162. Applications of ENDOR Spectroscopy to Radical Cations in Freon Matrices

Part 2[1])

The Radical Cation of 2,3-Diazabicyclo[2.2.2]oct-2-ene

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The radical cation of 2,3-diazabicyclo[2.2.2]oct-2-ene (**1**), generated by γ-rays in a $CF_2ClCFCl_2$ matrix, has been fully characterized by its hyperfine data with the use of ESR, ENDOR, and TRIPLE resonance spectroscopy. The isotropic coupling constants for $\mathbf{1}^{+}$ are +3.14 mT for the two ^{14}N nuclei in the azo group, −0.336 mT for the two protons at the bridgehead C atoms, and +1.51 and +0.135 mT for the sets of four *exo*- and four *endo*-protons, respectively. MO calculations indicate that these values are consistent with an electron removal from an orbital represented by the antibonding combination (n_-) of the lone-pair atomic orbitals at the two N atoms. The corresponding radical anion $\mathbf{1}^{\overline{\cdot}}$ is persistent in fluid solution and its hyperfine data, combined with MO calculations, point to an electron uptake into the antibonding π orbital (π^*) of the azo group. It is, thus, reasonable to classify $\mathbf{1}^{+}$ as a σ and $\mathbf{1}^{\overline{\cdot}}$ as a π radical.

Introduction. – Azoalkanes are precursors of alkanediyls, because of their facile loss of N_2 [2]. The radical anions of several azoalkanes are persistent in fluid solution and have been studied by ESR spectroscopy [3]. By contrast, the radical cations of azoalkanes are short-lived, and only in a recent paper [4], ESR spectra attributed to such species in freon matrices have been described. Analysis of these spectra is rather problematic due to the substantial ^{14}N hyperfine anisotropy which does not average out in rigid solution.

Some time ago, we have found that the radical cation of 2,3-diazabicyclo[2.2.2]oct-2-ene (**1**) persists in freon matrices. This work was in progress, when Prof. *Williams* kindly informed us [5] about the specific conditions under which an essentially isotropic ESR spectrum of $\mathbf{1}^{+}$ is obtained in such an environment. While [5] provides information about the major hyperfine features, our use of ENDOR and TRIPLE resonance spectroscopy under the same conditions has enabled us to characterize $\mathbf{1}^{+}$ by more complete and more precise hyperfine data. A communication on our part appears, therefore, justified, in addition to [5] which has already been submitted for publication.

Experimental. – Diazabicyclooctene **1** was synthesized according to [6] with the use of cyclohexa-1,3-diene and diethylazodicarboxylate as the starting material. The radical cation $\mathbf{1}^{+}$ was prepared by γ-irradiation of **1** (^{60}Co source) in $CFCl_3$, CF_3CCl_3, or $CF_2ClCFCl_2$ matrices at 77 K. The ESR, ENDOR, and TRIPLE resonance studies were carried out on a *Bruker-ESP-300* spectrometer system.

Results and Discussion. – In $CFCl_3$ and CF_3CCl_3 matrices, $\mathbf{1}^{+}$ retains anisotropic features up to the softening points. On the other hand, in a $CF_2ClCFCl_2$ matrix, the spectrum of $\mathbf{1}^{+}$ becomes essentially isotropic at 110 K [5]. Such a spectrum

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[1]) Part 1, see [1].

($g = 2.0022 \pm 0.0005$), shown in the *Figure*, exhibits 13 almost equidistant hyperfine components spaced by *ca.* 1.55 mT. In the corresponding proton ENDOR spectrum, displayed in the same *Figure*, the position of the low-frequency signal *(exo)* at 6.67 MHz is given by ($|a/2| - \nu_H$) where $|a/2| = 21.13$ and $\nu_H = 14.46$ MHz are half the coupling constant (in MHz) and the frequency of the free proton, respectively [7]. (The high-frequency counter-signal at ($|a/2| + \nu_H$) = 35.59 MHz is outside the range accessible to our RF source.) The pertinent coupling (a) is 1.51±0.01 mT; in [5], it has been taken as the average spacing (1.55 mT) of the ESR components. Its assignment to the four equivalent *exo*-protons in the two ethano moieties of $\mathbf{1}^{+}$ is straightforward, considering similar long-range couplings in structurally related radicals [8]. Reduction in the total width of the ESR spectrum by *ca.* 3 mT, as a consequence of the dideuteriation in the *exo*-positions of $\mathbf{1}^{+}$ [5], confirms this assignment.

The four remaining proton ENDOR signals at higher frequencies *(Figure)* occur as pairs centered at ν_H. The two signals (br) at 9.76 and 19.16 MHz are approximately half as intense as those *(endo)* at 12.57 and 16.35 MHz. This ratio was verified by a special TRIPLE resonance experiment [7]. The outer pair of signals is, thus, assigned to the two

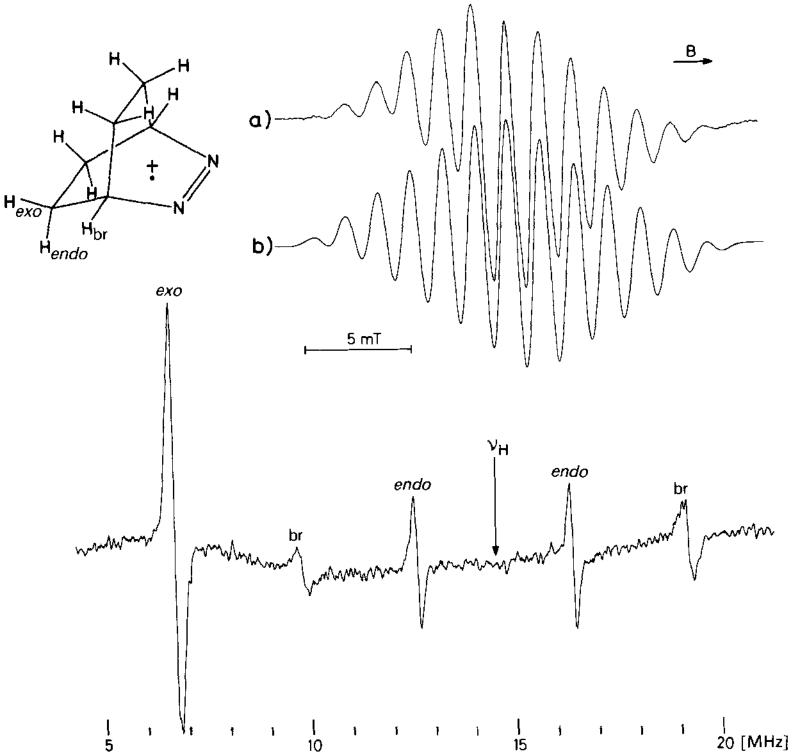

Figure. Top: *ESR spectra of* $\mathbf{1}^{+}$ (*a*) experimental; solvent, $CF_2ClCFCl_2$; temp., 115 K; *b*) simulated with the coupling constants given in the text and in the *Table*; line-shape, *Gaussian*; line-width, 1 mT). The simulation does not account for the incomplete averaging of the ^{14}N hyperfine anisotropy which broadens the outer components more strongly than the inner ones. Bottom: *corresponding proton ENDOR spectrum.*

Table. *Calculated and Observed Coupling Constants for the Radical Cation of 2,3-Diazabicyclo[2.2.2]oct-2-ene* (**1**)

Nuclei	s-Spin densities by INDO[a])	Coupling constants [mT] Calc.	Obs.
2 ^{14}N	+0.0512	+3.31[b])	+3.14 (3.1[a]))
2 $^{1}H_{br}$	−0.0065	−0.358[c])	−0.336
4 $^{1}H_{exo}$	+0.0267	+1.47[c])	+1.51 (1.55[a]))
4 $^{1}H_{endo}$	+0.0025	+0.138[c])	+0.135

[a]) [5]. [b]) Atomic conversion factor +64.7 mT [11]. [c]) INDO conversion factor +55.0 mT [9].

equivalent protons at the bridgehead C atoms and the inner pair to the four equivalent *endo*-protons in the two ethano moieties. The coupling constants associated with these pairs are 0.336 ± 0.003 mT for the two bridgehead protons and 0.135 ± 0.002 mT for the four *endo*-protons. Both values could not be determined in [5], since they are considerably smaller than the line-widths in the ESR spectrum (0.8–1.2 mT). According to the general TRIPLE resonance spectrum [7], the sign of 0.336 mT is opposite to that of 1.51 and 0.135 mT. Since the mechanism of the long-range coupling (spin transfer by delocalization) requires a positive sign for 1.51 mT, the value of 0.135 mT must also be positive, whereas 0.336 mT should have a negative sign.

The coupling constant of the two ^{14}N nuclei in the azo group was determined by the simulation of the ESR spectrum *(Figure)* as 3.14 ± 0.02 mT ([5]: 3.10 mT). In view of its large magnitude, the sign of 3.14 mT is undoubtedly positive.

In the *Table*, the coupling constants observed for $\mathbf{1}^{+}$ are compared with the corresponding values [5], calculated by the INDO method [9]. The excellent agreement between experiment and theory supports the prediction that the singly occupied orbital (SOMO) of $\mathbf{1}^{+}$ can, to a good approximation, be represented by an antibonding combination (n_{-}) of the two N lone-pair atomic orbitals. This conclusion is in accordance with the photoelectron spectrum of **1** [10] in which the band of lowest energy is attributed to an electron removal from a n_{-} like orbital. As has been stated in [5], $\mathbf{1}^{+}$ should, thus, be classified as a σ radical, the large ^{14}N coupling constant being due to a substantial *s*-character of the SOMO at the two N atoms.

It is noteworthy that the radical anion $\mathbf{1}^{\overline{\cdot}}$ can readily be generated by reduction of **1** with alkali metals in fluid ethereal solution [3b]. From the ESR (g = 2.0040 ± 0.0001) and proton ENDOR spectra of $\mathbf{1}^{\overline{\cdot}}$ in 1,2-dimethoxyethane at 213 K, with K^{+} as the counterion, the following coupling constants [mT] were determined: 0.878 ± 0.005 (2 ^{14}N), 0.274 ± 0.002 (4 H_{exo}), 0.073 ± 0.001 (4 H_{endo}), 0.0205 ± 0.0005 (2 H_{br}), and 0.053 ± 0.001 (1 ^{39}K). The general TRIPLE resonance spectrum indicates that the sign of 0.274 mT (presumably positive) is opposite to those of 0.073 and 0.0205 mT (presumably negative). The expectation that $\mathbf{1}^{\overline{\cdot}}$ has to be classified as π radical is borne out by INDO calculations [9] in which the SOMO of $\mathbf{1}^{\overline{\cdot}}$ is represented by the antibonding π orbital (π*) of the azo group.

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