$$C_{13}H_{21}ClNO_3{}^+.Cl^-$$

Crystal packing and the hydrogen-bonding interactions are shown in Fig. 2. Each cation acts as donor in three distinct hydrogen bonds, namely one $O-H\cdots Cl^-$ and two $N-H\cdots Cl^-$ bonds (Table 2). The chloride ions involved are c-glide-related and their translation equivalents along z, resulting in a hydrogen-bonding network that links the hydrophilic residues in bands parallel to c. The hydrophobic portions of the cations intermesh in the region of the yz plane at $x = \frac{1}{2}$.

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Bond Length and Reactivity. Structure of a Tetraalkyl Pyrophosphate, Bis(2-oxo-1,3,2λ⁵-dioxaphosphorinan-2-yl) Oxide,* C₆H₁₂O₇P₂

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Abstract. $M_r = 258\cdot11$, orthorhombic, $P2_12_12_1$, $a = 8\cdot619$ (2), $b = 10\cdot612$ (2), $c = 11\cdot401$ (2) Å, $V = 1042\cdot8$ (5) Å^3, $Z = 4$, $D_x = 1\cdot644$ (2) g cm^{-3}, $\lambda(Mo\,K\alpha) = 0\cdot71069$ Å, $\mu = 4\cdot0$ cm^{-1}, $F(000) = 536$, $T = 293$ K. $R = 0\cdot039$ for 2168 observed reflections. The mean P—OP bond length is $1\cdot602$ Å, which appears to represent an upper limit for good leaving groups in the 1,3,2-dioxaphosphorinane 2-oxide system. The ring flattening at phosphorus is appreciably different in the two independent rings (torsion angles $40\cdot6, 40\cdot5$ *cf.* $28\cdot5, 27\cdot3°$).

Introduction. As part of an extensive investigation of the relationship between the length of a bond in the crystal and its reactivity towards heterocyclic cleavage in solution (Jones & Kirby, 1984), we have reported

crystal structures for a series of five dialkyl aryl phosphates [1, Ar = (*a*) phenyl, (*b*) 3-nitrophenyl, (*c*) 2-nitrophenyl, (*d*) 4-chloro-2-nitrophenyl, and (*e*) 2,4-dinitrophenyl; Jones, Sheldrick, Kirby & Briggs, 1984].

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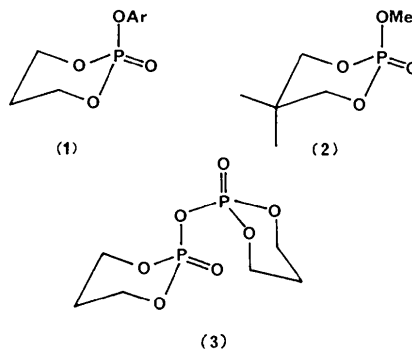
* *P,P'*-Oxybis(1,3,2λ⁵-dioxaphosphorinane 2-oxide).

The relationship can be expressed, apparently generally, in terms of a linear correlation between the length of the bond (C—OR, P—OR) and the free energy of activation for its hydrolytic cleavage (or, generally more conveniently, the pK_a of the conjugate acid, ROH, of the leaving group, which can be shown to be related to reactivity by a linear free-energy relationship) (Jones & Kirby, 1979, 1984). The series of phosphate triesters is no exception: we find a good linear relationship ($r = 0.992$ for five data points) between the length of the P—OAr bond for compounds (1a–d) and also of the P—OMe bond of (2) (Van Nuffel, Lenstra & Geise, 1980) and the pK_a's of ArOH and MeOH (Jones & Kirby, 1984).

However, the point for compound (1e), which has the best leaving group, shows an appreciable negative deviation from this line (Fig. 1). This is of interest because, unlike other series of compounds we have examined in detail, phosphate triesters do not react in solution by a dissociative process; that is to say, the P—OR bond does not cleave spontaneously. Before we speculate on the significance of this point we clearly need more data. We have therefore investigated the symmetrical pyrophosphate (3), in which both phosphorus atoms are attached to a very good (dialkyl phosphate anion) leaving group, and report here its crystal and molecular structure.*

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* The crystal structure of one tetraalkyl pyrophosphate has been reported previously. Both Bukowska-Strzyżewska & Dobrowolska (1978) and Cook & White (1976) have published structures of relatively low precision (R 0.121 and 0.092 respectively) for a pyrophosphate related to (3), but derived from 2,2-dimethyl-propane-1,3-diol rather than the unsubstituted propane-1,3-diol. These structures differ in some details, but more from each other than from the more accurate structure of (3).
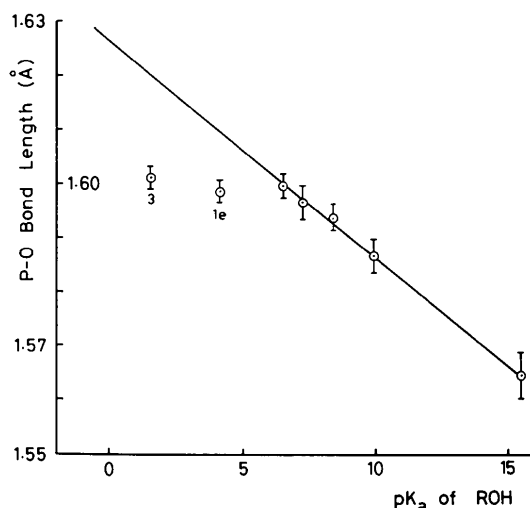

Fig. 1. Plot of P—OR bond length (R = Ar, Me) vs pK_a of ROH for esters (1a)–(1e) and (2), and for pyrophosphate (3) (mean value). The line is calculated (least squares, correlation coefficient 0.992) for the points for (1a)–(1d) and (2).

Experimental. Bis(2-oxo-1,3,2λ^5-dioxaphosphorinan-2-yl) oxide (3) was prepared by the partial hydrolysis of 2-chloro-1,3,2λ^5-dioxaphosphorinane 2-oxide (Lanham, 1959). Acetone (5·0 ml) containing water (0·90 g, 50 mmol) was added dropwise to an ice-cold solution of the phosphorochloridate (16·0 g, 10·2 mmol) and triethylamine (10·0 g, 10·0 mmol) in dry acetone (50 ml). After stirring for 2 h the white precipitate was filtered off and the solvents removed *in vacuo*. The crude residue was dissolved in chloroform (50 ml), washed with water (2 × 25 ml), dried (MgSO$_4$), then evaporated *in vacuo* to a brown oil. Flash chromatography on silica gel (200 g, eluent CHCl$_3$ containing 4% 2-propanol) gave the pyrophosphate ester (3, 2·18 g, 17%), which after recrystallization from ether/dichloromethane had m.p. 409–411 K (lit. 410–410·5 K; Khorana, Tener, Wright & Moffatt, 1957). Single crystals (well formed colourless blocks) were grown by the diffusion of diethyl ether into a solution in methylene chloride and sealed in glass capillaries to avoid slow hydrolysis by atmospheric moisture.

Crystal 0·35 × 0·27 × 0·19 mm. Stoe two-circle diffractometer with monochromated Mo $K\alpha$ radiation, $2\theta_{max}$ 55°. Layers recorded: 0–9kl and (with same crystal remounted) $hk0$–12; 3605 and 3761 reflections respectively, including in both cases a full set of Friedel opposites. R_{int} 0·023 for 2551 unique reflections, 2168 with $F > 4\sigma(F)$ used for all calculations (program system *SHELXTL*, written by GMS). Index ranges after merging: $h -11\rightarrow11$, $k\,0\rightarrow13$, $l\,0\rightarrow14$. No absorption correction. Cell constants refined from 2θ values of 32 reflections (same crystal on Stoe–Siemens four-circle diffractometer).

Structure solution by conventional direct methods followed by tangent recycling. Refinement on F to R 0·039, wR 0·034 [all non-H atoms anisotropic; H atoms included using a riding model with C—H 0·96 Å, H—C—H 109·5°, U(H) = 1·2 U_{eq}(C); 136 parameters, weighting scheme $w^{-1} = \sigma^2(F) + 0·0002F^2$, $S = 1·4$, slope of normal probability plot 1·2]. Max. Δ/σ 0·1. Max. and min. heights in final $\Delta\rho$ map +0·6 (near P) and −0·5 e Å^{-3}. Absolute structure (Jones, 1984) weakly indicated by an η refinement (Rogers, 1981); $\eta = +0·86$ (24). Atomic scattering factors as incorporated in *SHELXTL*.

Discussion. Final atomic coordinates are given in Table 1 with derived parameters in Table 2.*

The structure of the pyrophosphate (3) has the advantage that it gives us two dioxaphosphorinane

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

	x	y	z	U_{eq}*
P(1)	5271 (1)	4431 (1)	4787 (1)	39 (1)
P(2)	2367 (1)	5732 (1)	5181 (1)	41 (1)
O(2)	3857 (2)	5340 (1)	4433 (1)	38 (1)
O(11)	4525 (2)	3097 (1)	4858 (1)	49 (1)
O(13)	6289 (2)	4466 (2)	3662 (1)	47 (1)
O(14)	6098 (2)	4802 (2)	5837 (2)	64 (1)
C(14)	5711 (3)	3871 (3)	2591 (2)	53 (1)
C(15)	5179 (3)	2560 (3)	2833 (2)	57 (1)
C(16)	3953 (3)	2523 (2)	3765 (3)	55 (1)
O(21)	1116 (2)	4723 (2)	4905 (2)	50 (1)
O(23)	1854 (2)	6981 (2)	4588 (2)	57 (1)
O(24)	2711 (2)	5847 (2)	6419 (2)	78 (1)
C(24)	878 (3)	6992 (3)	3539 (3)	56 (1)
C(25)	−427 (3)	6078 (2)	3647 (2)	47 (1)
C(26)	173 (3)	4776 (2)	3831 (2)	46 (1)

* Equivalent isotropic U calculated from anisotropic U.

Table 2. *Bond lengths* (Å), *bond angles and torsion angles* (°)

O(2)—P(1)	1·606 (3)	O(2)—P(2)	1·597 (3)
O(11)—P(1)	1·557 (3)	O(13)—P(1)	1·554 (3)
O(14)—P(1)	1·448 (3)	C(14)—O(13)	1·462 (4)
C(14)—C(15)	1·491 (5)	C(15)—C(16)	1·499 (5)
C(16)—O(11)	1·472 (4)	O(21)—P(2)	1·552 (3)
O(23)—P(2)	1·552 (3)	O(24)—P(2)	1·447 (3)
C(24)—O(23)	1·462 (4)	C(24)—C(25)	1·491 (5)
C(25)—C(26)	1·490 (5)	C(26)—O(21)	1·471 (4)

O(2)—P(1)—O(11)	104·2 (2)	O(2)—P(1)—O(13)	101·9 (2)
O(11)—P(1)—O(13)	107·3 (2)	O(2)—P(1)—O(14)	114·7 (2)
O(11)—P(1)—O(14)	114·0 (2)	O(13)—P(1)—O(14)	113·4 (2)
O(2)—P(2)—O(21)	105·7 (2)	O(2)—P(2)—O(23)	102·7 (2)
O(21)—P(2)—O(23)	107·6 (2)	O(2)—P(2)—O(24)	112·2 (2)
O(21)—P(2)—O(24)	113·5 (2)	O(23)—P(2)—O(24)	114·3 (2)
P(1)—O(2)—P(2)	129·2 (2)	P(1)—O(11)—C(16)	118·1 (3)
P(1)—O(13)—C(14)	119·1 (2)	O(13)—C(14)—C(15)	110·7 (3)
C(14)—C(15)—C(16)	111·9 (3)	O(11)—C(16)—C(15)	110·7 (3)
P(2)—O(21)—C(26)	121·7 (3)	P(2)—O(23)—C(24)	121·8 (3)
O(23)—C(24)—C(25)	111·2 (3)	C(24)—C(25)—C(26)	110·7 (3)
O(21)—C(26)—C(25)	110·2 (3)		

O(11)—P(1)—O(2)—P(2)	68·3 (2)*	O(13)—P(1)—O(2)—P(2)	179·8 (2)
O(14)—P(1)—O(2)—P(2)	−57·2 (3)	O(2)—P(1)—O(11)—C(16)	67·0 (3)
O(13)—P(1)—O(11)—C(16)	−40·6 (3)	O(14)—P(1)—O(11)—C(16)	−167·2 (3)
O(2)—P(1)—O(13)—C(14)	−68·7 (3)	O(11)—P(1)—O(13)—C(14)	40·5 (3)
O(14)—P(1)—O(13)—C(14)	167·4 (3)	O(21)—P(2)—O(2)—P(1)	−89·4 (2)
O(23)—P(2)—O(2)—P(1)	157·9 (2)	O(24)—P(2)—O(2)—P(1)	34·7 (3)
O(2)—P(2)—O(21)—C(26)	−80·7 (3)	O(23)—P(2)—O(21)—C(26)	28·5 (3)
O(24)—P(2)—O(21)—C(26)	156·0 (3)	O(2)—P(2)—O(23)—C(24)	83·9 (3)
O(21)—P(2)—O(23)—C(24)	−27·3 (3)	O(24)—P(2)—O(23)—C(24)	−154·3 (3)
P(1)—O(11)—C(16)—C(15)	51·2 (4)	P(1)—O(13)—C(14)—C(15)	−50·5 (4)
O(13)—C(14)—C(15)—C(16)	57·1 (4)	C(14)—C(15)—C(16)—O(11)	−57·7 (4)
P(2)—O(23)—C(24)—C(25)	−46·3 (3)	P(2)—O(23)—C(24)—C(25)	44·3 (4)
O(23)—C(24)—C(25)—C(26)	−58·9 (4)	C(24)—C(25)—C(26)—O(21)	59·5 (4)

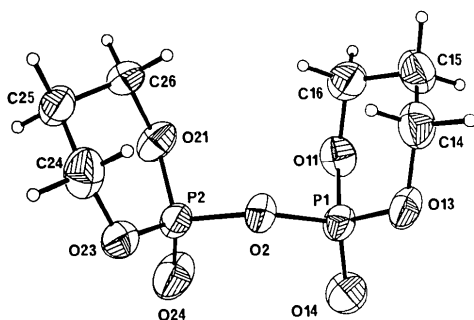* Sign convention as defined by Klyne & Prelog (1960).

Fig. 2. Thermal ellipsoid plot (50% probability) for (3), showing the atom-numbering scheme.

rings, and two exocyclic P—OP bonds in the same molecule. The gross features of (3) are as expected from previous work (Fig. 2). The rings adopt the usual chair conformations, with pronounced flattening at phosphorus, and with the P—OP bond axial. The mean P—OP bond length is 1·602 Å, not significantly longer than in the 2,4-dinitrophenyl ester (1e) – or even in esters (1d) and (1c) – supporting the idea that the bond-length extension may have reached a limit around 1·600 Å for good oxyanion leaving groups in the 1,3,2-dioxaphosphorinane 2-oxide system (Fig. 1).

The flattening of the ring at the phosphorus centre is substantially greater for ring 2 than for ring 1, as shown by the dihedral angles of 28·5 and 27·3° for C(26)—O(21)—P(2)—O(23) and O(21)—P(2)—O(23)—C(24), compared with 40·6 and 40·5° for C(16)—O(11)—P(1)—O(13) and O(11)—P(1)—O(13)—C(14), respectively. The latter figures are similar to those measured for esters (1) – five of the six ring dihedral angles for ring 1 are within 1° of those in the phenyl ester (1a). However, this further flattening around P(2) is not accompanied by any further lengthening of the P(2)—O(2) bond such as would be expected if it reflected further progress along the pathway for bond cleavage (Dunitz, 1979). In fact P(2)—O(2) is if anything shorter than P(1)—O(2) (by three standard deviations, 1·597 compared with 1·606 Å). Whether or not the conformational differences simply reflect packing forces, this adds support to the idea that P—OP bond lengthening has reached a limit in (3).

Although the differences in P—OR bond length in the series of compounds represented in Fig. 1 are small in absolute magnitude, as we would expect in a system of low intrinsic reactivity (Jones & Kirby, 1984), both the trend to longer bonds and its disappearance are well defined. It has always been clear that the linear relationship between bond length and reactivity can hold over only a limited range of reactivity. If a bond is going to break if a good enough leaving group is involved, it must eventually become easier to stretch as it gets longer. It appears that in the series (1–3), where the P—OR bond does not break spontaneously in solution, the reverse is the case. We are currently looking for evidence of this sort of behaviour in other systems.

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Bond Length and Reactivity. Structure of 1-Methoxymethoxy-3,5-dinitrobenzene, $C_8H_8N_2O_6$*

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Abstract. $M_r = 228 \cdot 17$, orthorhombic, $P2_12_12_1$, $a = 5 \cdot 387\,(2)$, $b = 11 \cdot 053\,(2)$, $c = 16 \cdot 783\,(3)$ Å, $V = 999 \cdot 3\,(5)$ Å^3, $Z = 4$, $D_x = 1 \cdot 516\,(8)$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0 \cdot 71069$ Å, $\mu = 1 \cdot 0$ cm^{-1}, $F(000) = 472$, $T = 293$ K. $R = 0 \cdot 041$ for 1654 observed reflections. The C—O bond length to the leaving group (referred to acetal hydrolysis) is $1 \cdot 431\,(3)$ Å; this forms part of a linear correlation between bond length and reactivity in formaldehyde acetals MeOCH$_2$—OR. The conformation about the acetal centre is close to ($-sc, -sc$) with torsion angles as expected for an acyclic acetal.

Introduction. Our work on bond length and reactivity in tetrahydropyranyl acetal (1) and glucoside systems (Jones & Kirby, 1984; Briggs, Glenn, Jones, Kirby & Ramaswamy, 1984) has shown that there is a very simple relationship between the length of an acetal C—OR bond and the rate at which it is broken hydrolytically: in a given series, the longer the bond, the more easily it is broken. Furthermore, there is some evidence that this generalization also holds for comparisons of acetals from different series. Thus in aryl α-glucosides (2), which are many orders of magnitude less reactive than the parent tetrahydropyranyl acetals (1), the exocyclic acetal C—OAr bond is always substantially shorter than the C—OAr bond of the corresponding axial acetal (1).

(1)   (2)   (3)
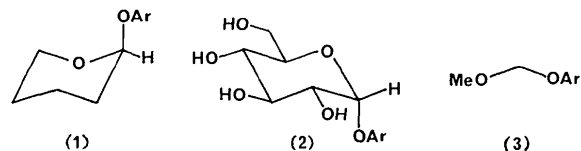
As an initial test of the strength of this second generalization, we recently determined the crystal structure of (3, Ar = 2,4-dinitrophenyl) (Jones, Sheldrick, Glenn & Kirby, 1983). The reactivity of this acetal is known to lie between that of the 2,4-dinitrophenyl derivatives of (1) and (2), and a similar relationship was found for the length of the C—OAr bond broken in the reaction.

A more reliable measure of the ease with which a bond can be stretched and, presumably, broken is the sensitivity of its length to the nature of the leaving group. The slope of the (good) linear plot of the length of the C—OAr bond of axial acetals (1) against the pK_a of the conjugate acid (ArOH) of the leaving group, is some $6 \cdot 5$ times greater than that of the corresponding plot for α-glucosides (Briggs *et al.*, 1984), which show very little dependence on Ar. It is thus of interest to measure the sensitivity of the C—OR bond length of a series of formaldehyde acetals, MeOCH$_2$—OR, to the nature of the group R. Five structures containing this unit have been reported recently (Jones, Kennard, Kirby & Osborne, 1978; Jones, Kennard, Kirby, Osborne & Malik, 1978; Egert, Cruse & Kennard, 1983; Jones, Sheldrick, Kirby & Briggs, 1984; Jones *et*

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* Crystal Structures of Acetals. 24. Part 23: Jones, Sheldrick, Kirby & Briggs (1984).