

(Figure 1) between the two CH₂-O distances of 1.45 and 1.41, both ± 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 postulated² 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 (C₁₄-H₆O₆)P(OC₃H₇)₃ makes the former a more likely possibility. In order to explain both the increased rate of acid-catalyzed ¹⁸O exchange and the negative shift of the ³¹P n.m.r. of strained cyclic phosphates relative to their unstrained analogs, a decrease in the π -bonding between the 3d phosphorus orbitals and the 2p orbitals of the ring oxygens has been proposed.¹⁷ 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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(8) D. A. Usher, E. A. Dennis, and F. H. Westheimer, *ibid.*, **87**, 2320 (1965).

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Concerning Linear Fluorine Nuclear Magnetic Resonance Shielding-Stabilization Energy (Ionization Potential) Relationships. The *para*-Substituted Triphenylmethyl Cations¹

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 π -electron charge density at the *p*-carbon atom.² While this shielding-charge

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density relationship and similar ones for certain H¹ and C¹³ n.m.r. shieldings³ are of interest, the lack of any independent experimental method or rigorous theoretical method for determination of the π -charge densities severely limits at this time the practical utility of the relationship.

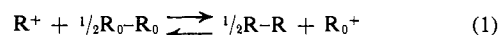
Inherent in LCAO-MO theory of the effects of conjugative substituents are approximately linear relationships between π -electronic energy and atomic π -electron charge density.⁴ Thus there is theoretical basis⁵ for both direct shielding- π -charge density and shielding- π -electronic energy relationships. 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, δ_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 solution⁶ (as their fluoroborate salts). These δ_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, ΔI , for the formation of the cation from the corresponding radical⁷) vs. the corresponding shielding parameter, δ_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 δ_F .

A simple HMO calculation⁸ 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 3.0β relative to aromatic carbon) gives $d\Delta I/d\Delta q_{p-C} = -2.6\beta$ or ~ 160 kcal. From the previously obtained relationship^{2c} $\delta_F = 220\Delta q_{p-C}$, one obtains from this crude theoretical calculation the correct order of magnitude value of ~ 0.6 kcal./p.p.m. for the slope of Figure 1.

The stabilization energies of Figure 1 have been obtained as ΔF° , for the reaction at 298°K.



(2) (a) P. C. Lauterbur, *Tetrahedron Letters*, **8**, 274 (1961); (b) H. Spiesscke 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).

(3) (a) G. Fraenkel, R. E. Carter, A. McLachlan, and J. H. Richards, *J. Am. Chem. Soc.*, **82**, 5846 (1960); (b) T. Schaefer and W. G. Schneider, *Can. J. Chem.*, **41**, 966 (1963); (c) V. R. Sandel and H. H. Freedman, *J. Am. Chem. Soc.*, **85**, 2328 (1963).

(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*-CH₃, have been obtained in H₂SO₄ from the carbinol. Equivalent results were obtained in H₂SO₄ and in CH₃CN for δ_F of the *p*-OCH₃ trityl cation.

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

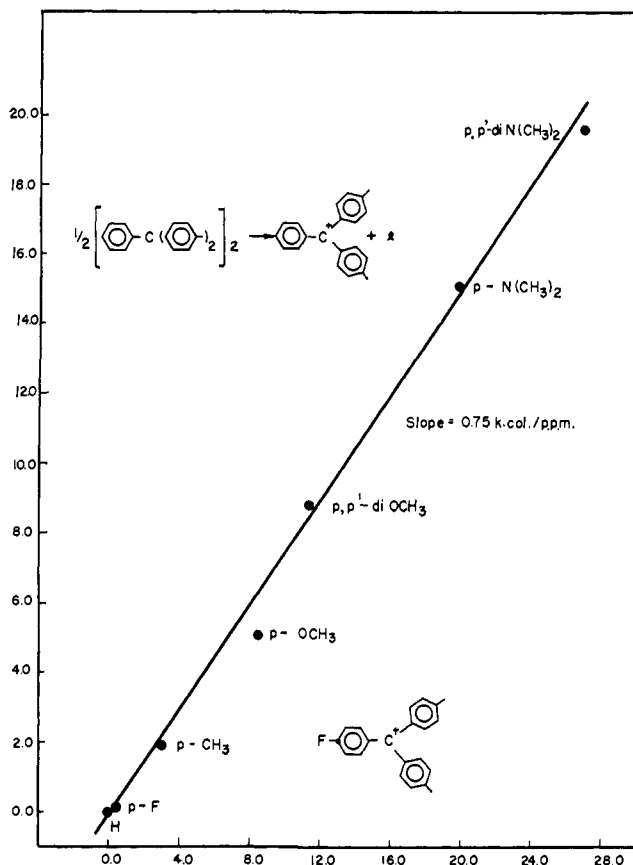
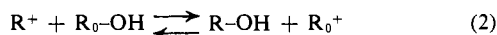


Figure 1. Relationship between effects of *para* substituents on stabilization energy and fluorine n.m.r. shielding for trityl cations. Ordinate: stabilization energy, kcal./mole, CH_3CN solutions; abscissa: δ_F , p.p.m., CH_3CN or H_2SO_4 solutions.

where R^+ is the *para*-substituted trityl cation, R_0^+ is the unsubstituted trityl cation, R-R is the symmetrical *para*-disubstituted hexaphenylethane, and $\text{R}_0\text{-R}_0$ is hexaphenylethane. It has been argued that $\Delta F_1^\circ \cong \Delta E^\circ_{\text{electronic}}$ and that $\Delta E^\circ_{\text{electronic}}$ is associated largely with the cation state.⁷ The basis for the argument is the approximate equality of ΔF_1° with the corresponding ΔF_2° for the reaction at 298°K.



where $\text{R}_0\text{-OH}$ is triphenylmethanol and R-OH is the *para*-substituted triphenylmethanol. The approximate equality $\Delta F_1^\circ \cong \Delta F_2^\circ$ provides support for the argument, particularly since reaction 1 is measured in acetonitrile and reaction 2 in aqueous solutions.⁷

Preliminary measurements of the temperature coefficient of the Jenson cell have been carried out, and the results appear to provide even more convincing evidence that $\Delta F_1^\circ \cong \Delta E^\circ_{\text{electronic}}$. Table I lists values of ΔF_1° at 298°K. and the presently available values of the corresponding ΔH_1° obtained from e.m.f. measurements at 10 and at 25°. The observation that $\Delta F_1^\circ \cong \Delta H_1^\circ$ (or $\Delta S_1^\circ \cong 0$) provides evidence which apparently excludes⁹ the possibility of any substantial contribution of solvent effects to values of ΔF_1° .

The relationship $\delta_F = C_1 E^\circ_{\text{electronic}} + C_2$ yields for a reaction series having a given state change between

(9) (a) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 80-84; (b) L. G. Hepler, *J. Am. Chem. Soc.*, **85**, 3089 (1963).

Table I. Enthalpy Stabilization Energies

<i>para</i> subst.	ΔF_1° , ^a kcal.	ΔH_1° , ^b kcal.
H,H,H	(0.0)	(0.0)
CH_3 , CH_3 ,H	3.2	2.8
OCH_3 , OCH_3 ,H	8.7	8.0
$\text{N}(\text{CH}_3)_2$,H,H	15.1	14.9

^a At 298°K., experimental error ± 0.1 . ^b At 290°K., experimental error ± 0.8 .

products and reactants: $\Delta \delta_F = C_1 \Delta E^\circ_{\text{electronic}}$. The approximate equality or proportionality between corresponding values of ΔF° and $\Delta E^\circ_{\text{electronic}}$ then leads us to anticipate linear shielding-free-energy relationships. The present discussion appears to provide some theoretical basis for recently reported¹⁰ empirical relationships of this kind.

(10) R. W. Taft, *et al.*, Preprints of Papers, Division of Petroleum Chemistry, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965, p. A19.

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Stabilization Energies of Substituted Methyl Cations. The Effect of Strong Demand on the Resonance Order¹

Sir:

Lossing and students have found excellent correlation of the ionization potentials of *meta*- and *para*-substituted benzyl radicals² with Brown's σ^+ values.³ This result coupled with applications of ionization and appearance potentials to condensed phase reactivities⁴ and the previously known substantial effects of certain substituents on the appearance potential of the substituted methyl cation^{4a} prompted us to a systematic investigation of the appearance potentials (*A*) of the general system

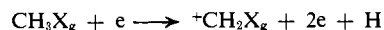


Table I summarizes the values of *A* for the substituted methyl cations which we have determined by the re-tarding-potential difference method⁵ on a modified Bendix Model 14-101 time-of-flight mass spectrometer. The energy spread of the pseudo-monoenergetic electron beam was approximately 0.1 e.v. and Xe, Kr, and NO (depending on the *A* value) were used to calibrate the electron energy scale. The substituent effect of X is given as the stabilization energy relative to CH_3^+ , $\text{S.E.} \equiv -(A_{\text{CH}_3\text{X}} - A_{\text{CH}_3})$. The effects obtained are unique in their magnitude; it seems unlikely that a larger range of substituent effects on energy will be found.

(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

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