The dihedral angles between the two carboxylate planes of Hadc residues [13.8 (7) and 3.8 (7)° respectively] differ considerably from the 62° in LiHadc.H_2O, 66° in KHadc, 61° in RbHadc and 74° in NH_4Hadc. Planar centrosymmetric Hadc residues were observed in NaHadc.$2H_2O$ and CsHadc.H_2O. The striking feature of the structure is the nearly coplanar arrangement of the extended layers of guanidinium cations and Hadc residues (Fig. 2). The dihedral angles between separate Hadc and guanidinium entities vary from 3.5 to 13.6°, whereas in guanidinium hydrogen maleate, forms I and II, these angles are 33.2 and 16.5°, respectively (Golič, Leban, Detoni, Orel & Hadži, 1985). It seems that the planar guanidinium ions force the Hadc to assume the nearly planar conformation.

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Bond Length and Reactivity.† Structure of the Diphenyl Phosphate Ester of 2,6-Dichlorobenzyl Alcohol

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Abstract. 2,6-Dichlorobenzyl diphenyl phosphate, $C_{19}H_{15}Cl_2O_4P$, $M_r = 409.21$, monoclinic, $P2_1/c$, $a = 11.471\ (2)$, $b = 12.555\ (3)$, $c = 13.159\ (2)$ Å, $\beta = 91.83\ (2)°$, $V = 1894$ Å^3, $Z = 4$, $D_x = 1.435$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.45$ mm^{-1}, $F(000) = 840$, $T = 293$ K. Final $R = 0.056$ for 2248 unique observed reflections. The key torsion angle, between the benzylic C—O bond and the plane of the ring (C_{ar}—C_{ar}—C—O), which controls the strength of the ring-π–$\sigma^*_{C—OX}$ interaction is 77.3 (4)°, similar to that found for other derivatives of this alcohol [Jones, Dölle, Kirby & Parker (1989). *Acta Cryst.* C**45**, 231–234] and this benzylic C—O bond length is 1.464 (4) Å.

Introduction. We recently reported (Jones, Dölle, Kirby & Parker, 1989) crystal structures for three derivatives (1) of 2,6-dichlorobenzyl alcohol, which for steric reasons adopt a conformation in which the C—O*X* bond is close to perpendicular (torsion angle 73 ± 5°) to the ring, and is longer for better 'leaving groups' O*X*. After several months in the refrigerator

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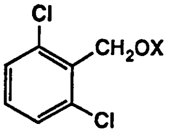
† Previous paper in this series: Jones, Edwards & Kirby (1989).

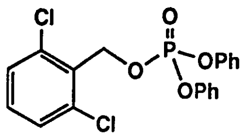
Table 1. *Atomic coordinates* (× 10^4) *and equivalent isotropic displacement parameters* ($Å^2 \times 10^3$) *for* (2)

	x	y	z	U_{eq}*
P	8873 (1)	2053 (1)	4509 (1)	48 (1)
Cl(1)	6025 (1)	2694 (1)	6459 (1)	90 (1)
Cl(2)	7349 (1)	− 1367 (1)	5801 (1)	112 (1)
O(1)	8342 (2)	2749 (2)	3614 (2)	62 (1)
O(2)	9571 (2)	1196 (2)	3913 (2)	55 (1)
O(3)	9607 (2)	2586 (2)	5265 (2)	64 (1)
O(10)	7775 (2)	1484 (2)	4912 (2)	53 (1)
C(10)	7795 (3)	1033 (3)	5938 (3)	58 (1)
C(11)	6601 (3)	639 (3)	6146 (2)	48 (1)
C(12)	5718 (3)	1336 (3)	6393 (3)	57 (1)
C(13)	4609 (4)	1011 (4)	6591 (3)	78 (2)
C(14)	4362 (4)	− 46 (5)	6542 (3)	88 (2)
C(15)	5189 (5)	− 781 (4)	6305 (3)	85 (2)
C(16)	6312 (4)	− 432 (3)	6108 (3)	64 (1)
C(21)	7875 (3)	3773 (3)	3775 (2)	51 (1)
C(22)	6695 (4)	3888 (4)	3894 (3)	66 (2)
C(23)	6257 (4)	4920 (4)	3987 (3)	82 (2)
C(24)	7008 (6)	5769 (4)	3967 (3)	92 (2)
C(25)	8166 (5)	5631 (4)	3867 (4)	90 (2)
C(26)	8602 (4)	4625 (3)	3755 (3)	70 (2)
C(31)	9069 (3)	490 (3)	3191 (3)	47 (1)
C(32)	8742 (3)	849 (3)	2240 (3)	57 (1)
C(33)	8278 (4)	140 (3)	1544 (3)	73 (2)
C(34)	8176 (5)	− 918 (3)	1781 (4)	78 (2)
C(35)	8537 (4)	− 1269 (3)	2730 (4)	76 (2)
C(36)	8978 (3)	− 564 (3)	3446 (3)	59 (1)

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

a fourth derivative, the diphenyl phosphate ester (2) crystallized. The leaving group in this case, the diphenyl phosphate anion, is the best of the series, because it is the least basic. We report the crystal and molecular structure of (2).


(1)


(2)

Experimental. The ester was prepared by the addition of 0.98 ml (4.8 mmol) of diphenyl phosphorochloridate in CH_2Cl_2 (5 ml) to a stirred solution of the alcohol (4 mmol) and pyridine (0.63 ml, 8 mmol) in the same solvent (10 ml). After stirring for 3 h the reaction mixture was partitioned between CH_2Cl_2 and water, the organic layer dried over $MgSO_4$, and the solvent evaporated off *in vacuo*. Purification by flash chromatography [Merck Kieselgel 60 (40–63 μm), eluant CH_2Cl_2] gave the phosphate [(2) 53%] as a yellow oil, which solidified after several months at 269 K to give colourless prisms, m.p. 332–333 K. (Found: C, 55.8, H, 3.50; $C_{19}H_{15}Cl_2O_4P$ requires C, 55.8, H, 3.69%.)

A colourless crystal 0.4 × 0.3 × 0.3 mm was mounted in a glass capillary. A hemisphere of data (6690 reflections, $\pm h$, $+k$, $\pm l$) was collected on a Siemens *R*3 diffractometer using monochromated Mo $K\alpha$ radiation ($2\theta_{max}$ 50°). Three check reflections showed no significant intensity change. No absorption or extinction correction was applied. Merging equivalents gave 3349 unique reflections (R_{int} 0.019), of which 2248 with $F > 4\sigma(F)$ were used for all calculations (program system Siemens *SHELXTL-Plus*; Sheldrick, 1990). Cell constants were refined from $\pm\omega$ values of 44 reflections in the 2θ range 20–23°, measured from the same crystal on a Stoe–Siemens diffractometer.

Table 2. *Selected bond lengths* (Å) *and angles* (°) *for* (2)

P—O(1)	1.574 (3)	P—O(2)	1.566 (3)
P—O(3)	1.447 (3)	P—O(10)	1.555 (2)
Cl(1)—C(12)	1.741 (4)	Cl(2)—C(16)	1.729 (4)
O(1)—C(21)	1.412 (4)	O(2)—C(31)	1.409 (4)
O(10)—C(10)	1.464 (4)	C(10)—C(11)	1.490 (5)

O(1)—P—O(2)	101.4 (1)	O(1)—P—O(3)	117.4 (1)
O(2)—P—O(3)	111.5 (1)	O(1)—P—O(10)	102.2 (1)
O(2)—P—O(10)	106.8 (1)	O(3)—P—O(10)	115.9 (1)
P—O(1)—C(21)	122.2 (2)	P—O(2)—C(31)	124.4 (2)
P—O(10)—C(10)	120.2 (2)	O(10)—C(10)—C(11)	108.1 (3)
C(10)—C(11)—C(12)	121.1 (3)	C(10)—C(11)—C(16)	122.4 (3)
C(12)—C(11)—C(16)	116.5 (3)	Cl(1)—C(12)—C(11)	118.8 (3)

The structure was solved by routine direct methods and subjected to anisotropic full-matrix least-squares refinement on F. H atoms were included using a riding model. The final R was 0.056, with wR 0.049. The weighting scheme was $w^{-1} = \sigma^2(F) + 0.0002F^2$. 235 parameters; S 1.8; max. Δ/σ 0.001; max. $\Delta\rho$ ± 0.39 e $Å^{-3}$.

Discussion. Final atom coordinates are given in Table 1, and derived parameters in Table 2. A plot of (2), showing the atom-numbering scheme, appears as Fig. 1.

The molecular packing is illustrated in the supplementary material.[†] The shortest non-bonded contacts between non-H atoms are C(32)···O(3) 3.43, C(22)···C(12) 3.45 Å (second atoms at x, $\frac{1}{2} - y$, $-\frac{1}{2} + z$) and O(2)···Cl(2) 3.55 Å ($2 - x$, $-y$, $1 - z$).

The benzyl phosphate side chain adopts the extended conformation, with P—O(10)—C(10)—C(11) 174.7 (2)°, thus minimizing steric interactions between the two most crowded centres. The key torsion angle O(10)—C(10)—C(11)—C(12) which controls the strength of the ring-π-$\sigma^*_{C—OX}$ interaction (Jones, Dölle, Kirby & Parker, 1989) is 77.3 (4)°, similar to those found for the two carboxylic esters described previously. The length of the C—O*X* bond,

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[†] Lists of structure factors, H-atom parameters and anisotropic thermal parameters, together with complete tables of bond lengths, bond angles and torsion angles, and packing diagrams have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54748 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA0048]

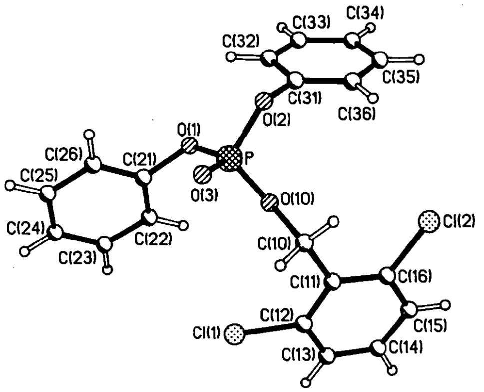

Fig. 1. Molecular structure of (2), showing the atom-numbering scheme.

C(10)—O(10), is identical, within experimental error, with that for the 3,5-dinitrobenzoate ester already reported. This is to be expected, since the pK_a's of diphenyl phosphoric and 3,5-dinitrobenzoic acids differ by less than one unit, and the slope of the plot of bond length *vs* pK_a of the leaving group is only 0.003 Å/pK_a unit.

This plot was one of the original objectives of the work with these 2,6-disubstituted benzyl compounds (1). We had found earlier (Jones & Kirby, 1979, 1984) that there is a good linear relationship between these parameters for many different series of compounds. But for derivatives of 1-phenylethanol, where the conformation about the benzylic C_α—Ar bond varies, the relationship was clearly not linear. This was ascribed to the variation with this dihedral angle of the ring-π–$\sigma^*_{C—OX}$ interation, which was found to be the single most important factor affecting the length of the C—O*X* bond (Edwards, Jones & Kirby, 1986). The (best-least-squares) line drawn through the augmented data set has a correlation coefficient $r = 0.94$, clearly not very strong evidence for a linear relationship. Unfortunately the data are too few to support firm conclusions.

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Bond Length and Reactivity. Structure of 2-*endo*-Bornyl *p*-Toluenesulfonate

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Abstract. $C_{17}H_{24}O_3S$, $M_r = 308.45$, triclinic, $P\bar{1}$, $a = 7.9995\,(14)$, $b = 9.870\,(2)$, $c = 11.975\,(2)$ Å, $\alpha = 112.84\,(2)$, $\beta = 105.10\,(2)$, $\gamma = 93.56\,(2)°$, $V = 826.9$ Å^3, $Z = 2$, $D_x = 1.238$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.19$ mm^{-1}, $F(000) = 332$, $T = 293$ K. Final $R = 0.049$ for 2445 unique observed reflections. The C—O*X* bond length is normal for an ester at a secondary centre.

Introduction. We have suggested two rules that relate the length of a bond to the rate at which it is broken in ionic reactions in solution (Edwards, Jones &

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