78941-77-2; **2h**, 98736-36-8; **2k**, 98736-37-9; **2l**, 98736-43-7; **2m**, 98736-44-8; **3a**, 84293-23-2; **3b**, 84293-21-0; **3c**, 84293-22-1; **4a**, 98736-38-0; **4b**, 98736-39-1; **4c**, 98736-40-4; **5a**, 98736-41-5; **5b**, 98736-42-6; **5c**, 98759-92-3; **6**, 15872-28-3; **7**, 17397-31-8; $MeNH_2$, 74-89-5; $PhCH_2NH_2$, 100-46-9; t-$BuNH_2$, 75-64-9; Me_2NH, 124-40-3; MeNHPh, 100-61-8; Ph_2NH, 122-39-4; AcNH-p-$C_6H_4NH_2$, 122-80-5; p-$NO_2C_6H_4NH_2$, 100-01-6; AcNH-o-$C_6H_4NH_2$, 34801-09-7; o-$NH_2C_6H_4NH_2$, 95-54-5; $NH_2(CH_2)_2NH_2$, 107-15-3; p-$NH_2C_6H_4NH_2$, 106-50-3; pyrrolidine, 123-75-1; indoline, 496-15-1; glycine, 56-40-6.

Conformations of Hexahydropyridazine Cation Radicals

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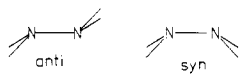
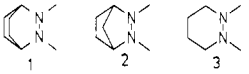
The variable temperature ESR spectra of the cations of 1,2-dimethylhexahydropyridazine (**3**) *cis*- and *trans*-1,2,3,6-tetramethylhexahydropyridazine (**4** and **5**), *trans*-3,4-dimethyl-3,4-diazabicyclo[4.4.0]decane (**6**), and 1,2,3,3,6,6-hexamethylhexahydropyridazine (**7**) are reported and demonstrate that these species exist in half-chair conformations. The 3,6-diaxial methyl form of 5^+ is about 1 kcal/mol stabler than its 3,6-diequatorial ring reversal form. The UV spectra of solutions containing these cations and those of three other hexahydropyridazine cation radicals are described.

Tetraalkylhydrazine cation radicals $R_4N_2^+$ have approximately sp^2-hybridized nitrogen atoms and hence a p-rich atomic orbital centered at each nitrogen. There is a strong electronic preference for coplanarity of these p-rich orbitals, producing π and π^* MOs. The π MO is doubly occupied and the π^* singly occupied, a situation which has been described as a "three-electron π bond".[1] Bending at N in $R_4N_2^+$ is unusually easy, and constricting the RNR and RNN bond angles by linking the R groups in rings has been shown to induce bending of the nitrogens at equilibrium, increasing the fraction of s hybridization in the π system. If the nitrogen lone pairs remain coplanar, bending at N can either cause the alkyl groups to be staggered, shown as anti, or to be eclipsed, as in syn. The



symmetries of the bonding π and antibonding π^* orbitals change between syn- and anti-bent structures, which affects their spectroscopic properties because π and π^* mix with the σ and σ^* orbitals when the nitrogens are bent. A given amount of bend syn causes larger mixing than the same amount of bend anti, producing a larger increase in both the nitrogen ESR splitting constant a(N) and the wavelength for the π,π^* transition in the $R_4N_2^+$ optical spectrum, λ_m.[2] Both steric and electronic effects favor anti bend in acyclic and *N,N*-cycloalkyl examples. In contrast, the *N,N'*-bicyclic cations 1^+ and 2^+ show relatively large a(N) values (13.9 and 16.0 G, respectively), which we have



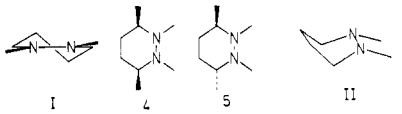
argued indicates they are syn bent at nitrogen.[2] Because their bicyclic structures hold the ring CNNC dihedral angle near 0°, anti bending forces twisting of the 3e-π bond, while syn bending allows it to remain untwisted, rationalizing syn bending of 1^+ and 2^+.

Table I. ESR Splitting Constants for Radical Cations of Hexahydropyridazines[a]

compd	temp, °C	a(2 N), a(2 CH_3)	other splittings	LW for simulation, G
3	−100	ca. 12.8	27.6 (2 H)	1.2
4	+60	13.65 (2 H)	ca. 13.65 (2 H)	
		12.62 (6 H)		0.3
	−100	ca. 12.9	27.5 (1 H)	1.5
5	+85	ca. 13.0	8.2 (2 H)	1.2
	−105	ca. 13.2_5	3.6 (2 H)	1.5
6	−105	ca. 12.7	23.2 (2 H), 4.2 (2 H)	1.2
7	+60	ca. 13.0		1.0
	−60	ca. 12.8		1.7

[a] Generated by $(4\text{-}BrC_6H_4)_3N^+SbCl_6^-$ oxidation in butyronitrile and reported in gauss = 0.1 mT. The a values reported are believed to be accurate to about 0.1 G.

The six-membered ring monocyclic compound, dimethylhexahydropyridazine **3**, might be expected to give a half-chair radical cation I if the nitrogens remained flat in the cation (ring CNNC angle about 0° again). We



published room temperature ESR spectra 4^+ and 5^+ several years ago[3] with ring tertiary hydrogen splittings which did not agree with our predictions for I conformations of these species. We expected 5^+ to have pseudoequatorial C_3,C_6 methyl groups and hence pseudoaxial tertiary hydrogens. Since 4^+ would be rapidly equilibrating between equal energy I structures and pseudoaxial splittings are much larger than pseudoequatorial splittings, we expected a(2 H) for 5^+ to be much larger than a(2 H) for 4^+ if they were in half-chair conformations I. We observed the opposite, a(2 H) of 6.2 G for 5^+ and a(2 H) of 13 G for 4^+, and suggested that these cations were in boat conformations II. This paper reports low-temperature ESR and UV spectra of these and related cations which show that the assumption we made in 1971 that 5^+ would be stablest with

(1) Nelsen, S. F. *Acc. Chem. Res.* **1981**, *14*, 131.
(2) Nelsen, S. F.; Blackstock, S. C.; Yumibe, N. P.; Frigo, T. B.; Carpenter, J. E.; Weinhold, F. *J. Am. Chem. Soc.* **1985**, *107*, 143.
(3) Nelsen, S. F.; Hintz, P. J. *J. Am. Chem. Soc.* **1971**, *93*, 7104.

0022-3263/85/1950-4749$01.50/0

Table II. UV Spectra of Oxidized Hexahydropyridazines in Acetonitrile Solution

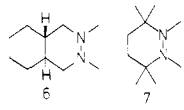
	electrochemical flow cell oxidation		
compd	$R_4N_2^+$ band λ_m, nm (ϵ min)[a]	long λ band λ_m, nm (ϵ min)[a]	NO^+PF_6 oxidn λ_m, nm (ϵ min)[a]
3	231 (1200)	300 (700)	249 (1900)
4	unobsd[b]	283 (1900)	248 (2200)
5	249 (1300)	292 (1400)	
6	254 (1700)	none	263 (3000)
7	247 (1800)	267 (1100)	
8	238 (1700)	300 (500)	
9	259 (1700)	unobsd	
10	255 (1100)	unobsd	

[a] Calculated for 100% yield of a single species absorbing at this wavelength and only included for comparative purposes. [b] No maximum observed for flowing solution. A peak with λ_m 245 (1300) grows in upon letting the solution stand.

pseudoequatorial methyl groups was incorrect and led to the wrong conclusions about their conformations.

Results and Discussion

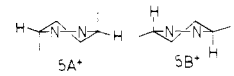
ESR. The ESR splitting constants for 3^+–7^+ in butyronitrile are compared in Table I. The splittings reported are not highly accurate because of the complexity of these spectra. The nitrogen splitting is expected to be



6 7

about the same size as the methyl hydrogen splitting and was not usually resolved from it, and the small γ-splittings also were not resolved; the observed line width was over 1 G in all cases except for 4^+ at 60 °C, where the nitrogen and methyl splittings were successfully resolved. Nevertheless, these spectra do show which type of conformation is occupied for hexahydropyridazine cations. Either rapidly equilibrating conformations or a "frozen" boat conformation for 4^+ would produce a ring tertiary hydrogen a(2 H) splitting, but what is seen is a large single hydrogen splitting, which we attribute to H_a in "frozen" half-chair (I) 4^+. Although frozen half-chair 4^+ has in principle two different a(N) values and two different methyl splittings, their sizes should be similar, and it is not surprising that we failed to resolve them. We also failed to resolve the splitting for the equatorial tertiary ring hydrogen. The bicyclic cation 6^+ has a large a(2 H) and a small a(2 H), which we attribute to the axial and equatorial β-hydrogen splittings of the I conformation, respectively. The transfused carbocyclic ring of 6^+ would seem to preclude a hexahydropyridazine ring boat conformation of reasonably low energy, because this would require the carbocyclic ring to be very twisted. Furthermore, the nitrogen splitting for 1^+, which is required to have its hexahydropyridazine ring in a boat conformation by its bicyclo[2.2.2]octyl structure, has a significantly larger a(2 N) value than do 3^+–7^+.

The cation with the most significant ESR spectrum is 5^+. It does indeed show a(2 H) about half the size of a(2 N) = a(6 H) at room temperature as previously reported,[3] but the two hydrogen splitting proved to be unusually temperature sensitive. As seen in Table I, a(2 H) increases a factor of 2.2 between −105 and +85 °C. Such large temperature sensitivity can only be rationalized if 5^+ is equilibrating between conformations having quite different a(2 H) values. We suggest that 5^+, like 4^+, is "frozen" on the ESR time scale at −105 °C in a I conformation and that at high temperature it is equilibrating with the ring-reversed I conformation so that a weighted average of the two a(2 H) values is observed. These conformations are shown as $\mathbf{5A}^+$ and $\mathbf{5B}^+$ (the N-methyl groups have been left out for clarity). The low a(2 H) value observed at low

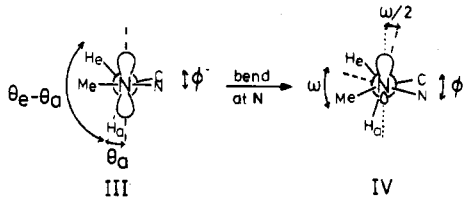


$\mathbf{5A}^+$ $\mathbf{5B}^+$

temperature shows that the stabler conformation is that with equatorial tertiary hydrogens, $\mathbf{5A}^+$. The temperature sensitivity of the a(2 H) coupling allows estimation of the energy gap between $\mathbf{5A}^+$ and $\mathbf{5B}^+$. Assuming $a(2\ H_a)$ for $\mathbf{5B}^+$ is about 27 G and $a(2\ H_e)$ for $\mathbf{5A}^+$ is about 3.6 G at high temperature, the 8.1 G 2 H splitting observed at 85 °C represents a 19% contribution of $\mathbf{5B}^+$ to the equilibrium, which would mean that $\mathbf{5B}^+$ is about 1.0 kcal/mol less stable than $\mathbf{5A}^+$. If $\Delta S°$ for the equilibrium is near 0, as it is expected to be for ring reversal forms of six-membered rings, $\Delta G°$ would still be about 1 kcal/mol at −105 °C. There would then only be about 4.5% $\mathbf{5B}^+$ in the equilibrium mixture at low temperature, which is consistent with our failure to observe $\mathbf{5B}^+$ in the ESR spectrum of 5^+ at low temperature. Most of the lines of $\mathbf{5B}^+$ would overlap with those of $\mathbf{5A}^+$, and the differences in their spectra would only be observed in the rings of the spectrum, where the intensities are low. Although the diaxial methyl ring reversal form being the stabler one surprised us enough to cause us to reject this as a reasonable possibility in 1973,[3] subsequent work has made such a result unsurprising. There is a clear reluctance to have even three adjacent equatorial methyl groups in the neutral forms of **4** and **5**, and no conformations with diequatorial N-methyl groups were detected by ^{13}C NMR for either, although the diequatorial conformation is the stabler one for **3**.[4] The flattening at nitrogen which accompanies electron removal would increase steric interactions between the adjacent methyl groups of the all equatorial methyl conformation $\mathbf{5B}^+$ relative to those in the neutral compound. Although the steric interactions between the methyls of $\mathbf{5B}^+$ could be relieved by bending at the nitrogen atoms, this would force twisting of the three-electron π bond. Ring reversal to the diaxial methyl conformation $\mathbf{5A}^+$ avoids this twisting and appears to be the least destabilizing option for relieving methyl buttressing.

The sizes of the axial and equatorial splittings at C_3 and C_6 in hexahydropyridazine cations also deserve comment. We failed to resolve the equatorial splittings in 3^+ or 4^+, although $a(H_a)$ was 27.5–27.6 G, and because we would have seen an $a(H_e)$ splitting above 3 G, $a(H_a)/a(H_e)$ is above 9 for these systems. This is anomalous if the simple McConnell equation for β-splittings, $a(H_\beta) = B\rho_N^\pi \cos^2\theta$ is employed, because $a(H_a)/a(H_e)$is $\cos^2\theta_a/\cos^2\theta_e$ by this equation. The phasing angle, θ_e–θ_a, to be used is probably somewhat less than the 120° it would be for a tetrahedral β carbon atom. For cyclohexene, which can be considered an imperfect structural model for half-chair hexahydropyridazine cation, electron diffraction[5] gave θ_e–θ_a of 115.5°, θ_a of 16.7°, and internal ring dihedral angle ϕ (the C_4-C_3,C_2=C_1 angle in cyclohexene, see structure *III* for a hexahydropyridazine cation) of 15.4°, and Allinger MM2 molecular mechanics calculations[6] gave θ_e–θ_a = 117.0°, θ_a = 15.8°, and θ = 16.1°. Even with θ_a = 0° and θ_e–θ_a = 115°, $a(H_a)/a(H_e)$ should only be 5.6 from the $\cos^2\theta$ ratio. We suggest that the higher observed ratio is most likely to be caused by deformation from planarity at nitrogen. All

(4) Nelsen, S. F. *Acc. Chem. Res.* **1978**, *11*, 14.
(5) Chang, J. F.; Bauer, S. H. *J. Am. Chem. Soc.* **1969**, *91*, 1898.
(6) Allinger, N. J. *J. Am. Chem. Soc.* **1977**, *99*, 8127; *QCPE* 395.



III IV

splittings observed are time averages over a range of bending values because hydrazine radical cations are so easily bent at nitrogen. Bending anti at the hydrazine nitrogens is easier then bending syn, and anti bending raises ϕ and increases ω, (see IV), changing the direction of the lone pair axis from perpendicular to the NN bond. Because $\langle \cos^2 \theta \rangle = 0.5$ and methyl group rotation is rapid at these temperatures, $a(NCH_3) = B/2$, so B is about 25.6 G for 3^+. Since $a(H_a)$ was observed at 2% 6 G, B clearly does not accurately give the $\cos^2 \theta$ dependence predicted by the simple McConnell equation; B differs for different β-hydrogens. Kawamura and co-workers[7] have pointed out that the scaling factor B in the McConnell equation for β-hydrogens syn to spin-bearing orbital at carbon decreases as bending increases, and it seems likely that B increases for anti hydrogens, which would lead to an increase in $a(H_a)/a(H_e)$ over that calculated by the simple McConnell equation. B probably decreases for anti hydrogens at large enough amounts of bending. Another factor is that as anti bending increases, mixing of the equatorial CH bond with the remote nitrogen should increase, and since the spin at the remote nitrogen is opposite in sign, this will also decrease $a(H_e)$ and increase the $a(H_a)/a(H_e)$ ratio. We did resolve $a(H_e)$ for 5^+ and 6^+, and $a(H_a)/a(H_e)$ is 5.5 for 6^+, closer to the ratio predicted by the simple McConnell equation. Allinger MM2 calculations do not predict a significant change in θ_a or ϕ for fusion of a six-membered ring trans at C_4,C_5 in cyclohexene, giving essentially the same geometry in the region of the double bond for cyclohexene and *trans*-bicyclo[4.4.0]dec-3-ene. This gives no support for the idea that the lower $a(H_a)$ and higher $a(H_e)$ for 6^+ compared to 3^+ is caused by a change in ϕ value which makes θ_a and θ_e larger in 6^+. If 6^+ were "stiffer" than 3^+, and had less equilibrium bend at nitrogen, the observed decrease in $a(H_a)$ and the higher $a(H_a)/a(H_e)$ ratio could be rationalized without a significant change in ϕ.

UV. The experiments which initially forced us to reexamine the conformations of hexahydropyridazine cation radicals involved attempts to measure their UV spectra. As previously described,[2] syn- and anti-bent $R_4N_2^+$ show different distribution in $a(N)$ vs. λ_m plots because the mixing of s character into the nitrogen lone pair orbitals of the syn-bent species is greater than for the anti-bent species due to orbital symmetry effects. Hydrazine radical cations in which the α-hydrogens are not Bredt's Rule protected[8] are not isolably stable and decompose slowly. Generation of solutions containing $R_4N_2^+$ for λ_m determination for such compounds proved convenient using a flow electrochemical cell.[2] A solution of the hydrazine in acetonitrile containing 0.1 M *n*-Bu_4NClO_4 as supporting electrolyte was flowed over a porous carbon electrode maintained at a potential high enough to cause over 90% conversion to the cation radical and was shown to give λ_m values close to those obtained by dissolution of isolable $R_4N_2^+$ salts. When the flow and oxidation were stopped, the $R_4N_2^+$ absorption was observed to decrease

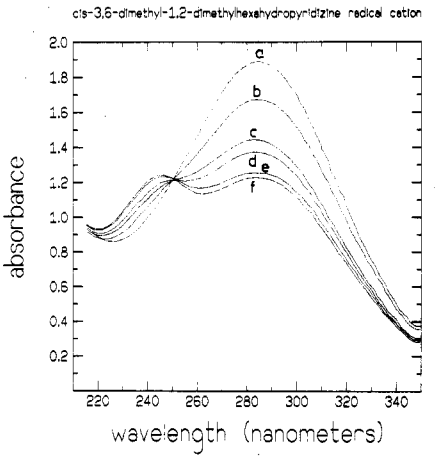
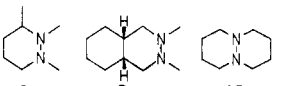


Figure 1. UV spectrum for **4** flow cell oxidation: (a) flowing solution; (b–f) current and flow stopped for 2, 4, 5, 7, and 8 min.

over a period of tens of minutes for unprotected examples, as the cation radicals decomposed. Hexahydropyridazines **3–7** as well as **8–10** were studied by this method, but gave different results from other hydrazines.



8 9 10

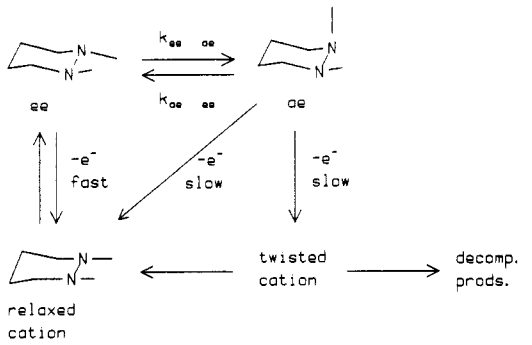
Although the expected behavior of seeing a single near-UV band in the region where the radical cation should occur was seen for **6**, **9**, and **10**, anomalous longer wavelength absorption bands were produced for the other compounds. The long wavelength band was weaker than the $R_4N_2^+$ band for **3**, **7**, and **8** but comparable in intensity for **5**, and only the long wavelength band was observed while the solution was flowing for **4**. When the flow and oxidation were stopped, the long wavelength bands decreased in intensity over a period of minutes, and the ratio of $R_4N_2^+$ to long wavelength band increased, although this was superimposed on a slower decrease in $R_4N_2^+$ band intensity as the cation radical decomposed. The increase in $R_4N_2^+$ intensity as the long wavelength band decreased was most noticeable for **4**, where no $R_4N_2^+$ maximum was resolved under flowing conditions; see Figure 1.

We initially considered the possibility that an unstable conformation of $R_4N_2^+$ was generated for some hexahydropyridazines and that we were observing its relaxation to the stabler radical cation conformation, but this hypothesis is unreasonable. The ESR spectra of hexahydropyridazine cation radicals, as other examples of $R_4N_2^+$, show that they undergo conformational interconversion rapidly on the ESR time scale at room temperature, and a radical cation conformational change with a barrier high enough for the process requiring minutes at room temperature is not a viable possibility. Furthermore, experiments in which the effluent from the flow cell was trapped at low temperature and also examined directly at room temperature by leading the flow through an ESR cell showed that the species causing the long wavelength absorption did not give an ESR spectrum. We suggest that the species giving the long wavelength absorption is not a radical but some hydrazine decomposition product produced upon oxidation in the flow cell. We noted that there is a rough correlation between the intensity of the long wavelength band relative to the $R_4N_2^+$ band and the amount of ae conformation present at equilibrium[4] for the neutral hexahydropyridazine (see Scheme I).

10 exists exclusively in the ee conformation, and **9** should be very predominantly ee because it has an axial alkyl

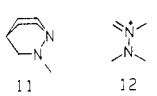
(7) Kawamura, T.; Matsunaga, M.; Yonezawa, T. *J. Am. Chem. Soc.* **1978**, *100*, 92.
(8) Nelsen, S. F.; Kessel, C. R.; Brien, D. J. *J. Am. Chem. Soc.* **1980**, *102*, 702.

Scheme I



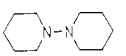
group imposed by its structure. ee conformations are known to predominate over ae conformations for **6** and for **3**, and although ae predominates for **8**, the ee conformation is detectable. Compounds **5** and **4**, for which the long wavelength species predominates upon flow cell oxidation, have no ee conformation detectable by NMR or PE spectroscopy. Conformational studies of methylated diazadecalins have shown that the ee conformation is even higher in energy relative to the ae conformation for the cis ring carbon dimethyl substitution pattern of **4** than it is for the trans dimethyl substitution pattern of **5**.[9]

Low-temperature CV studies have demonstrated that the relatively high barrier of 10.3 kcal/mol or greater between ee and ae conformations of hexahydropyridazine leads to conformationally dependent oxidation behavior.[10] When the potential at the electrode is increased faster than the ae conformation can convert to the more rapidly oxidized ee conformation, a kinetic resolution of the oxidation waves occurs because ae transfers an electron to the electrode far more slowly than does ee (see Scheme I). In our published kinetic analysis, we did not show a twisted cation as an intermediate between ae and the relaxed cation, because the latter is a product of oxidation of ae and we had no evidence for such an intermediate. We did note that the reduction scan wave observed for ae-rich compounds was never quite as large as expected and that second oxidation scan experiments did not allow proper measurement of $k_{ee \rightarrow ae}$,[11] which would be consistent with an intermediate twisted cation which did not give relaxed cation completely. The conditions of the oxidation using the flow electrochemical cell are rather different from those used in the CV experiments, because the potential of the electrode in the flow cell is maintained at a high value to ensure rapid electron transfer as the hydrazine comes in contact with the electrode. Electrode potential control is also very imprecise because of the geometry of the electrode. We postulate that at high potential, ae is oxidized to a twisted cation, which decomposes rapidly, as the cation from **11**, which is forced to be twisted by its bicyclic skeleton, is known to do even in CV experiments.[12] De-



11 **12**

composition of a twisted cation would be expected to generate protons and α-hydrazinyl radicals, which would be oxidized to α-aminoimmonium ions of general structure **12**. We do not know what species actually cause the long wavelength absorptions observed nor how decomposition of these species generates oxidizing agents capable of producing hydrazine cation radicals but believe the structural pattern of compounds giving the long wavelength absorptions strongly implicates decomposition of the oxidation products of ae hexahydropyridazines. Most hydrazines do not have a high barrier between conformations with twisted and those with coplanar lone pairs and do not show such behavior in the flow oxidation cell. The only hydrazine which is not a hexahydropyridazine for which a long wavelength absorption was produced is *N,N'*-bipiperidinyl (**13**), which shares with ae hexahydropyridazines the structural feature of ring α-hydrogen CH bonds being forced to have large overlap with the lone pair by six-membered rings and gauche lone pairs in the neutral form. It is quite possible that potentials high enough to



13

generate dications are present in the flow cell (we thank a referee for this suggestion). Dications of all unprotected hydrazines certainly decompose very rapidly. We would expect, however, that a twisted radical cation would be even more difficult to oxidize to a dication than would an untwisted radical cation, because the dication has a full double bond between the nitrogens and should be exceptionally difficult to twist. We do not see why production of the non-hydrazine cation decomposition product would correlate with the fraction of ae conformation present if these products were coming only from dications.

When **3**, **4**, and **6** were oxidized from $NOPF_6$, a maximum in the $R_4N_2^+$ region was produced without generating the long-wavelength band seen in the flow cell, although the λ_m observed was several nanometers longer in wavelength than that observed in the flow experiment. Despite this uncertainty, all of our data put hexahydropyridazine cation radical λ_m values in the range 248–263 nm, which is significantly shorter than those seen for acylic hydrazine cations and especially for the isolable *N,N'*-bisbicyclic anti-bent examples.[2]

Conclusion

The ESR results establish that relaxed hexahydropyridazine cation radicals exist in half-chair six-membered ring conformations. The shorter wavelength UV absorption is consistent with less bending at nitrogen than occurs for acyclic $R_4N_2^+$, which seems reasonable on structural grounds. A half-chair ring constrains the internal CNNC dihedral angle near 0°, which would force the lone pair orbitals out of planarity if the methyl groups bent in the anti sense. The UV λ_m values and ESR a(N) values for 3^+–6^+ are somewhat smaller than those for the bridged hexahydropyridazine derivatives 1^+ and 2^+, which are forced to have boat six-membered rings, implying less bending at nitrogen for half-chair than for boat radical cation conformations. We suggest that the nitrogens of the half-chair hexahydropyridazine radical cations studied here are flatter at nitrogen than other $R_4N_2^+$ examples because of the conformational constraints of their six-membered rings.

The suggestion that the fate of an ae hexahydropyridazine upon oxidation depends on the potential of the electrode seems to us to be a novel suggestion. Our results are consistent with a high electrode potential causing formation of a twisted cation which mostly deprotonates, while a lower electrode potential (as in CV work) or a

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chemical oxidant produces the relaxed radical cation. Additional studies will be required to see if this idea has merit.

Experimental Section

Preparations of the compounds studied here have been previously reported; **3–5**, **8**, and **10**,[13] **6**,[14] and **7** and **9**.[15] The techniques used for ESR and UV spectra were the same as those in our previous work.[2,15] Spectra were recorded on a Varian E-15 spectrometer, with temperature maintained with a V-4557 variable temperature Dewar and vacuum-jacketed carrier tube and a V-4540 variable temperature control. A copper constantan thermocouple and Leeds and Northrup temperature potentiometer (Model 8693-2) was used to measure the temperature (by using a dummy tube replacing the sample tube without changing the nitrogen flow rate). The field was calibrated at room temperature with 10^{-4} M Fremy's salt in saturated aqueous potassium carbonate, by using $a(N) = 13.09$ G, and the corrections were assumed to be temperature independent.

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Registry No. **3**, 26163-37-1; **3** (radical cation), 98705-11-4; **4**, 26171-64-2; **4** (radical cation), 35018-93-0; **5**, 38704-91-5; **5** (radical cation), 35018-94-1; **6**, 60387-16-8; **6** (radical cation), 98757-92-7; **7**, 60678-80-0; **7** (radical cation), 98719-94-9; **8**, 38704-92-6; **8** (radical cation), 98719-77-8; **9**, 60678-81-1; **9** (radical cation), 98757-93-8; **10**, 3661-15-2; **10** (radical cation), 98719-78-9; $NO^+PF_6^-$, 16921-91-8.

Supplementary Material Available: Expected and simulated ESR spectra for the spectra reported in Table I (8 pages). Ordering information is given on any current masthead page.

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Electrophilic Fluorination of Unsaturated Systems with the Recently Developed Acetyl Hypofluorite

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Acetyl hypofluorite (AcOF, **1**) is a relatively new reagent which is prepared in situ from F_2 and is an excellent source for electrophilic fluorine. Unlike the other known fluoroxy reagents, it reacts smoothly and quickly at −78 °C with many types of olefins to produce acetylated fluorohydrins. It is particularly important as a major tool for introducing the ^{18}F radio isotope into biologically interesting systems. AcOF has been added to arylethenes, isolated aliphatic double bonds, and steroidal olefins with absolute regiospecificity (Markovnikov mode) and good stereoselectivity (syn addition). The more deactivated enones react with **1** with full regio- and stereospecificity, providing they are located in rigid systems or conjugated to an aromatic ring. Other enones, as well as acetylenes, seem to be less reactive when treated with **1**. Raising the temperature usually results either in the destruction of the substrate due to thermal radical decomposition of **1** or in full recovery of the starting material. Electron-rich double bonds such as enol acetates react with **1** very rapidly, and after short treatment with base the corresponding α-fluoro ketones are obtained in good yields.

Acetyl hypofluorite was first synthesized from elemental fluorine in our laboratories about 4 years ago.[1] During this short period it has been found to be quite applicative for synthetical purposes[2] and a major reagent for efficient introduction of the radioisotope ^{18}F into biologically interesting compounds.[3] The latter is an essential component for many research or diagnostic studies connected with the highly important technique of Positron Emitting Transaxial Tomography (PETT).[4] Since AcOF has potentially great importance in this field, several variants of its synthesis have already been described[5] along with some of its physical and spectral features.[6]

However, because of the short period that has passed since its discovery and because of its promptly found applications in nuclear medicine, not much has yet been investigated concerning some of the basic chemical behavior of AcOF with various unsaturated centers. We wish to report here on the scope of the reactions of **1** with different types of π bonds, reactions which present further opportunities for the introduction of this important halogen to specific sites usually difficult to fluorinate, let alone efficiently introduce the ^{18}F radioisotope.

In general, acetyl hypofluorite reacts with olefins to produce the highly important fluorohydrin derivatives.

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