is the substrate of the borohydride reduction, then one of the new hydrogens in the dihydro product IV must come from the borohydride and the other from the solvent methanol. This postulate was verified by repeating the above experiment using sodium borodeuteride as reducing agent. The monodeuterated product IV which was obtained in this manner was indistinguishable from its only hydrogen-containing analog by tlc, infrared, and nmr spectroscopy. It showed, however, the correct molecular weight by high-resolution mass spectroscopy [molecular ion found at *m/e* 408.2743 (calcd 408.2734)].

Thus the unusual photoreduction of a carbon–carbon bond by borohydride seems to support our original views about the nature of the chromophoric system in the pyrodelphinium alkaloids.

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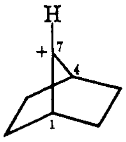
Can Deformed Classical Carbonium Ions Be Nonplanar?

Sir:

Although there is yet but little direct experimental evidence,[1] it is generally believed that carbonium ions tend strongly toward planarity. This belief is strengthened by numerous theoretical calculations which indicate that the simplest classical carbonium ion, CH_3^+, is most stable in the planar D_{3h} form.[2] However, the possibility has been raised recently that certain classical carbonium ions in strained systems may prefer a nonplanar arrangement.[3] Specifically, such a nonplanar ion at the 7 position of norbornane might accommodate the observation that solvolysis of a nonsymmetrically deuterium-labeled 7-norbornyl tosylate proceeds with predominant retention of configuration.[3]



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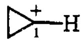

II

The possibility that carbonium ions in strained systems, such as at the 7 position of norbornane, may be nonplanar is not wholly unreasonable. The endocyclic angle around C_7 in norbornane itself is about 95°;[4] therefore, the 7-norbornyl cation (I) would be expected to have a $C-C^+-C$ angle restricted to a value much less than the ideal one (∽120°). The possibility exists that such a deformation from the preferred cation geometry could "loosen" the intramolecular forces so that planarity would be less strongly favored than in an undeformed ion, or even disfavored relative to some nonplanar structure.[3] To test this hypothesis we have performed several series of calculations.[5]

The first series of calculations consisted of two sets of *ab initio* LCAO–MO–SCF computations on the methyl cation. In one, the HCH angle, θ, was held at 120°; in the other, θ was fixed at 90°. For each value of θ calculations were performed for geometries with the third hydrogen out of the HCH plane, this CH bond making angles, φ, of 0, 5, 15, and 30° with regard to the plane of the other atoms. The basis set used consisted of Whitten's three s-type Gaussian groups[6] for carbon, Huzinaga's carbon p's,[7] and Whitten's hydrogen 1s group (hydrogen scale, $\eta^2 = 2.5$).[6] Such a basis set, of essentially Hartree–Fock atomic orbitals, has been shown in the past to give geometrical parameters in polyatomic systems to within a few per cent.[8] The results of these calculations, summarized in Table I and Figure 1, indicate that as the angle θ is decreased from 120 to 90°, the methyl cation prefers planarity even more strongly than at equilibrium.

Table I. *Ab Initio* Energies for CH_3^+ [a]

φ,[b] deg	ΔE_{rel}[c]	ΔE_{rel}[d]	$\Delta E'_{rel}$[e]
0	0.0	0.0	16.59
5	0.27	0.28	16.87
15	2.13	2.47	19.06
30	8.38	9.81	26.40

[a] Kilocalories per mole. [b] For Table I and Table II, $\theta = \angle HCH$; ϕ is the angle of deformation of the remaining C–H bond out of the plane. [c] Relative to the equilibrium energy, −39.178263 au, for $\theta = 120°$, $\varphi = 0°$, and bond length of 1.084 Å. [d] Relative to the $\theta = 90°$, $\varphi = 0°$ conformation ($E = -39.151822$ au). [e] Relative to the true equilibrium value for $\theta = 120°$, $\varphi = 0°$.

A second series of computations, parallel to the first but with many more points, was performed on CH_3^+ using the MINDO (modified intermediate neglect of differential overlap) method.[9] The results, some of which are given in Table II and Figure 1, show the same trend: the smaller the value of θ, the more strongly planarity is favored. However, the magnitude of the effect is not so pronounced as in the results of the more rigorous *ab initio* calculations. This calibration of the MINDO results for methyl cation, however, provides a basis for expecting that calculations for larger systems

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(1) For a review, see R. C. Fort and P. von R. Schleyer, *Advan. Alicyclic Chem.*, **1**, 283 (1966).

(2) R. E. Kari and I. G. Csizmadia, *J. Chem. Phys.*, **46**, 1817 (1967); G. von Bünau, G. Diercksen, and H. Preuss, *Intern. J. Quant. Chem.*, **1**, 645 (1967); S. D. Peyerimhoff, R. J. Buenker, and L. C. Allen, *J. Chem. Phys.*, **45**, 734 (1966).

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

(8) See 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, p 39; also see Allen, *et al.*[2]

(9) N. C. Baird and M. J. S. Dewar, *J. Chem. Phys.*, in press; N. C. Baird, M. J. S. Dewar, and R. Sustmann, *ibid.*, in press; J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *ibid.*, **47**, 2026 (1967).

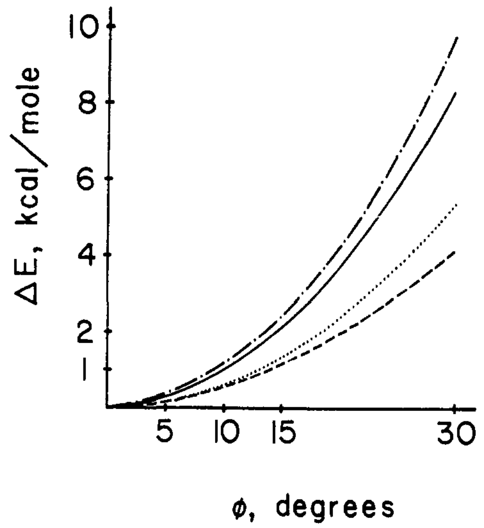

Figure 1. *Ab initio* and MINDO energies for the methyl cation, all referenced to the same zero of energy (at $\varphi = 0$ for each θ): (- · -) *ab initio*, $\theta = 90°$; (——) *ab initio*, $\theta = 120°$; (·····) MINDO, $\theta = 90°$; (-----) MINDO, $\theta = 120°$.

Table II. MINDO Energies for CH_3^+ [a]

φ,[b] deg	ΔE_{rel}[c]	ΔE_{rel}[d]	$\Delta E'_{\mathrm{rel}}$[e]
0	0.0	0.0	4.94
5	0.14	0.17	5.11
15	1.15	1.35	6.29
30	4.17	5.37	10.31

[a] Kilocalories per mole. [b] See Table I. [c] Relative to the equilibrium heat of formation, 274.18 kcal/mol for $\theta = 120°$, $\varphi = 0°$, and bond length of 1.084 Å. [d] Relative to the $\theta = 90°$, $\varphi = 0°$ conformation ($E = 279.12$ kcal/mol). [e] Relative to the true equilibrium value, $\theta = 120°$, $\varphi = 0°$.

will lead to the same qualitative conclusions as *ab initio* computations on the same systems, were it practicable to do them.

A third series of computations, using the MINDO method, was done for the isopropyl cation. For each of three values of θ, 120, 110, and 100°, where θ is now the isopropyl CCC angle, calculations for three values of φ, 0, 15, and 30°, were performed (Table III and Figure 2). Again, as θ decreases, the tendency toward planarity about the trigonal carbon increases.

Table III. MINDO Energies for $(CH_3)_2CH^+$ [a]

φ,[b] deg	ΔE_{rel}[b,c]	ΔE_{rel}[b,d]	$\Delta E'_{\mathrm{rel}}$[b,e]
0	0.0	1.34	3.14
15	0.72	2.14	4.25
30	3.07	4.78	7.32

[a] Kilocalories per mole. [b] Energies relative to the presumed heat of formation, 209.33 kcal/mol, for $\theta = \angle CCC = 120°$, $\varphi = 0°$, and bond lengths of 1.48 Å for C–C and 1.093 Å and 1.084 Å for C–H. [c] $\theta = 120°$. [d] $\theta = 110°$. [e] $\theta = 100°$.

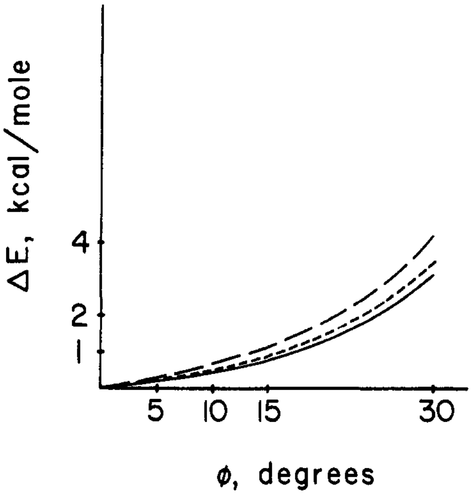

Figure 2. MINDO energies for the isopropyl cation, plotted in the same way, and with the same scale, as Figure 1: (— —) $\theta = 100°$; (-----) $\theta = 110°$; (——) $\theta = 120°$.

Finally, two MINDO computations for the 7-norbornyl cation itself (I) were done, one with the substituents around C_7 planar, the other with the hydrogen 15° out of the $C_1C_7C_4$ plane. The results indicate that the planar (C_{2v}) structure is favored by 1.15 kcal/mol. This value, corresponding to a $C_1C_7C_4$ angle (θ) of 101°, is almost the same as the value of 1.11 kcal/mol calculated for the isopropyl cation of similar geometry (Table III; $\theta = 100°$, φ varied from 0 to 15°).

We conclude that classical carbonium ions prefer planarity, even when distorted from the optimum geometry ($\theta < 120°$). In fact, an in-plane distortion ($\theta < 120°$) increases the resistance to out-of-plane deformations. Examination of the *ab initio* wave functions for the methyl cation affords an understanding of this behavior. As φ increases, the formerly empty $2p_z$ begins to replace the in-plane orbitals in contributing to the bonding of the out-of-plane hydrogen. When $\theta = 90°$, the orbital replaced is primarily the 2s, whereas for $\theta = 120°$, replacement of the in-plane p's predominates. The net phasing-out, and concomitant depopulation, of the 2s for $\theta = 90°$ relative to $\theta = 120°$ makes nonplanarity more unfavorable in the former case, because in carbon the 2s orbital is of lower energy than the 2p.[10] To draw a crude analogy: it is more expensive to go from sp ($\theta = 90°$) than from sp^2 ($\theta = 120°$) to sp^3 for the out-of-plane CH bond.[10a]

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(10) Huzinaga's[7] and Whitten's[6] calculations indicate that the carbon 2s is lower in energy than the 2p by about 170 kcal/mol.

(10a) NOTE ADDED IN PROOF. MINDO calculations on the methyl cation indicate that with a HCH angle fixed at 90°, it is easier to move the remaining hydrogen in the plane than with a HCH angle of 120°. Furthermore, with $\angle HCH = 90°$, the in-plane deformation is easier than the out-of-plane, whereas the opposite is true for $\angle HCH = 120°$. Further details, with *ab initio* results, will be reported later.

(11) National Science Foundation Predoctoral Fellow, 1965–1969.

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