1-Phospha-2,10-dioxabicyclo[4.4.0]decane 1-Oxide

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Abstract. $C_7H_{13}PO_3$, orthorhombic, $P2_12_12_1$, $a = 10\cdot950$ (10), $b = 9\cdot966$ (20), $c = 7\cdot512$ (20) Å, $Z = 4$, $D_x = 1\cdot427$ g cm^{-3}, μ(Mo $K\alpha$) $= 2\cdot39$ cm^{-1}. The structure was refined to $R = 0\cdot036$ for 1622 unique diffractometer data. The *cis*-fused six-membered rings adopt chair conformations; the relatively low O–P–C–H dihedral angle is consistent with the influence of non-bonded H$\cdots$H repulsions.

Introduction. This bicyclic phosphonate was synthesized as a model compound capable of existing in two isomeric forms analogous to *cis*- and *trans*-decalin. Deuterium-exchange studies should lead to a clearer understanding of the stereochemical aspects of α-phosphinyl-stabilized carbanions. Only one isomer was isolated (Chérest & Whitham, 1976), and the conformation could not be unambiguously assigned by spectroscopic methods.

Crystals (m.p. 60–61°C) were obtained from acetone. Intensities were determined at $10\cdot0 \pm 1\cdot0$°C with an automated Stoe STADI-2 two-circle diffractometer, graphite-monochromated Mo $K\alpha$ radiation, and two crystals (layers $h0$–$8l$, 2909 reflexions; $hk0$–10, 2133). Lp corrections were applied, but none for absorption, and interlayer scale factors were obtained by a linear least-squares analysis of common reflexions. Equivalent reflexions were averaged to give 1684 unique data, of which 1622 with $I > \sigma(I)$ based on counting statistics were employed for structure determination. Cell dimensions were obtained by a least-squares fit to diffractometer ω-angle measurements for all the zero-layer reflexions.

The P atom was located from the Patterson function, and the C and O atoms from difference syntheses. Idealized H atom coordinates were calculated geometrically, and a riding model was employed for refinement: the C–H vectors were held constant in magnitude and direction, but the C atoms were free to move; both atoms contributed to the derivative calculation. For structure refinement the C–H distances were fixed at $1\cdot00$ Å; the H atom positions were recalculated geometrically from the refined positions of the other atoms with C–H set to $1\cdot08$ Å for the calculation of non-bonded distances. The structure was refined by full-matrix least squares with individual isotropic temperature factors for H and anisotropic temperature

factors for the other atoms, complex neutral-atom scattering factors, and the weighting scheme $w = 1/[\sigma^2(F) + 0\cdot00438F^2]$, which gave a flat analysis of variance in terms of sin θ and the magnitude of F_o. Measurements with Cu $K\alpha$ radiation were used to establish the absolute configurations of the particular crystals employed, thus eliminating a possible source of coordinate error. Refinement converged to $R' = \Sigma w^{1/2} \Delta / \Sigma w^{1/2}|F_o| = 0\cdot041$ with a corresponding R of $0\cdot036$. Positional (all atoms) and isotropic thermal parameters (H atoms) are given in Tables 1 and 2,*

Table 1. *Atom coordinates* ($\times 10^4$)

	x	y	z
P(1)	−741 (1)	−1768 (1)	−7524 (1)
O(1)	−1731 (2)	−2737 (2)	−7690 (3)
O(2)	−1174 (2)	−302 (2)	−6978 (3)
O(3)	−65 (2)	−1547 (2)	−9338 (2)
C(1)	−1671 (3)	−196 (4)	−5161 (4)
C(2)	−696 (3)	−515 (4)	−3794 (4)
C(3)	−157 (2)	−1900 (3)	−4017 (3)
C(4)	391 (2)	−2130 (3)	−5886 (3)
C(5)	1527 (2)	−1258 (3)	−6198 (3)
C(6)	2009 (2)	−1383 (3)	−8099 (4)
C(7)	1094 (2)	−824 (3)	−9420 (3)

Table 2. *Hydrogen atom coordinates* ($\times 10^4$) *and isotropic temperature factors* (Å^2 $\times 10^3$)

	x	y	z	U
H(1)	−1999	813	−4944	102 (16)
H(2)	−2419	−895	−5016	112 (19)
H(3)	−1101	−450	−2485	62 (10)
H(4)	28	217	−3909	50 (9)
H(5)	558	−2030	−3041	47 (8)
H(6)	−865	−2635	−3794	46 (8)
H(7)	670	−3166	−5983	53 (9)
H(8)	2235	−1571	−5287	35 (7)
H(9)	1297	−221	−5945	24 (6)
H(10)	2172	−2428	−8396	92 (14)
H(11)	2854	−830	−8213	131 (19)
H(12)	1466	−916	−10746	78 (12)
H(13)	935	221	−9122	41 (8)

Table 3. *Bond lengths and librationally corrected bond lengths* (Å)

O(1)—P(1)	1·457 (3)	1·465	C(2)—C(1)	1·515 (6)	1·523
O(2)—P(1)	1·590 (4)	1·600	C(7)—C(6)	1·516 (6)	1·524
O(3)—P(1)	1·566 (4)	1·574	C(3)—C(2)	1·511 (6)	1·515
C(4)—P(1)	1·783 (4)	1·793	C(6)—C(5)	1·528 (5)	1·533
C(1)—O(2)	1·474 (4)	1·477	C(4)—C(3)	1·543 (5)	1·549
C(7)—O(3)	1·461 (4)	1·466	C(5)—C(4)	1·536 (5)	1·542

Table 4. *Bond angles* (°)

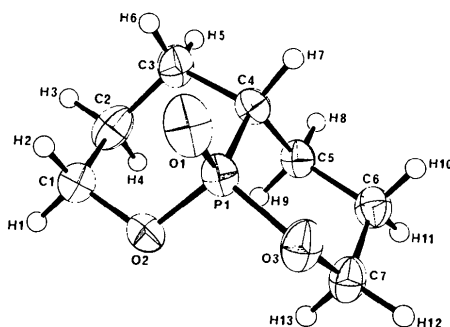| O(2)—P(1)—O(1)	114·1 (2)	C(6)—C(7)—O(3)	111·5 (3)
O(3)—P(1)—O(1)	111·7 (2)	C(3)—C(2)—C(1)	113·0 (3)
O(3)—P(1)—O(2)	103·7 (2)	C(7)—C(6)—C(5)	110·7 (3)
C(4)—P(1)—O(1)	116·2 (2)	C(4)—C(3)—C(2)	112·9 (3)
C(4)—P(1)—O(2)	102·4 (2)	C(6)—C(5)—C(4)	112·1 (3)
C(4)—P(1)—O(3)	107·5 (2)	C(5)—C(4)—C(3)	111·7 (3)
C(1)—O(2)—P(1)	114·5 (3)	C(3)—C(4)—P(1)	109·1 (3)
C(7)—O(3)—P(1)	121·1 (2)	C(5)—C(4)—P(1)	110·1 (3)
C(2)—C(1)—O(2)	110·6 (3)		

Fig. 1. *ORTEP* diagram of 1-phospha-2,10-dioxabicyclo[4.4.0]-decane 1-oxide, showing 50% probability ellipsoids for the anisotropic atoms.

bond lengths and angles in Tables 3 and 4. Fig. 1 is an *ORTEP* diagram of the molecule.

Discussion. The anisotropic temperature factors (H atoms excluded) are in good agreement with the rigid-body-motion model of Schomaker & Trueblood (1968): $R_g = [\Sigma \Delta^2 / \Sigma U_{ij}^2]^{1/2}$ for the agreement between the observed and calculated U_{ij} was 0·059. Librational tensors, with respect to axes parallel to **x**, **y** and **z**, were:

L_{11} 73 (4), L_{12} 10 (2), L_{13} −20 (3), L_{22} 34 (3), L_{23} −12 (2), L_{33} 44 (4) 10^{-4} rad²; S_{11} 1 (4), S_{12} 0 (3), S_{13} −4 (4), S_{22} 14 (3), S_{23} −7 (2), S_{33} −15 (4) 10^{-4} rad Å; T_{11} 284 (8), T_{12} −26 (8), T_{13} −40 (7), T_{22} 288 (13), T_{23} 13 (8), T_{33} 267 (8) 10^{-4} Å² (relative to an origin at $x = 0·0183, y = −0·1398, z = −0·6754$ which makes **S** symmetric). These values were used to calculate the librationally corrected bond lengths given in Table 3.

The molecule consists of *cis*-fused six-membered rings, both in the chair conformation. All the dihedral angles fall in the ranges ±60 ± 10 and 180 ± 10° except those about P(1)—C(4) and P(1)—O(3); the closest to eclipsed conformations are O(3)—P(1)—C(4)—C(5) 38·5, C(4)—P(1)—O(3)—C(7) −39·2 and O(1)—P(1)—C(4)—H(7) 46·4°. The P—C bond is the longest in the molecule and so presumably has the lowest torsional barrier; the rotation about the P—C bond and the compensating twists around the rings may serve to reduce the H(4)···H(9) repulsion (2·11 Å). P(1)—O(3) [1·566 (4) Å] is significantly shorter than P(1)—O(2) [1·590 (4) Å] and the angle at O(3) [121·1 (2)°] is wider than the angle at O(2) [114·5 (3)°], consistent with greater multiple-bond character in P(1)—O(3) than P(1)—O(2). The formation of only a *cis* product may reflect the stability of the Li derivative of the carbanion formed by losing proton H(7) (employed in the final stage of the preparation); for the *cis* carbanion, the Li⁺ ion can interact simultaneously with the lone pairs on C(4) and O(1).

References

Chérest, M. & Whitham, G. H. (1976). Personal communication.
Schomaker, V. & Trueblood, K. N. (1968). *Acta Cryst.* B24, 63–76.