Heterocyclic Radical Ions. VI. Long-Range Proton Electron Spin Resonance Splittings in Bicyclic Hydrazine Cations

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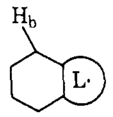
Abstract: The esr spectra of dimethyldialkylhydrazine cations derived from azodicarboxylate adducts with butadiene, cyclopentadiene, and 1,3-cyclohexadiene are reported. The "W-plan" long-range (γ) splittings are observed to have approximately the same sensitivity to charge density as β, and significantly greater than α splittings. The "homoconjugated" vinyl hydrogen splittings are somewhat more sensitive to charge density than β splittings. The nitrogen splitting increases with ring strain; a(N) for 2,3-diaza-2,3-dimethylbicyclo[2.2.1]heptene cation was 35% greater than that for 2,3-diaza-2,3-dimethylbicyclo[2.2.2]octane.

Unusually large γ-proton splittings have been observed in the esr spectra of a number of rigid bicyclic radical anions[2,3] since the first report of Russell and Chang.[2a] Enhanced γ splittings are observed when a "W" arrangement of the C_γ–H bond and the axis of the spin-bearing p orbital on the α-carbon is attained, and homohyperconjugation has been suggested as an important mechanism for spin delocalization. Enhanced splittings are also observed for γ-vinyl hydrogens. It is not at all apparent how important spin polarization mechanisms are, compared to hyperconjugation mechanisms, in delocalizing odd electron density to protons attached to γ-carbons. For β-protons, the observed splitting follows the relation[4] $a(H_\beta) = (B' + B\cos^2\theta)\rho C_\alpha^\pi$, where θ is the dihedral angle between the C_β and H_β bond and the C_α p-orbital axis. It is often supposed that the B' term corresponds to spin polarization, while the B term represents the contribution from hyperconjugation. For neutral radicals B is about 54[5] and B' is small.[6] Apparently hyperconjugation accounts for most of the observed $a(H_\beta)$ values except when θ is close to 90°. The B term clearly depends on charge density. Methyl splittings for many aromatic radical cations are substantially greater than those for the radical anions and the differences are greater than those seen for α-proton splittings[7] (which are caused almost entirely by spin polarization). Russell's group[8] has presented arguments favoring use of $B/2$ of 20 for radical anions, and 40 for cations, although they point out that there is every reason to expect B to vary continuously with charge density.

Arguing that the charge effect on splitting constants for γ protons might be much the same as for β protons (hyperconjugation giving a much bigger increase than spin polarization as charge density is decreased), we wished to extend studies of long-range splittings to cationic systems. To make a direct comparison with systems studied as radical anions, a symmetrical "label" with two adjacent p orbitals bearing as large a spin density as possible and having sufficient stability for esr measurements to be made conveniently was required. These requirements are fulfilled by tetraalkylhydrazine cations.[9] Suitable bicyclic tetraalkylhydrazine derivatives are easily prepared by lithium aluminum hydride reduction of diethyl azodicarboxylate Diels–Alder adducts.[10] These compounds have the decided disadvantage for esr studies that the splittings of interest are masked by the huge number of lines from the nitrogen and methyl groups, so that the γ-proton splittings can only be analyzed in the outer wings of the spectrum, which causes experimental problems in getting sufficient resolution and intensity. Methyl deuteration would only make the situation worse because of the magnitude of the methyl splittings, and sufficiently high ^{15}N labeling would not lead to enough simplification to justify the expense.

Results

The dimethyldialkylhydrazines derived from hydrogenated and unhydrogenated adducts of butadiene,



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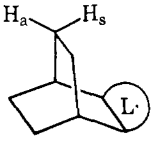

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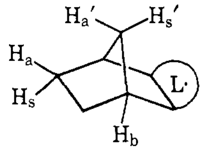

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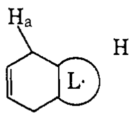

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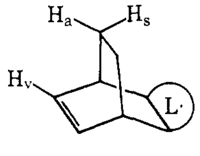

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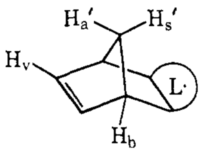

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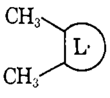

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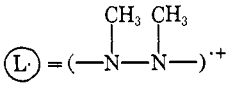
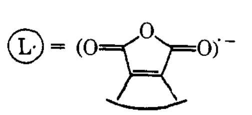
a, 
$(\mathrm{L\cdot}) = (\overset{\mathrm{CH_3}}{\overset{|}{\text{—N}}}\text{—}\overset{\mathrm{CH_3}}{\overset{|}{\text{N}}}\text{—})^{\cdot +}$

b, 

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[1] Alfred P. Sloan Fellow, 1968–1970.

[2] (a) G. A. Russell and K-y. Chang, *J. Amer. Chem. Soc.*, 87, 4381 (1965); (b) G. A. Russell, G. W. Holland, and K. Y. Chang, *ibid.*, 89, 6629 (1967).

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[6] There is still some confusion as to the magnitude of B'. See D. H. Levy and R. J. Myers, *ibid.*, 43, 3063 (1965).

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[10] (a) H. R. Snyder and J. G. Michels, *J. Org. Chem.*, 28, 1144 (1963); (b) J. E. Anderson and J. M. Lehn, *J. Amer. Chem. Soc.*, 89, 81 (1967); (c) N. P. Marullo and J. A. Alfort, *J. Org. Chem.*, 33, 2368 (1968).

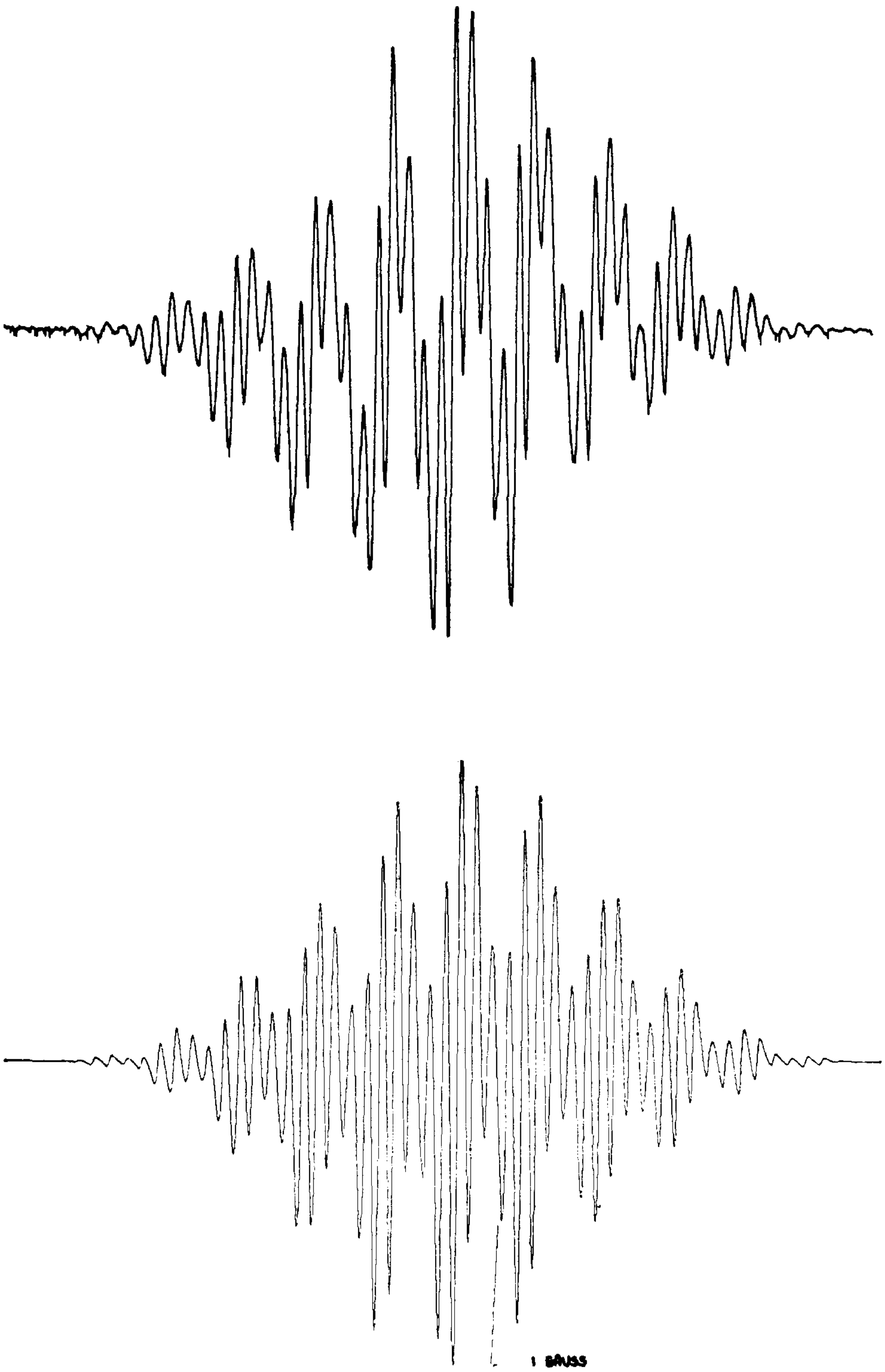

Figure 1. The esr spectrum of 2,3-diaza-2,3-dimethylbicyclo[2.2.2]octane cation radical (top), and a computer simulation using the splitting constants given in the text (bottom).

cyclopentadiene, and 1,3-cyclohexadiene were oxidized electrolytically in acetonitrile, and the esr spectra of **1a**–**6a** recorded. Since the methyl and nitrogen splittings were large and of similar size, all of the spectra consisted of groups of overlapping multiplets, and the long-range splittings of the bicyclic compounds were only observed unobscured in the wings of the spectrum. For **2a**, the outer lines were quintets, as expected for the four equivalent H_a hydrogens. The H_s splitting, expected to be considerably smaller, was not resolved. The outer lines of **5a** were also quintets (Figure 1) so we could neither resolve $a(H_s)$, nor a difference between $a(H_v)$ and $a(H_a)$. **3a** gave the most complicated long-range splitting pattern, consisting of an overlapping triplet of multiplets with at least seven components. To obtain such a result some of the long-range splittings of **3a** must be approximately multiples of others, but we cannot distinguish between $a(3\text{ H}) \approx 2a(2\text{ H})$ and $a(1\text{ H}) \approx 3a(2\text{ H}) \approx 2a(2\text{ H})$, for these patterns. By reducing at the biscarbamate stage with deuterium gas.[11]

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(11) W. R. Roth and M. Martin, *Justus Liebigs Ann. Chem.*, **782**, 1 (1967).

Table I. Comparison of Esr Splittings Constants for Some Hydrazine Cations and Semifuraquinones

Compd	*A* (hydrazine cation) splitting (no. of H)	Assignment	*B* (semifuraquinone) splitting (no. of H)	Assignment
7	13.4 (2 N)	N		
	12.7 (12)	Me	6.10 (6)	Me
1	13.9 (4)	H_b	7.63 (4)	H_b
	12.8 (2 N)	N		
	12.2 (6)	Me		
2	13.6 (2 N)	N		
	12.4 (6)	Me	1.36 (4)	
	2.45 (4)	H_a	0.27 (4)	H_s
3	15.6 (2 N)	N	2.04 (2)	H_a
	12.8 (6)	Me	1.03 (1)	$H_{a'}$
	4.78 (2)	H_a	0.47 (1)	$H_{s'}$
	1.72 (2)[a]	H_s or H_b	0.37 (2)	H_s or H_b
	0.86 (2)	H_b or H_s	0.27 (2)	H_b or H_s
4	13.2 (2 N, 4 H)	N, H_b	6.35 (4)	H_b
	12.3 (6)	Me	0.19 (2)	H_v
5	14.4 (2 N)	N	1.55 (2)	H_a
	12.0 (6)	Me	1.18 (2)	H_v
	3.0 (4)	H_a, H_v	0.33 (2)	H_s
6	18.3 (2 N)	N	1.41 (1)	$H_{a'}$
	12.5 (6)	Me	0.79 (3)	H_v, H_s
	3.56 (2)	H_v	0.40 (2)	H_b
	2.07 (1)	$H_{a'}$ or $H_{s'}$		
	1.34 (1)	$H_{s'}$ or $H_{a'}$		

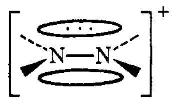
[a] $H^{a\prime}$ is probably 1.7 or 3.0 G (see text).

we prepared 5,6-*exo*-**3a**-d_2 (**3a** with H_a deuterium labeled). This material oxidized to a radical lacking the 4.78-G two-hydrogen splitting of **3a**, but with a much more complex smaller splitting pattern, consistent with $a(2\ D) \approx 0.8$ G. This result assures assignment of the largest long-range splitting of **3a** to H_a. The spectrum of **6a** had a ten-line pattern for the outer group, with lines 4–7 being more intense, and lines 4 and 7 being noticeably broadened. This is expected for $a(2\ H) \approx a(1\ H) + a(1\ H)$. The splittings of two hydrogens present in **6a** were not resolved, and these are expected to be the H_b hydrogens by comparison with spectra of the related semiquinone and semifuraquinone.

The observed splittings and assignments made are summarized in Table I.

Discussion

In Table I we compare the hydrazine cation splittings for those observed for semifuraquinone anions, because the electronic properties of these spin labels are the same in that each has a nodal plane bisecting the 2,3 and 5,6 bonds of the bicyclic systems. We presume that the hydrazine cations are sp^2 hybridized at nitrogen, which leaves three electrons in an ethylene-like π system as in **8**. This is in contrast to the starting hydrazines, which nmr studies have proven[10b] to be nonplanar at nitrogen. The splittings of tetramethylhydrazine (**7a**)[9] are entirely consistent with this interpretation. Furthermore, the long-range splittings of the bicyclic hydrazine cations are qualitatively like those of the related semifuraquinones, which is only reasonable if the nodal plane is present. For example, **3a** has $a(H_a) > a(H_a{}')$, and $a\ (H_b)$ small, in contrast to the related semidione, which lacks a nodal plane and has $a(H_{a'}) > a(H_a) = a(H_b)$.[2]



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We do observe a definite dependence of a(N) upon structure, consistent with a(N) increasing with increasing ring strain. The 2,3-diazabicyclo[2.2.2]octane system **2** has a nitrogen splitting close to that of tetramethylhydrazine, while that of the most strained compound, **6a**, has a nitrogen splitting 35% larger. This increase in a(N) seems not to be caused by larger $\rho_N{}^\pi$ (which is illogical anyway) since a(Me) remains more or less constant in this series; $a(\mathrm{Me}) = 13.4 \pm 0.4$ (or $\pm 3.2\%$). One possibility is that closing the C–N–N angle causes rehybridization to mix some s character into the spin bearing orbital on nitrogen, which would cause an increase[12] in a(N). Such an effect of ring strain has been postulated at carbon in cyclopropyl radical to explain the low $a(H_\alpha)$ splitting.[5] This would make the nitrogens slightly nonplanar in the bicyclic compounds; if so, they must be interconverting rapidly to give the observed spectra. Closing the C–N–N angle but keeping the system planar at the nitrogens might not be expected to affect a_N markedly.[13]

The observed ratio of methyl splittings for **7a**/**7b** is 2.09, and those for the methylene splittings of **1a**/**1b** and **4a**/**4b** are 1.82 and 2.08, respectively. Thus a ratio of about 2 for the long-range splittings with **a** and **b** spin labels is expected if γ-hydrogen splittings respond to charge density in the same way as β splittings (and if the changes in geometry are negligible). The observed ratios for the "W-plan" splittings are **2**, H_a, 1.8; **3**, H_a, 2.3; **5**, H_a, 1.9. The $H_{a'}$ ratio for **6** is about 1.5; unfortunately, that for **3** is not certain because of the ambiguity in the size of the splitting, but the 1.72 value would give a ratio of about 1.7, which would be consistent with the result for **5**. Both of the $H_{a'}$ ratios, which have the usual hyperconjuga-

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[12] Thus iminoxides, with some degree of s hybridization in the spin-bearing orbital, show large nitrogen splittings: J. R. Thomas, *J. Amer. Chem. Soc.*, **86**, 1446 (1964).

[13] M. Karplus and G. K. Fraenkel (*J. Chem. Phys.*, 35, 1312 (1961)) do not allow for a bond angle dependence in ^{13}C splittings. Lack of an effect of bond angle on a(Me) is expected: I. Bernal, P. H. Rieger, and G. K. Fraenkel, *ibid.*, 37, 1489 (1962).

tive contribution canceled by symmetry, are at the low end of the range, as might be expected. We conclude that the effect of charge on "W-plan" splittings is reasonably close to that on β-hydrogen splittings.

The vinyl hydrogen splittings do not show ratios nearly as close. The value of $a(\mathrm{H_v})$ for **6a** is greater than for **5a**, but this order is reversed in the semifuraquinones. The $a(\mathrm{H_v})$ ratios are 4.5 for **6**, but only 2.5 for **5**. It is possible that the difference in hybridization at nitrogen, reflected in the differing $a(\mathrm{N})$ values, is responsible for this difference in $a(\mathrm{H_v})$ although whether nitrogen is more sensitive than carbon to such effects is not known. In both cases, however, the $a(\mathrm{H_v})$ ratio is at least as sensitive to charge as are β splittings. The importance of homoconjugative interactions as a spin delocalization mechanism for **5** and **6** is still largely open.[2,3] We have recently questioned the reliability of the technique of probing for π spin density in the vinyl group (as required for homoconjugation to be important) by methyl substitution.[14] Our results here seem consistent with a homoconjugative contribution to $a(\mathrm{H_v})$, since such a contribution should be relatively more important for cationic than anionic systems. We do not doubt that there is also an important contribution due to spin polarization, and separation of these factors is not yet possible.

Experimental Section

Materials. The dimethylhydrazine precursors to **1a**-**4a** were prepared by literature procedures.[10b] Mass spectral analysis of *exo*-5,6-dideuterio-2,3-diaza-2,3-dicarbethoxynorbornane, prepared by the method of Roth and Martin,[11] and its LAH reduction product showed that our material was approximately 84% d_2, 13% d_1, and 3% d_0.

Esr spectra were determined by intramuros electrolytic oxidation in a platinum gauge electrode in a flat quartz cell in the cavity of a Varian E-3. Acetonitrile (stored over Linde 3A Molecular Sieve and distilled from calcium hydride) which was 0.05 *M* in sodium perchlorate was used as supporting electrolyte. The hydrazine cations were quite stable enough for esr work under these conditions, and persisted for hours if current was passed continuously. Splitting constants due to the alkyl portion of the molecule were determined by examination of the outer group of lines. All spectra were synthesized by computer as a check on the splitting constants so derived. The values of $a(\mathrm{N})$ and $a(\mathrm{Me})$ are probably not better than $\pm 2\%$ (0.3 G), for they depend on the accuracy of the "Fielddial" and line widths in excess of 250 mG were observed.

Acknowledgment. We wish to thank the National Science Foundation for generous support of this work and Robert Keppel for preparation of the precursors to **2a** and **5a**.

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Chemical and Spectroscopic Studies of the Decomposition of Bicyclic Azo Compounds Derived from Isopyrazoles

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Abstract: The reaction of isopyrazoles (IX) with 4-phenyl-1,2,4-triazoline-3,5-dione (X) affords the adducts XI in high yield. The decomposition of these azo compounds (XI) was studied; loss of nitrogen occurs both photochemically and thermally to afford 1,3 diradicals (XII) which either disproportionate intramolecularly (to XIX) or close to form the bicyclo[2.1.0]pentane derivatives (XXI). If the irradiation of XI is carried out in matrices at $T < 77$ °K, triplet signals which are consistent with the 1,3-diradical XII are obtained. The stability of the signals indicates that the triplet is the lowest state for this diradical. The reactions of bicyclo[2.1.0]pentane derivatives (XXI) were also studied; they reflect the extremely weak central bond (*D* 2-20 kcal).

The characterization of 1,3 diradicals is a subject of great current interest. These species are believed to be intermediates in the synthesis of several important classes of small ring compounds: cyclopropanes from pyrazolines,[1a] cyclobutanones,[1b] lactones,[1c] or olefins and carbenes;[1d] cyclopropenes from pyrazolenines,[2] or butenolides,[1c] and bicyclo[2.1.0]pentanes from diazanorbornenes.[3] In addition, their involvement is strongly implied in the cis-trans isomerization of cyclopropanes[4a] and of bicyclopentanes.[4b]

Most attempts to probe for the existence and properties of 1,3 diradicals have utilized cyclic azo compounds as precursors. Crawford and coworkers[1a,5] have demonstrated that both C-N bonds break in the rate-determining step of the thermal decomposition of 1-pyrazolines (I), as is the case with acyclic azo compounds,[6] and that a nitrogen-free diradical intermediate is formed. This has been supported for 2,3-diazabicyclo[2.2.1]hept-2-enes (II) by Allred's group,[7] although

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(1) (a) R. J. Crawford, R. J. Dummel, and A. Mishra, *J. Amer. Chem. Soc.*, **87**, 3023 (1965); (b) T. H. McGee, *J. Phys. Chem.*, **72**, 1621 (1968); (c) I. S. Krull and D. R. Arnold, *Tetrahedron Lett.*, 1247 (1969).

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