quently decomposed to the persulfurane. Such a finding is not completely unexpected; it has been noted that **1** and sulfur tetrafluoride react to give CF_3OSF_5.[6] Further work on these compounds and related materials is in progress and details will be reported in a subsequent publication.

(6) G. Pass and H. L. Roberts, *Inorg. Chem.*, **2**, 1016 (1962).

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Why a Cyclopropyl Group Is Good at Stabilizing a Cation but Poor at Transmitting Substituent Effects

Sir:

The cyclopropane ring is the most effective unsubstituted hydrocarbon neighboring group for stabilizing a primary carbocationic center—a property which has labeled it the saturated analog of a carbon–carbon double bond. However, cyclopropyl is remarkably ineffective at transmitting resonance effects, in contrast to good π-stabilizing groups. These seemingly disparate conclusions have been drawn from both experiment[1,2] and theory.[3,4] This communication presents some new theoretical results pertaining directly to this problem and provides a simple interpretation that we hope will untangle these contradictory observations.

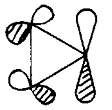
The first three columns of Table I present representative experimental data related to the relative stability of the parent cyclopropylcarbinyl cation along with our CNDO/2[5,6] results. The degree of agreement provides support for using simple quantum mechanical models to probe the question raised above.

Table I. Carbocation Stabilization by Some Hydrocarbon Groups

R	Appearance potential of RCH_2^+, eV	Log k_{rel} for solvolysis[a]	Methyl cation stabilization, energy, eV[b]	2-Cyclopropylcarbinyl substituent effect, eV[c]
H	14.4[d]	0	0	0
CH_3	12.9[d]	4.7	3.061	0.283
CH═CH	12.1[e]	6.7	3.499	0.280
C_6H_5	12.0[d]	8.4	4.253	0.431
c-C_3H_5	11.85[f]	9.5[g]	4.340	0.461

[a] Solvolysis of tertiary derivatives; H. C. Brown and M. H. Rei, *J. Amer. Chem. Soc.*, **86**, 5008 (1964); A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1963. [b] Calculated (CNDO/2) energy for the reaction: $RCH_2^+ + CH_4 \rightarrow RCH_3 + CH_3^+$. [c] Calculated (CNDO/2) energy for the reaction of 2-R-cyclopropylcarbinyl cation with cyclopropylmethane as in footnote *b*. [d] R. W. Taft, R. H. Martin, and F. W. Lampe, *J. Amer. Chem. Soc.*, **87**, 2491 (1965). [e] J. L. Franklin, *et al.*, *Nat. Stand. Ref. Data Ser.*, *Nat. Bur. Stand.*, **No. 26**, 43 (1969). [f] R. H. Martin, Ph.D. Thesis, Pennsylvania State University, 1965; cited in ref 1a. [g] Extrapolated from the value of C. D. Poulter and S. Winstein, *J. Amer. Chem. Soc.*, **91**, 3650 (1965).

A qualitative answer to why the cyclopropyl group is a more effective stabilizer than π substituents is easily obtained using the Walsh model for the bonding in cyclopropane[8] and simple perturbation theory considerations.[9,10] Despite the greater energy difference between the interacting levels in the cyclopropyl (ionization potential[10] = 10.9 eV) system the interaction is greater than the interaction of vinyl (ionization potential[10] = 10.5 eV) with an empty p orbital. This is because of the larger coefficient in the Walsh orbital, **1**, of



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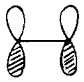

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cyclopropyl carbon adjacent to the p orbital [$\sqrt{2/3}$] compared to the coefficient of the corresponding AO in the HOMO, **2**, of vinyl [$\sqrt{1/2}$]. In other words the increase in H_{ij} overcomes the increase in ΔE in the perturbation expression[9]

$$E = E^\circ + (H_{ij}^2/\Delta E) \tag{1}$$

A similar analysis is applicable to benzyl cation where the HOMO energy is relatively high (9.2 eV[11]), but the relevant coefficient is only $\sqrt{1/3}$.

Substituents in the 2 position of the ring in the cyclopropylcarbinyl system have provided puzzling results for over a decade.[2] Sneen[2a,12] showed that a *trans*-2-phenyl substituent provides an acceleration of only a factor of 2.2 over the unsubstituted (cyclopropylcarbinyl) β-naphthalene sulfonate in solvolysis. Recently Traylor[2e] has found evidence for a remarkably small effect of a 2-methoxy substituent during a study of

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(1) The unique stability of the cyclopropylcarbinyl cation has been amply and elegantly demonstrated by a generation of physical organic chemists. See: (a) N. C. Deno, *et al.*, *J. Amer. Chem. Soc.*, **87**, 4533 (1965), and references cited therein; (b) H. G. Richey in "Carbonium Ions," Vol. III, G. A. Olah and P. v. R. Schleyer, Ed., Wiley Interscience, New York, N. Y., 1972, p 1295; K. B. Wiberg and A. J. Ashe, *ibid.*, p 1201; (c) G. A. Olah and G. Liang, *J. Amer. Chem. Soc.*, **95**, 3792 (1973).

(2) The absence of good through conjugation by cyclopropane is exemplified by: (a) R. A. Sneen, *et al.*, *J. Amer. Chem. Soc.*, **83**, 4843 (1961); (b) P. v. R. Schleyer and G. W. Van Dine, *J. Amer. Chem. Soc.*, **88**, 2321 (1966); (c) R. Fuchs and J. J. Bloomfield, *J. Org. Chem.*, **28**, 910 (1963); (d) R. G. Pews and N. D. Ojha, *J. Amer. Chem. Soc.*, **91**, 5769 (1969), and references cited therein; (e) R. S. Brown and T. G. Traylor, manuscript submitted for publication (we thank Professor Traylor for communicating his results prior to publication); (f) C. F. Wilcox, Jr., and J. N. Hsu, *J. Amer. Chem. Soc.*, **94**, 8232 (1972) (the second author was given erroneously as H. D. Banks in the journal).

(3) The charge distribution, rotational barriers, and geometry of cyclopropylcarbinyl cation have been theoretically investigated by many workers. Among these are: (a) R. Hoffmann, *J. Chem. Phys.*, **40**, 2480 (1964); (b) R. Hoffmann, *Tetrahedron Lett.*, **43**, 3819 (1965); (c) K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968); (d) L. Radom, J. A. Pople, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **94**, 5935 (1972); (e) W. J. Hehre and P. C. Hiberty, *J. Amer. Chem. Soc.*, **94**, 5917 (1972); (f) R. Hoffmann, "Special Lectures at the XXIIIrd International Congress of Pure and Applied Chemistry," Vol. 2, Butterworths, London, 1971, p 233.

(4) L. D. Kispert, C. Engelman, C. Dyas, and C. U. Pittman, Jr. (*J. Amer. Chem. Soc.*, **93**, 6948 (1971)) found small changes in bond orders, charge distributions, and rotational barriers in vinylcyclopropanes substituted with groups of varying electron deficiencies.

(5) CNDO/2[6] calculations were performed using Wiberg's parameterization[7] with the following geometries: C—C single bonds, 1.51 Å; C═C bonds, 1.34 Å; C═C aromatic bonds, 1.40 Å; C—C$^+$ bonds, 1.45 Å; C—H bonds to tetragonal carbons, 1.09 Å; C—H bonds to trigonal carbons, 1.05 Å; conformations were chosen so as to maximize conjugative overlaps and minimize steric repulsions.

(6) J. A. Pople and D. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970.

(7) K. B. Wiberg, *J. Amer. Chem. Soc.*, **90**, 59 (1958).

(8) A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949).

(9) (a) R. Hoffmann, *Accounts Chem. Res.*, **4**, 1 (1971); (b) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969.

(10) P. Bischof, R. Gleiter, E. Heilbronner, V. Hornung, and G. Schröder, *Helv. Chim. Acta*, **53**, 1645 (1970).

(11) See footnote *e* in Table I.

(12) See also: T. Shono, I. Nishiguchi, and R. Oda, *J. Org. Chem.*, **35**, 42 (1970).

"vertical stabilization" in a model system for the cyclopropylcarbinyl cation. Such results are especially puzzling when viewed in terms of the resonance model of the cyclopropylcarbinyl cation.[13]

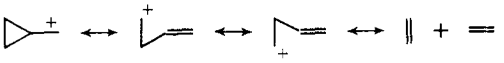
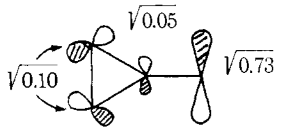


Table I, column IV, gives our calculated results for the stabilization of the cyclopropylcarbinyl cation by substituents in the 2 position. These stabilizations are all *ca.* one-tenth as large as the stabilization energies for the direct interaction of R with the carbinyl carbon given in Table I. This factor is consistent with the factor of 0.10 derived by simply taking the square of the coefficient of the in-plane p orbital at the 2 position of the ring in the LUMO of cyclopropylcarbinyl cation[14] derived from the CNDO/2 calculation.



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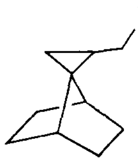
The factor of 10 (derived either from the CNDO results or from the simple perturbation argument) is quite sufficient to account for Sneen's phenyl substituent effect. The factor of 250,000,000 = $10^{8.4}$, the observed substituent effect of a phenyl attached directly to the cation (Table I), is predicted to be reduced to $10^{8.4/10} = 7$ for the cyclopropylcarbinyl system, sufficiently close (especially if entropy effects are considered) to Sneen's factor of 2.2.

This analysis is also consistent with the observed relative rates for methyl and vinyl substituents on the cyclopropylcarbinyl cation. Methyl in the 2 position of the ring would be expected to accelerate the solvolysis rate by $10^{4.7/10} = 3$; the observed[2b] value is a factor of 10. Recently[15] the $k_{\rm rel}$ for a dimethylvinyl substituted cyclopropylcarbinyl cation has been determined as 15. The $k_{\rm rel}$ for the corresponding tetramethylallyl cation can be estimated[16] as $\sim 10^{13.7}$ leading to a predicted $k_{\rm rel}$ for the cyclopropylcarbinyl system of $10^{1.37} = 23$.

A methoxy group adjacent to an incipient cationic center accelerates the rate of solvolysis by 10^{14}.[17] Our analysis for the effect of a methoxy substituent in the 2 position of the cyclopropylcarbinyl system would predict $10^{1.4} = 25$. We would tend to agree, therefore, with Traylor's assertion[2e] that the observed[18] factor of 791 is due to some ring cleavage accompanying solvolysis.

The analysis presented here nicely rationalizes the small observed rate enhancement (a factor of 4 at 25°) experienced upon comparing compounds **4** and **5**.[2f]



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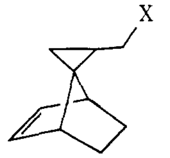
1:4



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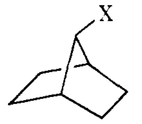

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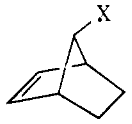
1:1.4 × 10′′



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Applying our treatment $10^{11.1/10} = 13$. This factor is further diminished when one considers that the strain associated with the 7 position of the norbornyl skeleton reduces still more the coefficient of the cyclopropyl p orbital at that position in the LUMO of the cation, **3**, a point made elegantly by Sargent[19] for the similar allylic systems.

In conclusion we feel that the perturbation arguments presented provide a clear qualitative explanation for the small effect of resonance stabilizing groups in the "intensely conjugated" [1a] cyclopropylcarbinyl system. The very same factor which makes cyclopropane an excellent stabilizing group, namely the concentration of electron density at one site in its interacting HOMO, assures, by depleting the coefficients at other sites, that the group is little responsive to substituent effects. The phenomenon cannot be generalized, but any case that does come up can be analyzed by the perturbation method given here. We feel that this approach has great potential in explaining the poor stabilization of other σ-delocalized ions by π donors.[18,20]

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(13) These resonance structures would, of course, be given very unequal weights. This resonance picture cannot then, however, correctly predict the extraordinary stability of the parent ion.

(14) (a) This refers only to the H_{ij}^2 parameter in the perturbation expression (eq 1). ΔE changes as well and accounts for some of the fluctuations encountered upon comparing columns 3 and 4 of Table I; these latter considerations have been alluded to by Dewar: M. J. S. Dewar and A. P. Marchand, *Annu. Rev. Phys. Chem.*, **16**, 321 (1965). (b) The coefficient at C_1 is small due to the mixing in of antibonding as well as bonding cyclopropane levels. Its magnitude is consistent with the known minor effect of substitution at that site.[2b]

(15) T. Sasaki, S. Eguchi, M. Ohno, and T. Umemuro, *Chem. Lett.*, 503 (1972).

(16) R. G. DeWolfe and W. G. Young, *Chem. Rev.*, **56**, 753 (1956).

(17) P. Ballinger, P. B. D. de la Mare, G. Kohnstam, and B. M. Presitt, *J. Chem. Soc.*, 3641 (1955).

(18) P. v. R. Schleyer, P. J. Stang, and D. J. Raber, *J. Amer. Chem. Soc.*, **92**, 4727 (1970).

(19) T. J. Mason, M. J. Harrison, J. A. Hall, and G. D. Sargent, *J. Amer. Chem. Soc.*, **95**, 1849 (1973).

(20) (a) C. F. Wilcox and H. D. Banks, *J. Amer. Chem. Soc.*, **94**, 8231 (1972); (b) K. L. Servis and J. D. Roberts, *J. Amer. Chem. Soc.*, **87**, 1331 (1965); (c) H. C. Brown, F. J. Chloupeck, and M.-H. Rei, *J. Amer. Chem. Soc.*, **86**, 1246 (1964); (d) E. J. Corey and H. Uda, *J. Amer. Chem. Soc.*, **85**, 1788 (1963).

(20e) Note Added in Proof. Professor P. v. R. Schleyer has recently informed us of unpublished work with H. Alper on the solvolysis of 2-substituted cyclopropylcarbinyl derivatives that yields a good correlation against σ^+ with a ρ of -3.6 including the methoxy substituent. Even if this substituent sensitivity represented solely "vertical" stabilization (contrary to the evidence in ref 2e) the central conclusion of this communication would still hold. Also, in Table I if the reaction of ethane to ethyl cation is used as the reference the cation stabilization energies are reduced by a factor of about 0.66.

(21) National Science Foundation Trainee, 1969–1973.

Effects of Substituents on the Mechanism of Stereomutation of Allyl Cations

Sir:

The stereomutation of allyl cations (I → I′, I′′, I′′′) can, in principle, take place by two mechanisms, either (Scheme I, paths A and A′) by simple stepwise rotation