·408 (3)	1·400 (3)	1·383 (3)	1·376 (4)	1·368 (3)

* van Nuffel, Lenstra & Geise (1980).

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Laser Dye Intermediates: Structures of 1,2,3,4-Tetrahydroquinolinium-7-sulfonate Monohydrate (I), $C_9H_{11}NO_3S.H_2O$, and Twinned 1,2,3,4-Tetrahydro-1-methylquinolinium-7-sulfonate (II), $C_{10}H_{13}NO_3S$

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Abstract. (I): $M_r = 231{\cdot}2$, monoclinic, $P2_1/c$, $a = 7{\cdot}979\ (4)$, $b = 9{\cdot}096\ (6)$, $c = 14{\cdot}492\ (6)$ Å, $\beta = 96{\cdot}03\ (4)^\circ$, $F(000) = 488$, $V = 1046{\cdot}0$ Å^3, $Z = 4$, $D_x = 1{\cdot}47$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 2{\cdot}9$ mm^{-1}, $T = 295$ K, final $R = 0{\cdot}057$ for 1374 unique reflections. (II): $M_r = 227{\cdot}3$, monoclinic, $P2_1/n$, $a = 9{\cdot}343\ (4)$, $b = 14{\cdot}235\ (6)$, $c = 7{\cdot}706\ (4)$ Å, $\beta = 95{\cdot}71\ (4)^\circ$, $F(000) = 480$, $V = 1019{\cdot}7$ Å^3, $Z = 4$, $D_x = 1{\cdot}48$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 2{\cdot}89$ mm^{-1}, $T = 295$ K, final $R = 0{\cdot}069$ for 1140 unique reflections. Crystals of (II) were found to be twinned, with components of the twin present in approximately equal amounts. The X-ray results showed the sulfonyl group to be in the *meta* position with respect to the quinoline moiety. Both (I) and (II) are zwitterions in the crystalline phases studied.

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