present calculations, while covalency effects seem to play a major role. This explanation would be also in line with the low $A_{\parallel}$ values observed in blue copper proteins where sulfur donor atoms are known to be present in the copper(II) coordination sphere.[48-50]

It seems, therefore, that MS-Xα is indeed able to describe the spectral properties of transition metal complexes, in a not too time-consuming way. Allowing for overlapping spheres appears to be absolutely necessary to improve the agreement with experimental data, and also the inclusion of higher order spherical harmonics may have a positive influence on the calculated values. However, we did not find improvement better than 10% by including harmonics up to $l = 5$.

At the moment the main limitations for the calculation of the EPR parameters is that the spin-orbit-dependent terms are available only through a perturbation procedure while it would be desirable to use a complete relativistic approach. This does not seem to be possible, in short, but less crude approaches than the one we also used should be attempted.

Other possible improvements of Xα model might be attempted following suggestions which were put forward from the analysis of Fermi contact hyperfine constants in atoms and ions. It was shown for ions, that, the MS-Xα model can yield results comparable with those obtained using the HF method either changing the form of the exchange potential or using different α values for different spins.[45,51-53] While the first type of correction cannot be easily applied to solids, the second might in principle be used. We tried this approach in the present calculation but did not find any substantial improvement, so that we preferred to stay with the traditional α values.

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The 1,2 Hydrogen Shift as an Accompaniment to Ring Closure and Opening: Ab Initio MO Study of Thermal Rearrangements on the C_2H_3N Potential Energy Hypersurface

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Abstract: Ab initio electronic structure calculations employing both 4-31G and DZP (double-ζ plus polarization) basis sets have been made for equilibrium geometries and transition states involved in thermal rearrangements on the C_2H_3N potential energy hypersurface. The principal rearrangements studied are those involving vinyl nitrene, 2*H*-azirine, methyl isocyanide, and acetonitrile. From the computed energies of stationary points and from the pathways connecting these points, several conclusions are drawn. First, singlet vinyl nitrene, although possessing a nonplanar equilibrium geometry, can undergo a ring closure with only a modest activation energy to form 2*H*-azirine. Second, the combined 1,2 hydrogen shift and ring opening required to form acetonitrile from 2*H*-azirine proceeds optimally but indirectly via methyl isocyanide as an intermediate. Thus hydrogen transfer precedes C–N bond breakage, necessitating a subsequent ring closure and reopening. Third, although no direct pathway leading from 2*H*-azirine to acetonitrile was located, there is a higher energy but direct pathway leading to acetonitrile from an excited singlet state of vinyl nitrene.

Introduction

The C_2H_3N molecular system exhibits a number of stable structures (local energy minima) including 1*H*-azirine, 2*H*-azirine, ketenimine, methyl isocyanide, and acetonitrile (methyl cyanide). The rearrangement of methyl isocyanide to acetonitrile has been the subject of numerous theoretical and experimental investigations,[1-6] and is thus the best understood rearrangement of C_2H_3N. Considerable experimental and theoretical attention has also been given to the photochemical rearrangements of 2*H*-azirine and of substituted azirines.[7-12] Some related molecular systems which exhibit numerous rearrangements[13] include the isoelectronic CHNO system,[14,15] which has been the subject of several theoretical investigations, and the C_6H_5N system,[16,17] which includes the species phenyl nitrene and cyanocyclopentadiene. The thermal rearrangements in the latter system resemble those in the smaller C_2H_3N system which is the subject of our present investigation.

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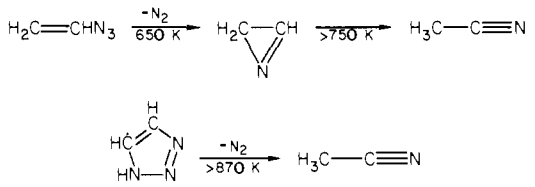
A series of C_2H_3N rearrangements which have recently been studied[18,19] are those initiated by the gas-phase pyrolysis of vinyl azide or of its tautomer 1*H*-1,2,3-triazole. In these experiments the formation of various C_2H_3N species such as 2*H*-azirine and acetonitrile was monitored by UV PES (UPS). The principal conclusions from these studies were that vinyl azide decomposes at 650 K to form 2*H*-azirine and N_2, with the azirine converting to acetonitrile above 750 K, and that the more stable 1*H*-1,2,3-triazole decomposes to acetonitrile and N_2 above 870 K. It is



the purpose of the present investigation to explore theoretically the C_2H_3N hypersurface in order to determine the energies and geometries of the transition states (saddle points) separating the various stable molecular forms involved in these transformations which overall couple a 1,2 hydrogen shift[20] with ring closure and opening.

Methods

Ab initio calculations for the C_2H_3N molecular system were carried out at the Institute for Molecular Science (IMS) using the IMSPACK series of programs and at the University of Michigan using the GAUSSIAN 80 program.[21] Equilibrium structures and saddle points were located using energy gradients at the SCF (single determinantal) level with an extended (4-31G) basis set. Energy differences were computed using both 4-31G and polarization basis sets, the latter being a double-ζ (DZ) basis set augmented by polarization functions for all atoms (DZP).[22,23] These computational levels are designated as HF/4-31G and HF/DZP//HF/4-31G, respectively. The DZP basis set either included all six second-order Gaussians for each C or N atom, giving a total of 63 basis functions for C_2H_3N, or, in some cases, included only the five true *d* functions for each C or N, giving a total of 60 basis functions for C_2H_3N. The two DZP basis sets are designated as DZP(6) and DZP(5), respectively, with the unspecified designation DZP referring to DZP(6). In a few cases geometries were reoptimized at the SCF level using the DZP(6) basis set; this level is designated HF/DZP.

Correlation effects were incorporated by second-order Møller–Plesset perturbation theory (MP2) or by configuration interaction involving single and double electronic excitations (CISD); with the DZP basis set and HF/4-31G optimized geometries these levels are designated as MP2/DZP//HF/4-31G and CISD/DZP//HF/4-31G, respectively. The MP2 and CISD calculations assumed frozen cores, while the CISD calculations assumed in addition several frozen virtual orbitals, three with both the 4-31G and DZP(5) basis sets. Quadruple excitation corrections (QC) were estimated by the Davidson–Silver procedure.[24]

Two methods were used for the location of transition states (saddle points). The first of these is the energy minimization method,[25,26] in which the energy as a function of n internal coordinates is minimized with respect to $n-1$ coordinates. The energy and geometry are thus parametrically dependent upon the remaining coordinate, say x_n, and may be represented by an energy profile $V(x_n)$ and a pathway $\mathbf{P}(x_n)$, where $\mathbf{P}(x_n)$ is an $n-1$ component vector comprised of the optimized coordinates $x_1(x_n), x_2(x_n), \ldots, x_{n-1}(x_n)$. One of us has recently shown[26,27] that a maximum in $V(x_n)$ necessarily occurs at a transition state provided that the pathway leads continuously from reactants to products and that the surface is describable by a quadratic form in the neighborhood of the maximum. Under the weaker condition that the pathway be continuous only along some segment including a maximum in $V(x_n)$, it was also shown that a maximum can only occur at a transition state, although the transition state may not be for the reaction of interest. Although an injudicious choice of the coordinate x_n may result in a failure[25,26] to locate any transition state, much less the desired transition state, one merit of the method is that a stationary point located by its use is known, without the necessity of making a second-derivative test, to be a saddle point having one and only one negative eigenvalue of the Hessian matrix, that is, to be a transition state.

The second method used to locate transition states involves an alternating sequence of energy maximizations along a single coordinate, say x_n, and energy minimizations with respect to the remaining $n-1$ internal coordinates.[28] The single coordinate x_n is typically taken to correspond to a linear synchronous transit pathway from reactants to products.[29] In this method it is necessary to be able to compute gradients with respect to coordinates which are linear combinations of the customary internal coordinates (bond angles and lengths). Further, it is necessary to establish that a transition state, once located, does indeed lie on a pathway connecting the desired reactants and products, although the above definition of x_n may make this method more likely to succeed than the energy minimization method. The intrinsic reaction coordinate (IRC)[30] may be followed in both directions from the transition state in order to establish the identity of the species connected by the pathway containing the given transition state.

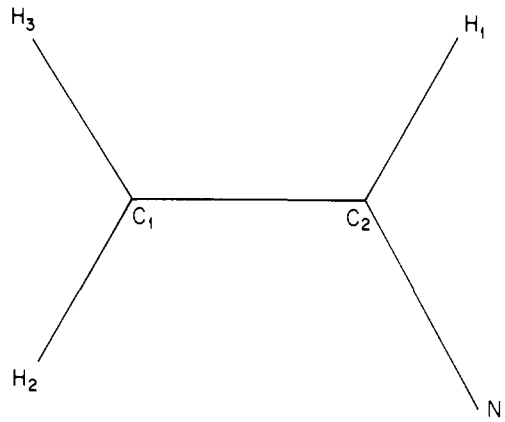


Figure 1. Atom designations used in defining internal coordinates in Table III for C_2H_3N. Structure shown to scale for $1\pi^2n^2$ state of vinyl nitrene.

Results

A. Vinyl Nitrene. The first molecule considered was singlet vinyl nitrene, as it is possibly the product initially formed by loss of N_2 from vinyl azide. Another possibility is that the ring closure to form 2*H*-azirine accompanies the loss of N_2 in such a way that the free nitrene itself is not formed. Subject to the constraint of planar geometry, an equilibrium geometry was located at the HF/4-31G level. The DZP energy was then computed at the 4-31G equilibrium geometry. As a test of the HF/DZP//HF/4-31G level of calculation, the geometry was reoptimized, but still constrained to be planar, using the DZP basis set. The energies in Table I show only a modest lowering of 1.2 kJ mol^{-1} from reoptimization of the planar geometry. In each case the

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electronic configuration is $1\pi^2n^2$ rather than $1\pi^22\pi^2$.

The HF/4-31G planar structure for this state of singlet vinyl nitrene is characterized by internal coordinates (angströms and degrees) of C_1–C_2 = 1.341, C_2–N = 1.364, and ∠N–C_2–C_1 = 119.0 and ∠H–C_2–C_1 = 119.5. The full list of HF/4-31G coordinates is given in Table III and is based on the definitions in Figure 1. The reoptimized HF/DZP structure is similar, with C_1–C_2 = 1.357, C_2–N = 1.349, ∠N–C_2–C_1 = 118.4, and ∠H–C_2–C_1 = 118.9.

Of particular significance is the result that a planar geometry for singlet vinyl nitrene is unstable with respect to an out-of-plane bending mode. This is revealed by our calculation at the HF/DZP level of the eigenvalues of the mass-weighted Cartesian force constant (Hessian) matrix associated with the out-of-plane displacements. The matrix was computed by numerical (first-difference) differentiation of the analytically computed gradient and possessed one negative eigenvalue, corresponding to a twisting of the CH_2 group with respect to the CHN group.

Given the instability found at the HF/DZP level for the $1\pi^2n^2$ singlet state of planar vinyl nitrene with respect to an out-of-plane deformation we searched at the HF/4-31G level for a nonplanar equilibrium geometry. We located a nonplanar local minimum with an energy below that of the planar structure by 2.2 kJ mol^{-1} at the HF/4-31G level and by 7.2 kJ mol^{-1} at the HF/DZP//HF/4-31G level. The principal difference between the planar and nonplanar structures (Table III) is in their dihedral angles; the H_3–C_1C_2–N angle is 14.1° in the nonplanar form as compared to 0° in the planar form.

In order to have a more reliable value for the energy difference between the planar and nonplanar forms, the energies were recomputed at the CISD/DZP(5)//HF/4-31G level; the energy difference was found to be 20.8 kJ mol^{-1}. When higher order correlation effects (QC) were included via the Davidson–Silver procedure, the nonplanar form is found at this CI(SD+QC)/DZP(5)//HF/4-31G level to be 29.7 kJ mol^{-1} lower in energy than the unstable planar form (Table II).

B. Other Electronic States of Vinyl Nitrene. We have computed HF/4-31G optimized geometries and HF/DZP//HF/4-31G energies for several electronic states of vinyl nitrene other than the $1\pi^2n^2$ singlet described above. The energies are given in Tables I and II and the geometries in Table III. First, there is the closed-shell singlet $1\pi^22\pi^2$ with a HF/DZP//HF/4-31G energy which is only 24.1 kJ mol^{-1} above that of the $1\pi^2n^2$ singlet. This and all other energy differences given in Table II are adiabatic, not vertical, differences. Unlike the $1\pi^2n^2$ state, the $1\pi^22\pi^2$ state is associated with a planar structure which is stable with respect to out-of-plane deformations. The most striking difference in their internal coordinates (Table III) is the very large C_1–C_2–N angle of 134.6° in the $1\pi^22\pi^2$ state as compared with 119.0° in the $1\pi^2n^2$ state. Both the C_1–C_2 and the C_2–N distances are smaller in the higher energy state. As before, we also carried out CISD calculations, with $1\pi^22\pi^2$ as the reference configuration. The CI(SD+QC)/DZP(5)//HF/4-31G energy (Table II) is found to be +51.8 kJ mol^{-1} relative to that for the nonplanar structure.

We have also carried out unrestricted Hartree–Fock (UHF) calculations for the "triplet" (M_s = +1) and "singlet" (M_s = 0) A″ states of the open-shell configuration $1\pi^2n^12\pi^1$, with the results being given in Tables I–III. The "triplet", with a UHF/DZP(5)//UHF/4-31G energy 279.7 kJ mol^{-1} *below* that of the $1\pi^2n^2$ singlet, is characterized by an expectation value of S^2 equaling 2.269, close to the value of 2 for a "pure" triplet. The "singlet", with a UHF/DZP(5)//UHF/4-31G energy 212.4 kJ mol^{-1} below that of the $1\pi^2n^2$ singlet is characterized by an expectation value of S^2 equaling 1.174, thus indicating substantial triplet character in the UHF wave function and thus a poor representation of a true spin singlet. These results do indicate that the electronic ground state of vinyl nitrene is undoubtedly a triplet, as has also been found in the MNDO studies[19] of Bock et al. and in ab initio studies[31,32] for the related molecule methyl nitrene. However, in

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Table I. Energies (au) for C_2H_3N Equilibrium Structures and Transition States

molecule	symmetry	4-31G HF	4-31G CISD	4-31G CI(SD+QC)	DZP(6)//HF/4-31G HF	DZP(6) HF	DZP(5)//HF/4-31G HF	DZP(5)//HF/4-31G MP2	DZP(5)//HF/4-31G CISD	DZP(5)//HF/4-31G CI(SD+QC)
vinyl nitrene										
$1\pi^2n^2$ (TS1)	C_s	−131.575 38	−131.832 35	−131.859 41	−131.792 39	−131.792 86	−131.791 87	−132.171 82	−132.164 93	−132.209 81
a^2a^2	C_1	−131.576 22	−131.839 95	−131.872 07			−131.794 62		−132.172 88	−132.221 12
$1\pi^22\pi^2$	C_s	−131.564 11	−131.822 94	−131.851 12	−131.783 22		−131.782 77	−132.159 99	−132.156 04	−132.201 33
$1\pi^2n^12\pi^1$ (M_s = +1)[a]	C_s	−131.683 43					−131.898 96			
$1\pi^2n^12\pi^1$ (M_s = 0)[a]	C_s	−131.652 07					−131.873 31			
2*H*-azirine	C_s	−131.613 03	−131.899 67	−131.930 52	−131.863 46	−131.864 81	−131.862 75	−132.286 33	−132.260 28	−132.307 18
TS2	C_s	−131.509 85			−131.776 20		−131.775 44	−132.219 24	−132.183 37	−132.236 65
methyl isocyanide	C_{3v}	−131.694 23			−131.920 62	(−131.920 03)[c]	−131.920 20		−132.306 29	−132.350 71
TS3	C_s	−131.602 60			(−131.842 04)[b]	(−131.847 56)[c]	−131.844 39		−132.231 88	−132.279 04
acetonitrile	C_{3v}	−131.728 29			−131.951 48		−131.950 97		−132.340 43	−132.385 44
TS4	C_1	−131.532 58					−131.760 16	−132.189 53	−132.160 45	−132.216 25
ketenimine	C_s	−131.673 47					−131.897 63		−132.286 99	−132.332 40

[a] UHF triplet or singlet for M_s = +1 or 0. [b] Reference 5; DZP basis set used at geometry taken from ref 3. [c] Reference 6; the *d* polarization functions constructed from *p* functions.

Table II. Relative Energies (kJ mol^{-1}) for C_2H_3N Equilibrium Structures and Transition States

molecule	symmetry	4-31G HF	DZP(6)//HF/4-31G HF	DZP(6) HF	DZP(5)//HF/4-31G HF	CISD	CI(SD+QC)
vinyl nitrene							
$1\pi^2n^2$ (TSl)	C_s	401.7	417.6	0	417.6	460.6	461.1
a^2a^2	C_1	399.6			410.4	439.7	431.4
$1\pi^2 2\pi^2$	C_s	431.4	441.7		441.4	484.1	483.2
$1\pi^2n^1 2\pi^1$ ($M_s = +1$)[a]	C_s	117.8			136.5		
$1\pi^2n^1 2\pi^1$ ($M_s = 0$)[a]	C_s	200.1			203.8		
2*H*-azirine	C_s	302.9	231.0	−188.9	231.4	210.4	205.4
TS2	C_s	573.6	460.1		460.6	412.1	390.8
methyl isocyanide	C_{3v}	89.5	81.0	(−333.8)[b]	80.8	89.5	91.2
TS3	C_s	330.0		(−143.6)[b]	279.5	284.9	279.5
acetonitrile	C_{3v}	0	0		0	0	0
TS4	C_1	514.2			500.8	472.4	444.3
ketenimine	C_s	143.9			139.7	140.2	139.3

[a] UHF triplet or singlet for $M_s = +1$ or 0. [b] Reference 6.

the remainder of this study we shall confine our attention to rearrangements involving the closed-shell singlet states of vinyl nitrene and of other molecular species in the C_2H_3N system.

We may summarize our vinyl nitrene results (Table II) as follows: the ground state is a spin triplet with an energy only 136.5 kJ mol^{-1} higher than that of acetonitrile at the HF/DZP(5)//HF/4-31G level; the planar singlet derived from the $1\pi^2n^2$ configuration is unstable with respect to an out-of-plane deformation; the planar singlet derived from the $1\pi^2 2\pi^2$ configuration is stable but at a higher energy. Further conclusions about vinyl nitrene are given in section D.

Before proceeding to discuss other C_2H_3N species, it is interesting to note that a gas-phase reaction[33] presumably producing triplet vinyl nitrene is that of N(^{4}S) with C_2H_4, displacing an H atom. A related reaction is that of O with C_2H_4, producing the vinyloxy radical CH_2CHO, with one more electron than vinyl nitrene. The HF/DZP optimized geometry reported[34,35] for the ^{2}A″ state with configuration $\pi_{CC}{}^2\pi_O{}^1$ is very similar to our singlet ($\pi_{CC}{}^2$) vinyl nitrene HF/DZP geometry, with C–C = 1.335 Å, C–O = 1.325 Å, and ∠C–C–O = 120.8° in the vinyloxy radical as compared with C–C = 1.325 Å, C–N = 1.349 Å, and ∠C–C–N = 118.4° in the nitrene. However, the lowest energy state of the radical was found to be a ^{2}A″ state described as $\pi_C{}^1\pi_{CO}{}^2$, corresponding to the formyl methyl radical.

C. 2*H*-Azirine. An optimized geometry for 2*H*-azirine (symmetry C_s) was determined at the HF/4-31G level, with the energy recalculated using the DZP basis set. As with planar vinyl nitrene, a reoptimization of the geometry using the DZP basis set was also carried out. As shown in Table II, the energy of 2*H*-azirine relative to planar vinyl nitrene is almost twice as great (−186.6 kJ mol^{-1}) at the HF/DZP//HF/4-31G level as it is at the 4-31G level (−98.8 kJ mol^{-1}). It appears that the polarization functions in the DZP basis produce a greater lowering of the energy in the strained ring system 2*H*-arizine than they do in the open vinyl nitrene system. The optimized HF/DZP and the HF/DZP//HF/4-31G values of the difference differ, however, by only 2.3 kJ mol^{-1}. Further, correlation effects also lower the energy of 2*H*-azirine more than they do that of planar vinyl nitrene as indicated in Table II by the relative energy for 2*H*-azirine of −255.6 kJ mol^{-1} at the CI(SD+QC)/DZP(5)//HF/4-31G level as compared with the HF/DZP(5)//HF/4-31G value of −186.1 kJ mol^{-1}. The latter value is not significantly different from either the HF/DZP(6)//HF/4-31G (−186.5 kJ mol^{-1}) or the HF/DZP(6) (−188.9 kJ mol^{-1}) values.

We have not computed the energy of the isomer 1*H*-azirine, although reported[36] GTO energies without geometry optimization of −130.5478 and −130.5935 au for the 1*H* and 2*H* isomers, respectively, suggest a much higher energy (120.0 kJ mol^{-1} in these calculations) for the 1*H* isomer.

D. Ring Closure: Vinyl Nitrene to 2*H*-Azirine. It was pointed out in section A that planar vinyl nitrene is unstable with respect to an out-of-plane deformation. Geometry optimizations were carried out at the HF/4-31G level for a series of six values of the N–C_2–C_1 angle θ, ranging from 119.0°, the value in planar vinyl nitrene, to 70.1°, the value in 2*H*-azirine. The optimizations were complete with respect to the 11 remaining internal coordinates. At each θ the C_s symmetry was deliberately broken in the initial coordinates. Thus the ring closure described by decreasing θ was found to be accompanied by CH_2 rotation, leading without further constraint to 2*H*-azirine. The HF/DZP//HF/4-31G energies along this pathway were found to decrease smoothly to the 2*H*-azirine value, suggesting that there is little or no barrier to formation of 2*H*-azirine from vinyl nitrene, despite our location at the HF/4-31G level of a nonplanar minimum for vinyl nitrene with θ = 116.1°. Thus the nonplanar equilibrium structure corresponds to a shallow minimum.

Our conclusion is that singlet planar vinyl nitrene is itself a transition state for the interchange of the two CH_2 hydrogens in 2*H*-azirine by a process of ring opening and CH_2 rotation. Thus this form is designated as a transition state (TS1) in Tables I–III. Conversely, vinyl nitrene, if formed, should either close to form 2*H*-azirine or cross into the triplet manifold; we do not expect significant stability for the nonplanar singlet structure.

E. Ring Opening: 2*H*-Azirine to Methyl Isocyanide. Our several attempts to locate the transition state for the ring opening of 2*H*-azirine to produce the stable product acetonitrile, as observed by Bock and Solouki,[18] produced a surprise. The optimum route to acetonitrile appears to proceed via methyl isocyanide. That is, the 1,2 hydrogen shift to form a CH_3 group accompanies the breakage of the C–C, not the H_2C–N bond in 2*H*-azirine. A transition state (TS2 in Tables I–III) with C_2 symmetry and a HF/DZP//HF/4-31G energy of +229.0 kJ mol^{-1} relative to 2*H*-azirine (only +42.5 kJ mol^{-1} relative to vinyl nitrene) was located by minimizing the HF/4-31G energy with respect to 11 internal coordinates for a succession of 13 values of the H–C_2–C_1 angle α, ranging from 150.1°, the value in 2*H*-azirine, to 19.0°, the value in methyl isocyanide, where this H atom is attached to C_1 rather than C_2. At each value of α the symmetry C_s was restored by the optimization process, not by constraint. The maximum along this energy optimization pathway occurs near α = 70° with the energy stated above (Table II). Since this maximum occurs along a pathway leading continuously (by inspection) from 2*H*-azirine to methyl isocyanide, it is *necessarily*[26] a saddle point with one and only one negative eigenvalue of the Hessian matrix. Thus the latter matrix need not be, and was not,

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Table III. Internal Coordinates for C_2H_3N Equilibrium Structures and Transition States at HF/4-31G Level

coordinate[a,b]	vinyl nitrene $1\pi^2n^2$ (TS1)	a^2a^2	$1\pi^22\pi^2$	$1\pi^2n^12\pi^1$ ($M_s = +1$)	$1\pi^2n^12\pi^1$ ($M_s = 0$)	2*H*-azirine	methyl isocyanide	TS2[c]	TS3[d]	TS4[e]	acetonitrile	ketenimine
C_1–C_2	1.341	1.346	1.324	1.386	1.399	1.457	2.580[f]	1.758	1.875	1.388	1.455	1.299
C_2–N	1.364	1.347	1.341	1.337	1.305	1.241	1.161	1.261	1.187	1.220	1.142	1.212
C_2–H_1	1.077	1.077	1.092	1.077	1.078	1.062	3.117[g]	1.135	1.070[h]	1.164	2.092[o]	1.946[p]
C_1–H_2	1.072	1.071	1.070	1.071	1.070	1.070	1.079	1.070	1.070	1.069	1.081	1.070
C_1–H_3	1.073	1.073	1.068	1.070	1.070	1.070	1.079	1.070	1.070	1.072	1.081	1.070
C_1–C_2–N	119.0	116.1	134.6	123.6	124.0	70.1	0.0	54.8	75.8	151.8	180.0	176.6
C_1–C_2–H_1	119.5	120.9	121.7	119.9	119.4	150.1	19.0	70.0	84.3[i]	84.1	29.0	157.7
H_2–C_1–C_2	119.5	119.4	122.0	121.4	121.0	120.6	109.9	116.2	114.4[j]	119.6	110.3	120.6
H_3–C_1–C_2	122.3	122.4	120.2	120.9	120.8	120.6	109.9	116.2	114.4[k]	121.1	110.3	120.6
H_1–C_2–C_1–N	180.0	168.4	180.0	180.0	180.0	180.0		180.0	180.0[l]	154.9		180.0
H_2–C_1–C_2–N	0.0	14.1	0.0	0.0	0.0	−99.2		−103.9	−67.3[m]	162.2		−90.4
H_3–C_1–C_2–N	180.0	−160.2	180.0	180.0	180.0	99.2		103.9	67.3[n]	−30.8		90.4

[a] See Figure 1 for designations of atoms. [b] The first five coordinates are distances in Å; the remaining are angles or dihedral angles in degrees. [c] TS2 denotes transition state connecting 2*H*-azirine and methyl isocyanide. [d] TS3 denotes transition state connecting methyl isocyanide and acetonitrile. [e] TS4 denotes transition state connecting excited vinyl nitrene ($1\pi^22\pi^2$) and acetonitrile. [f] The bonded distance C–N is 1.419. [g] The bonded distance C_1–H_1 is 1.079. [h] The distance C_1–H_1. [i] The angle N–C_1–H_1. [j] The angle N–C_1–H_2. [k] The angle N–C_1–H_3. [l] The dihedral angle H_1–C_1–N–C_2. [m] The dihedral angle H_2–C_1–N–C_2. [n] The dihedral angle H_3–C_1–N–C_2. [o] The bonded distance C_1–H_1 is 1.081. [p] The bonded distance H_1–N is 1.002.

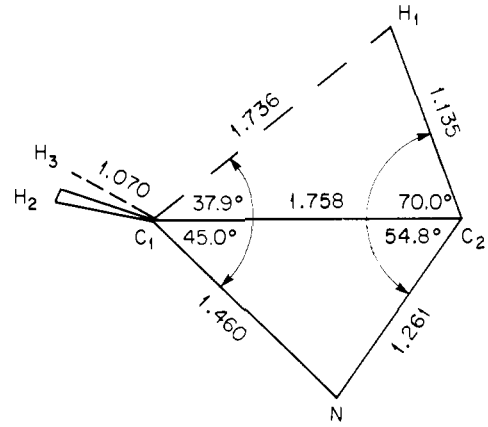


Figure 2. Structure of the transition state (TS2) connecting 2*H*-azirine and methyl isocyanide along a pathway maintaining C_s symmetry by energy minimization rather than by constraint. Structural parameters are those obtained at HF/4-31G level.

computed at this stationary point. However, we did follow the IRC in both directions from TS2, verifying that it does indeed lie on a pathway connecting 2*H*-azirine and methyl isocyanide. The shape of this transition state (TS2) is shown in Figure 2. As noted in Table II, the transformation of 2*H*-azirine to methyl isocyanide is exothermic by 150.2 kJ mol^{-1} at the HF/DZP//HF/4-31G level. The shortness of the C_2–H_1 distance (1.135 Å) as compared with the C_1–H_1 distance (1.736 Å) indicates that H_1, which is the H atom being transferred, is essentially bonded to C_2 at TS2, much as it is in the reactant 2*H*-azirine (C_2–H_1 = 1.062 Å), a result compatible with the exothermicity of the transformation to methyl isocyanide.

F. Methyl Isocyanide to Acetonitrile. To complete the passage from 2*H*-azirine to acetonitrile via methyl isocyanide it is necessary to pass over another transition state. Although the rearrangement of methyl isocyanide to acetonitrile has been thoroughly investigated by others,[3-6] we have reexamined this region of the C_2H_3N surface in order to have a consistent set of energies. Tables I–III give our results together with some values taken from the literature. The relevant transition state (TS3) has a HF/DZP(5)//HF/4-31G energy of 198.7 kJ mol^{-1} relative to methyl isocyanide or 48.1 kJ mol^{-1} relative to 2*H*-azirine. By comparison, the energy of TS2, on the pathway from 2*H*-azirine to methyl isocyanide, is 229.2 kJ mol^{-1} at the same level of calculation relative to 2*H*-azirine, clearly much higher than that of TS3. Our conclusion is that 2*H*-azirine molecules with sufficient energy to surmount TS2 can easily continue over TS3 to form acetonitrile. It should be noted that the combined pathway maintains C_s symmetry throughout and may be described as a ring opening coupled with a 1,2 hydrogen shift to form methyl isocyanide followed by the ring closure and reopening required to convert the isocyanide to the cyanide (acetonitrile).

G. Excited Vinyl Nitrene to Acetonitrile. Although we have located a reaction pathway proceeding from 2*H*-azirine to acetonitrile via methyl isocyanide, passing through two transition states (TS2 and TS3 in Table I) and preserving C_s symmetry throughout, we decided to search for a transition state along a more direct pathway. This search was made according to the second method described in the Methods section; namely, a linear synchronous transit pathway was defined using the HF/4-31G optimized coordinates of 2*H*-azirine and acetonitrile, with the single variable x_n representing the degree of progression along this coordinate. Not only does this coordinate by definition involve the coupling of ring opening with the 1,2 hydrogen shift, together with changes in all other bond lengths and angles, but also there was imposed a 60° rotation of the CH_2 group as it receives an H to become a CH_3 group. That is, the CH_3 group in H_3CCN was taken to be rotated by 60° relative to the orientation it would have had if the H were transferred with C_s symmetry maintained. Thus the molecule possessed only C_1 symmetry except at the reactant (C_s) and product (C_{3v}) limits.

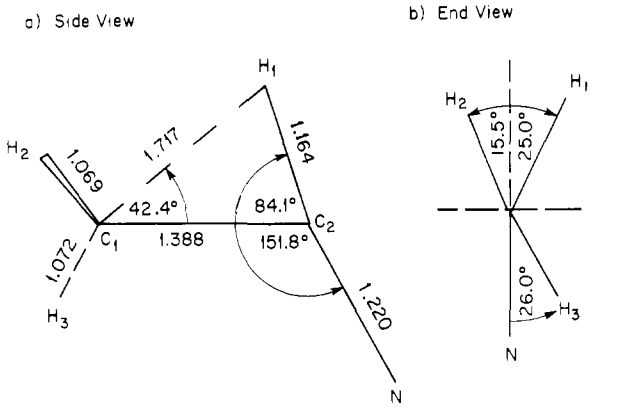


Figure 3. Structure of the transition state (TS4) connecting excited vinyl nitrene and acetonitrile along a pathway with only C_1 symmetry except at the reactant and product limits. Structural parameters are those obtained at HF/4-31G level. (a) Side view. (b) End view showing angles between bonds and the CCN plane.

Using the above procedure together with a 4-31G basis set, we located a transition state (TS4) with only C_1 symmetry (Figure 3). The HF/DZP(5)//HF/4-31G energy (Table II) is 83.2 kJ mol^{-1} relative to singlet vinyl nitrene or +268.4 kJ mol^{-1} relative to 2*H*-azirine. When we followed the IRC, we discovered that, whereas one direction leads to acetonitrile as expected, the other direction leads not to 2*H*-azirine, but rather to the excited $1\pi^2 2\pi^2$ singlet state of planar vinyl nitrene! It is seen in Figure 3 that the transition state TS4 resembles a distorted vinyl nitrene, with a large ∠C–C–N of 152.0°. Again the shortness of the C_2–H_1 distance (1.164 Å) as compared to the C_1–H_1 distance (1.717 Å) indicates that H_1 is essentially bonded to C_2 at TS4, much as it is in the reactant excited vinyl nitrene (1.092 Å). Despite a number of attempts, we have not been able to locate a "direct" pathway leading from 2*H*-azirine to acetonitrile.

H. Correlation Effects on Transition States. The transition state TS4 lies 40.2 kJ mol^{-1} at the HF/DZP(5)//HF/4-31G level above TS2. Although they lie on different pathways, excited vinyl nitrene to acetonitrile and 2*H*-azirine to methyl isocyanide, respectively, both could be involved in conversions of C_2H_3N species to acetonitrile. Accordingly, correlation effects on these two transition state energies were calculated at the CISD level using the DZP(5) basis set. The resulting stabilizations are −0.40794 and −0.40028 au for TS2 and TS4, respectively. Additionally, the Davidson–Ssilver corrections (QC) are −0.05328 and −0.05581 au for TS2 and TS4, respectively, so that TS2 is more stabilized than TS4 by 13.5 kJ mol^{-1}, increasing their difference to 53.5 kJ mol^{-1} at this CI(SD+QC)/DZP(5)//HF/4-31G level. Thus the optimum route which we have located from 2*H*-azirine or vinyl nitrene to acetonitrile is that proceeding via methyl isocyanide. At this same level, TS2 lies 185.4 kJ mol^{-1} higher in energy than 2*H*-azirine; this barrier is comparable to our value of 188.3 kJ mol^{-1} or to the 189.5 kJ mol^{-1} value calculated[4] at the MBPT/DZP level for the barrier to isomerization of methyl isocyanide to acetonitrile via TS3. We also note that when correlation is included, the energy of TS2 not only falls below that of planar singlet vinyl nitrene (TS1), and thus below that of excited vinyl nitrene, but also falls below that of the nonplanar vinyl nitrene structure. The energy difference between TS2 and TS1 has values of +43.0, −124.5, and −70.3 kJ mol^{-1} at the HF/DZP(5)//HF/4-31G, MP2/DZP(5)//HF/4-31G, and CI(SD+QC)/DZP(5)//HF/4-31G levels, respectively. These results suggest that singlet vinyl nitrene lies at a very high energy and may not be formed as a free species during the pyrolysis of vinyl azide. Rather, as pointed out by Bock et al.,[19] N_2 elimination and ring closure to form 2*H*-azirine may occur simultaneously. Similarly we note that the energy of TS4, although higher than that of TS2, is lower than that of excited ($1\pi^2 2\pi^2$) vinyl nitrene at the MP2/DZP(5)//HF/4-31G or CI(SD+QC)/DZP(5)//HF/4-31G levels; it cannot be the transition state for the excited vinyl nitrene to acetonitrile rearrangement, as there must be another saddle point at a higher energy.

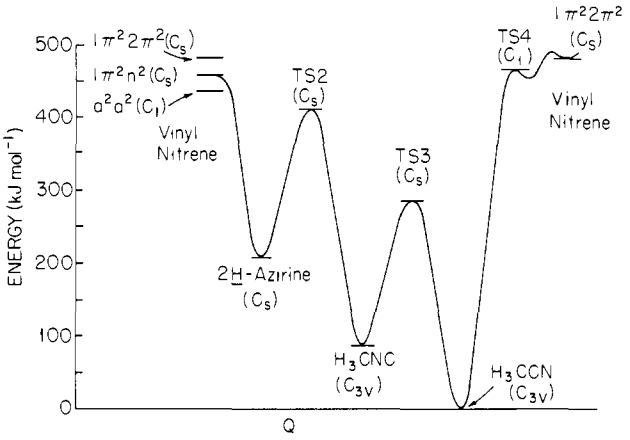
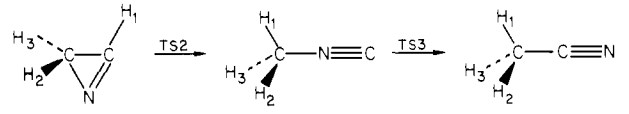


Figure 4. Summary of CISD/DZP(5) relative energies in kJ mol^{-1} at HF/4-31G geometries for the rearrangements of vinyl nitrene–2*H*-azirine–methyl isocyanide–acetonitrile. Structures of transition states TS2 and TS4 are given in Figures 2 and 3, respectively. The reaction coordinate is unspecified in the figure.

I. Ketenimine. Another C_2H_3N isomer is ketenimine, $H_2C{=}C{=}NH$, with symmetry C_s. Our geometry optimized HF/4-31G energy is −131.67347 au (Table I), slightly below a literature values[37] of −131.6731 au. It is the second most stable C_2H_3N species which we have considered, with an energy relative to acetonitrile which is not very sensitive to the level of calculation; the energy differences (Table III) in kJ mol^{-1} range from 143.9 at the HF/4-31G level to 139.3 at the CI(SD+QC)/DZP(5)//HF/4-31G level. We have searched for a transition state on a pathway leading from ketenimine to acetonitrile by a 1,3 hydrogen shift, but have not so far been successful in locating one. A C_2H_3N species not considered in our study is aminoacetylene, $H_2NC{\equiv}CH$.

Discussion and Summary

A least-motion pathway for the rearrangement of 2*H*-azirine to the more stable acetonitrile might simply involve a hydrogen shift coupled with ring opening (breaking of the C–N single bond), with a plane of symmetry maintained throughout the rearrangement. We were unable to find such a direct transition state. Instead we found an indirect pathway proceeding via methyl isocyanide (TS2 and TS3). The least-motion pathway described above simply does not provide an orbital on the CH_2 group for the attachment of the H being transferred, as the C–N bond being broken lies on the opposite side of the C–C bond. A possible solution to this dilemma is represented by the pathway which we have located. First, the H atom may attach itself to the CH_2 if the C–C bond is broken instead of the C–N single bond, leading



to the transition state (TS2) in Figure 1 and methyl isocyanide as an intermediate. Second, the passage to acetonitrile is completed via TS3.

We shown in Figure 4 a summary of relative energies at the CISD/DZP(5)//HF/4-31G level. The lowest spin-singlet of vinyl nitrene, designated as $a^2a^2(C_1)$, possesses a nonplanar equilibrium geometry but probably only a small barrier to ring closure to form 2*H*-azirine.

Under collision-free conditions, the 2*H*-azirine molecules that attain enough energy to go over the TS2 barrier have an energy well above the TS3 barrier (see Figure 4) and will finally form only acetonitrile. However, if collisions with walls or other molecules deactivate the system sufficiently, methyl isocyanide

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should be obtained as a product as well. No isocyanide has been reported in the experimental studies[18,19] of the rearrangements of 2*H*-azirine to acetonitrile. Apparently no attempt was made to identify methyl isocyanide, which in any event would be rapidly converted to acetonitrile if the temperature were 650 K or above.[38] There are also possibilities involving bimolecular pathways which we have not considered in this study. Finally, it is of interest that recent experimental studies[39] of the gas-phase thermal isomerization of 3*H*-isoxazoles to α-carbonylacetonitrile derivatives have pointed to 2*H*-azirines as intermediates.

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Registry No. Vinyl nitrene, 64987-66-2; 2*H*-azirine, 157-16-4; methyl isocyanide, 593-75-9; acetonitrile, 75-05-8; ketenimine, 17619-22-6.

Ab Initio CI Study of Chemical Reactions of Singlet and Triplet NH Radicals

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Abstract: Reactions of the NH radical in its low electronic states ($^3\Sigma^-$, $^1\Delta$, $^1\Sigma^+$, and $^3\Pi$) with hydrogen and ethylene have been investigated by the multireference double-excitation (MRD) CI method employing mainly the 4-31G basis set. The 4-31G** basis set has been utilized for special points of interest. It is confirmed that the relative energies of these low-lying states calculated by this method are in satisfactory agreement with the experimental data. The insertion of NH($^3\Pi$) into H_2 is predicted to proceed maintaining the planar (C_{2v}) symmetric structure with an extremely low-energy barrier. NH($^1\Delta$) inserts into hydrogen and cyclo-adds to ethylene with no barrier at all. The minimum-energy path for the addition of NH($^3\Sigma^-$) to ethylene has been searched for. The activation barrier height is calculated to be not larger than 24 kcal/mol. The CH_2CH_2NH radical has various local energy minima, among which the face-to face (FF) singlet diradical is the most stable. Cyclization of the singlet FF diradical to form the ground-state aziridine has virtually no energy barrier. It has been demonstrated that the singlet and triplet diradical states in the face-to-edge (FE) conformation are correlated with the first excited singlet (S_1) and the lowest triplet (T_1) state of aziridine, respectively. Implications of all these results are discussed in comparing the reactivities of CH_2 and O as isoelectronic homologues of NH.

I. Introduction

The imidogen radical NH is an intriguing chemical species which is isoelectronic with CH_2 and O. Despite an intuitive anticipation of a similarity of its chemical behavior to those of such isoelectronic homologues, its chemistry has hitherto been far less well explored. It has so far only been disclosed experimentally that the first excited singlet NH($^1\Delta$) inserts readily into a paraffin single bond in the gas[1] as well as in the liquid[2] phase, while the ground-state triplet NH($^3\Sigma^-$) can undergo addition toward radical species[3,4] and olefins[5] in the gas phase. The chemical reactivity of NH in its higher lying electronic states is still comparatively unknown. It is felt that systematic investigations of the chemistry of the NH radicals would not only be academically rewarding but practically important, particularly in relation to their possible participation in chemical cycles involved in the upper atmosphere.

Theoretical considerations of the characteristics of NH reactions have also been surprisingly scanty. The only example of such studies is an ab initio SCF treatment of the CH_2CH_2NH diradicals to be formed by the addition of NH($^3\Sigma^-$) to ethylene.[6] Emphasis there has been placed at the stabilities of such diradicals relative to aziridine as the ring-closed product. The results are highly illuminating but insufficient to be used at present as a theoretical guide for the reaction in question.

The present investigation employs ab initio MO configuration-interaction (CI) treatments for description of reactions in which the NH radicals in various low-lying electronic states ($^1\Delta$, $^1\Sigma^+$, $^3\Sigma^-$, and $^3\Pi$) are involved. Molecular hydrogen and ethylene were chosen as prototypes of reaction partners. Search for the minimum-energy paths and characterization of the electronic structures of the reacting systems along reaction paths are the matters of our primary concern. Particular attention has been paid to the diradical character as well as the thermochemical stability of the aforementioned CH_2CH_2NH intermediate. The state correlations of various stable conformations of the CH_2CH_2NH diradicals, both singlet and triplet, with ring-closed aziridine in different electronic states will also be elucidated. The results of these treatments provide an useful qualitative guide for the consideration of the dynamic phase of the NH reactions which

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