Electronic Structure of Carbonium Ions. Methyl and Ethyl Cations[1a]

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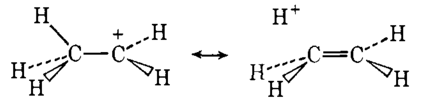
Abstract: *Ab initio* wave functions have been obtained for CH$_3^+$ and CH$_4$ and for CH$_3$CH$_2^+$ and CH$_3$CH$_3$ by means of the LC (Hartree–Fock)-AO–MO–SCF scheme. According to the calculated energy differences between the cations and their hydrocarbon precursors, the ethyl cation has an "extra stabilization" of 18 kcal/mole over the methyl cation, in rather good agreement with experimental results. Population analyses, energy term separation, and correlation diagrams provide insight into the electronic structure of carbonium ions in general and lend a new explanation for the stabilizing effect of methyl substitution at a positive center.

The ethyl cation is an obvious and convenient model for larger alkyl cations because it is the simplest system in which appears the effect of alkyl substitution onto a carbonium ion center. Like most carbonium ions, however, the ethyl cation is far too reactive to allow thorough experimental investigation. Rigorous quantum theory therefore provides the most reliable and detailed source of information on the forces governing the structures and stabilities of the ethyl cation and other simple alkyl cations.

Numerous *ab initio*[1-5] and semiempirical[6-10] calculations on alkyl cations other than the methyl cation have appeared recently. Those dealing explicitly with the ethyl cation[1,5,6-10] fall into two general categories. The first comprises the relatively crude π electron calculations[7] which attempt to evaluate the energy associated with hyperconjugation. In these calculations



the three methyl hydrogens are treated as a pseudoatom triply bound to the methyl carbon. Such treatments explicitly take into account only those orbitals or linear combinations of orbitals of the proper symmetry to mix in with the cation pseudo-π system. The energetic consequences of such mixing can be taken care of only *ad hoc*, through the use of adjustable parameters, because these methods manifestly cannot adequately reproduce the proper balance of one-electron effects (nuclear–electron attraction and electron kinetic energy) *vs.* two-electron effects (electron–electron repulsion and exchange energies). The importance of hyperconjugation is thus consistently overestimated[11] and resulting calculated charge densities disagree greatly with those found using more refined and reliable techniques.

Calculations on the ethyl cation in the second category include the σ electrons and are used to estimate quantities other than resonance energies. Both *ab initio* and semiempirical schemes have been investigated, and it is worthwhile noting that even the two-electron containing semiempirical schemes can yield results opposite to *ab initio* wave functions for some important cases. Thus *ab initio* calculations[2] for the ethyl and vinyl cations show them to be more stable than the isomeric bridged structures, protonated ethylene and protonated acetylene, respectively, while semiempirical calculations give the reverse.[9,10] Small basis set *ab initio* wave functions also can be misleading; thus Preuss, *et al.*,[5] found the ethyl cation and protonated ethylene structures to be of equal energy (-77.779 hartrees) due to an inadequate representation of the hydrogens.

Method of Calculation. *Ab initio* calculations, in the Roothaan[13] LCAO–MO–SCF approximation, are reported in detail for the methyl cation **3** and the ethyl cation **4**, for their parent hydrocarbons, methane **1** and ethane **2**, for the π-localized ethyl cation **5**, and for protonated ethylene **6** (Figures 1 and 3). *Ab initio* results for several of these structures have been summarized in previous reports.[1b,2] Structure **5** differs from **4** only in that the empty p orbital on the CH$_2^+$ group of the latter has been left out of the calculation. The computations for **1–3** done earlier in this laboratory[14-16] were redone with the more flexible hydrogen basis used for the other structures.

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(1) (a) Supported in part by the Power Branch of the Office of Naval Research, Contract Number N00014-67-A-0151-0016; (b) J. E. Williams, Jr., V. Buss, L. C. Allen, P. v. R. Schleyer, W. A. Lathan, W. A. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 2141 (1970); (c) G. V. Pfeiffer and J. G. Jewett, *ibid.*, **92**, 2143 (1970).

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(4) D. T. Clark and D. M. J. Lilley, *Chem. Commun.*, 549 (1970).

(5) F. Fratev, R. Janoschek, and H. Preuss, Arbeitsbericht der Gruppen Quantenchemie, Max-Planck Institut für Physik und Astrophysik, Number 10, p 140, 1968; *Int. J. Quantum Chem.*, **3**, 873 (1969).

(6) H. Fischer, H. Kollman, H. O. Smith, and K. Miller, *Tetrahedron Lett.*, 5821 (1968); K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968); G. Klopman, *J. Amer. Chem. Soc.*, **91**, 89 (1969); J. E. Baldwin and W. D. Foglesong, *ibid.*, **90**, 4311 (1968); R. E. Davis, A. S. N. Murthy, and A. Ohno, *Tetrahedron Lett.*, 1595 (1968), and preceding papers; H. O. Ohorodnyk and D. P. Santry, *J. Amer. Chem. Soc.*, **91**, 4711 (1969); C. Trindle and O. Sinanoglu, *ibid.*, **91**, 4054 (1969); T. Yonezawa, K. Shimizu, and H. Kato, *Bull. Chem. Soc., Jap.*, **40**, 1302 (1967); G. J. Gleicher, *J. Amer. Chem. Soc.*, **90**, 3397 (1968).

(7) N. Muller and R. S. Mulliken, *ibid.*, **80**, 3489 (1958); A. Streitwieser and P. M. Nair, *Tetrahedron*, **5**, 149 (1959); A. Ron, E. A. Halevi, and P. Pauncz, *J. Chem. Soc.*, 630 (1960); S. Ehrenson, *J. Amer. Chem. Soc.*, **86**, 847 (1964).

(8) R. Hoffmann, *J. Chem. Phys.*, **40**, 2480 (1964).

(9) T. Yonezawa, H. Nakatsuji, and H. Kato, *J. Amer. Chem. Soc.*, **90**, 1239 (1968).

(10) J. J. Dannenberg and T. D. Berke, 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, Abstract PHYS 163.

(11) Extensive delocalization through an alkyl cation pseudo-π system should give rise to a long wavelength transition (at *ca.* 290 mμ) observable in the electronic spectra of these cations (S. F. Mason, *Quart. Rev., Chem. Soc.*, **15**, 339 (1961)), but only end absorption is actually found.[12]

(12) G. A. Olah, C. U. Pittman, Jr., R. Waack, M. Doran, *J. Amer. Chem. Soc.*, **88**, 1488 (1966).

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Table I. Structures for Species **1–6**[a]

No.	Structure	R(CC)[b]	$\sphericalangle$HC$^+$H[c]	$\sphericalangle$HCCH
1	Methane			
2	Ethane	1.534		60, 60, 60[d] (staggered)
3	Methyl cation		120	
4	Ethyl cation	1.48	120	90, 90[e]
5	Ethyl cation, π localized	1.48	120	90, 90[e]
6	Protonated ethylene	1.46[f]		Ethylene moiety planar[a]

[a] Reasons for choice of values of structural parameters for **1** and **6** are detailed in ref 2; geometries for all other species are idealized or derived from **4**. [b] All lengths in ångströms; for tetragonal carbon R(CH) = 1.096; for trigonal carbon R(C$^+$H) = 1.084 with the exception of the bridge hydrogen in **6**. [c] Angles in degrees; CH_3 groups are kept tetrahedral. [d] Smallest dihedral angles in this conformation. [e] Dihedral angles between hydrogens of CH_2^+ and unique methyl hydrogen. [f] $R(CH_{\text{bridge}})$ = 1.33.[a]

Table II. *Ab Initio* Total Energies and Energies Components for Ethyl and Methyl Cation and Their Neutral Hydrocarbon Precursors[a]

No.	Species	E_t[b]	V_{nn}[b]	V_{ee}[b]	T[b]	V_{ne}[b]
1	Methane	−40.1788	13.3738	25.9622	40.1788	−119.6982
2	Ethane	−79.1851	42.2306	67.3506	79.1851	−267.9515
3	Methyl cation	−39.2072	9.6478	19.0193	39.2074	−107.0819
4	Ethyl cation	−78.2426	37.1830	57.1808	78.2425	−250.8490

[a] All energies in hartrees (1 hartree = 627.502 kcal/mol) and scaled to satisfy the virial theorem. [b] E_t = total energy relative to electrons and nuclei all at infinitive separations; V_{nn} = nuclear repulsion energy; V_{ee} = electron–electron interaction inergy; T = electron kinetic energy; V_{ne} = nuclear–electron attraction energy.

Table III. *Ab Initio* Total Energies and Energy Components for Cations **5** and **6**[a]

No.	Species	E_t	V_{nn}	V_{ee}	T	V_{ne}
5	π Localized ethyl cation, 90, 90	−78.2235	37.1562	57.1161	78.2235	−250.7194
	Difference **4** → **5**	+11.9	−16.7	−40.4	−11.9	+81.0
6	Protonated ethylene	−78.2285	37.7902	57.5040	78.2285	−251.7512
	Difference **4** → **6**	+8.8	+379.0	+201.8	−8.8	−564.0

[a] Absolute energies in hartrees and scaled to satisfy the virial theorem. Energy differences in kilocalories per mole.

The basis set for all calculations consisted of Whitten's[17] three s-type groups (total of ten Gaussians) and Huzinaga's[18] five Gaussian p orbitals on carbon, and Whitten's five *s*-type Gaussians grouped into a four-component and a long-range one-component group on each hydrogen, both groups scaled with η^2 = 1.44. *Ab initio* calculations with such a basis give structural parameters to within a few per cent[19] and threefold barriers to within ±0.4 kcal/mol.[20]

Structures for the species **1–6** are as reported previously and are summarized in Table I. Population analyses are given in Figures 1 and 3, total energies and energy components in Table II and III, and the nuclear coordinates and the molecular orbital energies in Table IV.

Role of the Methyl Group in Stabilizing the Ethyl Cation.

The stabilization of carbonium ions resulting from the substitution of methyl groups for hydrogens attached to the positive center has long been known by organic chemists. For instance, experimental heats of formation show the ethyl cation to be more stable than the methyl cation by an amount 31[21]–42[22] kcal/mol greater than the difference in the heat of formation[23] between ethane and methane. This "extra" methyl stabilization energy in alkyl cations may be rationalized using disarmingly straightforward logic. The most obvious difference between a highly reactive, and in this sense, unstable cation such as **4** and its unreactive, neutral precursor **2**, is the presence in **4** of an electron-deficient center. The instability associated with such a positively charged center can be offset by neutralizing the charge, or at least dispersing it throughout the molecular framework. The stability of **4** relative to **3** therefore seems to imply that methyl groups are better electron suppliers than hydrogens. This conclusion is widely accepted.[24–26]

This argument, however, is seriously flawed. The positive center in **4** is only a part of the molecule. Increasing the electron density at such an electron-deficient site will undoubtedly increase the nuclear–

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(14) W. H. Fink and L. C. Allen, to be published.

(15) W. H. Fink and L. C. Allen, *J. Chem. Phys.*, **46**, 2261 (1967).

(16) J. E. Williams, Jr., R. Sustmann, L. C. Allen, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 1037 (1968).

(17) J. L. Whitten, *J. Chem. Phys.*, **39**, 349 (1963); **44**, 359 (1966).

(18) S. Huzinaga, *ibid.*, **42**, 1293 (1965).

(19) L. C. Allen in P. O. Löwdin, "Quantum Theory of Atoms, Molecules, and the Solid State: A Tribute to John C. Slater," Academic Press, New York, N. Y., 1966.

(20) L. C. Allen, *Chem. Phys. Lett.*, **2**, 597 (1968).

(21) J. L. Franklin in "Carbonium Ions," Vol. I, G. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1969; D. Bethell and V. Gold, "Carbonium Ions: An Introduction," Academic Press, New York, N. Y., 1967.

(22) Calculated using data of J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966), and of C. E. Melton and W. H. Hamill, *J. Chem. Phys.*, **41**, 3464 (1964), and F. A. Elder, C. Giese, B. Steiner, and M. Inghram, *ibid.*, **36**, 3292 (1962). The agreement in the ionization potential for C_2H_5 in the last two works, the former using electron impact, the latter photoionization, makes the higher value of 42 kcal/mole more probable.

(23) American Petroleum Institute, Project 44, "Selected Values of the Thermodynamic Properties of Hydrocarbons," Carnegie Institute of Technology, Pittsburgh, Pa., 1952 onward.

(24) J. D. Roberts and M. C. Caserio, "Basic Principles of Organic Chemistry," W. A. Benjamin, Inc., New York, N. Y., 1964; R. W. Taft, Jr., and I. C. Lewis, *Tetrahedron*, **5**, 210 (1959).

(25) E. S. Gould in "Mechanism and Structure in Organic Chemistry," Holt Rinehart, and Winston, New York, N. Y., 1959, Chapter 7.

(26) M. J. S. Dewar, "Hyperconjugation," Ronald Press Co., New York, N. Y., 1962.

electron attractions at that site and thus lower its energy, but this does not necessarily mean that the energy of the cation as a whole will decrease.[27] While the question of the electron-releasing ability of methyl relative to hydrogen is still an ambiguous one, there is a more effective way of stabilizing a cationic center which does not depend on the electron-donating ability of the methyl group.

It is convenient in discussing the ethyl cation to make the usual separation of effects into σ *vs.* π effects. The π effects—including any that might be called π inductive effects—we loosely term hyperconjugative and discuss in the next section. Throughout this paper we refer to the "empty" p orbitals of **3**–**5** as p_π orbitals, comprising, with the parallel p_π orbital of the methyl group, the "pseudo-π" or π_z system. The π-type p orbitals perpendicular to the π system are the p_y orbitals and make up the π_y system.

From Table II the difference in reaction energies between 1 and 2, which equals the "extra" methyl

$$CH_4 \longrightarrow CH_3^+ + H^- \qquad (1)$$

$$C_2H_6 \longrightarrow C_2H_5^+ + H^- \qquad (2)$$

stabilization energy for the ethyl cation, is found to be 18 kcal/mol. This differs from the experimental values mentioned above for two major reasons. The four species **1**–**4** contain different numbers of atoms and bonds and thus their energies are at different distances from their respective true Hartree–Fock energies, and also zero-point energy changes are not included in our *ab initio* calculations. Estimates of the zero-point energy difference between **1** and **2** from the values of Pitzer and Catalano,[28] and of the corresponding difference between **3** and **4** from the (incomplete) set of calculated frequencies for $(CH_3)_3C^+$ and $(CH_3)_2CH^+$ given by Olah, *et al.*,[29] indicate that correcting the experimental stabilization energy for zero-point energies will lower it significantly—probably by 15 kcal/mol. Electron correlation (intramolecular van der Waals) energy changes—which are outside the scope of the Hartree–Fock model—may be also fairly large for each of the two reactions (1 and 2). It is very likely, however, that the difference in correlation energies between the two reactions will not be very significant—no more than 1 or 2 kcal/mol.

To find the origin of the extra methyl stabilization, we turn first to the population analyses presented in Figure 1, which might help us decide as to the electron-donating ability of CH_3 relative to hydrogen. Unfortunately, because the electrons are divided between the different nuclei in an artificial way,[30] the accuracy of the electronic distribution as represented by population analysis does not necessarily go hand in hand with the quality of other calculated values, such as the total energy. And, in fact, with an inferior basis set the distribution of electrons might yield more reasonable atomic charges than one which results from the highly sophisticated basis we are using in the present calculation. Thus a minimum Slater-type basis set (with optimized exponents) showed[31a] that for methane the hydrogens had a positive charge each of 0.021, leaving an excess of 0.084 electron on the carbon atom. This is clearly more realistic than the population analysis of methane shown in Figure 1 which renders the carbon negative by 1.072 electrons.

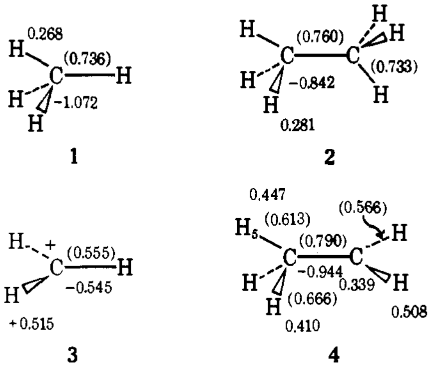

Figure 1. *Ab initio* formal atomic charges and overlap populations (in parentheses) for the methyl and ethyl cations and their parent hydrocarbons.

The positive atomic charge on the hydrogens gives the amount by which hydrogen is a better electron donor than methyl, for in ethane, because of its symmetry, the charge on each methyl group is zero. This value, 0.268 in our calculation and 0.021 in Pitzer's, seems to indicate that in neutral molecules the methyl group is indeed electron-withdrawing relative to hydrogen.

Turning to the cationic compounds, we find that in CH_3^+ the hydrogens have transferred 0.515 electron each to the positive center, whereas in the ethyl cation the methyl group has donated only 0.323 electron. Again the methyl group is losing less electrons than is hydrogen, but we note that the difference now is only 0.192 electron as compared to 0.268 in the neutral precursors. Thus it seems that in carbonium ions in which hyperconjugation is an important factor, the methyl group is a better electron donor than in hydrocarbons, and since the value of 0.268 is probably highly exaggerated, we conclude that the methyl group, if bonded directly to a cationic center, might even be a better electron donor than hydrogen. However, the atomic population based analysis presented here is not really convincing because, not only is it a very rough and uncertain estimate of the charge distribution as indicated, but so far we have not taken into account what is happening in other parts of the molecular system as well. A more complete understanding of the problem follows from the reasoning developed below.

The experimental CH homolysis of ethane is only 6 ± 2 kcal/mol lower than that of methane,[21] so the extra methyl stabilization arises as a result of changes occurring during ionization of the radicals derived from **1** and **2**. Furthermore, since we expect the relief in nuclear repulsion (Table II) to occur mainly in the radical formation step, in which the tetrahedral carbon changes to trigonal coordination,[2,31b] the effects we are looking for can be found only in the electronic energy changes for reactions 1 and 2. In order to examine

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(27) Hoffmann found several years ago (ref 8) that the experimental stability order for simple alkyl cations was correctly reproduced by extended Hückel theory, even though this theory predicts methyl groups to be electron-withdrawing relative to hydrogen.

(28) K. S. Pitzer and E. Catalano, *J. Amer. Chem. Soc.*, **78**, 4844 (1966).

(29) G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. W. McIntyre, and I. J. Bastieu, *ibid.*, **86**, 1360 (1964).

(30) R. S. Mulliken, *J. Chem. Phys.*, 23, 1833 (1955).

(31) (a) R. M. Pitzer, *ibid.*, **46**, 4871 (1967); (b) J. E. Williams, R. Sustmann, L. C. Allen, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 1037 (1969).

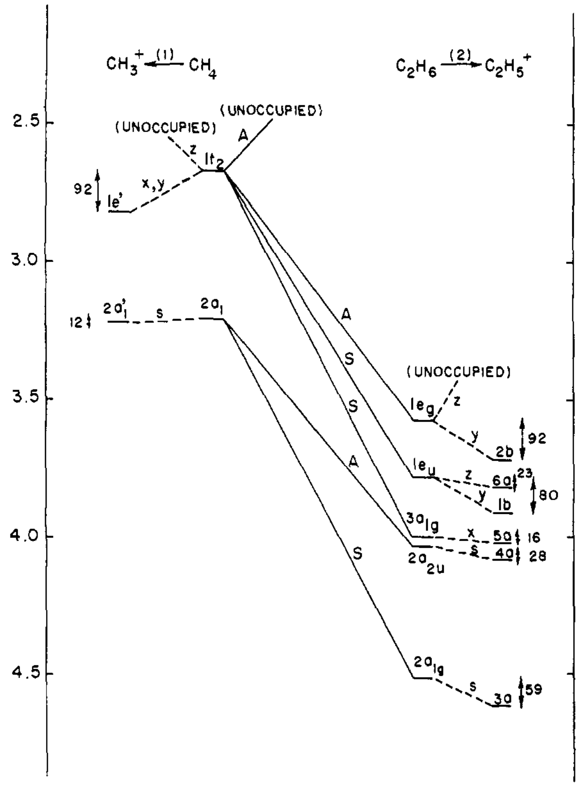


Figure 2. Correlation diagram of the MO partitioned energies e_i for reactions 1 and 2.

energetic changes in the MO's, we use the partitioned total energy quantities, e_i, rather than the ionization potential related eigenvalues of the Hartree–Fock equations, ϵ_i. The e_i add up to the total electronic energy and the component composition of the two types of one-electron energies are contrasted in the following definitions

$$\epsilon_i = V_{ne}(i) + T(i) + V_{ee}(i)$$

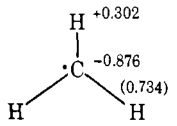
$$e_i = V_{ne}(i) + T(i) + 1/2V_{ee}(i)$$

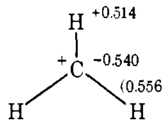
The e_i for **1**–**4** are used to construct the valence-electron correlation diagram[32] of Figure 2.

Correlations between methane and ethane connect bonding orbitals with a high percentage of a given atomic orbital from the carbon of methane with the corresponding linear combination of carbon orbitals on ethane. These are either a symmetric (labeled S) or antisymmetric (labeled A). Correlations for the RH → R^+ transformations are labeled with the symmetry of the carbon orbital characterizing the MO's being correlated: s = 2s (actually the third carbon s-type group[17]), x = $2p_\sigma$, y = $2p_y$, z = $2p_\pi$.

Figure 2 shows the lowering in e_i for each occupied MO of **1** or **2** relative to the corresponding MO of **3** or **4**. The difference between the sums of these energy lowerings for **1**–**3** *vs.* **2**–**4** accounts for the "extra" methyl stabilization energy in the ethyl cation. From the highest occupied orbitals (the triply degenerate $1t_2$ of methane and the doubly degenerate pairs $1e_u$ and $1e_g$) the sum of MO stabilizations for reaction 1 is equal to approximately 184 kcal/mol. The triply degenerate $1t_2$ of methane correlates with the $1e_g$, $1e_u$, and $3a_{1g}$, and the corresponding stabilization energy for reaction 2 is 211 kcal/mol, or 27 kcal/mol more. Of this, 12 kcal/mole is due to hyperconjugation (see below). By far the largest effect, however, is found in the difference in energy lowerings resulting from the MO's involving bonding with the carbon 2s, and the major effect here (59 kcal/mol) arises from CC σ bonding. Inspection of Figure 1 and of the coefficients of the wave functions (not given here because of space limitations) reveals that the immediate effect of the decreased electron–electron repulsion about the positive center is to allow more electrons into the 2s orbital of this carbon and to decrease the relative importance of the 2p orbitals in bonding. Both the α-hydrogens and their CH overlap regions become depopulated because the hydrogen 1s orbitals are of much higher energy (ionization potential) than the carbon 2s orbitals.[15,17,18] Also, the CC overlap population changes little upon ionization, but because the methyl carbon has an orbital energetically comparable and hence[26,32] available for mixing with the positive carbon 2s (its own 2s) a greater percentage of that overlap is 2s–2s. Since electrons in the 2s orbitals see more of the carbon nuclei than do those in 2p's, the 2s–2s bonding is stronger than any bonding involving the 2p or hydrogen orbitals.

A positively charged electron-deficient species such as **3** or **4** is stabilized not by intramolecular neutralization or dispersal of its excess charge but by optimal utilization of its electrons for filling the regions of high positive potential. The electron-deficient aspect is necessary because it makes electron repulsion less important and allows more electrons into smaller regions around the nuclei. The difference in the electronic structure between neutral and positively charged species is most clearly seen in the regrouping of electrons which takes place upon removal of an electron from the methyl radical to generate the methyl cation. A





geometry search yielded for the methyl radical a CH bond length of 1.077 Å, in agreement with other *ab initio* calculations,[33] and 1.091 Å for the methyl cation. The shorter bond length of the radical compared to methane is easily explained either by the decreased nuclear repulsion around the carbon due to the lowering of its coordination number from 4 to 3 or by the change of its hybridization state.

The longer bond length in the cation is somewhat unexpected and warrants some further discussion. The effect of the decreased electron–electron repulsion is visible in the increase of the population of the carbon atomic orbitals. Removing an electron from the methyl radical and not counting the population of the p_π orbital (which is 1 in the radical and 0 in the cation)

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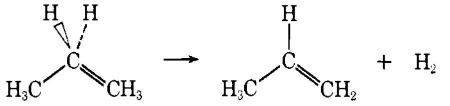
[32] For changes involving only angular coordinates, we may draw correlation diagrams—such as Walsh diagrams [A. D. Walsh, *J. Chem. Soc.*, 2260 (1953)]—using the molecular orbital energies ϵ_i, provided the bonding in the systems investigated is not ionic [S. D. Peyerimhoff, R. J. Buenker, and L. C. Allen, *J. Chem. Phys.*, **45**, 734 (1966)]. This is not true in general for reactions like 1 and 2, which represent bond-length changes and involve large amounts of charge separation. Furthermore, in diagrams like Figure 2, where the "coordinate" used as the abscissa is discontinuous and of no meaningful physical denotation, the fact that the e_i add up to the total electronic energy makes their use preferable to using ϵ_i.

[33] V. Buss, unpublished STO-3G calculations; see also G. Herzberg, *Proc. Roy. Soc., Ser. A*, **262**, 291 (1961).

actually result in an increase of negative charge on the carbon from +0.124 to −0.540. This charge comes from the hydrogen atoms, which each lose about 0.19 electron, and from the carbon–hydrogen bonding region (the overlap population of which decreases from 0.734 to 0.556). Both the weaker bonds and the increased positive charge on the hydrogens account for the increased bond length.

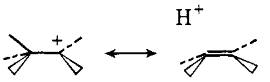
The ethyl cation **4** has an extra stabilization over **3** because: (a) the electron deficiency of the positive center is transmitted into the methyl group resulting in an additional gain of nuclear–electron attraction, an effect which is not present in the parent ethane; (b) very efficient bonding involving the carbon 2s orbitals is possible, while in the methyl cation the carbon 2s cannot effectively mix with any of the available orbitals.

Reaction 2 is one of a number of reactions in which a CC bond between tetragonal carbons becomes shorter and more stable when one of the carbons becomes trigonal through loss of a substituent and all or part of the associated pair of bonding electrons. We can without further calculation apply the above analysis directly to such reactions, *e.g.*, the dehydrogenation of propane to form propene



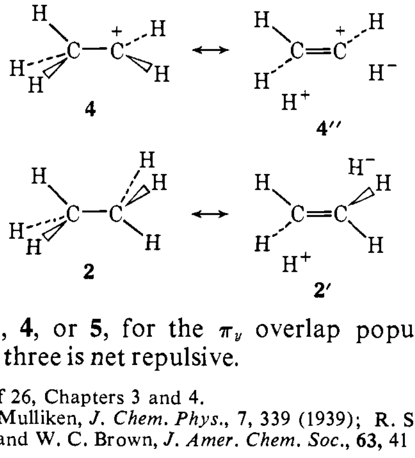
Here a mild electron deficiency is induced on the central carbon of propene by effectively dispersing a CH bond pair on the corresponding carbon of propane into the double bond and away from the methyl–methine CC bond. According to our analysis of the ethyl cation, this CC bond should become shorter and stronger, as is experimentally observed, and we thus account for the well-known stabilization of double bonds by alkyl substituents.[34]

Hyperconjugation *vs.* Bridging. By omitting the p_π orbital on C_1 of **4** and repeating the calculation, we obtain structure **5**. In **5**, hyperconjugative resonance (**4** ↔ **4**,′), illustrated below, is completely suppressed.



4 **4′**

The change in energy components for **4** → **5** is given in Table III. As expected,[26] "second-order" hyperconjugation[35] (**4** ↔ **4**,″ **2** ↔ **2′**) is apparently not important,



in either **2**, **4**, or **5**, for the π_y overlap population in each of the three is net repulsive.

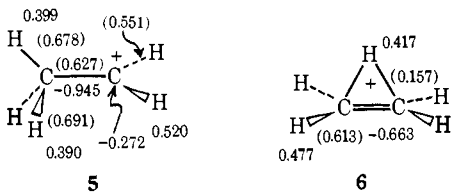


Figure 3. *Ab initio* formal atomic charges and overlap populations (in parentheses) for π-localized ethyl cation and protonated ethylene.

The hyperconjugation energy in the ethyl cation is the energy change for the reaction **5** → **4**,[36] or, from Table III, 11.8 kcal/mol.[38] This energy change is substantial, but not nearly as great as the calculated delocalization energy in the cyclopropenyl cation, 88 kcal/mol.[4] This is as expected, because as hyperconjugation becomes important (indicated by resonance structure **4′**) some of the CH binding energy in the methyl group must be lost. Hence, the methyl group CH overlap populations in the π-localized structure **5** are greater than those in **4** (Figures 1 and 3).

Analysis of the energy components for each of the molecular orbitals in **4** and **5** indicates that the changes in CH bonding are primarily responsible for the decrease in nuclear–electron attraction that takes place during the localization reaction (Table III). However, the lowered electron density and electron–electron repulsion around the positive carbon of **5**, relative to the positive carbon in **4**, allows some polarization of the CC σ bond toward the electron-deficient center in **5**, thus compensating in part for the loss in attractive potential. To be specific, about half the electrons donated in **4** to the positive carbon through the π_z system reach the corresponding carbon in **5** through the σ system, where proximity to the carbon nucleus and hence attractive potential is greater.

The energy component changes for a different delocalization process, the formation of the bridged ion **6**, contrast sharply with the one just discussed (Table III). The nuclear–electron attraction strongly favors **6** over **4** and moderates the large increase in nuclear repulsions. Such moderation of nuclear repulsion by electronic energy is generally to be expected. As a molecular system becomes more compact, the attractive regions between nuclei become smaller and more attractive. The electrons in these regions are more strongly bound, but because the volume to which they are effectively confined has diminished, these electrons interact more with each other resulting in an increase of the V_{ee} term. The bridge proton itself, as distinct from the orbitals centered on it, increases the stabilities of the molecular orbitals having large amounts of CC bonding character through its field effect (which is much stronger in the CC than in the CH overlap regions). Further stabilization of the CC bonding resulting from the 2s–2s overlap in the $2a_1$ MO of **6**

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(34) See ref 26, Chapters 3 and 4.

(35) R. S. Mulliken, *J. Chem. Phys.*, 7, 339 (1939); R. S. Mulliken, C. A. Rieke, and W. C. Brown, *J. Amer. Chem. Soc.*, **63**, 41 (1941).

(36) Strictly speaking, this energy change is the "vertical" resonance or hyperconjugation energy.[37] The "true" hyperconjugation energy could be found by obtaining the minimum energy CC bond length in **5** and subtracting the energy of **4** from the optimized energy of **5** thus found. The change in hyperconjugation energy resulting from this procedure, however, is expected, on general chemical grounds, to be small.

(37) See *e.g.*, A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961, Chapter 9.

(38) With the MINDO method this value is 12.8 kcal/mol,[39] in surprisingly good agreement with our *ab initio* results.

(39) N. C. Baird, *Theor. Chim. Acta*, **16**, 239 (1970).

Table IV

			Nuclear coordinates[b]			Molecular orbital energies[b]		
No.	System[a]	Atom	*x*	*y*	*z*	MO	ϵ_i	e_i
1	Methane	C	0.0	0.0	0.0	$1a_1$	−11.2266	−15.5434
		H	0.6904	0.0	−1.9257	$2a_1$	−0.9479	−3.2046
		H	0.6904	−1.6911	0.9764	$1t_2$	−0.5436	−2.6741
		H	0.6904	1.6911	0.9764			
		H	−2.0712	0.0	0.0			
2	Ethane	C	0.0	0.0	0.0	$1a_{1g}$	−11.2439	−16.7126
		C	−2.8989	0.0	0.0	$1a_{2u}$	−11.2434	−16.7126
		H	0.6904	0.0	−1.9527	$2a_{1g}$	−1.0286	−4.5111
		H	0.6904	−1.6911	0.9764	$2a_{2u}$	−0.8435	−4.0349
		H	0.6904	1.6911	0.9764	$1e_u$	−0.6068	−3.7835
		H	−3.5893	0.0	1.9527	$3a_{1g}$	−0.4974	−3.9941
		H	−3.5893	1.6911	−0.9764	$1e_g$	−0.4890	−3.5747
		H	−3.5893	−1.6911	−0.9764			
3	Planar methyl cation	C^+	0.0	0.0	0.0	$1a_1'$	−11.7185	−15.5565
		H	2.0485	0.0	0.0	$2a_1'$	−1.2907	−3.2236
		H	−1.0242	1.7740	0.0	$1e'$	−0.9581	−2.8199
		H	−1.0242	−1.7740	0.0			
4	Planar ethyl cation, 90, 90	C^+	0.0	0.0	0.0	1a	−11.7034	−16.7529
		C	−2.7968	0.0	0.0	2a	−11.5305	−16.7640
		H	1.0242	1.7740	0.0	3a	−1.3457	−4.6054
		H	1.0242	−1.7740	0.0	4a	−1.1328	−4.0795
		H	−3.4872	0.0	1.9527	1b	−0.9627	−3.9100
		H	−3.4872	1.6911	−0.9764	5a	−0.8442	−4.0201
		H	−3.4872	−1.6911	−0.9764	6a	−0.8350	−3.8204
						2b	−0.7892	−3.7208
5	Planar ethyl cation, π localized	C^+	Coordinates as for **4**			1a	−11.7257	−16.7641
		C				2a	−11.5119	−16.7547
		H				3a	−1.3488	−4.6008
		H				4a	−1.1375	−4.0958
		H				1b	−0.9762	−3.9165
		H				5a	−0.8452	−4.0167
		H				6a	−0.8194	−3.7960
						2b	−0.7812	−3.7191
6	Protonated ethylene	C	1.3795	0.0	0.0	$1a_1$	−11.6389	−16.7977
		C	−1.3795	0.0	0.0	$1b_1$	−11.6381	−16.7976
		H	0.0	0.0	2.1047	$2a_1$	−1.3996	−4.7363
		H	2.4038	1.7740	0.0	$2b_1$	−1.1169	−4.0783
		H	2.4038	−1.7740	0.0	$1b_2$	−0.9647	−3.9736
		H	−2.4038	1.7740	0.0	$3a_1$	−0.9023	−3.9405
		H	−2.4038	−1.7740	0.0	$1a_2$	−0.8350	−3.7552
						$4a_1$	−0.7890	−3.8775

[a] For values of internal coordinates see Table I. [b] Coordinates in bohrs (1 bohr = 0.52917 Å); energies in hartrees (1 hartree = 627.502 kcal/mol).

arises because the electron deficiency in **6** is equally shared between both carbons. That is, the $2a_1$ is not centered on (or polarized toward) either carbon, as is the case in **4**, but is rather spread over both, which reduces T and increases the overlap population and V_{ne} relative to the 3a MO of **4**. Of course, movement of the hydrogen in **4** (H_5 in Figure 1) to the bridge position of **6** entails loss of some CH binding energy. In addition the 2p orbitals lose the CC bonding character they have in the 5a of **4** and are relegated to bonding in the ethylenic CH bonds in the $3a_1$ of **6**. Both of these result in the destabilization of the $3a_1$—the only major destabilization indicated by the e_i of an MO resulting from the process **4** → **6** (see Table IV).

As Table III indicates, the net effect of the changes in electronic structure and energy in **4** → **6** is not quite enough to overcome the increase in nuclear repulsions, and so **4** is favored by 9.0 kcal/mol. We expect that this energy difference would not change significantly if we were to make the refinements necessary to push our calculations to the Hartree–Fock limit. Furthermore, we do not expect the correlation energies for the two ions to be very different, for reasons given earlier.[2] In fact, the Hollister–Sinanoglu[40] method predicts a correlation energy change of 0.2 kcal/mol (*i.e.*, negligible for our purposes) for the **4** → **6** isomerization.

It has been stated (*e.g.*, by Dewar[26]) that molecular orbital methods will always overestimate delocalization energies because these methods do not take into account correlation effects. That is, by correlating their motions, electrons can stay out of each other's way and thus better avoid repulsive interactions. Since in a delocalized species the electrons should be farther apart than in a corresponding localized isomer, it is argued that correlation should be a smaller effect for the delocalized form, *i.e.*, should favor the more crowded structure. We now have in hand, however, near-Hartree–Fock wave functions for the species involved in the delocalization processes in Table V. Obviously, if we use the size of the electron–electron interaction energies as measures of roughly how much might be gained from electron correlations, then the *delocalized* forms, except the π-localized ethyl cation, should be favored by correlation effects. As we have argued,[2,4] these effects should be small for the reactions noted above. On the other hand, semiempirical MO

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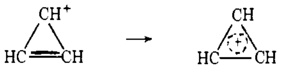
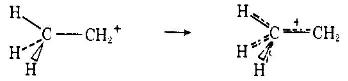
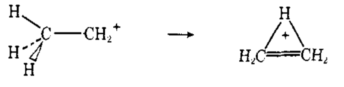
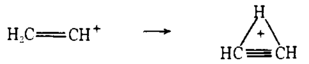
(40) C. Hollister and O. Sinanoglu, *J. Amer. Chem. Soc.*, **88**, 13 (1966).

Table V

	27	*a*
	118	*a*
	−40	This work
	202	This work
	110	*b*

[a] Reference 8. [b] Reference 3.

schemes do in general overestimate resonance effects.[2,7,9,10,35,37] This is due to inadequate treatment of two-electron effects, especially electron–electron repulsions, rather than to neglect of correlation energies.

Conclusions

The stabilities of alkyl cations are not dominated by their ability to neutralize or disperse positive charge, but by optimum utilization of the most stable orbitals. The electron-deficient nature of these molecules is important because it lowers electron–electron repulsion, thus allowing electrons to crowd close together at places of high positive potential. As a result of the greater ability of a methyl carbon than of a hydrogen substituent to take advantage of this lowered repulsion (by forming strong bonds with the cationic carbon through involvement of the 2s orbitals), the ethyl cation is more easily formed from its neutral precursor than is the methyl cation.

Stable Carbocations. CXII. Preferential Formation of the Bicyclo[3.3.0]-1-octyl Cation from Bicyclooctyl Precursors and Its Rearrangement to the 2-Methylnorbornyl Cation[1]

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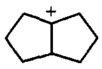
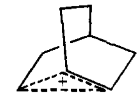
Abstract: The bicylo[3.3.0]-1-octyl cation (I) is formed from all bicyclooctyl precursors in FSO$_3$H–SbF$_5$–SO$_2$ClF or in SbF$_5$–SO$_2$ClF solutions at −78°. When I is heated to 0°, it irreversibly rearranges to 2-methylnorbornyl cation.

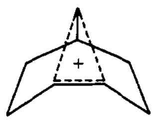
In the solvolytic studies of bicyclo-2-octyl derivatives,[2–7] it was shown that two distinct carbocation intermediates are involved, the asymmetrical nonclassical ion II formed from *exo*-bicyclo[3.2.1]-2-octyl isomers and the symmetrical nonclassical ion III formed from *endo*-bicyclo[3.2.1]-2-octyl isomers. Similar observations were made in the solvolyses of both *exo*- and *endo*-2-norbornecarbinyl[8–12] and 7-norbornanecarbinyl systems.[13,14]



I

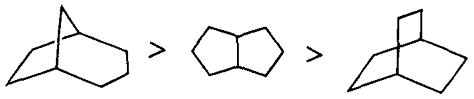


II



III

The solvolytic products involve both bicyclo[2.2.2]- and [3.2.1]octyl structures. No further rearrangement products were observed. However, when initial rearrangement can produce bicyclo[3.3.0]octyl cations, bicyclo[3.3.0]octyl products are dominant.[15–20] In the aluminum bromide catalyzed isomerization of a series of bicyclooctanes, the following stability order is revealed.[21]



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