The Radical Cation of Azatriquinane: An ESR Study

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Azatriquinane (= 10-azatricyclo[5.2.1.$0^{1,10}$]decane; **1**) was oxidized to its radical cation $\mathbf{1}^{\bullet+}$ by γ- irradiation in a $CF_2ClCFCl_2$ matrix at 77 K. A prominent feature of the ESR spectrum of $\mathbf{1}^{\bullet+}$ is the ^{14}N-hyperfine anisotropy which broadens the components with $M_I(^{14}N) = \pm 1$. The observed coupling constants are $a_N = +2.5$ and $a_H = +4.0$ mT for the ^{14}N nucleus and the three methine β-protons, respectively. While the a_N value points to pyramidalization at the N-atom comparable to that in the radical cation of quinuclidine (= 1-azabicyclo[2.2.2]octane; **4**), an eclipsing of the singly occupied orbital at this atom by the three $C-H_\beta$ bonds is indicated in view of the large a_H value. Theoretical calculations on the geometry of $\mathbf{1}^{\bullet+}$ are in accord with the conclusions drawn from the experimental findings.

Introduction. – Azatriquinane (= 10-azatricyclo[5.2.1.$0^{1,10}$]decane; **1**)[1]) has been recently synthesized [1]. It can be considered both as a cyclic dehydrotriisopropylamine (**2**) [2] and a perhydro derivative of the hypothetical cycl[2.2.2]azinyl radical ($\mathbf{3}^{\bullet}$) [3]; moreover, its triene analogue, azatriquinacene, has been proposed as a precursor to 1,16-diazadodecahedrane [4]. An X-ray crystal structure was obtained for the HBF_4 salt of **1** [4], and the geometry of **1** was calculated at the 6-31G* *ab-initio* level of theory [5]. In contrast to its acyclic analogue **2** which is planar [2] or slightly nonplanar [6], **1** should be distinctly cup-shaped and of C_3 symmetry, with the five-membered rings arranged in a twisted conformation [5]. At the level of the applied theory, pyramidalization at the N-atom of **1** is predicted to be comparable to that in the structurally related quinuclidine (= 1-azabicyclo[2.2.2]octane; **4**).

The vertical ionization energy of **1** was determined by photoelectron (PE) spectroscopy as 7.80 eV [5] which is a little lower than the corresponding value of **4** (8.05 eV) [7], but substantially higher than that of **2** (7.18 eV) [2]. Ionization of an amine primarily implies removal of an electron from the N lone pair and causes flattening of the molecule at the N-atom. The radical cations of acyclic and monocyclic amines are thus generally planar [8]. However, in those of polycyclic amines such as **4**, and, even more so, 1-azanorbornane (= 1-azabicyclo[2.2.1]heptane; **5**), planarity cannot be achieved because of the rigid molecule framework [9]. It has thus been of interest to investigate the structure of $\mathbf{1}^{\bullet+}$ by ESR spectroscopy, in order to inquire into the geometry of this tricyclic radical cation.

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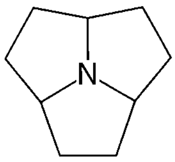
1) The systematic *IUPAC* name of **1** is octahydro-2aα,4aα,6aα-1*H*-pyrrolo[2,1,5-*cd*]pyrrolizine.



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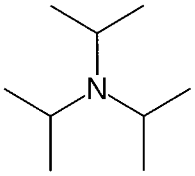

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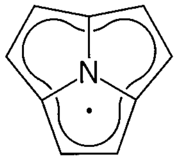

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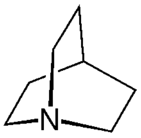

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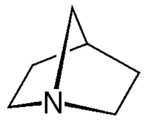

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Results. – Oxidation of **1** to $\mathbf{1}^{\cdot+}$ failed when the amine was treated with SbF_5 in CH_2Cl_2 at 195 K, although this method was successful for trialkylamines having their vertical ionization energies below 8 eV [10]. On the other hand, an ESR spectrum of a radical cation ($g = 2.0035 \pm 0.0001$) was readily observed upon γ-irradiation of **1** with a ^{60}Co source in a 'mobile' $CF_2ClCFCl_2$ matrix. At 77 K, this spectrum exhibited a three-proton quartet spaced by 4.00 ± 0.05 mT. Raising the temperature to 125 K led to the appearance of additional much broader lines flanking the original quartet at a distance of 2.5 ± 0.1 mT, as shown in *Fig. 1.* This finding is interpreted in terms of ^{14}N-hyperfine anisotropy which can be accounted for by the formula [11a]

$$\text{l.w.} = \text{A} + \text{B}\ M_\text{I} + \text{C}\ M_\text{I}^2$$

where l.w. is the line-width and M_I are the quantum numbers of the ^{14}N-nuclear spin. The central quartet has $M_\text{I}(^{14}\text{N}) = 0$ and l.w. = A = 0.4 mT, whereas the broad lateral lines are due to components with $M_\text{I}(^{14}\text{N}) = \pm 1$ and l.w. = A + C = 0.8 mT ($B \approx 0$). The observed spectrum is thus consistent with that expected for $\mathbf{1}^{\cdot+}$, being characterized by the coupling constants $|a_\text{N}| = 2.5$ and $|a_\text{H}| = 4.0$ mT for the ^{14}N nucleus and the three methine β-protons, respectively (*Fig. 1*)2). Hyperfine splittings from the twelwe methylene γ-protons are not resolved (< 0.1 mT).

The spectrum of $\mathbf{1}^{\cdot+}$ disappeared when the $CF_2ClCFCl_2$ matrix was warmed above its softening point (130 K). It was replaced by a multiline-hyperfine pattern presumably due to a radical arising from the matrix by the abstraction of a Cl atom ($|a_\text{F}| = 1.81$ and $|a_\text{Cl}| = 0.42$ mT).

Discussion. – Planar radical cations of trialkylamines give rise to a ^{14}N-coupling constant, a_N, of + 2.0 mT3)), deviations from which do not exceed 0.1 mT [10]. In such species, the singly occupied orbital at the N-atom has a 'pure p-character' with the a_N value being due to p,s-spin polarization [11b]. A direct s-contribution to the orbital by pyramidalization increases a_N, so that the observed ^{14}N-coupling constant can be taken

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2) In ESR spectroscopy, protons separated from a π-center by 0, 1, 2, ... sp^2-hybridized C-atoms are denoted α, β, γ... .

3) The positive signs of a_N and a_H are required by theory.

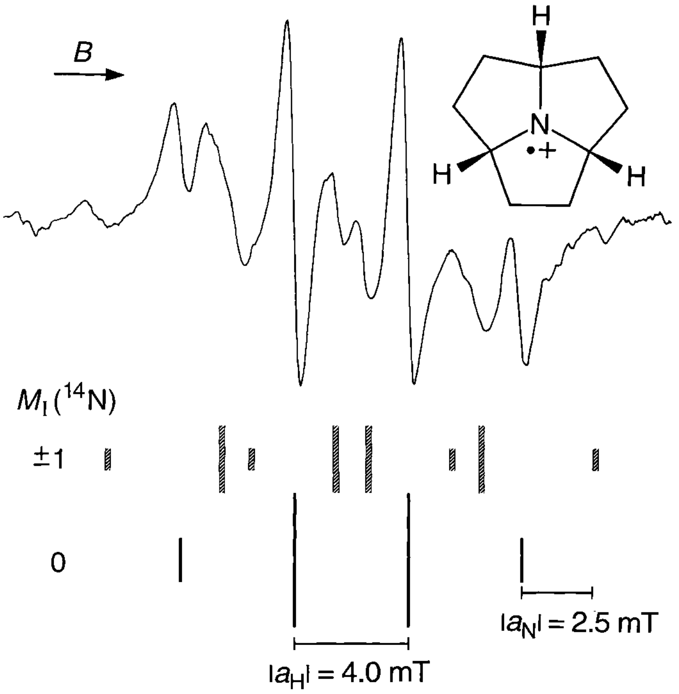


Fig. 1. *ESR Spectrum of* $\mathbf{1}^{\cdot+}$ *in a* $CF_2ClCFCl_2$ *matrix at 125 K and the corresponding stick diagram*

as a measure of nonplanarity of the radical cation. As mentioned in the *Introduction*, the bicyclic radical cations $\mathbf{4}^{\cdot+}$ and $\mathbf{5}^{\cdot+}$ represent examples of this effect on a_N; their ^{14}N-coupling constants are + 2.51 and + 3.02 mT, respectively [9]. The similar geometry at the N-atom in **1** and **4** is thus shared by their radical cations $\mathbf{1}^{\cdot+}$ and $\mathbf{4}^{\cdot+}$ which have practically the same a_N value. An increase of 0.5 mT relative to the ^{14}N-coupling constants for planar radical cations of amines points to a moderate pyramidalization at the N-atom. The finding that such an increase is twice as large for $\mathbf{5}^{\cdot+}$ than for $\mathbf{1}^{\cdot+}$ and $\mathbf{4}^{\cdot+}$ is not unexpected, considering the enhanced resistance to flattening of the strained framework in **5**.

The geometry at the N-atom in trialkylamines and their radical cations is reflected by the sum, $\sum\varphi$, of the three CNC angles φ and by the distance, d, of the N-atom from the plane of the three attached C neighbors. Planarity requires $\sum\varphi = 360°$ and $d = 0$, while a decreasing $\sum\varphi$ and an increasing d indicate that pyramidalization becomes more pronounced. The *Table* gives these values calculated by the AM1 [12] and, in part, the *ab-initio* 6-31G* [13] procedure for $\mathbf{1}/\mathbf{1}^{\cdot+}$, $\mathbf{2}/\mathbf{2}^{\cdot+}$, $\mathbf{4}/\mathbf{4}^{\cdot+}$, and $\mathbf{5}/\mathbf{5}^{\cdot+}$. As anticipated, they comply with the flattening of the amine on passing from the neutral molecule to its radical cation and they correlate with a_N in the sequence $\mathbf{2}^{\cdot+} < \mathbf{1}^{\cdot+} \approx \mathbf{4}^{\cdot+} < \mathbf{5}^{\cdot+}$.

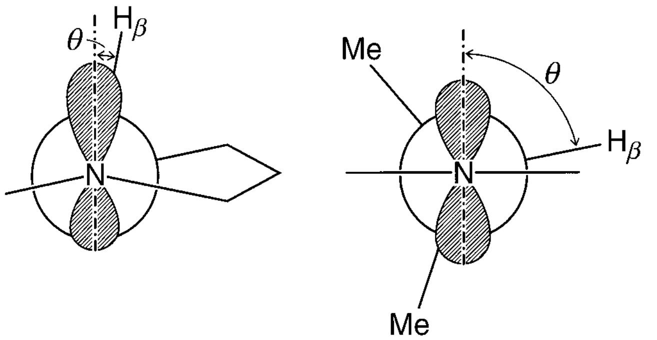
The coupling constant, $a_H = +4.00$ mT[3]), of the three methine β-protons in $\mathbf{1}^{\cdot+}$ is likewise informative with respect to the structure of the radical cation. As for the β-protons in general, it arises by direct p,s-spin delocalization from the p-orbital at the spin-bearing center to 1s-AOs of the H-atoms (hyperconjugation) [11b]. (In this

Table. *Geometry Parameters for* **1/1$^{\bullet+}$**, **2/2$^{\bullet+}$**, **4/4$^{\bullet+}$**, *and* **5/5$^{\bullet+}$**, *Calculated by the AM1, and in Part, the 6-31G** (values in italics) *Procedure*[a]) vs. *the Coupling Constants* a_N *and* a_H of *β-Protons*

	1	**1$^{\bullet+}$**	**2**	**2$^{\bullet+}$**	**4**	**4$^{\bullet+}$**	**5**	**5$^{\bullet+}$**
$\sum\varphi$ [°]	326 *331*	343 *346*	349[b]) *360*	360	325	340	308	325
d [pm]	52 *47*	36 *24*	28[c]) *0*	0	52	39	65	52
a_N [mT]		+2.50		+2.02[d])		+2.51[e])		+3.02[e])
θ [°]	0 *12*	0 *13*	88 *90*	89	58	60	44/75[f])	47/75[f])
$\cos^2\theta$		1.00 *0.95*		0		0.25		0.47/0.07[f])
a_H [mT]		+4.00		+0.15[d])		+0.94[e])		+1.51/+0.30[e])[f])

[a]) See text for the meaning of the geometry parameters. [b]) Experimental values 358 [2] and 350° [6]. [c]) Experimental values 5 [2] and 26 pm [6]. [d]) Taken from [10]. [e]) Taken from [9]. [f]) *Exo/endo* protons.

respect, the small s contribution to the p-orbital at the N-atom in nonplanar radical cations of amines can be neglected, although it is responsible for the increase in the ^{14}N-coupling constant.) The a_H value of a β-proton is proportional to $\cos^2\theta$, where θ is the dihedral angle between the C−H$_\beta$ bond and the axis of the p-orbital [14]. The *Table* also lists the angles θ calculated by the same procedures as $\sum\varphi$ and d for the four amines and their radical cations; they are, in each case, similar for the neutral molecule and its ionized form. The $\cos^2\theta$ values for the radical cations meet the expected proportionality to the pertinent a_H. Most striking is the difference between **1$^{\bullet+}$** and **2$^{\bullet+}$**. Whereas in the former the C−H$_\beta$ bonds almost eclipse the orbital axis at the N-atom ($\cos^2\theta \approx 1$), they are nearly perpendicular to such an axis in the latter. This point is illustrated in *Fig. 2* by the relevant *Newman* projections for **1$^{\bullet+}$** and **2$^{\bullet+}$**.



1$^{\bullet+}$ **2$^{\bullet+}$**

Fig. 2. Newman *projections at the N-atom along a N−C bond in* **1$^{\bullet+}$** *and* **2$^{\bullet+}$**

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