Temperature Effects on the Electron Spin Resonance Spectra of Tetraalkylhydrazine Radical Cations

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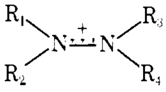
Abstract: The ESR spectra of tetramethyl-, tetrabenzyl-, and unsymmetrical dibenzyldimethylhydrazine radical cation at various temperatures are reported. Second-order splittings were partially resolved for tetramethylhydrazine radical cation, and a (CH_3) decreases as the temperature is raised. The value for $\Delta G^\ddagger$ (−70°) for CH_2–N rotation in tetrabenzylhydrazine radical cation is 4.9 ± 0.4 kcal/mol.

Tetraalkylhydrazine radical cations (I) are interesting species because they have a rather unusual electronic configuration, being isoelectronic with olefin radical anions. It has been shown[1] that the nitrogen hyperfine splitting [a(N)] is sensitive to alkyl group structure, varying from 11.9 G for $1\cdot^+$ to 18.5 G for $2\cdot^+$. Because the spin density is localized on the two nitrogens except for hyperconjugation effects, such a large variation of a(N) requires varying degrees of nonplanarity in I. For $3\cdot^+$, nonplanarity at nitrogen was indicated by a high value of a(N), 17.1 G in butyronitrile at 23°, and by freezing the hydrogen splittings into two sets of four ($\Delta G^\ddagger$ ca. 3.4 kcal/mol at −110° for the interconversion process). Furthermore, a(N) was observed to decrease as the temperature was raised, as would be expected for a nonplanar species, with a sizable barrier to inversion, and as observed for two other bicyclic hydrazines having large a(N) values.[1]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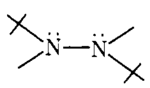
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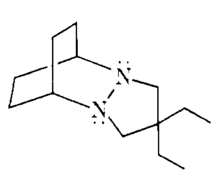
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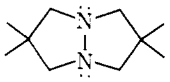
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In contrast, tetraethylhydrazine cation radical ($4\cdot^+$) [a(N) = 13.0 G] was found to have both a(N) and a(H) increase as the temperature is raised. To further investigate the effects of structure upon a(N) and a(H), we have determined the temperature effect upon the ESR spectra of three additional hydrazine radical cations, tetramethyl, tetrabenzyl, and unsymmetrical dimethyldibenzyl ($5\cdot^+$–$7\cdot^+$).

$(R)_2N—N(R)_2$

4, R = CH_2CH_3

5, R = CH_3

6, R = CH_2Ph

$(PhCH_2)_2NN(CH_3)_2$

7

Results

Tetramethylhydrazine Radical Cation ($5\cdot^+$). Although the ESR spectrum of $5\cdot^+$ has been reported previously,[2] we reinvestigated this molecule at various temperatures in butyronitrile, using tris(p-bromophenyl)aminium hexachloroantimonate as the oxidizing agent. We had never been able to attain peak-to-peak line widths under ca. 300-350 mg for tetraalkylhydrazine radical cations. We now found that $5\cdot^+$ gives much narrower lines if the concentration is kept under 10^{-3} *M*, and far more lines than previously observed. For example, the center multiplet in the spectrum, a quintet with a peak separation of a(N)-a(H) in the first-order approximation (and as observed at concentrations high enough to study the weak lines in the wings) appears as the ill-resolved multiplet shown in Figure 1. The minimum peak-to-peak line width here is about 80 mG. At second order,[3] the "quintet" shown is a badly overlapping pattern containing 55 lines, and the extra lines observed are clearly caused by partial resolution of second-order structure.[4] Since a(N) and a(H) are nearly equal for $5\cdot^+$, many of the second-order components are unresolved. It is clear that the inherent line width for these radicals is quite narrow, and that the complexity of the second-order splittings is responsible for the large line widths previously reported.

The splitting constants observed for $5\cdot^+$ at various temperatures appear in Table I. As previously observed in other examples, anisotropic line broadening effects broaden the $\bar{M}_n \neq 0$ lines as the temperature is lowered, making evaluation of a(N) impossible at low temperatures.

Tetrabenzylhydrazine Radical Cation ($6\cdot^+$). The room temperature ESR spectrum of $6\cdot^+$ showed the expected quintet [a(N) = 12.70 (2N)] of nonets [a(H) = 8.14 (8H)], but the appearance of the spectrum changed dramatically as the temperature was lowered. In addition to $\bar{M}_n \neq 0$ broadening, an alternating line width effect[5] sets in, and the $\bar{M}_n$ odd lines were indistinguishable at −70°. At −100°, the $\bar{M}_n \neq 0$ lines were so broadened they merely gave a poor base line, and the remaining lines appeared as two quintets (still somewhat distorted from 1:4:6:4:1 intensities) for $a(H_A)$ = 9.58(4H), $a(H_B)$ = 6.33(4H) G, which average to the value expected from higher temperature measurements, where H_A and H_B are rapidly interconverting. The data are presented in Table I.

Unsaturated Dibenzyldimethylhydrazine Radical Cation ($7\cdot^+$). Our principal interest in this compound was to determine the relative size of the nitrogen splittings. We had never successfully analyzed an unsymmetrically substituted I molecule and wished to establish whether this was because of the increased complexity derived by having inequivalent nitrogen splittings and to establish whether a change as small as substitution of one alkyl group for another would cause a resolvable difference in the a(N) values observed. Although the ESR spectrum of $7\cdot^+$ was quite complex at room temperature, it proved possible to analyze the splittings, as the simulation in Figure 2 demonstrates. At +32°, a(N) = 13.7_9, a(N′) = 12.5_0, a(Me) = 13.2_3(6H), $a(CH_2)$ = 8.0_2(4H). The spectrum undergoes changes as the temperature is lowered, and a reasonable simulation for the −61° spectrum was obtained by using the changes in a(N), $a(CH_3)$, and $a(CH_2)$ expected from the studies of $5\cdot^+$ and

Table I. Temperature Dependence of the ESR Splitting Constants for $5\cdot^+$ and $6\cdot^+$

$(CH_3)_2NN(CH_3)_2$ ($5\cdot^+$)			$(PhCH_2)_2NN(CH_2Ph)_2$ ($6\cdot^+$)		
T, °C	a(N)[c]	a(H)[c]	T, °C	a(N)[c]	a(H)[c]
+20	13.3_8	12.6_1	+30	13.0_2	8.3_4
0	13.3_5	12.6_5	0	12.9_7	8.2_3
−20	13.3_2	12.6_9	−40	12.9_4	8.1_3
−40	13.2_8	12.7_2	−70	~12.7	8.0_4
−60[a]		12.7_9	−100		7.96 (av)[b]
−80		12.8_5			
−100		12.8_8			
−120		12.9_5			

[a] In butyronitrile, oxidation with tris(p-bromophenyl)aminium hexachloroantimonate. [b] $a(H_A) = 9.5_8(4H)$, $a(H_B) = 6.3_3(4H)$. [c] In gauss.

Table II. Temperature Variation of Hydrazine Radical Cation Splittings

Species	Slopes,[a] mg/deg a(N)	Slopes,[a] mg/deg a(CH)
$5\cdot^+$	+1.4	−2.2
$6\cdot^+$	+1.8	+2.9
$4\cdot^{+b}$	+3.0	±6.8
$3\cdot^{+b}$	−7	<+0.8

[a] Slope of a plot of a vs. T. A positive number indicates an increase as the temperature is raised. [b] Data from ref 1.

$6\cdot^+$, but there is substantial broadening in the spectrum. The splitting constants at −61° were approximately $a(N) = 13.6$, $a(N') = 12.3$, $a(CH_3) = 13.4$, $a(CH_2) = 7.7$ G. We were unfortunately unable to observe an alternating line width effect and freeze out $N\text{-}CH_2$ rotation for this compound.

Discussion

Temperature Variation of Splittings. The splittings of hydrazine cation radicals were observed to vary approximately linearly with temperature over the temperature range investigated, and the slopes observed are summarized in Table II.

The negative slope for a(N) of $3\cdot^+$ is good evidence that this species is nonplanar at nitrogen with a substantial activation energy for inversion, and the positive slopes for the three acyclic compounds indicate that they are substantially less bent, or perhaps planar, in agreement with the significantly lower values of a(N) observed.

The positive slopes for a(H) of tetraethyl- and tetrabenzylhydrazine radical cation are those expected[6] since, at higher temperature, the higher energy conformations with the $CH_2\text{-}R$ bond eclipsed with the other substituents should become relatively more populated. A geometrically similar situation ($CH_2\text{-}R$ bond roughly parallel to the spin-bearing orbital, so $a(H_\beta)$ is lowest at low temperatures) is attained in 9-ethyl and 9-benzylxanthyl radical, both of which show +1.8 mG/deg slopes for $a(H_\beta)$.[7] For n-propyl radical, the $CH_2\text{-}CH_3$ bond is roughly perpendicular to the spin-bearing orbital and, in contrast, a large negative slope (ca. −29 mG/deg) was observed.[8]

It is more difficult to rationalize the negative slope (−2.2) for a(H) of tetramethylhydrazine. Because of the symmetry and rapid rotation of the methyl group, rotational effects on a(H) should not occur over the temperature range studied. Wood and coworkers[9] argued that, for a planar radical, since they predicted hyperconjugation to decrease as the vibrational amplitude increased, a negative slope would result. This prediction has apparently not been verified experimentally. Both ethyl radical[8] and 9-methylxanthyl radical[7] showed no temperature variation for $a(CH_3)$. $tert$-Butyl radical shows a positive slope of ca. +3.7 for $a(CH_3)$ and a negative slope of ca. −2.6 for $a(^{13}C)$, causing Wood and coworkers[9] to suggest that these results [combined with the relatively large $a(^{13}C)$] proved that $tert$-butyl radical is nonplanar, an assertion which has aroused some controversy.[10] It is interesting to note that Fessenden and Schuler[8] found $a(CH_3)$ for isopropyl radical to have a (rather smaller) positive slope (ca. +1.0). It appears, then, that the negative slope of $a(CH_3)$ for $5\cdot^+$ (and $7\cdot^+$, see Results) is rather unusual, although it is by no means clear that a geometrical conclusion can be drawn from this fact.

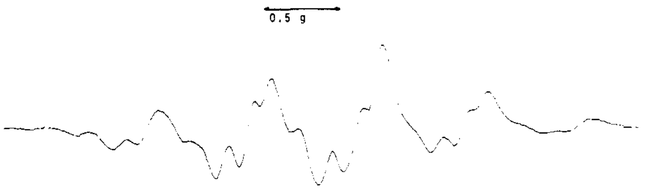


Figure 1. The central multiplet of the $(CH_3)_2NN(CH_3)_2\cdot^+$ ESR spectrum at +2°, showing partially resolved second-order splittings.

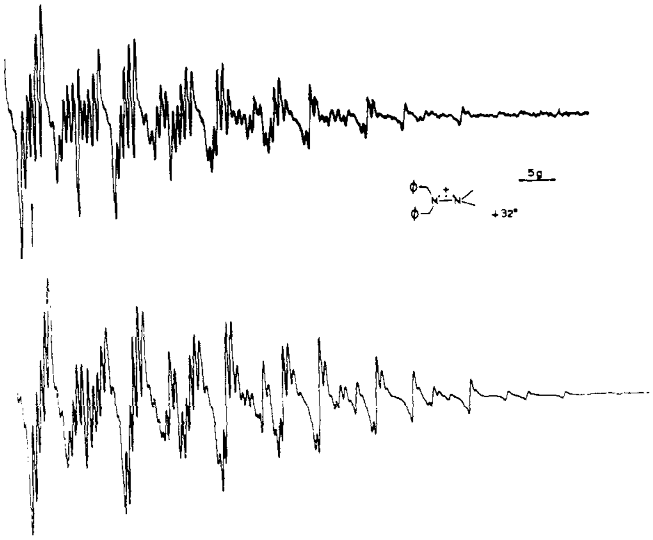
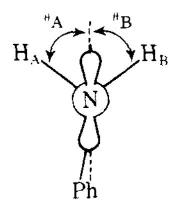


Figure 2. The ESR spectrum of $[(PhCH_2)_2NN(CH_3)_2]\cdot^+$ at +32°, together with a simulation using the splitting constants quoted in the text, a Lorentzian line shape, and a line width of 0.3 G.

Conformation of $6\cdot^+$. Since the nitrogen splitting of $6\cdot^+$ is near the low end of the range observed for hydrazine radical cations, it is presumably close to being planar, which should allow application of the usual β splitting eq 1 in analyzing the conformation attained.

$$a(H_\beta) = (B_0 + B_2 \cos^2 \theta)\rho_N^\pi \tag{1}$$

Making the usual assumptions[11] of a 120° phasing angle and a negligible B_0, the $a(H_A)/a(H_B)$ ratio is consistent with either $\theta_A = -56.5°$, $\theta_B = +63.5°$ (see II), or $\theta_A =$



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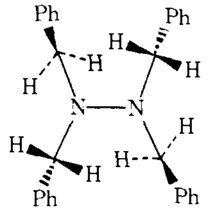

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Table III. Comparison of $X_{\mathrm{R-H}}$ with σ^*

Substituent	$X_{\mathrm{R-H}}$	σ^{*a}	Est $X_{\mathrm{R-H}}{}^b$
H	(0)	+0.490	(0)
CH_2Ph	0.074_3	+0.115	0.09_5
CH_3	0.123_6	0.000	(0.12_4)
CH_2CH_3		−0.100	0.14_9
$C(CH_3)_3$		−0.300	0.19_9

[a] From ref 19. [b] Estimated $X_{\mathrm{R-H}} = (0.49 - \sigma^*)(0.1236)/(0.49)$, so $\Delta\sigma^*$ has been multiplied by a constant which reproduces the observed value of $X_{\mathrm{Me-H}}$.

+20, $\theta_B = +140°$. The latter pair may be positively ruled out, because the CH_2 splitting would have to be larger than $a(CH_3)$ for tetramethylhydrazine (where $\langle\cos^2\theta\rangle$ is 0.5), whereas the observed splitting is substantially smaller. The conformation indicated by the ESR of $\mathbf{6}\cdot^+$ is that shown as III, which appears reasonable on steric grounds, and is consistent with the positive slope of $a(CH_2)$. The exact values of θ derived in this simple way are subject to error not only because B_0 may well not be negligible, and the phasing angle is not exactly 120° (which we believe[11] only lead to fairly small errors), but also because the nitrogens are likely not to be perfectly planar.[1] An indication that something is wrong with the θ values derived may be obtained by back-calculating $a(H_A)$ and $a(H_B)$ using them. Making the reasonable assumption that $\rho_N{}^\pi$ is similar for $\mathbf{5}\cdot^+$ and $\mathbf{6}\cdot^+$, one obtains $B\rho_N{}^\pi = 2a(CH_3\text{–}\mathbf{5}\cdot^+)$, which gives $a(H_A) = 7.7$, $a(H_B) = 4.8$ G, considerably lower than the observed values. This result is consistent with our expectation that $\mathbf{6}\cdot^+$ is not quite planar,[1] or at least that fairly large deviations from planarity occur because of an unusually broad energy minimum, even compared with alkyl radicals.

Benzyl Rotation in $\mathbf{6}\cdot^+$. The temperature of maximum broadening (T_c) for the alternating line width effect in $\mathbf{6}\cdot^+$ was about −70°. Since $k(T_c) = 6.22 \times 10^6 \Delta a$,[12] $k(-70°) = 2.02 \times 10^7\ \mathrm{sec}^{-1}$, corresponding to $\Delta G^\ddagger(-70°)$ of ca. 4.9 ± 0.4 kcal/mol (the 0.4-kcal/mol error is totally arbitrary and corresponds to a 15° uncertainty in T_c, which is difficult to determine accurately). Since hydrazine radical cations have the spin-bearing orbitals essentially parallel, and double nitrogen inversion activation energies are quite low,[1] the barrier observed here can only be reasonably attributed to CH_2–N rotation. Dewar and Jennings[13] assumed that CH_2–N rotation in neutral **6** was lower than the 8.2 kcal/mol (−105°) barrier they observed and attributed to N–N rotation. It is clear that CH_2–N rotation in $\mathbf{6}\cdot^+$ must be easier than in the neutral compound, because the radical cation is substantially more planar and has less steric hindrance to rotation, but it is difficult to estimate the difference in barrier heights expected. Malatesta and Ingold[14] found inequivalence for the benzyl hydrogens of 1,1-dibenzylhydrazyl radical at 0°, requiring that the barrier to equilibrating them is at least 7 kcal/mol. The reason for this result is not clear, but the barrier to N-CH_2 rotation expected on steric grounds should be considerably lower.

Nitrogen Splittings of Unsymmetrical Hydrazine Radical Cations. The larger nitrogen splitting of $\mathbf{7}\cdot^+$ may be confidently assigned to the dimethylamino nitrogen, because $a(CH_3)/a(N)$ for $\mathbf{5}\cdot^+$ is 0.94, and this assignment gives $a(CH_3)/a(N)$ for $\mathbf{7}\cdot^+$ of 0.96, whereas the opposite assignment would give the ratio as 1.06. Thus $\mathbf{7}\cdot^+$ has $a(N(CH_3)_2)$ 0.41 G (3%) larger than that of $\mathbf{5}\cdot^+$, and $a(N(CH_2Ph)_2)$ 0.52 G (4%) smaller than that for $\mathbf{6}\cdot^+$. Since benzyl is somewhat less electron releasing than CH_3, this result is expected from qualitative considerations.

It would clearly be of interest to be able to estimate how much nitrogen splittings would differ in other unsymmetrical hydrazine radical cations. The only other literature data are for $(MeHNNH_2)\cdot^+$, which is reported to have $R_N = a(N)/a(N') = 0.77_5$[15] or 0.78_7,[16] and for $(Me_2NNH_2)\cdot^+$, $R_N = 0.604$[15] or 0.608.[16] If these differences in $a(N)$ are assumed to be caused by differences in $\rho_N{}^\pi$ (which would be true if differences in geometry at nitrogen were small enough to ignore[17]), it may be stated that the effect of replacing a hydrogen by a methyl group in going from hydrazine to methylhydrazine radical cation is to move a fraction $X_{\mathrm{Me-H}}$ of the spin (charge) from the NH_2 nitrogen to the NHMe nitrogen. The nitrogen splitting ratio should then be $R_N = (1 - X_{\mathrm{Me-H}})/(1 + X_{\mathrm{Me-H}})$, requiring $X_{\mathrm{Me-H}}$ to be 0.123_6. For $(Me_2NNH_2)\cdot^+$, if the effect is not quite additive (as one would expect[18]), $R_N = (1 - X_{\mathrm{MeH}})^2/(1 + X_{\mathrm{MeH}})^2 = 0.608$, making it appear that the $X_{\mathrm{Me-H}}$ obtained from the monomethyl compound has utility. Proceeding similarly, the 0.906 observed value for R_N for $\mathbf{7}\cdot^+$ requires $X_{\mathrm{Me-Bz}}$ to be 0.049_3, so $X_{\mathrm{Bz-H}}$ is apparently 0.074_3. To estimate the effect of other alkyl groups upon R_N, it would seem reasonable to compare X values with the best known Hammett-type substituent constants for alkyl groups, σ values,[19] which is done in Table III. It is apparent that σ^* for benzyl and methyl are closer than are the corresponding $X_{\mathrm{R-H}}$ values but, if a linear relationship between $X_{\mathrm{R-H}}$ and σ^* is assumed (for lack of a better way to proceed), the last column of Table III indicates that R_N for ethyltrimethylhydrazine radical cation would be 0.95, leading to a difference in the two $a(N)$ values of about 0.65 G. Even replacing one methyl by ethyl in a hydrazine radical cation should lead to an easily detectable difference in the nitrogen splitting constants, although further work would be required to establish how successful σ^* would be in quantitative predictions of $a(N)$ values.

Experimental Section

Tetrabenzylhydrazine (**6**) was prepared by alkylation of hydrazine,[13] mp 140–141.5° (lit.[13] 139–140°).

Unsaturated dibenzyldimethylhydrazine (**7**) was prepared by reductive methylation[20] of unsymmetrical dibenzylhydrazine.[13] A mixture of 1.06 g (5 mmol) of unsymmetrical dibenzylhydrazine, 4 ml of formalin (50 mmol), 0.95 g (15 mmol) of sodium cyanoborohydride, and 22 ml of acetonitrile was stirred magnetically and treated over a 3-hr period with 35 drops of acetic acid. After stirring for 2 additional hr, 5 ml of concentrated hydrochloric acid was added, and the solvent was removed by rotary evaporation. After basification with sodium hydroxide, extraction into ether, and drying with potassium carbonate, the product was crystallized from pentane, giving 750 mg (62%) of white needles, mp 54–56°, having the proper empirical formula and spectral properties for **7**.

The ESR techniques employed have been described.[1]

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(4) Fessenden's Table I[3] lacks entries for 12 equivalent H and 2 equivalent N. The proper entries are: shift in units of $a^2/4\nu_0$ (intensity). For 12H, $k_z = 0$: 84 (1), 60 (11), 40 (54), 24 (154), 12 (275), 4 (297) 9 (132). $k_z = 1$: 82 (1), 58 (11), 38 (54), 22 (154), 10 (275), 2 (297). $k_z = 2$: 76 (1), 52 (11) 32 (54), 16 (154), 4 (275). $k_z = 3$: 66 (1) 42 (11), 22 (54), 6 (154). $k_z = 4$: 52 (1), 28 (11), 8 (54). $k_z = 5$: 34 (1), 10 (11). $k_z = 6$: 12 (1).

For 2N, $k_z = 0$: 12 (1), 4 (1), 0 (1). $k_z = 1$: 19 (1), 1 (1). $k_z = 2$: 4 (1). We note that the number of components and shifts are the same for 2N as for 4H, but that the intensities are different.

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(17) The fact that a(N) average increases[15] in going from hydrazine (11.5) to methylhydrazine (12.25) to dimethylhydrazine (12.87), in spite of increased hyperconjugation, suggests that the geometry is indeed changing. Changes in amount of hyperconjugation would be expected to make a(N) decrease in this series. Both effects should be minimized for tetralkylhydrazines, and we have ignored them.

(18) The difference between $(1 - X_{\text{Me-H}})^2$ and $(1 - 2X_{\text{Me-H}})$ is too small to be significant here but, when more accurate data are in hand, the expressions of the former form work better. See R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963); and S. F. Nelsen and J. M. Buschek, *J. Am. Chem. Soc.*, **96**, 2392 (1974).

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Electron Transfer between Tetraalkylhydrazine Radical Cations and Tetraalkylhydrazines

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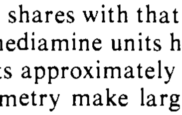
Abstract: The radical cations of both tetramethyl and tetraethyl *sym*-hexahydrotetrazine have the odd electron localized in one hydrazine unit, and intramolecular electron transfer between the methylene bridged hydrazine units is slow on the ESR time scale. The intermolecular electron transfer rate is also unusually slow between 3,3,7,7-tetramethyl-1,4-diazabicyclo[3.3.0]octane and its radical cation, because less than 0.7 g of line broadening is observed when the ESR spectrum of the radical cation is recorded in a solution over 0.8 M in the neutral hydrazine.

We recently reported[1] that the radical cation of tetraazatricyclododecane (**1**) gives an ESR spectrum showing splittings for four equivalent nitrogens and two sets of eight equivalent hydrogens at −100°. Although all that is required by this ESR result is a low activation energy for electron transfer among the nitrogens, we argued from the low $E_{1/2}$ for electrolytic oxidation that the charge was actually delocalized over all four nitrogens in **1**$\cdot^{+}$. The structure of **1** shares with that of Dabco (**2**) the feature of having ethylenediamine units held with their lone pair (C–C) lone pair units approximately colinear. Substantial changes from this geometry make large changes in the amount of lone pair–lone pair interaction as measured by photoelectron spectroscopy[2] and cause the radical cations to have such short lifetimes that their re-reduction is not detectable in a cyclic voltammetry experiment.[3] Because of the unusual effect of methylene bridging to enable 1,3 interactions between two units to occur in **1**, we thought it would be of interest to examine the monocations of *sym*-hexahydrotetrazines **3**, which incorporate two methylene-bridged tetraalkylhydrazines.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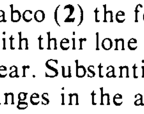
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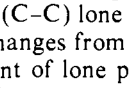
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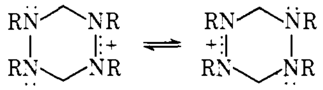
Results

Hexahydrotetrazine ESR Spectra. From the known ESR spectra of six ring hydrazines,[4] it is easy to distinguish whether the odd electron is localized in one hydrazine unit, which will give a spectrum with two equivalent nitrogen splittings and a(N) near 13 G, from that of a four nitrogen delocalized or rapidly equilibrating $\mathbf{3}\cdot^{+} \rightleftarrows \mathbf{3'}\cdot^{+}$ system, which would have four equivalent nitrogens with a splitting about half as large. Both **3**$\cdot^{+}$ (R = CH_3) and **3**$\cdot^{+}$ (R = CH_2CH_3) give ESR spectra of the former type at room temperature, clearly demonstrating that intramolecular electron transfer is slow. Similar spectra were observed both by electrolytic oxidation in acetonitrile, and chemical oxidation in butyronitrile. The splittings observed appear in Table I. The ESR spectrum of **3**$\cdot^{+}$ (R = CH_2CH_3) showed only rather broad lines, and we were unable to resolve the difference between a(N) and $a(CH_2)$. The observation of a four hydrogen quintet with the splitting expected for a 1,2-diethylhydrazine[4] and of such a large nitrogen splitting clearly requires localization of the odd electron in only one hydrazine unit, however. For **3**$\cdot^{+}$ (R = CH_3), we could resolve the difference between $a(CH_3)$ and a(N). Because of the accidental equality of $a(CH_2)$-a(N) and a(N)-$a(CH_3)$, however, most of the lines observed consist of overlapping components having different magnetic quantum numbers. Although the relative intensities of the observed lines at room temperature were fairly close to those expected on the basis of the degeneracies of the lines, large deviations appeared at low temperatures. As expected from the low temperature ESR spectra of other tetraalkylhydrazine radical cations,[4] anisotropic line broadening seriously


$\mathbf{3}\cdot^{+}$ $\mathbf{3'}\cdot^{+}$

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