which is just the unsymmetrical limit of the $[2_s + 1_s]$ interaction. With moderate donor dienes (D), cyclobutanones are formed, but with a strongly donating diene, the $[2_s{}^D + 2_a{}^K]$ interaction is too feeble to compete with a $[4_s{}^D + 2_s{}^K]$ interaction leading to a Diels–Alder reaction at the carbonyl group.[71]

If a diene were sufficiently electron-deficient relative to a ketene, then the out-of-plane ketene HOMO should prompt behavior like that of a typical, slightly electron-rich, dienophile; that is, a concerted Diels–Alder reaction with "inverse electron demand" should occur at the CC bond of ketene. While this behavior is observed with α,β-unsaturated ketones,[72] extensive tests of this prediction have not been carried out. Finally, with very electron-deficient alkenes, the $[1_s + 1_s]$ interaction involving the ketene HOMO and ketenophile LUMO will determine control of the initial bonding interaction, and formation of a cyclobutanone *via* a dipolar intermediate is predicted.[27] Figure 9 shows this rich mixture of rationalization and prediction. We have applied similar arguments to other cumulene reactions.[27]

Conclusions

Through an understanding of the properties of the frontier molecular orbitals of unsaturated species, it has become possible to rationalize or predict the facility of a reaction between two addends, the favored geometry of approach, and the products of the reaction. **Violations**—there are some! But the theory is capable of refinement through inclusion of extrafrontier interactions and steric and coulombic effects, as well as through the input of quantitative experimental data about unsaturated systems. These refinements, as well as the applications of these principles to the design of new reactions and the synthesis of old molecules by new tricks, are the directions in which our research is progressing.

(71) J. P. Gouesnard, *Tetrahedron*, **30**, 3113 (1974), and references therein.

(72) H. Ulrich, "Cycloaddition Reactions of Heterocumulenes", Academic Press, New York, N.Y., 1967.

# Theoretical Approaches to the Structure of Carbocations

Warren J. Hehre[1]

Department of Chemistry, University of California, Irvine, California 92664

Among the most impressive accomplishments in organic chemistry during the last decade has been the development of a variety of experimental tactics for the direct observation of reactive carbocation intermediates in solution.[2] The pioneering systematic efforts of Olah and his coworkers have resulted in a multitude of NMR, vibrational ir, and Raman and ESCA spectroscopic data on literally hundreds of carbon-containing ions under stable long-lived conditions in superacid media. Despite this flourish of activity, however, the detailed geometrical structure of not a single such ion is known to date. Consider the case of the *tert*-butyl cation. Here the ^1H and ^{13}C NMR spectra[3,4] depict the obvious structure, one with two different kinds of carbon atom, but—on the time scale of the experiment—with all hydrogens equivalent. The ESCA measurements,[5] of the carbon inner-shell shieldings, concur fully. Interpretation of the ir and Raman data[6] suggests parallels with the corresponding spectra of isoelectronic trimethylborane, leading to the assignment of a planar (or nearly planar) carbon skelton for the *tert*-butyl cation. In addition, evidence based on vibrational selection rules seems to favor an ion of C_{3v} symmetry (Ia) rather than a propeller-shaped, C_{3h} symmetry, form (Ib). Other methyl group arrangements, leading to lower overall symmetry, are certainly possible but were not considered in the analysis.

Ia   Ib
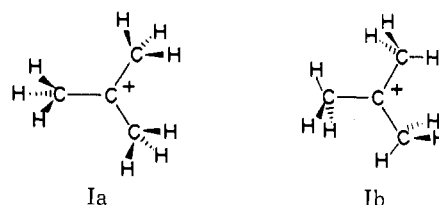
(2) G. A. Olah, *Angew. Chem., Int. Ed. Engl.*, **12**, 173 (1973).

(3) G. A. Olah, E. B. Baker, T. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and I. J. Bastien, *J. Am. Chem. Soc.*, **86**, 1360 (1964).

(4) G. A. Olah and A. M. White, *J. Am. Chem. Soc.*, **91**, 5801 (1969).

(5) G. A. Olah, G. D. Mateescu, L. A. Wilson, and M. H. Gross, *J. Am. Chem. Soc.*, **92**, 7231 (1970).

(6) G. A. Olah, A. Commeyras, J. DeMember, and J. L. Bribes, *J. Am. Chem. Soc.*, **93**, 459 (1971).

Warren J. Hehre received his BA degree from Cornell University in 1967 where he studied under Roald Hoffmann, and his Ph.D. from Carnegie–Mellon University in 1971 with John Pople. After spending 2 years in Lionel Salem's lab at the University of Paris he joined the faculty of the University of California, Irvine. His research interests center around the development of simple molecular orbital methods and their application to problems of chemical structure and energetics.
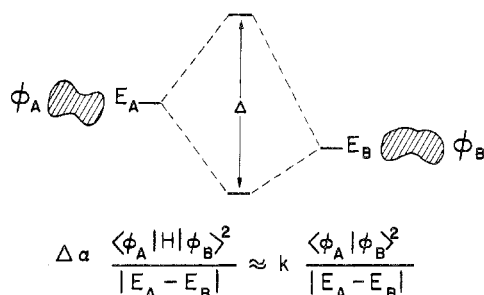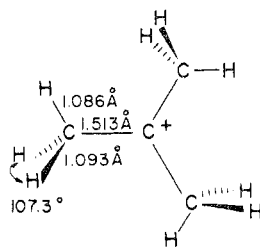
Figure 1. Energy levels split as a result of interaction.

Figure 2. Geometrical consequences of charge transfer.

It would seem, then, that while the gross structural features and overall symmetry of metastable species such as the *tert*-butyl cation are amenable to experimental characterization, details of molecular geometry (bond lengths and bond angles) are not. Lacking such quantitative information from direct observation, we turn to theory, in particular the molecular orbital theory which has itself undergone impressive development in recent years. Indeed, simple ab initio schemes have now advanced to a point where a priori calculations of the geometrical structure of small organic molecules and ions (up to, say, ten heavy atoms) may be performed routinely. More important, it is now well established that even minimal basis set theories, as, for example, the STO-3G method,[7] are quite capable of supplying details of molecular structure to a high enough degree of accuracy so as to be quantitatively useful. For example, mean deviations from experiment of STO-3G calculated equilibrium bond lengths and bond angles in the set of neutral hydrocarbons containing up to four heavy atoms are only $\simeq$0.02 Å and $\simeq$2°, respectively.[8] Similar but slightly larger errors have been reported for the much more extensive set of one and two heavy-atom molecules containing first-row heteroatoms.[9]

The theoretical STO-3G structure of the *tert*-butyl cation, in its predicted C_{3h} symmetry equilibrium conformation,[10] shows a number of interesting features. Most conspicuous, perhaps, is a shortening of

the C–C linkages from "normal" single-bond values (1.541 Å in propane[8b] at the STO-3G level, 1.520 Å in propene[8b]). While the six out-of-plane methyl C–H bonds have lengthened from the usual values (1.086 and 1.085 Å in propane and propene, respectively),

the in-plane set of three remain as expected. Finally, a curious angular distortion has occurred in the individual methyl groups, resulting mainly in the bending of the two out-of-plane CH's toward one another.

All of these structural features might easily have been anticipated with the aid of simple perturbation theoretic arguments.[11] Recall that, upon interaction, energy levels split, and the magnitude of the splitting, Δ, is given by perturbation theory to second order as proportional to the square of the matrix element between them and inversely so to their energy separation (Figure 1). Not knowing the detailed form of the perturbation Hamiltonian, we replace the matrix element in the numerator by a simple overlap expression involving the two interacting fragments. From the diagram it is apparent that, if in total two electrons are involved in the interaction (either by one of the two levels being filled and the other empty or both being singly occupied), net stabilization results. On the other hand, if both interacting levels are fully populated, energetic destabilization follows. (This is akin to the repulsion experienced between approaching helium atoms and the resultant instability of the He$_2$ molecule.)

Accompanying energetic stabilization resulting from the interaction of filled and empty orbitals is a net transfer of charge. This gives rise to a number of interesting structural consequences, illustrated in Figure 2 for the special case of the donor or acceptor molecular orbital being delocalized over a diatomic fragment. Withdrawal of electrons from an orbital which is bonding between the two centers A and B results in elongation of the linkage connecting them. Correspondingly, donation into an unfilled function of the same character leads to shortening of the A–B bond. On the other hand, the AB linkage tightens in response to charge removal from an antibonding molecular orbital and lengthens if electrons are forced into a function of such character.

Consider those geometrical consequences commensurate with the stabilizing two-electron interaction between the empty p lobe on the carbonium center and the occupied π symmetry orbital on methyl (right-hand side of Figure 3). Here electrons are delocalized away from the methyl group and into the region connecting the two carbon centers, effecting the observed shortening. We pay a price for this new "hyperconjugative" linkage in that bonding electron density is removed from two of the methyl group C–H linkages, resulting in their lengthening. A further consequence of electron displacement from methyl is that the nonbonded repulsive interaction

(7) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969). All theoretical structures and energy differences discussed herein are derived from calculations at the STO-3G level.

(8) (a) W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Am. Chem. Soc.*, **93**, 808 (1971); (b) L. Radom, W. A. Lathan, W. J. Hehre, and J. A. Pople, *ibid.*, **93**, 5339 (1971); (c) W. J. Hehre and J. A. Pople, *ibid.*, in press.

(9) (a) W. A. Lathan, W. J. Hehre, L. A. Curtiss, and J. A. Pople, *J. Am. Chem. Soc.*, **93**, 6377 (1971); (b) W. A. Lathan, L. A. Curtiss, W. J. Hehre, J. B. Lisle, and J. A. Pople, *Prog. Phys. Org. Chem.*, **11**, 175 (1974).

(10) L. Radom, J. A. Pople, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **94**, 5935 (1972). These authors suggest that the C_{3v} form lies 1.4 kcal/mol higher in energy.
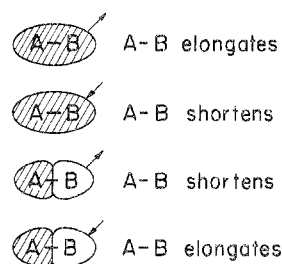
(11) For vivid discussions of the general approach see: (a) R. Hoffmann, *Acc. Chem. Res.*, **4**, 1 (1971); (b) W. L. Jorgensen and L. Salem, "The Organic Chemist's Book of Orbitals", Academic Press, New York, N.Y., 1973.
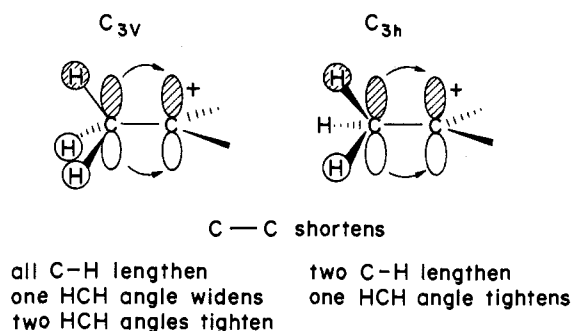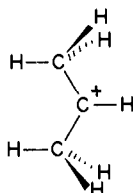
C — C shortens

all C-H lengthen	two C-H lengthen
one HCH angle widens	one HCH angle tightens
two HCH angles tighten	

Figure 3. Changes in geometry arising from the interaction of a methyl group and the empty p orbital at a carbonium center.

between these out-of-plane hydrogens is diminished, leading to the calculated reduction in HCH bond angle. Throughout all this the third, in-plane, carbon–hydrogen bond remains unaffected, for it is not involved in the methyl group orbital from which electrons are withdrawn. Similar arguments may be used to predict the qualitative structural features of the *tert*-butyl cation in its C_{3v} symmetry form (left-hand side of Figure 3).

Whereas the prediction of a propeller-shaped ground-state conformation for the *tert*-butyl cation (contrary to Olah's ir and Raman assignments[6]) is not particularly surprising in terms of minimizing steric repulsions between neighboring methyl groups, what is somewhat unexpected is the preferred arrangement of the two methyls in the secondary isopropyl system.[12] Here the pair of in-plane methyl hydrogens point toward one another, quite the opposite tendency than that displayed in the known geometrical structures of molecules such as propane, dimeth-


ylamine, and dimethyl ether and of propene and acetone. In the ground-state conformations of these molecules, one might be tempted to visualize the possibility of overlap between the two pairs of out-of-plane methyl hydrogens leading to the formation of a


X = CH₂, NH, O   X = CH₂, O
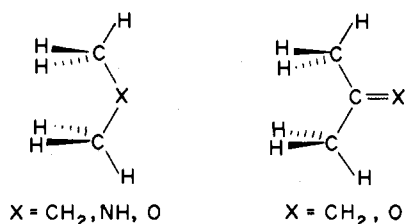
π-electron cycle. As each methyl rotor supplies two electrons to the total, the overall character of the ring is determined by the contribution of the central grouping. If this contribution approaches two electrons, then the cycle will be overall 6π electron and "aromatic". This is the case for the neutral molecules noted above. The situation is entirely different for

(12) D. Cremer, J. S. Binkley, J. A. Pople, and W. J. Hehre, *J. Am. Chem. Soc.*, **96**, 6900 (1974).
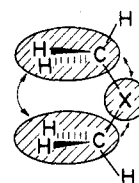
the isopropyl cation where the carbonium center makes no contribution of electrons to the cycle. We are left then with the possibility of a 4π-electron "antiaromatic" arrangement, a sufficient cause for the methyl groups to rotate into a conformation where substantial overlap is no longer possible.
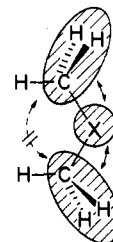
Rotation of a single methyl rotor away from an eclipsed position would also serve to limit the unfavorable interaction, thus providing the likely rationale behind the calculated ground-state conformation for the *tert*-butyl cation. It is, of course, possible
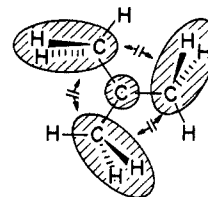
to rationalize the isopropyl cation structure simply by stating that methyl groups prefer to stagger adjacent CH bonds more than they do carbon–carbon linkages. Similarly, the difference in conformational preference between the isopropyl cation and, say, propene is easily accommodated if one is willing to consider the unsaturated linkage as a "banana" bond. This author finds this sort of reasoning unrewarding.

Note that in addition to speculations regarding the equilibrium conformation of the isopropyl cation, the simple model also leads naturally to a number of qualitative statements regarding the rotational barriers of molecules where experimental probes have been possible. For example, because the number of electrons localized on the central carbon in the vinylic systems (CH₃)₂C=X decreases in going from isobutylene to acetone to the dimethylfluorocarbonium ion, one would expect a corresponding decrease in preference for a ground-state eclipsed conformation. Indeed, methyl torsion in acetone[13a] is known experimentally to be more facile than in isobutylene[13b] (0.78 vs. 2.21 kcal/mol), whereas the fluorine-substituted ion is predicted by the quantitative ab initio calculations to exhibit very little conformational preference at all.[13c,d] In all of these unsaturated mol-

(13) (a) R. Nelson and L. Pierce, *J. Mol. Spectrosc.*, **18**, 344 (1965); (b) V. W. Laurie, *J. Chem. Phys.*, **34**, 1516 (1961); (c) W. J. Hehre and P. C. Hiberty, *J. Am. Chem. Soc.*, **96**, 2665 (1974); (d) W. J. Hehre, J. A. Pople, and A. J. P. Devaquet, *ibid.*, in press; (e) P. H. Kasai and R. F. Myers, *J. Phys. Soc. Jpn.*, **30**, 1096 (1959); (f) E. Hirota, C. Matsumura, and Y. Morino, *Bull. Chem. Soc. Jpn.*, **40**, 1124 (1967); (j) V. W. Laurie and J. Wollrab, *Bull. Am. Phys. Soc.*, 327 (1963).

Table I

Conformations of Double Rotor Molecules CH_3-X-CH_3

Contribution of X to the cycle	Overall character of cycle	Preferred conformation of methyl groups	Examples
0 electrons	Antiaromatic	"Staggered"	$(CH_3)_2CH^+$
	Nonaromatic		$(CH_3)_2CF^+$
			$(CH_3)_2C=O$
			$(CH_3)_2C=CH_2$
2 electrons	Aromatic	"Eclipsed"	$(CH_3)_2CH_2$

ecules the π population of the central carbon is never much greater than a single electron (i.e., the charge density is delocalized over two centers). We might expect, therefore, an even greater preference for an eclipsed arrangement in molecules such as propane, dimethylamine, and dimethyl ether, where both π electrons are localized at the central atom. Indeed, rotational barriers here range from 2.72 kcal/mol for dimethyl ether[13e] to 3.33 kcal/mol for propane,[13f] with that in dimethylamine falling midway in between[13f] (3.20 kcal/mol). A summary is presented in Table I.

It is in dealing with questions of structure of primary ions that theory may be of greatest use. Here, more than anywhere else, unambiguous experimental characterization has been severely impeded, due in part to the proclivity of these systems to undergo facile intramolecular rearrangement. Perhaps the simplest is the case involving interaction between a heteroatom lone pair and the vacant p orbital of a carbonium center. The delocalization of electrons which results (away from the former and into a bonding π symmetry orbital connecting the two sites) leads to a
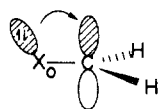

shortening of the carbon–heteroatom linkage from a normal single bond value. Thus, the crystal structure of the perchlorate salt of *N,N*-dimethylisopropylideniminium—$(CH_3)_2C=N(CH_3)_2{}^+$—shows a carbon–nitrogen bond length of 1.30 Å,[14] far removed from that of a single linkage (1.48 Å in methylamine at the STO-3G level[9b]) and, in fact, very close to what one would expect of a full carbon–nitrogen double bond (i.e., 1.27 Å in formaldimine[9b]). The theoretical calculations, on $^+CH_2NH_2$, concur, suggesting a bond length of 1.29 Å[9b] (Figure 4). The calculations also show the lone pair on oxygen to be highly delocalized on account of interaction with the carbonium center, but percentagewise, at least, the resulting bond shrinkage is not as prominent. Contraction of the normal carbon–fluorine linkage as a result of n electron delocalization appears also to be significant, but is of lesser magnitude than the effects noted in the nitrogen and oxygen systems. We may easily un-

derstand the observed ordering of bond length contractions, $NH_2 > OH > F$, by again invoking the results of the simple perturbation treatment of interacting orbitals. Stabilization resulting from the union of the filled (heteroatom lone pair) and empty (carbonium center) orbitals is, recall, inversely proportional to their energy separation. This gap is, of course, smallest in the case of amino substitution (lowest lone-pair ionization potential[15]) and largest when the substituent is fluorine.

In the above examples the only geometrical consequence of significance was the formation of a new bond between the interacting fragments. Because the electrons used in its construction were drawn from lone-pair orbitals with little or no bonding character of their own, secondary geometrical effects, that is, those within the donor grouping itself, are not expected to be important. Electron withdrawal from an orbital which is bonding or antibonding with respect to its local environment would, however, be expected to lead to interesting secondary consequences. Thus, charge donation from the π system of ethylene into a vacant carbonium center results not only in a new linkage being formed between the two fragments but also in a weakening (and hence lengthening) of the original double bond. What results, of course, is the suggestion of the symmetrical nature of the allyl cation, a contention which is well borne out by quantitative theory.[16]
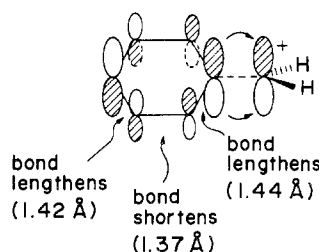
Allyl cation

bond lengthens (1.39 Å)
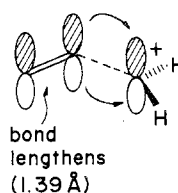
Ethylene $r(C=C) = 1.31$ Å

A far less trivial example is the geometric reorganization which accompanies interaction of a carbonium center and a phenyl ring, leading to the formation of a benzyl cation. Here, electrons are removed from an orbital which is bonding between the ipso and ortho ring positions, and between meta and para positions, but antibonding between ortho and meta sites. While four of the ring bonds lengthen as a direct result, the other two (connecting ortho and meta carbons) actu-

Benzyl cation

bond lengthens (1.42 Å)   bond shortens (1.37 Å)   bond lengthens (1.44 Å)

Benzene $r(C=C) = 1.39$ Å

(14) L. M. Trefonas, R. L. Flurry, Jr., R. Majeste, E. A. Meyers, and R. F. Copeland, *J. Am. Chem. Soc.*, **88**, 2145 (1966).

(15) Experimental ionization potentials: NH_3, 10.2 eV; H_2O, 12.6 eV; HF, 15.8 eV. "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions", J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, NSRDS-NBS 26, National Bureau of Standards, Washington, D.C., 1969.

(16) L. Radom, P. C. Hariharan, J. A. Pople, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **95**, 6531 (1973).
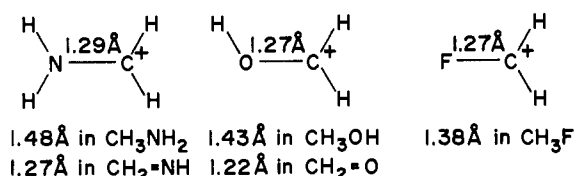
1.48Å in CH_3NH_2 1.43Å in CH_3OH 1.38Å in CH_3F
1.27Å in $CH_2 \cdot NH$ 1.22Å in $CH_2 \cdot O$

Figure 4. STO-3G geometries of NH_2-, OH-, and F-substituted carbonium ions.

ally contract in response to the electron withdrawal.

Although an organic chemist would easily have reached the same conclusion regarding the geometries of the allyl and benzyl cations, simply by stressing the importance of valence structures of the form
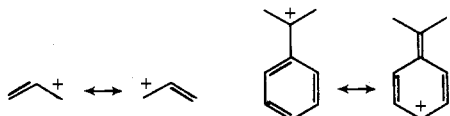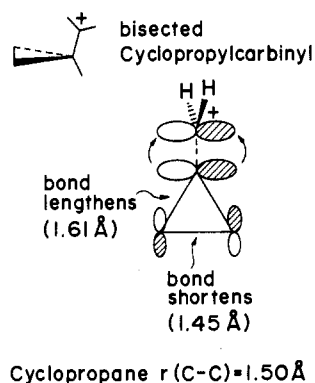
we seriously doubt whether the resonance theory would provide him with much insight into the geometry of an interesting related system, cyclopropylcarbinyl. Here we must probe interactions between the degenerate pair of valence molecular orbitals on cyclopropane[17] (the Walsh orbitals) and the carbonium center. In an eclipsed orientation of the two groups it is the symmetric Walsh component which interacts with the carbonium center. Due to poor orbital overlap, however, the magnitude of interaction is small, and distortions to the cyclopropane ring which follow

eclipsed
Cyclopropylcarbinyl

bond lengthens (1.51 Å)

bond lengthens (1.51 Å)

Cyclopropane r(C–C) = 1.50Å
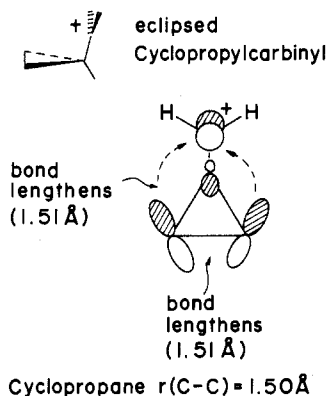
(in this case, a lengthening of all three ring bonds) only slight. The quantitative molecular orbital calculations clearly show this to be the case.

Twisting the carbonium center by 90°)such that it bisects the ring) makes it available for interaction with the asymmetric member of the Walsh duo. This time the two fragments are disposed so as to overlap optimally, and the geometric distortions arising from the resultant charge transfer away from the small ring (a lengthening of two of its linkages accompanied by a shortening of the third) are clearly visible in the theoretical structure of the ion. Since the interaction we are considering, between filled, cyclopropane, and empty, carbonium center, orbitals, is of benefit energetically, it follows that the bisected conformation of the two groups, in which it is maximized, will be the preferred. Though a static cyclopropylcarbinyl cation has yet to be observed and characterized experimentally,[18a,b] both secondary

(17) For a discussion of the valence orbitals on cyclopropane and cyclobutane see: R. Hoffmann and R. B. Davidson, *J. Am. Chem. Soc.*, **93**, 5699 (1971).

bisected
Cyclopropylcarbinyl

bond lengthens (1.61 Å)

bond shortens (1.45 Å)

Cyclopropane r(C–C) = 1.50Å

methylcyclopropylcarbinyl and tertiary dimethylcyclopropylcarbinyl cations are known to exist in a bisected conformation under conditions of long life in superacid media.[18a] Furthermore, the barrier hindering rotation about the carbonium center in dimethylcyclopropylcarbinyl has been estimated, by study of the temperature dependence of its NMR spectrum, to be 13.7 kcal/mol,[18c] substantiating the contentions of the simple perturbation model regarding the difference in stabilizing abilities of the two Walsh cyclopropane orbitals. The theory's assignment of an even larger (25.7 kcal/mol) conformational preference in the primary ion adds additional support.[18d]

The carbonium center in cyclobutylcarbinyl shows very little preference to bisect or to eclipse the small ring, quite the opposite behavior than was noted for cyclopropylcarbinyl. Indeed, we find the barrier hindering rotation away from a bisected ground-state structure to be only 4 kcal/mol. Again the orbital interaction model provides the rationale behind the change in behavior, and in doing so leads to the suggestion of an interesting geometrical consequence. In an eclipsed arrangement, the carbonium center interacts with the symmetric component of the degenerate pair of cyclobutane valence orbitals. Overlap

eclipsed
Cyclobutylcarbinyl
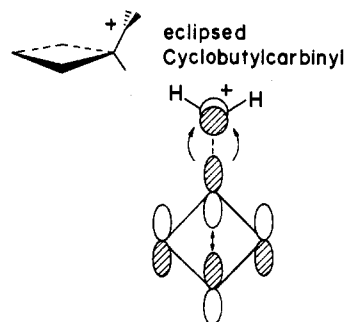
between the fragment orbitals is favorable, and one would expect the resultant charge transfer to be significant. In addition to a lengthening of all four cyclobutane C–C bonds, the most obvious geometrical consequence is one resulting from a lessening of anti-

(18) (a) G. A. Olah, C. L. Jeuell, D. P. Kelly, and R. D. Porter, *J. Am. Chem. Soc.*, **94**, 146 (1972); the NMR spectra of $C_4H_7^+$ in superacid media have been observed. The reported ^{13}C shifts do not correspond to a static cyclopropylcarbinyl cation, nor are they readily interpretable in terms of a rapidly equilibrating set of such species. Rather, Olah has proposed a σ-delocalized ground-state structure for the ion. Brown does not agree, arguing that the observed carbon–hydrogen coupling constants do indeed fit the equilibrating cyclopropylcarbinyl cation picture. See: (b) D. P. Kelly and H. C. Brown, *ibid.*, **97**, 3897 (1975); (c) D. S. Kabakoff and E. Namanworth, *ibid.*, **92**, 3234 (1970). (d) For further discussion see: W. J. Hehre and P. C. Hiberty, *ibid.*, **96**, 302 (1974).

bonding density between carbons displaced opposite to one another. This leads to distortion of the ring into a diamond shape, the carbonium center being linked to one of the obtuse apices.[19]

Interaction of the two fragments oriented in such a way that the carbonium center bisects the small ring also gives rise to the distortion of the latter into a diamond shape. Only this time the carbonium center
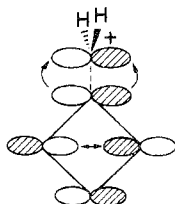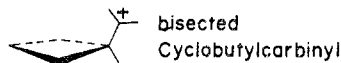
finds itself attached to an acute apex.[19] An overall view of cyclobutylcarbinyl suggests the obvious: that roation about the linkage connecting small ring and carbonium center results in the lateral motion of atomic positions in the latter. In simple language we
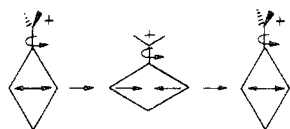
have here an example of a *Molecular Cam.* Although it is highly unlikely that the parent cyclobutylcarbinyl cation is a stable species (no doubt undergoing ring expansion to the less strained cyclopentyl system), it is certainly conceivable that the tertiary (dimethyl-substituted) ion will prove amenable to experimental characterization and be a suitable test for the coupling of rotational and vibrational motions which we propose. Alternatively one might probe for ring distortions and mode coupling in the geometrical structures and vibrational spectra of molecules such as cyclobutanecarboxaldehyde and cyclobutanecarboxylic acid.

The power of the simple perturbation model is illustrated most beautifully in considering the interaction of a methyl group with a carbonium center.[20] Two limiting conformations are possible, bisected and eclipsed, referring to the disposition of one of the methyl group's C–H bonds relative to CH_2^+. In the
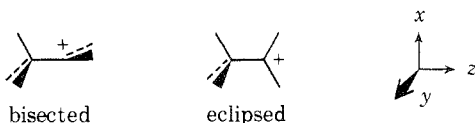
former arrangement interaction between the π_x component of the degenerate pair of methyl group orbitals and the p lobe at the carbonium center is permitted on symmetry grounds. Interaction is also possible between the two fragments in the eclipsed geometry, only this time it is the methyl group π_y orbital which is involved (Figure 5). We can immediately see that, according to the simple model, the magnitude of in-

(19) The possibility of geometrical distortions of this type has already been commented on by Hoffmann and Davidson.[17]

(20) R. Hoffmann, L. Radom, J. A. Pople, P. v. R. Schleyer, W. J. Hehre, and L. Salem, *J. Am. Chem. Soc.*, **94**, 6221 (1972).
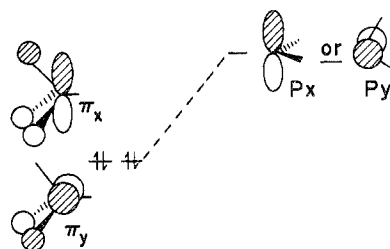
Figure 5. Stabilization resulting from interaction of a methyl group and an empty p orbital is independent of conformation.
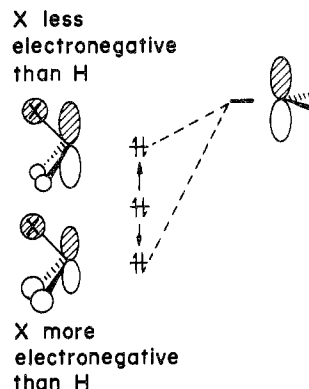
Figure 6. Raising and lowering the energy of a single methyl group orbital leads to a favoring of one conformation over the other.

Table II
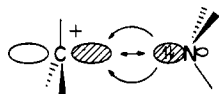**Rotational Barriers (kcal/mol) in**
Substituted Ethyl Cations

X	$E\left(\begin{smallmatrix}X\\ \diagdown\end{smallmatrix}\!\!\!\!\overset{+}{\diagup}\right) - E\left(\begin{smallmatrix}X\\ \diagdown\end{smallmatrix}\!\!\!\diagdown\!\!\!\diagup\right)$
H	0.0
BH_2	10.4
F	−8.4

teraction is independent of conformation, and that the resultant ethyl cation should show no preference for either a bisected or eclipsed geometry. Indeed, the variety of quantitative molecular orbital calculations performed on the system show this to be the case.[8a,9b,21] Let us now suppose that we replace one of the methyl hydrogens (for convenience we choose the one lying in the *x–z* plane) by some chemical group, X. In doing so it is important to realize that such substitution leaves unaltered the energy of the methyl π_y orbital (and hence its ability to interact with a carbonium center in an eclipsed geometry), and only succeeds in raising or lowering that of the π_x function (Figure 6). In particular, if X is less electronegative than hydrogen, the energy of π_x will increase, as will the ability of the methyl group to stabilize a carbonium center in a bisected conformation. Hence such an arrangement will be preferred. On the other hand, substitution by a group of greater electronegativity will lower the energy of π_x, making it less favorable than π_y in competing for the chance to stabilize the positively charged center. In this case the ion should adopt an eclipsed geometry. The theoretical (STO-3G) data presented in Table II fully substantiate these conclusions.

Thus far we have dealt entirely with situations where a carbonium center is afforded stabilization

(21) P. C. Hariharan, W. A. Lathan, and J. A. Pople, *Chem. Phys. Lett.*, **14**, 385 (1972).

through the π system by a group to which it is already σ bonded. Alternatively we might consider direct interaction of a carbonium center and an electron-rich group to which it is not already attached via the σ system. For example, the structure of protonated methylamine might be thought of in terms of interaction between the lone pair of ammonia and the vacant p orbital on CH_3^+. More interesting are situa-

tions in which electron density is drawn not from a localized lone pair but from a σ or π orbital which is actually involved in molecular bonding. Thus, we might visualize the bridged ethyl cation to be formed as a result of intermolecular interaction of the ethylene π system and a bare proton. Correspondingly, substitution of the methyl cation for H^+ provides us with one way of looking at protonated cyclopropane.
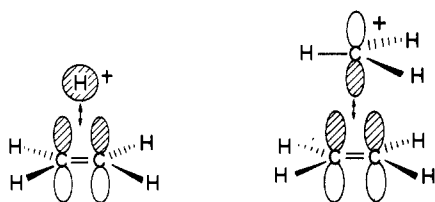
Note that the simple orbital interaction picture does not distinguish between the symmetric approach of the electrophile to the double bond—leading to a bridged structure—and attack on a single carbon resulting in the formation of an acyclic ion (Figure 7). While it is not known experimentally with any certainty whether species such as protonated ethylene and cyclopropane exist as cyclic or open ions,[22] the best levels of theoretical calculation which have been performed to date indicate both to prefer symmetric hydrogen- (and methyl-) bridged structures.[23] In addition, the weight of experimental evidence is clearly in favor of a cyclic geometry for the 2-phenylethyl cation (interaction of $C_6H_5^+$ with the ethylene π system).[24] Theoretical calculations concur.[25] In all of these cases the extreme geometrical distortion accompanying bridging is chosen in preference to incorporation of a primary carbonium center into the ion. Bridging normally does not occur when the alternative is formation of a secondary or a tertiary carbonium center.[26] Thus, the proton addition complex involving propene is better represented in terms of a secondary isopropyl cation rather than some hydrogen- or methyl-bridged structure.[27] Similarly, methyl

(22) What is believed to be the case is that either such species exist as bridged forms or else they undergo rapid equilibration between equivalent acyclic structures.

(23) (a) B. Zurawski, R. Ahlrichs, and W. Kutzelnigg, *Chem. Phys. Lett.*, **21**, 309 (1973); (b) P. C. Hariharan, L. Radom, J. A. Pople, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **96**, 599 (1974).

(24) For a recent review see: C. J. Lancelot, D. J. Cram, and P. v. R. Schleyer in "Carbonium Ions", G. A. Olah and P. v. R. Schleyer, Ed., Vol. 3, Wiley, New York, N.Y., 1972, p 1347.

(25) W. J. Hehre, *J. Am. Chem. Soc.*, **94**, 5919 (1972).

(26) A possible exception to this statement is the secondary 2-norbornyl cation. For opposing viewpoints see: (a) G. A. Olah, G. Liang, G. D. Mateescu, and J. L. Riemenschneider, *J. Am. Chem. Soc.*, **95**, 8698 (1973); and references therein, and (b) H. C. Brown and K. T. Liu, *ibid.*, **97**, 600 (1975), and references therein.

(27) For a thorough discussion of the $C_3H_7^+$ surface see: L. Radom, J. A. Pople, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **94**, 311 (1972).
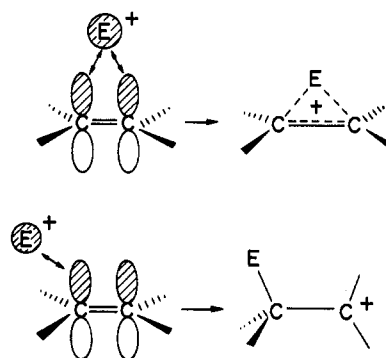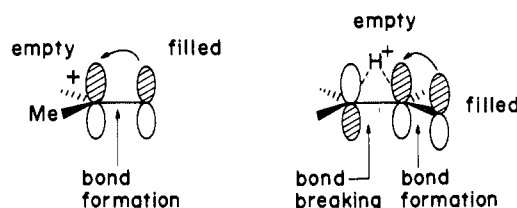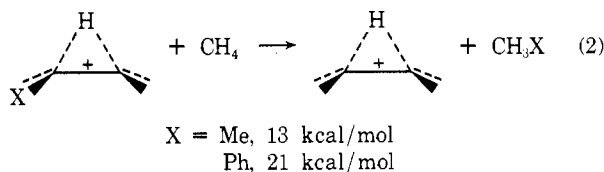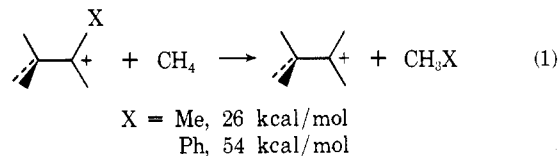
Figure 7. Qualitatively at least, the simple perturbation molecular orbital picture does not distinguish between symmetric or antisymmetric approach of an electrophile.

and phenyl cation adducts also seem to adopt acyclic geometries. We might conclude then that substitution on a localized carbonium center is apt to be of greater consequence energetically than that on a bridged ion, where the positive charge has already been significantly dispersed across the molecular framework. Specifically, charge transfer from, say, a methyl group into the carbonium center of the open ethyl cation results primarily in the formation of a new "π" bond between donor and acceptor sites. On the other hand, electrons donated into the lowest vacant molecular orbital of the hydrogen-bridged ethyl cation go into a function which is antibonding. In this instance charge transfer actually results in a weakening of the carbon–carbon bond of the bridged ethyl cation, and we might expect the overall stabilizing ability of the substitutent to be significantly dimin-

ished. The theoretical (STO-3G) energies of reactions 1 and 2 indeed show this to be the case, stabilization

$$\text{reaction (1)}$$

X = Me, 26 kcal/mol
Ph, 54 kcal/mol

$$\text{reaction (2)}$$

X = Me, 13 kcal/mol
Ph, 21 kcal/mol

given the open ethyl cation being approximately twice that imparted to the bridged species for both methyl and phenyl substituents.

σ bonds also provide an excellent source of electrons,[28] and structures of such ions as the protonated alkanes may easily be formulated in terms of their interaction with localized positive charge centers such as H^+ or CH_3^+. One can see, for example, that the

(28) G. A. Olah, G. Klopman, and R. H. Schlosberg, *J. Am. Chem. Soc.*, **91**, 3261 (1969).
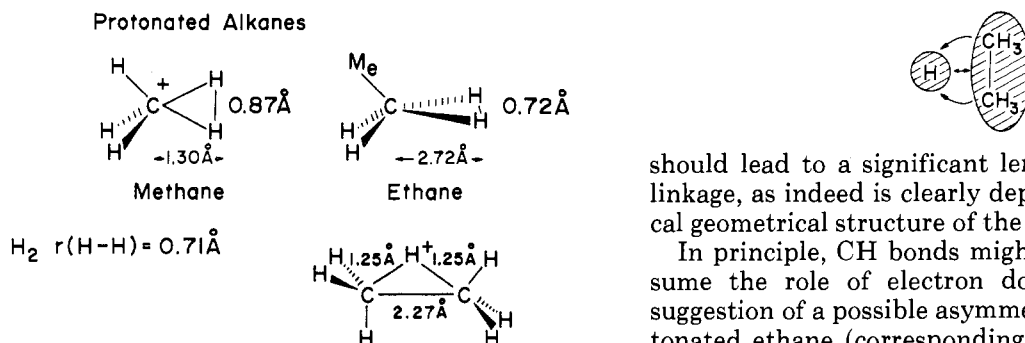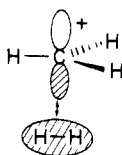
Protonated Alkanes

Figure 8. STO-3G geometries of protonated methane and ethane.

theoretical (STO-3G) structure for CH_5^{+}[8a,9a] looks very much like a loose complex between the methyl cation and H_2 (Figure 8). More extensive calcula-


tions, including those in which partial account is taken for valence-shell correlation energy, favor a like structure.[29] One of the possible structures for protonated ethane[8a,b] shows even a more marked resemblance to an intermolecular addition complex involving the hydrogen molecule, in this situation the open ethyl cation providing the acceptor site.

The theory's choice for the ground-state structure of $C_2H_7^{+}$ (11 kcal/mol more stable than the hydrogen–ethyl cation complex at the STO-3G level)[8a,9b] may be considered to result from the interaction of a bare proton and the carbon–carbon σ-bonding orbital of ethane. Electron donation from σ to the proton

(29) V. Dyczmons and W. Kutzelnigg, *Theor. Chim. Acta*, **33**, 239 (1974).

should lead to a significant lengthening of the C–C linkage, as indeed is clearly depicted by the theoretical geometrical structure of the ion[30] (Figure 8).

In principle, CH bonds might also be asked to assume the role of electron donors, leading to the suggestion of a possible asymmetric structure for protonated ethane (corresponding to an interaction between methane and the methyl cation).[31] While no
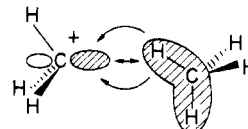
such geometrical minimum has been located on the $C_2H_7^{+}$ potential surface, one structure found for protonated propane does indeed correspond to complex formation involving the bonding σ orbital of a carbon–hydrogen linkage.

The variety of examples which we have presented have been directed at demonstrating the utility of simple arguments, based on the perturbation treatment of interacting orbitals, in anticipating the detailed findings of the quantitative ab initio calculations. Together, these two techniques provide a powerful, and yet intelligent, means of elucidating the structure and conformation of reactive carbocation intermediates.

(30) At the extended basis 4-31G level this structure appears to relapse to a higher symmetry D_{3d} geometry (the same symmetry as ethane itself), corresponding to protonation at the center of the carbon–carbon bond. See ref 9b for a discussion.

(31) L. Radom, L. A. Curtiss, J. A. Pople, and P. v. R. Schleyer, to be submitted.

Mechanism of Cobalamin-Dependent Rearrangements

Bernard M. Babior

Department of Medicine, Tufts–New England Medical Center Hospital, Boston, Massachusetts 02111

The corrins are an extensive family of compounds among which are included a unique group of cobalt-containing organometallic reagents of great biological significance. These compounds were found at the end of a long search for the agent that cured pernicious anemia, a disease which, before the discovery of corrins, was almost always fatal.

In 1922, Minot and Murphy found that pernicious anemia could be cured by liver fed in very large quantities.[1] Twenty-six years later, the isolation of the therapeutic principle in liver was announced independently by Smith[2] and by Folkers.[3] The substance they isolated was a beautiful red crystalline compound that prevented pernicious anemia at doses of only 1–2 μg per day. Over the next several years partial structures of this compound, which was given the names vitamin B_{12} and cobalamin, were de-

Bernard M. Babior received an M.D. from the University of California School of Medicine, San Francisco, in 1959, and a Ph.D. in biochemistry from Harvard University in 1965. After postdoctoral training he joined the faculty of Harvard Medical School. In 1972 he moved to Tufts Medical School where he is currently Associate Professor of Medicine. He studies the biochemistry of corrinoids and the physiology and biochemistry of white blood cells.

(1) G. R. Minot and W. P. Murphy, *J. Am. Med. Assoc.*, **87**, 470 (1926).

(2) E. L. Smith and L. F. J. Parker, *Biochem. J.*, **43**, VIII (1948).

(3) E. L. Rickes, N. G. Brink, F. R. Koniuszy, T. R. Wood, and K. Folkers, *Science*, **107**, 396 (1948).