faces" and the deviations from axiality are restricted, which suggests a certain tetragonal symmetry character. For centers B and B' according to this model, the four irons would appear equivalent up to a point. In the $[Fe_4S_4]^{3+}$ state in Chromatium HiPIP protein, the EPR spectrum is considered as axial within the accuracy of the "powder" measurements[4] but the fits of the "Mössbauer" spectra are realized with two types of irons.[14] Connection with centers B and B' is not straightforward.[15]

Conclusion

In this article we have presented the $\tilde{g}$ tensors of species created by γ-irradiation that we believe to be paramagnetic forms of 4Fe-4S "cubes". We have discussed the relations between the tensorial directions and the structure of the diamagnetic "cube", and we have proposed plausible assumptions to account for the results. This study is simply the first of this kind. In other compounds where the "cube" would be arranged in a different way in the crystal unit cell, one should not have certain ambiguities that we have encountered here. A true appreciation of the paramagnetic species considered will be provided by comparison between EPR results of various compounds.

Acknowledgment. We are grateful to Dr. R. Cox and Dr. J. Laugier for helpful discussions.

Registry No. $(Bu_4N)_2[Fe_4S_4(SPh)_4]$, 52586-83-1.

Supplementary Material Available: Tables of positional parameters and isotropic thermal parameters of the cations (Table SII), bond distances and angles of the cations (Table SIII), and anisotropic thermal parameters of the anion (Table SIV) (3 pages); a list of observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.

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A Dynamic ^1H NMR and ab Initio MO Investigation of the Barrier to Pyramidal Inversion in Azetidine

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Abstract: Conformational interconversion in azetidine was investigated by low-temperature ^1H NMR spectroscopy and ab initio molecular orbital theory. Coalescence of the α- and β-proton signals was observed with $\Delta G^{\ddagger}$ (154 K) = 30 kJ mol^{-1}. Analysis of changes in the line shape yielded $\Delta H^{\ddagger} = 21 \pm 4$ kJ mol^{-1} and $\Delta S^{\ddagger} = -45 \pm 25$ J mol^{-1} K^{-1}. Three stationary points were located using RHF theory and analytical gradient techniques at the 6-31G** basis set level. Harmonic frequency analysis was used to characterize two as equivalent minima, a puckered ring with an equatorial N-H bond, separated by the third, a transition structure with C_{2v} symmetry, and to provide an estimate for zero-point vibrational energy (ZPVE) corrections to the barrier to nitrogen inversion. The computations confirm the low measured value for the nitrogen inversion. A value of 27.1 kJ mol^{-1} is obtained after inclusion of correlation corrections up to third order in Moller-Plesset perturbation theory (MP3), and taking account of ZPVE differences. Parallel calculations on aziridine and ammonia yield values of 77.9 and 22.3 kJ mol^{-1}, respectively, for the barrier to pyramidal inversion.

The effect of angular constraint on barriers to pyramidal inversion at tricoordinated atomic centers has been well documented for a variety of atoms[1] and in particular for nitrogen.[2] Barriers hindering pyramidal inversion at tricoordinated N substituted by alkyl groups or hydrogen atoms in systems without constraints at the inverting center have been found experimentally to fall in the range 16 to 30 kJ mol^{-1}. This group of amines is typified by ammonia, whose inversion barrier has been measured[3] at 24.1 kJ mol^{-1}. It has been demonstrated that ab initio calculations *at the RHF level* are able to reproduce this value accurately provided that a large polarized basis set is employed.[4,5] If one of the angles at the inverting center is fixed (as in a small ring) at a small value, the barrier to inversion is increased. The barrier to inversion in aziridine has been observed by gas-phase NMR to be 79.9 kJ mol^{-1} after correction for zero-point vibrational energy differences ($\Delta G^{\ddagger}$ = 72.1 kJ mol^{-1}, 338 K).[6] The inversion barriers in 1-methylaziridine and 1,2,2-trimethylaziridine in solution have been shown to have similar values, $\Delta G^{\ddagger} = 79$[7,8] and = ~77 kJ mol^{-1},[9] respectively, suggesting that N-alkylation does not have a dramatic effect on the barrier to inversion. As the barriers to inversion in 1-methylazetidine and 1,3,3-trimethylazetidine had been shown to be 42[10] and 34 kJ mol^{-1},[11] respectively, the recent report[12] that the inversion barrier in azetidine, measured in the gas phase by NMR spectroscopy, is 75 kJ mol^{-1} came as a surprise,[13] especially

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Table I. Calculated Total Energies (Hartrees) and Zero-Point Vibrational Energies (ZPVE, kJ mol^{-1}): 6-31G** Basis Set

structure	RHF	MP2	MP3	ZPVE
ammonia				
C_{3v}	−56.195 545	−56.382 843	−56.395 655	96.8
D_{3h}	−56.186 762	−56.373 043	−56.385 610	92.2
aziridine				
C_s	−133.048 991	−133.501 241	−133.526 861	198.3
C_{2v}	−133.019 223	−133.470 083	−133.495 259	192.5
azetidine				
C_s	−172.091 759 (−172.078 768)[b]	−172.686 506	−172.723 417	280.8[a] (282.4)[b]
C_{2v}	−172.082 053 (−172.068 348)[b]	−172.674 625	−172.711 610	276.6[a] (277.9)[b]

[a] Calculated numerically. [b] 6-31G* basis set.

as computations had supported the lower value.[16]

Azetidines are of particular interest, primarily because they represent an intermediate case in the question of the role of angular constraints in determining the magnitude of inversion barriers. Also of interest, since correlation energy changes have been shown to be very small in conformational changes in small molecules, is an indication of whether this is true in larger molecules.

There is no reported experimental determination of the barrier to N inversion in azetidine itself. We present herein the results of low-temperature dynamic ^{1}H NMR experiments and large basis set ab initio calculations to establish a value for the inversion barrier. Parallel calculations on aziridine and ammonia serve to support the results for the larger system.

Method

Experimental. Azetidine was obtained from the Aldrich Chemical Co. and used without further purification. ^{1}H NMR spectra were obtained on a Varian XL-200 NMR spectrometer (200 MHz). Temperatures were calibrated using the methanol procedure (and extrapolated into the very low temperature region).

Obtaining low-temperature ^{1}H NMR spectra of azetidine is not without problems. It is not very soluble in nonpolar solvents and can also react with some freons. Line-broadening data are obtained in very dilute solutions of ca. 1:2 CF_2Cl_2–$CFCl_3$ with 2 drops of $CDCl_3$ as lock. Azetidine is more soluble in $CHFCl_2$ (plus 2 drops of CD_2Cl_2) or in $(CD_3)_2O$, and data could also be obtained in these solvents using ca. 1% w/w solutions. Coalescence temperatures were about 10–15° lower in the dimethyl ether solvent and one has to worry about the possible effects of hydrogen-bonding interactions. Using freshly prepared solutions of azetidine in $CHFCl_2$ (made at −78 °C and never warmed above this temperature), the most complete set of line-broadened spectra was obtained. At −130 °C, the nonequivalent α protons show chemical shifts of δ 3.63 and 3.02; the nonequivalent β protons are found at δ 2.26 and 1.78 (relative to $CHFCl_2$: δ 7.41). No low-temperature coupling constant could be obtained because of the broadness of the lines. The NH proton is typically very broad at −80 °C (quadrupolar relaxation) and becomes sharper as the temperature is dropped (δ ca. 1.6 at −125 °C). Activation parameters were obtained by the usual matching of computer-simulated spectra with the experimental ones (simple two-site exchange of either α or β protons). The spectra were simulated using the experimentally observed average coupling constants, but we had to ignore the additional couplings (e.g., geminal) which will probably show up in the "frozen-out" spectra. This, however, makes a negligible difference to our results since the comparisons involved were always with broad peaks, i.e., still not completely "frozen-out".

Theoretical. Ab initio molecular orbital calculations have been carried out using the Gaussian 82[17] system of programs. The geometries of equilibrium structures and transition structures of ammonia, aziridine, and azetidine have been determined at the Hartree–Fock (HF) level using analytical gradient procedures and the 6-31G** basis set.[18,19] Correlation energy corrections were estimated by Moller–Plesset perturbation theory truncated to third order (MP3).[20] Harmonic vibrational frequencies[21] were determined in order to characterize the stationary points as minima or as saddle points and to provide an estimate for the zero-point vibrational energy correction to the inversion barriers. For the latter purposes, the frequencies were scaled by 0.9 to account for their overestimation at this level of theory.[22,23]

Results and Discussion

^{1}H NMR Studies. The most complete set of ^{1}H NMR line-broadening data for azetidine as obtained in $CHFCl_2$ solution in the temperature range −100 to −130 °C. Coalescence of the α protons, for which the most reliable data could be obtained, occurs at T_c −119 °C. Matching of computer-simulated spectra at this temperature yields a rate of exchange of $k_c = 293$ s^{-1}, from which a free energy of activation could be estimated via the Eyring equation ($\Delta G^\ddagger = 30$ kJ mol^{-1}):

$$k_c = (T_c k_B/h) \exp(-\Delta G^\ddagger/RT_c) \quad (1)$$

Under the usual assumption that for an intramolecular process the entropy of activation is negligible, $\Delta S^\ddagger \sim 0$, this value provides an estimate of the inversion barrier which can be directly compared to the value obtained by molecular orbital theory. Although the accessible temperature range is rather narrow, we have attempted to extract enthalpies and entropies of activation directly form rates at various temperatures obtained by matching of computer-simulated to observed spectra. Under the conditions mentioned above ($CHFCl_2$ solution, α protons), satisfactory straight lines could be obtained from a plot of ln (k/T) vs. $1/T$, according to the equation:

$$k = (Tk_B/h) \exp(-(\Delta H^\ddagger - T\Delta S^\ddagger)/RT) \quad (2)$$

The values thus derived are $\Delta H^\ddagger = 20 \pm 5$ kJ mol^{-1} and $\Delta S^\ddagger = -62 \pm 30$ J mol^{-1} K^{-1}. For the β protons, a similar treatment yields $\Delta H^\ddagger = 19 \pm 4$ kJ mol^{-1} and $\Delta S^\ddagger = -67 \pm 20$ J mol^{-1} k^{-1}, although over a narrower temperature range (20°), analysis of the spectral changes in $(CD_3)_2O$ yielded the following results: α protons, $\Delta H^\ddagger = 25 \pm 4$ kJ mol^{-1}, $\Delta S^\ddagger = -8 \pm 25$ J mol^{-1} K^{-1}; β protons, $\Delta H^\ddagger = 21 \pm 4$ kJ mol^{-1}, $\Delta S^\ddagger = -44 \pm 23$ J mol^{-1} K^{-1}. Errors are estimated by assuming worst-case uncertainties in the temperature measurement and rate determination of 2 K and 10%, respectively, and are larger than those derived from standard deviations of the linear least-squares fits to the data points. Indeed, as is shown below, coalescence of the α and β protons occurs in the same transformation and involves the same transition structure. Therefore, the discrepancy between the values for these two in-

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Table II. Calculated Nitrogen Inversion Barriers (kJ mol^{-1}, 6-31G**)

structure	RHF	RHF + ZPVE[a]	MP2	MP3	MP3 + ZPVE[a]	experiment
ammonia	23.1	19.0	25.7	26.4	22.3	24.1[b,c]
aziridine	78.2	73.0	81.9	83.0	77.8	79.9[c,d], 72.1[d,e]
azetidine	25.5	21.6	31.2	31.0	27.1	21,[f] 30[g]
	(26.3)[h]	(22.3)[h]				

[a] ZPVE values have been scaled by 0.9. [b] Reference 3. [c] ZPVE contribution not included; see the RHF and MP3 values. [d] Reference 6. [e] $\Delta G^{\#}$ (65 °C). [f] This work, $\Delta H^{\#}$. [g] This work, $\Delta G^{\#}$ (−119 °C). [h] 6-31G* basis set.

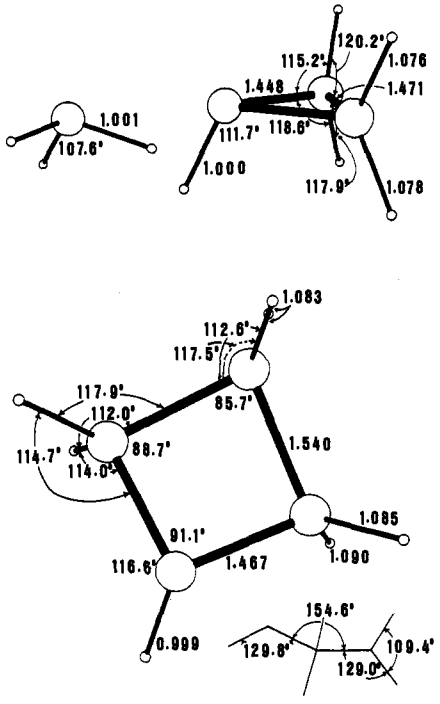

Figure 1. Equilibrium geometries of NH_3, aziridine, and azetidine, calculated at the RHF level with the 6-31G** basis set. Bond distances are in angstroms, angles in degrees.

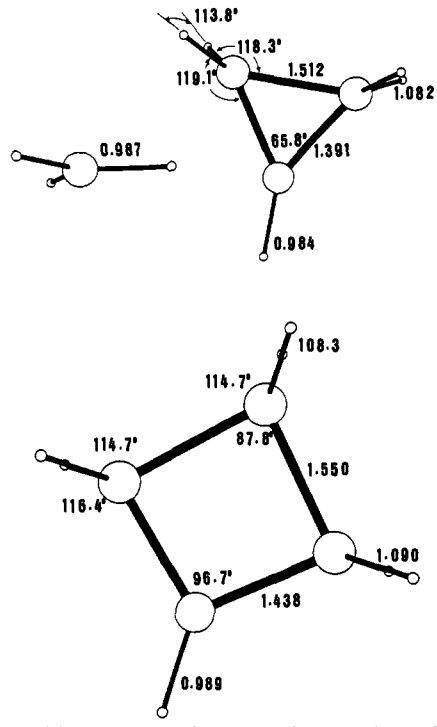

Figure 2. Transition structures for pyramidal inversion at N in NH_3, aziridine, and azetidine, calculated at the RHF level with the 6-31G** basis set. Bond distances are in angstroms, angles in degrees.

dependently analyzed processes in two different solvents provides a realistic estimate of the uncertainty in the activation parameters which is consistent with the estimated error bounds above. As the data for the two solvents are similar, simple averaging of the four sets of data yields $\Delta H^{\ddagger} = 21 \pm 4$ kJ mol^{-1} and $\Delta S^{\ddagger} = -45 \pm 25$ J mol^{-1} K^{-1}. We are uncertain as to the significance of the rather large negative entropy of activation. Values in the range −21 kJ mol^{-1} K^{-1} to −26 kJ mol^{-1} have been measured for inversion of aziridines in the gas phase[6a,b] and decalin solution.[6c] The internal contribution to the entropy of activation which arises from the structural changes that occur during inversion in isolation may be estimated theoretically to be about −5 kJ mol^{-1} K^{-1}. The part which ensues form reorganization of the solvent may be larger because of possible strong solvent–solute interactions through hydrogen bonding, but is more difficult to assess.

Theoretical. The calculated structures at the equilibrium geometry and at the transition geometry are shown in Figures 1 and 2, respectively. Numerical data are presented in Tables I and II.

Ammonia. The geometric parameters, NH = 1.001 Å and HNH = 107.6°, are in excellent agreement with experimental values, NH = 1.012 Å and HNH = 106.7°, as expected.[4,5] The lowest harmonic vibrational frequency, 1142 cm^{-1}, is about 10% higher than the experimentally derived value, 1022 cm^{-1}.[24] The instantaneous nuclear displacement vectors, shown in Figure 3, lead directly along the reaction coordinate for pyramidal inversion. at the transition structure, Figure 2, the N–H bonds are slightly shorter , 0.987 Å. The Cartesian displacement vectors for the single normal coordinate with an imaginary frequency, 909i cm^{-1}, are orthogonal to the molecular plane (Figure 4). The calculated barrier height at the RHF level, 23.1 kJ mol^{-1}, agrees very well with the experimental value,[3] 24.1 kJ mol^{-1}, as does the MP3 value, 26.4 kJ mol^{-1} (Table II).

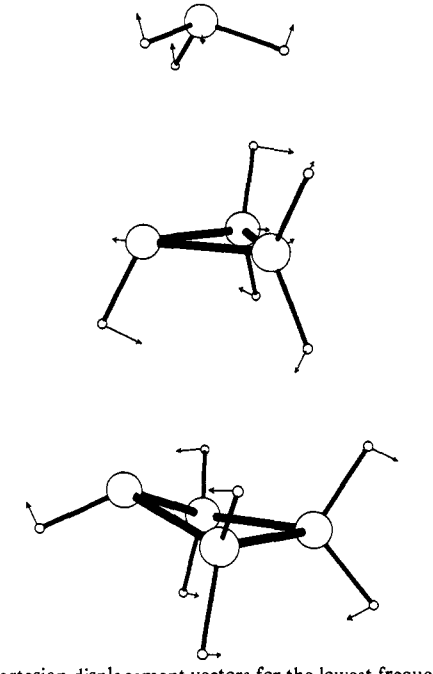

Figure 3. Cartesian displacement vectors for the lowest frequency normal modes at the equilibrium geometries: NH_3, 1142 cm^{-1}; aziridine, 846 cm^{-1}; azetidine, 224 cm^{-1}.

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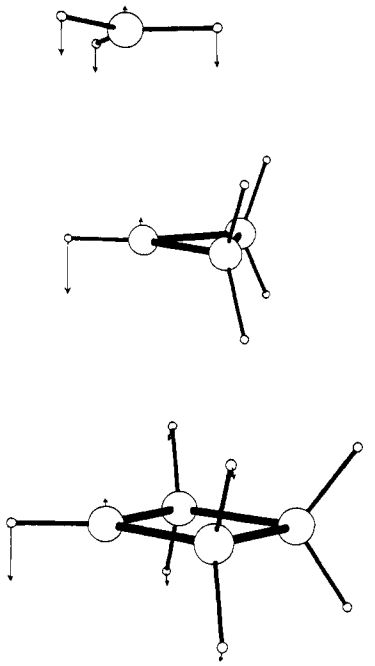
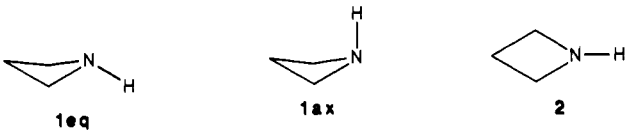


Figure 4. Cartesian displacement vectors for the normal modes with imaginary frequency in the transition structure: NH_3, 909*i* cm^{-1}; aziridine, 999*i* cm^{-1}; azetidine, 617*i* cm^{-1}.

Aziridine. The equilibrium structure of aziridine has been determined by microwave spectroscopy.[25] The RHF//6-31g** structure (Figure 1) agrees well with the experimental structure as well as structures previously calculated with smaller basis sets.[26,27] All of the bond lengths are shorter than the experimental lengths, the most significant deviation occurring for the C–N bond (calcd 1.448 Å, obsd 1.475). The N–H bond length is essentially the same as it is in NH_3. The transition structure for pyramidal inversion (Figure 2) has C_{2v} symmetry. All of the bonds terminating at N are shorter than in the equilibrium structure. Again, the N–H bond is the same as in planar NH_3. The C–N bonds are shorter by 0.057 Å and the C–C bond is longer by 0.041 Å, relative to the equilibrium geometry. The C–H bonds are somewhat longer. The Cartesian displacement vectors for the lowest frequency vibration, 846 cm^{-1}, are shown in Figure 3. The N–H out-of-plane bending motion is strongly coupled to a breathing motion of the ring and twisting of the HCH planes. Thus, reduction of the out-of-plane angle is accompanied by shortening of the C–N bonds and lengthening of the C–C bond. The estimated lowest vibrational frequency, 761 cm^{-1} (=0.9 × 846 cm^{-1}), corresponds well with that assigned by Mitchell and co-workers[28] to the CH_2 rocking motion in the gas phase, 772 cm^{-1}. The N–H deformations were assigned to two modes at 904 and 1096 cm^{-1} of symmetry a″ and a′, respectively. The latter assignment is inconsistent with the present calculations which indicated that the N–H deformation dominates in the fifth vibrational mode at 1084 cm^{-1}. After scaling, the estimated value, 976 cm^{-1} (=0.9 × 1084 cm^{-1}), coincides reasonably well with an observed transition at 998 cm^{-1}, which was attributed to a CH_2 wag. The vibrational analysis of aziridine will be discussed in detail elsewhere.[29]

The instantaneous Cartesian displacement vectors for the single normal mode associated with the imaginary frequency, 998.8*i* cm^{-1}, are shown in Figure 4. This mode is highly localized to motion of the N–H bond. The calculated barrier to inversion at both the RHF and MP3 levels of theory, 78.2 and 83.0 kJ mol^{-1}, respectively, agrees well with the value, 79.9 kJ mol^{-1}, determined by dynamic NMR in the gas phase by Carter, Drakenberg, and Bergman (CDB).[6a] CDB have estimated the ZPVE correction to the barrier, 3.8 kJ mol^{-1}. The calculated value is 5.2 kJ mol^{-1} after scaling by 0.9.

Azetidine. In principle, azetidine may exist in two conformational forms distinguishable by the orientation, pseudoequatorial or pseudoaxial, of the N–H bond, relative to a puckered ring. The calculations confirm previous theoretical[26,30,31] and experimental[32–35] results that azetidine has a puckered ring and that the N–H bond is in the pseudoequatorial position, **1eq**. There is no local



minimum which corresponds to a conformation with a puckered ring and with the N–H bond in the pseudoaxial orientation, **1ax**, despite an earlier interpretation of the far-IR spectrum which suggested the contrary.[36] The equilibrium structure of azetidine is shown in Figure 1. The four-membered ring is folded by 154.4° across the α-carbon atoms, compared to 150.3° derived from electron diffraction and microwave measurements of Gunther, Schrem, and Oberhammer.[35] The C–N bond lengths, 1.467 Å, and C–C bond lengths, 1.540 Å (exptl[35] 1.473 and 1.563 Å, respectively), are longer than the corresponding bonds in aziridine. The *average* value of the bond angles at the pyramidal N atom, 108.1°, is almost the same as in ammonia, 107.6°, in sharp contrast to aziridine where the average bond angle at N is 94.8°. This result suggests that the electronic configuration at N is more similar to that found in unhindered amines and that the barrier hindering pyramidal inversion at N should be comparable also. The lengths of the C–H bonds at the β carbon, both 1.083 Å, are similar to the equatorial C–H bond lengths at the α carbon, 1.085 Å. The pseudoaxial C–H bonds at the α-carbon atoms are somewhat longer as expected from simple PMO arguments, since there will be some delocalization of the N nonbonded electrons into the α_{C-H} orbitals.

The Cartesian displacement vectors for the normal coordinate with the lowest frequency, 224.1 cm^{-1}, are shown in Figure 3. This mode describes puckering of the ring and has little contribution from flattening of the geometry at N. The lowest fundamental observed experimentally[33] is at 207.2 cm^{-1}, which is consistent with that expected from the calculations, 201.7 cm^{-1} (=0.9 × 224.1). The motion leading to inversion at N is strongly coupled to the β-CH_2 rock in the next two lowest vibrational normal modes, with frequencies, 709.9 and 822.5 cm^{-1}, and with α-CH_2 motions of a′ symmetry in modes 6 and 7, which have frequencies 1010.2 and 1034.3 cm^{-1}, respectively. In short, the nitrogen inversion coordinate is not an isolated normal mode as in the case of ammonia, and is more strongly coupled to nearly degenerate rocking and twisting motions of the methylene groups than is the case in aziridine. A complete vibrational analysis of azetidine will be presented elsewhere.[29]

The only other stationary point, **2**, on the ground-state potential hypersurface that corresponds to the connectivity of azetidine is shown in Figure 2. This structure has C_{2v} symmetry. Harmonic frequency analysis reveals it to be the transition state to pyramidal inversion at the nitrogen. Evidently, inversion of the ring is

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concurrent with the inversion at nitrogen. The barrier to inversion at the RHF level is 21.6 kJ mol^{-1}, after inclusion of the zero-point vibrational energy correction. Introduction of the MP3 correlation correction raises the value to 27.1 kJ mol^{-1}.

The instantaneous displacement vectors for the reaction coordinate at the transition structure describe motion with frequency 617.2i cm^{-1} and are shown in Figure 4. As in the case of ammonia and aziridine, the deformation at the transition structure corresponds almost entirely to pyramidalization of the nitrogen atom. There are no significant components corresponding to puckering of the ring, rocking of the α- or β-CH_2 groups, or twisting of the α-CH_2 groups. These latter motions are coupled in modes with real frequencies, one of which is very low, 202.7 cm^{-1}. Most of the loss of ZPVE which leads to the low inversion barrier for azetidine arises from differences in the frequencies of the lowest three vibrational modes of the equilibrium structure and the transition structure, including the mode with imaginary frequency in the latter.

Conclusions

The temperature-dependent ^{1}H NMR spectrum of azetidine has been measured and analyzed to yield an estimate for the nitrogen inversion barrier: $\Delta G^{\ddagger}$ (154 K) = 30 kJ mol^{-1}. Approximate values for the activation enthalpy, $\Delta H^{\ddagger} = 21 \pm 4$ kJ mol^{-1}, and entropy, $\Delta S^{\ddagger} = -45 \pm 25$ J mol^{-1} K^{-1}, were also estimated. The equilibrium geometry and the geometry of the transition structure of azetidine were determined by ab initio RHF molecular orbital theory (Figures 1 and 2). The contribution of electron correlation energy was estimated to third order in Moller-Plesset perturbation theory (MP3), and the barriers were corrected for zero-point vibrational energy differences. The values of the barrier thus derived (RHF + ZPVE 21.6 kJ mol^{-1}; MP3 + ZPVE 27.1 kJ mol^{-1}) confirm that the inversion barrier in azetidine is low as is typical of unhindered amines and not elevated by angular constraints imposed by the ring, as happens in aziridine.

Unlike ammonia and aziridine, the normal vibrational mode with the lowest frequency in azetidine (Figure 3) does not lead directly along the reaction coordinate but rather involves deformation of the ring skeleton. In the transition structure of each of the three compounds, however, the normal mode with the imaginary frequency (Figure 4) involves almost exclusively out-of-plane motion of the NH bond and is therefore aligned with the reaction coordinate at the top of the barrier.

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Influence of Disc-Rod-Sphere Phase Transitions in Nematic Lyotropics on a Unimolecular Isomerization Reaction

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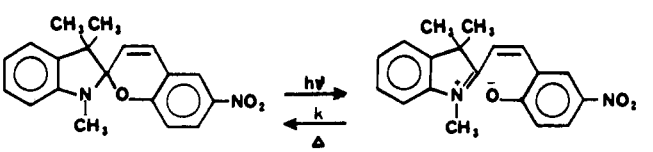
Abstract: The unimolecular isomerization of a photochromic merocyanine to an indolinospiropyran was performed in the nematic lyophases formed by potassium laurate (KL) or sodium decyl sulfate (SDS) with 1-decanol and water. In both systems there are discontinuities in reaction rates as a function of concentration or temperature which correspond to the phase transitions from disc- to rod- to sphere-like aggregates. Because of the change in molecular shape during the reaction, the order parameters of the reactant and products are quite different, and also reflect the differences between the rod- and disc-like phases in their ability to order the solute. The micropolarity and bulk viscosities of these phases are not very different, but microviscosity changes are the most likely explanation for the rate discontinuities at the phase transitions.

It has recently been established that bimolecular reactions conducted in nematic lyotropic liquid crystalline phases are profoundly influenced by the nature of the aggregate.[1] Such nematic lyotropic phases consist of either cylindrical (N_C) or disk-like (N_L) aggregates, and a phase transition can occur between them by changing either the temperature of the system or the concentration of one of the phase constituents.[2] The isotropic (I) phases of these same systems are thought to consist of conventional spherical micellar aggregates. Thus, in typical experiments disc-rod-sphere transitions can be examined with respect to their influence on kinetics and products of a variety of reactions.

Several factors can be involved in modulating the reactivity of a solute in these media; the local order, polarity, viscosity, as well as the sites of solubilization may change with aggregate size and shape. To simplify the problem, we undertook a study of a

Scheme I



2 1

unimolecular reaction—the isomerization of a photochromic merocyanine **1** to an indolinospiropyran[3] **2** (Scheme I)—in two nematic lyophases. The first phase consists of potassium laurate (KL), 1-decanol, and water, whereas the second contains sodium decyl sulfate (SDS), 1-decanol, and water. The phase diagrams of these systems have been studied in detail,[4,5] and both have easily

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