196. Radical Cations and Radical Anions of Three Bridgehead Azopolycycloalkanes: A Fluid-Solution ESR Study

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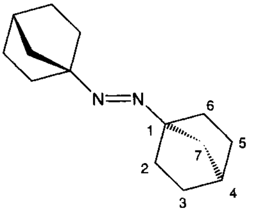
The radical mono-ions of three azoalkanes in which the azo group is connected to the polycyclic alkane moieties at the bridgehead C-atoms, *i.e.* 1,1'-azonorbornane (**1**), 1,1'-azotwistane (**2**), and 1,1'-azobicyclo[3.2.1]octane (**3**), were studied in fluid solution by ESR spectroscopy. According to the ESR parameters and MO models, the radical cations of **1**–**3** should be considered as σ radicals, whereas the corresponding radical anions are π radicals. INDO calculations point to a remarkable dependence of the ^{14}N-coupling constants on the geometry at the N-atoms in the radical cations of aliphatic azo compounds.

Introduction. – The radical anions of azoalkanes have been known for a long time [1] [2]. Until 1988, there was no report on radical cations of azoalkanes being detected by ESR spectroscopy. The use of freon matrices and irradiation by γ rays made it possible to record ESR spectra of 2,3-diazabicyclo[2.2.2]oct-2-ene (**4**) [3][4] and some other radicals attributed to azoalkane cations [5] in rigid solution. Only very recently, the radical cation of (*E*)-1,1'-azonorbornane (= (*E*)-1,1'-azobicyclo[2.2.1]heptane; **1**) was reported to be stable in fluid solution [6].

Here, we report, in addition to **1**+, on the radical cations of (*E*)-1,1'-azotwistane (= (*E*)-1,1'-azotricyclo[4.4.0.$0^{3,8}$]decane; **2**) and (*E*)-1,1'-azobicyclo[3.2.1]octane (**3**), as well as on the radical anions of **1**–**3**.



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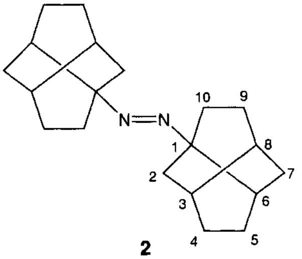

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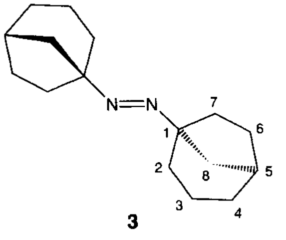

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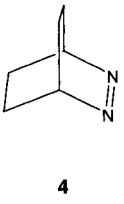

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Experimental. – The syntheses of **1**–**3** are given in [7][8]. Oxidation of **1**–**3** to their radical cations was performed with tris(2,4-dibromophenyl)ammoniumyl hexachloroantimonate [9] in a CH_2Cl_2 (dried over molecular sieves) soln. The radical anions **1**", **2**", and **3**" were generated by K-metal reduction of the neutral compounds in DME (for **1**) or THF (for **2** and **3**). All reactions were carried out under high vacuum. The ESR spectra were recorded on a *Varian E 9* spectrometer. g Factors were determined using a *Bruker ER 035 M* gaussmeter and a *Marconi Instruments 2440* microwave counter. The ENDOR spectra were taken on a *Bruker ESP 300* spectrometer.

Results. – *Radical Cations.* The ESR spectrum of **1**+ was identical with that already reported in [6]. The ESR spectra of **2**+ and **3**+ (*Fig. 1*) consisted of a *quintet* pattern, similar to the one of **1**+, with a 1:2:3:2:1 intensity ratio due to hyperfine interaction with two equivalent ^{14}N nuclei. The ^{14}N-coupling constants, a_N, are 1.26 [6], 1.16, and 1.19 mT for **1**+, **2**+, and **3**+, respectively (*Table 1*). The *quintet* in the ESR spectrum of **3**+ is additionally split into *triplets* by a ^1H-coupling constant, a_H (0.28 mT), of two equivalent protons. According to INDO calculations [10], this coupling constant should belong to the bridgehead protons at C(5) (see *Formula*) of the bicyclo[3.2.1]octane moieties[1]).

A better resolution of the ESR spectra, in order to determine further ^1H-coupling constants, was not achieved. Moreover, we failed to obtain ENDOR spectra, as the ESR spectra of all three radical cations could not be saturated up to a microwave power of 200 mW.

Radical Anions. The ESR spectra of the radical anions of **1**–**3** together with ENDOR spectra of **1**" and **2**" are displayed in *Fig. 2*. The 1,1'-azonorbornane radical anion, **1**", was stable in a DME solution in the temperature range between –80 and –50°. It was not possible to detect ESR spectra of **2**" and **3**" in DME; however, when THF was used as the solvent, **2**" and **3**" were sufficiently stable from –80 to –70° to be studied by ESR spectroscopy. The ESR spectra of **1**", **2**", and **3**" show a 1:2:3:2:1 *quintet* (*Fig. 2*) spaced by 0.8 mT, due to the coupling constant a_N of two equivalent ^{14}N nuclei. The patterns of the ESR spectra remained unchanged in the accessible temperature range, thus indicating no change in the symmetry of all three radical anions. In addition to a_N, ^1H-coupling constants could be detected by ENDOR spectroscopy for **1**" and **2**" (*Fig. 2* and *Table 2*); but their values, *i.e.* 0.021, 0.033, 0.045, and 0.069 mT (for **1**"), and 0.045, 0.072, and 0.089 mT (for **2**") (*Table 2*), are too close to each other to be assigned to individual positions.

Table 1. *Hyperfine Coupling Constants* [mT] *and g Factors of* **1**+, **2**+, *and* **3**+ (counterion, $SbCl_6^-$; solvent, CH_2Cl_2).

Radical cation	a_N	a_H	g Factor
1+	1.26±0.02	–	2.0010±0.0001
2+	1.16±0.02	–	2.0012±0.0001
3+	1.19±0.02	0.28±0.02	2.0011±0.0001

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[1]) The INDO open-shell calculations [10] were performed using coordinates of neutral **3**. As no crystal-structure data are available, the geometry of **3** was calculated by a MM1 force-field method modified for azo compounds [11]. For the ESR experiments, a racemic mixture of **3** was used; therefore, the INDO calculations were based on the geometries of (*R*,*S*)-**3**, (*R*,*R*)-**3**, and (*S*,*S*)-**3**. For all of these isomers, the coupling constant of the bridgehead H-atom at C(5) (for C-atom numbering, see *Formula*) was the major one.

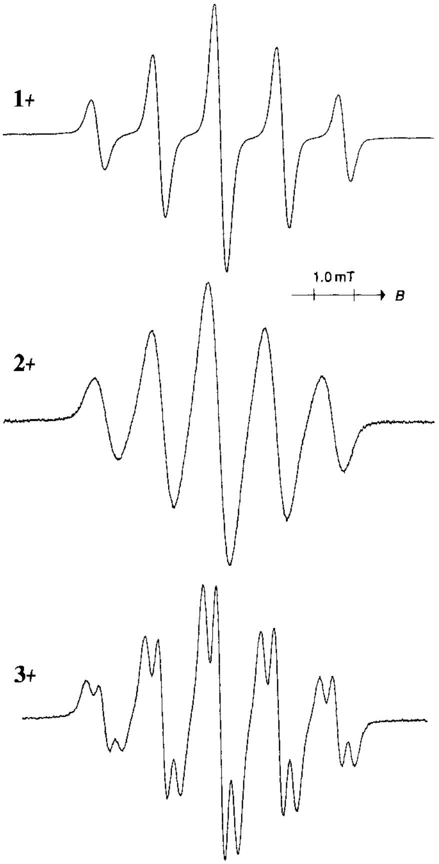

Fig. 1. *ESR Spectra of* **1+** (top), **2+** (middle), *and* **3+** (bottom) (solvent, CH_2Cl_2; counterion, $SbCl_6^-$; $T = -78°$)

Table 2. *Hyperfine Coupling Constants* [mT] *and g Factors of* **1**″, **2**″, *and* **3**″ (counterion, K^+; solvent, DME (for **1**″) or THF (for **2**″ and **3**″)).

Radical anion	a_N	a_H	g Factor
1″	0.80±0.02	0.021[a] 0.033[a] 0.045[a] 0.069[a]	2.0041±0.0001
2″	0.81±0.02	0.045[a] 0.072[a] 0.089[a]	2.0041±0.0001
3″	0.81±0.02	–	2.0042±0.0001

[a] Detected by ENDOR spectroscopy, not resolved in the ESR spectra.

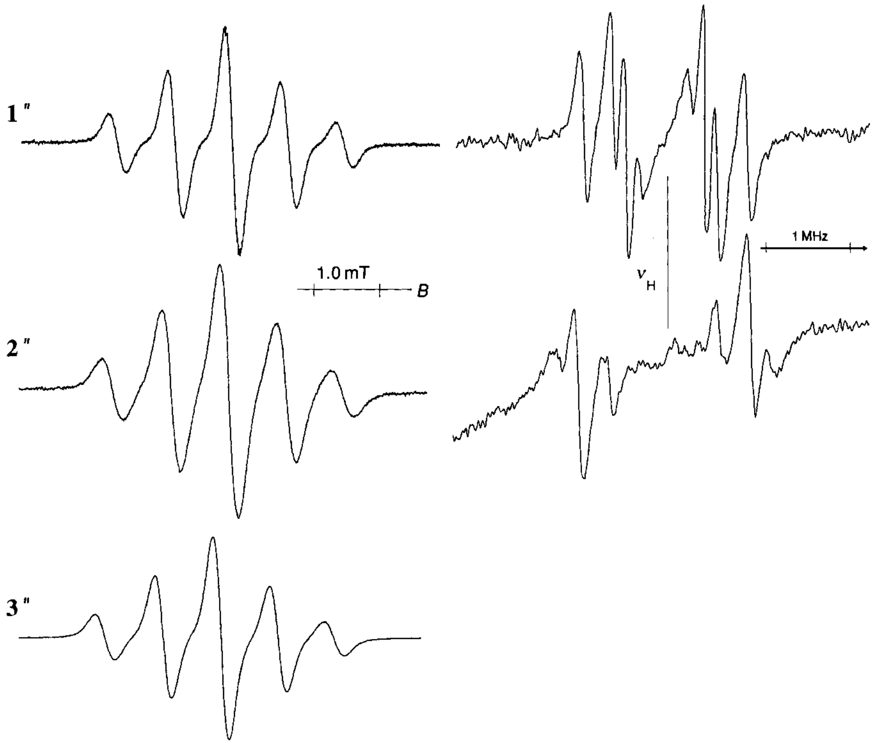

Fig. 2. *ESR Spectra of* **1**" (left, top), **2**" (left, middle), *and* **3**" (left, bottom) *and ENDOR spectra of* **1**" (right, top), **2**" (right, middle) (solvents, DME (for **1**"), THF (for **2**" and **3**"); counterion, K^+; $T = -78°$).

Discussion. – *General.* The radical ions of the three azoalkanes possess rather similar values a_N, *i.e.* 1.2 mT for the cations and *ca.* 0.8 mT for the anions, respectively. Thus, the nature of the polycyclic substituents plays a minor role in the spin distribution of the radical mono-ions. The ESR spectra are dominated by patterns due to ^{14}N-coupling constants. The ^{1}H hyperfine splittings are masked by the broad ESR lines; thus, their values must be below 0.1 mT, indicating that only a small part of the spin population is delocalized into the alkyl substituents. Moreover, UV/VIS spectra of **1**–**3** show nearly identical absorption maxima (**1**: 369 [7], **2**: 369 [7], **3**: 367 [7] nm) implying comparable electronic structures of the chromophoric azo groups. Therefore, we decided to use the simplest azo compound, diimine (H–N=N–H), as a probe for open-shell INDO [10] calculations in order to discuss the a_N values in terms of the geometry at the N-atoms and its effect on the s character of the singly occupied orbitals (SOMO's). For these calculations, the H–N and N=N distances at 1.02 Å and 1.2 Å, respectively, were held constant and the H–N=N bond angles varied, thus achieving (*E*) (C_{2h} symmetry), linear ($D_{\infty h}$ symmetry), and (*Z*)(C_{2v} symmetry) geometries.

Radical Cations. Compared to 2,3-diazabicyclo[2.2.2]oct-2-ene (**4**), the radical cations of the (*E*)-azo compounds **1**–**3** show remarkably smaller a_N values, *i.e. ca.* 1.2 (**1**+, **2**+, and **3**+) *vs.* 3.14 mT (**4**+). The INDO calculations on the radical cations of diimine indicate that the s-spin density and, consequently, the a_N value significantly depends on the geometry at the N-atoms (*Fig. 3*): for a (*E*)-configuration of diimine, a_N amounts to *ca.* 1.4–2.3 mT, whereas changing to (*Z*)-configuration increases a_N to *ca.* 3.0–3.4 mT. Thus, the nearly identical a_N values point to a similar structure of the –N=N– group in $\mathbf{1}^{+}$, $\mathbf{2}^{+}$, and $\mathbf{3}^{+}$. Furthermore, the calculations indicate that the SOMO is represented by an antibonding σ orbital. This finding is in line with the results obtained from the analysis of PE spectra of various azoalkanes (see *e.g.* [12] [13]).

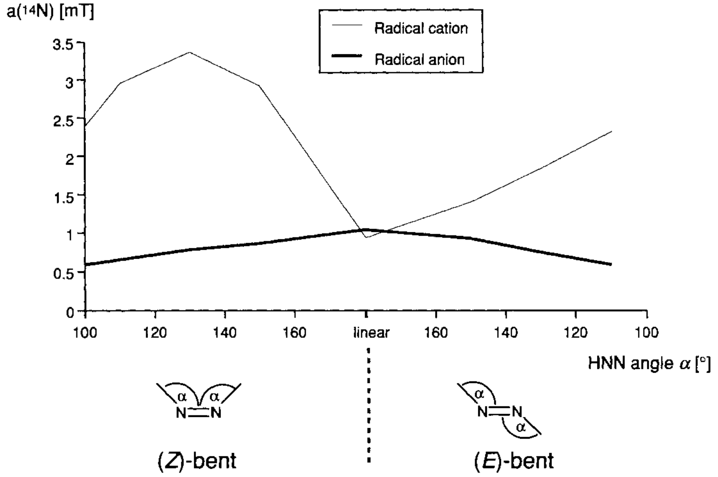

Fig. 3. *^{14}N Hyperfine-coupling constants of H–N=N–H depending on geometry, according to INDO calculations.*

Radical Anions. The ^{14}N-coupling constants of **1**″, **2**″, and **3**″ are identical (0.8 mT; *Table 2*) within experimental error. This, again, points to a similar structure of the three radical anions. The radical anion of azo(1,1-dimethylethane) has an a_N of 0.824 mT [1] and the corresponding values found for **4**″ (0.878 mT [4]) and other radical anions possessing the (*Z*)-configurated azo group, *e.g.* 3,3,5,5-tetramethyl-1-pyrazoline (0.918 mT [14]) or 2,3-diazabicyclo[2.2.1]hept-2-ene (0.871 mT [14]), are of comparable size. INDO calculations on (H–N=N–H)″ (*Fig. 3*) display a π^*-type SOMO bearing a vertical nodal plane between the two N-atoms. The s-spin population in this type of orbitals is, as expected, much less dependent on the geometry of the molecular framework than that in the σ-type radicals.

Conclusions. – The hyperfine data and the model calculations of the radical mono-ions of **1**–**3** establish that, in line with [3][4][6] but in contrast to the results in [5], the radical cations are of σ-type, whereas the radical anions can be regarded as π-type radicals. This finding is further supported by the g factors of the radical ions: the range of the g factors of

1+, **2**+, and **3**+ is 2.0010–2.0012 (*Table 1*), characteristic of σ radicals [15], being below 2.0023 (the g factor of the free electron). On the other hand, the g factors of **1**″, **2**″, and **3**″ are much higher (2.0041–2.0042, *Table 2*), thus providing evidence for π radicals.

Comparison with compound **4**, having the (*Z*)-configurated azo group, confirms the remarkable dependence of the s character of the σ-type SOMO upon the geometry at the N-atoms in the radical cations. A similar behavior was already found for the radical cations of hydrazines (see, *e.g.* [16]) and diimines [17][18]. However, to establish more general rules for a_N, the hyperfine data for more radical cations of azoalkanes should be available, and a more detailed model than our crude 'diimine approximation' has to be developed.

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