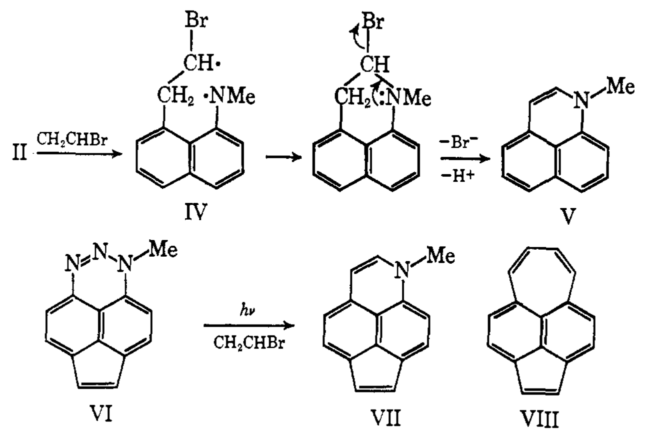

IV V VI VII VIII

Yellow N-methylacenaphtho[5,6-*bc*]pyridine (VII),[5] mp 126–127°, derived from VI in *ca.* 30% yield, is the simplest heterocyclic analog of the nonbenzenoid aromatic hydrocarbon VIII[9] so far recorded.[10] The aromaticity of VII is reflected in a substantial downfield shift in the nmr spectrum relative to that of V (*e.g.*, protons on C_2 and C_3 appear at τ 3.78 and 4.38 in V and τ 2.69 and 3.00 in VII; *cf.* ref 2 and 3).

Our results supplement data on the photolysis of cyclic diazoamino compounds communicated recently by Burgess, Carrithers, and McCullagh.[7] We are currently exploring extensions of these photolyses in the presence of vinyl bromide and other halo olefins.

Acknowledgment. We are grateful to the Science Research Council for the award of a Research Studentship (to P. F.)

[9] V. Boekelheide and G. Vick, *J. Am. Chem. Soc.*, 78, 653 (1956).

[10] Examples of other heterocycles related to hydrocarbon VIII are described in ref 2 and 3, and by I. S. Ponticello and R. H. Schlessinger, *J. Am. Chem. Soc.*, 90, 4190 (1968).

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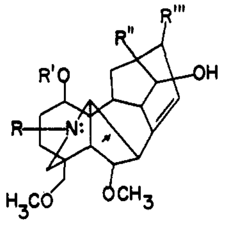
The Photoreduction of Desmethoxypyrodelphonine

Sir:

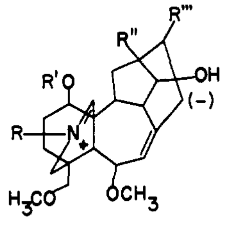
Eight years ago we showed[1] that pyrodelphonine (Ia) and pyroneoline (Ib) display an unexpected ultraviolet absorption spectrum [Ia, λ_{max} 245 mμ (log ϵ 3.8); Ib, λ_{max} 236 mμ (log ϵ 3.85)] which disappears on acidification. We postulated at that time that the free electron pair of the nitrogen, the σ bond marked by an arrow in formula I, and the π-electron pair of the double bond are part of the unprecedented chromophore and that the excited state of this system may be portrayed as a mesomeric hybrid between the limiting structures I and II. Six years later Cookson and his collaborators published a paper[2] entitled "σ-Coupled π Electron Systems. A New Type of Chromophore," in which several more examples of such chromophoric systems are given, but the authors claim that this type has "*remained previously unrecognized.*"[3]

It appeared to us probable that if the excited state of the pyro compounds resembles II, it might be reducible with sodium borohydride. Since, however, many reactions of the pyrodelphonine system involve the R''' methoxyl,[4] we wished to perform our photochemical experiments on compound Ic in which this group is missing. The desired derivative was readily accessible from compound III. The preparation of the N-formyl analog of III (*i.e.*, V) from α-oxopyrodelphinine is known,[5] and we have prepared compound III itself by the same sequence of steps starting from pyrodelphinine.[6] Pyrolysis of compound III followed by alkaline hydrolysis yielded the desired product Ic [amorphous glass homogeneous in thin-layer chromatography; uv λ_{max} 231 mμ (log ϵ 3.96); nmr poorly resolved quadruplet (1 H), τ 4.86 (vinylic hydrogen); molecular ion found at *m/e* 405.2524 (calcd 405.2515)]. Compound Ic was completely stable in methanolic solution in the presence of an excess of sodium borohydride at room temperature in the dark.

When the same solution was irradiated at 0° with a quartz mercury vapor lamp (100 W) for 4.5 hr a mixture of products was formed. The major component of this mixture was isolated by preparative thin-layer chromatography, and it was the expected product IV

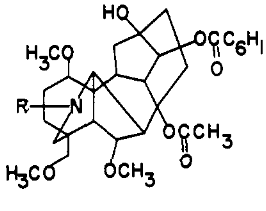


I a, b, c

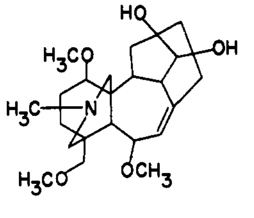


II a, b, c

a ($R = CH_3$, $R' = CH_3$, $R'' = OH$, $R''' = OCH_3$)
b ($R = CH_3{-}CH_2$, $R' = H$, $R'' = H$, $R''' = OCH_3$)
c ($R = CH_3$, $R' = CH_3$, $R'' = OH$, $R''' = H$)



III ($R = CH_3$)
V ($R = CHO$)



IV

[amorphous glass homogeneous in tlc; nmr broad singlet (1 H), τ 4.61 (vinylic hydrogen); molecular ion found at *m/e* 407.2666, (calcd 407.2671)]. If our views are correct and the excited state resembling IIc

[1] K. Wiesner, H. W. Brewer, D. L. Simmons, D. R. Babin, F. Bickelhaupt, J. Kallos, and T. Bogri, *Tetrahedron Letters*, No. 3, 17 (1960).

[2] R. C. Cookson, J. Henstock, and J. Hudec, *J. Am. Chem. Soc.*, 88, 1060 (1966).

[3] In a letter to K. W., Professor Cookson admitted that we have "expressed[1] in valence-bond language much the same thought about the spectrum of our pyro alkaloids" as Cookson, *et al.*[2]

[4] K. Wiesner, D. L. Simmons, and R. H. Wightman, *Tetrahedron Letters*, No. 15, 23 (1960).

[5] K. Wiesner, F. Bickelhaupt, D. R. Babin, and M. Gotz, *Tetrahedron*, 9, 254 (1960).

[6] To be described in a full paper.

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.

Acknowledgment. We thank the National Research Council, Ottawa, and the S. B. Penick Company, Orange, N. J., for the support of these studies.

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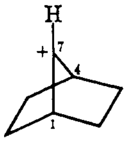
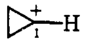
Can Deformed Classical Carbonium Ions Be Nonplanar?

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]



I



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 ($\sim$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]	$\Delta E'_{\text{rel}}$[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).

(3) P. G. Gassman, J. M. Hornback, and J. L. Marshall, *J. Am. Chem. Soc.*, 90, 6238 (1968); F. B. Miles, *ibid.*, 90, 1265 (1968).

(4) For a summary of the literature, see G. Dallinga and L. H. Toneman, *Rec. Trav. Chim.*, 87, 795 (1968).

(5) Only one theoretical calculation dealing with this problem in secondary classical cations is known to us. W. Kutzelnigg, *Tetrahedron Letters*, 4965 (1967), using an extended Hückel method, has provided evidence that the cyclopropyl cation II prefers a planar, rather than a nonplanar, arrangement around the carbonium ion center. For calculations on planar and nonplanar cyclobutyl cations, see K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968); K. B. Wiberg and G. Szeimies, *J. Am. Chem. Soc.*, in press; R. E. Davis and A. Ohno, *Tetrahedron*, **24**, 2063 (1968).

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

(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).