DIAZIRIDINE; THE OXIDATION OF CYCLIC HYDRAZINES AND ITS INHIBITION

James P. Snyder

Belfer Graduate School of Science, New York and

Chemical Laboratory II, The H.C. Ørsted Institute, University of Copenhagen

Universitetsparken 5, DK-2100 Copenhagen, Denmark

Cyclic hydrazines are extremely labile to air oxidation[1] in contrast to the corresponding acyclic heterosystems. Similarly cyclic semicarbazides are converted to azo alkanes under very mild conditions by metal oxidants. Semicarbazide, an open chain analog, under the same conditions experiences only metal-complex formation.[2] In an attempt to understand the influence of geometry on the reducing capacity of hydrazines, we have undertaken semiempirical m.o. calculations for the smallest member of the cyclic class; diaziridine[3] (CH_4N_2) and its conjugate acid. In this connection the geometry of CH_4N_2 and the mechanism for its conformational interconversion has been studied by the CNDO-BW parameterization.[5] The results provide a rationale for the observation that protonation of cis-hydrazines converts them to a stable form convenient for storage and handling.

The lowest energy diaziridine conformation is properly predicted to be the trans isomer 1. The energy minimized structural parameters of this species (R(C-N)=1.374, R(N-N)=1.346, R(C-H)= 1.095, R(N-H)=1.020Å, < HCH=116.5°, < NCN=58.6°, < (NH,NNC)=70.7°, < HNN=131.7°), are in fair agreement with postulated "reasonable" geometries[6] and a structure derived from the CNDO calculations of Seitz et al.[4,8] Forms 2(cis), 3(half-planar) and 4(planar) are computed to be less stable than the trans conformer by the energy values given in Figure 1. These results are in accord with the observation of a single isomer, undoubtedly the trans species, in the nmr spectra of a wide variety of diaziridines[4] and in agreement with a recent ab initio calculation on structures 1 and 2.[6b] The relatively high energy of planar form 4 strongly suggests that trans conformers (1/1') are interconverted through transition state 3 by a pair of consecutive single inversions on nitrogen. The cis isomer intervenes (E_a = 16.4 kcal/mole).[7] Seitz et al. provide the same overall description of the conformational dynamics of diaziridine but with considerably different energy requirements.[4b,8] A similar result has been deduced intuitively for synchronous nitrogen inversion in 2,3-diazabicycloheptanes and - octanes.[9]
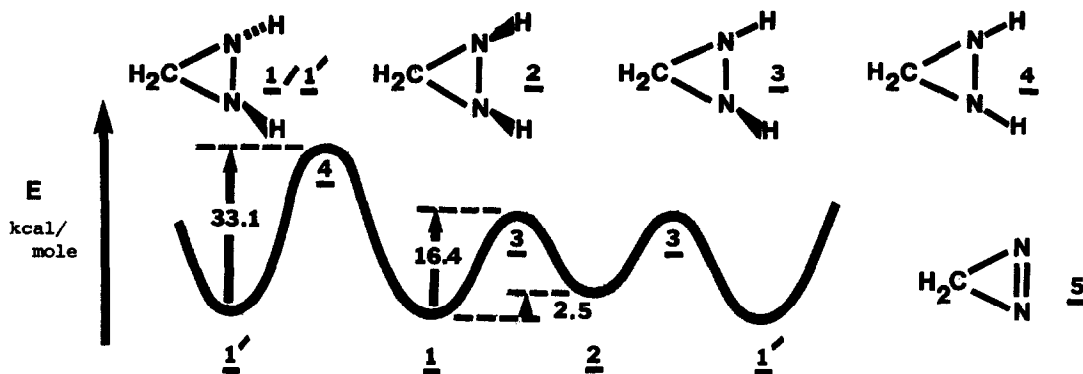
Figure 1 Computed energy relationships between diaziridine structures.

A final structural feature of importance is the electron distribution in the cis and trans diaziridine isomers. As has been concluded for diazirine[10] 5, the nitrogen lone electron pairs strongly interact and are considerably delocalized throughout the sigma framework of the molecule. The two high lying molecular orbitals which can be identified with the lone pairs are the symmetric (n_+) and antisymmetric (n_-) combinations: trans 1: $-11.45(n_+)$, -11.76eV(n_-), Δ_{trans} = 0.31eV; cis 2: $-11.50(n_-)$, -12.19eV(n_+), Δ_{cis} = 0.69eV. In concert with the ab initio result[6b] $(\Delta_{trans}$ = 0.92, Δ_{cis} = 2.4eV) the lone pair interaction is considerably greater for the cis isomer than for the trans, although the CNDO-BW computed quantities are too small by a factor of about one third.[11] A crude index of lone pair delocalization by the CNDO-BW method is the percentage of electrons in the n_+/n_- m.o.'s found on nitrogen: n_-(trans, 61, cis, 74%), n_+(trans, 78; cis, 41%).

The differential capacity for oxidation of cyclic versus acyclic hydrazines may consequently be seen as a result of electronic structure following from the geometries of the systems in question. Conformationally stable entities in the rigid cyclic system (1/2) cannot avoid persistent eclipsing interaction between lone electron pairs. By contrast in the acyclic series the potential surface[14,15] displays both cis and trans isomers (Figure 2) as transients at energy maxima separating degenerate gauche forms. The former equilibrium thus contains a species (2) with strong direct interaction[16] between the nitrogen lone pairs. The resultant HOMO is antibonding between nitrogens. Removal of an electron from such a species should be an energetically favorable process which promotes increased bonding across the N-N bond.[17] The existence of a non-negligible direct interaction between the lone pairs in the trans case results in a certain degree of antibonding character in the n_+ HOMO in this conformer as well. Thus the possibility that the more abundant

cyclic <u>trans</u> hydrazine is undergoing oxidation to some extent cannot be neglected. These energy

considerations are clearly not met in the acyclic series.[18] Accordingly non-cyclic hydrazines

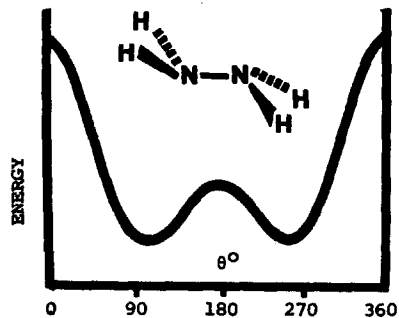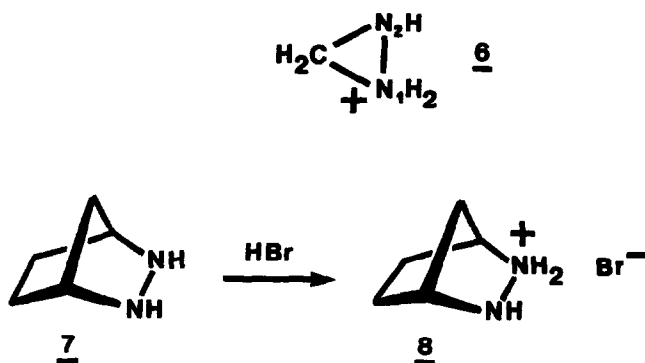(and presumably semicarbazides as well) are less easily oxidized than their cyclic counterparts.

Figure 2   Rotational energy barriers
for the hydrazine molecule.[14,15]

If lone pair interaction is indeed responsible for the short lifetimes of cyclic hydrazines

in the presence of very mild oxidants, removal of this interaction by protonation or complexation,

for example, should ameliorate the observed reactivity. A CNDO-BW calculation for protonated

diaziridine <u>6</u> supports this expectation. No m.o.'s can be identified with the type of interaction

described above for <u>trans</u> <u>1</u> and <u>cis</u> <u>2</u>. The degenerate contributions of nitrogen lone-pairs in

the latter are replaced in the main by a HOMO in <u>6</u> which yields 62% of the electrons on N_2 and

only 3% on N_1. In complete agreement with these notions the highly air-labile hydrazine <u>7</u> upon

treatment with HBr generates salt <u>8</u> and/or the corresponding di-hydrobromide quantitatively.[21]

These salts are indefinitely stable to air oxidation and should prove useful as uncontaminated

sources for the hydrazine.[22]

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