

Fig. 2. Packing plot of (2) projected down *a*. Hydrogen bonds are indicated by dashed lines.

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Bis(cyclohexylammonium) Propargyl Phosphate Dihydrate,
 $2C_6H_{14}N^+ \cdot C_3H_3O_4P^{2-} \cdot 2H_2O^*$

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Abstract. $M_r = 370.43$, monoclinic, $P2_1/c$, $a = 14.186$ (5), $b = 6.355$ (2), $c = 21.417$ (9) Å, $\beta = 105.55$ (5)°, $U = 2034$ Å³, $Z = 4$, $D_x = 1.21$ Mg m⁻³, $F(000) = 808$, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu(\text{Mo } K\alpha) = 0.16$ mm⁻¹, room temperature, $R = 0.080$, $R_w = 0.057$ for 1978 unique reflections. The P–OR bond length, 1.626 (4) Å, is appreciably longer than in related ester dianions with $R = \text{Me}$, Et. A complex hydrogen-bonding network links the hydrophilic residues in bands parallel to z .

Introduction. As part of an investigation of correlations between bond length and reactivity, we have determined crystal structures for a large number of acetals (Jones, Sheldrick, Kirby & Briggs, 1984, and references therein). It is important to establish whether the

observed linear correlations (between the length of a bond in the crystal and the free energy of activation for its cleavage in solution) can be extended to related compounds. Our approach is to measure the length of the X–OR bond in a series of compounds in which the effective electronegativity of oxygen is varied by increasing electron demand by the group R . This is the first paper in a series on phosphate monoester dianions (1).

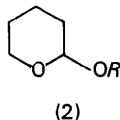


(1)

These compounds are of particular interest because their hydrolysis has many features in common with that of the tetrahydropyranyl acetals (2), for which we first observed a bond-length–reactivity correlation (Jones &

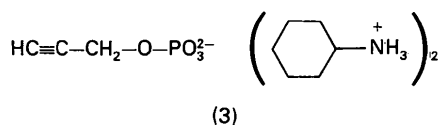
* Phosphate Ester Dianions. 1.

Kirby, 1978). Both series undergo unimolecular heterolysis to eliminate RO^- , in reactions which may involve very late transition states. Reactivity is both very sensitive to the nature of the group RO , and controlled primarily by differences in ground-state energy (Craze & Kirby, 1978; Kirby & Varvoglis, 1967). Thus both might be expected to show marked variations of bond length with reactivity.



Ideally we would like to measure the structures of dianions (1) in the absence of perturbations, such as H bonding, from the counter-ion or ions. We have therefore tried to grow crystals of phosphate monoester dianions with large alkali-metal or aprotic organic cations. These attempts failed completely. The PO_3^{2-} group is sharply destabilized in the absence of H bonding (Abell & Kirby, unpublished): it holds tenaciously to water molecules acquired from the atmosphere or 'dry' solvents, and will remove a proton from nominally much weaker acids, e.g. amidinium cations. We are thus forced to use cyclohexylammonium salts, which inevitably have a complex H-bonding network in the crystal. Even these salts often crystallize with molecules of water in the lattice, and may lose a molecule of cyclohexylamine on slow evaporation.

The bis(cyclohexylammonium) salts of alkyl phosphates are easily prepared by the oxidation of inorganic phosphite in the alcohol as solvent (Kirby, 1963). We report here the structure of the salt (3) of propargyl (2-propynyl) phosphate. Irregular colourless plates of (3) were obtained on slow evaporation from aqueous ethanol.



Experimental. D_m not determined. Stoe two-circle diffractometer. Crystal $0.4 \times 0.2 \times 0.08$ mm mounted about b (monochromated Mo $K\alpha$ radiation, $2\theta_{max}$ 50° , layers 0–7). No absorption correction. 6515 intensities recorded. Merging equivalents gave 3689 unique reflections (R_{int} 0.025), 1978 of which with $F > 4\sigma(F)$ were used for all calculations. Cell constants refined from 2θ values of 21 reflections in the range $19^\circ < 2\theta < 23^\circ$, using the same crystal remounted on a Stoe four-circle diffractometer. Structure solved by routine direct methods (revealing 17 non-H atoms) and refined on F to R 0.080, R_w 0.057 [weighting scheme

$w^{-1} = \sigma^2(F) + 0.00015F^2$; all non-H atoms refined anisotropically, acetylenic and water H subject to the restraint $X-H = 0.96 \pm 0.02$ Å, other H using a riding model with $X-H$ 0.96 Å, $H-X-H$ 109.5° , $U(H) = 1.2 U(X)$; interlayer scale factors refined]. No correction for secondary extinction. Maximum features in final $\Delta\rho$ map were $+0.66$ (near P), $-0.50 e \text{ \AA}^{-3}$. Max. Δ/σ 0.03. All calculations performed with program system *SHELXTL* (Sheldrick, 1978).

Table 1. Atom coordinates ($\times 10^4$) and isotropic temperature factors ($\text{\AA}^2 \times 10^3$)

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
P	1069 (1)	651 (2)	1551 (1)	34 (1)
O(1)	2168 (2)	1612 (6)	1685 (1)	57 (1)
O(2)	630 (2)	1484 (5)	933 (1)	49 (1)
O(3)	623 (2)	1576 (5)	2010 (1)	48 (1)
O(4)	1148 (2)	-1702 (5)	1591 (1)	44 (1)
C(1)	2877 (3)	967 (10)	2198 (2)	67 (3)
C(2)	3699 (5)	2475 (13)	2332 (2)	83 (3)
C(3)	4351 (5)	3742 (15)	2457 (3)	115 (4)
N(1)	844 (2)	5556 (6)	2474 (1)	38 (1)
C(11)	1767 (3)	5358 (8)	2957 (2)	47 (2)
C(12)	1688 (4)	3536 (9)	3364 (2)	57 (2)
C(13)	2672 (4)	3260 (10)	3827 (2)	82 (3)
C(14)	2968 (5)	5251 (11)	4165 (2)	99 (3)
C(15)	3042 (5)	7042 (11)	3762 (3)	106 (4)
C(16)	2038 (4)	7339 (9)	3300 (2)	70 (3)
N(2)	1573 (2)	5561 (7)	779 (1)	44 (1)
C(21)	2654 (3)	5605 (8)	909 (2)	40 (2)
C(22)	3007 (3)	3918 (8)	564 (2)	58 (2)
C(23)	4130 (3)	3973 (9)	683 (2)	67 (2)
C(24)	4477 (4)	6133 (9)	565 (2)	69 (2)
C(25)	4104 (4)	7787 (9)	913 (3)	76 (2)
C(26)	2985 (3)	7753 (8)	784 (2)	56 (2)
OW(1)	-993 (3)	4089 (7)	484 (1)	66 (2)
OW(2)	-695 (3)	-1665 (7)	285 (2)	85 (2)

Table 2. Bond lengths (Å) and angles ($^\circ$)

O(1)—P	1.626 (4)	O(2)—P	1.510 (4)
O(3)—P	1.503 (4)	O(4)—P	1.501 (5)
C(1)—O(1)	1.405 (6)	C(1)—C(2)	1.476 (10)
C(2)—C(3)	1.202 (12)	C(11)—N(1)	1.489 (6)
C(11)—C(12)	1.522 (8)	C(11)—C(16)	1.487 (8)
C(12)—C(13)	1.532 (7)	C(13)—C(14)	1.492 (10)
C(14)—C(15)	1.499 (11)	C(15)—C(16)	1.552 (9)
C(21)—N(2)	1.482 (6)	C(21)—C(22)	1.508 (8)
C(21)—C(26)	1.498 (8)	C(22)—C(23)	1.542 (8)
C(23)—C(24)	1.509 (9)	C(24)—C(25)	1.509 (9)
C(25)—C(26)	1.535 (8)		
O(1)—P—O(2)	100.4 (3)	O(1)—P—O(3)	106.3 (3)
O(2)—P—O(3)	113.8 (3)	O(1)—P—O(4)	108.0 (3)
O(2)—P—O(4)	114.4 (3)	O(3)—P—O(4)	112.6 (3)
P—O(1)—C(1)	119.0 (4)	O(1)—C(1)—C(2)	109.6 (6)
C(1)—C(2)—C(3)	177.3 (9)	N(1)—C(11)—C(12)	110.0 (5)
N(1)—C(11)—C(16)	112.7 (5)	C(12)—C(11)—C(16)	111.0 (5)
C(11)—C(12)—C(13)	108.9 (5)	C(12)—C(13)—C(14)	110.6 (6)
C(13)—C(14)—C(15)	111.6 (6)	C(14)—C(15)—C(16)	109.0 (6)
C(11)—C(16)—C(15)	109.3 (6)	N(2)—C(21)—C(22)	110.5 (4)
N(2)—C(21)—C(26)	109.7 (5)	C(22)—C(21)—C(26)	112.1 (5)
C(21)—C(22)—C(23)	111.2 (5)	C(22)—C(23)—C(24)	111.1 (5)
C(23)—C(24)—C(25)	110.9 (6)	C(24)—C(25)—C(26)	112.2 (5)
C(21)—C(26)—C(25)	109.6 (5)		

Discussion. Final atom coordinates and derived parameters are presented in Tables 1 and 2,* diagrams of the structure in Figs. 1 and 2. The P—OR bond length [P—O(1)] in the ester (3) is 1.626 (4) Å, *cf.* the simple monoester dianions for which data are available: 1.579 (6) Å in diammonium methyl phosphate ($R = 9.0\%$; Garbassi, Giarda & Fagherazzi, 1972); 1.56 (2) Å in dipotassium ethyl phosphate ($R = 11.9\%$; McDonald & Cruickshank, 1971); and 1.64 (2) Å in dipotassium phenyl phosphate ($R = 11\%$; Caughlan & Mazhar-ul-Haque, 1967). The propargyl group is weakly electron withdrawing compared with Me or Et, so a longer P—O bond would be expected. Since, however, these structures are not of high precision, it would be premature to draw conclusions at this stage. [The mean P—OR bond length of 1.614 (4) Å for all the phosphate monoester dianions with $R < 10\%$ in the Cambridge Database — 32 separate bonds for 22 different esters, mostly of sugar phosphates — may be a better standard for comparison]. We are currently investigating further phosphate dianions in order to obtain more reliable correlations.

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and Table 3 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39045 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

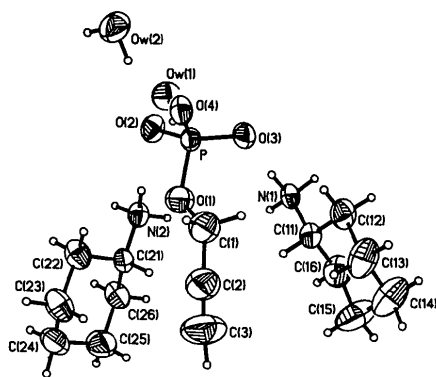


Fig. 1. Thermal-ellipsoid plot of the asymmetric unit, showing the atom-numbering scheme.

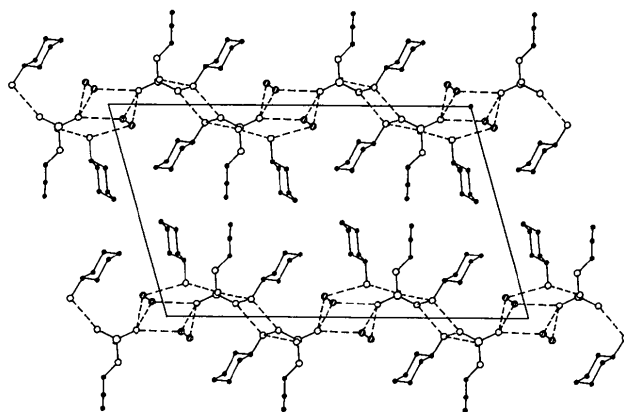


Fig. 2. Packing plot of the structure projected down *b*. Shaded circles, water O; open circles, P, N and phosphate O; filled circles, C. Hydrogen bonds indicated by dashed lines. H atoms omitted for clarity.

The packing plot (Fig. 2) shows bands of hydrophilic (near $x = 0$) and hydrophobic (near $x = \frac{1}{2}$) residues running parallel to *z*. A network of H bonds (Table 3, deposited) connects the $-N^+H_3$, H_2O and PO_3^{2-} groups.

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