Calculation of the Bond Angles and Conformation of Methyl Ethylene Phosphate and Related Compounds

D. A. Usher, Edward A. Dennis, and F. H. Westheimer

*Contribution from the James Conant Bryant
Laboratory, Harvard University,
Cambridge, Massachusetts. Received April 17, 1965*

Minimization of calculated bond angle strain and eclipsing strain in five-membered rings can readily be accomplished with the aid of a digital computer, and in the four compounds studied (three heterocyclic and one homocyclic) leads to bond angles and to dihedral angles closely in accord with the experimental values determined from X-ray data. The calculated angles are insensitive to the values chosen for the force constants for angular bending.

Five-membered cyclic esters of phosphoric acid,[1] phosphonic acid,[2] and sulfuric acid[3] show extraordinarily large rates of hydrolysis when compared with their acyclic and six-membered analogs. The major part of the enhancement of the rate of hydrolysis of methyl ethylene phosphate (I, R = CH_3) over related acyclic triesters has been attributed to thermochemical strain in the five-membered ring.[4,5] Preliminary calculations showed that angle strain in the ring probably makes a substantial contribution to the over-all strain energy.[6]

I

II
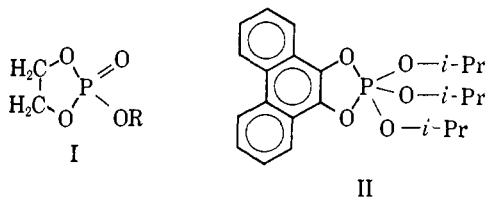
In an attempt to gain further insight into the nature of the strain energy and of the transition state for acid-catalyzed hydrolysis, we have extended the previous calculations[6] of bond angles and strain energy in these cyclic esters. Calculations were made by an extension of the methods previously outlined[6,7]; related calculations have been made by Pitzer and co-workers,[8] Hendrickson,[9] and Wiberg.[10] The bond angles in the ring were adjusted by a process of iterative refinement so as to minimize the total energy due to angle bending and bond eclipsing. The bond lengths,

which were assumed to remain constant,[7] and the "preferred" bond angles were taken from published data on related acyclic compounds.[11] The calculations were made on an IBM 7094.

Initially, calculations were made for planar molecules with the assumption that all angle bending force constants were equal. In spite of this simplified approach, the internal bond angles are in quite good agreement with those obtained by X-ray diffraction[12,13] (see Table I).

The extension to nonplanar molecules involves a great deal more computation, and in order to perform a large number of calculations with different force constants, the restriction has at present been made that four of the atoms be coplanar. The crystal structure of I (R = CH_3) has now been determined by Steitz and Lipscomb by X-ray diffraction methods,[14] and for this compound the above restriction would appear to be justified.

The following ranges were used for the computations with I: angle bending force constants,[15] C–C–OP, 82–110; C–O–P, 110–170; O–P–O, 70–140 (kcal./mole radian^2); bond eclipsing energies,[16] CH_2–CH_2, 2.5–3.0; CH_2–O, 0.5–1.5; CO–P, 0.0–1.0 (kcal./mole). The predicted internal bond angles are little affected by changes in the angle bending and bond eclipsing force constants. A decrease in the OP̂O bending force constant from 140 to 70 kcal./mole radian^2 (with the other parameters held constant at about the center of their ranges) gave changes in the bond angles varying from 1.3 to 2.7°. However, the absolute value of the strain energy and the variation of the strain energy with changes in the preferred OP̂O angle are sensitive to the values of the force constants and bond eclipsing constants. For example, halving the OP̂O bending constant decreases the calculated strain energy by about 1.5 kcal./mole. For I (R = CH_3) the calculated minimum in energy is within 0.3–0.8 kcal./mole of that of the planar form; the calculated dihedral angle of about 13° (found[14] 11°) is thus poorly defined.

The relief of strain (3–6 kcal./mole) in the phosphate ring (I) on passing from the ground state (preferred OP̂O = 109.5°) to a transition state with a preferred OP̂O of 90°, is in sharp contrast to the large increase of strain (5–7 kcal./mole) which would be expected for

(1) J. Kumamoto, J. R. Cox, Jr., and F. H. Westheimer, *J. Am. Chem. Soc.*, **78**, 4858 (1956); H. G. Khorana, G. M. Tener, R. S. Wright, and J. G. Moffatt, *ibid.*, **79**, 430 (1957).

(2) A. Eberhard and F. H. Westheimer, *ibid.*, **87**, 253 (1965).

(3) E. T. Kaiser, M. Panar, and F. H. Westheimer, *ibid.*, **85**, 602 (1963).

(4) J. R. Cox, Jr., R. E. Wall, and F. H. Westheimer, *Chem. Ind.* (London), 929 (1959).

(5) P. C. Haake and F. H. Westheimer, *J. Am. Chem. Soc.*, **83**, 1102 (1961).

(6) F. H. Westheimer, Special Publication No. 8, The Chemical Society, London, 1957, p. 1.

(7) F. H. Westheimer in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 523–555.

(8) C. W. Beckett, N. K. Freeman, and K. S. Pitzer, *J. Am. Chem. Soc.*, **70**, 4227 (1948); K. S. Pitzer and W. E. Donath, *ibid.*, **81**, 3213 (1959).

(9) J. B. Hendrickson, *ibid.*, **83**, 4537 (1961).

(10) K. B. Wiberg, *ibid.*, **87**, 1070 (1965).

(11) "Tables of Interatomic Distances and Configurations in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958.

(12) P. J. Wheatley, *Acta Cryst.*, **6**, 369 (1953).

(13) G. A. Jeffrey, *ibid.*, **4**, 58 (1951).

(14) T. A. Steitz and W. N. Lipscomb, *J. Am. Chem. Soc.*, **87**, 2488 (1965).

(15) T. Shimanouchi, M. Tsuboi, and Y. Kyogoku, *Advan. Chem. Phys.*, **7**, 435 (1964). $E = \frac{1}{2}k(\Delta\vartheta)^2$, where E is energy in kcal./mole, k is the force constant, and $\Delta\vartheta$ is the angular deflection in radians.

(16) C. C. Lin and J. D. Swalen, *Rev. Mod. Phys.*, **31**, 841 (1959).

Table I

	a	b	c	d	e
			Angle, deg.		
			Methyl Ethylene Phosphate[a]		
Atom	P	O	CH_2	CH_2	O
Calcd.[b]	98.3 ± 1.9	112.8 ± 1.1	104.9 ± 1.1	105.5 ± 0.9	113.5 ± 1.4
Exptl.[c]	99.1 ± 0.5	112 ± 0.7	107.8 ± 1.1	106 ± 0.9	112 ± 0.7
			Ethylenethiourea[d]		
Atom	CS	NH	CH_2	CH_2	NH
Calcd.	110.9	111.7	102.8	102.8	111.7
Exptl.[e]	110	112	102	103	113
			Isoprene Sulfone[d]		
Atom	S	CH_2	$C(CH_3)$	CH	CH_2
Calcd.	100.6	103.3	116.6	116.4	102.9
Exptl.[f]	98.3	106.3	114.2	117.0	104.2
			Cyclopentene[a,g]		
Atom	CH	CH_2	CH_2	CH_2	CH
Calcd.	111.2	103.2	105.4	103.2	111.2
Exptl.[h]	111.5	102.9	106.3	Dihedral angle between abde and bcd is 24° (found[h] 22° 16′)	

[a] Nonplanar molecule; angles given for the most stable configuration on the assumption that atoms abde are coplanar. [b] Average values given. [c] See ref. 14. [d] Planar molecule. [e] See ref. 12. [f] See ref. 13. [g] The torsional constants given by Beckett, et al.,[8] were used, but the angle bending force constants were reduced to 96 kcal./mole radian^2. [h] G. W. Rathjens, J. Chem. Phys., 36, 2401 (1962), and calculations made from the data therein.

a preferred OP̂O of 120°. This result supports the previous hypothesis[5] of an OP̂O angle of 90° in the transition state for the acid-catalyzed hydrolysis of I (R = H). Furthermore, the suggested trigonal bipyramid structure, with the five-membered ring joined in the basal–axial positions has recently been found[17] for the pentaoxyphosphorane II.

P^{31} n.m.r. studies have shown that the phosphorus nuclei of those cyclic esters which undergo rapid hydrolysis are less shielded than those of the analogous more stable esters.[2,18,19] It has therefore been suggested[2,3,19] that ring strain reduces the 2p–3d π-bonding[20] between the phosphorus atom and the alkyl oxygens in the ring. A decrease in the amount of double bond character should perhaps be reflected in an increased P–OC bond length,[20] but Lipscomb and Steitz have now shown by X-ray crystallography that the three ester P–OC bond lengths of I (R = CH_3) are identical.[14] A bond length of 1.57 Å. implies[20] a π-bond order of 0.2 to 0.3, and it seems probable that this partial double bonding will be removed in the transition state.[3] Preliminary calculations suggest that the resultant bond lengthening (as found[17] in the pentaoxyphosphorane II) could account for a further 0.6–1.0 kcal./mole relief of strain.

(17) W. C. Hamilton, S. J. La Placa, and F. Ramirez, *J. Am. Chem. Soc.*, **87**, 127 (1965).
(18) R. A. Y. Jones and A. R. Katritzky, *J. Chem. Soc.*, 4376 (1960).
(19) G. M. Blackburn, J. S. Cohen, and Lord Todd, *Tetrahedron Letters*, 2873 (1964).
(20) D. W. J. Cruickshank, *J. Chem. Soc.*, 5486 (1961).