Long-range coupling in strained derivatives of the 2,3-diazabicyclo[2.2.1]hept-2-ene radical anion: An EPR, ENDOR and TRIPLE-resonance study

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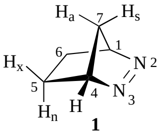
Radical anions of 2,3-diazabicyclo[2.2.1]hept-2-ene 1 and its 18 substituted and tricyclic derivatives (2a–11c) have been characterized by their hyperfine data with the use of EPR and ENDOR spectroscopy. The structural modifications of 1, yielding 2a–11c, are methyl and/or phenyl substitutions in the 1,4-positions, introduction of methyl groups or a spirocyclopentane ring in the 7,7-positions and annelation by a cyclopropane, cyclobutane, cyclobutene, cyclopentane or cyclopentene ring in the 5,6-*endo*-positions. Although these modifications do not markedly alter the π-spin and charge distribution in $1^{\cdot-}$, they have a strong effect on the long-range coupling constant of the γ-protons in the 5,6-*exo*-positions: the pertinent $a_{H(\gamma)}$ value varies from +0.26 to +0.64 mT. The effect is particularly impressive for the 5,6-*endo*-annelation by a cycloalkane or a cycloalkene ring and it goes along with only slight changes in the geometry of the carbon framework in $1^{\cdot-}$. Thus, owing to the through-bond mechanism of π,σ-spin transfer (homohyperconjugation), the coupling constant, $a_{H(\gamma)}$, of the 5,6-*exo*-protons responds sensitively to such changes in the geometry.

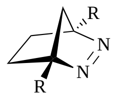
The propensity of cyclic *Z*-azoalkanes to lose dinitrogen upon thermal or photolytic excitation and, therewith, to yield unusual hydrocarbons has aroused much interest in the last three decades, which resulted in a palette of available compounds of this class.[1] In particular, 2,3-diazabicyclo[2.2.1]hept-2-ene **1** and its derivatives have been the focus of numerous mechanistic studies concerned with the extrusion step and fragmentation, giving rise to radicals, diradicals and radical ions.

As the radical cations of cyclic *Z*-azoalkanes expel very rapidly dinitrogen with a concomittant 1,2-shift,[2] they are, in general, too short-lived to be detected by EPR spectroscopy. Exceptionally, the radical cation of the relatively strain-free 2,3-diazabicyclo[2.2.2]oct-2-ene was sufficiently persistent in a Freon matrix to be fully characterized by its hyperfine data.[3] A few radical cations generated in this medium were presented as those of *E*-azoalkanes,[4] but only the radical cations of some compounds having their *E*-configured azo group protected by bulky hydrocarbons[5,6] and those of two heavily substituted 4-methylenedihydropyrazoles[7] could be studied in fluid solution. In contrast, the radical anions of both *E*- and cyclic *Z*-azoalkanes proved to be much more resistant to the extrusion of dinitrogen, and so have been amply investigated by EPR and ENDOR spectroscopy.[6–9] Unlike azoarenes, such as azobenzene with a half-wave reduction potential of −1.38 V *vs*. standard calomel electrode (SCE),[10] conversion of azoalkanes to their radical anions requires a highly negative voltage; notably, **1** fails to exhibit a reduction wave in the range 0 to −2.8 V.†[,11] Therefore, reaction with strong reducing agents, preferably alkali metals in ethereal solvents, is used to generate radical anions of azoalkanes from their neutral precursors.

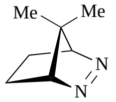
Some years ago, the EPR and ENDOR spectra of the radical anions of **1** and its 1,4-dimethyl (**2a**), 1,4-diphenyl (**2b**), 7,7-dimethyl (**3**) and 1,4-diphenyl-7,7-dimethyl (**4b**) derivatives were described in a paper dealing with a series of cyclic *Z*-azoalkanes.[9] Here, these studies are complemented by those of the radical anions generated from 14 polycyclic derivatives of **1**, in which the 1,4-positions are substituted by two methyl (**a**) or two phenyl groups (**b**) or one methyl and one phenyl group (**c**), while the 7,7-positions bear two methyl substituents (**5a**–**9b**) or a spiro-linked cyclopentane ring (**10a**–**11c**).[12,13] A particular structural modification of **1** to yield **5a**–**11c** is the annelation by a cycloalkane or a cycloalkene ring in the 5,6-*endo*-positions. It imposes an additional strain on the carbon framework of the



1
x = *exo* a = *anti*
n = *endo* s = *syn*



2a R = Me
2b R = Ph



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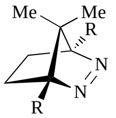
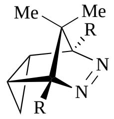
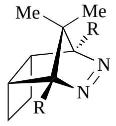


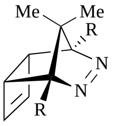
4b R = Ph



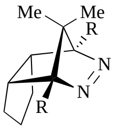
5a R = Me



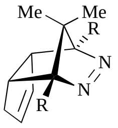
6a R = Me
6b R = Ph



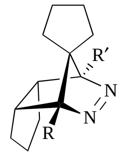
7a R = Me
7b R = Ph



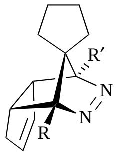
8a R = Me
8b R = Ph



9b R = Ph



10a R = R′ = Me
10b R = R′ = Ph
10c R = Me, R′ = Ph



11a R = R′ = Me
11b R = R′ = Ph
11c R = Me, R′ = Ph

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† The half-wave potentials of −0.8 to −0.9 V *vs*. SCE, which were previously reported for three cyclic *Z*-azoalkanes inclusive **1**,[9] are incorrect. The observed reversible waves presumably arise from reduction of dioxygen present in incompletely degassed acetonitrile solutions.

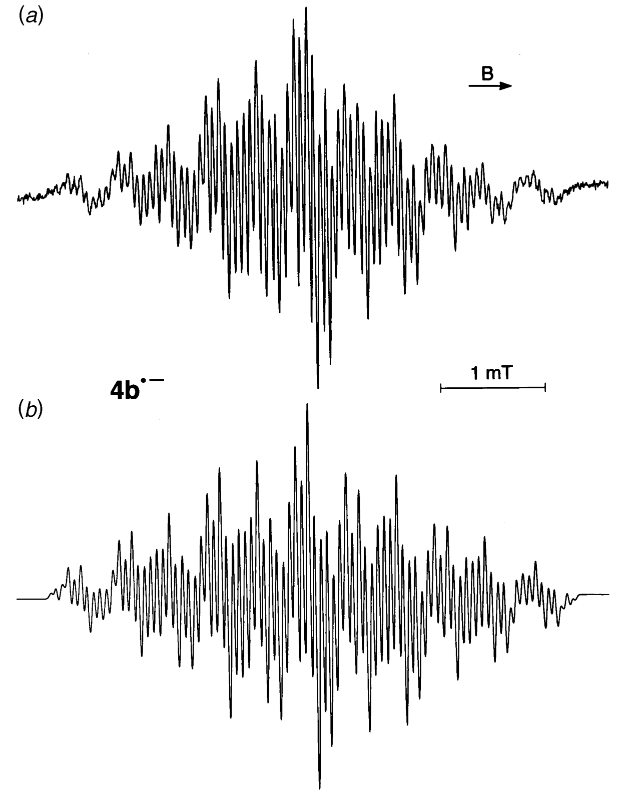


Fig. 1 (*a*) EPR spectrum of $\mathbf{4b}^{\bullet-}$; solvent DME, counterion K^+, temperature 293 K. (*b*) Simulation with the use of coupling constants given in Table 1; line-shape Lorentzian, line-width 0.016 mT; the effect of ^{14}N-hyperfine anisotropy is not accounted for.

radical anions and has a surprisingly great effect on the large coupling constant arising from a long-range interaction with the two γ-protons in the 5,6-*exo*-positions. This value thus serves as a sensitive probe for structural modifications of the carbon framework.

Results

The radical anions $\mathbf{1}^{\bullet-}$–$\mathbf{11c}^{\bullet-}$ were generated by reaction of the corresponding neutral compounds with potassium mirror in 1,2-dimethoxyethane (DME) at 195 K. With the exception of $\mathbf{2a}^{\bullet-}$ and $\mathbf{2b}^{\bullet-}$ which decayed at higher temperatures,[9] they could be studied by EPR spectroscopy up to 298 K. (The low persistence of $\mathbf{2a}^{\bullet-}$ and $\mathbf{2b}^{\bullet-}$ was caused by the destabilizing effect of 1,4-dimethyl or diphenyl substitution which, in these two radical anions, is not counterbalanced by the stabilization due to the substituents in the 7,7-positions.) The EPR spectra exhibited a pronounced ^{14}N-hyperfine anisotropy which progressively increased the line-width on going from the central component with $M_I(^{14}N) = 0$ to the peripheral ones with $M_I(^{14}N) = \pm 1$ and ± 2. In addition, the components with $M_I(^{14}N) = -1$ and -2 in the high-field half of the spectrum were more strongly affected by the line-broadening than those with $M_I(^{14}N) = +1$ and $+2$ in the low-field half. As the effects of ^{14}N-hyperfine anisotropy attenuated at higher temperatures, the analyses of the EPR splitting pattern were performed on spectra taken at 293 K. They made use of the coupling constants a_H determined from the pairs of ^1H-ENDOR signals centred at $\nu_H = 14.56$ MHz and observed at 203 K. The ^{14}N-ENDOR signals appeared in the frequency range 10–13 MHz on raising the temperature to 243 K. They were centred at half the coupling constant a_N and often overlapped with proton signals. The ^{39}K-ENDOR signals escaped detection, because of the low sensitivity of our instrument in the pertinent frequency range below 1.5 MHz. Therefore, the coupling constants a_K for the counterion K^+ had to be determined solely from the EPR spectra. Best fit of the simulated to the experimental EPR derivative curves was achieved with the use of a computer program[14] by slightly varying the a_N, a_H and a_K values. The EPR spectra and their computer simulations are exemplified in Fig. 1 by those of $\mathbf{4b}^{\bullet-}$. Usefulness of the ENDOR technique, in particular for radical anions of low symmetry (C_1), is illustrated in Fig. 2.

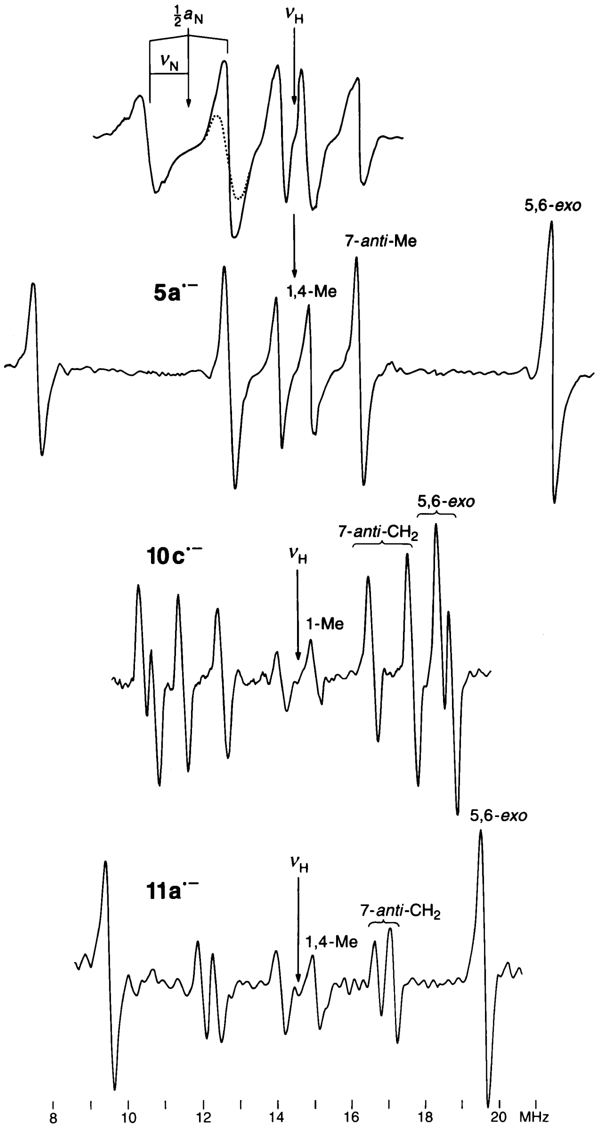


Fig. 2 ^1H-ENDOR spectra of $\mathbf{5a}^{\bullet-}$, $\mathbf{10c}^{\bullet-}$ and $\mathbf{11a}^{\bullet-}$; solvent DME, counterion K^+, temperature 203 K. For $\mathbf{5a}^{\bullet-}$, the low-frequency ^{14}N-ENDOR signal, observed at 243 K, is also shown at the top; its high-frequency counterpart is obscured by the outermost proton signal.

Table 1 lists the hyperfine data, a_H, a_N and a_K, for all 19 radical anions $\mathbf{1}^{\bullet-}$–$\mathbf{11c}^{\bullet-}$, together with their g factors. According to the EPR nomenclature, protons separated by 0,1,2,3,4,5, . . . sp^3-hybridized carbon atoms from a spin-bearing π-centre are denoted α,β,γ,δ,ε,φ, ...[15a] With respect to the azo π-system of $\mathbf{1}^{\bullet-}$, the protons in the 1,4-positions are thus β, whereas those in the 5,6- and 7,7-positions have to be classified as γ. Moreover, the protons of the methyl substituents in 1,4- and 7,7-positions are γ and δ, respectively, while those of the 7,7-spirocyclopentane ring and of the cycloalkane rings annelated in the 5,6-*endo*-positions are δ and ε. Although the protons of 1,4-phenyl substituents and at the double bond in the 5,6-*endo*-annelated cycloalkene rings are attached to sp^2-hybridized carbon atoms, they pass for δ, ε and φ, because no measurable spin population seems to be transferred to these atoms from the spin-bearing azo π-centres. Assignments of the coupling constants to magnetic nuclei in the individual positions is based on

Table 1 ^{1}H-, ^{14}N- and ^{39}K-coupling constants, a_{H}, a_{N} and a_{K} in mT, and g factors[a] of the radical anions **1**$^{\bullet-}$ to **11c**$^{\bullet-}$. Solvent DME, temperature 293 K, counterion K^{+}

	Position							
	2,3	1,4	5,6-*exo*	5,6-*endo*	7-*anti*	7-*syn*	Counterion	g
1$^{\bullet-}$[b]	+0.855(2N)	+0.044(2H$_{\beta}$)	+0.340(2H$_{\gamma}$)	−0.073(2H$_{\gamma}$)	−0.223(1H$_{\gamma}$)	−0.122(1H$_{\gamma}$)	+0.055(1K)	2.0039
2a$^{\bullet-}$[b,c]	+0.852(2N)	−0.027(6H$_{\gamma}$)	+0.422(2H$_{\gamma}$)	−0.057(2H$_{\gamma}$)	−0.215(1H$_{\gamma}$)	−0.115(1H$_{\gamma}$)	+0.050(1K)	2.0039
2b$^{\bullet-}$[b,c]	+0.848(2N)	*d*	+0.434(2H$_{\gamma}$)	−0.062(2H$_{\gamma}$)	−0.216(1H$_{\gamma}$)	−0.118(1H$_{\gamma}$)	+0.046(1K)	2.0038
3$^{\bullet-}$[b]	+0.848(2N)	+0.065(2H$_{\beta}$)	+0.406(2H$_{\gamma}$)	−0.065(2H$_{\gamma}$)	+0.139(3H$_{\delta}$)	+0.012(3H$_{\delta}$)	+0.058(1K)	2.0039
4b$^{\bullet-}$	+0.845(2N)	*d*	+0.488(2H$_{\gamma}$)	−0.042(2H$_{\gamma}$)	+0.126(3H$_{\delta}$)	*f*	+0.056(1K)	2.0038
5a$^{\bullet-}$	+0.839(2N)	−0.023(6H$_{\gamma}$)	+0.492(2H$_{\gamma}$)	*e*	+0.135(3H$_{\delta}$)	*f*	+0.050(1K)	2.0039
6a$^{\bullet-}$	+0.842(2N)	−0.033(6H$_{\gamma}$)	+0.263(2H$_{\gamma}$)	*e*	+0.122(3H$_{\delta}$)	*f*	+0.057(1K)	2.0038
6b$^{\bullet-}$	+0.842(2N)	*d*	+0.270(2H$_{\gamma}$)	*e*	+0.138(3H$_{\delta}$)	*f*	+0.052(1K)	2.0040
7a$^{\bullet-}$	+0.812(2N)	−0.033(6H$_{\gamma}$)	+0.618(2H$_{\gamma}$)	*e*	+0.123(3H$_{\delta}$)	*f*	+0.058(1K)	2.0039
7b$^{\bullet-}$	+0.820(2N)	*d*	+0.637(2H$_{\gamma}$)	*e*	+0.132(3H$_{\delta}$)	*f*	+0.057(1K)	2.0039
8a$^{\bullet-}$	+0.830(2N)	−0.031(6H$_{\gamma}$)	+0.271(2H$_{\gamma}$)	*e*	+0.126(3H$_{\delta}$)	*f*	+0.052(1K)	2.0041
8b$^{\bullet-}$	+0.836(2N)	*d*	+0.272(2H$_{\gamma}$)	*e*	+0.134(3H$_{\delta}$)	*f*	+0.051(1K)	2.0041
9b$^{\bullet-}$	+0.836(2N)	*d*	+0.359(2H$_{\gamma}$)	*e*	+0.130(3H$_{\delta}$)	*f*	+0.056(1K)	2.0040
10a$^{\bullet-}$	+0.823(2N)	−0.033(6H$_{\gamma}$)	+0.290(2H$_{\gamma}$)	*e*	+0.175(2H$_{\delta}$)	*f*	+0.052(1K)	2.0040
10b$^{\bullet-}$	+0.829(2N)	*d*	+0.285(2H$_{\gamma}$)	*e*	+0.195(2H$_{\delta}$)	*f*	+0.050(1K)	2.0040
10c$^{\bullet-}$	+0.816(2N)	−0.033(3H$_{\gamma}$) *d*	+0.295(1H$_{\gamma}$) +0.275(1H$_{\gamma}$)	*e*	+0.220(1H$_{\delta}$) +0.162(1H$_{\delta}$)	*f*	+0.052(1K)	2.0040
11a$^{\bullet-}$	+0.826(2N)	−0.033(6H$_{\gamma}$)	+0.358(2H$_{\gamma}$)	*e*	+0.184(1H$_{\delta}$) +0.155(1H$_{\delta}$)	*f*	+0.058(1K)	2.0040
11b$^{\bullet-}$	+0.838(2N)	*d*	+0.367(2H$_{\gamma}$)	*e*	+0.210(1H$_{\delta}$) +0.165(1H$_{\delta}$)	*f*	+0.057(1K)	2.0041
11c$^{\bullet-}$	+0.826(2N)	−0.033(3H$_{\gamma}$) *d*	+0.385(1H$_{\gamma}$) +0.350(1H$_{\gamma}$)	*e*	+0.210(1H$_{\delta}$) +0.129(1H$_{\delta}$)	*f*	+0.054(1K)	2.0040

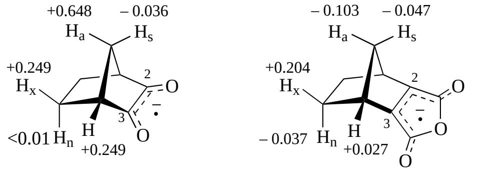
[a] Experimental error ±0.002 mT in a_{H} and a_{K}, ±0.005 mT in a_{N} and ±0.0001 in g. [b] Values taken from ref. 9. [c] Temperature 203 K. [d] Coupling constants of the protons in the phenyl substituents too small to be observed. [e] Coupling constants of the protons in the annelated cycloalkane or cycloalkene rings too small to be observed. [f] Coupling constants of the protons in the methyl group or the remaining protons in the spirocyclopentane ring too small to be observed.

the differences in nature and numbers of equivalent nuclei and on the well-established relation that the absolute values of the γ-proton-coupling constants, $a_{\mathrm{H}(\gamma)}$, are larger for the *exo*- than for the *endo*-positions and for the *anti*- than for the *syn*-positions.[16–18] The signs of a_{H} follow the results of the general-TRIPLE-resonance experiment carried out on the ^{1}H-ENDOR signals[19] with the justified assumption that the large $a_{\mathrm{H}(\gamma)}$ value due to the protons in the 5,6-*exo*-positions is positive. In the case of the ^{14}N- and ^{39}K-coupling constants, a_{N} and a_{K}, the positive sign was taken for granted. For a_{N}, this sign is in accord with the finding that the ^{14}N-hyperfine components are broader in the high- than in the low-field half of the EPR spectrum,[15b,20] while for a_{K}, it complies with the increase of this value upon raising the temperature.[21]

Discussion

γ- and δ-Couplings

The major hyperfine interaction in alkyl-substituted planar π-radicals and radical ions is due to α- and β-protons.[15a] The β-coupling arises from π,σ-delocalization or hyperconjugation and it depends on geometry, namely on the dihedral angle θ between the C−H(β) bond and the 2p$_z$-axis at the spin-bearing π-centre ($\cos^2\theta$ dependence).[22] Moreover, as hyperconjugation is enhanced by a positive π-charge, the radical cations exhibit larger β-proton-coupling constants, $a_{\mathrm{H}(\beta)}$, than the radical anions for a comparable geometry and π-spin distribution.[15a] The sign of $a_{\mathrm{H}(\beta)}$ is, in general, the same as that of the spin population at the π-centre, and it is thus positive for large $a_{\mathrm{H}(\beta)}$ values. π,σ-Spin polarization plays a significant role only for small coupling constants $a_{\mathrm{H}(\beta)}$ when θ is close to 90°, *i.e.* the β-protons lie in the nodal plane of the π-system; in such cases, the small $a_{\mathrm{H}(\beta)}$ value can have a sign opposite to that of the spin population at the π-centre.[23,24] The coupling constants, $a_{\mathrm{H}(\gamma)}$ and $a_{\mathrm{H}(\delta)}$, of the γ- and δ-protons in planar, alkyl-substituted π-radicals and radical ions are usually less by one order of magnitude than the $a_{\mathrm{H}(\beta)}$ values and they may have either sign, depending on the dominant mechanism of spin transfer.[25]



12$^{\bullet-}$ **13**$^{\bullet-}$

Fig. 3 Proton-coupling constants for **12**$^{\bullet-}$ and **13**$^{\bullet-}$ in mT; signs required by theoretical calculations and analogy with **1**$^{\bullet-}$ (Table 1)

On the other hand, in radicals and radical ions having a π-system incorporated in a rigid, nonplanar, bi- or poly-cyclic carbon framework, the hyperfine interaction with the γ- and δ-protons often exceeds that with the β-protons. First well-founded reports on long-range γ-couplings were published on semidione anions by Russell and co-workers.[26,27] A radical anion structurally related to **1**$^{\bullet-}$ is that of 2,3-dioxobicyclo-[2.2.1]heptane **12**.[16,17,26] However, for reasons pointed out below, the radical anion of the corresponding semifuraquinone (**13**)[17] is a more appropriate species to be compared with **1**$^{\bullet-}$ (Fig. 3).

Following the pioneering work by Russell, long-range γ- and δ-couplings were reported for further semidione anions,[28] radical anions of bicyclic *Z*-azoalkanes,[9] rigid polycyclic derivatives of nitroxides[29,30] and alkyls.[31–34] In particular, they were observed for radical cations, in which a hydrazine[35,36] or an ethene π-system[18,23,37] is embedded in a polycyclic saturated carbon framework. By far the largest coupling constants $a_{\mathrm{H}(\gamma)}$ and $a_{\mathrm{H}(\delta)}$ are found when the C−H(γ) or C−H(δ) bond is connected with the 2p$_z$-axis at a spin-bearing π-centre by a chain of sp^3-hybridized carbon atoms in a W-plan or zig-zag arrangement. Such a coupling is also denoted as through-bond interaction[38] or homohyperconjugation. Its mechanism is similar to that of the coupling to β-protons, as it likewise depends on the mutual orientation of the pertinent C−H bond and the 2p$_z$-axis at the π-centre. However, to the best of our knowledge, no relation analogous to the $\cos^2\theta$ dependence of $a_{\mathrm{H}(\beta)}$ exists for $a_{\mathrm{H}(\gamma)}$

and $a_{\mathrm{H}(\delta)}$, although some rather unsuccessful attempts were reported in this respect.[30] Homohyperconjugation, like hyperconjugation itself, is strongly enhanced by a positive charge at the π-centre, so that $a_{\mathrm{H}(\gamma)}$ and $a_{\mathrm{H}(\delta)}$ values are much larger for radical cations than for neutral radicals and radical anions with a comparable geometry and π-spin distribution. Impressive examples of large long-range couplings were reported for the radical cations of benzvalene (tricyclo[3.1.0.0^{2,6}]hex-3-ene)[23] and *trans*-sesquinorbornene[18] with $a_{\mathrm{H}(\gamma)} = +2.79$ and +1.35 mT, respectively, as well as for the radical cation of adamantylideneadamantene[37] with $a_{\mathrm{H}(\delta)} = +0.605$ mT. Owing to the mechanism of π,σ-spin delocalization through bonds, the sign of such $a_{\mathrm{H}(\gamma)}$ and $a_{\mathrm{H}(\delta)}$ values is the same as that of the spin population at the π-centre, *i.e.* it is generally positive. However, substantial, although not the largest, coupling constants $a_{\mathrm{H}(\gamma)}$ and $a_{\mathrm{H}(\delta)}$ have negative sign when, due to the nodal properties of the singly occupied π-orbital, contribution by π,σ-spin polarization dominates the hyperfine interaction. Both mechanisms of spin transfer in long-range couplings have been discussed in the literature.[17]

Hyperfine interactions in $\mathbf{1}^{\bullet -}$ to $\mathbf{11c}^{\bullet -}$

The singly occupied orbital of $\mathbf{1}^{\bullet -}$ is essentially the antibonding π-MO of the azo group which houses the bulk of the spin and charge population. Such a statement is in accord with the ^{14}N-coupling constant, $a_{\mathrm{N}} = +0.855$ mT, the range +0.8 to +0.9 mT being characteristic of both *E*- and *Z*-azoalkane radical anions.[6–9] This a_{N} value drastically decreases for the radical anions of azobenzene[10] and other azoarenes,[39] because a large part of the spin population shifts from the azo group to the aryl π-systems. The negative charge of the azo group leads to a close association of $\mathbf{1}^{\bullet -}$ with the counterion K^+, as indicated by the substantial coupling constant $a_{\mathrm{K}} = +0.055$ mT; in the ion pair $\mathbf{1}^{\bullet -}/\mathrm{K}^+$, the cation should favour a position proximate to the π-system of the azo group. The a_{N} and a_{K} values are rather insensitive to structural modifications of the carbon framework in the series $\mathbf{2a}^{\bullet -}$ to $\mathbf{11c}^{\bullet -}$ (Table 1), thus testifying that the π-spin distribution in the radical anions and the structure of the ion pairs are not seriously affected by such modifications.

The small magnitude of the coupling constant, $a_{\mathrm{H}(\beta)} = +0.044$ mT, of the β-protons in the bridgehead 1,4-positions of $\mathbf{1}^{\bullet -}$ points to a dihedral angle θ of *ca.* 80°. The positive sign of $a_{\mathrm{H}(\beta)}$ suggests that the π,σ-spin polarization, which would be solely effective for β-protons lying in the nodal plane of the π-system, is not yet dominant.[23,24] Methyl substitution in the 1,4-positions replaces the $a_{\mathrm{H}(\beta)}$ value by a coupling constant, $a_{\mathrm{H}(\gamma)}$ *ca.* −0.03 mT, of the alkyl γ-protons, while introduction of phenyl groups into these positions virtually eliminates the hyperfine splitting because the pertinent $a_{\mathrm{H}(\delta)}$, $a_{\mathrm{H}(\varepsilon)}$ and $a_{\mathrm{H}(\varphi)}$ values are too small to be observed.

A prominent hyperfine feature of $\mathbf{1}^{\bullet -}$ to $\mathbf{11c}^{\bullet -}$ is the large and positive coupling constant, $a_{\mathrm{H}(\gamma)}$, of the two γ-protons in the 5,6-*exo*-positions, a paradigm of a W-plan long-range interaction. It varies from +0.340 mT for $\mathbf{1}^{\bullet -}$ to +0.263 mT for $\mathbf{6a}^{\bullet -}$ and +0.637 mT for $\mathbf{7b}^{\bullet -}$, thus covering a range of 0.38 mT (Table 1). These variations will be discussed in the following section. On the other hand, the coupling constant, $a_{\mathrm{H}(\gamma)} = -0.073$ mT, of the γ-protons in the 5,6-*endo*-positions of $\mathbf{1}^{\bullet -}$ is much smaller and negative. Annelation at these positions by a cycloalkane or cycloalkene ring leads to a disappearance of such hyperfine splitting, as the coupling constants, $a_{\mathrm{H}(\delta)}$ and $a_{\mathrm{H}(\varepsilon)}$, of the ring protons escape detection.

W-Plan arrangement is also considered as being responsible for the substantial coupling constant, $a_{\mathrm{H}(\gamma)} = -0.223$ mT, of the γ-proton in the 7-*anti*-position of $\mathbf{1}^{\bullet -}$. Surprisingly, this $a_{\mathrm{H}(\gamma)}$ value is negative, as is that, $a_{\mathrm{H}(\gamma)} = -0.122$ mT, of the corresponding γ-proton in the 7-*syn*-position. The negative sign can be traced back to the location of the protons in the vertical nodal plane of the spin-bearing π-orbital of the azo group. In this respect, it is informative to compare the proton-coupling constants for $\mathbf{1}^{\bullet -}$ with those for $\mathbf{12}^{\bullet -}$ and $\mathbf{13}^{\bullet -}$ (Fig. 3). Thereby, one has to account for the relative π-spin populations at the two relevant π-centres 2 and 3, those at the carbon atoms 2 and 3 in $\mathbf{12}^{\bullet -}$ and $\mathbf{13}^{\bullet -}$ being only a fraction of the π-spin populations at the nitrogen π-centres in $\mathbf{1}^{\bullet -}$. A satisfactory agreement between the coupling constants a_{H} for $\mathbf{1}^{\bullet -}$ and $\mathbf{13}^{\bullet -}$ is achieved when the latter values are multiplied throughout by a factor 2.0 ± 0.4. In contrast, the hyperfine data for $\mathbf{12}^{\bullet -}$ hardly correlate with those for $\mathbf{1}^{\bullet -}$ and $\mathbf{13}^{\bullet -}$. Undoubtedly, this is because the nodal plane of the singly occupied orbital in $\mathbf{13}^{\bullet -}$, like that in $\mathbf{1}^{\bullet -}$, coincides with the mirror plane of the radical anion, whereas the corresponding orbital in $\mathbf{12}^{\bullet -}$ lacks such a nodal plane. Accordingly, the most drastic difference is found for the coupling constant of the γ-proton in the 7-*anti*-position.

The δ-protons of the freely rotating methyl substituents or of the spirocyclopentane ring in the 7,7-positions no longer lie in the nodal plane of singly occupied orbital of $\mathbf{1}^{\bullet -}$. Three protons of the *anti*-methyl substituent or two in the *anti*-oriented methylene group of the spirocyclopentane ring have small positive coupling constants, $a_{\mathrm{H}(\delta)} = +0.12$ to +0.22 mT, whereas the δ-protons of the *syn*-methyl substituent and the remaining two δ- and four ε-protons of the spirocyclopentane ring do not generally give rise to observable hyperfine splittings (Table 1).

Effect of structural modifications on the coupling constant, $a_{\mathrm{H}(\gamma)}$, of the *exo*-protons

As stated in the preceding section, the coupling constant, $a_{\mathrm{H}(\gamma)}$, of the two protons in the 5,6-*exo*-positions responds sensitively to structural modifications of the carbon framework in $\mathbf{1}^{\bullet -}$. Analysis of this $a_{\mathrm{H}(\gamma)}$ value in Table 1 indicates that its changes follow a systematic pattern in an additive way. For a single structural modification of $\mathbf{1}^{\bullet -}$, one derives an increment $\Delta a_{\mathrm{H}(\gamma)}$ which can serve to predict the coupling constant in each radical anion $\mathbf{2a}^{\bullet -}$ to $\mathbf{11c}^{\bullet -}$. Substitution in the 1,4-positions by two methyl or two phenyl groups leads to an increase $\Delta a_{\mathrm{H}(\gamma)}$ of +0.08 and +0.09 mT, respectively. Two methyl substituents in the 7,7-positions require a $\Delta a_{\mathrm{H}(\gamma)}$ value of +0.06 mT, while an introduction of the spirocyclopentane ring in these positions gives rise to $\Delta a_{\mathrm{H}(\gamma)} = +0.07$ mT. A much larger effect of opposite sign, $\Delta a_{\mathrm{H}(\gamma)} = -0.22$ mT, is found upon 5,6-*endo*-annelation by a cyclobutane or a cyclopentane ring. Interestingly, such a decrease turns into an increase, $\Delta a_{\mathrm{H}(\gamma)} = +0.15$ mT, when the annelated cyclobutane is replaced by a cyclobutene ring. The change of the annelated cyclopentane into a cyclopentene ring is less effective; nevertheless, it reduces $\Delta a_{\mathrm{H}(\gamma)}$ to −0.13 mT.

The increments $a_{\mathrm{H}(\gamma)}$ can be used in eqn. (1), where +0.34 mT

$$a_{\mathrm{H}(\gamma)} = +0.34 + \Sigma\Delta a_{\mathrm{H}(\gamma)}\ (\text{in mT}) \qquad (1)$$

stands for $\mathbf{1}^{\bullet -}$ and the summation is carried over all structural modifications. For example, the smallest and the largest $a_{\mathrm{H}(\gamma)}$ value, +0.263 mT ($\mathbf{6a}^{\bullet -}$) and +0.637 mT ($\mathbf{7b}^{\bullet -}$), emerge as (0.34 + 0.08 + 0.06 − 0.22) mT = +0.26 mT and (0.34 + 0.09 + 0.06 + 0.15) mT = +0.64 mT, respectively.

It is particularly noteworthy that mere introduction of the double bond into the cyclobutane and the cyclopentane ring increases the coupling constant by $\Delta\Delta a_{\mathrm{H}(\gamma)} = +0.15 - (-0.22) = +0.37$ and $-0.13 - (-0.22) = +0.09$ mT, respectively. This finding can be interpreted as follows. Molecular models suggest that the 5,6-*endo*-annelation by a four- or five-membered ring exerts an additional strain on the carbon framework of **1**, leading to a large decrease, $\Delta a_{\mathrm{H}(\gamma)}$, in the coupling constants of the protons in the corresponding *exo*-positions. Superimposed on this effect is that of the double bond, of which the π-orbitals overlap with those of the azo group (Fig. 4). The π,π-interaction resulting therefrom works against the effect of annelation by providing a positive contribution to $\Delta a_{\mathrm{H}(\gamma)}$ which overcompensates or diminishes its negative value. The much smaller impact of the double bond in the cyclopentene than in

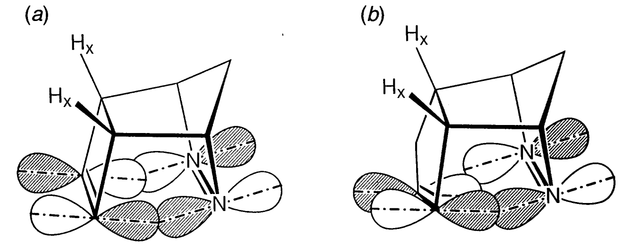


Fig. 4 Overlapping of the antibonding π-orbitals of the azo group with those of the double bond in (*a*) the 5,6-*endo*-annelated cyclobutene and (*b*) the cyclopentene ring. Hydrogen atoms or substituent groups in the 1,4- and 7,7-positions are omitted for clarity.

the cyclobutene ring is due to a shift of this bond away from the mirror plane bisecting the azo group, as such a shift reduces the overlap between the orbitals of the two π-systems and weakens their interaction (Fig. 4). This interpretation is supported by theoretical calculations (see below). The effect of the 5,6-*endo*-annelation by a cyclopropane ring is revealing. On the one hand, the strain on the carbon framework should be comparable to that of the cyclobutane ring, causing a similar decrease $\Delta a_{H(\gamma)}$. On the other hand, the Walsh orbitals of the cyclopropane ring could play the role of the π-orbitals and work against this decrease. As a result, both contributions almost exactly cancel to give a vanishing $\Delta a_{H(\gamma)}$ value of +0.01 mT.

Theoretical calculations

The INDO procedure[40] was applied to calculate the coupling constants, a_N and a_H, of the protons and ^{14}N nuclei in $\mathbf{1}^{\bullet-}$, $\mathbf{5a}^{\bullet-}$, $\mathbf{6a}^{\bullet-}$, $\mathbf{7a}^{\bullet-}$, $\mathbf{8a}^{\bullet-}$ and $\mathbf{9a}^{\bullet-}$,‡ using the geometry optimized by the AM1 method.[41] The magnitude and sign of the a_N and a_H values are well reproduced by these calculations, except the sign of the small coupling, $a_{H(\gamma)}$, of the protons in the 5,6-*endo*-positions, which is predicted to be positive, at variance with experiment. The negative sign found for this value, as opposite to the positive one of the large coupling constant, $a_{H(\gamma)}$, of its *exo*-counterpart, was previously confirmed by NMR spectroscopy for the γ-protons in the corresponding positions of a structurally related hydrazine.[36]

In particular, it is gratifying to note that theoretical calculations reflect the impressive changes in the coupling constant, $a_{H(\gamma)}$, of the protons in the 5,6-*exo*-positions, on going from the parent radical anion $\mathbf{1}^{\bullet-}$ to $\mathbf{5a}^{\bullet-}$–$\mathbf{9a}^{\bullet-}$. Surprisingly, the geometry of the carbon framework in $\mathbf{1}^{\bullet-}$ is not greatly affected by the structural modifications occurring in this series. Such a statement is justified by inspection of Table 2 which gives the calculated values of some selected geometry parameters pertinent to the annelation by a cycloalkane or a cycloalkene ring in the 5,6-*endo*-positions. The listed values are the bond angle C(4)–C(5)–H$_x$, the dihedral angle N(3)–C(4)–C(5)–H$_x$ and the distance, C$_n$–N, between an *endo*-carbon atom of the cycloalkane or cycloalkene ring and a nitrogen atom of the azo group. Significant effects are an increase in the angle C(4)–C(5)–H$_x$ and a decrease in the interatomic C$_n$–N distance upon introduction of the double bond into the 5,6-*endo*-annelated cycloalkane ring, especially on replacing the cyclobutane by cyclobutene ring ($\mathbf{6a}^{\bullet-} \longrightarrow \mathbf{7a}^{\bullet-}$: +5.9° and −12.1 pm). Both effects are in line with an attractive interaction between the π-orbitals of the double bond and the azo group (Fig. 4). Such an interaction lowers the energy, *E*(SOMO), of the singly occupied orbital, as indicated by the calculated values also given in Table 2.

Table 2 Bond angles, C(4)–C(5)–H$_x$, and dihedral angles, N(3)–C(4)–C(5)–H$_x$ in degrees, interatomic distances, C$_n$–N in pm, and energies, *E*(SOMO) in eV, of the singly occupied orbital, calculated for $\mathbf{1}^{\bullet-}$ $\mathbf{5a}^{\bullet-}$, $\mathbf{6a}^{\bullet-}$, $\mathbf{7a}^{\bullet-}$, $\mathbf{8a}^{\bullet-}$ and $\mathbf{9a}^{\bullet-}$

	C(4)–C(5)–H$_x$ (°)	N(3)–C(4)–C(5)–H$_x$ (°)	C$_n$–N/pm	*E*(SOMO)/eV
$\mathbf{1}^{\bullet-}$	110.7	175.2	—	3.63
$\mathbf{5a}^{\bullet-}$	115.4	156.1	284.7	3.25
$\mathbf{6a}^{\bullet-}$	112.2	168.6	291.2	3.32
$\mathbf{7a}^{\bullet-}$	118.1	167.4	279.1	3.11
$\mathbf{8a}^{\bullet-}$	109.8	175.9	298.0	3.28
$\mathbf{9a}^{\bullet-}$	113.7	170.6	278.9	3.09
	110.0	174.0	288.6	

Conclusions

Structural modifications of 2,3-diaza[2.2.1]bicyclohept-2-ene **1** reported in the present paper lead to only minor changes in the geometry of the carbon framework of $\mathbf{1}^{\bullet-}$ and they do not substantially alter the π-spin distribution. Nevertheless, they have a great impact on the long-range coupling to the γ-protons in the 5,6-*exo*-positions.

Experimental

Materials

The azoalkanes **1**–**11c** were synthesized according to known procedures.[12,13]

Instrumental

The EPR, ENDOR and TRIPLE-resonance spectra were taken on a Bruker-ESP-300 system.

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‡ The hyperfine data for $\mathbf{9a}^{\bullet-}$ with methyl substituents in the 1,4-positions are missing, because, in contrast to its phenyl analogue $\mathbf{9b}^{\bullet-}$, this radical anion was not studied by EPR and ENDOR spectroscopy in the present work. However, the relevant a_N and a_H values for $\mathbf{9a}^{\bullet-}$ should closely resemble those for $\mathbf{9b}^{\bullet-}$ (Table 1), as anticipated by comparison of the results for other radical anions, in which the 1,4-methyl substituents (**a**) were replaced by phenyl groups (**b**).

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