solvent. The salting-in effect of large anions and of denaturing and depolymerizing agents of the urea-guanidinium class could be explained by a direct interaction of the salt or organic molecule with amide groups. Similar effects may be suggested for the interaction of these compounds with F-actin.

# Communications to the Editor

## Molecular Structure of Methyl Ethylene Phosphate

*Sir:*

The five-membered cyclic phosphate esters, intermediates in the hydrolysis of ribonucleic acids, have been the subjects of recent detailed kinetic studies in the form of model compounds.[1-3] One of these, methyl ethylene phosphate (MEP), undergoes alkaline hydrolysis, which splits the $P-OCH_2$ bond, at a rate some $2 \times 10^6$ times faster than the rate of hydrolysis of trimethyl phosphate.[3] A similar increase relative to an acyclic analog is found in the rates of hydrolysis and of $^{18}O$ exchange during acid-catalyzed hydrolysis of
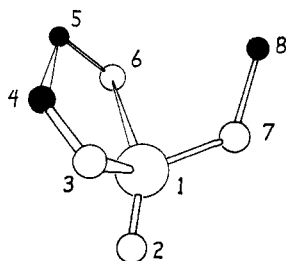


Figure 1. Molecular structure of methyl ethylene phosphate. Molecular parameters are $P_1-O_2 = 1.44$, $P_1-O_3 = 1.57$, $P_1-O_6 = 1.57$, $P_1-O_7 = 1.57$, $O_3-C_4 = 1.41$, $C_4-C_5 = 1.52$, $C_5-O_6 = 1.45$, $O_7-C = 1.44$ Å.; $O_2P_1O_3 = 116.0°$, $O_2P_1O_6 = 117.3°$, $O_2P_1O_7 = 108.7°$, $O_3P_1O_6 = 99.1°$, $O_3P_1O_7 = 105.7°$, $O_6P_1O_7 = 109.2°$, $P_1O_3C_4 = 112.0°$, $O_3C_4C_5 = 107.8°$, $C_4C_5O_6 = 106.0°$, $C_5O_6P_1 = 112.0°$, and $P_1O_7O_8 = 118.8°$. Standard deviations of distances are $\pm0.01$ Å. for bonds to $P_1$, and $\pm0.02$ Å. otherwise, while those of angles are $\pm0.6°$ about $P_1$, and $\pm0.9°$ otherwise. Dihedral angles are 10.9° between $O_3P_1O_6$ and $O_3C_4O_6$ plane normals, and 1.8° between $O_3P_1O_6$ and $O_3C_5O_6$ plane normals.

ethylene hydrogen phosphate. Furthermore, the $^{31}P$ n.m.r. peak shows a shift of $-17$ p.p.m. relative to that of 85% phosphoric acid.[4] Since most explanations of these phenomena have involved the bond angles in the strained five-membered ring and the P–OC bond lengths, low temperature single crystal X-ray diffraction methods have been employed in the present study in order to establish these angles and distances.

A total of 533 independent diffraction maxima were obtained from a single crystal grown from a melt at $-5°$ and maintained at $-40°$. Six self-correlating

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(3) J. R. Cox, Jr., R. E. Wall, and F. H. Westheimer, *Chem. Ind.* (London), 929 (1959).
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levels were collected with the use of a Weissenberg camera and Cu $K\alpha$ radiation on a crystal mounted on the [110] axis. The reciprocal lattice symmetry of $C_{2h}$, extinctions of $hkl$ when $h + k$ is odd and $h0l$ when $l$ is odd, led to the possible space groups Cc and C2/c. The latter was ruled out by the fact that there are four molecules of low symmetry in a unit cell, whose parameters are $a = 11.29$, $b = 5.96$, $c = 9.09$ Å., and $\beta = 113°$, yielding an X-ray density of 1.47 g. $cm.^{-3}$. The structure was solved from the Patterson function. Full-matrix least-squares procedures, including anisotropic temperature factors, have yielded a value (H atoms omitted) of $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.10$, which is uniformly low for all classes of reflections and rises only to $R = 0.16$ for the outermost 121 reflections. Bond distances, angles, and standard deviations are shown in the legend of Figure 1, while atomic parameters and errors are listed in Table I.

Table I. Final Structure Parameters[a]

| Atom | x | y | z |
|---|---|---|---|
| $P_1$ | $0.2500^b$ | $0.0236 \pm 0.0003$ | $0.2500^b$ |
| $O_2$ | $0.2441 \pm 0.0010$ | $0.1794 \pm 0.0013$ | $0.3858 \pm 0.0007$ |
| $O_3$ | $0.1318 \pm 0.0009$ | $0.1190 \pm 0.0011$ | $0.1061 \pm 0.0009$ |
| $O_4$ | $0.3772 \pm 0.0007$ | $0.0891 \pm 0.0012$ | $0.2288 \pm 0.0011$ |
| $O_5$ | $0.2518 \pm 0.0013$ | $0.2137 \pm 0.0011$ | $0.2795 \pm 0.0011$ |
| $C_6$ | $0.1293 \pm 0.0012$ | $0.3030 \pm 0.0024$ | $0.3357 \pm 0.0012$ |
| $C_7$ | $0.0718 \pm 0.0014$ | $0.3062 \pm 0.0017$ | $0.1536 \pm 0.0011$ |
| $C_8$ | $0.3936 \pm 0.0017$ | $0.3136 \pm 0.0021$ | $0.1892 \pm 0.0014$ |

[a] Coordinates are given in fractions of a unit cell edge. [b] The x and z coordinates of one atom are arbitrary in the space group Cc.

Molecular structural aspects of particular interest are (a) the $O_3PO_6$ bond angle of 99° which is 10° less than the tetrahedral angle and 5° less than that in dibenzylphosphoric acid[4]; (b) the reduction of the POC angle from 119° in the unstrained part to 112° in the five-membered ring of methyl ethylene phosphate; (c) the pucker of the five-membered ring, presumably because of H $\cdots$ H interactions between the $CH_2$ groups, in such a way that the normal of the $O_3C_4O_6$ plane is about 11° from the normal of the $O_3PO_6$ plane; (d) the equality of all three esterified P–O bonds apparently independent of angle strain; and (e) the good agreement of the P–OC bond lengths of 1.57 Å. with that of 1.56 Å. in dibenzylphosphoric acid,[5] which are significantly shorter than ring P–OC bonds of 1.60 and 1.76 Å. in a pentaoxyphosphorane.[6] The difference

(5) J. D. Dunitz and J. S. Rollett, *Acta Cryst.*, **9**, 327 (1956).
(6) W. C. Hamilton, S. J. LaPlaca, and F. Ramirez, *J. Am. Chem. Soc.*, **87**, 127 (1965).

(Figure 1) between the two $CH_2$–O distances of 1.45 and 1.41, both $\pm 0.02$ Å., is not regarded as statistically significant, but the lone short P–O bond is significantly shorter than the P–O bonds in the ester groups.

It has previously been postulated[2] that during acid hydrolysis this structure would form either the trigonal bipyramidal or the square-pyramidal activated complex with considerably greater ease than would a tetrahedral unstrained ester; and further that if a trigonal bipyramid is formed, the equatorial–apex positions, requiring an O–P–O bond angle of about 90°, would be most appropriate for the attachment of the five-membered ring. From our results we cannot choose between a trigonal bipyramidal and a tetragonal pyramidal activated complex, although the molecular structure of the pentaoxyphosphorane ($C_{14}$-$H_6O_6$)$P(OC_3H_7)_3$ makes the former a more likely possibility. In order to explain both the increased rate of acid-catalyzed $^{18}O$ exchange and the negative shift of the $^{31}P$ n.m.r. of strained cyclic phosphates relative to their unstrained analogs, a decrease in the $\pi$-bonding between the 3d phosphorus orbitals and the 2p orbitals of the ring oxygens has been proposed.[1,7] On the other hand, we find that the three P–OC bonds are identical in length, and hence are seeking a more detailed interpretation of these facts and of the geometry of the transition state from molecular orbital studies now in progress.

We point out that the bond angles in the five-membered ring as computed from force constant analysis, and described by Usher, Dennis, and Westheimer in an accompanying article,[8] were obtained in advance of our structure determination and are in agreement with those estimated earlier for ethylene phosphate ion.[9]

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(7) E. T. Kaiser, M. Panar, and F. H. Westheimer, *J. Am. Chem. Soc.*, **85**, 602 (1963).

(8) D. A. Usher, E. A. Dennis, and F. H. Westheimer, *ibid.*, **87**, 2320 (1965).

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

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## Concerning Linear Fluorine Nuclear Magnetic Resonance Shielding–Stabilization Energy (Ionization Potential) Relationships. The *para*-Substituted Triphenylmethyl Cations[1]

*Sir:*

The fluorine nuclear magnetic resonance shielding of *p*-fluorophenyl derivatives has been shown to be predominantly determined by, and apparently directly related to, the MO theory $\pi$-electron charge density at the *p*-carbon atom.[2] While this shielding–charge

density relationship and similar ones for certain $H^1$ and $C^{13}$ n.m.r. shieldings[3] are of interest, the lack of any independent experimental method or rigorous theoretical method for determination of the $\pi$-charge densities severely limits at this time the practical utility of the relationship.

Inherent in LCAO–MO theory of the effects of conjugative substituents are approximately linear relationships between $\pi$-electronic energy and atomic $\pi$-electron charge density.[4] Thus there is theoretical basis[5] for both direct shielding–$\pi$-charge density and shielding–$\pi$-electronic energy relationships. The latter relationship, however, appears to be of greater utility since it may be subjected to more rigorous tests and because this relationship can be directly utilized in the understanding of correlations between substituent shielding and reactivity parameters.[2c]

We wish to report the results of a substantial test of our proposed linear shielding–electronic energy relationship provided by the measurement of the fluorine n.m.r. shielding parameters, $\delta_F$, for a series of 4′-X- (or 4′,4″-diX-) substituted 4-F-trityl cations relative to the 4-F-trityl cation in *ca.* 0.5 *M* acetonitrile solution[6] (as their fluoroborate salts). These $\delta_F$ values may be compared with the stabilization energies of corresponding 4′-X- (or 4′,4″-diX-) substituted trityl cations relative to the trityl cation value, which were recently obtained from e.m.f. measurements in acetonitrile solution.[7]

Figure 1 plots the stabilization energy for the indicated series of *para*-substituted trityl cations (these energies are evidently only about 10% larger than the relative ionization potentials, $\Delta I$, for the formation of the cation from the corresponding radical[7]) *vs.* the corresponding shielding parameter, $\delta_F$. The reasonably linear relationship of slope, 0.75 kcal./p.p.m., illustrated in Figure 1 covers the wide ranges of *ca.* 20 kcal. in stabilization energy and of 28 p.p.m. in $\delta_F$.

A simple HMO calculation[8] for a series of model (hypothetical) coplanar *p*-X- (or 4-X-, 4-F-) substituted trityl cations (X = united atom with unshared pair of electrons having $\alpha = 0.0$ to $3.0\beta$ relative to aromatic carbon) gives $d\Delta I/d\Delta q_{p\text{-}C} = -2.6\beta$ or $\sim 160$ kcal. From the previously obtained relationship[2c] $\delta_F = 220\Delta q_{p\text{-}C}$, one obtains from this crude theoretical calculation the correct order of magnitude value of $\sim 0.6$ kcal./p.p.m. for the slope of Figure 1.

The stabilization energies of Figure 1 have been obtained as $\Delta F°$, for the reaction at 298°K.

$$R^+ + {}^1\!/_2R_0\text{--}R_0 \rightleftharpoons {}^1\!/_2R\text{--}R + R_0{}^+ \qquad (1)$$
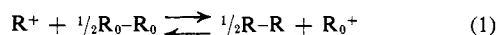
(2) (a) P. C. Lauterbur, *Tetrahedron Letters*, **8**, 274 (1961); (b) H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 731 (1961); (c) R. W. Taft, *et al.*, *ibid.*, **38**, 380 (1963); *J. Am. Chem. Soc.*, **85**, 3146 (1963); (d) T. K. Wu and B. P. Dailey, *J. Chem. Phys.*, **41**, 2996 (1964).

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(4) (a) C. A. Coulson, *Proc. Phys. Soc.* (London), **A65**, 933 (1952); (b) L. Goodman and H. Shull, *J. Chem. Phys.*, **23**, 33 (1955).

(5) (a) M. Karplus and T. P. Das, *ibid.*, **34**, 1683 (1961); (b) F. Prosser and L. Goodman, *ibid.*, **38**, 374 (1963).

(6) Measured as described by R. W. Taft, *et al.*, *J. Am. Chem. Soc.*, **85**, 709 (1963). Several values, *e.g.*, *p*-$CH_3$, have been obtained in $H_2SO_4$ from the carbinol. Equivalent results were obtained in $H_2SO_4$ and in $CH_3CN$ for $\delta_F$ of the *p*-$OCH_3$ trityl cation.

(7) E. D. Jenson and R. W. Taft, *ibid.*, **86**, 116 (1964).

(8) We are indebted to Mr. Harvey Kriloff for programming these calculations and to Professor Lionel Goodman for valuable discussions.