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**Jack Halpern,* B. L. Goodall, G. P. Khare**
**H. S. Lim, J. J. Pluth**
*Department of Chemistry, The University of Chicago*
*Chicago, Illinois 60637*

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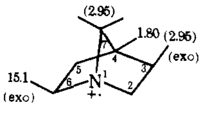
## An Electron Spin Resonance Study of the Bridgehead Aminium Radicals Derived from 1-Azabicyclo[2.2.1]heptane, 1-Azabicyclo[2.2.2]octane, and 1-Azaadamantane[1]

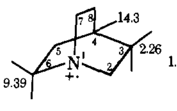
*Sir:*

The geometry and electronic configuration of transient chemical species have been the goal of numerous studies. Carbonium ions are known to prefer a planar geometry while unconjugated carbanions exist in a pyramidal configuration.[2] Carbon-centered free radicals are generally planar or nearly so.[2-4] However, out-of-plane deformation of a free radical is considerably easier than for a carbonium ion and many appropriately substituted or electronically compelled carbon-centered radicals have been shown to be nonplanar.[4] Krusic, Rettig, and Schleyer have recently concluded from ESR and INDO studies that the 1-adamantyl and 1-bicyclo[2.2.2]octyl radicals are pyramidal with the bridgehead carbon atoms about 0.4 Å out of a plane defined by the attached three carbons.[5] Mishra and Symons[6] have observed $a^{13C}$ = 136.7 G for the central carbon in the 1-adamantyl radical which corresponds to 12% 2s character and supports a distinctly pyramidal configuration.

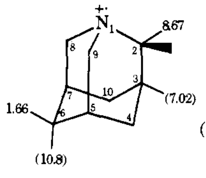
Many studies concerned with the stability and reactivity of free radicals and carbonium ions generated at the bridgehead positions of the bicyclo[2.2.1]heptyl, bicyclo[2.2.2]octyl, and adamantyl ring systems have been conducted.[2] We have demonstrated in previous studies[7] that dialkylaminium radicals, $R_2NH^{\cdot+}$, are planar about the nitrogen atom and we believed it would be of significance to investigate by ESR the corresponding bridgehead aminium radicals, **1–3**. On the basis of both Pauling's arguments[8] and INDO calculations,[9] it is expected that the out-of-plane bending force constant for an aminium radical should be intermediate between that of an alkyl radical and that of a carbonium ion. It follows that **2** and **3** should be less pyramidal as compared to the analogous carbon-centered radicals providing that the caged structures are sufficiently flexible to allow a flattening distortion about the bridgehead nitrogen atoms. The present results appear to support this conclusion.



$a^N$ = 30.2
**1**



25.1
**2**



21.6
**3**

28.5 $(CH_3)_3N^{\cdot+}$

20.7
**4**

The radicals were generated by ultraviolet photolysis of the corresponding amine-$Cl_2$ adducts in $CF_3SO_3H$ at 0 to −50°. The spectrum of **3** is shown in Figure 1 along with the simulated spectrum; hyperfine coupling constants in gauss are noted above for **1–4**.[10] Several features are worthy of note: (a) $a^N$ increases in the order **4** < **3** < **2** < **1**; (b) the proton hyperfine interactions for **2** and **3** are considerably larger than in the corresponding bridgehead carbon-centered radicals studied by Krusic et al.;[5] (c) the large $\delta$ coupling in **2** (14.3 G, verified by deuterium labeling) does not have its counterpart in **1**.

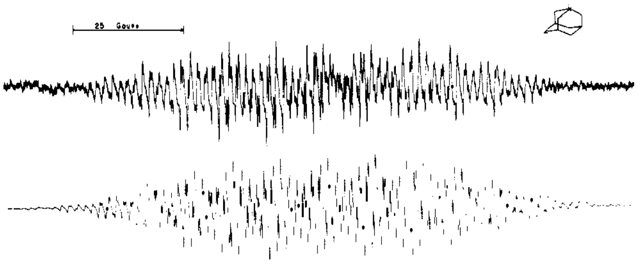


**Figure 1.** Experimental (above) and computer simulated (below) ESR spectra of the radical cation derived from 1-azaadamantane in $CF_3SO_3H$ at −50°.

On the basis of the ESR results and INDO calculations we conclude that the bridgehead radicals are pyramidal about the nitrogen atoms but that there is a trend toward planarity in going from **1** to **3**. Complete INDO geometry optimizations[11] for **1**, **2**, and **3** indicate that the nitrogen atom is external to a plane defined by the attached three carbon atoms by 0.44, 0.32, and 0.30 Å, respectively; the trimethylaminium radical is calculated to be planar. The calculated $a^N$ values are less definitive at 20.4, 20.9, and 18.8 G for **1**, **2**, and **3**, respectively; $a^N$ is calculated as 15.1 and 36.8 G for planar and tetrahedral (N is 0.49 Å out-of-plane of attached carbons) $(CH_3)_3N^{\cdot+}$, respectively. The observed $a^N$ values are quite small in view of a predicted coupling of 550 G for unit spin density in a nitrogen 2s orbital[13] but, as attested to by the INDO results and localized orbital considerations,[9] are not inconsistent with pyramidal geometries about the nitrogen atoms in **1–3**.

The calculated values for $a^H$ are in at least qualitative agreement with the experimental proton hyperfine coupling constants with the major trends reproduced. In particular, large values of $a_\delta{}^H$ for **2** and the axial protons in **3** are predicted as well as the low value of the $\delta$ hydrogen in **1**. The large $a^H$ of the exo $\beta$ hydrogens and negligible interaction with the endo $\beta$ protons in **1** are verified. Interestingly, movement of the bridgehead nitrogen inward predicts a calculated *decrease* in $a^H$ for $H_4$ in **2** but an *increase* for this proton in **1**. This supports other data[5] suggesting that a through-bond mechanism for spin delocalization[14] is operative in such bicyclic radicals and that a backlobe effect is probably unimportant. The small coupling to $H_4$ in **1** apparently results from a cancellation of the positive spin density on this proton induced via the $C_2$–$C_3$ and $C_5$–$C_6$ bonds by the negative spin density transmitted effectively through the shorter $C_7$ methylene bridge.

These and other aspects of these interesting bridgehead radicals will be discussed in the full publication of this work.

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(1) (a) Nitrogen-Centered Free Radicals. Part VIII. For Part VII see W. C. Danen and C. T. West, *J. Am. Chem. Soc.*, **96**, 2447 (1974). (b) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

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(11) A program, soon to be available through the Quantum Chemistry Program Exchange, for complete geometry optimization has been written by Professor K. F. Purcell of this department. By allowing treatment of both open and closed shell molecules according to either the CNDO or INDO prescriptions, the program is a generalization of those discussed in ref 12. The final geometries of **1**, **2**, and **3** are the energy minimum structures for $C_s$, $C_{3v}$, and $C_{3v}$ symmetries, respectively.

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**Wayne C. Danen,* Robert C. Rickard**
*Department of Chemistry, Kansas State University*
*Manhattan Kansas 66506*

*Received January 20, 1975*

## Structural Interpretation of Heme Protein Resonance Raman Frequencies. Preliminary Normal Coordinate Analysis Results[1]

*Sir:*

Much current interest attaches to the stereochemistry of the heme group and its consequences for biochemical function in heme proteins. In hemoglobin, the transition from a five-coordinate, out-of-plane, high-spin heme to a six-coordinate, planar, low-spin heme has been proposed as the stereochemical trigger for the cooperative binding of oxygen.[2] This transition produces appreciable frequency shifts in certain porphyrin ring vibrational modes, which can be sensitively monitored by the technique of resonance Raman spectroscopy. From an examination of various heme proteins, it has been possible to identify characteristic vibrational shifts associated with the electronic and stereochemical concomitants of changes in oxidation and spin state.[3]

We present here results of a normal coordinate analysis on octamethylporphyrin (OMP) designed to elucidate the parameters responsible for the observed vibrational shifts. Application of the porphyrin Urey–Bradley force field suggested by Nakamoto and coworkers[4] gave ~100 cm$^{-1}$ errors for the high-frequency $A_{2g}$ and $B_{1g}$ modes. Addition of two stretch–stretch interaction constants ($F_{C_\alpha C_m,C_\alpha C_m}$ = 0.4 mdyn/Å and $F_{C_\alpha N,C_\alpha N}$ = 0.6 mdyn/Å)[5a] and an adjustment of the CN stretching constant ($K_{CN}$ = 4.5 mdyn/Å) yielded eigenfrequencies in good agreement with the observed resonance Raman frequencies of ferrocytochrome c, as shown in Table I. The molecular parameters of bis(piperidine)-α,β,γ,δ-tetraphenylporphinatoiron(II)[6] were used with slight alteration to ensure $D_{4h}$ symmetry, and the methyl groups were treated as point masses.[5b] OMP adequately models those physiological porphyrins which have eight peripheral substituents attached to the pyrrole rings through saturated carbon atoms, as in c-type cytochromes. Peripheral vinyl groups, found in protoheme proteins, are known to couple the porphyrin ring and produce extra bands, but the basic vibrational patterns remain unaltered.[3b] Bands which are assigned to $A_{1g}$ and $A_{2g}$ are consistent with their reported depolarization ratios.[3] All the observed depolarized bands ($\rho = 3/4$) were reasonably assigned to $B_{1g}$ symmetry modes. The $B_{2g}$ modes, as had been earlier predicted,[3a] are not observed.

Low-spin hemes are planar but, in high-spin hemes, the iron atom lies out of the plane, and the pyrrole rings tilt in the same direction, producing a doming of the porphyrin.[7] This transition is reflected in relatively large frequency decrements, up to 35 cm$^{-1}$, in three Raman bands:[8] ~1640 (dp = depolarized), ~1580 (ap = anomalously polarized), and ~1500 (p = polarized) cm$^{-1}$. The potential-energy distribution (Table I) shows that the first two are mainly methine bridge C–C stretching, and the third is mainly pyrrole C–N stretching. The next calculation was of domed OMP, using the same force constants as for the planar case, in order to investigate the purely kinematic effects of doming. The shifts produced by a 19° dome angle (the angle of the pyrrole rings with respect to the mean heme plane) are compared in Table I with experimental frequency differences[3b] between ferrocytochrome c[10] and deoxyhemoglobin. The main kinematic effects of doming do show up in the spin-state marker bands and are in the right direction, but

Table I. Summary Results of Preliminary Normal Coordinate Calculations for Octamethylporphyrin

| Frequency, cm$^{-1}$ | | Frequency shift, cm$^{-1}$ | | | Potential-energy distribution |
|---|---|---|---|---|---|
| Exptl[a] | Calcd[b] | 19° dome[c] | + Force field[d] | Exptl[e] | (contributions above 10%) |
| 1626[f] | 1626 ($B_{1g}$) | 5 | 24 | 14 | 51% $C_\alpha C_m$,[g] 20% $C_\beta C_\beta$, 16% $C_\alpha C_\beta$ |
| 1592 | 1598 ($A_{1g}$) | 0 | 7 | 4 | 54% $C_\beta C_\beta$, 16% $C_\alpha C_m$ |
| 1585[f] | 1587 ($A_{2g}$) | 8 | 33 | 33 | 73% $C_\alpha C_m$, 16% δCH, 14% $C_{\alpha\beta}$ |
| 1547 | 1534 ($B_{1g}$) | 6 | 20[14] | 1 | 57% $C_\beta C_\beta$, 16% $C_\alpha C_m$ |
| 1497[f] | 1493 ($A_{1g}$) | 6 | 18 | 23 | 46% $C_\alpha N$, 17% $C_\alpha C_\beta$, 13% $C_\beta C_\beta$ |
| *h* | 1476 ($B_{2g}$) | 0 | 4 | *h* | 45% $C_\alpha C_m$, 37% $C_\alpha N$ |
| 1405 | 1424 ($B_{1g}$) | 5 | 8 | 3 | 60% $C_\alpha N$, 16% $C_\alpha C_m$ |
| 1400 | 1399 ($A_{2g}$) | 8 | 1 | *i* | 40% $C_\alpha N$, 28% δCH, 13% $C_\alpha C_\beta$ |
| *h* | 1387 ($B_{2g}$) | 0 | 2 | *h* | 75% $C_\alpha C_\beta$ |
| 1362 | 1376 ($A_{1g}$) | −6 | 3 | 4 | 38% $C_\alpha C_\beta$, 31% $C_\alpha C_m$, 17% $C_\beta C_\beta$ |
| 1310 | 1284 ($A_{2g}$) | −4 | −8 | 0 | 45% $C_\alpha C_\beta$, 37% δCH |
| 1228 | 1257 ($B_{1g}$) | −6 | −7 | 0 | 29% $C_\alpha C_\beta$, 58% δCH |

[a] Ferrocytochrome c data.[3b] [b] Planar octamethylporphyrin (see text). [c] Planar minus domed (19° angle), same force field. [d] Planar minus domed (19° angle), altered force field (see text). [e] Ferrocytochrome c minus deoxyhemoglobin. [f] Spin-state marker bands. [g] Coordinate labels as in ref 4. [h] These modes have not been detected. [i] Not detected in deoxyhemoglobin.