The Molecular Structure of 2α-Bromo-5β-bromomethyl-5α-methyl-2β-oxo-1,3,2-dioxaphosphorinane[1]

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FIVE-MEMBERED cyclic phosphate esters exhibit anomalously high rates of hydrolysis when compared with their six-membered and acyclic analogues.[2] It has been suggested[3,4] that a major factor in this rate enhancement is thermochemical strain in the five-membered ring. The nature of this strain is best understood in terms of the bond distances and angles for the respective phosphates. Molecular dimensions have been measured for a representative acyclic phosphate, dibenzylphosphoric acid,[5] and for a five-membered cyclic phosphate, methyl ethylene phosphate.[6] Reported herein is the first structural investigation of a six-membered cyclic phosphate, 2α-bromo-5β-bromomethyl-5α-methyl-2β-oxo-1,3,2-dioxaphosphorinane,[7] hereafter referred to as BBMOD.
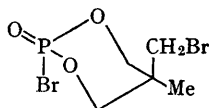
(BBMOD)

Crystal data: BBMOD = $C_5H_9PO_3Br_2$, M = 307·9. Orthorhombic, a = 13·470, b = 11·453, c = 6·240 Å. U = 962·7 Å³, D_m = 2·00 g. cm.⁻³, Z = 4, D_c = 2·12 g. cm.⁻³. Space group $P2_12_12_1$. 777 nonzero reflections were recorded with a single-crystal orienter equipped with a scintillation counter, using Mo-K_α radiation. The structure was solved by the heavy-atom method and

refined by full-matrix least-squares analysis to an R-value of 0·087. The resulting structure is shown in the Figure. Several carbon–carbon distances
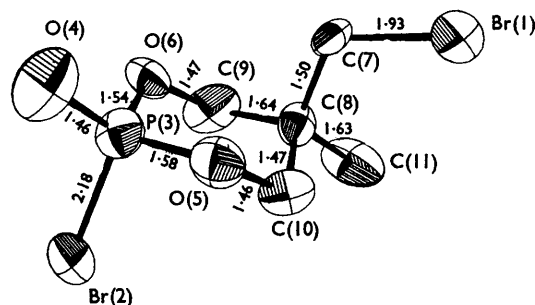

FIGURE. *Molecular structure of BBMOD. Average standard deviations are* ± 0·01 Å *for distances to* P(3) *and* ± 0·03 Å *otherwise.*

deviate considerably from the expected 1·54 Å; however, because the carbon co-ordinates are most seriously affected by series termination effects, these deviations are of doubtful significance. The conformation of BBMOD is best described as a distorted chair with the bromo and the bromomethyl groups in axial positions. The interior C–O–P angles which are larger by 6·5 to 8·5° than the 111·5° in cyclohexane[8] cause the phosphate end of the ring to be flattened somewhat. The normal

TABLE

Comparison of phosphate molecular dimensions

(The values in parentheses are the standard deviations in the last significant digit)

	BBMOD	Methyl ethylenephosphate[6]	Dibenzylphosphoric acid[5]
Bond Distances (Å)			
P=O	1·46 (2)	1·44 (1)	1·469 (4)
P–O (ring)†	1·58 (1)	1·57 (1)	1·545 (4)
	1·54 (1)	1·57 (1)	1·566 (4)
Bond Angles (°)			
O–P–O (ring)†	105·5 (7)	99·1 (6)	103·8 (2)
O=P–O	112·6 (8)	116·0 (6)	112·8 (2)
	114·9 (9)	117·3 (6)	108·3 (2)
C–O–P (ring)†	120 (1)	112·0 (9)	118·8 (3)
	118 (1)	112·0 (9)	122·3 (3)

† These dimensions refer to the P–O distances and O–P–O angles within the rings of the two cyclic esters. The listings for the dibenzylphosphoric acid are the corresponding dimensions in the acyclic compound.

to a least-squares plane through O(5), O(6), C(9), and C(10) (from which the atoms deviate by $\pm 0{\cdot}002$ Å) makes an angle of $39{\cdot}3°$ with the normal to the plane defined by O(5), P(3), and O(6). The angle with the normal to the plane, C(8), C(9), and C(10), is $52{\cdot}3°$. The net result of this flattening is a partial loss of distinction between equatorial and axial positions at P(3) and a concurrent reduction in the steric interactions between Br(2) and the hydrogens attached to C(9) and C(10).

In the Table the molecular dimensions pertinent to the ring strain are compared. It is immediately evident that there exist no significant differences in phosphorus–oxygen distances for the three compounds. The interior O–P–O angles, however, exhibit a minimum for the five-membered ring. Six-membered BBMOD is remarkably similar to the acyclic analogue in this respect which, according to the thermochemical strain theory, explains their similar rates of hydrolysis. In methyl ethylene phosphate the internal C–O–P angles are also significantly less obtuse than the corresponding internal angles in both the six-membered and acyclic phosphates. It is, however, the strain at the phosphorus which determines the ease with which the particular ester can form the proposed activated complex.[4]

[1] Work was performed at the Ames Laboratory of the U.S. Atomic Energy Commission.

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