



A computational study of cyclopropylnitrene

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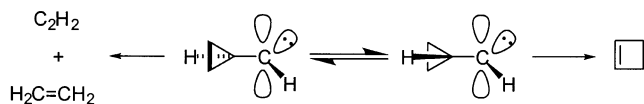
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Abstract—Calculations predict that singlet cyclopropylnitrene has a closed-shell configuration, in contrast to singlet phenylnitrene, and has little or no barrier to fragmentation. © 2002 Elsevier Science Ltd. All rights reserved.

Singlet methylcarbene ($\text{CH}_3\text{-C-H}$)¹ and singlet methylnitrene ($\text{CH}_3\text{-N}$)² are predicted to isomerize to ethylene and imine over barriers of 1–3 kcal/mol. Because these barriers are very small, these species have never been detected or chemically intercepted, and if they exist at all as true reactive intermediates, their lifetimes in solution must be sub-nanosecond.

Cyclopropylcarbenes are predicted to isomerize over larger barriers.³ In fact, cyclopropylcarbenes can be chemically intercepted and have lifetimes of ≈ 20 ns in solution at ambient temperature.⁴ The empty p orbital of the singlet carbene conjugates with a filled Walsh orbital of the cyclopropyl ring. This stabilizes the carbene and extends its lifetime.



This prompted us to calculate cyclopropylnitrene (**1**) to estimate its lifetime and suitability for laser flash photolysis studies. The calculations reveal important differences between cyclopropylcarbene and cyclopropylnitrene.

Geometry optimizations for singlet and triplet cyclopropylnitrenes were performed with the standard 6-31G* basis set,⁵ using complete active space (CAS) SCF calculations⁶ with a four-electron, four-orbital active space with GAUSSIAN-98^{7a} and with MOLCAS.^{7b} This (4,4) active space consisted of two p AO's on nitrogen and the highest occupied σ and

lowest unoccupied σ^* MOs of the two β C–C bonds of the cyclopropyl group.

The CASSCF(4,4)/6-31G* optimized bond lengths in the lowest electronic states (³A'', ¹A', and ¹A'') of cyclopropylnitrene **1** are shown in Fig. 1, and their relative energies are given in Table 1. The calculated singlet-triplet energy gap (ΔE_{ST}) of **1** is 27.88 kcal/mol at the CASPT2(8,8)/6-311G(2d,p) level with the triplet as the ground state. Experimentally, the singlet-triplet energy gap in methylnitrene is 31.2 kcal/mol, and with a triplet ground state.⁸ The calculated ΔE_{ST} of phenylnitrene is

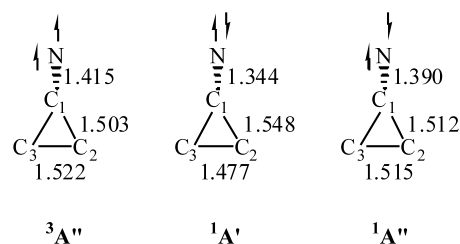


Figure 1. CASSCF(4,4)/6-31G* optimized bond lengths (Å) of three low-lying spin states of cyclopropylnitrene **1**.

Table 1. Relative energies (kcal/mol) of triplet and singlet cyclopropylnitrenes^a

Method	³ A''	¹ A'	¹ A''
CASSCF(4,4)/6-31G*	0.00	34.54	38.51
CASSCF(8,8)/6-31G*	0.00	30.68	39.04
CASPT2(8,8)/6-31G*	0.00	28.59	33.66
CASSCF(8,8)/6-311G(2d,p)	0.00	29.17	39.00
CASPT2(4,4)/6-311G(2d,p)	0.00	29.66	31.80
CASPT2(8,8)/6-311G(2d,p)	0.00	27.88	32.26

^a Energies were calculated with the CASSCF(4,4)/6-31G* optimized geometries, including corrections for differences in CASSCF(4,4)/6-31G* unscaled zero-point vibrational energies.

Keywords: cyclopropylnitrene; fragmentation reaction; CASSCF calculations.

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18.5 kcal/mol,⁹ phenylcarbene is $\approx 3\text{--}5$ kcal/mol,¹⁰ and cyclopropylcarbene is 1.5 kcal/mol.^{3a} Theory predicts that the aromatic nitrene has a smaller energy gap than its cyclopropyl analog, and unsurprisingly, that cyclopropyl nitrene has a larger ΔE_{ST} than cyclopropylcarbene.

The closed-shell singlet state ($^1A'$) has a shorter C–N bond length than the biradical-like open-shell singlet state ($^1A''$) in order to maximize conjugation with the ring. In phenylnitrene, the open-shell singlet state is ≈ 17 kcal/mol lower in energy than the closed-shell singlet.¹¹ However, in cyclopropyl nitrene, the energy of the closed-shell singlet is below that of the open-shell singlet at all levels of theory, illustrating the importance of the conjugative interaction. This interaction also reduces the ΔE_{ST} of cyclopropyl nitrene relative to methylnitrene by differential stabilization of the singlet state.

Thermolysis of azidocyclopropane led to hydrogen cyanide, ethylene, and 1-azetine.¹² Since singlet cyclopropyl nitrene prefers a closed-shell configuration, single-determinant methods should provide some insight into its preferences for rearrangement. Calculations on the optimal geometries of singlet cyclopropyl nitrene ($^1A'-1$), the reaction products, and possible transition states, **TS1** and **TS2**, were carried out at the HF/6-31G* level. The relative energies are given in Table 2.

At the HF/6-31G* level, the activation energy of the ring-expansion reaction ($1 \rightarrow \text{TS1} \rightarrow 2$) was 2.84 kcal/mol, and the activation energy of the fragmentation reaction ($1 \rightarrow \text{TS2} \rightarrow 3+4$) was 0.64 kcal/mol. Some calculated bond lengths for the intermediates and transition structure of the fragmentation reaction are shown in Fig. 2. The calculated activation energy of the ring-

expansion reaction is smaller than a published value of 9.3 kcal/mol, which was obtained by HF/3-21G calculations without a zero-point vibrational energy correction.¹³ From single-point energies (Table 2) at all correlated levels of theory attempted in this study (B3LYP, MP2 and CASPT2), singlet cyclopropyl nitrene is predicted to fragment spontaneously if one uses the HF/6-31G* derived geometries for the transition states. In addition, transition state searches with the (restricted) B3LYP or MP2 methods led to barrierless fragmentation.

CASSCF searches for the two transition states proved even more challenging. CASSCF(4,4)/6-31G* transition states could be located, but the final orbitals were inconsistent with those of the starting singlet cyclopropyl nitrene (**1**) and the (4,4) active space was too small to correctly describe the transition structures. However, using the correct orbitals and the CASSCF(8,8)/6-31G* level, transition state searches were unsuccessful in locating the two transition states, and both processes were barrierless. Since electron correlation at the CASPT2 level may also be important for these transition states, we explored a different approach.

Using an intrinsic reaction coordinate (IRC)¹⁴ search from the HF/6-31G* transition states (**TS1** and **TS2**), we obtained about 10–15 sets of Cartesian coordinates that connected each transition state to the singlet cyclopropyl nitrene (**1**) at the HF/6-31G* level. We then performed single-point energy calculations for each set of these Cartesian coordinates at the CASPT2(8,8)/6-311G(2d,p) level. These relative energies are shown in Figs. 3 and 4 for the ring-expansion (**TS1**) and fragmentation (**TS2**) reaction paths, respectively, at the HF/6-31G* and CASPT2(8,8)/6-311G(2d,p) levels.

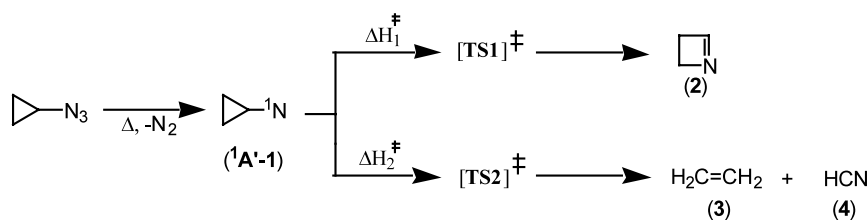
Table 2. Relative energies (kcal/mol) of intermediates and stationary points for cyclopropyl nitrene rearrangement and fragmentation^a

Structure	HF	B3LYP	MP2	MP4(SDQ)	CASPT2(8,8)/6-311G(2d,p)
$^1A'-1$	0.00	0.00	0.00	0.00	0.00
$^3A''-1$	-45.16	-17.24	-20.49	-23.50	-27.88 ^b
2	-59.56	-62.53	-70.44	-66.68	- ^c
Ethene + HCN	-68.70	-63.05	-74.49	-71.84	- ^c
TS1	2.84	-1.43	-5.78	-1.72	-1.11
TS2	0.64	-6.44	-7.85	-4.95	-8.61

^a Energies were calculated with the 6-31G* basis set and the HF/6-31G* optimized geometries, including corrections for differences in HF/6-31G* unscaled zero-point vibrational energies, unless noted otherwise.

^b Using the CASSCF(4,4)/6-31G* geometry.

^c Not calculated.



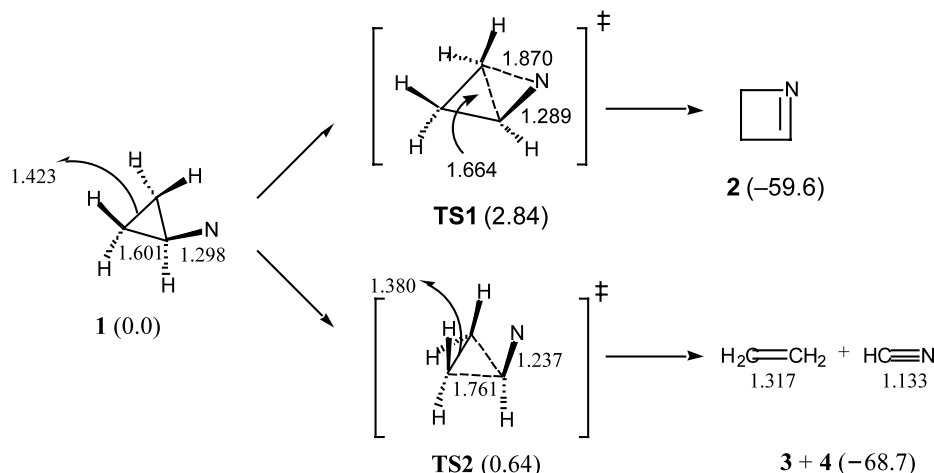


Figure 2. Intermediate and transition state structures for the ring-expansion (via **TS1**) and fragmentation (via **TS2**) reactions of cyclopropyl nitrene at the HF/6-31G* level. Relative energies (in kcal/mol) are listed in parentheses at the HF/6-31G* level. Bond lengths are shown in Å.

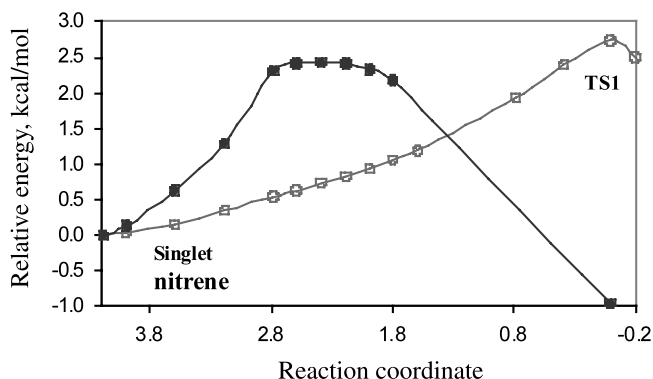


Figure 3. Relative energies (kcal/mol) along the ring-expansion reaction path at the HF/6-31G* level (open circles) and their single-point energies at the CASPT2(8,8)/6-311G(2d,p) level (filled circles).

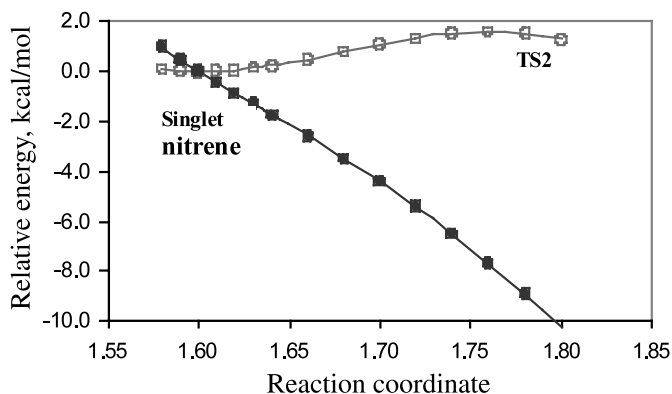


Figure 4. Relative energies (kcal/mol) along the fragmentation reaction path at the HF/6-31G* level (open circles) and their single-point energies at the CASPT2(8,8)/6-311G(2d,p) level (filled circles).

For the **TS1** ring-expansion process, the CASPT2(8,8)/6-311G(2d,p) level predicts that there will be a small barrier (≈ 2.4 kcal/mol) for the formation of azetidine (**2**) (Fig. 3). However, for the **TS2** fragmentation process, the CASPT2(8,8)/6-311G(2d,p) level confirms our earlier results that the fragmentation process is barrierless to generate ethene and HCN.

The HF/6-31G* calculations predict that the activation energy for fragmentation is about 2 kcal/mol smaller than that of the ring-expansion reaction. Single-reference methods which include electron correlation (B3LYP and MP2) predict that both processes are barrierless. CASPT2(8,8)/6-311G(2d,p) calculations on structures along the IRC reaction path at the HF/6-31G* level predict that the fragmentation reaction is barrierless, but the ring-expansion process has a small activation barrier (≈ 2.4 kcal/mol). The small barrier for ring expansion in cyclopropyl nitrene is similar to that for the rearrangement of methyl nitrene.² Also, for cyclopropyl nitrene, fragmentation will be more facile than ring expansion, a trend that is similar to cyclopropyl carbene.^{3a} In summary, the calculations here indicate that unlike cyclopropyl carbene, singlet cyclopropyl nitrene will have a sub-nanosecond lifetime, similar to methyl carbene and methyl nitrene, in solution at ambient temperature.

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