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ON THE STABILITY OF AZIRINYL AND DIAZIRINYL CATIONS

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Abstract: The stabilities of the experimentally unknown azirinyl and diazirinyl cations are discussed on the basis of results from ab initio molecular orbital calculations.

The aromatic 2π-electron cyclopropenyl cation ($C_3H_3^+$, 1) along with numerous derivatives has been synthesized[1] but none of the isoelectronic aza-analogs, the azirinyl cation ($C_2NH_2^+$, 2) and the diazirinyl cation (CN_2H^+, 3) or derivatives thereof, have been characterized. However, their involvement as intermediates has been implicated in reactions of haloazirines[2] and halodiazirines,[3] respectively.


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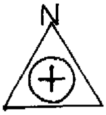
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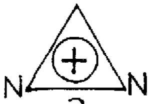
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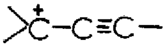
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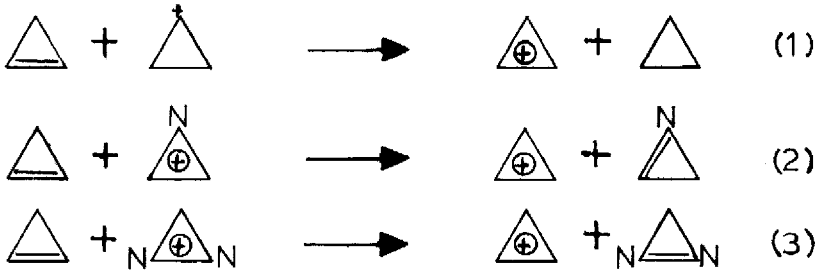
In the thorough ab initio study of $C_3H_3^+$ isomers by Radom et al.[4] only two of low energy were found, 1 and the propargyl cation (4); 1 was calculated to be 34.4 kcal/mol (6-31G*//STO-3G) more stable than 4. The published theoretical results for 3 are conflicting. Extended Hückel calculations by Hoffmann[5a] predicted 3 as unstable with respect to ring opening to the linear diazomethyl cation (5). Pittman et al,[5b] however, did not find this instability in their INDO study and concluded from the calculated geometries and charge distributions, that 3 as well as 2 were aromatically stabilized cations. Initiated by the experimental failures in isolating derivatives of 2 or 3[2,3,6] and the contradictory theoretical predictions,[5] this work reports the results from a computational study of 2, 3, and their isomers using ab initio molecular orbital theory.[7] Unless otherwise noted, all structural and electronic population data will refer to optimized geometries calculated with the minimal STO-3G basis set,[8a] while energy data refer to values obtained with the 6-31G* (split valence plus d-type polarization functions on C and N) basis set[8b] at these geometries (6-31G*//STO-3G). Conjunctive usage of these basis sets has been proven to describe the geometries and relative energies of closed and open isomeric structures fairly accurately.[9]

Four $C_2NH_2^+$ isomers are calculated to lie within an energy range of 15 kcal/mol. The azirinyl cation (2) is the lowest energy isomer with the propargyl cation-like $CNCH_2^+$ and $NCCH_2^+$ isomers 6.1 and 13.3 kcal/mol higher in energy, respectively; a linear isomer $HCNCH^+$ (triplet ground state)[10] is calculated to be 9.4 kcal/mol above 2. The charges in the N and C 2p(π) orbitals of 2 are 0.70 and 0.65, respectively, and this complete delocalization of the two π-electrons is reflected clearly in the ring dimensions. The calculated C-C and C-N bond lengths (1.364Å and 1.384Å) are similar to the typically aromatic C-C bond length (1.377Å) calculated in 1.[4]

The CN_2H^+ isomer of lowest energy is linear $HNCN^+$ (triplet), which is placed 12.1 kcal/mol below 5 (triplet) and 36.9 kcal/mol below 3 (singlet). The latter two ions may be the CN_2H^+ species observed in the mass spectra of diazomethane and diazirine, respectively.[11] The calculated energy separation (25 kcal/mol) is in accord with the difference in estimated heats of formation (16 kcal/mol).[11] The $HNCN^+$ ion has a N(H)-C bond length of 1.203Å and a C-N bond length of 1.434Å, corresponding to a major contribution from the resonance structure $H\text{-}\overset{+}{N}{\equiv}C\text{-}N$. An analogous major resonance structure is implied in 5, where the bond lengths are C≡N = 1.196Å and N-N = 1.433Å. As in 1 and 2, the π-electrons are delocalized in 3 with 2p(π) populations on N and C of 0.68 and 0.63, respectively. The calculated N-N and C-N bond lengths are 1.404Å and 1.375Å.

Thus the thermodynamic stability of the three-membered rings relative to the lowest energy open isomers decreases substantially (~30 kcal/mol) for each N replacing a CH group.[12]

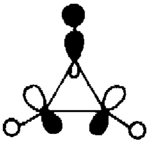
The stabilization energy due to delocalization of the π-electrons in the cyclopropenyl cation may be determined as 69.5 kcal/mol (6-31G*//STO-3G) from the exothermicity of reaction (1)[4]



Reactions (2) and (3), which compare the cyclopropene-cyclopropenyl cation pair with the 1-azirine-azirinyl and 3H-diazirine-diazirinyl cation pairs, are exothermic by 37.6 and 77.8 kcal/mol, respectively. This scheme consequently predicts (by subtraction of (2) and (3) from (1)) a "delocalization energy" of 31.9 kcal/mol for 2 and -8.3 kcal/mol (!) for 3, i.e. a reduction by nearly 40 kcal/mol occurs for every nitrogen introduced, despite that 2 and 3 were calculated as having complete delocalization of the π-electrons and "aromatic" geometries. Although simple Hückel theory does predict a diminishing resonance energy upon aza-substitution,[13] σ-effects must certainly account for a large part of the loss in stabilization energy.

The atomic net charges calculated in 1 indicate that a significant fraction of the excess positive charge is situated on the hydrogen atoms. Progressive exchange of CH with N localizes the charge on fewer atoms, leading to a differential increase in electrostatic repulsion in the rings over the open structures. The larger electronegativity and hence electronic demands of nitrogen apparently require at least one π-electron per nitrogen, viz. 1-azirine and 3H-diazirine, which both feature a regular double bond and are experimentally known. The resulting need for nitrogen to acquire compensation through polarization of the σ-systems gets reflected in the energies of the upper occupied molecular orbitals (Table).

The three highest lying occupied MO's in 1-3 are the π-orbital and two Walsh type σ-orbitals; the latter (6,7) are degenerate in 1 and positioned slightly below the π-orbital. The Walsh orbitals feature weak bonding with π-type overlap taking place outside the ring between nonoptimally directed atomic orbitals; (7) contains a directly antibonding component, but both do provide some C-H bonding. Aza substitution would tend to lower all the orbital energies due to the increase in effective nuclear charge, and the energy of the π-orbital does indeed decrease steadily by ca. 1.8 eV for each nitrogen added. In the azirinyl cation, orbital 6 is transformed into an orbital (8) with considerable lone pair character and almost no C-H bonding. Since exocyclic C-H bond orbitals possess large s character and lower energies than nitrogen lone pairs, the orbital is strongly destabilized and pushed above the π-orbital. Orbital 7 is stabilized (~1.9 eV) in 2, since it involves exchange of the C 2p orbital with a N 2p orbital. With two nitrogens in the ring, this orbital is severely destabilized (9), since the necessary σ-withdrawal from C generates large nitrogen orbital coefficients and consequently strong antibonding; the large N-N distance in 3 (1.404Å; the calculated N-N distance in 3H-diazirine is 1.266Å[9]) results. In the equilateral N_3^+ isomer the degenerate orbitals are well separated as the HOMO's from the π-orbital.[14]



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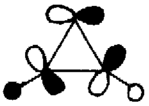

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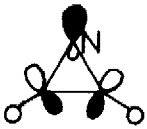

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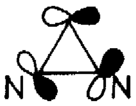

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The thermodynamic considerations presented (cyclic versus open structures, delocalization energies) indicate that substituted azirinyl cations could well be stable in nonnucleophilic media, but that the isolation of diazirinyl cations represents a considerable challenge. There is also evidence for decreasing kinetic stability in the series 1-3, if a correlation exists between kinetic stability and the HOMO-LUMO gap.[15] This orbital separation decreases from 17.5 eV in 1 through 16.1 eV in 2 to 15.7 eV in 3. Likely dissociation products for diazirinyl cations XCN_2^+ would be N_2 and CX^+. The reaction is calculated as endothermic by 35.4 kcal/mol for X=H, but a search at the STO-3G level for a simple substituent (e.g. CH_3, CN, NH_2) to further stabilize the ring has not been successful; the CX^+ fragment gains substantial preferential stability from the improved distribution of positive charge. Initial separation of a C-N bond might lead the dissociation through carbene-like intermediates. A bent singlet HCN_2^+ structure was located 15.1 kcal/mol (STO-3G//STO-3G) above 3 with a long C-N bond length of 1.63Å, indicating that the structure is only a loose complex. The corresponding triplet carbene opened up to the linear diazomethyl cation (5).

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Table. Total (E) and Orbital (ε) Energies for the Molecules 1-3.[a]

Molecule	1	2	3
E(STO-3G//STO-3G)	-113.62032	-129.33930	-145.04438
E(4-31G//STO-3G)[c]	-114.81364[b]	-130.71736	-146.59033
E(6-31G*//STO-3G)	-115.00369	-130.95777	-146.88241
ε(6-31G*//STO-3G)	-20.6(π)	-20.9	-22.4
ε(6-31G*//STO-3G)	-21.3	-22.4(π)	-23.3
ε(6-31G*//STO-3G)	-21.3	-23.1	-24.3(π)

(a) E in Hartrees, ε in eV. (b) Reference 4. (c) 4-31G basis set from reference 8c.

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(10) The UHF procedure spin contaminates the triplet states and lowers them artificially relative to the singlet states; the energy involved could amount to ~10 kcal/mol. Also, the three-membered rings are generally calculated as too unstable relative to the open isomers, probably by some 4 kcal/mol at the 6-31G*//STO-3G level (ref. 9).

(11) G.S. Paulett and R. Ettinger, J. Chem. Phys., 39, 825 (1963).

(12) The linear structure of N_3^+ is favored over the ring by 96.8 kcal/mol (STO-3G//STO-3G).

(13) For example, use of the parameters h_N=1.0, K_{CN}=1.0, and K_{NN}=1.0 gives a resonance energy of 1.59β for 2 and 1.46β for 3, compared to the 2β of 1.

(14) ε(6,7)=-24.5 eV; ε(π)=-26.3 eV (STO-3G//STO-3G).

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