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Nitrenium Ion Analogues of Nonclassical Carbocations: Cyclopropylnitrenium, Allylnitrenium, and Azetidenium Ions and Mechanisms for Their Interconversion

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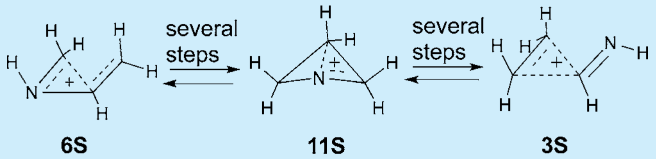
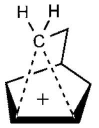
Ⓢ *Supporting Information*

ABSTRACT: Cyclopropylnitrenium **3S**, allylnitreium **6S**, and azetidenium (i.e., the nitrogen analogue of cyclobutylcarbenium) ions were examined using density functional theory and a complete basis set method. Similarly to the carbon analogues, the singlet states of these species have several local minima with nonclassical bonding. Structures characterized include **3S**, an N analogue of the bisected cyclopropylcarbinyl cation, **11S**, an N analogue of the bicyclobutonium ion, and **6S**, an unsymmetric 2-azidinylcarbinyl cation.



Studies of high energy carbocation intermediates have revealed many fascinating structures and reaction mechanisms that are not well described using classical bonding models.[1−3] The 2-norbornyl cation **1** and the cyclopropylcarbinyl cation **2** have been historically influential and continue to be examined. The former species exists as a single, symmetric potential energy minimum, having a pair of σ-electrons delocalized between three electron-deficient carbon atoms.[4−8] Cation **2** consists of three distinct, rapidly equilibrating isomers, including a bisected cyclopropylcarbinyl cation **2a**, a symmetric bicyclobutonium ion **2b**, and an unsymmetric bicyclobutonium ion **2c**.[9] The equilibration of these structures is so fast that attempts to generate the homoallylic cation, cyclobutylcarbenium ion, or the cyclopropylcarbinyl cation each produce the same mixture of stable products.[10] State of the art calculations are in good general agreement with experimental data on these species.[11−14]



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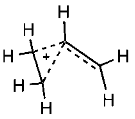
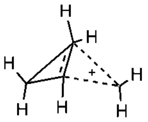


2A



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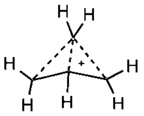

2C

Nitrenium ions are N-analogues of carbenium ions consisting of a dicoordinate nitrogen rather than a tricoordinate carbon. The higher electronegativity of the nitrogen atom predicts that these species will be more reactive than their carbon analogues. Additionally, nitrenium ions have low energy triplet states, and these can also be relevant to their chemical behavior.[15,16] Arylnitrenium ions have been studied extensively,[17,18] due to their roles as intermediates in mutagenic DNA-damaging reactions.[19−21] However, far less is known about nitrenium ions having substituents that are nonaromatic. Experimental[22−25] and theoretical[26−28] studies indicate that most of these species rearrange concertedly with their formation, usually through 1,2-alkyl or -H shifts. Elsewhere will be reported a computational survey[29] of nonaromatic nitrenium ions, which shows that barrierless 1,2-alkyl shifts, with a few exceptions, are the predominant behavior for singlet alkylnitrenium ions. In the course of that survey, it was found that the singlet cyclopropylnitrenium ion **3S**, neither spontaneously rearranges through the typical 1,2 alkyl shift nor exhibits a structure well described by classical localization of the σ-electrons. Rather, it minimizes to a C_s structure, analogous to **2a**. Further investigation revealed that **3S** exists on a surprisingly complex potential energy surface that includes distinct minima corresponding to an unsymmetric bicycloazetidonium ion **11S** (analogous to the bicyclobutonium ion **2b**) as well as a 2-aziridinylcarbinyl cation. Reported below are structure and energies for these nonclassical nitrenium ions as well as several isomers and transition states relevant to their interconversion mechanisms.

Computational Methods. The calculations described below were carried out using Gaussian09.[30] DFT calculations used the hybrid functional, M06-2X, developed by Truhlar et al.[31] along with the 6-311G(d,p) basis set.[32] Vibrational frequency calculations were carried out to determine if the stationary points were local minima (zero imaginary frequencies) or transition states (one imaginary frequency) (Table 1). Singlet nitrenium ions were stable to a RHF → UHF perturbation[33] and were thus assumed to be well-described by a single determinant. The M06-2X functional provides useful geometries and vibrational frequencies for reactive intermediates such as carbenes[34] and carbocations[35] in a cost-effective manner. To assess the feasibility of applying this methodology to larger nitrenium ions in the future, M06-2X results are compared to those from a more expensive, and accurate, complete basis set procedure (CBS-QB3) developed by

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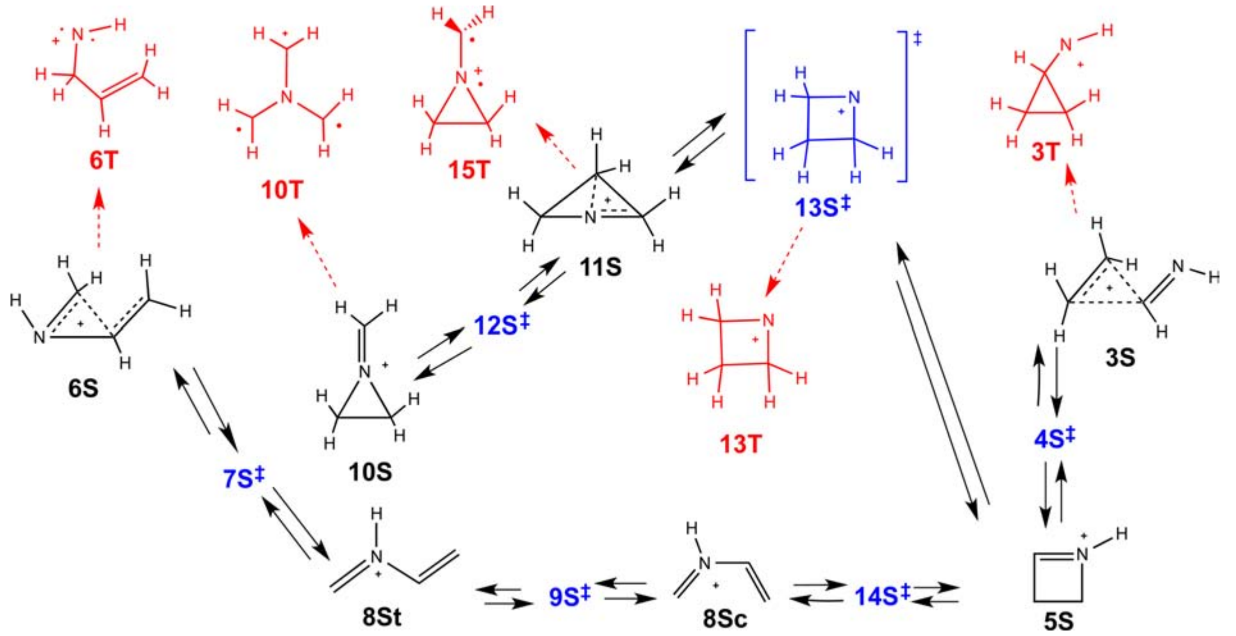


Figure 1. Stationary points on the $C_3H_6N^+$ potential energy surface shown with the mechanisms for their isomerization. Singlet minima are in black, singlet saddle points in blue, and triplets in red. Dashed lines connect singlets to the corresponding triplets.

Petersson et al.[36] which provides excellent thermochemical predictions for cationic intermediates.[37] However, because it employs a geometry optimization different from that used in the M06-2X calculations, CBS-QB3 energies are not available for some transition states and shallow local minima.

Singlet States. The geometries of singlet **3S** and triplet state **3T** cyclopropylnitrenium ion are shown in Figure 2. The singlet converges on a geometry with approximate C_s symmetry and features significant shortening of the distal ring C_2-C_3 bond (1.39 Å) as well as that of the C_1-N bond (1.25 Å). This is accompanied by lengthening of the proximal C_1-C_2 and C_1-C_3 bonds (1.77 Å) and planarization of the CH_2 groups. This planarization indicates increasing s character in the distal C−H bonds and thus increasing p character in the proximal C−C bonds as predicted by Bent's rule for a strongly electronegative substituent on cyclopropane.[38] In contrast, the triplet shows little σ-delocalization, adopting a more classical structure that shows more modest cyclopropyl bond length distortions of 1.46 Å for the distal C_2-C_3 bonds and 1.58 Å for the proximal $C_1-C_{2,3}$ bonds, along with pyramidalization of the CH_2 groups.

Table 1. Stationary Points on the $C_3H_6N^+$ Potential Energy Surface[a]

	DFT			CBS
	E (au)	ZPVE (au)	ΔE(a) (kcal/mol)	ΔG(a) (kcal/mol)
3S	−172.2698	0.0855	0.00	0.0
3T	−172.2145	0.0829	+33.0	+35.9
4S‡	−172.2617	0.0860	+5.4	c
5S	−172.3389	0.0893	−41.0	−41.2
6S	−172.2694	0.0866	+0.9	c
6T	−172.2006	0.0822	+41.3	+42.4
7S‡	−172.2691	0.0858	(+0.3)[b]	c
8St	−172.3378	0.0878	−41.2	−43.4
8Sc	−172.3339	0.0879	−38.7	−40.7
9S‡	−172.3295	0.0872	−36.4	c
10S	−172.3135	0.0878	−26.0	−24.1
10T	−172.2501	0.0825	+10.5	+10.9
11S	−172.2555	0.0866	+9.7	c
12S‡	−172.2548	0.0858	(+0.4)[b]	c
13S‡	−172.2039	0.0813	+38.7	+39.5
13T	−172.2124	0.0847	+35.5	+37.6
14S‡	−172.2799	0.0865	−5.7	c
15T	−172.1955	0.0815	+44.1	+47.2
16S	−172.3315	0.0874	−37.5	−34.4
17S‡	−172.1852	0.0812	+52.1	c

[a] Relative to **3S**. [b] Classical barrier relative to less stable reactant. [c] CBS-QB3 values not available.

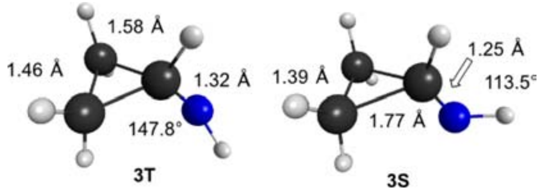
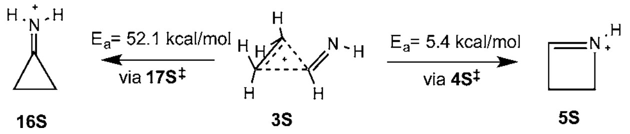


Figure 2. Geometries of **3T** and **3S**.

The 1,2-shift for **3S** could lead to two strained products: either 2,3-dihydroazetidinium ion **5S** or cyclopropylidenyliminium ion **16S**. While both products are more stable than the nitrenium ion, it appears that this strain is sufficient to create a modest barrier of 5.4 kcal/mol to **5S** and a more substantial barrier of 52.1 kcal/mol to **16S**.



Azetidenium ion **13** is the N analogue of the cyclobutyl cation. On the singlet surface, **13S**‡ is a transition state for the interconversion of **5S** to another nonclassical nitrenium ion **11S**. The geometries of the latter along with **13S** and **13T** are provided in Figure 3. Triplet **13T** has a planar ring system

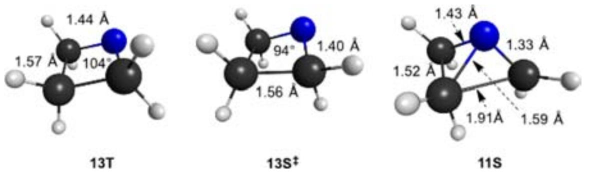


Figure 3. Geometries of **13T** and **13S**‡ and **11S**.

(dihedral angle <0.1°) and has C_{2v} symmetry. Singlet **13S**‡ deviates only slightly from planarity and has (nearly) C_s symmetry. In contrast the nonclassical species, **11S** is has a CNCC dihedral angle of 64° and deviates significantly from symmetry. The N is flanked by one CH_2 group having a short C−N bond (1.33 Å), one that is longer (1.43 Å) and one that is longer yet (1.59 Å). In all, this species resembles the unsymmetrical bicyclobutonium ion and is thus designated the bicycloazetidonium ion.

Bicycloazetidonium **11S** exists in a very shallow potential energy well and is predicted to readily isomerize via transition state **12S**‡ to *N*-methyleneaziridinium ion **10S**. The latter is some 35.7 kcal/mol more stable than its nonclassical precursor. The formal barrier, calculated at 0.3 kcal/mol, vanishes when zero-point vibrational energy is taken into account.

The optimized structure for **6S**, shown in Figure 4, also shows nonclassical bonding but is distinct from the structures derived from **3S** and **13S**. In many ways, **6S** could be considered a 2-aziridinylcarbinyl cation. Due to the ring nitrogen, however, it lacks the C_s symmetry seen in **3S**. As is the case with **11S**, **6S** is also separated from its ring-opened isomer **8 St** by a small, formal barrier (in this case 0.3 kcal/mol), which vanishes when zero-point vibrational energy is considered.

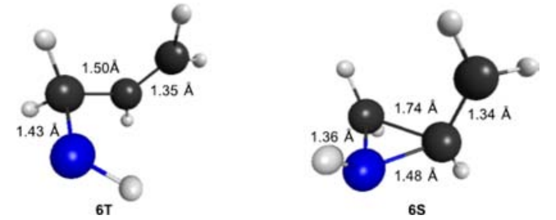


Figure 4. Geometries of allylnitrenium ions **6T** and **6S**.

Transition state **7S**‡ connects **6S** with *N*-methylenevinyliminium ion **8St**. The latter is a product of a formal 1,2-vinyl group shift in **6S**. Of course, **8St** is connected to its s-cis isomer **8Sc** via a C−N bond rotation (E_a = 2.3 kcal/mol) and the latter, in turn, can be derived from **5S** via ab electrocyclic ring opening (E_a = 33.0 kcal/mol).

Triplet States. The triplet states of **3**, **6**, and **13** as well as selected isomers were examined. Figure 1 shows these species (in red). The dashed arrows indicate that a given triplet structure was derived from optimizing the corresponding singlet geometry on the triplet surface. Rates or mechanisms for these intersystem crossing processes were not explicitly considered. As shown in Table 1, most of the triplet states lie significantly higher in energy than the singlet intermediates and are thus unlikely to play a significant role in the thermal process.

As shown in Table 1, **3T** is some 33 kcal/mol higher in energy than the singlet. By comparison phenylnitrenium ion has a singlet−triplet splitting of only ca. 18 kcal/mol in favor of the singlet.[39−41] In both examples the singlet is favored over the triplet due to its ability to accept electron density from the substituent. The larger effect for cyclopropyl is attributed to the formation of its distorted, nonclassical structure.

Similarly, **6** preferentially stabilizes the singlet state by relaxing to the 2-aziridinylcarbinyl cation geometry, allowing for increased electron donation to the N^+ center. As with **3** there is a marked change in the geometry of the singlet and triplet states. The triplet has its C−N bond rotated perpendicular to the plane formed by the remaining C atoms. More surprisingly, the rotomer that places the N−H bond eclipsed with respect to the $CH-CH_2$ bond is actually preferred over the antiperiplanar conformer by ca. 5.5 kcal/mol.

Optimization starting at the geometries of the bicycloazetidonium ion **11S** and *N*-methyleneaziridinium ion **10S** also provides structurally interesting, albeit high energy, triplet isomers. In the former case, the triplet is a completely planar (C_{3h}) trimethyleneammonium cation diradical, **10T**. The nonclassical ion **11S** optimizes to **15T**, and the latter actually more closely resembles **10S**, but with the C═N bond rotated perpendicular to the aziridine ring and some pyramidalization of the nitrogen.

The azetidenium ion **13** can be said to possess a triplet ground state, although in this case, the singlet is actually a transition state connecting two lower energy intermediates, **11S** and **5S**. In any case, **13T** is still significantly less stable than **5S** and **11S** and is unlikely to be populated under thermal conditions.

In conclusion, singlet nitrenium ions considered in this study, **3S**, **6S**, and **13S**, are connected by a series of transition states and intermediates. However, given the deep potential energy wells for some of the stable products (e.g., **5S**) and significant barriers, it is unlikely that generation of each of these species will provide identical product distribution as was seen for the $C_4H_7^+$ series. Rather, these calculations predict that generation of **3S** will result in formation of its ring expansion product **5S**. In fact, an early experimental study on a phenyl derivative of **5S** supports this prediction.[23] Given the nontrivial barrier to rearrangement, it may be possible to trap **3S** with external nucleophiles or observe it if prepared photolytically under low temperature conditions. Generation of allylnitrenium **6S** is predicted to form **8** from a vinyl migration. Given the low barrier to this migration, the prospects of trapping a free **6S** seem very remote. The nitrenium ion derived from azetidine **13S**‡ presents an interesting case. Given that this structure is a transition state, its attempted thermal generation (e.g., through heterolysis of a N-substituted azetidine) should result in a concerted rearrangement or intersystem crossing. However, the present calculations do not predict whether **10S**, **5S**, triplet products, or some mixture of these will form. It is likely that this will depend on the specifics of the generation process. Future efforts will seek to answer these questions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Complete reference for software used; energies and Cartesian coordinates for **3**−**17**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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