

Structural Information from Hydrazine Radical Cation Optical Absorption Spectra

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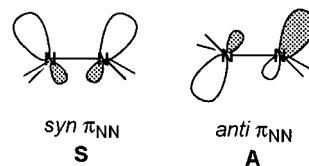
Transition energies (E_{op}) of the nitrogen-centered π, π^* absorption of tetraalkylhydrazine radical cations are quite sensitive to twist at the NN bond, nitrogen pyramidalization, and mixing of the σ orbitals with the π system. Thirty-one examples for which E_{op} varies from 63 to 107.5 kcal/mol are discussed with the aid of calculated values (E_{calc}) for the 0,0 transition energy using simple (no configuration interaction) neutral-in-cation-geometry calculations on AM1–UHF geometry-optimized radical-cation structures. Significant changes in the difference between E_{op} and E_{calc} are observed for bis-*N,N'*-bicyclic systems, which are *syn* pyramidalized at nitrogen (twist angles near 0° ; E_{op} about 23 kcal/mol larger than E_{calc}) and for bis-*N,N'*-bicyclic ones, which are *anti* pyramidalized (twist angles of 180° ; difference about 7 kcal/mol when calculations of 180° structures are employed). Within these classes, changes in E_{op} caused by changes in pyramidalization and σ, π interaction are predicted well by the calculations. The tetraisopropylhydrazine radical cation has $\lambda_{\text{max}} = 282$ nm, but its tetracyclohexyl analogue shows two transitions, at 276 and 386 nm. This surprising difference is attributed to tetracyclohexylhydrazine radical cation having both untwisted and significantly twisted (estimated twist angle $\approx 44^\circ$) forms occupied in solution, although the isopropyl compound only has the untwisted form significantly occupied.

Introduction

The position of an absorption maximum in an optical spectrum (λ_{max}) provides the transition energy (E_{op} (kcal/mol) = $2.859 \times 10^4 / \lambda_{\text{max}}$ (nm)), which corresponds to the vertical energy gap between the ground state and an excited state. Alkenes have a π ground state (that we will call a $\pi^2 \pi^{*0}$ electronic configuration), and many have a $\pi^* \pi^{*0}$ lowest excited state, ($\pi^1 \pi^{*1}$ configuration). Changing one alkyl substituent for another in tetraalkylalkenes has a small effect on the π, π^* transition energy. Tetraalkylhydrazine radical cations ($\mathbf{R}_4\mathbf{N}_2^+$) electronically prefer nearly planar nitrogen atoms and coplanar lone pair axes, making them structural analogues of tetraalkyl alkenes. These two systems even have comparable bond lengths for the two-atom π system. The NN bond length for the range reported for $\mathbf{R}_4\mathbf{N}_2^+$ is 1.32–1.36 Å,¹ which brackets the 1.33 average C=C bond length for tetraalkylalkenes.² The lowest energy transition for $\mathbf{R}_4\mathbf{N}_2^+$ is the nitrogen-centered π, π^* transition. We will refer to the π, π^* transition energy of $\mathbf{R}_4\mathbf{N}_2^+$ as E_{op} . It is very sensitive to changes in alkyl group structure.^{3,4} Hydrazine radical

cations have greater flexibility at their nitrogens than alkenes have at their sp^2 -hybridized carbons because $\mathbf{R}_4\mathbf{N}_2^+$ has an antibonding π electron ($\pi^2 \pi^{*1}$ configuration), and changing alkyl groups causes significant changes in the geometry about the nitrogens.

Pyramidalization at nitrogen lowers the π, π^* orbital energy gap ($\Delta E(\pi, \pi^*)$) because it lowers overlap between the p-rich orbitals at nitrogen.³ We measure pyramidalization using α' , the deviation of the average of the bond angles at nitrogen from the 120° of a planar atom, because this quantity correlates nearly linearly with formal hybridization and lone pair energies for amines.⁵ Pyramidalizing at the nitrogens in *syn* geometry (displacing the alkyl substituents to the same side of a plane through the NN bond, resulting in a lone pair, lone pair twist angle, θ , of 0°) results in larger overlap of the p-rich orbitals at nitrogen than pyramidalization in the *anti* geometry (displacing the substituents at each nitrogen



to opposite sides of a plane through the NN bond, resulting in $\theta = 180^\circ$). The outer cartoons of Figure 1 show the larger $\Delta E(\pi, \pi^*)$ for *syn* than for *anti* bent structures arising from direct π -rich orbital overlap. This difference in direct overlap does not lead to larger E_{op} for *syn* than for *anti* pyramidalization because σ, π mixing also affects $\Delta E(\pi, \pi^*)$ and is also sensitive to pyramidal-

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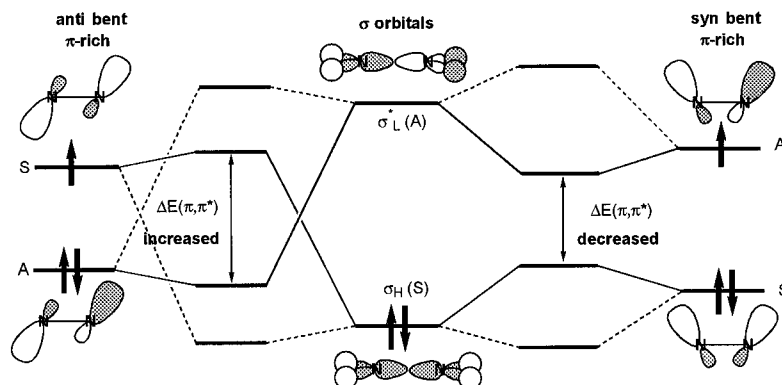


Figure 1. Orbital diagram illustrating the effects of pyramidalization at nitrogen in syn and anti geometries on $\Delta E(\pi, \pi^*)$ for H_2NNH_2^+ .

ization at nitrogen. Symmetry effects cause an opposite effect on $\Delta E(\pi, \pi^*)$ to occur for σ, π mixing and for direct π overlap. The NN and CN bonds lie in the nodal plane of the π system when the nitrogens are planar. This precludes mixing of the NN and CN orbitals with π and π^* orbitals. The highest occupied and lowest unoccupied σ orbitals have large contributions from the NN and CN bond orbitals (as well as contributions from other orbitals in the molecule when the attached groups are larger than the hydrogens considered in the drawings in Figure 1). The highest occupied σ orbital, which we will call σ_{H} , has *S* symmetry, and the lowest unoccupied σ orbital (σ_{L}^*) has *A* symmetry for both types of pyramidalization. Syn pyramidalization makes π symmetric (*S*) with respect to a plane bisecting the NN bond and π^* antisymmetric (*A*). Anti pyramidalization makes π *A* and π^* *S* with respect to the C_2 axis perpendicular to the NN bond. Because σ, π mixing is only allowed for orbitals of the same symmetry, syn pyramidalization mixes σ_{H} with π and σ_{L}^* with π^* . The pairs of orbitals that mix have fairly small energy gaps, leading to relatively large mixing. The π orbital is destabilized as it acquires σ_{H} character, and the π^* orbital is stabilized as it acquires σ_{L}^* character. This lowers $\Delta E(\pi, \pi^*)$, lowering E_{op} . The orbital symmetries only allow σ_{H} to mix with π^* , and σ_{L}^* to mix with π for anti pyramidalization, so here mixing stabilizes π and destabilizes π^* . The amount of mixing is significantly smaller for anti pyramidalization than for syn pyramidalization because the orbitals for which mixing is symmetry allowed are much farther apart in energy. The result of both direct π overlap and σ, π mixing is to make syn pyramidalization lower E_{op} significantly more than anti pyramidalization.³ Twisting about the NN^+ bond also occurs in some R_4N_2^+ and lowers E_{op} proportionately to $\cos \theta$. We measure θ using the angle between the bisectors of the CNC bonds in a Newman projection down the NN bond.

Results and Discussion

Calculation of Electronic Transition Energies.

Calculation of electronic transition energies is computationally difficult for most molecules. The orbital energy gap between doubly occupied orbitals and singly occupied or unoccupied orbitals is in fact very different from the vertical energy difference between the ground state and an excited state that has an electron promoted. Another way of saying this is that use of Koopmans' theorem, which assumes that orbital energy gaps are the same size

as state energy gaps, leads to large errors for transitions between orbitals of different occupancy. Large amounts of configuration interaction and large basis sets are typically required to calculate electronic transition energies. For the special case of radical cations there is a useful approximation that we believe was first explicitly demonstrated by Haselbach and co-workers.⁶ They compared photoelectron (PE) spectra of neutral compounds with the optical spectra of their radical cations. They showed that for cases that do not undergo significant structural change upon electron loss, if the first ionization band of the PE spectrum is used as zero energy, then the observed transition energies in the optical spectrum overlay well with the higher ionization bands of the PE spectrum. This means that Koopmans' theorem works well for these molecules when the orbitals are all filled because in these cases the PE band separations can be accurately calculated using Koopmans' theorem. Clark took this idea a step farther, approximating the transition energies for radical cations by taking the orbital energy differences for the neutral compound calculated at the radical cation geometry, the NCG approximation.⁷ He also included estimations of oscillator strengths in his calculations, which is necessary information because some of the energy gaps calculated do not correspond to the allowed transitions that contribute to the optical spectrum. The NCG method was shown to be useful for understanding the σ, π transitions observed for alkene radical cations.⁷ Weinhold and co-workers demonstrated using ab initio calculations that the NCG approximation is an excellent one even when the geometry change between neutral and cation oxidation states is very large, as it is for hydrazines.⁴ We employ NCG calculations on AM1-UHF geometry-optimized structures in this work and examine the relationship between the calculated energy differences (E_{calc}) and the observed E_{op} values to aid in interpreting E_{op} .

The substantial sensitivity of E_{op} to alkyl group structure for R_4N_2^+ suggests that information about the geometry of these species in solution ought to be present in these data. This work represents our third attempt to extract such information from the spectra with the assistance of NCG calculations. We concluded earlier that such an approach was not very useful because of large differences between the calculated and experimen-

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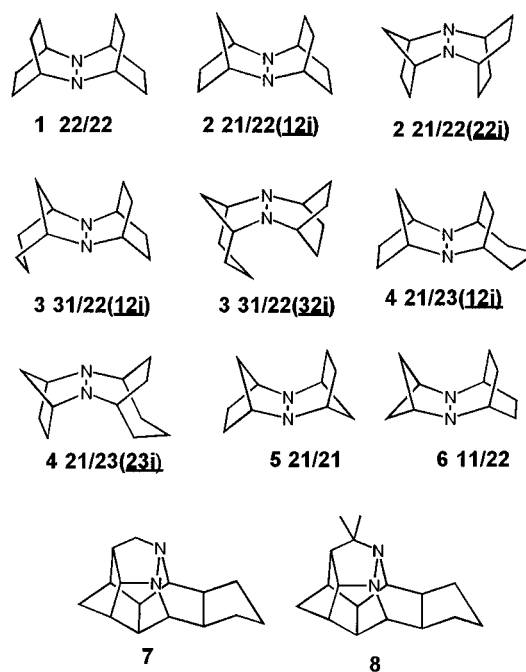
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Table 1. λ_{\max} and Transition Energies for Bis-N,N'-bicyclic Hydrazine Radical Cations

no.	cation from:		λ_{\max}^a (nm)	E_{op} (kcal/mol)	E_{calc}^b (kcal/mol)	ΔE^c (kcal/mol)	θ_{calc}^d (deg)	α'_{calc}^d (deg)
	bridged (invertomer)							
1	22/22		266	107.5	84.3	23.2	0 [3.3]	1.9 [1.4]
2	21/22(22i)		283	101.0	79.2 (73.5)	21.8 (27.5)	0 [1.6]	2.2 [1.8]
	21/22(12i)^e							
3	31/22(32i)		294 ^f	97.2	75.7 (70.1)	21.6 (27.1)	0 [0.7]	1.4 [0.9]
	31/22(12i)^g							
4	21/23(12i)		298	95.9	73.6 (76.0)	22.3 (19.9)	0	2.3
	21/23(23i)^h							
5	21/21		321	89.1	67.2	21.8	0	3.9
6	11/22		323	88.5	67.0	21.5	0	3.5
7			450	63.5	40.5	23.1	23.9	9.5, 11.2
8			454	63.0	40.3	22.7	24.7	8.6, 11.6
9	42/22(42i)		283	101.0	84.5 (85.0)	16.5 (16.0)	2.9 2.0	0.4, 0.8
	42/22(22i)ⁱ							
10	32/22(23i)		286	97.9	79.7 (82.2)	19.2 (16.8)	0	1.0
	32/22(22i)^j							
11	32/23(33i)		299	95.6	80.0 (82.6)	15.6 (13.0)	0	0.3
	32/23(22i)^k							

^a From ref 5 unless noted. ^b Numbers in parentheses are for the invertomer assigned as not occupied. ^c $\Delta E = E_{\text{op}} - E_{\text{calc}}$. ^d Numbers in brackets are values from X-ray crystal structures. ^e 2^+ , **21/22(22i)** is calculated to be 0.06 kcal/mol higher in enthalpy than the **12i** invertomer. ^f From ref 1d. ^g 3^+ , **31/22(32i)** is calculated to be 0.40 kcal/mol higher in enthalpy than the **12i** invertomer. ^h 4^+ , **21/32(23i)** is calculated to be 0.63 kcal/mol higher in enthalpy than the **12i** invertomer. ⁱ 9^+ , **42/22(22i)** is calculated to be 0.80 kcal/mol higher in enthalpy than the **42i** invertomer. ^j 10^+ , **32/22(22i)** is calculated to be 0.14 kcal/mol higher in enthalpy than the **23i** invertomer. ^k 11^+ , **32/32(33i)** is calculated to be 0.30 kcal/mol higher in enthalpy than the **22i** invertomer.

tal numbers.^{3,4} We now point out that AM1–NCG calculations work significantly better than we had thought. The most important consideration we neglected previously is that even if NCG calculations do account for the effects of changing alkyl group structure well, a large discrepancy between observed E_{op} and E_{calc} will remain. E_{calc} is an estimation of the ground-state ($\pi^2\pi^*$) to excited-state ($\pi^1\pi^*$) vertical energy difference for both species in their zeroth vibrational level. The geometry of ($\pi^1\pi^*$) $\mathbf{R}_4\mathbf{N}_2^+$ is very different from that of the ground state. With two antibonding electrons, the excited state electronically prefers being twisted to $\theta = 90^\circ$ at the NN bond. The large equilibrium geometry change between the states makes Franck–Condon overlap of their 0,0 vibrational levels vanishingly small, and the absorption band is an envelope for excitation to highly excited vibrational levels of the excited state. How much vibrational excitation will be required will depend on structure of the molecule examined. This work indicates that although the amount of vibrational excitation varies substantially for different substitution patterns, it is similar enough within related structural classes of $\mathbf{R}_4\mathbf{N}_2^+$ to make AM1–NCG calculations useful for correlating E_{op} data. Another significant factor is that σ,π mixing is important in determining E_{op} , and it does not just involve the NN and CN bonding orbitals, but the entire σ framework. This means that E_{op} values do not just depend on the geometric parameters about the nitrogens (the NN distance, α' , and θ). Correlations of E_{op} with compound structure cannot be expected to directly correlate with some of these geometric parameters at nitrogen even within a structural class. The utility of

Scheme 1. Bis-N,N'-bicyclics

AM1–NCG calculations for incorporating the strongly coupled effects of pyramidalization at nitrogen and σ,π mixing into determining E_{op} values will be documented in this work.⁸

E_{op} Values for Bis-N,N'-bicyclic $\mathbf{R}_4\mathbf{N}_2^+$. Bis-bicyclic $\mathbf{R}_4\mathbf{N}_2^+$ are isolable and can be purified, allowing reliable optical data to be obtained for them. Bis-N,N'-bicyclic compounds have the most structural constraints on the geometry about the nitrogens, and X-ray studies have shown that even AM1 calculations to do a rather good job at optimizing their structures in some cases.¹ Optical data are compared with calculations for several examples in Table 1, and their structures are shown in Schemes 1 and 2. With the probable exception of **9**⁺ (see below), these compounds are all syn pyramidalized at nitrogen. Changing the alkyl substituents varies λ_{\max} from 266 to 454 nm, corresponding to an E_{op} range of 44 kcal/mol.

(8) (a) We were using some bad data previously. Flow system oxidations were employed for systems we knew were unstable,^{3,8b} and we found a variety of tetraalkylhydrazine radical cations having five- and six-membered rings produce spectra with λ_{\max} values in the 230–260 nm region. From the results discussed here, we now believe it is clear that π,π^* absorptions for these compounds will not occur at such short wavelengths and do not trust the data reported³ for *N,N*-dimethyl-*N,N'*-bicyclic systems either. Despite the fact that the solutions clearly contain $\mathbf{R}_4\mathbf{N}_2^+$ from ESR studies, they also contain their decomposition products. We believe that matrix techniques will be required to obtain reliable optical spectra for such compounds. (b) Nelsen, S. F.; Yumibe, N. P. *J. Org. Chem.* **1985**, *50*, 4749.

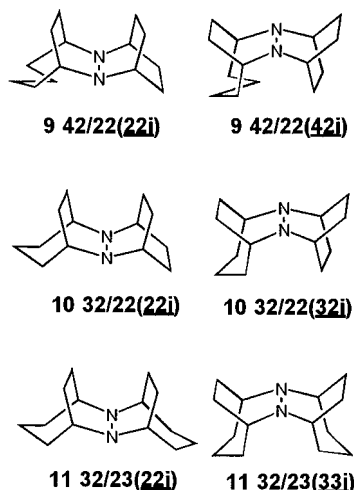
Scheme 2. Twisted Bis-N,N'-bicyclics That Are Calculated To Be Untwisted


Table 1 also includes AM1–NCG E_{calc} values for each compound, and a plot of E_{calc} vs E_{op} appears in Figure 2. Compounds **1**⁺–**6**⁺ are calculated to be untwisted at the NN bond ($\theta = 0^\circ$). The X-ray structures of **1**⁺,^{1a} **2**⁺ (reported here), and **3**⁺^{1d} show that only small twist angles are present in crystals, so AM1 estimates θ rather well for these compounds. Their nitrogens are not planar, so two different double-nitrogen inversion forms (invertomers) are possible for **2**⁺–**4**⁺. The sizes of the carbon bridges in the bicyclic systems on each side of the dinitrogen bridge common to both bicyclic rings, separated by a slash, are shown for each compound. Where the invertomers are different, they are designated by the sizes of the carbon bridges that are “inner” (directed toward each other by the pyramidalization at nitrogen). We had not previously realized that different invertomers have significantly different E_{calc} values.^{3,4} Using the wrong invertomer destroys the good correlation shown in Figure 2. The nitrogens are quite pyramidalized for the neutral compounds, causing 1,3-steric interactions between the bridges to be large. Only the invertomers having smaller steric interactions are occupied, so neutral **2**–**4** are in the **12i** invertomer.^{1d,9} The nitrogens are flattened in the cations, sharply decreasing the size of the 1,3-steric interactions. This makes interaction of bridgehead HC bonds eclipsing with NC bonds in the adjacent rings, a 1,2-steric interaction, much more important in determining relative energies of the radical cation invertomers. AM1 calculations get **12i** invertomers as most stable for **2**⁺–**4**⁺, but only by 0.06 and 0.4 kcal/mol for **2**⁺ and **3**⁺, respectively. One should not expect such calculations to be able to reliably predict which of two isomers so similar in energy is the more stable. Magnetic resonance and labeling studies have shown that one invertomer of **2**⁺ predominates, to an estimated extent of 70%.¹⁰ We previously assigned the predominate invertomer as **2**⁺(**12i**), but this assignment was only based on believing that we could correctly estimate a γ -exo splitting constant in the bicycloheptyl ring. The E_{calc} values differ substantially for the invertomers of both **2**⁺ (5.7 kcal/mol) and **3**⁺ (5.5 kcal/mol).

(9) Nelsen, S. F.; Wang, Y.; Powell, D. R.; Hayashi, R. K. *J. Am. Chem. Soc.* **1993**, *115*, 5246.

(10) Nelsen, S. F.; Petillo, P. A.; De Felippis, J.; Wang, Y.; Chen, L.-J.; Yunta, M. J. R.; Neugebauer, F. A. *J. Am. Chem. Soc.* **1993**, *115*, 5608.

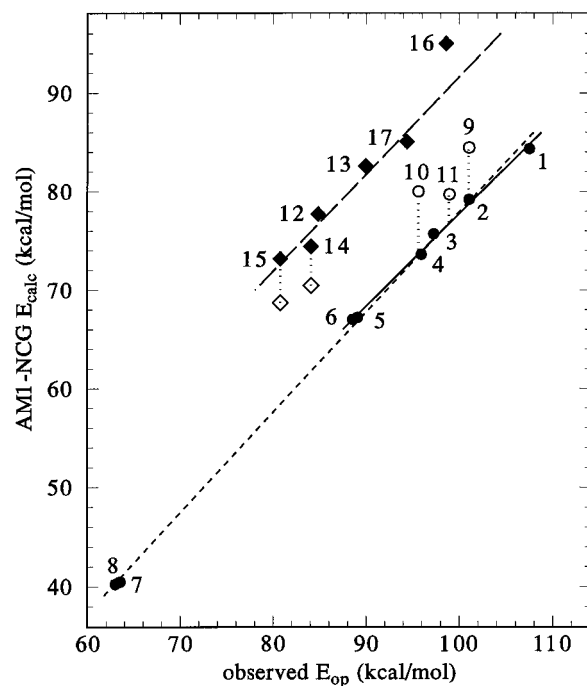


Figure 2. Plot of E_{calc} versus E_{op} for the data of Table 1. The open symbols represent compounds for which AM1 obtains the wrong θ , leading to large deviations from the correlations.

This shows that $C_\alpha C_\beta$ interactions as well as the NC_α interactions mentioned in the Introduction are very significant in determining E_{calc} ; 5.7 kcal/mol is 30% of the total range in E_{op} for **1**⁺–**6**⁺. On the basis of the E_{calc} , E_{op} correlation in Figure 1, we suggest that the correct assignment for the predominate invertomer is **2**⁺(**22i**). The **22i** invertomer is also that present in crystalline **2**⁺ NO_3^- (see the Supporting Information). The new assignment of the predominant invertomer as **2**⁺(**22i**) is also consistent with the behavior of **3**⁺, which has similar geometrical properties. **3**⁺ TsO^- crystallizes in the **32i** invertomer,^{1d} also changing from that of the neutral compound. The **3**⁺(**32i**) invertomer also fits the E_{calc} , E_{op} correlation better than the **12i** invertomer. The ENDOR spectrum of **3**⁺ demonstrates that the splitting constants of the $H_{\gamma\text{-exo}}$ hydrogens of the bicyclo[2.2.2]octyl ring, which are syn and anti to the one carbon bridge of the bicyclo[3.2.1]octyl ring, are nearly the same. This shows that the two invertomers of **3**⁺ are actually nearly equal in free energy in solution.^{1d} We therefore only see one π, π^* optical absorption band for what is known from ENDOR measurements to be a mixture of both invertomers, indicating that AM1 calculations overestimate the difference in transition energies for the invertomers of **3**⁺. We do not know how to rationalize the experimental fact that **3**⁺(**32i**) has such a small α' value. Contracting a bridge from two methylene groups to one clearly leads to a significant increase in α' for other cases.

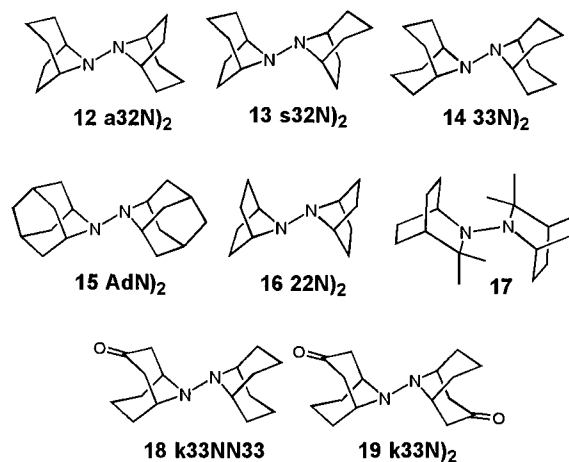
The E_{op} versus E_{calc} plot for the $\theta = 0^\circ$ compounds **1**⁺–**6**⁺ using the invertomer assignments of Table 1 gives a correlation line (the solid line in Figure 2) having a maximum deviation of 0.55 kcal/mol (for **4**⁺(**12i**)). This corresponds to only a 3 nm shift in λ_{max} , little more than the 2 nm resolution of the spectrometer used for these measurements. The E_{calc} values are surprisingly close to plotting linearly with the E_{op} values for these syn-pyramidalized, $\theta = 0^\circ$ compounds, indicating that the calculations are properly accounting for the complex

interplay between α' and σ, π interactions that determines E_{calc} . Including $\mathbf{7}^+$ and $\mathbf{8}^+$ introduces variation in θ , a quantity to which E_{op} is clearly very sensitive. There are so many geometrical constraints built into $\mathbf{7}^+$ and $\mathbf{8}^+$ that we expect both α' and θ to be calculated well. Including them more than doubles the E_{op} range covered, but the correlation with E_{calc} remains excellent. The least-squares line (drawn with short dashes in Figure 2) is $E_{\text{op}} = 0.98 (\pm 0.01)E_{\text{calc}} + 23.25 (\pm 1.02)$ kcal/mol. The maximum deviation that this line predicts in E_{op} (for $\mathbf{1}^+$) corresponds to a λ_{max} 3 nm less than the observed value. AM1–NCG calculations for these specially constrained compounds give E_{calc} values that differ from E_{op} essentially only by being too small by about 23 kcal/mol.

Three other bis-N,N'-bicyclic compounds have been studied, $\mathbf{9}^+$, $\mathbf{10}^+$, and $\mathbf{11}^+$ (see Scheme 2). They were omitted from the correlation lines in Figure 1 not only for the obvious reason that they do not fit on the line, but also because we believe that they are twisted at their NN bonds, while AM1 calculations get θ near 0° optimized structures. The X-ray structure of neutral $\mathbf{9}$ is anti pyramidalized, $\theta = 164.4^\circ$, but AM1 optimizes it in syn-pyramidalized geometry with $\theta = 9.3^\circ$. We do not know whether $\mathbf{9}^+$ is syn or anti pyramidalized, but its ESR spectrum has a hydrogen splitting over 10 G,¹¹ requiring that it is significantly twisted at the NN bond. E_{calc} and E_{op} are so sensitive to changes in θ that this parameter must be correct for a calculation to give the right answer. The data for $\mathbf{9}^+$ – $\mathbf{11}^+$ are plotted in Figure 2 as open circles. They lie 5.5, 2.9, and 6.6 kcal/mol, respectively, above the dotted regression line for the other bis-N,N'-bicyclic compounds. We attribute these deviations to AM1 calculations obtaining untwisted structures, while the real structures are significantly twisted. The excellent correlation for $\mathbf{1}^+$ – $\mathbf{8}^+$ occurs because they have so many structural constraints built in that AM1–UHF calculations get the changes in their structures as ring sizes are changed to be nearly correct.¹²

E_{op} Values for Bis-N,N'-bicyclic $\mathbf{R}_4\mathbf{N}_2^+$. Bis-N,N'-bicyclic cations $\mathbf{12}^+$ – $\mathbf{19}^+$ (Scheme 3) have fewer structural constraints than their N,N' analogues because they lack N,N' rings, and NN bond twist costs little energy, so errors in calculated θ are likely. Both the neutral and radical cation oxidation states of $\mathbf{12}$ ($\mathbf{a32N}_2$),^{1a} $\mathbf{14}$ ($\mathbf{33N}_2$),^{1f} and $\mathbf{15}$ (\mathbf{AdN}_2) (this work) crystallize in $\theta = 180^\circ$ conformations. AM1 incorrectly gets their neutral forms to be substantially twisted, and optimizes $\mathbf{14}^+$ and $\mathbf{15}^+$ with $\theta_{\text{calc}} \sim 159^\circ$, 0.4 kcal/mol more stable than $\theta_{\text{calc}} = 180^\circ$ conformations (Table 2). Because all should be in $\theta = 180^\circ$ conformations, both these and the other compounds in this series were calculated restricting θ to 180° . The dashed line in Figure 2 is a correlation line for the

Scheme 3. Bis-N,N'-bicyclics



compounds with saturated alkyl substituents (omitting $\mathbf{16}^+$ ($\mathbf{22N}_2$), see below). This line for $\theta_{\text{calc}} = 180^\circ$ conformations, $E_{\text{op}} = 1.01 (\pm 0.13)E_{\text{calc}} + 7.02 (\pm 10.46)$, also has a slope of nearly 1, but the constant is only about one-third as large as that for the bis-N,N'-bicyclics. We suggest that the difference in constant obtained for these correlations is likely to largely represent differences in the vibrational excitation component of $\Delta E = E_{\text{op}} - E_{\text{calc}}$ for these structurally rather different classes of compounds.

The E_{calc} values for the twisted AM1 energy minima for $\mathbf{14}^+$ and $\mathbf{15}^+$ are plotted as open diamonds in Figure 2. They fall 4.5 and 3.9 kcal/mol below the $\theta = 180^\circ$ E_{calc} values, showing how sensitive E_{calc} is to twisting about the NN bond. We think it is clear that the AM1 minimum energy structures for $\mathbf{14}^+$ and $\mathbf{15}^+$ lie below the correlation line for the $\theta = 180^\circ$ bis-N,N'-bicyclic compounds because they are incorrectly calculated to be twisted about 21° from having coplanar lone pairs and that the Scheme 2 bis-N,N'-bicyclics (shown as open circles in Figure 1) have E_{calc} values that lie above the correlation line for the other N,N' compounds because they are incorrectly calculated to be nearly untwisted. $\mathbf{16}^+$ has a significantly larger deviation than any of the other compounds in Figure 2, so the NCG calculation is not working as well. We suggest as a probable reason the much smaller CNC bond angle for this compound (96.1° by AM1–UHF) than for any of the others. The AM1 Hamiltonian ignores 1,3-overlaps, causing inherent problems for small ring compounds, where such overlap is significant. AM1 basically fails to be very useful for most three- and four-membered ring compounds. Ignoring 1,3-overlaps may cause problems for 7-azabicycloheptyl systems as well.

Substitution of keto for CH_2 γ to nitrogen raises E_{op} for $\mathbf{18}^+$ and $\mathbf{19}^+$ relative to $\mathbf{14}^+$. The calculations get this result, although the observed changes are +0.5 and +2.3 kcal/mol and the calculated ones +0.3 and +0.9 kcal/mol, respectively. From X-ray structures of the neutral compounds, it is unlikely that significant geometry changes at nitrogen occur between them. The increase in E_{op} presumably arises from poorer σ, π mixing with the half-oxidized π system by the keto-substituted σ -framework.

Model Calculations on Tetramethylhydrazine Radical Cation. As emphasized above, significant σ, π interactions that involve the entire σ -framework are present. Increases in α' caused by decreasing bridge size

(11) Wang, Y. Ph.D. Thesis, University of Wisconsin, 1993.

(12) (a) There are slight deviations in both $d(\text{NN})$ and α' for all $\mathbf{R}_4\mathbf{N}_2^+$ for which X-ray structures have been obtained. The AM1–UHF $d(\text{NN})_{\text{calc}}$ values are too small. For the compounds discussed here, $d(\text{NN})_{\text{calc}} - d(\text{NN})_{\text{X-ray}}$ (Å): $\mathbf{1}^+$ ($\mathbf{22/22}^+$) -0.010 , $\mathbf{2}^+$ ($\mathbf{22i}$) ($\mathbf{21/22}^+$) -0.006 , $\mathbf{3}^+$ ($\mathbf{32i}$) ($\mathbf{31/22}^+$) -0.004 , $\mathbf{12}^+$ ($\mathbf{a32N}_2$) -0.024 , $\mathbf{14}^+$ ($\mathbf{33N}_2$) -0.043 , $\mathbf{15}^+$ (\mathbf{AdN}_2) -0.024 , $\mathbf{23}^+$ ($\mathbf{33NNiPr}_2$) -0.037 , $\mathbf{30}^+$ (\mathbf{ioio}) ($\mathbf{i-Pr}_2\mathbf{N}_2$) -0.026 , $\mathbf{31}^+$ (\mathbf{ioio}) ($\mathbf{i-Pr}_2\mathbf{N}_2$) -0.024 . $\alpha'_{\text{calc}} - \alpha'_{\text{X-ray}}$ (deg) values: $\mathbf{1}^+$ ($\mathbf{22/22}^+$) $+0.5$, $\mathbf{2}^+$ ($\mathbf{22i}$) ($\mathbf{21/22}^+$) $+0.4$, $\mathbf{3}^+$ ($\mathbf{32i}$) ($\mathbf{31/22}^+$) $+0.5$, $\mathbf{12}^+$ ($\mathbf{a32N}_2$) -0.6 , $\mathbf{14}^+$ ($\mathbf{33N}_2$) -1.5 , $\mathbf{15}^+$ (\mathbf{AdN}_2) -1.3 , $\mathbf{23}^+$ ($\mathbf{33NNi-Pr}_2$) -0.8 (at each nitrogen), $\mathbf{30}^+$ ($\mathbf{i-Pr}_2\mathbf{N}_2$) 0.0 , $\mathbf{31}^+$ ($\mathbf{cHx}_2\mathbf{N}_2$) 0.0 . (b) AM1 calculations get the changes in α' as structure is changed to be about right.^{1a} Because ab initio 6-31G* calculations do a far poorer job on this parameter,⁹ they presumably would not do as good a job at correlating these E_{op} data. We have not tried such calculations, which would be very time-consuming, and for which an NCG program is not available to us.

Table 2. λ_{\max} and Transition Energies for Bis-N,N-bicyclic Hydrazine Radical Cations

cation from:							
no.	abbreviation	λ_{\max}^a (nm)	E_{op} (kcal/mol)	E_{calc}^b (kcal/mol)	ΔE^c (kcal/mol)	θ_{calc}^d (deg)	α'_{calc}^d (deg)
12	a32N ₂	337 ^e	84.8	77.7	7.1	180 [180]	3.2 [4.4]
13	s32N ₂	318 ^e	89.9	82.6	7.3	180	3.5, 5.5
14	33N ₂	340 ^e	84.1	74.4	9.7	180 [180]	2.2 [3.7]
				(70.5)	(13.6)	159.4	1.8
15	AdN ₂	354 (4290)	80.8	73.2	7.6	180 [180]	2.1 [3.4]
				(68.7)	(12.1)	158.5	1.8
16	22N ₂	290 (1830) ^f	98.6	95.0	3.6	180	4.5
17		303 ^g	94.4	85.1	9.3	180/0	0.0
18	k33NN33	338 ^h	84.6	74.7	9.9	179.6	2.0
19	k33N ₂	331 ^h	86.4	75.3	11.1	180	2.0

^a The numbers in parentheses are ϵ , $\text{M}^{-1} \text{cm}^{-1}$, only given for data first published here. ^b E_{calc} values for $\theta = 180^\circ$ conformations. The numbers in parentheses for **14**⁺ and **15**⁺ are for the twisted AM1-UHF energy minima, $\theta = 159^\circ$, which have ΔH_f 0.4 kcal/mol smaller than that calculated at $\theta = 180^\circ$. ^c $\Delta E = E_{\text{op}} - E_{\text{calc}}$. ^d Numbers in brackets are values from X-ray crystal structures. ^e λ_{\max} from ref 1a. ^f From the Ph.D thesis of D. J. Steffek, University of Wisconsin, 1982. ^g λ_{\max} from ref 4. ^h λ_{\max} from Nelsen, S. F.; Teasley, M. F.; Kapp, D. L.; Kessel, C. R.; Grezzo, L. A. *J. Am. Chem. Soc.* **1984**, *106*, 791.

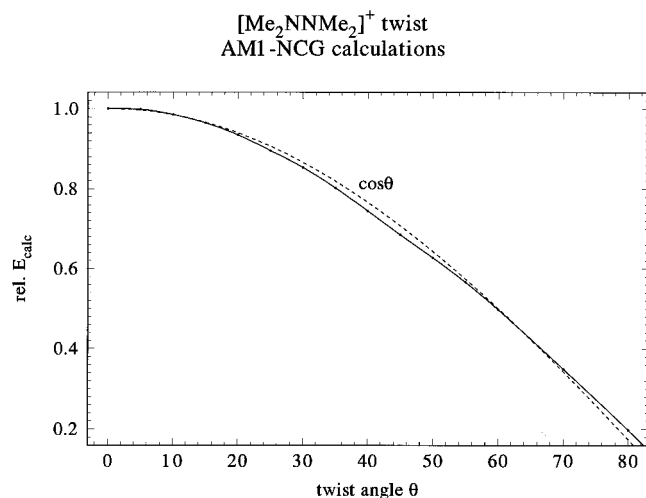


Figure 3. Plot of $E_{\text{calc}}/E_{\text{calc}}(\text{syn-bent energy minimum})$ versus θ for $(\text{Me}_2\text{N})_2^+$, with a $\cos \theta$ curve superimposed as the dashed line.

lower E_{op} , but the changes in σ, π interaction caused by the changes in alkyl group preclude extracting α' just from E_{op} , even if θ is known to be 0 or 180° . We have examined the effect of forcing changes in α' , θ , and $d(\text{NN})$ on E_{calc} for tetramethylhydrazine radical cation to see if E_{calc} changes can be obtained simply from these parameters when the alkyl groups remain constant.¹³ Not surprisingly, they cannot. The most useful thing arising from these model calculations is that forcing θ to increase from the 0° *syn*-pyramidalized C_2 minimum does not significantly affect α' (which starts at only 0.4 and decreases as θ increases), affects $d(\text{NN})$ little, and produces E_{calc} values close to $E_{\text{calc}} = E_{\text{calc}}^0 \cos \theta_{\text{calc}}$ (see Figure 3).¹⁴ We therefore suggest that reliable estimated θ values (θ_{est}) or E_{op}^0 (the E_{op} value for an untwisted analogue) ought to be obtained using $\theta_{\text{est}} = \cos^{-1}(\pm E_{\text{op}}/E_{\text{op}}^0)$, if an appropriate model is available. If the $\theta = 0$ AM1-UHF structures are considered models, the $\cos \theta$

(13) Enforcing *syn* [anti] pyramidalization decreases E_{op} by ~ 7.2 [3.1] kcal/mol/ $^\circ$ in α' and is accompanied by a $\sim 3.2 \times 10^{-2}$ [1.2×10^{-2}] Å per degree in α' increase in $d(\text{NN})$. Increasing $d(\text{NN})$ at $\alpha' = 0$ causes E_{op} to decrease by ~ 2.1 kcal/mol per 10^{-2} Å at the optimum geometry; the slope slightly decreases as $d(\text{NN})$ increases.

(14) The small deviations from the $\cos \theta$ relationship expected on simplest grounds appear to be associated with changes in $d(\text{NN})$. The optimized $d(\text{NN})$ shortens slightly as θ is increased, the change reaching -0.005 Å at -30° , but then lengthens to the same as at 0° by $\theta = 60^\circ$, and $d(\text{NN})$ is longer by 0.012 Å at 80° .

relationship used with the regression line predicts that **10**⁺ is twisted about 15° and **9**⁺ and **11**⁺ are twisted about 23° .

π, π^* Transition Energies for Other Hydrazine Radical Cations. Tetra- α -branched hydrazines do not need bis-bicyclic substitution patterns for isolability, and reliable optical data can be obtained.^{1c} Table 3 contains the same data as Table 1 for some other tetraalkylhydrazine radical cations. The E_{op} values for three mono-N,N'-bicyclics, **20**⁺–**22**⁺ (Scheme 4) cover a range of 10 kcal/mol, and their differences are estimated to within 1 kcal/mol by AM1-NCG. As can be noted from the ΔE column, the constant for converting E_{calc} to E_{op} for these compounds lies between those for the *syn* bent and $\theta = 180^\circ$ anti bent compounds, which emphasizes that comparisons must be made within a structural class to get reliable estimates for differences in E_{op} from AM1-NCG E_{calc} values. The significantly twisted isopropylated N,N-bicyclic **23**⁺ and **24**⁺ (Scheme 4) have ΔE values similar to those of the monocyclic isopropylated compounds but distinctly larger ones than the $\theta = 180^\circ$ bis-N,N-bicyclic ones. NN bond torsion may be more difficult with isopropyl groups than with bicycloalkyl groups, but we do not know how to reliably estimate what ΔE will be for examples having substituents that have not been studied. The calculations overestimate the effect of γ -keto substitution for **23**⁺ \rightarrow **24**⁺, getting a 2.7 kcal/mol increase in E_{op} , while the observed change is 1.7 kcal/mol. They underestimated it for **14**⁺ \rightarrow **18**⁺ and **19**⁺.

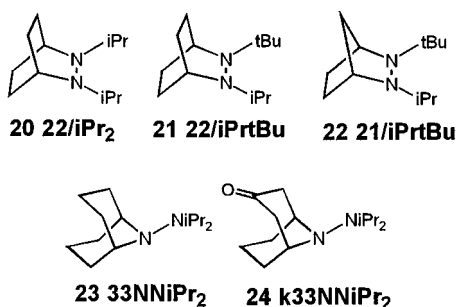
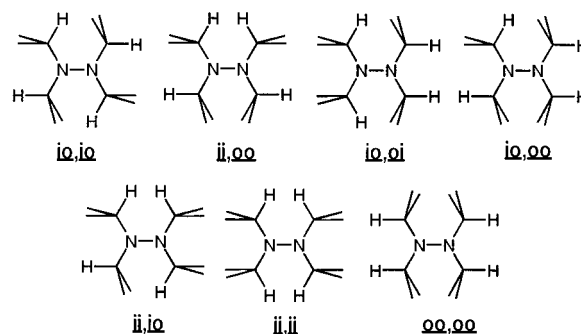
The next five entries in Table 3 are for compounds that lack N,N' rings and contain methyl or ethyl groups, which can give lifetime problems.⁸ We believe from the NCG calculations that the λ_{\max} values reported probably do correspond to the structures indicated, and not to decomposition products.⁸ Even the seemingly trivial change of replacing methyl groups by ethyl groups in comparing **25**⁺ to **26**⁺ raises E_{op} by 4.6 kcal/mol. As inferred from ESR splitting constants,¹⁵ the methyl groups of **26**⁺ are calculated to assume positions alternating above and below the nearly planar $(\text{CH}_2)_4\text{N}_2$ core. Changing methyl to ethyl groups apparently introduces larger σ, π interactions because of the presence of $\text{C}_\alpha\text{--C}_\beta$ bonds aligned well for overlap with the NN π system. This presumably causes the calculated flattening at nitrogen (α'_{calc} increasing from 119.6 to 120.0°) and decrease in the NN bond length (by 0.009 Å), resulting in increase in E_{calc} by 5.9

(15) Nelsen, S. F.; Echegoyen, L. *J. Am. Chem. Soc.* **1975**, *97*, 4930.

Table 3. λ_{\max} and Transition Energies for Some Other Hydrazine Radical Cations

cation from:		λ_{\max}^a (nm)	E_{op} (kcal/mol)	E_{calc} (kcal/mol)	ΔE (kcal/mol)	θ_{calc}^b (deg)	α'_{calc}^b (deg)
no.	abbreviation						
Mono-N,N'-bicyclic Compounds							
20	22/ <i>i</i> -Pr ₂	280 (2900)	102.1	87.4	14.8	2.3	0.7
21	22/ <i>i</i> -Pr- <i>t</i> -Bu	296 (1980)	96.6	80.9	15.7	161	0.8, 1.2
22	21/ <i>i</i> -Pr- <i>t</i> -Bu	310 (2210)	92.2	76.9	15.3	162	1.1, 1.7
Compounds Lacking an N,N' Ring							
23	33NN- <i>i</i> -Pr ₂	324 (3310)	88.2	73.8	14.5	22.8	0.4, 1.5 [1.2, 2.3]
24	k33NN- <i>i</i> -Pr ₂	318 (3030)	89.9	75.1	14.8	23.2	0.4, 1.6
25	Me ₂ N) ₂	303 ^c	94.4	81.0	13.4	0.0	0.2, 0.3
26	Et ₂ N) ₂	289 ^c	98.9	86.9	12.0	4.7	0.0
27	<i>i</i> -PrMeN) ₂	286 ^c	100.0	82.1	17.9	10.6	0.1
28	<i>t</i> -BuMeNNMe ₂	331 ^c	86.4	74.8	11.6	158.6	0.2, 1.2
29	<i>t</i> -BuMeN) ₂	414 ^c	69.1	69.5	-0.4	148.0	0.0, 0.1
30	<i>i</i> -Pr ₂ N) ₂	282 (3170)	101.4	80.3	10.5	23.8 [7.9]	0.0 [0.1, 0.4]
31	cHx ₂ N) ₂	276 (2590) 386 (2060)	103.6 74.1				

^a The numbers in parentheses are ϵ , $\text{M}^{-1}\text{cm}^{-1}$. ϵ values are only given for data first published here. ^b Numbers in brackets are values from X-ray crystal structures. ^c λ_{\max} from ref 4.

Scheme 4. Monobicyclics**Scheme 5.** N-C Rotamers of *i*-(Pr₂N)₂**Table 4.** Comparison of AM1-UHF Parameters for Rotamers of *i*-Pr₂N)₂⁺ and cHx₂N)₂⁺

rotamer	<i>i</i> -Pr ₂ N) ₂ ⁺		cHx ₂ N) ₂ ⁺	
	$\Delta\Delta H_{\text{f}}^a$ (kcal/mol)	θ_{calc} (deg)	$\Delta\Delta H_{\text{f}}^a$ (kcal/mol)	θ_{calc} (deg)
io,io	0.0	24	0.0	14
ii,oi	2.7	22	3.2	12
ii,oo ^b	3.7	42	3.2	19
io,oo	4.7	47	6.7	49
ii,ii ^b	4.9	24	5.2	23
io,oi ^b	5.1	25	3.5	43
oo,oo ^b	9.3	62	13.4	62

^a $\Delta\Delta H_{\text{f}} = \Delta H_{\text{f}}(\text{other rotamer}) - \Delta H_{\text{f}}(\text{io,io})$. ^b These rotamers can have C_2 symmetry.

kcal/mol, which mimics the observed increase in E_{op} . Although it is tempting to use a relationship $\theta_{\text{est}} = \arccos(\pm E_{\text{op,unknown}}/E_{\text{op,model}})$ to extract estimates of θ for acyclic compounds, we suspect that the importance of σ, π interaction will make such estimates quantitatively inaccurate unless the alkyl groups substituted are very similar. We next will discuss a puzzling result that fits the "very similar" alkyl group criterion.

Conformations of 30⁺ and 31⁺. The experimental result that caused us to reconsider the relationship between E_{op} and structure for hydrazine radical cations was the unanticipated difference in optical spectra between the tetraisopropyl (30⁺) and tetracyclohexyl (31⁺) cases. 31⁺ shows two absorption maxima above 250 nm, in contrast to all other stable R_4N_2^+ . These bands differ in E_{op} by 29.5 kcal/mol, two-thirds of the total range of E_{op} values for all R_4N_2^+ studied. The difference in absorption spectrum between 30⁺ (solutions almost colorless) and 31⁺ (solutions distinctly reddish because the 386 nm band extends significantly into the visible region) is easily observed visually. Such large differences in E_{op} would only occur if 31⁺ has two occupied conformations of quite different θ , with the small E_{op} one having θ far from 0°. How could this occur for 31⁺ if 30⁺ only has a small θ conformation occupied? The secondary alkyl groups of these compounds undergo substantial non-bonded steric interactions, forcing them into conformations having the tertiary C_{α} -H bonds with twist angles near 0 or 180° with the NN bond, which we will call inner and outer alkyl group rotamers, respectively. The most stable conformation is calculated to be that labeled io,io in Scheme 5. 30⁺ crystallizes as both nitrate and tosylate salts in the io,io form, which has each tertiary hydrogen tucked between methyl groups of the adjacent isopropyl

group.^{1c} The large E_{op} value for 30⁺ suggests that it has a small θ in solution, probably nearer the 7.9° observed in the crystal^{1c} than the $\theta_{\text{calc}} = 23.8^\circ$. The relative energies and θ values for the AM1-UHF-optimized rotamers of 30⁺ appear in Table 4. The $\cos \theta_{\text{calc}}$ relationship works consistently for the 30⁺ rotamers, $E_{\text{calc}}/\cos \theta_{\text{calc}} = E_{\text{calc}}^0$ values averaging to 85.8 kcal/mol with a total range of +1.8 to -1.7 kcal/mol. Using $E_{\text{calc}}^0 = 85.8$ produces $\Delta E = 15.6$ -17.5 kcal/mol if θ is in the range 0-12°. This range of ΔE values is more consistent with those for similar compounds than the 10.5 kcal/mol value obtained using the 23.8° AM1-UHF enthalpy minimum. If the high E_{op} form of 31⁺ is assumed to have $\theta = 0^\circ$ and to be a model for 30⁺, a $\cos \theta$ relationship gives $\theta = 12^\circ$ for 30⁺. The $\cos \theta$ relationship implies that two NN rotamers of 31⁺, one untwisted and the other with $\theta \approx 44^\circ$, must have such similar energies that both are populated in solution. We presume that the large θ conformation has a different alkyl group rotamer than

io,io. Although it might seem implausible that simply exchanging four isopropyl groups for cyclohexyl groups would make a different alkyl group rotamer become significantly populated, there seems to be no other explanation for the optical spectrum of **31**⁺. We attempted to optimize the structures of the rotamers of **31**⁺ and compare the results with those for **30**⁺ in Table 4. AM1-UHF calculations do get the relative energies and θ_{calc} values of the rotamers of **30**⁺ and **31**⁺ to be significantly different (although we have no good way of finding and might not have found the global minima). The io,io and ii,io rotamers of the cyclohexyl compound are calculated to be less twisted than those of the isopropyl one, which is consistent with the slightly larger E_{op} , although the calculations appear to overestimate θ for both. The calculations estimate over a 3 kcal/mol higher enthalpy for all rotamers other than oi,oi, which is inconsistent with twisted and untwisted rotamers of **31**⁺ having similar energies. AM1 calculations do not predict the two absorption bands which are observed. Nevertheless, both untwisted and twisted forms of **31**⁺ have been isolated in crystals. Crystals of the Ar₄B⁻ salt (Ar = *m,m'*-bis-(trifluoromethyl)phenyl) are clear and colorless and have untwisted cations in the io,io rotamer (see the Supporting Information). Solution of these crystals gives the reddish solutions. Crystals of the tosylate, nitrate, and hexafluoroantimonate salts of **31**⁺ give the same optical spectrum upon solution, but they are opaque and red and not very well formed. The SbF₆⁻ salt gave the best-looking crystals, but like those of **30**⁺ salts and neutral **30**,^{1c} they are disordered and have two molecules twisted 90° with respect to each other present. The cyclohexyl regions are extremely complex. It appears that formally C₂ rotamers are present and that there is considerable twisting about the NN bond, but disorder is too serious to provide accurate structural information for these red crystals, and details of this structure will not be reported. KBr pellets containing **31**⁺SbF₆⁻ have λ_{max} ca. 420 nm, at longer wavelength than the longer wavelength solution maximum, and also show a second maximum below 350 nm; the exact position remains uncertain because of increasing absorbance of KBr at shorter wavelengths.

Conclusions

AM1-NCG E_{calc} values correlate well with E_{op} values for syn-pyramidalized bis-N,N'-bicyclics **1**⁺-**8**⁺, for which there is good evidence that AM1 calculations get nearly the correct α' and θ values. On the basis of this correlation, compounds **9**⁺-**11**⁺ must be significantly twisted, a result that AM1 calculations fail to reproduce. AM1 calculations incorrectly get bis-N,N'-bicyclic compounds to be significantly twisted from $\theta = 180^\circ$, but if structures constrained to the experimental untwisted

geometries are used, good correlation of E_{op} with E_{calc} is also obtained for these compounds. The difference between E_{op} and E_{calc} is significantly different for these classes of **R₄N₂⁺**. This is reasonable because E_{op} clearly does not correspond to a 0,0 vibrational transition, and the amount of excitation energy involved is expected to be different for compounds of different substitution pattern. The optical spectrum of tetracyclohexylhydrazine radical cation (**31**⁺) demonstrates that untwisted and twisted conformations are comparable in free energy, despite the fact that a twisted conformation is not observed for its tetraisopropyl analogue (**30**⁺).

Experimental Section

Preparations of the compounds appear elsewhere.¹ The optical data reported were measured in acetonitrile solution at room temperature, on a diode array spectrometer with resolution of 2 nm. Crystal data for **2**⁺NO₃⁻ (**21/22**⁺), **15**(AdN)₂, **15**⁺TsO⁻, and **31**⁺Ar₄B⁻ (**cHx₂N**)₂⁺ are reported in the Supporting Information.¹⁶ **2**⁺ is present in two crystallographically different forms, both in the (**22i**) invertomer, which have α' values at the nitrogens of 1.9 and 1.6°, close to those observed for **1**⁺ (2.0 and 1.5°)^{1b} and significantly larger than the 0.9° of **3**⁺(**32i**).^{1d} The structures at the nitrogens of both oxidation states of **15** are extremely similar to those of **14**.^{1f,17} The AM1 calculations were carried out using the VAMP package,¹⁸ and the NCG calculations also were done using a program kindly provided by Timothy Clark.

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Supporting Information Available: Crystal data for **2**⁺NO₃⁻ (**21/22**⁺), **15**(AdN)₂, **15**⁺TsO⁻, and **31**⁺Ar₄B⁻ (**cHx₂N**)₂⁺, thermal ellipsoid drawings, and crystal coordinates (11 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(16) The authors have deposited atomic coordinates for these structures with the Cambridge Crystallographic Data Centre. The coordinates may be obtained, upon request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K.

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