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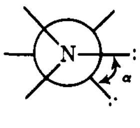
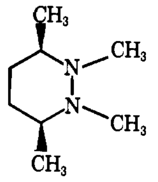
Geometry of Hydrazine Cation Radicals

Sir:

The simplest example of a molecule containing a vicinal lone pair–lone pair interaction is hydrazine, the geometry of which has received a fair amount of study, both experimentally and theoretically.[1] Because interaction of the lone-pair orbitals is destabilizing, hydrazines which are free to rotate adopt a gauche conformation, **1**, α approaching 60–90°, to minimize overlap, although steric constraints can force α to assume almost any value.[2] A consequence of the destabilizing electronic interaction is that hydrazines are particularly easily oxidized. Although hydrazinium cation radicals which have N–H bonds are so unstable that flow systems are required for detection by esr,[3] tetraalkylhydrazinium cation radicals are conveniently stable for esr study.[4] We have been interested in the geometry of hydrazinium radicals, since it should be quite different from that of the hydrazine. When an electron is removed, considerable flattening at the nitrogens should occur. Esr studies of hydrazinium radicals have been interpreted as showing the proper nitrogen splitting for sp^2 hybridization at nitrogen[3] (odd electron in pure p orbitals), but the present state of knowledge about nitrogen splittings does not allow very much accuracy in prediction of a(N) values.



1



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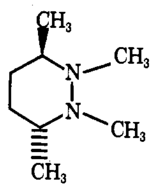

3

The esr splitting for a hydrogen on the carbon α to a hydrazinium nitrogen (a "β" splitting in the usual esr nomenclature) should be given by the relationship $a(\mathrm{H}) = (A + B\cos^2\theta)\rho_\alpha$, where A is small, B is large (about 50 G for a p orbital on carbon and apparently[4] about the same size for the spin-bearing orbital at a hydrazinium nitrogen), θ is the dihedral angle between the C–H bond and the spin-bearing orbital axis, and ρ_α is the spin density at the hydrazinium nitrogen. In a six-ring hydrazinium radical cation, for any one conformation the splitting for the two hydrogens of an α-methylene group would be different, since different θ values would be involved, but ring flipping and nitrogen inversion are expected to be fast on the esr time scale at accessible temperatures. The observed splitting will therefore reflect a weighted average value of θ over all the conformations which are populated.

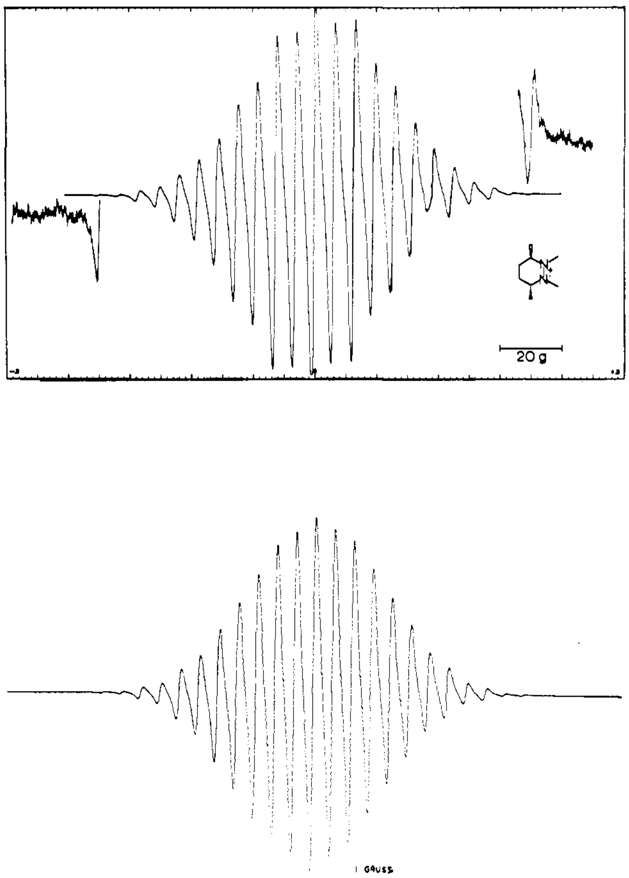

Figure 1. Esr spectrum of $\mathbf{3}\cdot^{+}$ compared with a simulation using the splittings quoted in the text.

We wish to report esr results for *cis*- and *trans*-1,2,3,6-tetramethylhexahydropyridizine[5] (**2** and **3**, respectively) which demonstrate that even in a relatively unstrained six-membered ring, the hydrazinium group is not planar. Electrolytic oxidation of the hydrazines in acetonitrile (0.05 *M* in sodium perchlorate) gave the hydrazinium radical cations, and the esr spectra were recorded. The spectrum of $\mathbf{2}\cdot^{+}$ consisted of 13 groups of lines, and analyzed for $a(6\mathrm{H}) = 12.4$ G, $a(2\mathrm{N}) \approx a(2\mathrm{H}) = 13.1$ G. In contrast, the spectrum of $\mathbf{3}\cdot^{+}$ consisted of 21 lines with a separation of about half that observed for the cis compound, and analyzed for $a(6\mathrm{H}) \approx a(2\mathrm{N}) \approx 12.4$, $a(2\mathrm{H}) \approx 6.2$ (Figure 1). It is clear that averaged values are being observed for the methine hydrogen splittings, and that these C–H bonds are, on the average, better aligned for overlap with the hydrazinium spin-bearing orbitals in $\mathbf{2}\cdot^{+}$ than in $\mathbf{3}\cdot^{+}$.

Assuming that the hydrazinium group was flat, $\mathbf{2}\cdot^{+}$ would exist in the equilibrating half-chair conformations **2a** $\rightleftharpoons$ **2b**, and the methine hydrogen splitting observed would be the average of that for a pseudoaxial and a pseudoequatorial hydrogen, since **2a** and **2b** are of equal energy. The corresponding conformations for the trans compound, **3a** and **3b**, are not of equal energy, because of the 1,3-dipseudoaxial $\mathrm{CH_3}$–H interactions of **3b**. Because the ratio of **3a**/**3b** would be considerably

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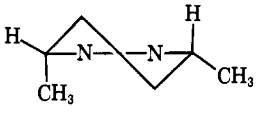
[1] M. S. Gordon, *J. Amer. Chem. Soc.*, **91**, 3122 (1969), and references therein.

[2] J. E. Anderson, *ibid.*, **91**, 6374 (1969).

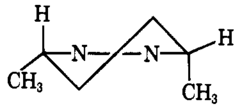
[3] J. Q. Adams and J. R. Thomas, *J. Chem. Phys.*, **37**, 1904 (1963).

[4] S. F. Nelsen, *J. Amer. Chem. Soc.*, **88**, 5666 (1966).

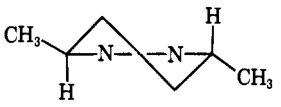
[5] Anderson[2] has prepared **3** previously; final purification was by preparative vpc. The low-temperature nmr spectra are consistent with the structures.



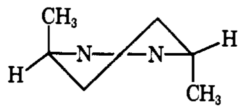
2a



2b

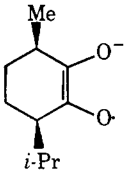


3a

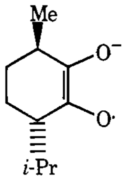


3b

greater than 1, the methine hydrogen splitting observed for **3**$\cdot^+$ would be nearly that expected for a pseudoaxial hydrogen, making the ratio of methine hydrogen splittings for **2**$\cdot^+$/**3**$\cdot^+$ < 1, since pseudoaxial hydrogens have a lower θ value and hence a larger splitting than pseudoaxial ones. Essentially this experiment has been done by Russell's group,[6] using the authentically flat semidione spin label, and giving the predicted result. The cis compound **4** showed the smaller splittings (10.8 and



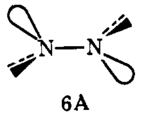
4



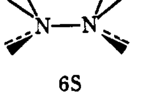
5

6.7 for the two different α hydrogens). Since the conformations corresponding to **2a** and **2b** are not equal in energy, the splitting for the hydrogen on the carbon-bearing isopropyl is nearer the pseudoaxial value, and the other nearer the pseudoequatorial value. The trans compound **5** with both hydrogens almost exclusively pseudoaxial had a(2H) = 12.4. Since the hydrazinium cation radical label gave the reverse of this result, cis/trans splitting of about 2, the hydrazinium portion of the molecule is clearly not flat.

Deviation from planarity could occur in two basically different ways, to move toward an anti conformation (**6A**) or toward a syn one (**6S**). If the bending were



6A



6S

toward **6A**, the prediction of the cis/trans methine splitting ratio being <1 would still hold, for the ring conformation would then be between a half-chair and a chair. Only if the hydrazine were bent toward the syn (**6S**) conformation would this ratio become >1. In this case, the ring would adopt a conformation tending toward a boat, and then the cis compound **2**$\cdot^+$ has the sterically more favorable conformations with C–H$_\beta$ more nearly aligned with the spin-bearing orbitals on nitrogen ("bowsprit" type), while **3**$\cdot^+$ has pairs of conformations of equal energy which average the β hydrogens between favorable and unfavorable θ angles.[7]

Discussion of the amount of deformation from planarity and its consequences will occur in future publications.

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[6] G. A. Russell, G. R. Underwood, and D. C. Lini, *J. Amer. Chem. Soc.*, **89**, 6636 (1967).

C_2O, CN_2, and C_3O Molecules[1]

Sir:

In the course of an investigation of the reactions of carbon atoms and molecules with each other at temperatures near 4°K,[2,3] a recurring infrared band appeared at 2244 cm^{-1}. It had also been observed by Jacox, *et al.* (JMMT),[4] when C_3O_2 was photolyzed in an argon matrix at 4°K. We report here the assignment of this band to the CCCO molecule formed by the trapping of carbon atoms with CO and their subsequent reaction to yield C_2O and then C_3O. CNN was prepared in a similiar way and the vibrational assignment of Milligan and Jacox[5] corroborated.

The furnace, variable-temperature dewar, and spectrometers used in the matrix-isolation experiments were similar to those described previously.[3] A beam of ^{12}C (or ^{13}C) atoms was vaporized from TaC[6] at temperatures near 3000°K by packing a thin-walled (0.008 in.) tantalum tube with graphite and allowing the carbon to essentially vaporize "through" the carbided tube.[3] ^{13}C was vaporized in the same way from 96% isotopically enriched graphite obtained from Mound Laboratory, Monsanto Chemical Co. At the highest temperatures some Ta atoms are also in the vapor and CO (from the graphite) is eliminated with difficulty. The carbon atoms were condensed with an argon: ^{12}C^{16}O mixture (200:1) onto a CsI window at 4°K. ^{12}C^{18}O was also used as a reactant (from Miles Laboratories, enriched to 92%). CNN was prepared by trapping carbon atoms in a pure N_2 matrix.

All isotopic combinations of the available C and CO were allowed to react, and the result for ^{13}C + ^{12}C^{18}O is shown in the ir absorption spectra in Figure 1. The bands in the originally formed matrix are in the top tracing, and subsequent diffusions are shown in descending order. The CCO band at 1928 cm^{-1} is formed immediately, and the C_3O band (2204 cm^{-1}) and the doublet of C_3O_2 (2228, 2243 cm^{-1}) grow in with further warming and quenching. In the region of 1800–2000 cm^{-1} $Ta(CO)_n$ bands also are formed[7] and unfortunately obscure the other, apparently weak, absorption band of C_3O expected in that frequency range. A stretching frequency for C_3O is also expected near 1000

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[1] The authors gratefully acknowledge the support of the Air Force Office of Scientific Research (NC-AFOSR 68-1588) and the National Science Foundation (GP-25411).

[2] K. R. Thompson, R. L. DeKock, and W. Weltner, Jr., *J. Amer. Chem. Soc.*, **93**, 4688 (1971).

[3] W. Weltner, Jr., and D. McLeod, Jr., *J. Chem. Phys.*, **45**, 3096 (1966).

[4] M. E. Jacox, D. E. Milligan, N. G. Moll, and W. E. Thompson, *ibid.*, **43**, 3734 (1965).

[5] D. E. Milligan and M. E. Jacox, *ibid.*, **44**, 2850 (1966).

[6] T. F. Lyon in "Condensation and Evaporation of Solids," E. Rutner, P. Goldfinger, and J. P. Hirth, Ed., Gordon and Breach, New York, N. Y., 1964, pp 434–449.

[7] R. L. DeKock, *Inorg. Chem.*, **10**, 1205 (1971).