Extended Hückel Theory. IV. Carbonium Ions

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pyridine, while Positions 2, 6 become more negative. Thus in this calculation, coordination with BH_3 not only produces charge transfer from N to B but also from N to neighboring carbons (N–C overlap population also is greater in $PyBH_3$). This could be an artifact of a computation which uses the same Coulomb integrals for N regardless of environment. On the other hand one can construct an explanation for the anomalous $PyBH_3$ hydrogen chemical shifts reported by Brey *et al.*[6] by superimposing upon this charge distribution the effect of increasing ring currents.

The B,N naphthalene[20] and B,N biphenyl linked via either B–B[21] or B–N[20] have also been examined. In the naphthalene analog, the gap between filled and unfilled orbitals is large and only slightly smaller than in borazine. This situation, quite different from the benzene, naphthalene progression, indicates the trend which culminates in a colorless hexagonal boron nitride. The B–N linked biphenyl analog prefers to be slightly twisted, while the B–B linked compound should be planar. (The N hydrogens which are the source of steric difficulties in the planar form are positively charged and thus "smaller.") The total charge distributions which are shown in Fig. 6 may be of some interest when the NMR spectra of these compounds are examined.

[20] A. W. Laubengayer, P. C. Moews, Jr., and R. F. Porter, J. Am. Chem. Soc. **83**, 1337 (1961).

[21] R. J. Brotherton, L. L. Peterson, and A. L. McCloskey, Abstracts, 144th Meeting, American Chemical Society, Los Angeles, 1963.

ACKNOWLEDGMENTS

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Extended Hückel Theory. IV. Carbonium Ions

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The conformations, relative stabilities, and electronic distribution of a sample of the more important carbonium ions and positively charged hypothetical transition states are examined. The species studied include the methyl, ethyl, isopropyl, tertiary butyl, and higher alkyl carbonium ions; protonated ethylene, acetylene, benzene, cyclopropane; the cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl carbinyl, allyl, and benzyl cations; the carbonium ions based on norbornane, norbornene, norbornadiene. Significant charge delocalization for a classical carbonium ion geometry is observed—the extent of this phenomenon is wider than anticipated. For the alkyl carbonium ions it is shown that the order of stabilities may be obtained from a calculation in which the polarity of the C–H bond is C^-–H^+. Protonated ethylene and acetylene show local minima for a symmetrical complex, but with rearrangement to an unsymmetrical cation favored. Protonated cyclopropane prefers an unsymmetrical three-center bonded structure, protonated benzene stabilizes in the familiar benzenium. The orientation of the empty carbonium p orbital with respect to other π-type orbitals determines the conformation in cyclopropyl carbinyl, benzyl, and allyl. The peculiar nature of the cyclopropane electron distribution is studied. The carbonium ions based on the bicyclo[2.2.1]-heptane structure show some nonclassical features; confirming experimental conclusions, the unusual 7-norbornadienyl cation is calculated to prefer an unsymmetrical geometry. Difficulties in applying the extended Hückel theory to charged species make some of the conclusions from the calculations less certain.

THE theoretical literature on carbonium ions is almost exclusively limited to conjugated molecules[1]; the experimental literature on the other hand abounds with speculations regarding positively charged species of every possible variety.[1,2] In part, the more speculative aspects of various structural proposals are due to the fact that the ions are such transitory and elusive entities that only indirect evidence, amenable to many interpretations, is available; in part, they have been almost encouraged by the absence of a guiding theoretical framework. The problem is difficult—carbonium ions are electron-deficient compounds and their structural variety and problems will be similar to the hardly simple boron hydrides.[3]

In this contribution, the extended Hückel theory, described in the first paper of this series,[4] is applied to

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[1] A. Streitwieser, Jr., *Molecular Orbital Theory for Organic Chemists* (John Wiley & Sons, Inc., New York, 1961), Chap. 12.

[2] (a) *The Transition State*, Special Publication No. 16 (The Chemical Society, London, 1962); (b) Extensive work by S. Winstein and J. D. Roberts and co-workers; see list of references on p. 387 of Ref. 1; (c) J. A. Berson in *Molecular Rearrangements*, edited by P. de Mayo (Interscience Publishers, Inc., New York, 1963), p. 111; (d) F. W. McLafferty, *Mass Spectrometry of Organic Ions* (Academic Press Inc., New York, 1963), Chap. 7.

[3] W. N. Lipscomb, *Boron Hydrides* (W. A. Benjamin, Inc., New York, 1963).

[4] R. Hoffmann, J. Chem. Phys. **39**, 1397 (1963).

a sampling of carbonium ions. The parameters for carbon and hydrogen are identical to those used in the work on the hydrocarbons.[4] The cations investigated fall into four classes:

(1) Carbonium ions formed by loss of H^- from normal or branched alkanes (methyl, ethyl, isopropyl, *tert*-butyl,[5] etc.).

(2) Ions formed by coordination of H^+ to a stable molecule, and often implicated as transition states in electrophilic reactions (ethylene, acetylene, benzene, cyclopropane+H^+).

(3) Cations in which π delocalization plays a role in determining conformation and stability (benzyl, allyl, cyclopropyl carbinyl).

(4) Carbonium ions suspected of nonclassical behavior (norbornyl, norbornenyl, norbornadienyl).

It was anticipated that if the success of the extended Hückel theory for neutral molecules depended on an approximate cancellation of electron–electron repulsions and nuclear–nuclear repulsions in Eq. (1) below, then the theory would run into difficulties for charged species. The total Hartree-Fock molecular energy for the neutral molecule may be written as

$$E=2\sum\epsilon_i+\sum_{n,n'}E_{nn'}-\sum_{e,e'}E_{ee'}, \qquad (1)$$

where ϵ_i are one-electron energies, $\sum E_{nn'}$ the sum of nuclear–nuclear repulsions and $\sum E_{ee'}$ symbolically represents the sum of electron–electron repulsion matrix elements. The hypothesis set forth in the first paper was: (1) The prescribed method of choosing H_{ii} and H_{ij} constitutes an intelligent guess for the matrix elements of a Hartree–Fock Hamiltonian, whose eigenvalues are the ϵ_i. (2) Total energies may be obtained as simply $2\sum\epsilon_i$ since the last two terms in Eq. (1) cancel approximately, or at least their difference varies slowly with R. A consequence of these conjectures is that the energy of a positive ion formed by loss of an electron from a neutral molecule cannot be given simply by an orbital energy sum, since there are now fewer electron repulsions and the missing electron repulsion term is certainly not a slowly varying function of R. Similarly a nuclear repulsion term is added if a cation is formed by addition of a proton to a neutral molecule. It would seem a simple matter to evaluate this additional repulsion as a function of separation, certainly in the case of the completely classical nuclear–nuclear repulsion, and to add it on to the orbital sum. Unfortunately, the inclusion of such a repulsion eliminates completely the shallow potential minima for the carbonium ions. It was decided then to attempt to disregard the added repulsion for cations (for anions it is an attraction) and to proceed with care in locating conformational minima. In two cases difficulties were encountered, apparently due to the failure to take into account a short-range repulsive term. In the protonated acetylene and benzene the best potential minima corresponded to arrangements of hydrogens much too close to each other. These are discussed in the relevant sections.

In summary, in the following discussion, those conclusions which depend on energetic considerations when large variations in internuclear distances take place are in doubt. Where only the orientation of one part of a molecule is varied, or where the arguments are concerned with electron distribution, the calculations are believed to be reliable. Finally, it should be kept in mind that the calculations refer to isolated, unsolvated species.

STABILITY OF ALKYL CARBONIUM IONS

It is widely assumed that a methyl group is a better electron donor than hydrogen. In part, the argument is tied to the experimental order of stability of carbonium ions, i.e., in order of increasing stability: methyl, ethyl, isopropyl, *tert*-butyl. A quantitative estimate of the stability difference may be obtained by comparing the heats of formation of the ions (262, 224, 190, and 160 kcal/mole, respectively[6]) with the same quantities for the parent hydrocarbons (−16.0, −16.5, −19.5, and −25.3[7]). The usual argument is that the tertiary cation is more stable than the secondary since there are more methyl groups in the former to act as electron donors. The implicit assumption is that electroneutrality is a good thing, i.e., the more negative charge donated to the positive site, the more stable the carbonium ion.

The proponents of this argument also point out that a polarity of the C–H bond such as C^-–H^+ is inconsistent with the stability order; for if C is more electronegative than H, the CH_3 will be electron withdrawing with respect to H.[8] Now good limited-basis SCF functions for simple hydrocarbons are becoming available; they clearly indicate that the hydrogen carries a net positive charge in the population analysis.[9] In my previous work this polarity was reproduced and a methyl group was indeed found to be electron withdrawing with respect to a hydrogen; nevertheless, it was shown that this did not prevent the computation of a reasonable charge distribution for toluene.[4] In this work we have therefore undertaken a study of alkyl carbonium ions to see if the correct stability order could be predicted with our ordering of $-CH_3$ and –H electronegativity. The results indicate that it can.

In Table I are listed calculated total energies for some carbonium ions. Unless the cation is specified as planar, its geometry is taken as that of the parent hydrocarbon with a hydrogen removed. We will also use the term

[5] The notation used in this paper departs from standard usage in that $CH_3CH_2^+$ is termed ethyl carbonium ion, instead of methyl carbonium, etc.

[6] (a) F. H. Field and J. L. Franklin, *Electron Impact Phenomena* (Academic Press Inc., New York, 1957); (b) R. R. Benecker and F. A. Long, J. Phys. Chem. **65,** 1565 (1961), prefer 259, 228, 200, and 176 kcal/mole, respectively.

[7] F. D. Rossini, K. S. Pitzer, R. L. Arnett, R. M. Braun, and G. C. Pimentel, *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds* (Carnegie Press, Pittsburgh, Pennsylvania, 1953).

[8] M. J. S. Dewar, *Hyperconjugation* (Ronald Press Company, New York, 1962).

[9] Acetylene: A. D. McLean, J. Chem. Phys. **32,** 1595 (1960); ethane: R. M. Pitzer and W. N. Lipscomb, J. Chem. Phys. **39,** 1995 (1963).

TABLE I. Total energies of some carbonium ions.

Molecule	$-E$	Molecule	$-E$
CH_3^+	108.984	neo-$C_5H_{11}^+$ prim	526.753
planar	110.001		
$C_2H_5^+$ stag	213.952	n-$C_6H_{13}^+$ sec-2	631.172
ecl	213.866	sec-3	631.138
planar	215.009	prim	630.871
$C_3H_7^+$ sec	318.569	n-$C_7H_{15}^+$ sec-2	735.377
sec planar	319.874	sec-3	735.348
prim	318.157	sec-4	735.355
n-$C_4H_9^+$ sec	422.746	n-$C_8H_{17}^+$ sec-2	839.581
prim	422.428	sec-3	839.552
i-$C_4H_9^+$ tert	422.916	sec-4	839.564
tert planar	424.573		
prim	422.370	n-$C_9H_{19}^+$ sec-2	943.786
n-$C_5H_{11}^+$ sec-2	526.962	sec-3	943.757
sec-3	526.921	sec-4	943.769
prim	526.656	sec-5	943.774
		prim	943.492

"tetrahedral carbonium ion" for this form, as well as "trigonal" for the form planar about C^+. Methyl, ethyl, isopropyl, and *tert*-butyl were studied in planar geometries; this meant an investigation of various possible hydrogen arrangements in the planar form for isopropyl and *tert*-butyl, since simple angular distortion at the central carbon atom did not necessarily lead to the most favorable conformation. The energies in Table I are for the best possible geometrical arrangement, in which at each primary C, one H is coplanar with all the carbons. The process studied theoretically may be described by the sequence of transformations

$$RH \rightarrow R_{tetr}^+ \rightarrow R_{trig}^{+*} \rightarrow R_{trig}^+,$$

where R_{trig}^{+*} is the simply flattened trigonal cation and R_{trig}^+ the cation of optimum conformation. The prediction of absolute stabilities in the series is impossible since one cannot determine by our method what energy

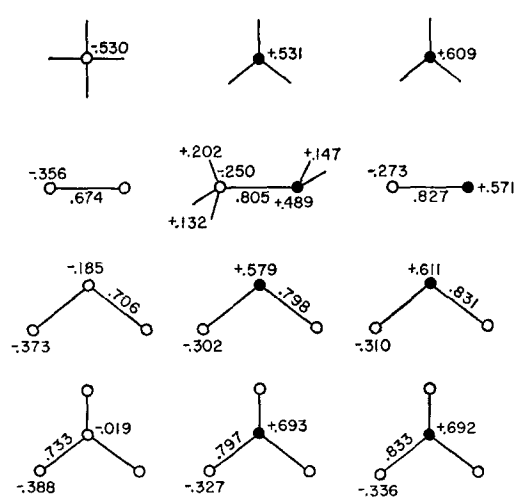


FIG. 1. Population analyses for methyl, ethyl, isopropyl, *tert*-butyl tetrahedral and trigonal carbonium ions compared with their parent hydrocarbons. For tetrahedral ethyl the charge distribution on the hydrogens is also illustrated. From left to right: RH, R^+ tetrahedral, R^+ trigonal.

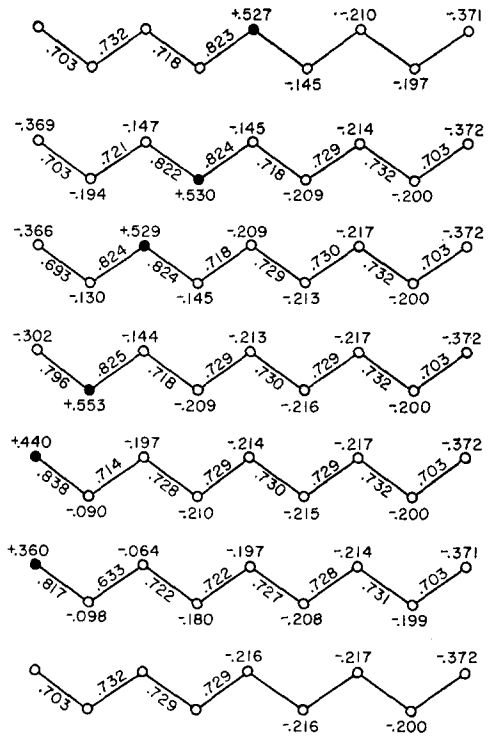


FIG. 2. Population analyses for the tetrahedral carbonium ions of *n*-nonane. Full circle indicates position of ionization; of the two primary ions the lower corresponds to a hydrogen missing in the plane of the C chain. For comparison the *n*-nonane charge distribution is shown at bottom.

should be assigned to $H+e^-$ in the reaction

$$RH \rightarrow R^+ + H + e^-.$$

We can, however, obtain the stabilizations relative to methyl cation. These are 0.95, 1.59, and 1.99 eV for ethyl, isopropyl, and *tert*-butyl, respectively, compared to the experimental 1.63, 2.97, and 4.02 eV. The qualitative trend is correct. The calculated stabilizations relative to methyl may be analyzed stepwise as follows:

	ethyl	isopropyl	*tert*-butyl
$RH \rightarrow R_{tetr}^+$	0.92	1.31	1.35
$R_{tetr}^+ \rightarrow R_{trig}^{+*}$	0.03	0.25	0.57
$R_{trig}^{+*} \rightarrow R_{trig}^+$	0.00	0.03	0.07.

The actual computed reorganization energies for the process $R_{tetr}^+ \rightarrow R_{trig}^+$ are 1.02, 1.05, 1.30, and 1.66 eV for methyl, ethyl, isopropyl, and *tert*-butyl, respectively.

It should be noted from a comparison of the various energies in Table I with those of the parent hydrocar-

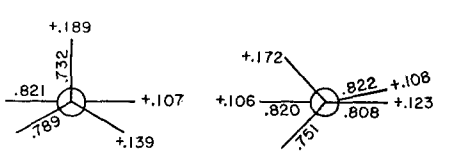


FIG. 3. Hydrogen charges and C–H overlap populations in two rotamers of trigonal $C_2H_5^+$.

bons[4] that there is constancy for the type of carbon ionized (assuming constant reorganization energies). In the longer chain alkanes, investigated in their completely extended *trans* configurations, there appears a difference in the energy of the carbonium ion formed by loss of a terminal hydrogen of up to 0.1 eV, depending on whether the missing hydrogen is in the carbon plane (more stable, listed in Table I), or not. This difference is interesting, along with its effect on the charge distribution—it is probably not significant since it will be removed by subsequent reorganization. The charge distributions in the carbonium ions are illustrated in Fig. 1, which compares tetrahedral and planar common carbonium ions with their parent hydrocarbons; and in Fig. 2 for the possible carbonium ions derived from *n*-nonane. An important correlation between the charge distribution on carbons in the parent alkane and the stability of the corresponding cation should be noted—in general, the more positive the original site, the more stable the ion. The correlation is not perfect, as may be seen from the interior sites in *n*-nonane; it also runs counter to the above mentioned electroneutrality principle. Nevertheless, it is an interesting and verifiable prediction that in a medium sized normal alkane the most stable carbonium ion will be the one localized on the penultimate carbon.

In Fig. 1, one may look for correlations between charge distribution and stability. First it should be noted that, accepting the RH charges, the placing of a positive charge on the central carbon would give that atom a charge of +0.470, +0.644, +0.815, and +0.981, respectively. The cation charges, with the exception of methyl, are increasingly less positive than these figures indicating that stability, as in the verbal argument, is associated with ability to get rid of positive charge. On the other hand, the actual charges are such that the

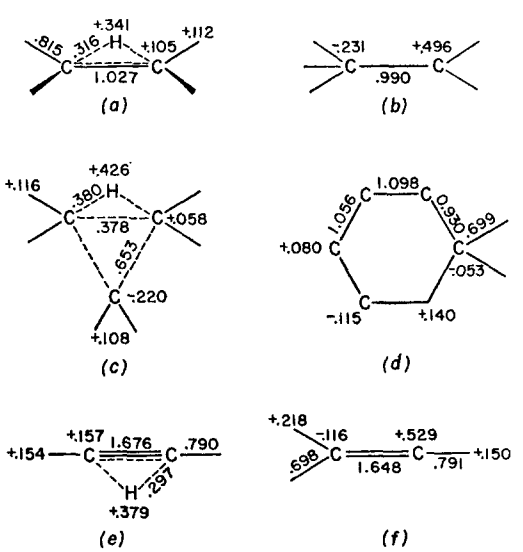


FIG. 4. Carbonium ions of protonated ethylene, acetylene, cyclopropane, benzene: (a) bridged symmetrical $C_2H_5^+$; (b) unsymmetrical $C_2H_5^+$; (c) bridged $C_3H_7^+$; (d) benzenium $C_6H_7^+$; (e) symmetrical $C_2H_3^+$; (f) unsymmetrical $C_2H_3^+$.

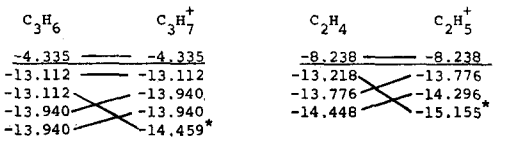


FIG. 5. Effect of bridging H on bonding and antibonding levels in $C_3H_7^+$ and $C_2H_5^+$. Energy levels below line are occupied. Individual levels below those listed are not affected significantly. Starred orbital is primarily the three-center bond.

tert-butyl central C is more positive than isopropyl, indicating that the methyl group is a better electron acceptor than H (but the reverse would be concluded from the methyl–ethyl pair!). The primary energy gain in the stabilization of the cations is in the step $RH \rightarrow R_{tetr}^+$, with what, for want of a better term, we may call hyperconjugative charge transfer away from the ionized site. Stabilization gained in the step $R_{tetr}^+ \rightarrow R_{trig}^+$ appears to be primarily steric in nature, since, as may be seen from Fig. 1, the ionized site is in general more positive for the trigonal cation. The total picture is not clear, but it appears that there are two effects operative, an inductive effect in which the methyl group is an electron acceptor, and a hyperconjugative effect in which methyl groups act as electron donors, and which operates only in the cation.

Some interesting phenomena may be noted in the population analysis. One is the significant increase in bond order between C^+ and its neighbors on going from RH to R_{tetr}^+ to R_{trig}^+. Another occurs only in R_{tetr}^+ and may be termed the "trans" effect. Thus in $C_2H_5^+$ the hydrogen *trans* to the hole acquires much more positive charge than other hydrogens. This is also true in the higher carbonium ions, where the presence of a carbon chain *trans* to the hole is associated with increased stability and charge delocalization. Finally, while there is practically no difference in energy or carbon charge between the two rotamers of trigonal $C_2H_5^+$, there is a difference in hydrogen populations, illustrated in Fig. 3. These results are in qualitative accord with conclusions regarding the conformational dependence of secondary deuterium isotope effects in solvolysis.[10]

It should also be noted that as far as hydrogens are concerned the calculation shows virtually no propagation of inductive effects, i.e., unless there is steric hindrance, hydrogen charges depend only on the atom to which H is bonded. Exceptions occur when the neighboring atom has a vacant *p* orbital. The conclusions of this section regarding the inductive effect of –H and $-CH_3$ are diametrically opposite to currently accepted ideas. The latter have been eminently successful in consistently correlating a vast body of chemical information. It remains to be seen if calculations of the type reported here can yield better results.

[10] V. J. Shiner, Jr., B. L. Murr, and G. Heinemann, J. Am. Chem. Soc. **85**, 2413 (1963); V. J. Shiner, Jr., and J. S. Humphrey, Jr., J. Am. Chem. Soc. **85**, 2416 (1963); V. J. Shiner, Jr., H. R. Mahler, R. H. Baker, Jr., and R. R. Hiatt, Ann. N. Y. Acad. Sci. **84**, 583 (1960).

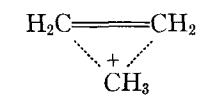
$C_2H_5^+$–ETHYL CATION OR PROTONATED ETHYLENE

This species has been viewed from two perspectives; first as an ethyl carbonium ion based on the ethane geometry, second as a protonated ethylene. If the ethane geometry is retained, but an H^- removed, $C_2H_5^+$ prefers the staggered conformation by an energy calculated as 2.0 kcal/mole. However, for the same C–C distance, the form of the carbonium ion planar at $-CH_2^+$ is favored over the staggered ethanelike conformation by a computed 24 kcal. In this trigonal form the barrier to internal rotation is sixfold and is calculated to be negligible (less than 0.001 kcal). The population analysis for the tetrahedral and trigonal forms may be seen in Fig. 1.

To study the protonated ethylene, we locate C_2H_4 in the xy plane with the y axis passing through the carbons. H^+ clearly prefers to approach the molecule along the z axis, reaching, according to my calculation, the configuration of minimum energy about 1.2 Å above the origin. The molecular diagram for this geometry may be found in Fig. 4; it is apparent that a three-center bond or alternatively, a π complex, is being formed. The way in which individual energy levels of ethylene are perturbed in this species is shown in Fig. 5. The symmetrical complex is a local minimum; it is stable with respect to motion of the bridge proton in the xy plane; however, there exists a more stable structure, corresponding to an unsymmetrical $CH_3CH_2^+$. Keeping C=C at 1.34 Å the difference between the bridge and the $CH_3CH_2^+$ structures is calculated as 2.0 kcal. The actual energy differences computed are suspect since no account has been made of C–C bond length distortion, nor can this reliably be made with this calculation. I have also not studied the combination of H^+ approach and $=CH_2$ deformation—there are too many degrees of freedom in the motion. Thus it has not been determined whether there is an activation energy in going from the symmetrical to the unsymmetrical structure. Nevertheless, I believe this calculation is the first theoretical confirmation of the organic chemists' concept of what happens in the primary stage of addition to the double bond. A more detailed study of this reaction, with substituents of varying electronegativity, is being contemplated.

$C_3H_7^+$–PROTONATED CYCLOPROPANE

A species of this composition is prominent in hydrocarbon mass spectra and there has been some speculation that it may involve a ring structure.[2d,11] This cation, or its derivatives, also merits consideration as a transition state in reactions involving 1, 3 hydride shifts. In this calculation a protonated cyclopropane is examined, carbon ring located in the xy plane, with origin at center of ring, and a carbon atom on the positive x axis. Testing several likely routes for the extra proton, while keeping the C_3H_6 geometry intact, it is found that the preferred approach is along the negative x axis, i.e., in the plane of the carbons and in the direction of the center of a C–C bond. The equilibrium position is reached 0.85 A from the bond center; the population analysis for this bridge bonded structure is illustrated in Fig. 4. With C–C distances fixed this form does not want to go over to the "ethylene alkonium ion",[12]



whose energy is calculated as 0.250 eV above the three-center structure. If C–C distances are allowed to vary, the protonated structure appears to be unstable with respect to ethylene and CH_3^+. The experimental evidence is not conclusive, but an analysis of the products of deamination of aminopropanes labeled with ^{14}C or deuterium[13,14] indicates that the transition state is not symmetrical or an "ethylene alkonium ion."

The distribution of electrons in cyclopropane itself has been an intriguing problem. Our calculations support to some extent the orbital picture of Walsh,[15] who suggested that one may obtain a simple view of cyclopropane bonding if one begins with an sp^2 hybrid set, the pure p orbital in the plane of the ring. A plot of the total electronic density distribution yields the very small angle of $7.5\pm1°$ between the C–C line and the point of maximum density on a line perpendicular to the C–C axis. The degenerate, highest occupied level pair is almost entirely composed of p orbitals in the carbon plane; since H^+ interacts primarily with the highest filled orbitals, it is not surprising that the most stable $C_3H_7^+$ has the proton located out from the center of a bond. The way in which the cyclopropane orbitals are perturbed by the proton bridge is indicated in Fig. 5.

$C_6H_7^+$–BENZENIUM CATION

This ion is exceedingly important as the prototype of intermediates in aromatic substitution. Benzene was placed in the xy plane with the x axis passing through two carbons, origin in center of ring. A proton was then brought close to the ring along, respectively the x, y, and z axes. The *least* favorable direction was that in which a symmetrical approach was made along the z axis. The best approach was along the x axis, i.e., onto a C–H. In this case, however, we encountered the failure of the method mentioned in the introductory section, i.e., the energy minimum resulted for intruding H^+ and ring H both on the x axis and separated by only 0.3 Å. If this unrealistic minimum due to an underestimation

[11] P. N. Rylander and S. Meyerson, J. Am. Chem. Soc. **78,** 5799 (1956).

[12] J. D. Roberts and M. Halmann, J. Am. Chem. Soc. **75,** 5759 (1953) and references therein.

[13] O. A. Reutov and T. N. Shatkina, Tetrahedron **18,** 237 (1962).

[14] G. J. Karabatsos and C. E. Orzech, Jr., J. Am. Chem. Soc. **84,** 2838 (1962).

[15] A. D. Walsh, Trans. Faraday Soc. **49,** 179 (1949).

of short-range repulsions is discounted, another minimum occurs for the geometry generally ascribed to the benzenium cation, i.e., two hydrogens, out-of-plane, both symmetrically bonded to a ring carbon. In our calculation the minimum occurs for an HCH angle of 100°, with the populations shown in Fig. 4. The charge distribution agrees qualitatively with that expected from a resonance argument and with the calculations of Pickett *et al.*[16]

$C_2H_3^+$–PROTONATED ACETYLENE

This calculation ran into the same difficulties as $C_6H_7^+$. For C_2H_2 located on the x axis, an approach by H^+ along x leads to an equilibrium position with the two hydrogens very close to each other. If this situation is set aside, a similarity to $C_2H_5^+$ is noted. The cylindrically symmetrical favored approach is along y, with a local minimum about 1.2 Å from the x axis. If the acetylene hydrogens are allowed to distort, a more stable unsymmetrical C_{2v} form is preferred. The population analysis for this geometry, as well as for the form at the local minimum, is illustrated in Fig. 4.

$C_4H_7^+$–CYCLOPROPYL CARBINYL CATION

The molecule considered here is the classical carbonium ion of methyl cyclopropane. The species is of particular interest in a study of the orientation of the trigonal carbonium grouping in various environments since cyclopropane is somewhat set apart from other saturated species in its electronic distribution. We have alluded to this in the section on $C_3H_7^+$, and if the Walsh representation is valid, the carbonium ion should prefer to orient itself so that $-CH_2^+$ and the tertiary hydrogen are coplanar. In this way maximum π overlap is achieved between the carbonium p orbital and the π-like top filled orbitals of cyclopropane. This is indeed confirmed by this calculation, which studied orientations of the $-CH_2^+$ group 0, 30, 60, and 90 degrees removed from coplanarity. 0° is preferred to 90° by 0.384 eV. While this energy is no doubt too large, the orientation is certainly significant, in view of the fact that the $CH_3CH_2^+$ barrier is negligible and that methyl cyclopropane itself definitely prefers a staggered conformation. The population analysis confirms that in the 0° form a stabilizing interaction takes place:

	Charges			Overlap populations		
	1	2	4	1–4	1–2	2–3
0°	+0.082	−0.095	+0.271	0.956	0.569	0.681
90°	+0.013	−0.188	+0.482	0.872	0.637	0.606
methyl cyclopropane	−0.038	−0.245	−0.374	0.730	0.655	0.621.

The exocyclic C–C distance is 1.54 Å in methyl cyclopropane, 1.50 Å in cyclopropyl carbinyl, so that the comparison is not precise—nevertheless it is obvious that the 90° form is more "normal."

Some calculations were made for a "tricyclobutonium ion"[17] in the geometry of a C–H$^+$ sitting at various distances on the threefold axis of cyclopropane. No minimum at all was found for this form; moreover for C$^+$ less than 2.5 Å above center of ring the molecule has an orbitally degenerate ground state. The bicyclobutonium ions appear to be too unsymmetrical to be reliably studied by this method.

In view of the surprisingly large $C_4H_7^+$ barrier, larger cyclic carbinyls were investigated. The following energy differences between the 90° and 0° rotamers were calculated

cyclobutylcarbinyl	−0.088
cyclopentyl (planar)	+0.058
cyclohexyl (equatorial)	+0.022.

Compared with cyclopropyl (+0.384) and allyl (+0.253, next section) these are small, emphasizing the peculiarity of cyclopropane. I have no explanation as to why cyclobutylcarbinyl prefers the 90° form; in this geometry there is considerable 1,4 charge transfer as well as 1,3. Axial cyclohexyl carbinyl also prefers the 90° geometry, but this is understandable since at 0° steric difficulties are maximized. The axial–equatorial difference between the most stable rotamers is 0.118 eV, significantly less than that computed for methyl cyclohexane in I.

$C_3H_5^+$–ALLYL CATION

This model chosen initially was an unsymmetrical one, consisting of a $-CH_2$ 1.50 Å removed from an ethylene with C=C 1.34 Å. The planar conformation was most stable, with a calculated advantage over the perpendicular form of 0.253 eV. The molecular diagram is shown in Fig. 6. Again stabilization occurred along with positive charge transfer into the ethylene moiety; sample charges in the perpendicular form being −0.292, +0.033, and +0.612 at Positions 1, 2, and 3, respectively. A symmetrical cation, with C–C 1.40 Å possesses the charge distribution shown in Fig. 6.

$C_7H_7^+$–BENZYL CATION

A model was constructed with ring distances of 1.40 Å, exocyclic C–C 1.50 Å. The planar form emerged 0.300 eV

[16] L. W. Pickett, N. Muller, and R. S. Mulliken, J. Chem. Phys. **21**, 1400 (1953).

[17] R. H. Mazur, W. N. White, D. A. Semenov, C. C. Lee, M. S. Silver, and J. D. Roberts, J. Am. Chem. Soc. **81**, 4390 (1959) and references therein.

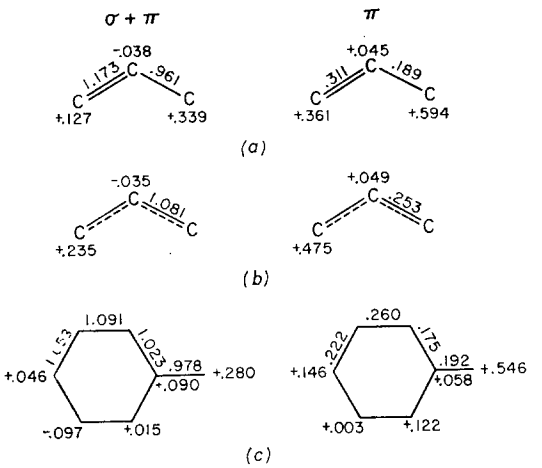


FIG. 6. Total and π charge distributions in (a) unsymmetrical allyl, (b) symmetrical allyl, and (c) planar benzyl.

more stable than that with ring and $-CH_2$ forming perpendicular planes. The results of the population analysis are shown in Fig. 6 for the planar conformation; the charge distribution for the π system agrees well with that computed by simple Hückel theory. Stabilization in this case, as in $C_4H_7^+$ and $C_3H_5^+$, is accompanied by the assumption of the most favorable π overlap geometry and the movement of positive charge into the benzene ring. For comparison the perpendicular form has charges of +0.144, −0.084, −0.088, −0.128, and +0.547 at Positions 1, 2, 3, 4, and 7 respectively.

$C_7H_{11}^+$, $C_7H_9^+$, AND $C_7H_7^+$: IONS BASED ON THE BICYCLO[2.2.1]HEPTANE STRUCTURE

The cations of norbornane, norbornene, and norbornadiene have been the subject of much speculation.[2b,c,18,19]

TABLE II. Calculated energies of norbornane, norbornene, norbornadiene, cyclohexane, and their cations. In the case of epimers, the label refers to the "hole."

Molecule		$-E$
norbornane		693.871
norbornyl	2(planar)	665.953
	7(planar)	665.362
	2(exo)	665.081
	2(endo)	664.769
	7(tetrahedral)	664.390
norbornene		660.550
norbornenyl	5(planar)	632.463
	7(planar)	632.076
	7(anti)	631.238
	7(syn)	631.068
	5(endo)	631.406
	5(exo)	631.470
norbornadiene		626.999
norbornadienyl	7(planar)	598.571
	7(tetrahedral)	597.682
cyclohexane		625.463
cyclohexyl	(axial)	596.057
	(equatorial)	596.374

[18] H. C. Brown and H. M. Bell, J. Am Chem. Soc. **85,** 2324 (1963); S. Winstein, A. H. Lewin, and K. C. Panda, J. Am. Chem. Soc. **85,** 2325 (1963).

[19] E. J. Corey, J. Casanova, Jr., P. A. Vatikencherry, and R. Winter, J. Am. Chem. Soc. **85,** 169 (1963).

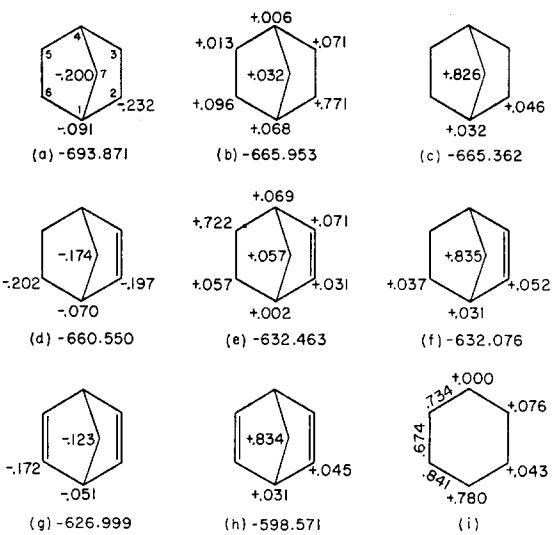


FIG. 7. Charge distributions in ions based on bicyclo[2.2.1] heptane; (a) norbornane, (b) 2-norbornyl, (c) 7-norbornyl, (d) norbornene, (e) 5-norbornenyl, (f) 7-norbornenyl, (g) norbornadiene, (h) 7-norbornadienyl, (i) cyclohexyl. The charge distributions illustrated for (b), (c), (e), (f), (h), and (i) are differences between the parent hydrocarbon and the cation.

My method of calculation is not sufficiently reliable that much can be safely concluded from comparisons of structures differing in many degrees of freedom, such as the extremes forwarded in the nonclassical carbonium ion controversy.[18] Rather the procedure will be adopted of viewing the cations as classical, but looking in the resultant electron distribution for one nonclassical feature, namely unusual delocalization. The species studied were the neutral molecules mentioned above, the epimeric tetrahedral and trigonal forms[20] of the 2- and 7-norbornyl, 5- and 7-norbornenyl, and 7-norbornadienyl cations [the numbering system is shown in Fig. 7(a)]. For the last two, one symmetric distortion of C_7 from the classical position was examined.

The charge distributions of the parent hydrocarbons and the trigonal ions are indicated in Fig. 7. For the ions, the numbers shown are *differences* in charge between the neutral molecule and the cation. In Table II

TABLE III. Population analyses for *n*-propyl carbinyl cation.

	0°	30°	60°	90°
E	−423.435	−423.420	−423.384	−423.363
$Q(1)$	+0.524	+0.524	+0.523	+0.522
$Q(2)$	−0.108	−0.115	−0.131	−0.139
$Q(3)$	−0.195	−0.169	−0.114	−0.086
$Q(4)$	−0.370	−0.366	−0.358	−0.353
$n(1-2)$	0.862	0.857	0.847	0.841
$n(2-3)$	0.730	0.710	0.668	0.645
$n(3-4)$	0.703	0.702	0.702	0.701

[20] The coordinates of C. F. Wilcox, Jr., J. Am. Chem. Soc. **82,** 414 (1960) were used for norbornane, with hydrogens at RCH_2R' placed symmetrically in the plane bisecting RCR′ and perpendicular to it, with tetrahedral HCH angles. For norbornene and norbornadiene a model was constructed with C_2–C_3 1.34 Å, and both atoms in the original norbornane plane. The hydrogens in the carbonium ions were placed in the RCR′ plane and radially out from the midpoint of the line joining C_1 and C_4.

calculated energies are listed, and a comparison with experimental solvolysis reactivities[20] shows that for the three epimeric pairs the reactivities are correlated with the relative stabilities of the tetrahedral carbonium ions.[21] If all the ions are compared on an absolute scale by taking as a measure of stability the difference in energy between the hydrocarbon and the cation, the anti-7-norbornenyl and 7-norbornadienyl ions do not emerge as particularly stable. This contrast with their experimental reactivity, hinting at unusual behavior, is exposed below.

For all of the ions excess stability is paralleled by the ability to transfer charge away from the ionized site. To judge whether unusual nonbonded charge transfer is taking place, a comparison standard for "normal" 1,3 charge delocalization is needed. To this end I have carried out calculations on the carbonium ions of *n*-propyl carbinyl and the 4-carbonium ion of butene-1. For the former, an extended staggered *n*-propyl chain was assumed and various orientations of $-CH_2^+$ were studied. The orientation is specified by the angle between the $-CH_2$ plane and the plane of the carbon chain. The population analysis is shown in Table III. The coplanar form is preferred and corresponds to maximum 1–2 and minimum 1–3 charge transfer (compare with charge distribution in *n*-butane). The 90° geometry involves the greatest 1–3 (and 1,4) interaction, as would be expected from the favorable orientation of the carbonium *p* orbital. The norbornane and cyclohexane calculations are consistent with this effect; an examination of models indicates that cyclohexane corresponds to an angle of 60°; 2-norbornyl to rough angles of 0°, 90°, and 45° with respect to Sites 4, 6, and 7; and approximately 60° with respect to Site 2 in 7-norbornyl.

The conformational problems in a molecule containing a carbonium ion 1,3 to a double bond are complicated. Sixteen conformations were studied for the model compound, the 4-carbonium ion of butene-1: two possible orientations, eclipsed and staggered, of the C_3 hydrogens with respect to C_1=C_2; two choices for the location of C_4, *exo* or *endo*, for each of the above, and four rotamers at the ionized site, i.e., plane of $-CH_2^+$ 0°, 30°, 60°, and 90° relative to plane containing C_2, C_3, and C_4. As for butene-1,[4] the most stable conformation was nonplanar, eclipsed, *exo*, and as for *n*-propyl carbinyl, with CH_2^+ coplanar with C_2, C_3, and C_4. There was some evidence of increased stabilization of *endo* forms with a favorably oriented carbinyl group, but steric considerations dominated. Charge transfer from 4 to 3 and 4 to 2 as a function of orientation was similar to that in *n*-propyl carbinyl, but that from 4 to 1 was more variable. It should be noted that all these calculations are for unstrained conformations and that the problem of stability and charge transfer in strained compounds is much more complicated.

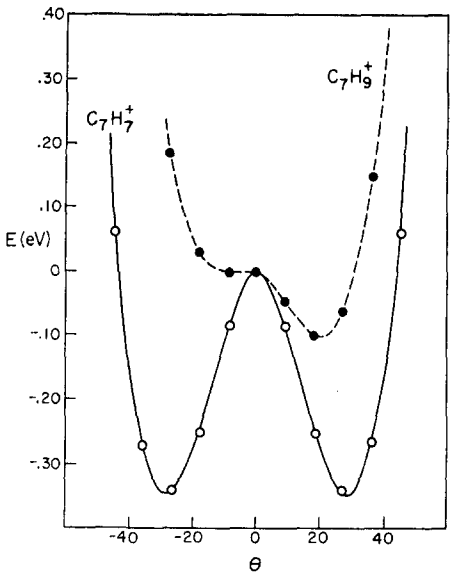


FIG. 8. Potential energy curves for distortion of C_7 in 7-norbornenyl and 7-norbornadienyl.

Returning to the trigonal cations of the bicyclic compounds, we see that charge transfer is limited in (f) and (h) of Fig. 7, while significant in the 6 position of (b) and 3 of (e). All of this is consistent with the conclusions of the above paragraph. It should be noted that the problem of where the hydrogens really are in (b) was not attacked, but the reader is referred to the section on $C_3H_7^+$.

For norbornene, 7-norbornenyl, norbornadiene, and 7-norbornadienyl I have also investigated distortions in which C_7 is moved on an arc in the plane bisecting C_2–C_3 and C_5–C_6, constrained by keeping C_1–C_7 and C_4–C_7 at 1.54 Å. The examination of this distortion was prompted by the study of Story and Saunders[22] which indicated asymmetry. The deformation is measured by the angle of deviation θ from the symmetric form. Norbornene and norbornadiene prefer $\theta \approx 0°$. The calculated potential curves for the 7-cations, shown in Fig. 8, confirm the conclusions of Story and Saunders. 7-norbornadienyl, a most amazing ion which does not take full advantage of the symmetry offered to it, clearly deserves to be called nonclassical. Distortion and stabilization are correlated with improved charge transfer; for example, the following relative charge distributions are obtained (compare with Fig. 7):

	1	2	5	7
7-norbornenyl (θ=18.5°)	+0.036	+0.168	+0.001	+0.660
7-norbornadienyl (θ=27°)	+0.046	+0.213	−0.010	+0.568.

[21] In the case of cyclohexyl, *cis*-4-*t*-butylcyclohexyl tosylate is solvolyzed faster than the *trans* epimer [S. Winstein and N. J. Holness, J. Am. Chem. Soc. **77**, 5562 (1955)], contrary to the calculated trend. However, this may be due to the domination of the conformational energy difference. The calculated energy difference should be considered only qualitative, see Ref. 4.

[22] P. R. Story, M. Saunders, J. Am. Chem. Soc. **84**, 4876 (1962).

At the 7-norbornadienyl minimum ($\theta \approx 30°$) C_7–C_2 is less than 2.0 Å and a positive overlap population is developing. It was felt that the method was not sufficiently reliable to allow the study of distortions parallel to C_1–C_4.

A $C_7H_7^+$ formed from a C–H on the sixfold axis of a benzene ring was also studied.[23] No minimum was found and for short distances this geometry did not yield a closed-shell molecule.

In conclusion, it seems to me that the reactivity of these bicyclic compounds is determined by two factors: (1) the stability of the incipient classical carbonium ion, which is correlated to the ability to transfer charge to other sites in the molecule; the extent of such charge transfer is considerable, (2) the additional stabilization (and charge transfer) gained from an unusual deformation such as that studied for 7-norbornadienyl.

Note added in proof: A further discussion of nonclassical carbonium ions in the norbornene and bicyclo[3.1.0]hexane systems may be found in R. Hoffmann, J. Am. Chem. Soc. (to be published). With respect to theoretical calculations on alkyl carbonium ions, mention should have been made of the work of N. Muller and R. S. Mulliken, J. Am. Chem. Soc., **80,** 3489 (1958), who obtained excellent agreement with the experimental stabilities of these ions using a hyperconjugation method.

ACKNOWLEDGMENTS

I would like to thank E. J. Corey for making me aware of some of the problems in this field and for many valuable discussions. This work was supported by a research grant from the National Institutes of Health,

[23] S. Winstein and C. Ordronneau, J. Am. Chem. Soc. **82,** 2084 (1960).

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Threshold Laws for Processes of Autoionization

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An examination is made of some new data obtained by photon and electron impact, in an attempt to determine more accurately the threshold laws for processes of autoionization. In the cases of Kr and Xe, it is found that marked interference can occur between the two competing processes of direct and autoionization. The results, and also some of the apparently anomalous ionization efficiency data obtained by electron impact for several of the metals, can be interpreted in terms of configuration-interaction phenomena involving excited states of very short lifetimes.

INTRODUCTION

IN two earlier papers,[1,2] an examination was made of processes of excitation induced by electron and photon impact, for cases where the products become subsequently ionized, and hence detectable in a mass spectrometer.

The results of this work suggested that to a degree of resolution of 0.05 eV, the threshold laws governing such processes were indistinguishable from a step function and a δ function, respectively, of the energy of the existing particle.[3]

A very simple statistical model, due to Wannier[4], accounted for the threshold behavior of n-fold ionization processes very well. In this model, the interaction between the charged particles leaving the collision complex was neglected. An earlier, more elaborate treatment by the same author,[5] in which an attempt was made to include the effect of this interaction, proved much less satisfactory.

This simple model can be extended to deal with the threshold behavior of excitation processes, and would predict a step function and a δ function for electron and photon impact, respectively. This agreement with the earlier experiments was surprising, because in these processes, the force field operating is no longer of simple Coulomb type. If it is allowable to neglect in this way the interaction of the product particles, it might be

[1] F. H. Dorman, J. D. Morrison, and A. J. C. Nicholson, J. Chem. Phys. **32,** 378 (1960).

[2] J. D. Morrison, H. Hürzeler, M. G. Inghram, and H. E. Stanton, J. Chem. Phys. **33,** 821 (1960).

[3] For the purposes of this paper, a curve is regarded as indistinguishable from a δ function or a step function if it or its first differential with respect to the energy, respectively, has appreciable value at only one point on the energy scale, and has fallen to one-tenth of this value at 0.05 eV on both sides of this point.

[4] G. H. Wannier, Phys. Rev. **100,** 1180 (1956).

[5] G. H. Wannier, Phys. Rev. **90,** 817 (1953).