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# Aromatic Nitrenium Ions Based on 1*H*-Azepine. 1. Ab Initio Studies at the RHF, UHF, and CASSCF Levels

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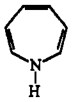
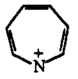
*Summary:* Ab initio molecular orbital studies at the HF, MP2, and CASSCF levels of theory of the singlet and triplet nitrenium ions derived from 1*H*-azepine show significant structural differences between the compounds of different spin states.

Nitrenium ions are proposed intermediates in several chemical reactions and are the putative carcinogens formed in vitro from aromatic amines.[1] Several computational studies of arylnitrenium ions, in which the nitrogen is directly attached to an aromatic ring, have appeared in the literature.[1,2] Studies of aromatic nitrenium ions, in which the nitrogen is contained in an aromatic ring, are much more rare.[3] The unsubstituted singlet azepine nitrenium ion is the heterocyclic analog of tropylium, and as such might be expected to show enhanced stability. Recent experimental studies on fused ring multicyclic azepines have led Cann to postulate nitrenium ion intermediates although no such species have been observed.[4]



**1**



**2**

We report here the first ab initio molecular orbital studies of the aromatic nitrenium ions based on the azepine ring system. Optimizations were done at the RHF/3-21G and CASSCF/3-21G levels with RMP2//RHF/3-21G and CASSCF//RHF/3-21G single point calculations for 1*H*-azepine, **1**, and singlet azepine nitrenium ion, **2s**; the triplet nitrenium ion, **2t**, was done at the UHF/3-21G level with UMP2//UHF/3-21G single-point calculations.[5,6] Calculations were done using the Gaussian 86, 90, and 92 suite of programs on various platforms.[7] Minima at both the HF and CASSCF levels were confirmed by calculation and analysis of the frequencies for negative values. The geometric parameters are summarized in Table I and the absolute and relative energies are given in Table II.

**Table I. HF/3-21G Geometries of 1, 2s, 2t, and 2tc**

| | atoms | 1 | 2s | 2t | 2tc |
|---|---|---|---|---|---|
| bond length$^a$ | 1–2 | 1.404 | 1.319 | 1.434 | 1.344 |
| | 2–3 | 1.321 | 1.398 | 1.341 | 1.365 |
| | 3–4 | 1.475 | 1.371 | 1.436 | 1.463 |
| | 4–5 | 1.323 | 1.403 | 1.398 | 1.336 |
| | 5–6 | 1.475 | 1.371 | 1.399 | 1.463 |
| | 6–7 | 1.321 | 1.398 | 1.415 | 1.365 |
| | 7–1 | 1.405 | 1.319 | 1.285 | 1.344 |
| angles$^b$ | 1–2–3 | 126.950 | 129.750 | 119.320 | 121.476 |
| | 2–3–4 | 126.220 | 127.570 | 128.910 | 126.779 |
| | 3–4–5 | 126.690 | 127.940 | 129.160 | 129.610 |
| | 4–5–6 | 126.670 | 127.900 | 130.270 | 129.610 |
| | 5–6–7 | 126.220 | 127.580 | 125.510 | 126.779 |
| | 6–7–1 | 126.950 | 129.740 | 123.070 | 121.476 |
| | 7–1–2 | 123.990 | 129.530 | 143.760 | 144.270 |
| dihedral angles$^b$ | 1–2–3–4 | 4.500 | 0.105 | 0.035 | 0.000 |
| | 2–3–4–5 | −25.903 | −0.211 | −0.195 | 0.000 |
| | 3–4–5–6 | −0.061 | 0.130 | 0.105 | 0.000 |
| | 4–5–6–7 | 25.933 | 0.029 | 0.082 | 0.000 |
| | 5–6–7–1 | −4.403 | −0.060 | −0.068 | 0.000 |
| | 6–7–1–2 | −36.492 | −0.032 | −0.162 | 0.000 |
| | 7–1–2–3 | 36.419 | 0.039 | 0.207 | 0.000 |

$^a$ In angstroms. $^b$ In degrees.

**Table II. Energies (Hartrees) of 1, 2s, 2t, and 2tc**

| | 3-21G$^a$ | MP2/3-21G// 3-21G$^b$ | CASSCF(6,7) | ZPE$^c$ | $S^2$ |
|---|---|---|---|---|---|
| 1 | −284.074 042 9 | −284.694 178 2 | *d* | 78.66 | |
| **2s** | −283.262 286 4 | −283.883 389 3 | −283.350 095$^e$ | | |
| | | | −283.350 762 4$^f$ | 72.04 | |
| **2t** | −283.230 267 7 | −283.776 797 9 | −283.164 814$^e$ | 68.31 | 2.437 |
| **2tc** | −283.227 592 9 | −283.785 362 | −283.129 181$^e$ | 71.61 | 2.338 |

$^a$ RHF for 1 and **2s**, UHF for **2t** and **2tc**. $^b$ RMP2//RHF for 1 and **2s** UMP2//UHF for **2t** and **2tc**. $^c$ In kcal/mol. $^d$ CASSCF not run for this molecule. $^e$ CAS//HF/3-21G single-point value. $^f$ CAS/3-21G optimized value.

The optimized geometry of neutral 1*H*-azepine, **1**, is a boat, with a plane of symmetry through the nitrogen atom and bisecting the C4–C5 bond. The alternating bond lengths, shorter between atom pairs C2 and C3, C4 and C5, C6 and C7, are indicative of discrete single and double bonds in a conjugated nonaromatic system.

In the azepine nitrenium ion, **2**, there are two atomic orbitals on the nitrogen which can accommodate the nonbonding electron pair, leading to either a ground-state singlet (paired) or triplet (unpaired). The singlet nitrenium ion, **2s**, is planar, with bond lengths and angles that show, similar to **1**, the molecule possesses a symmetry plane passing through the nitrogen and perpendicular to the plane containing the atoms of the ring (Table I). Significant double bond character is observed for N1–C2 and

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(1) For an excellent review on nitrenium ions, see: Ford, G.; Herman, P. S. *J. Chem. Soc., Perkins Trans. 2* **1991**, 607.

(2) Abramovitch, R. A.; Shi, Q.; Olivetta, S. *Heterocycles* **1992**, *33*, 483. Favey, E. D.; Cramer, J. C. *Tetrahedron Lett.* **1992**, *33*, 1705. Li, L.; Abramovitch, R. A.; Houk, K. N. *J. Org. Chem.* **1989**, *54*, 2911. Ford, G.; Herman, P. S. *J. Am. Chem. Soc.* **1989**, *111*, 3987. Ford, G.; Scribner, J. D. *J. Am. Chem. Soc.* 1981, *103*, 4281.

(3) Krough-Jespersen, K. *Tetrahedron Lett.* **1980**, *21*, 4553. Schmid, V. R. W. *Helv. Chem. Acta* **1962**, *17*, 1982. Smith, D. A. Unpublished results.

(4) McHugh, K. B.; Howell, W. M.; Doran, J. J.; Cann, M. C. *J. Heterocycl. Chem.* **1990**, *27*, 1839. Cann, M. C. *J. Org. Chem.* **1988**, *53*, 1112. Cann, M. C.; Lezensky, D. *J. Heterocycl. Chem.* **1988**, *25*, 863.

(5) All attempts using the CASSCF method for geometry optimization or single point calculations of the triplet failed to converge.

(6) (a) 3-21G: Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939. (b) MP2: Moeller, C.; Plesset, M. S. *Phys. Rev.* **1934**, 46, 818. Binkley, J. S.; Pople, J. A. *Int. J. Quantum Chem.* **1975**, 9, 229.

(7) (a) *Gaussian 90, Revision H*: Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whitesides, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A. Gaussian Inc., Pittsburgh, PA, 1990. (b) *Gaussian 92, Revision B*: Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1992.

(8) Hegarty, D.; Robb, M. A. *Mol. Phys.* **1979**, *38*, 1795. Eade, R. H. E.; Robb, M. A. *Chem. Phys. Lett.* **1981**, *83*, 362.

0022-3263/93/1958-0006$04.00/0

**Table III. Comparison of RHF/3-21G vs CASSCF(6,7) Geometries of 2s**

| | atoms | RHF | CAS |
|---|---|---|---|
| bond length | 1–2 | 1.319 | 1.332 |
| | 2–3 | 1.398 | 1.401 |
| | 3–4 | 1.371 | 1.384 |
| | 4–5 | 1.403 | 1.402 |
| | 5–6 | 1.371 | 1.384 |
| | 6–7 | 1.398 | 1.401 |
| | 7–1 | 1.319 | 1.332 |
| angles | 1–2–3 | 129.750 | 129.750 |
| | 2–3–4 | 127.570 | 127.810 |
| | 3–4–5 | 127.940 | 127.840 |
| | 4–5–6 | 127.900 | 127.830 |
| | 5–6–7 | 127.580 | 127.820 |
| | 6–7–1 | 129.740 | 129.750 |
| | 7–1–2 | 129.530 | 129.190 |
| dihedral angles | 1–2–3–4 | 0.105 | 0.025 |
| | 2–3–4–5 | –0.211 | 0.027 |
| | 3–4–5–6 | 0.130 | 0.000 |
| | 4–5–6–7 | 0.029 | 0.000 |
| | 5–6–7–1 | –0.060 | 0.000 |
| | 6–7–1–2 | –0.032 | 0.000 |
| | 7–1–2–3 | 0.039 | 0.000 |

C7–N1 while bond distances C3–C4 and C5–C6 indicate partial double-bond character. The bond angles in **2s** averaged 128.57 ± 1.12°, in excellent agreement with the value of the internal angles of a regular heptagon. This geometry suggests that the empty $p_z$ atomic orbital on nitrogen is fully conjugated with the $\pi$ orbitals around the ring, thus producing a planar cyclic fully conjugated $C_{2v}$ system of six $\pi$ electrons, i.e., an aromatic system.

A single configuration RHF wavefunction is generally considered inadequate to describe a system such as **2**, which involves charge delocalization through conjugation. We therefore performed multiconfigurational studies using the CASSCF method.[8] The active space was defined as the three occupied and three unoccupied $\pi$ molecular orbitals plus the unoccupied $p_z$ orbital on the nitrogen. This CASSCF(6,7) calculation involved 490 configurations and led to a wavefunction that was 88.1% composed of the ground state, with the six electrons in the carbon–carbon double bonds. The first excited singlet configuration contributed 1.4% while the rest of the configurations composed the other 10.5% (see Table IV, supplementary material, for a listing of all contributions which contributed more than 0.01% to the total wavefunction). The optimized geometric parameters of **2s** from the RHF and CASSCF calculations were not significantly different, cf. Table III, although the CAS-optimized structure is 55.5 kcal/mol lower in energy. The CAS//RHF/3-21G and CAS/3-21G energies differ only by 0.42 kcal/mol. The MP2 correlation correction lowers the energy of the RHF-optimized structure by 389.7 kcal/mol. Thus, it appears that configurations above the ground state reference configuration do not contribute significantly to the wavefunction nor do they significantly alter the molecular structure.

Examination of the bond lengths and angles in the triplet nitrenium ion, **2t**, reveals a lack of symmetry. The C–C bond lengths are, in general, intermediate between single and double except for the short C2–C3 and C7–N1 distances, which are indicative of double bonds. The angles in **2t** also differed from the previous systems and ranged from a minimum of 119.32° for C1–C2–C3 to a maximum of 143.76° for C7–N1–C2. This widening of the nitrogen angle in the triplet has been observed for other nitrenium ions.[1,2] In **2t**, each of the nonbonding atomic orbitals on nitrogen is singly occupied; the increase in the C7–N1–C2 angle from 127.6° in **2s** to 143.3° in **2t** may be attributed to the half-filled orbitals occupying a smaller volume of space than do doubly occupied orbitals. To our surprise, this cyclic seven-electron system was planar (cf. Table I) even though other azaaromatics such as pyridine are known both experimentally and theoretically to become nonplanar upon excitation to the triplet.[9] Despite numerous attempts, no other stable structures could be located for the triplet.

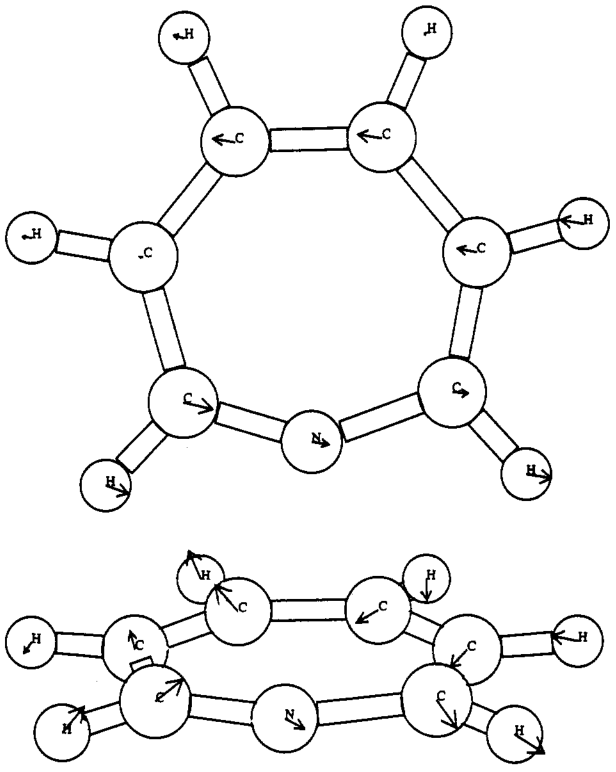

**Figure 1.** Vibrational mode associated with the geometric distortion in **2t**.

The MP2 single-point correlation correction led to a stabilization of 342.9 kcal/mol, comparable to that seen for the **2s** system. However, CAS//RHF/3-21G single-point calculation gave rise to an energy 41.1 kcal/mol *higher* than the RHF energy (see Table V, supplementary material, for a listing of all contributions which contributed more than 0.01% to the total wavefunction). The reason for this is not clear.

By simple Huckle theory the orbitals in **2t** containing the two nonbonded electrons should be degenerate. Thus, one would expect this molecule to undergo some kind of distortion that will lower its symmetry and split the degenerate orbitals. The loss of geometric symmetry is obvious as is the orbital splitting: the energies of the two SOMO's are –0.646 79 and –0.510 12 au. The vibrational mode associated with this distortion is shown in Figure 1. On the other hand, a number of open-shell molecules (e.g., the allyl radical[10]) have been shown to inaccurately prefer $C_s$ to $C_{2v}$ symmetry due to Hartree–Fock doublet insta-

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(9) Buma, W. J.; Groenen, E. J. J.; van Hemert, M. C. *J. Am. Chem. Soc.* **1990**, *112*, 5447.

(10) Benard, M.; Paldus, J. *J. Chem. Phys.* **1980**, *72*, 6546. McKelvey, J.; Hehre, W. J. *Mol. Phys.* **1973**, *25*, 983. Cook, D. B. *J. Chem. Soc., Faraday Trans. 2* **1986**, *82*, 187.

bility.[11,12] Alternatively, this distortion may be a pseudo- or second-order Jahn Teller effect due to vibronic mixing of energetically close triplet states.[9] In azaaromatic systems, this distortion usually leads to a nonplanar or boat conformation, rather than an in-plane distortion as observed for **2t**. Further studies are planned to address this question.

We therefore calculated the triplet nitrenium ion constrained to $C_2$ symmetry, **2tc**. This molecule is a true minima (i.e., no negative frequencies) on the constrained potential energy surface, but is not a stable structure on the unconstrained surface. That is, removal of the constraints followed by optimization led only to **2t**. The optimized geometry of **2tc** is planar with bond lengths different from **2t** but similar to **2s** (Table I); short bonds occur between carbons C2–C3, C4–C5, and C6–C7. The two N–C bonds in **2tc** are significantly shorter than in **2t** and significantly longer than in **2s**. However, the endocyclic bond angles in **2tc** were similar to those in **2t**. Examination of a series of the molecular orbitals HOMO-4 through LUMO+1 reveals that p–$\pi$ conjugation between the nitrogen atom and the adjacent carbons was not present (see Table VI, supplementary material, for a listing of all contributions which contributed more than 0.01% to the total wavefunction).[13]

Calculated energies for all compounds, given in Table II, confirm expectations that the aromatic structure **2s** is more stable than the nonaromatic triplet structure **2t** at all levels of theory. $E_{2t} - E_{2s}$ is 20.1 kcal/mol at the HF/3-21G level, 66.9 kcal/mol upon inclusion of correlation at the MP2//HF/3-21G level, and 116.3 kcal/mol at the CAS//RHF/3-21G. Inclusion of ZPE correction does not change the relative stabilities of the singlet versus the triplet.

The present ab initio calculations lead to the following conclusions. Both the singlet and triplet azepine nitrenium ions are planar systems. The singlet is aromatic and significantly more stable than the triplet, which undergoes distortion from $C_2$ symmetry due either to Hartree–Fock doublet instability or vibronic coupling associated with second-order Jahn Teller effects. The singlet is adequately represented by a single determinant (RHF) wavefunction; the same cannot be said with certainty for the triplet.

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**Supplementary Material Available:** Tables IV, V, and VI listing configurations which contribute greater than 0.01% of the total CAS wavefunction for **2s**, **2t**, and **2tc** and Gaussian archive files for 1, **2s**, **2t**, and **2tc** (8 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(11) For a general discussion of this instability problem, see: Chambaud, G.; Levy, B.; Millic, P. *Theor. Chim. Acta* **1978**, *48*, 103. We thank the many readers of the OSC Chemistry mail exploder for their input and suggestions relating to this problem.

(12) Inclusion of electron correlation is usually sufficient to resolve this problem; however, all our attempts to calculate either the MP2/3-21G, CISD/3-21G, or CAS/3-21G optimized structures for this system led to convergence problems.

(13) Molecular orbitals were visualized as Jorgensen–Salem plots using the program PSI88 (Jorgensen, J. L. *QCPE* **1980**, *12*, program 340) or using the AVS Chemistry Viewer.