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# CHELOTROPIC REACTIONS: THE THERMAL DESTRUCTION OF DIAZIRINE

James P. Snyder*[16]

Belfer Graduate School of Science, New York, and

Dept. of General and Organic Chemistry, H. C. Ørsted Institute,

Universitetsparken 5, Copenhagen, Denmark

Russell J. Boyd, M.A. Whitehead

Dept. of Chemistry, McGill University, Montreal, Canada

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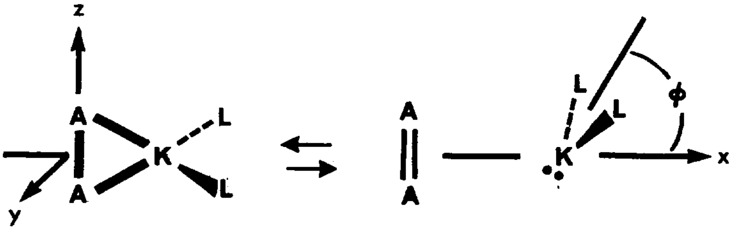
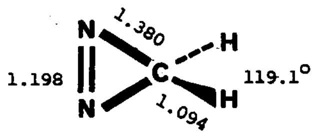
Chelotropic reactions have been evaluated theoretically[1] with regard to requirements for energetically economic reaction pathways. Thus orbital symmetry conservation arguments predict the concerted decomposition of three membered rings to occur in an unsymmetrical fashion. The moiety KL$_2$ is presumed to depart by a simultaneous displacement of atoms L in the X and Z directions.[1] Stereospecific extrusion of N$_2$[2], N$_2$O[3], n-BuS$^-$[4] and SO$_2$[5] from three membered rings fulfills the geometrical requirements, if concertedness obtains.





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The geometry preserving addition of singlet methylene to olefins[6] is likewise a chelotropic process. Extended Hückel calculations for the methylene-ethylene combination support an unsymmetrical but nonetheless concerted transition state.[7] We should like to report a somewhat more detailed theoretical investigation of the related system, singlet methylene, nitrogen and diazirine (1).[8] Gross features of the generally accepted view of three membered ring formation and destruction are preserved. However several significant but previously unrecognized mechanistic details emerge from the present calculations.

A recently parameterized SCF-MO-CNDO procedure[9] predicts geometries for singlet methylene ($^1A_1$ ∠HCH, 104.4°; RCH, 1.098Å; $^1\Delta_g$(180°) RCH, 1.094Å) and diazirine (1) in good to excellent agreement with experiment.[10,11] For the two reaction pathways considered below, the energy of each of the potential surface points studied has been minimized with respect to the N-N and C-H bond lengths and the HCH angle. For the unsymmetrical case minimization was carried out for two additional spatial coordinates (i.e. $R_z$ and φ of. Figure 1).

The lowest energy pathway is unsymmetrical and is found to involve no activation energy in the ring forming direction (curve a; Figure 2). Several events are of particular interest: (i) During the initial stage of the reaction ($R_x$ = 2.8-1.9Å), changes in computed electron density indicate a flow of electrons from $N_2$ to $CH_2$. For distances shorter than 1.9 Å, electrons are transferred in the reverse direction. (ii) The internal geometry of the system responds significantly to electronic interactions only during the second stage of the reaction as electrons begin to be transferred from carbon to nitrogen. Thus the HCH angle opens gradually from its equilibrium value of 104.4° to 126.9° ($R_x$ = 1.37) then recloses to 119.1°, the equilibrium value for diazirine. Simultaneously angle φ varies from 90° to 0°. These motions are depicted sequentially in Figure 1. (iii) Carbon of the methylene fragment moves off the x-axis a maximum of 0.093 Å ($R_x$ = 1.80). Extended Hückel calculations for the methylene-ethylene addition predict by contrast a value of approximately 0.6 Å for the carbon deviation at large fragment separation (ca. 3.0 Å).[7]

Of significance is observation (i) that the computed reaction occurs in two distinct electronic phases. The first ($R_x$ = 2.8-1.9Å), well into the descent region of the potential energy surface, is characterized by a sacrifice of electrons from nitrogen to carbon. While this sequence of events undoubtedly reflects the electrophilicity of singlet methylene, it is reproduced for other chelotropic 3-ring forming reactions not involving $CH_2$.[12] If the bi-directional electron flow principle proves to be general, analysis of certain reactions by consideration of HOMO/LUMO symmetries and relative atom electronegativities alone could be misleading.[13]

A second revealing feature of the computed hyperplane _a_ concerns the origin of the postulated unsymmetrical departure of $KL_2$ from 3-membered rings. In the present calculation the methylene lone electron pair, confined to the average HCH plane in an $sp_z$-type orbital at infinite separation, retains its relative spatial orientation upon passage through the intermediate states _aa_, _ab_ and _ac_ (Figure 1). The highest occupied MO for interaction of $CH_2$ ($^1A_1$) and $N_2$ receives its largest contribution from $p_z$/s AO's on carbon. Thus the HCH fragment may be described by a pivotal motion about the carbon "lone-pair" orbital with concomitant HCH angle deformation and rehybridization on carbon. Destruction of diazirine by a symmetrical linear ($C_{2v}$) pathway leads to a hyperplane of type _b_ in Figure 2. The HCH angle gradually opens to 180° by a symmetry allowed process resulting in linear $CH_2(^1\Delta_g)$ and nitrogen.[14,15] The symmetrical decomposition is computed to be 21.1 kcal/mole less

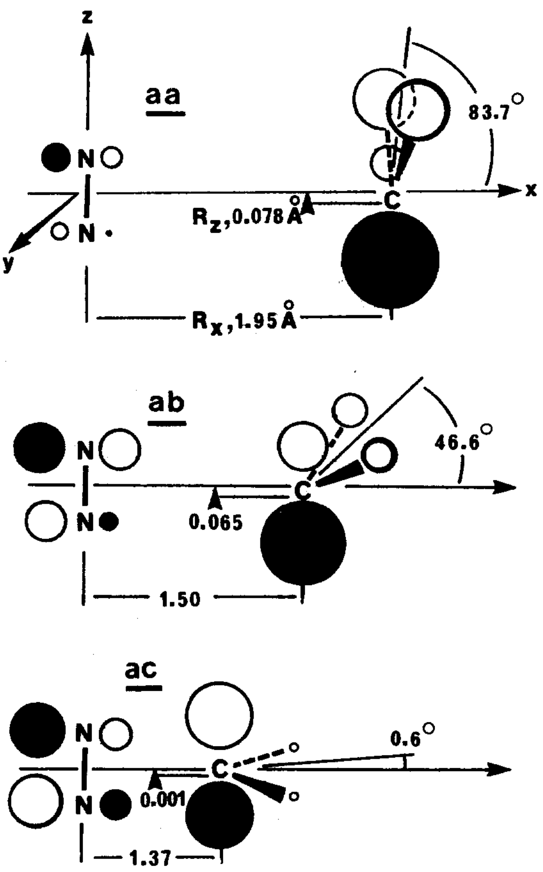

Figure 1. Unsymmetrical addition of $CH_2$ ($^1A_1$) to nitrogen. Circle radii represent the relative contributions made by the carbon $p_z/s$, the nitrogen $p_x/s$ and the hydrogen 1s atomic orbitals to the HOMO of the interacting fragments. (∠HCH = 105.4, 124.2 and 126.9° respectively)

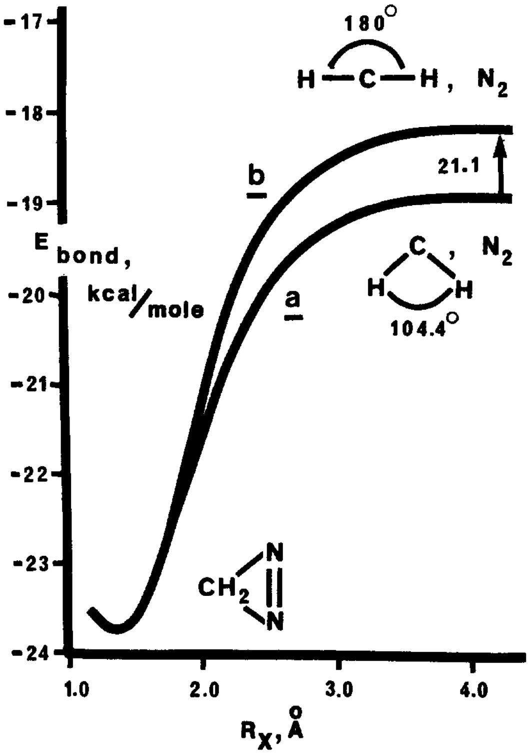

Figure 2. Hyperplanes for the interaction of singlet methylene and nitrogen on the diazirine potential surface. Energy values are relative to those of neutral atoms at infinite separation; (a) unsymmetrical pathway, (b) symmetrical $C_{2v}$ decomposition.

favorable than the unsymmetrical case in good agreement with the measured differences in energy between the two lowest singlets of methylene (ca. 20 kcal/mole).[10] Such a picture suggests that the unsymmetrical expulsion of $CH_2$ ($^1A_1$) from diazirine may be a consequence of the system's tendency to avoid utilizing an excited $CH_2$ configuration. Similarly any $KL_2$ fragment ejected from a three membered ring must choose between these symmetry permitted but energetically distinguishable alternatives.

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