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ESR Study of the 2,3-Diazabicyclo[2.2.2]oct-2-ene Radical Cation in Freon Matrices

Ffrancon Williams* and Qing-Xiang Guo*

Department of Chemistry, University of Tennessee
Knoxville, Tennessee 37996-1600

Peter A. Petillo and Stephen F. Nelsen*

Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

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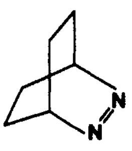
Despite recent interest in the structure and reactivity of azoalkane radical cations,[1-4] only one report[4] claims to have characterized such intermediates by ESR spectroscopy. Surprisingly, this study[4] concluded that the azoethane and azopropane radical cations are π_{NN} rather than the $\sigma(n_-)$ species anticipated from the photoelectron spectra of the neutral compounds,[5] this interconversion being attributed to a conformational preference in the π cation[4] although it is not clear why this effect should overcome the large difference (2.6 eV) in vertical ionization energies.[5d] In contrast, we now report ESR results demonstrating that the rigid 2,3-diazabicyclo[2.2.2]oct-2-ene (**1**) radical cation has the expected σ structure with a $b_2(n_-)$ SOMO[5d,6] in C_{2v} symmetry.



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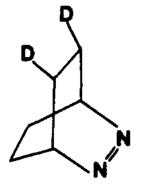
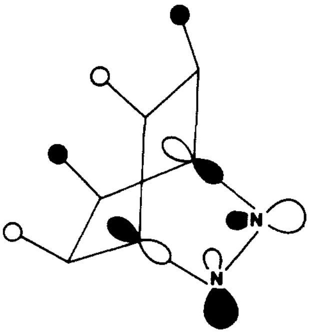


1-d₂

Blackstock and Kochi[3] have previously carried out an ESR study of the radiolytic oxidation of **1** in a $CFCl_3$ matrix. They established that the signal carrier produced by γ irradiation at 77 K photorearranges to the cyclohexene radical cation on exposure to blue light (λ > 415 nm). Unfortunately, they were unable to analyze the complicated ESR spectrum of the original oxidized species and consequently could not decide whether it was due to **1**$^{\bullet+}$ or some other intermediate such as the cyclohexane-1,4-diyl radical cation[7] derived from **1**$^{\bullet+}$ by loss of nitrogen.

Our interest in these species led us to study the oxidation in other Freon matrices. Above 80–90 K, the ESR spectra of the oxidized species in $CF_2ClCFCl_2$, $CFCl_2CFCl_2$, CF_3CCl_3, and CF_2ClCCl_3 changed reversibly from an asymmetric pattern[8] similar to that previously reported in $CFCl_3$[3] to an isotropic spectrum of 13 components which can be analyzed (Figure 1) as an overlapping quintet of quintets corresponding to the relation $a(2N) = 2a(4H) = 31.0$ G.[9] These major couplings[10-12] agree with those calculated for the $^2B_2$ ground state of **1**$^{\bullet+}$ (Table I), the 15.5 G coupling to the four anti hydrogens[13] confirming the σ-delocalized character of the b_2 SOMO depicted below.[14]



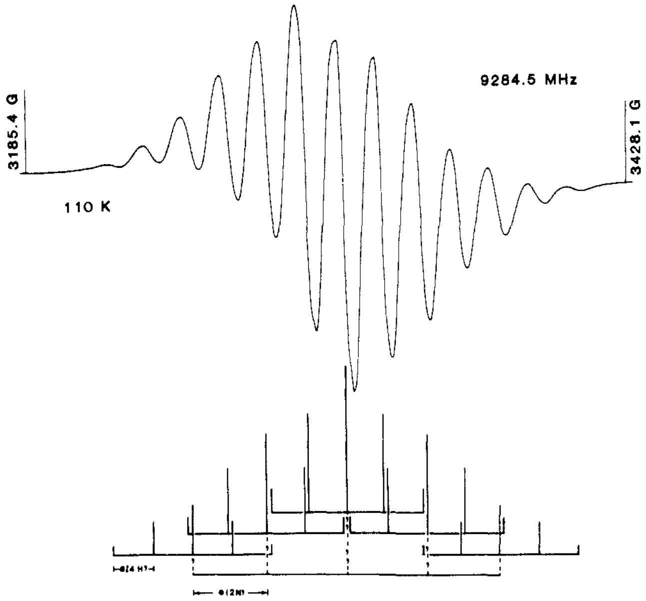


Figure 1. ESR spectrum of a γ-irradiated 1 mol% solution of 2,3-diazabicyclo[2.2.2]oct-2-ene in $CF_2ClCFCl_2$ (dose, 0.3 Mrad) at 110 K with a stick-diagram reconstruction of the hyperfine pattern for the radical cation. A spectrum computed from the hyperfine parameters of Table I and a line width of 5 G matched both the positions and relative intensities of the 13 lines. The corresponding spectrum of a γ-irradiated $CF_2ClCFCl_2$ (blank) sample showed only weak anisotropic signals from matrix radicals.

The photoconversion to the cyclohexene radical cation[3] was also observed in the $CF_2ClCFCl_2$ (Figure 2, (a) and (b)) and $CFCl_2CFCl_2$ matrices[15] and can now be represented by reaction 1, the putative cyclohexane-1,4-diyl radical cation intermediate being undetectable under photobleaching conditions.[7] Subsequently,

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(1) (a) Engel, P. S.; Keys, D. E.; Kitamura, A. *J. Am. Chem. Soc.* **1985**, *107*, 4964. (b) Bae, D. H.; Engel, P. S.; Hoque, A. K. M. M.; Keys, D. E.; Lee, W.-K.; Shaw, R. W.; Shine, H. J. *J. Am. Chem. Soc.* **1985**, *107*, 2561. (c) Hoque, A. K. M. M.; Kovelsky, A. C.; Lee, W.-K.; Shine, H. J. *Tetrahedron Lett.* **1985**, 5655.

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(5) (a) Haselbach, E.; Heilbronner, E. *Helv. Chim. Acta* **1970**, *53*, 684. (b) Haselbach, E.; Schmeizer, S. *Helv. Chim. Acta* **1971**, *54*, 1575; **1972**, *55*, 1745. (c) Brundle, C. R.; Robin, M. B.; Kuebler, N. S.; Basch, H. *J. Am. Chem. Soc.* **1972**, *94*, 1451. (d) Houk, K. N.; Chang, Y.-M.; Engel, P. S. *J. Am. Chem. Soc.* **1975**, *97*, 1824.

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(8) The asymmetry probably results from g anisotropy; $g_{iso} = 2.0020$ (3) and $g_{\parallel} = 2.0034$ (5).

(9) This analysis of the ESR spectrum has subsequently been corroborated by proton ENDOR measurements: Gerson, F.; Qin, X.-Z. *Helv. Chim. Acta* **1988**, *71*, 1498. We thank Professor Gerson for informing us of these results.

(10) $a(2N)$ is within the range (28–36 G) of nitrogen couplings for structurally related radicals such as the iminoxyls[11] and o,o′-disubstituted arylnitroso radical cations.[12]

(11) Cf. Neugebauer, F. A. In *Landolt-Börnstein, New Series, Group II, Volume 9, Magnetic Properties of Free Radicals*; Fischer, H., Hellwege, K.-H., Eds.; Springer-Verlag: Berlin-Heidelberg, 1979; Part c1, pp 123–178.

(12) Cf. (a) Sosonkin, I. M.; Belevskii, V. W.; Strajov, G. N.; Domarev, A. N.; Yarkov, S. P. *J. Org. Chem. USSR* **1982**, *18*, 1504. (b) Murabayashi, S.; Shiotani, M.; Sohma, J. *J. Phys. Chem.* **1979**, *83*, 844. (c) Detsina, A. N.; Efremova, N. V.; Starichenko, V. F. *J. Org. Chem. USSR* **1982**, *18*, 970.

(13) ESR spectra of the radical cation from the stereospecifically labeled **1**-d_2 (*cis-anti*-5,6-dideuterio-**1**), prepared by a method similar to that described by Edmunds and Samuel (Edmunds, A. J. F.; Samuel, C. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1179) confirmed that the 15.5 G coupling is to the anti hydrogens. Although the spectra from **1**-$d_2^{\bullet+}$ did not become isotropic in $CF_2ClCFCl_2$, $CFCl_2CFCl_2$, and CF_3CCl_3 at the higher temperatures, comparison with the corresponding anisotropic spectra of **1**$^{\bullet+}$ showed that the spectral width was reduced by ca. 31 G, as expected.

(14) Cf. (a) Snow, L. D.; Williams, F. *Faraday Discuss. Chem. Soc.* **1984**, *78*, 57. (b) Nelsen, S. F.; Kapp, D.; Snow, L. D.; Williams, F., unpublished work cited in *Faraday Discuss. Chem. Soc.* **1984**, *78*, 97–100.

(15) The photofragmentation of **1**$^{\bullet+}$ was not observed in CF_3CCl_3 and CF_2ClCCl_3, indicating that these matrices can prevent the extrusion of molecular nitrogen from the photoactivated state.

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Table I. Comparison of Calculated and Experimental Isotropic Hyperfine Couplings for $\mathbf{1}^{\bullet+}$

interatomic distances[a] (pm)				nuclei	AM1[b] spin densities		INDO[c] spin densities ρ_s	calcd hfcs (G) from INDO spin densities	expt. hfcs (G)
					ρ_s	ρ_s[d]			
C(1)-N(2)	155.2	C(1)-H_{br}	112.0	$2\,^{14}N$	0.0474	0.0517	0.0512	19.4,[e] 28.1,[f] 33.1[g]	31.0
N(2)-N(3)	117.3	C(5)-H_{syn}	112.2	$2\,^{1}H_{br}$	-0.0107	-0.0033	-0.0065	-3.5,[h] -3.3[i]	(3.6)[j]
C(1)-C(6)	154.2	C(5)-H_{anti}	112.5	$4\,^{1}H_{syn}$	0.0010	0.0010	0.0025	1.4,[h] 1.3[i]	
C(5)-C(6)	152.6			$4\,^{1}H_{anti}$	0.0243	0.0177	0.0267	14.4,[h] 13.5[i]	15.5[k]

[a] Optimized geometry by AM1 method corresponding to a ΔH_f for $\mathbf{1}^{\bullet+}$ of 241.985 kcal/mol. The CNN angle is 117.3 deg. [b] Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902. [c] Pople, J. A.; Beveridge, D. L.; Dobosch, P. A. *J. Chem. Phys.* **1967**, *47*, 2026. [d] After spin annihilation. [e] Using the INDO proportionality constant of 379.4 G. [f] Using the calculated atomic value of 550 G (Morton, J. R.; Rowlands, J. R.; Whiffen, D. H. *National Physical Laboratory Bulletin*; no. BPR 13, 1962). [g] Using the calculated atomic value of 646 G (Morton, J. R.; Preston, K. F. *J. Magn. Reson.* **1978**, *30*, 577). [h] Using the INDO parameter of 540 G. [i] Using the atomic value for hydrogen of 506.7 G. [j] Measured from hf substructure of parallel features in the anisotropic spectrum recorded in $CFCl_3$ at 130 K. [k] ENDOR measurements[9] give 15.09 G.

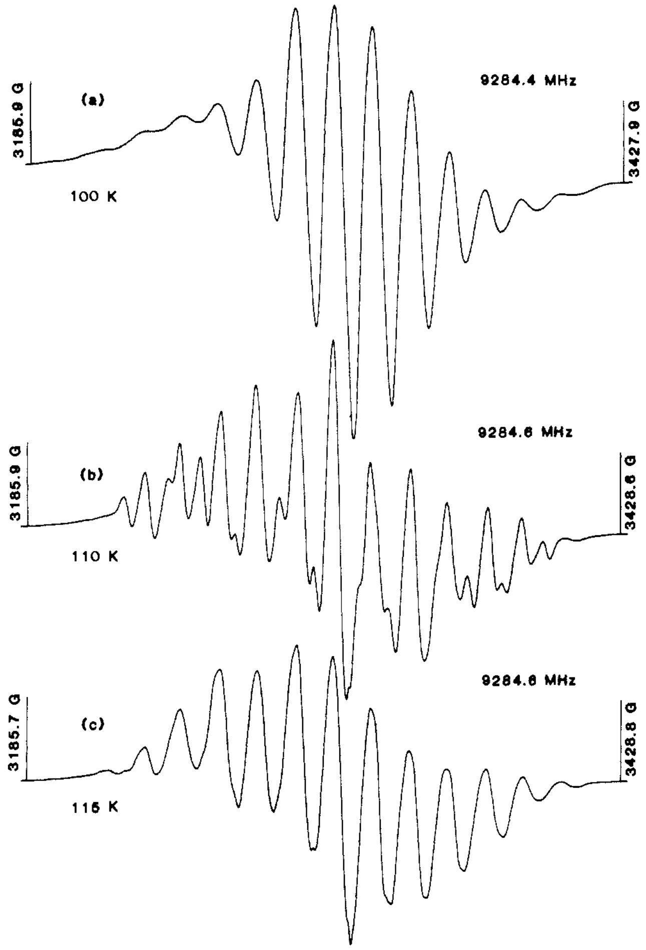
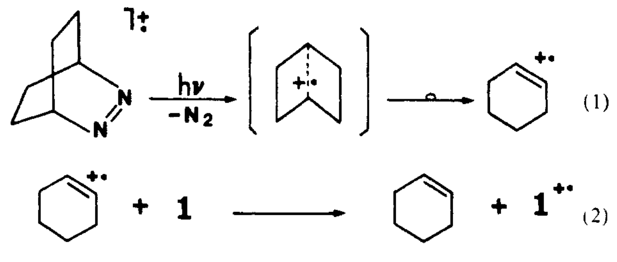


Figure 2. ESR spectrum of a γ-irradiated 1 mol% solution of 2,3-diazabicyclo[2.2.2]oct-2-ene in $CF_2ClCFCl_2$ (dose, 0.3 Mrad) recorded consecutively (a) at 100 K, (b) at 110 K after photobleaching at 100 K with blue light ($\lambda < 400$ nm; glass filter C. S. no. 7-54) from a 450-W xenon lamp, and (c) at 115 K. Spectra (a), (b), and (c) are assigned to $\mathbf{1}^{\bullet+}$, cyclohexene$^{\bullet+}$, and $\mathbf{1}^{\bullet+}$ respectively. The resolution of the inner lines of the cyclohexene$^{\bullet+}$ spectrum depends on both the freon matrix and the temperature.

the spectrum of $\mathbf{1}^{\bullet+}$ reappeared on warming the $CF_2ClCFCl_2$ matrix from 110 to 115 K (Figure 2, (b) and (c)). This thermal transformation does not occur in $CFCl_3$ and can be attributed to the bimolecular electron-transfer reaction 2[16] which becomes possible in the mobile $CF_2ClCFCl_2$ matrix.[17] Thus, reactions 1 and 2 constitute a photochemically assisted chain reaction for the conversion of **1** to cyclohexene via their radical cations, the loss of nitrogen in the photofragmentation of $\mathbf{1}^{\bullet+}$ resulting in a more powerful oxidant which regenerates $\mathbf{1}^{\bullet+}$.



Acknowledgment. We are indebted to Sheng Dai for his help with the computations. Professor F. Gerson (University of Basel) kindly informed us that proton ENDOR measurements agree with the interpretation of the ESR spectrum of $\mathbf{1}^{\bullet+}$ given here and in the preprint of our communication, and we also thank Professor P. H. Rieger (Brown University) for his interest in the work. This research was supported at the University of Tennessee by the Division of Chemical Sciences, U.S. Department of Energy (Grant DE-FG05-88ER13852), and at the University of Wisconsin by the National Science Foundation (Grant CHE-8415077).

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Photosensitized Cleavage of a Thymine Dimer by an Antibody

Andrea G. Cochran,[1] Renee Sugasawara,[2] and
Peter G. Schultz*[,1]

Department of Chemistry, University of California
Berkeley, California 94720
Igen, Inc., 1530 East Jefferson Street
Rockville, Maryland 20852

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The development of monoclonal antibody technology has provided ready access to homogeneous, high affinity ligand binding sites which recognize a large number of structurally diverse molecules.[3] Consequently, the development of strategies for the introduction of catalytic activity into antibodies should allow the design of biological catalysts with a wide range of specificities. One such strategy involves the generation of antibodies whose binding sites are complementary to the rate-limiting transition state of the reaction of interest. For example, antibodies elicited to transition-state analogues for acyl transfer and pericyclic reactions were found to accelerate the corresponding reactions 10^4-10^6-fold.[4-10] Alternatively, it should be possible to obtain

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(1) University of California.

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