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# Tetraalkylhydrazine radical cations. Effect of alkyl structure upon geometry

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(*R*)-*trans*-*N,N'*-Di(5-bromosalicylidene)-1,2-cyclohexanediamine [(*R*)-10b] was recrystallized from acetone-methanol (85%): yellow needles, mp 186–188°,  $[\alpha]^{25}_D -220^\circ$  (*c* 0.096, CH<sub>3</sub>OH, 2-dm).

Anal. Calcd for C<sub>20</sub>H<sub>20</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>2</sub>: C, 50.02; H, 4.20. Found: C, 50.06; H, 4.31.

(*R*)-(-)-1,2-Propanediamine [(*R*)-11a]. Technical grade (±)-11a was resolved by a method previously reported.<sup>28</sup> After 15 recrystallizations from dilute acetic acid, decomposition of the (+)-tartaric acid salt with sodium hydroxide gave (-)-11a which was extracted into benzene,  $[\alpha]^{25}_D -35^\circ$  (*c* 0.97, C<sub>6</sub>H<sub>6</sub>, 2-dm) [lit.<sup>28</sup>  $[\alpha]_D -34.8^\circ \pm 0.4^\circ$  (C<sub>6</sub>H<sub>6</sub>)]. The concentration of (-)-11a in benzene was determined by titration with 0.101 *N* hydrochloric acid as outlined above for (-)-10a.

(*R*)-*N,N'*-Di(5-bromosalicylidene)-1,2-propanediamine [(*R*)-11b] was recrystallized from acetone (61%): yellow needles, mp 119–121°,  $[\alpha]^{25}_D -110^\circ$  (*c* 0.23, CH<sub>3</sub>OH, 2-dm) [lit.<sup>45</sup> mp 119°].

Anal. Calcd for C<sub>17</sub>H<sub>16</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>2</sub>: C, 46.39; H, 3.66. Found: C, 46.32; H, 3.69.

(*R*)-*N,N'*-Disalicylidene-1,2-propanediamine [(*R*)-11c] was recrystallized from methanol (47%): yellow needles, mp 54–56°,  $[\alpha]^{25}_D -339^\circ$  (*c* 0.49, CH<sub>3</sub>OH) [lit. mp 89°<sup>43</sup> and 62–63°<sup>48</sup>].

(45) A. P. Terent'ev, G. V. Panova, and E. G. Rukhadze, *Zh. Obshch. Khim.*, **34**, 3013 (1964); *J. Gen. Chem. USSR*, **34**, 3049 (1964).

Anal. Calcd for C<sub>17</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>: C, 72.32; H, 6.43; N, 9.92. Found: C, 72.46; H, 6.43; N, 9.83.

(*S*)-*N*-(5-Bromosalicylidene)- $\alpha$ -(*p*-nitrobenzyl)ethylamine [(*S*)-21], prepared from (*S*)-(+)- $\alpha$ -(*p*-nitrobenzyl)ethylamine hydrochloride<sup>46</sup> [mp 194–195°,  $[\alpha]^{25}_D +21^\circ$  (*c* 1.22, H<sub>2</sub>O)], was recrystallized from acetone-methanol (76%): yellow needles, mp 115–116°,  $[\alpha]^{25}_D +180^\circ$  (*c* 1.01, absolute C<sub>2</sub>H<sub>5</sub>OH).

Anal. Calcd for C<sub>16</sub>H<sub>15</sub>BrN<sub>2</sub>O<sub>3</sub>: C, 52.91; H, 4.16. Found: C, 52.93; H, 4.13.

(*S*)-*N,N'*-Di(5-bromosalicylidene)- $\alpha$ -(*p*-aminobenzyl)ethylamine [(*S*)-22], prepared from (*S*)-(+)- $\alpha$ -(*p*-aminobenzyl)ethylamine dihydrochloride<sup>47</sup> [mp 270° dec,  $[\alpha]^{25}_D +16^\circ$  (*c* 1.23, H<sub>2</sub>O)], was recrystallized from methylene chloride-acetone (81%): yellow needles, mp 163–164°,  $[\alpha]^{25}_D +200^\circ$  (*c* 0.20, absolute C<sub>2</sub>H<sub>5</sub>OH).

Anal. Calcd for C<sub>23</sub>H<sub>20</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>2</sub>: C, 53.51; H, 3.91. Found: C, 53.44; H, 3.43.

Methyl *N*-salicylidene-L-tyrosinate [L-23] was recrystallized from methyl acetate: mp 166–167°,  $[\alpha]^{25}_D -268^\circ$  (*c* 2.07, CH<sub>3</sub>OH) [lit.<sup>8</sup> mp 166–167°,  $[\alpha]^{25}_D -270^\circ$  (*c* 2.0, CH<sub>3</sub>OH)].

(46) W. Gruber and I. C. Gunsalus, *J. Org. Chem.*, **21**, 1024 (1956).

(47) G. F. Holland, C. J. Buck, and A. Weissman, *J. Med. Chem.*, **6**, 519 (1963).

## Tetraalkylhydrazine Radical Cations. The Effect of Alkyl Structure upon Geometry

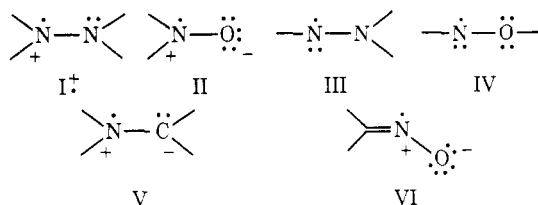
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Contribution from the Department of Chemistry, University of Wisconsin—Madison, Madison, Wisconsin 53706. Received September 10, 1973

**Abstract:** The esr spectra of 25 tetraalkylhydrazine radical cations are reported;  $a(N)$  varied from 11.9 to 18.8 G depending upon the structure of the alkyl groups present. The effect of temperature upon the esr spectra was investigated for representative compounds. All showed anisotropic broadening of the  $\bar{M}_N \neq 0$  lines at low temperatures. For the bridgehead diazabicyclo[3.3.0] and -[4.4.0] systems (19–20<sup>+</sup> and 11<sup>+</sup>, respectively), the splittings for the eight equivalent  $\beta$  hydrogens observed at room temperature showed an alternating line-width effect as the temperature was lowered, and at low temperatures two sets of four equivalent hydrogens were observed. Estimated  $\Delta G^\ddagger$  values for the interconversion process (interpreted as double nitrogen inversion) were about 3.4 and 4.5 kcal/mol, respectively. The nitrogen splitting increased as the temperature was lowered for three compounds with larger  $a(N)$  splittings, but decreased for tetraethylhydrazine cation (4<sup>+</sup>). INDO calculations on N<sub>2</sub>H<sub>4</sub><sup>+</sup> suggest that hydrazine cation radicals deviate from planarity toward the eclipsed conformation (1c<sup>+</sup>), and indicate  $\beta$  values of 14–37° for the series of compounds investigated. Acceptance of these  $\beta$  values requires accepting that N<sub>2</sub>H<sub>4</sub><sup>+</sup> itself has a  $\beta$  value of about 11° in solution; if it is actually planar, the  $\beta$  values indicated above must be decreased.

Hydrazine radical cations (I<sup>+</sup>) may be formally considered to be members of a class of radicals containing a nitrogen bearing an odd electron which is adjacent to an atom bearing a lone pair of electrons. Other members of this class of radicals include the neutral species dialkyl nitroxides (II),<sup>2</sup> hydrazyls (III),<sup>3</sup> alkoxyamino radicals (IV),<sup>4</sup> and  $\alpha$ -amino carbon radicals

(V);<sup>5</sup> other resonance forms can obviously be drawn for I–V. All of I–V show the relatively low  $a(N)$  (nitrogen esr splitting) one would expect for a  $\pi$  system containing three electrons (one of which must be “anti-bonding”), which we will refer to as “three-electron  $\pi$  bond.” In contrast, iminoxy radicals (VI) have larger



$a(N)$  values, demonstrating an unmistakable degree of  $\sigma$  hybridization in the spin-bearing orbital on nitrogen.<sup>6</sup>

(5) D. E. Wood and R. V. Lloyd, *J. Chem. Phys.*, **52**, 3840 (1970).

(6) For leading references, see ref 2b, p 562.

(1) Undergraduate research participant.

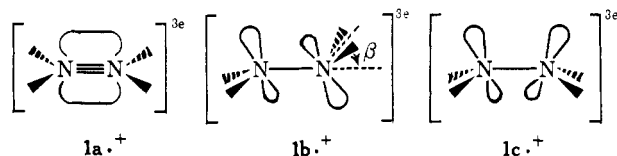
(2) For reviews, see (a) A. R. Forrester, J. M. Hay, and R. H. Thomson, "Organic Chemistry of Stable Free Radicals," Academic Press, New York, N. Y., 1968, pp 180–246; (b) S. F. Nelsen in "Free Radicals," Vol. II, J. K. Kochi, Ed., Wiley-Interscience, New York, N. Y., 1973, pp 539–556.

(3) (a) For a review of aryl derivatives, see ref 2a, pp 137–179; (b) D. E. Wood, C. A. Wood, and W. A. Lathan, *J. Amer. Chem. Soc.*, **94**, 9278 (1972); (c) R. Fantechi and G. A. Helcké, *J. Chem. Soc., Faraday Trans. 2*, **68**, 924 (1972); (d) V. Malatesta and K. U. Ingold, *J. Amer. Chem. Soc.*, **95**, 6110 (1973); (e) S. F. Nelsen and R. T. Landis, *ibid.*, **95**, 2719 (1973).

(4) W. C. Danen and C. T. West, *J. Amer. Chem. Soc.*, **93**, 5582 (1971).

The literature is quite ambiguous on the geometry of the three-electron  $\pi$  bond species I–V. The most studied example has been that of dialkyl nitroxides, often assumed to be planar at nitrogen,<sup>2</sup> which has been supported by an X-ray structure determination.<sup>7a</sup> Other workers,<sup>2,7b</sup> however, have argued for significant deviations from planarity. Detailed information is not yet available for III–V, although various approximate MO calculations have not agreed as to whether the bent or planar form should be most stable for III.<sup>3b,c</sup>

Three structures seem likely for a hydrazine radical cation ( $1\cdot^+$ ), the planar structure ( $1a\cdot^+$ ), the staggered one ( $1b\cdot^+$ ), and the eclipsed one ( $1c\cdot^+$ ). Hydrazine

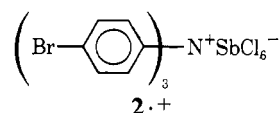


radical cation itself was argued to be planar from the magnitude of  $a(N)$  by Adams and Thomas,<sup>8</sup> but this same piece of data has been used to argue for nonplanarity.<sup>9</sup> More recent solid-state studies have been interpreted as verifying the planar structure ( $1a\cdot^+$ ) for  $N_2H_4\cdot^+$  at crystal defects,<sup>10</sup> but Fantechi and Helcké<sup>9c</sup> favored the staggered form ( $1b\cdot^+$ ) at high temperatures and the planar one at lower temperatures for  $N_2H_4\cdot^+$  absorbed on a zeolite matrix. The radical cations of hydrazine, mono-, di-,<sup>11</sup> and trialkylhydrazines are so unstable in solution that flow systems are required for esr studies. Since trialkylhydrazyls (III) are far more easily oxidized than the related hydrazines,<sup>12</sup> NH deprotonation is clearly responsible for the observed instability. In contrast, many tetraalkylhydrazine radical cations are quite stable enough in solution for convenient esr work.<sup>13</sup> We report our studies of tetraalkylhydrazine radical cations more fully<sup>14</sup> here. These studies take advantage of the unique four point attachment of substituents upon  $1\cdot^+$ , which allows a maximum degree of control over geometrical constraints placed upon the  $1\cdot^+$  system by the  $\sigma$  framework of the substituents. This work demonstrates that at least some, and perhaps all tetraalkylhydrazine radical cations are nonplanar, and surprisingly, that the eclipsed conformation ( $1c\cdot^+$ ) is preferred in at least some cases.

## Results

**Esr Spectra.** In conjunction with electrolytic study of hydrazine oxidation,<sup>13</sup> we determined the esr spectra of several tetraalkylhydrazine radical cations in acetonitrile (containing sodium perchlorate or tetrabutyl-

ammonium perchlorate as electrolyte), using *intra muros* electrolytic oxidation at room temperature for radical generation. To allow low-temperature studies, we also used butyronitrile as solvent in some cases; the small splitting changes do not warrant redetermination of all systems in all solvents. Unfortunately, we were unable to obtain nearly as good resolution in either solvent in the small cell necessary to fit in the variable-temperature esr dewar (the cell must fit into a cylinder which is 4 mm in diameter) as in the larger cell we used at room temperature (11-mm cylinder). For this reason, we have started using external electrolytic oxidation to convert all of the hydrazine in the sample to the radical cation, followed by transfer to a cylindrical esr tube, and sealing. This gives significantly better resolution in many cases, but of course requires substantial stability for the radical cations studied. Coulometry demonstrated one-electron oxidation, as earlier shown by cyclic voltammetry, and the esr signal persists for many hours to many days for unstrained tetraalkylhydrazine radical cations. A particularly convenient method of sample preparation which avoids electrochemistry (and the presence of a 100-fold excess of supporting electrolyte) altogether is to use chemical oxidation. We have chosen to employ tris(*p*-bromophenyl)amminium hexachloroantimonate<sup>15</sup> ( $2\cdot^+$ ) as the



oxidant, because it has several convenient features.

It is easily storable as the solid and has a convenient  $E_{1/2}$  value of +1.05 V (*vs.* sce in  $CH_3CN$ <sup>16</sup>), which is high enough to be able to assume complete electron transfer from our hydrazines to  $1\cdot^+$  and to ensure a slow enough electron transfer rate in the reverse direction not to broaden the esr spectra of the hydrazine radical cations. Its intense blue color allows visual "titration" with hydrazine to reach the desired mixture (no excess of either  $2\cdot^+$  or hydrazine), and the oxidation remains rapid enough at  $-78^\circ$  to prepare samples of  $1\cdot^+$  which are much less stable than those available by the external electrolytic method.

The esr splittings observed for several tetraalkylhydrazine radical cations ( $3\cdot^+$ – $26\cdot^+$ ) at room temperature are summarized in Table I. All of these radicals showed uniform (or nearly uniform) esr line widths at room temperature. For systems 27–29, which contain *N*-aminopiperidine part-structures, the esr spectra clearly had nonuniform line widths, as expected from esr studies of the isoelectronic piperidinyloxy radicals.<sup>4,17</sup> We have not analyzed the splittings of these complex spectra.

Interestingly, the esr spectra of all of the tetraalkylhydrazine cation radicals which we have investigated show obvious nonuniform line-width effects at low temperatures. In all cases, the lines with  $\bar{M}_N \neq 0$ , become noticeably broadened somewhere between  $-50$  and  $-100^\circ$ , and often become so broad that only the  $\bar{M}_N = 0$  lines are observed below  $-100^\circ$ . This dis-

(7) (a) G. J. Kruger and J. C. A. Boeyens, *Proc. Nat. Acad. Sci. U. S.*, **61**, 422 (1968); (b) J. Douday, Y. Ellinger, A. Rassat, R. Subra, and G. Berthier, *Mol. Phys.*, **17**, 217 (1969).

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(9) R. Poupo and B. L. Silver, *J. Amer. Chem. Soc.*, **93**, 575 (1971).

(10) (a) C. L. Marquardt, *J. Chem. Phys.*, **53**, 3248 (1970); (b) M. H. Reilly and C. L. Marquardt, *ibid.*, **53**, 3257 (1970); (c) J. A. Brivati, J. M. Gross, M. C. R. Symons, and D. J. A. Timling, *J. Chem. Soc.*, 6504 (1965).

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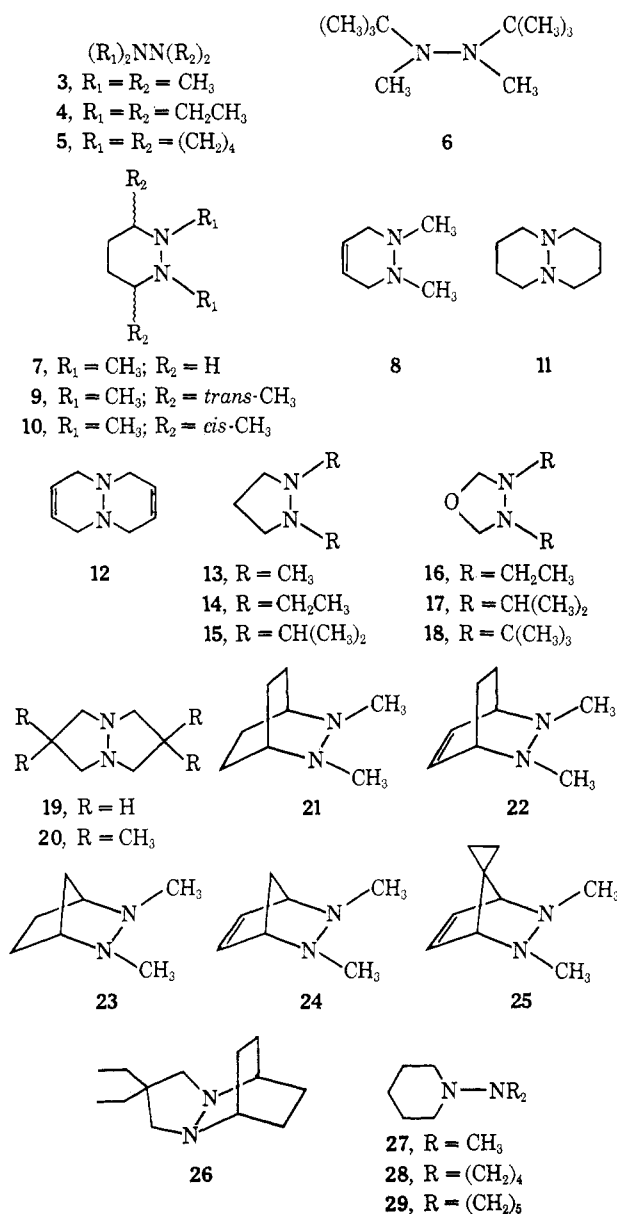
(13) S. F. Nelsen and P. J. Hintz, *J. Amer. Chem. Soc.*, **94**, 7108 (1972).

(14) (a) S. F. Nelsen and P. J. Hintz, *J. Amer. Chem. Soc.*, **92**, 6215 (1970); (b) *ibid.*, **93**, 7104 (1971).

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(16) B. T. Seo, *et al.*, *J. Amer. Chem. Soc.*, **88**, 3498 (1966).

(17) A. Hudson and H. H. Hussain, *J. Chem. Soc. B*, 251 (1968).



appearance of the lines caused by the nitrogen splitting is attributed to anisotropic broadening (see Discussion).

Our most instructive case of nonuniform line-width appearance as the temperature is lowered is that of 3,3,7,7-tetramethyl-1,5-diazabicyclo[3.3.0]octane cation ( $20^{+\cdot}$ ), for which spectra at various temperatures are shown in Figures 1 and 2. In this case there is unusually good resolution of the lines at room temperature, allowing one to follow the line broadening easily by examining the peak-to-peak amplitude changes. To aid in visualization of these changes, a plot of observed amplitude *vs.* temperature for the  $\bar{M}_N = \pm 2$ ,  $\bar{M}_H = 0(\pm 2, 0)$  and  $\pm 1, 0$  lines (undergoing anisotropic broadening), as well as the  $0, \pm 1$  lines is displayed in Figure 3. Broadening of the  $\pm 2, 0$  lines is clearly detectable at as high temperatures as  $-44^\circ$ , but as the temperature is lowered, even the  $0, \pm 1$  lines become quite broadened. We interpret this as being a result of an alternating line-width effect (see Discussion). At  $-91$  and  $-116^\circ$ , all of the lines but the  $0, 0, 0, \pm 2$ , and  $0, \pm 4$  (which are very weak) lines are extremely broadened. At still lower temperatures, many lines begin to grow up out of the noise (see the  $-121$  and  $-130^\circ$

**Table I.** Room Temperature ESR Splittings<sup>a</sup> for Tetraalkylhydrazine Radical Cations

Hydra- zine	Solvent <sup>b</sup>	$a(2N)$	$a_\beta(CH_3)$	$a_\beta(CH_2)$	Other splittings
3	MeCN	13.4	12.7 (12)		
4	PrCN <sup>d</sup>	13.0		7.1 (8)	
5	MeCN	12.9		18.5 (8)	$\sim 0.3$ (8 $H_v$ ) <sup>c</sup>
5	PrCN	12.8		18.4 (8)	$\sim 0.3$ (8 $H_v$ ) <sup>c</sup>
6	$CH_2Cl_2$	$\sim 11.9$	$\sim 11.9$ (6)		
7	MeCN	13.1	12.5 (6)	14.2 (4)	
8	MeCN	13.5	12.6 (6)	13.5 (4)	
9	MeCN	$\sim 12.4$	$\sim 12.4$ (6)		$\sim 6.2$ (2)
10	MeCN	$\sim 13.1$	$\sim 12.4$ (6)		$\sim 13.1$ (2)
11	MeCN	13.9		4.0 (8)	
12	MeCN	14.0		14.0 (8)	
13	MeCN	15.0	12.8 (6)	14.0 (4)	0.7 (2 $H_v$ )
14	MeCN	$\sim 14.2$		$\sim 0.142$	8.4 (4) $NCH_2CH_3$
15	MeCN	$\sim 14.2$		$\sim 14.2$ (4)	4.6 (2)
16	MeCN	13.7	13.0 (6)	13.0 (4)	
17	MeCN	14.4		14.2 (4)	9.9 (4) $NCH_2CH_3$
18	MeCN	14.0		14.0 (4)	4.8 (2)
19	MeCN	17.6		15.6 (8)	0.8 (4 $H_v$ )
20	PrCN	16.8		15.5 (8)	
21	MeCN	13.9	12.7		2.46 (4 $H_a$ )
22	$CH_2Cl_2$	14.7	12.46		3.70 (2 $H_v$ ), 2.46 (2 $H_a$ )
23	MeCN	16.0	13.1		4.8 (2 $H_{ax}$ ), 1.7 (1 $H_a$ ), 0.8 (1 $H_a$ )
24	MeCN	18.81	12.77 (6)		3.74 (2 $H_v$ ), 2.14 (1 $H_a$ ), 1.39 (1 $H_a$ )
25	PrCN	18.74	12.66 (6)		3.68 (2 $H_v$ ), 1.02 (2 $H$ )
26	MeCN	18.5		15.8 (4)	2.7 (4 $H_a$ )

<sup>a</sup> In gauss, number of equivalent H in parentheses. <sup>b</sup> Containing 0.05 M  $Bu_4NClO_4$  or  $NaClO_4$  as supporting electrolyte, electrolytic oxidation, unless otherwise noted. <sup>c</sup> Not resolved; needed to fit simulated spectrum to observed. <sup>d</sup>  $2^{+\cdot}$  as oxidant, no supporting electrolyte.

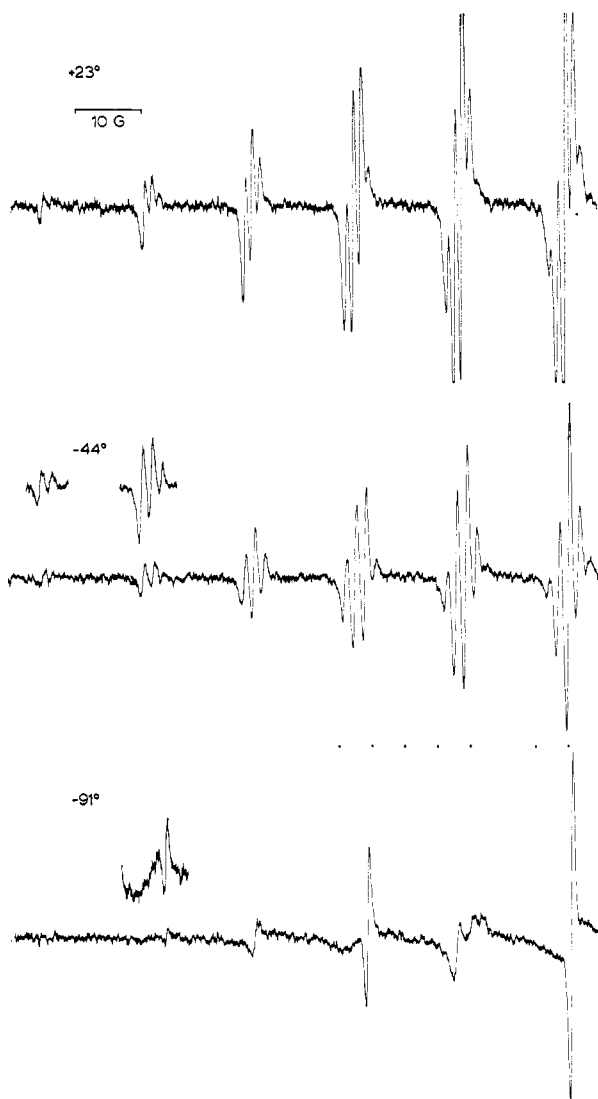
spectra of Figure 2), which we interpret as freezing out nitrogen flipping of  $20^{+\cdot}$  to give a spectrum showing two sets of four equivalent hydrogens. The variation of  $a(N)$  and  $a(H)$  with temperature is summarized in Table II.

Completely analogous behavior is shown by the unmethylated compound  $19^{+\cdot}$ , although in this case the

**Table II.** Temperature Variation of Splittings for Hydrazine Cation Radicals

Compound	Temp, $^\circ C$	$a(N)$	$a(H)$
$20^{+\cdot}$ <sup>a</sup>	23	17.12	15.61
	-8	17.44	15.83
	-26	17.53	15.86
	-44	17.69	15.87
	-64	17.84	15.88
	-82	17.96	15.87
	-91	17.94	15.89
	-116		15.89
	-130		23.5, 8.1
			7.02
$4^{+\cdot}$ <sup>b</sup>	+60	13.15	6.93
	+25	13.05	6.83
	0	13.03	6.70
	-40	12.86	6.54
	-80	12.64	6.08
	-100		5.92
	-120		

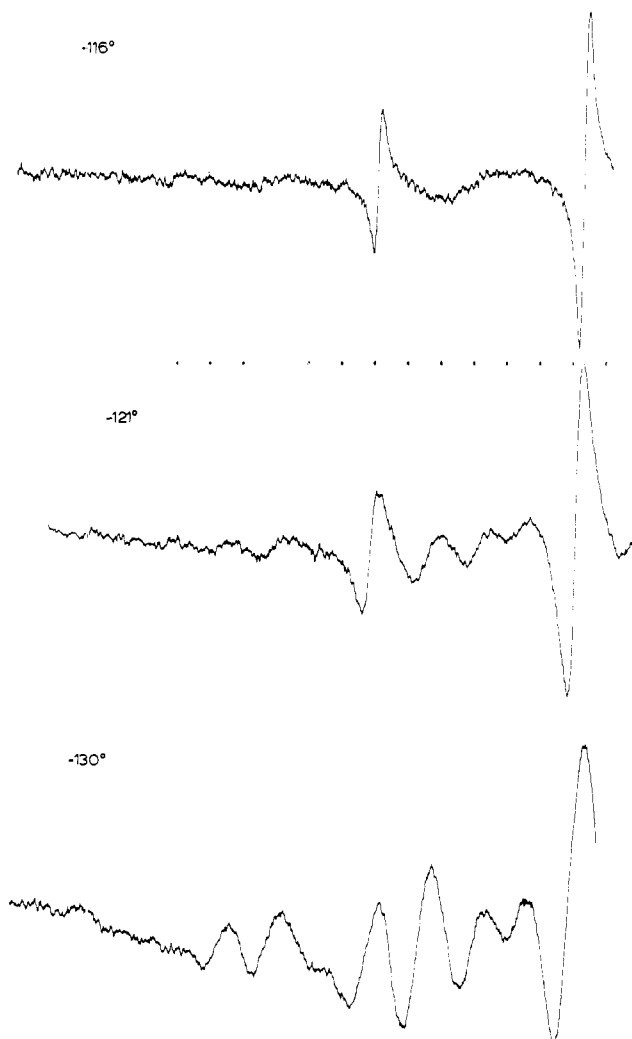
<sup>a</sup> In butyronitrile, oxidation with  $2^{+\cdot}$ . <sup>b</sup> In butyronitrile, electrolytic oxidation.



**Figure 1.** Temperature variation of the esr spectrum of  $20\cdot^+$ ; only half of the spectrum is shown.

four hydrogen  $\gamma$  splitting causes serious overlap of the lines. We observed  $a(2\text{ N}) = 17.05$ ,  $a(8\text{ H}) = 15.12$  and  $0.70$  at  $40^\circ$  in methylene chloride (electrolytic oxidation), and splittings of  $17.75$ ,  $15.15$ , and  $0.70$  at  $-100^\circ$ . The diazadecalin system  $11\cdot^+$  did not give nearly as clear a picture of what was going on, because the near equality of  $a(2\text{ N})$  and  $a(8\text{ H})$  causes serious overlap at all temperatures, and only 13 broad lines separated by about 14 G are observed after most of the temperature range. At  $-82^\circ$  ( $2\cdot^+$  oxidation in butyronitrile) intermediate lines could be discerned, and by  $-120^\circ$ , the spectrum consisted of a series of broad lines very similar to those of  $20\cdot^+$  at low temperature; for  $11\cdot^+$ , we observed splittings of  $22.4$  (4 H) and  $6.2$  (4 H).

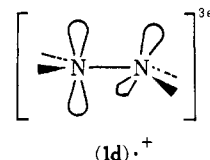
For the case in Table I showing the largest nitrogen splitting,  $24\cdot^+$ , the splitting increased from 18.8 G at room temperature to 19.6 at  $-80^\circ$  (in methylene chloride); at still lower temperatures the anisotropic line broadening began to become large. Tetraethylhydrazine radical cation ( $4\cdot^+$ ) was also studied at various temperatures, and the results of this study appear in Table II. We occasionally observed significantly better resolution at lower temperatures than at room temperature, and for  $21\cdot^+$  we resolved the syn splitting at



**Figure 2.** Temperature variation of the esr spectrum of  $20\cdot^+$ ; only half of the spectrum is shown.

$-80^\circ$  in methylene chloride, where the observed splittings were  $13.61$  (2 N),  $13.06$  (6 H),  $2.62$  (4  $H_a$ ), and  $0.59$  (4  $H_s$ ). A similar experiment did not give resolution of the syn splittings of  $26\cdot^+$ , however.

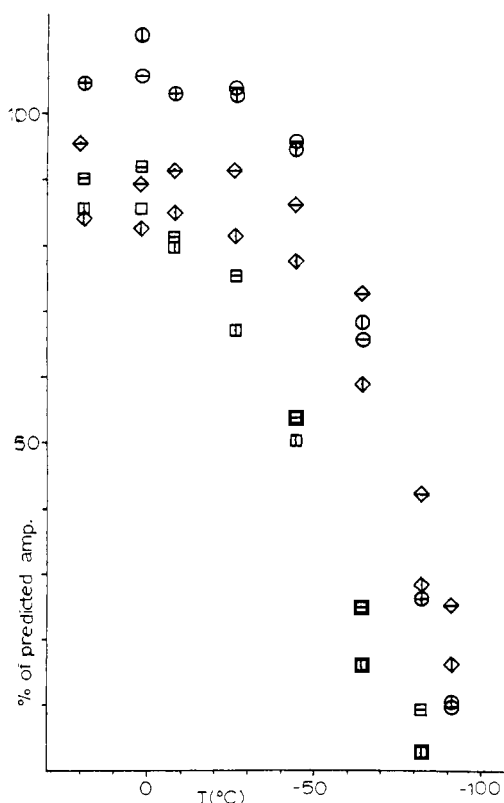
**INDO Calculations.** In spite of the fact that MO calculations have been published for  $N_2H_4\cdot^+$  previously,<sup>5b,c</sup> we performed a series of INDO calculations covering a wider range of possible geometries, including  $1c\cdot^+$  and the half-bent conformation  $1d\cdot^+$ , to



more fully explore the results predicted. Although it is tempting to ascribe the high symmetry apparent in the molecular formulation to the equilibrium geometry of  $1\cdot^+$ , it is not obviously necessary that the molecule has the nitrogens equivalent, although the observed esr spectra require rapid equilibration of the two nitrogens, if they are not instantaneously equivalent. Our results are presented graphically in the Discussion section.

## Discussion

**Room Temperature Esr Spectra.** The observed nitro-



**Figure 3.** Visualization of line broadening for 3,3,7,7-tetramethyl-1,5-diazobicyclo[3.3.0]octane radical cation ( $20\cdot^+$ ) as a function of temperature. The peak-to-peak amplitude of the first derivative esr spectrum, calculated as the percentage of the value predicted if the lines were uniform in line width, is plotted against temperature: ( $\oplus$ )  $M_N = 0$ ,  $M_H = 1$ ; ( $\ominus$ )  $M_N = 0$ ,  $M_H = 1$ ; ( $\diamond$ )  $M_N = 1$ ,  $M_H = 0$ ; ( $\square$ )  $M_N = 2$ ,  $M_H = 0$ .

gen splittings cover the range from 11.9 to 18.8 G. Because all of these compounds have the same "three-electron  $\pi$  system" bearing the odd electron, the spin density at each nitrogen must be 0.5 minus "leakage" into the hydrocarbon substituents. Such leakage effects cannot account for the observed 58% spread in  $a(N)$  without substantial changes in the effective  $Q(N)$  (to be used in the McConnell equation  $a(N) = Q_N \cdot (\rho_N)$ ), which could only reasonably arise if differing amounts of s character were present in the spin-bearing orbitals. Because  $a(N)$  for our compounds is distinctly larger than that for the planar (or nearly so)  $N_2H_4\cdot^+$  (11.5 G), in spite of the fact that more leakage to substituents must be occurring (we note the substantial  $a(H_\beta)$  splittings of Table I), it is apparent that conformation  $1a\cdot^+$  cannot explain the observed nitrogen splittings of tetraalkylhydrazine radical cations. Deviation from planarity ( $\beta \neq 0$ ) would increase the s character of the spin-bearing nitrogen orbitals, and lead to larger  $a(N)$  values. We therefore equate increased  $a(N)$  with increased s hybridization and increased  $\beta$ . Examining Table I, there is a clear trend that containing both nitrogens in a five-membered ring raises  $a(N)$  more than does containing them in a six-membered ring. The large increase in  $a(N)$  for the series  $21\cdot^+$ – $24\cdot^+$  is not reasonably explainable simply on the basis of increased "strain" (as we over enthusiastically suggested earlier<sup>14a</sup>), and we will defer discussion of this point to a future publication.

The question of whether deviation from planarity of tetraalkylhydrazines is in the sense of the staggered ( $1b\cdot^+$ ) or eclipsed ( $1c\cdot^+$ ) conformation is not an easy one to answer on a purely experimental basis, but as we have previously noted,<sup>14b</sup> the large difference in the methine hydrogen splittings for  $9\cdot^+$  and  $10\cdot^+$  cannot be rationalized with either the staggered or planar conformations, and requires deviation from planarity toward the eclipsed conformation  $1c\cdot^+$ . Since the nitrogen splittings for the six-ring compounds are among the lowest in our series, the  $\beta$  splittings indicate that even for these compounds, the radical cations are not planar at nitrogen. As we have also discussed previously,<sup>14a</sup> the long-range splittings observed for  $23\cdot^+$  and  $24\cdot^+$  require that there be a node between the two nitrogens in the MO containing the odd electron. As Hoffmann<sup>18</sup> has pointed out, the highest occupied orbital for a hydrazine in a staggered conformation ( $1b\cdot^+$ ) and that for an eclipsed ( $1c\cdot^+$ ) both have such a node (although the former is an  $n_1 + n_2$  orbital, and the latter  $n_1 - n_2$ ), so this information does not help in assigning the type of deviation from planarity. The methyl splittings of Table I are much more constant than the nitrogen splittings, as expected since the total nitrogen spin density must be fairly constant.

**Low-Temperature ESR Spectra.** Nonuniform line shapes can occur in esr spectra for a variety of reasons; such phenomena have been reviewed most generally by Hudson and Luckhurst.<sup>19</sup> Although the esr spectra for  $3\cdot^+$ – $26\cdot^+$  show uniform line-width behavior at room temperature, the spectra change markedly at low temperature, and we attribute these changes to two different effects, anisotropic line broadening (usually observed), and alternating line-width effects (observed in a few cases).

The theory of anisotropic line broadening has been discussed by Fraenkel<sup>20</sup> and in the text of Gerson.<sup>21</sup> They point out that the anisotropic contribution to the line width ( $\Delta H$ ) can be resolved into terms depending on the square of the g tensor, the square of the anisotropic hyperfine tensor, and the product of the two, resulting in a semiempirical equation for line width for a radical containing a single  $I = 1$  nucleus of the form shown in eq 1. Since there is a  $1/r^3$  relationship for the

$$(\Delta H)_{\text{aniso}} = A\tilde{M}_i^2 + B\tilde{M}_i + C \quad (1)$$

size of the electron–nuclear interaction, significant anisotropies are only observed for nuclei bearing significant spin densities, typically  $^{13}\text{C}$  and  $^{14}\text{N}$ . When two nitrogen nuclei are present (our case), the line-width formula is more properly that given in eq 2, where  $J_N$  de-

$$^{5/3}\tilde{M}_N^2 + B\tilde{M}_N + C' \quad (2)$$

fines the nuclear spin angular momentum. The average contribution of the first term of eq 2 to the line width is  $^{38/3}A'$  for  $\tilde{M}_N = \pm 2$ ,  $^{17/3}A'$  for  $\tilde{M}_N = \pm 1$ , and  $^{8/3}A'$  for  $\tilde{M}_N = 0$ .<sup>20</sup> This  $A'$  term leads to broadening of both the high- and low-field lines equally, while the  $B$  term, proportional to  $\tilde{M}_N$ , broadens the spectrum nonuniformly (the low-field side more broadened for

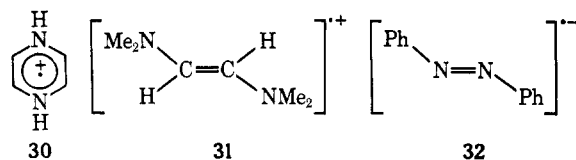
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positive  $\rho_N^{20}$ ). Reported anisotropic splitting parameters for cases similar to ours include  $A' = 0.0144$ ,  $B = 0.0269$  for pyridazine cation **30**,<sup>22</sup> and  $A' = 0.033$ ,  $B = 0.030$ ,  $C' = 0.072$  for 1,2-bis(dimethylamine)-ethylene cation, **31**.<sup>23</sup> For azobenzene anion **32**, which



is similar to our case in that the  $I = 1$  nuclei are directly bonded, the  $\tilde{M}_N \neq 0$  lines were broadened so much at low temperature that they disappeared.<sup>24</sup> This was our experience with **1**<sup>+</sup>. This phenomenon allows positive identification of the nitrogen splitting, and has been used in simplification of a 2-tetrazene spectrum.<sup>25</sup> Because of line overlaps, the tetraalkylhydrazine radical cation spectra usually do not allow calculation of the anisotropic splitting parameters. For **20**<sup>+</sup> at  $-64^\circ$ , we obtained  $A' = 0.026$ ,  $B = 0.011$ ,  $C' = 0.43$  (giving line widths of 0.78, 0.59, 0.50, 0.57, and 0.74 for the  $\tilde{M}_N = 2, 1, 0, 1$ , and  $2$  lines, a reasonable fit to the observed values of 0.78, 0.61, 0.50, 0.59, 0.73) by measuring the peak-to-peak line width in expansions of portions of the spectra. It should be pointed out that second-order effects are important in making  $C'$  unusually large for these spectra.

**Alternating Line-Width Effect.** When hydrogen splittings are not actually equivalent, but merely averaged by rapid interconversion of two forms which interchange the splittings, the  $\tilde{M}_H$  odd components are broadened at intermediate interchange rates, often being broadened so much that they are not observed. This broadening of every other line of a multiplet is called the alternating line-width effect, and has been recently reviewed by Sullivan and Bolton.<sup>26</sup> If tetraalkylhydrazines are actually nonplanar as we have argued, compounds containing endocyclic hydrazine units should have  $\beta$  hydrogens which are in principle nonequivalent, and if inversion of the nitrogens becomes slow enough, should show an alternating line-width effect. As stated in the results, we saw this for **20**<sup>+</sup>. In Figure 4 we show the stick spectrum for **20**<sup>+</sup> at rapid nitrogen flipping rates in a, the changes in intensity expected<sup>26</sup> for the maximum broadening point in b, and superimpose the anisotropic effect in c. Comparison with Figure 1 shows that the expected behavior is observed. At very low temperatures the quintet spectrum expected for two sets of four hydrogens is observed, and the observed splittings of 23.5 and 8.1 G average to 15.8 G, close to the value required by the higher temperature, rapidly averaging spectra (see Table II). The temperature of maximum broadening probably falls in the range  $-110 \pm 5^\circ$ , since no  $\tilde{M}_N$  odd lines could be discerned between  $-91$  and  $-120^\circ$ .

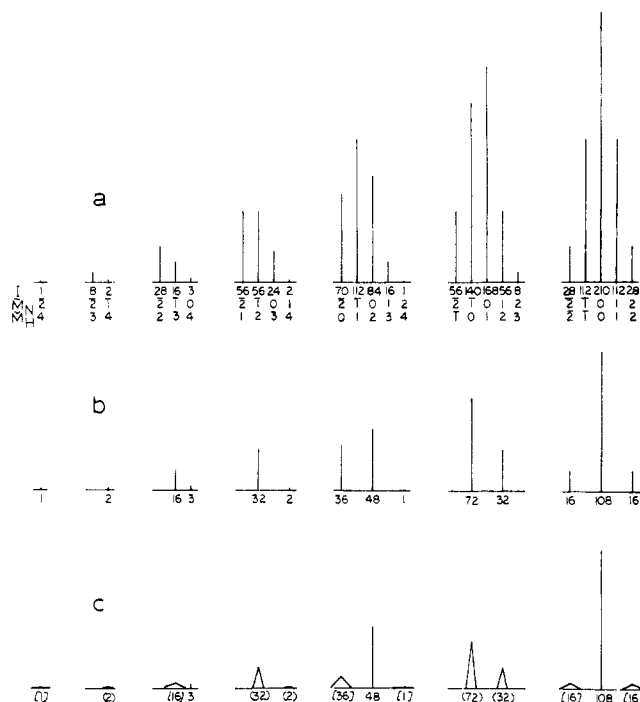
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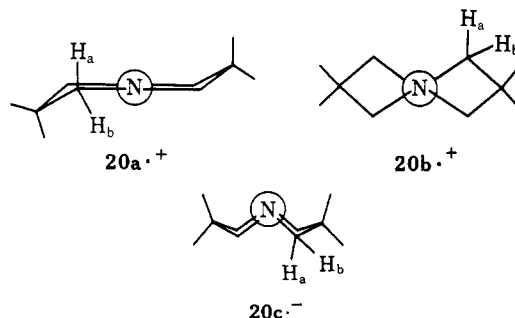
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**Figure 4.** Stick representation of the temperature variation of the ESR spectrum of 3,3,7,7-tetramethyl-1,5-diazabicyclo[3.3.0]octane radical cation (**20**<sup>+</sup>). (a) Room temperature;  $a(2\text{ N}) > (8\text{ H})$ . The rows of numbers show the relative intensity, the value of  $\tilde{M}_N$ , and the value of  $\tilde{M}_H$ . (b) Alternating line-width effect when  $a(4\text{ H}) \neq a(4\text{ H}')$ ,  $\text{H} \rightleftharpoons \text{H}'$ , if all broadened lines ( $\tilde{M}_H$  odd) are so broadened they cannot be observed. The  $\tilde{M}_H$  odd components of the  $\tilde{M}_N$  even lines are also broadened, changing the intensity pattern for the  $\tilde{M}_H$  even lines from those shown in (a). (c) Anisotropic broadening effect added, arbitrarily showing  $\tilde{M}_N = \pm 2$  lines twice as broad as the  $\tilde{M}_N = \pm 1$  lines.

Using the equation<sup>27</sup>  $k(T_c) = 6.22 \times 10^6(\Delta a(\text{H}))$ , we obtain  $k(-110 \pm 5^\circ) = 9.58 \times 10^7$ , corresponding to  $\Delta G^\ddagger = 3.4 \pm 0.1$  for the process interconverting the two sets of hydrogens. Of the three most reasonable conformations for **20**<sup>+</sup>, the planar one, **20a**, is a possibility only if  $\text{C}_3\text{N}_2$  ring flipping is what is being frozen out. We do not believe this to be reasonable, since freezing out ring flipping in cyclopentene-like rings is unprecedented,<sup>27</sup> and also because the observed hydrogen splittings in the frozen form would require an unreasonable degree of puckering in these rings. Instead, we suggest that double nitrogen inversion in either **20b** or **20c** is what is being frozen out. Although



we prefer the eclipsed conformation **20c** by analogy with our other evidence, the only piece of information which we believe points to this conformation in this

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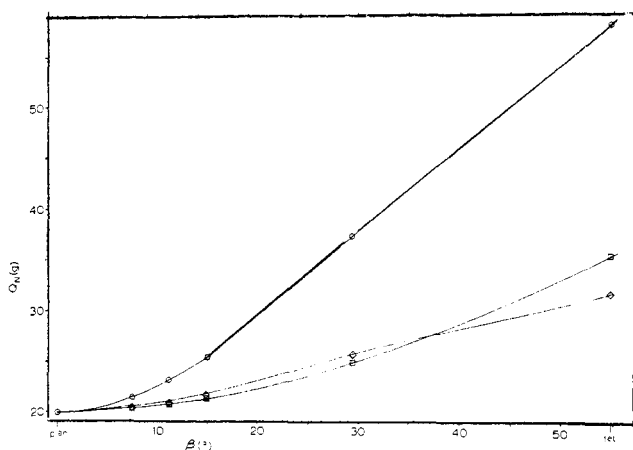
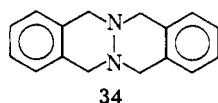
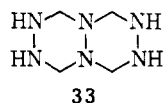


Figure 5.  $Q_N$  values given by INDO calculations for  $N_2H_4^{+\cdot}$ . (O) eclipsed conformation (**1c** $^{+\cdot}$ ); (□) staggered (**1b** $^{+\cdot}$ ); (◇) half-bent (**1d** $^{+\cdot}$ ).

experiment is the increase in  $a(N)$  in comparing **19** $^{+\cdot}$  to **20** $^{+\cdot}$ . Placing the methyls on **19c** $^{+\cdot}$  in going to **20c** $^{+\cdot}$  could force the  $C_3$  and  $C_7$  carbons apart, flattening the system and leading to a lower nitrogen splitting. It is not obvious to us that methyl for hydrogen substitution in the staggered conformation should make any difference in  $a(N)$ . Interpretation of  $\beta$  splittings for C-H bonds adjacent to sp-hybridized spin-bearing orbitals do not lead to as simple analyses as for those next to pure p hybridized orbitals, and although progress is being made in interpretation of such splittings,<sup>28</sup> we do not believe it is wise at this time to attempt to calculate the degree of bending in our cases from the  $\beta$  splittings observed.

For the 9,10-diazadecalin cation radical (**11** $^{+\cdot}$ ), we do not have as accurate a measure of  $T_c$  because of the problem of overlapping lines at the high temperature end, but we could detect  $\tilde{M}_H$  odd lines of the frozen form at  $-82^\circ$ , requiring that  $T_c$  be above this temperature. Estimating  $-60^\circ$  for  $T_c$ ,  $\Delta G^\ddagger = 4.5$  kcal/mol ( $-60^\circ$ );  $\Delta G^\ddagger$  is certainly greater for **11** $^{+\cdot}$  than for **20** $^{+\cdot}$ .  $\Delta G^\ddagger$  for double inversion of the unoxidized form of **20** is 11.95 ( $-55^\circ$ ), and 12.1 kcal/mol ( $-29^\circ$ ),<sup>29</sup> and although that for **11** is unknown,  $\Delta G^\ddagger$  for double inversion for the closest related compounds available are 16.6 ( $+58^\circ$ )<sup>29</sup> for **33** and 12.4<sup>30</sup> for **34**. Most, but



not all, of the barrier to double inversion at nitrogen disappears upon removal of an electron.

**INDO Calculations.** We only explored a few rather symmetrical types of deformation from planarity, and there are obviously many unsymmetrical deformations we ignored (for instance,  $\beta_1 \neq \beta_2$  for both B and C type conformations). Of the conformations we did calculate, the planar was stablest for the  $N_1-N_2$  distance of 1.3 Å, and the staggered conformation for moderate  $\beta$  value at a 1.4 Å distance, in agreement with the work

of Fantechi and Helcké.<sup>30</sup> There is abundant evidence that INDO will not give the proper conformation as having the lowest total energy, however. In two closely related examples, CNDO failed badly in predicting the correct angle of rotation ( $\theta$ ) for hydrazine itself ( $\theta = 66^\circ$ ,<sup>31</sup> compared to the  $90-95^\circ$  given by experiment<sup>32</sup>), and three types of MO calculations gave the incorrect prediction<sup>3b</sup> of which nitrogen has the largest splitting for dialkylhydrazyl radicals,<sup>3d</sup> which we interpret as being caused by minimization at the wrong geometry. We believe a more reasonable use of INDO calculations is to examine the trends in  $a(N)$  for various conformations. For hydrazine itself, the INDO calculations for both  $a(N)$  and  $a(H)$  fit the observed solution spectrum best for **1c** $^{+\cdot}$  with  $\beta \sim 11^\circ$  (although the minimum energy comes at  $\beta \sim 11^\circ$  for **1b** $^{+\cdot}$  at 1.4 Å,  $\beta = 0^\circ$  for 1.3 Å). The INDO results can only fit experiments with a modest deviation from planarity, since the effective  $Q(N)$  value for  $N_2H_4^{+\cdot}$  in solution is  $Q = 11.5/0.5 = 23$ . For a plot of INDO  $Q(N)$  vs.  $\beta$ , see Figure 5. To use the  $N_2H_4^{+\cdot}$  calculations in discussion of our tetraalkylated compounds, it is necessary to allow for spin which "leaks" to the  $\beta$  hydrogens. Although the best approach might well be to calculate several conformations for each of our compounds, the cost would be prohibitive, especially when compared to the insight likely to be gained. Fessenden and Schuler,<sup>33</sup> and later Fischer<sup>34</sup> have pointed out that  $\rho_c^\pi$  for methylated methyl radicals is consistently described by using  $\rho_c^\pi = (1 - \Delta)^n$ , where  $\Delta = 0.081$  for a methyl group and  $n$  is the number of methyl groups attached to the spin-bearing carbon. Although one could argue that  $\Delta$  ought to be larger for a methyl group attached to the half-positive nitrogen of a hydrazine radical cation than to the carbon of a methyl radical, the use of a larger  $\Delta$  would lead to lower  $\rho_N$  values, and higher effective  $Q(N)$  values, so we will use the same  $\Delta$  as for carbon systems in this discussion. We therefore suggest that  $\rho_N^\pi = 1/2(1 - 0.081)^2 = 0.422$  for tetramethylhydrazine, giving an effective  $Q(N)$  value of 31.7 for **3** $^{+\cdot}$ . The  $Q(N)$  value for **20** $^{+\cdot}$  is therefore  $>41.4$  (one could argue that  $\Delta$  for the alkyl groups of **20** $^{+\cdot}$  should be larger than whatever was used for  $CH_3$ ; we ignore this small difference). The *smallest*  $\beta$  value giving such a large  $Q(N)$  is about  $37^\circ$  for the eclipsed conformation, and staggered or half-bent conformations do not give such high  $Q(N)$  values until quite impossibly high  $\beta$  values are reached. If  $N_2H_4^{+\cdot}$  is actually planar in solution, and not somewhat bent as the INDO calculations indicate, the  $\beta$  values derived from Figure 5 would be too large by some amount, which we would guess to be about  $11^\circ$ .

**Temperature Dependence of  $a(N)$ .** Three compounds with large  $a(N)$  values, **19** $^{+\cdot}$ , **20** $^{+\cdot}$ , and **24** $^{+\cdot}$ , all showed increasing values of  $a(N)$  as the temperature was lowered, as expected for a nonplanar conformation.<sup>35</sup> In contrast,  $N_2Et_4^{+\cdot}$ , **4** $^{+\cdot}$ , showed the opposite trend, decreasing  $a(N)$  as the temperature is lowered. Although this might be cited as evidence for a planar

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radical, one still would not be able to explain the size of the nitrogen splitting at any temperature on the basis of the planar conformation. If a planar radical has positive correlation of  $a(N)$  and temperature, a slightly bent one ought to have a (smaller) positive correlation as well, since one certainly would not expect a discontinuity in the correlation for the planar conformation; there is no doubt that  $20^+$  is bent more than  $4^+$ .

## Conclusion

We have presented evidence that all the tetraalkylhydrazine radical cations we have investigated are bent somewhat from strict planarity of both nitrogens and the four attached carbons. Evidence from  $\beta$  splittings of **9** and **10**, as well as INDO derived evidence for the compounds with larger nitrogen splittings, suggests that the deviation from planarity is in the eclipsed sense ( $1c^+$ ). Using INDO calculations, observed  $Q(N)$  values indicate that  $\beta$  values from about  $14$  to  $37^\circ$  are attained, depending upon structure; these correlations assume that  $N_2H_4^+$  in solution is in the eclipsed conformation, with  $\beta$  of about  $11^\circ$ . If  $N_2H_4^+$  is actually planar in solution, as several workers agree it is in the solid, the  $\beta$  values for tetraalkylhydrazine radical cations estimated from the same INDO calculations are certainly too high. Future work will be required to be able to estimate the amount of deformation from planarity of hydrazine radical cations with more confidence.

## Experimental Section

We prepared **2** by the literature method.<sup>15</sup> Hydrazines **3**, **5**, **6**–**19**, **21**–**24**, and **26**, have been described previously.<sup>13</sup>

**Tetraethylhydrazine (4).** Tetraethyl-2-tetrazene<sup>36</sup> was heated in a round-bottomed flask, and a stream of nitrogen was directed over the surface and through a 20-cm glass helices packed column heated at  $340^\circ$ , at a pressure of about 3 mm. The effluent from the column was trapped at liquid nitrogen temperature. Tetraethylhydrazine was isolated by vpc, and had a slightly longer retention time than diethylamine, which was the major product.

**1,2-Di-tert-butyl-1,2-dimethylhydrazine (6).** Attempts to isolate **6** from reaction of 1,2-di-tert-butylhydrazine<sup>37</sup> with formaldehyde and sodium cyanoborohydride<sup>38</sup> met with total failure to even detect **6**. We successfully prepared **6** by deoxygenating 1,2-di-tert-butylloxadiazolidine (**18**) using sodium cyanoborohydride. A mixture of 930 mg (5 mmol) of the oxadiazolidine, 2 ml of formalin (25 mmol), 800 mg of sodium cyanoborohydride (12.7 mmol), and 15 ml of acetonitrile was treated with 25 drops of acetic acid over a 10-min period, and stirred for 12 hr. The mixture was extracted several times with pentane, giving 400 mg of a mixture of starting oxadiazolidine and **6** after distillation (bp  $70$ – $80^\circ$  (120 mm)), which was separated by vpc (**6** had the shorter retention time): nmr  $\delta$  1.04 (s), 2.33 (s) in 3:1 ratio; mass spectrum  $m/e$  172, 115, 59; exact mass, 172.174 (Calcd for  $C_{10}H_{24}N_2$ , 172.194).

**3,3,7,7-Tetramethyl-1,5-diazabicyclo[3.3.0]octane (20).** A mixture of 14 g (62.5 mmol) of 2,2-dimethyl-1,3-dibromopropane,<sup>38</sup> 1.02 g (3.13 mmol) of hydrazine hydrate, 9 g of potassium carbonate, and 15 ml of DMSO was heated at  $140^\circ$  under nitrogen. The nmr spectrum of the mixture showed a gradual disappearance of dibromide, and formation of a product with absorptions at  $\delta$  2.73 and 1.2. After 5 days, the mixture was filtered, made acidic with 10% HCl, extracted with ether ( $4 \times 25$  ml), basified with sodium

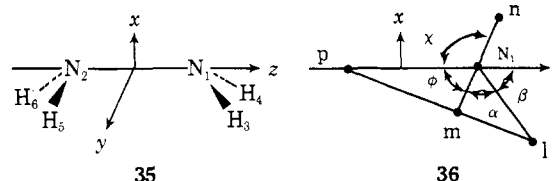
hydroxide pellets, and extracted with pentane. Concentration gave 1.8 g of crude **4**, which was purified by vpc. The product gave the reported nmr spectrum.<sup>29</sup>

**2,3-Dimethyl-7,7-spirocyclopropyl-2,3-diazanorbornene (25).** A solution of 5.05 g (19 mmol) of diethyl 7,7-spirocyclopropyl-2,3-diazanorbornene-2,3-dicarboxylate<sup>39</sup> in 70 ml of ether was added to 4.0 g (105 mmol)  $LiAlH_4$  in 150 ml of dry ether, and the mixture was stirred with nitrogen for 13 hr. The excess hydride was quenched by successive addition of 4 ml of  $H_2O$ , 4 ml of 5% aqueous NaOH, and 12 ml of  $H_2O$ . The mixture was filtered, the solid was washed with ether, and the ether solutions were dried with  $MgSO_4$  and concentrated. Distillation gave 1.36 g (9.07 mmol, 48%) of **25**: bp (22 min)  $65$ – $68^\circ$ ; nmr ( $CDCl_3$ )  $\delta$  0.68 (AA'BB', 4 H), 2.56 (s, 6 H), 3.23 (m, 2 H), 6.48 (m, 2 H); ir ( $CHCl_3$ ) no NH or  $C=O$ .

**Esr spectra** were recorded on a Varian E.15 system, calibrated with Fremy's salt. The Varian room temperature electrolysis cell was employed at room temperature, and the aqueous solution cell was used at low temperature, after being fitted with a gold foil electrode. A 4-mm o.d. glass tube could be used with methylene chloride solutions which had been oxidized with  $2^+$ , but a 3-mm tube was necessary for butyronitrile solutions near room temperature. Temperatures were measured with on Leeds and Northrop 8693-2 potentiometer (copper-constantan thermocouple). The spectra were simulated with the coupling constants reported in Table I to verify that the splittings reported are close to being correct.

## INDO Calculations

For our numbering system, see **35**. We kept the  $H_3N_1H_4$  and  $N_2N_1H_3$  angles equal throughout, requiring that a line passing through point m (the midpoint of the equilateral triangle formed by  $H_3$ ,  $H_4$ , and point p, which is on the  $N_1N_2$  line one NH distance from  $N_1$ ) and  $N_1$  is colinear with the  $N_1$ -lone pair orbital axis. Defining the  $N_1$ -lone pair orbital axis as the  $n, N_1$  line, let  $\angle(n, N_1N_2)$  be  $\chi$  ( $\chi = 90^\circ$  in the planar form,  $109.46666^\circ$  in the tetrahedral form). Noting that the  $H_3$ – $H_4$  distance is  $2Y$ , where  $Y$  is the  $y$  coordinate of  $H_3$ , see the  $xz$  planar projection in **36**, showing angles  $\phi$  ( $\chi -$



$180^\circ$ ),  $\alpha$ , and  $\beta$  ( $180^\circ - \phi + \alpha$ );  $l$  is the midpoint of the  $H_3$ ,  $H_4$  line segment. Since we used the NH distance as  $1.0 \text{ \AA}$  throughout,  $N_1 - m = \cos^2 \phi$  and  $N_1 - l = (\cos^2 \phi + (Y^2/3)^{1/2}) = r$ . The  $x$  coordinate of  $H_3$  is then  $(- )r \sin \beta$ , and the  $z$  coordinate  $r \cos \beta$  plus half the  $N_1$ – $N_2$  distance. The coordinates thus generated were used with Pople's INDO program.<sup>40</sup>

**Acknowledgments.** We thank the National Science Foundation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Wisconsin Alumni Research Foundation for financial support of this research. We also thank John Buschek for conversion of the INDO program (ref 40) to the MACC Univac 1108 computer.

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