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An *ab initio* Molecular Orbital Study on the Addition Reaction of Triplet Nitrene to Ethylene

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A minimal basis set, contracted from an extensive set of primitive Gaussian type functions (GTF), was used to expand the molecular orbitals (MO) within the framework of self consistent field (SCF) theory. The results revealed that aziridine is formed in its first excited triplet state (T_1) when ethylene is reacted with triplet nitrene. The equilibrium geometry of aziridine in its T_1 state had a tetrahedral CCN bond angle.

Key words: Aziridine – Addition reaction of triplet nitrene

Introduction

Nitrenes have long been considered as important intermediates in organic chemistry. Much of the progress in nitrene chemistry has been made by investigation of the parallels between nitrene and carbene species. According to a qualitative theory, originated by Skell [1], the stereospecificity of carbene cycloaddition to olefins may be related to the multiplicity of the electronic state of the carbene molecule. The extension of Skell's method into nitrene chemistry has been previously studied experimentally by several authors [2, 3].

Any general nitrene species (R – N) may exist in several electronic states which are iso-configurational in electronic structure. As an illustration one can consider the simplest nitrene (N – H) whose three lowest electronic states are obtained by assigning the two electrons in the 1π-shell to different spin orbitals.

$$\begin{array}{ccc}
\uparrow & & \downarrow \\
\uparrow\downarrow N-H & \uparrow\downarrow N-H & \uparrow\downarrow N-H \\
\uparrow & \uparrow\downarrow & \uparrow \\
{}^3\Sigma^- & {}^1\Delta & {}^1\Sigma^+
\end{array}$$

———Increasing Energy———→

Both experimentally and by SCF – MO calculations the triplet state is found to be the most stable species for N – H [4]. Electron spin resonance results also indicate that the triplet is the ground state for many other nitrenes [5].

The basic hypothesis advanced by Skell and adopted in the above experimental work [2, 3] is that (a) the singlet species should react in one single step process to yield the three-membered ring stereospecifically while (b) the triplet species should initially form a diradical intermediate which possesses small barriers to rotations about single bonds with the result that by the time ring closure does occur all stereochemical integrity will have been lost. These ideas are well represented by Fig. 1.

The fundamental question we are primarily concerned in this communication is whether the first excited triplet state (T_1) of aziridine is indeed in a ring distorted nuclear configuration as implied by Fig. 1.

Computational Method

The Gaussian orbital basis used in this study was formed by variationally fitting sets of Gaussian type functions (GTF) to Slater type orbitals (STO) [6, 7]. As described and examined by Klessinger [8] these basis sets are not expected to give absolute energies approaching the Hartree-Fock limit but one hopes that these basis sets represent a near optimal compromise between computational efficiency and results which might parallel more exact energy surfaces.

In the basis set chosen each 1*s* orbital was expanded in terms of 5 primitive Gaussians

$$\phi_{1s}(\xi, r) = \sum_{i=1}^{5} c_i^{(1s)} \eta_{1s}(\xi^2 \alpha_i^{(1s)}, r).$$

Each 2*s* Slater orbital and each 2*p* Slater orbital was expanded in 3 primitive Gaussians.

$$\phi_{2s}(\xi, r) = \sum_{i=1}^{3} c_i^{(2s)} \eta_{2s}(\xi^2 \alpha_i^{(2s)}, r)$$

$$\phi_{2p}(\xi, r) = \sum_{i=1}^{3} c_i^{(2p)} \eta_{2p}(\xi^2 \alpha_i^{(2p)}, r)$$

The contraction coefficients and orbital exponents for the primitive Gaussians as determined for expansions of the above basis functions (BF) are those published by Klessinger [8]. For aziridene this represents 76 primitive GTF contracted to 20 BF.

The SCF–MO computations for species with closed electronic shells were performed according to Roothaan [9] and the energies of the singlet and triplet excited electronic configurations, involving the promotion of an electron from orbital *b* to orbital *a*, were calculated by the virtual orbital technique [9]

$$^1E_{b\to a} = E_0 + (\varepsilon_a - \varepsilon_b) - J_{ab} + 2K_{ab}$$

$$^3E_{b\to a} = E_0 + (\varepsilon_a - \varepsilon_b) - J_{ab}$$

where ε_b and ε_a are the occupied and virtual orbital energies respectively, J_{ab} is the coulomb and K_{ab} is the Exchange integrals over these (*a* and *b*) molecular orbitals. The SCF MO calculations on nitrate were performed according to Roothaan's open shell formalism [10].

All SCF–MO computations were performed using the above basis set with the IBMOL-IV program system on an IBM 360/65 computer system at the University of Toronto.

Results and Discussion

The calculations on the ground state of aziridine were performed at the experimental geometry determined by microwave spectroscopy [11], thus no attempt at optimization of geometry for this particular basis set was made. The value found for the total energy is somewhat higher than the results from the Double Zeta quality work [12, 13]. The character of the individual molecular orbitals is however the same as found in the more accurate calculations [12, 13].

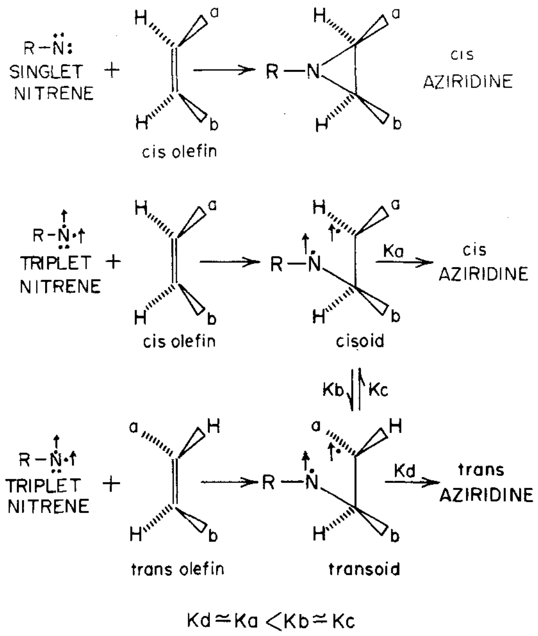

Fig. 1. Schematic description of nitrene addition to olefins

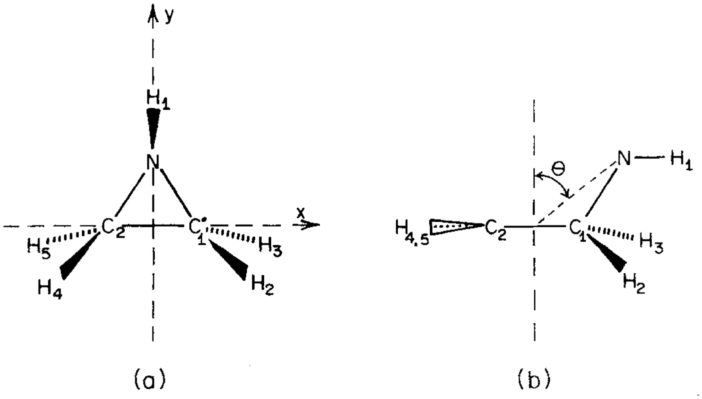

Fig. 2. (a) Coordinate system for aziridine in its equilibrium nuclear configuration
(b) Illustration of the ring distortion in aziridine (The extent of ring distortion is measured by the angle θ)

The highest occupied orbital, 8a, is predominately the nitrogen lone pair as evidenced from the contour plots in the plane containing the N–H bond and perpendicular to the CCN triangle.

The SCF–MO calculations on NH ($^3\Sigma^-$ and $^1\Delta$), C_2H_4 (^1A_g) and C_2H_5N ($^1A_1$) yielded the following total energy values –54.75080, –54.62938, –77.74336 and –132.55322 hartree respectively. The first excited triplet state (T_1) of aziridine was calculated by the virtual orbital technique [9] as –132.20843 hartree. These energy values allow one to draw a state, or more precisely a electronic configuration, correlation diagram (Fig. 3). As shown in Fig. 3 the cyclization is clearly favourable for the singlet NH reaction but there is a strong indication that the triplet reaction should procede through an intermediate of some distorted geometry which has a lower energy than the T_1 in the ground equilibrium nuclear configuration. This ring distorted T_1 species may then be deactivated to the S_0 state without passing through such a highly unfavourable energy level as the one shown Fig. 3.

A partial geometrical optimization has been carried out on the ring distorted aziridine which is illustrated in Fig. 2b. Rotation about the CN bond showed that the proton attached to the nitrogen is now in the CCN plane and it points away from C_2. The CNH bond angle was found to be nearly tetrahedral similarly to the bond angles about C_1. The CH_2 moiety involving C_2 was chosen to have 120° bond angle (the HCH bond angles in aziridene are 117°) and its plane was taken to be perpendicular to the CCN plane.

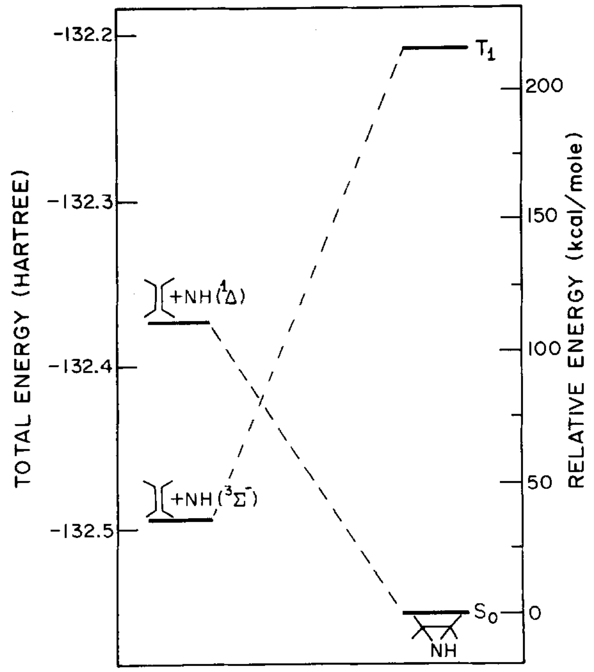

Fig. 3. Energy relationships between aziridine and its fragments

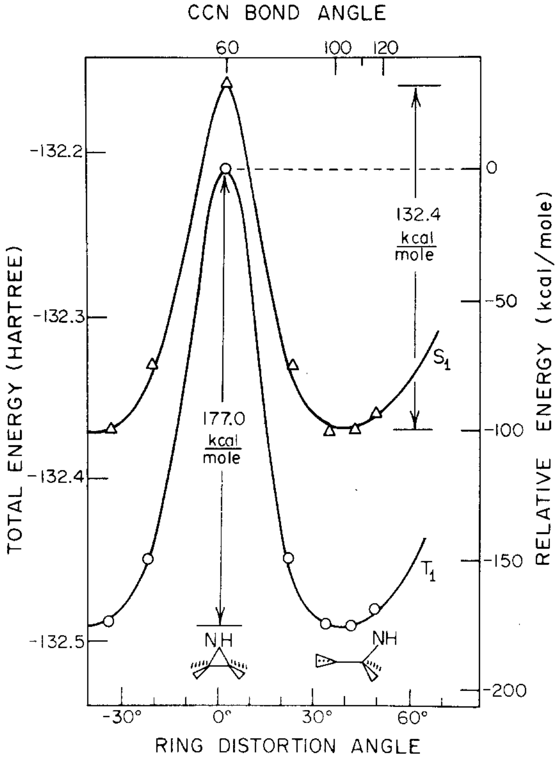

Fig. 4. Energy cross-section showing the effect of ring distortion upon the S_1 and T_1 states of aziridine

All further energy surface investigations were aimed at finding the minima for the first excited singlet and triplet (S_1 and T_1) states. The designation S_1 and T_1 will be most convenient because in many geometries considered no non-trivial elements of symmetry are present. Calculations were then performed at CCN angles of 80°, 100°, 110° and 120°. These points are shown in Fig. 4 where a ring distortion angle, θ, (as illustrated in Fig. 2) is introduced for convenience. At each of these CCN angles the other bond angles were adjusted according to the previous paragraph. This result clearly indicates that in the first excited singlet and triplet states have the open (diradical) structure in contrast to the electronic ground state (S_0) which has only one minimum at the equilibrium nuclear configuration (*cf.* Fig. 2).

This conclusion supports Skell's hypothesis that ethylene and triplet nitrene yields an open diradical structure in the primary step (*cf.* Fig. 1) and it is also in general agreement with the recent investigation of the ethylene and sulfur atom addition reaction [14].

Semi-quantitative studies by Hayes and Siu [15, 16] have considered symmetrical ring-open forms of aziridine ($CH_2=NH-CH_2$) and postulated a 30% diradical character (as opposed to a resonating π-system $CH_2=\overset{+}{N}H-\overset{-}{C}H_2 \rightleftarrows \overset{-}{C}H_2-\overset{+}{N}H=CH_2$) character for this open form. Salem had previously demonstrated [17] that such diradical systems would have equal preference for concerted and non-concerted modes of ring closure and hence open forms with large diradical character should possess small degrees of stereochemical preference.

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