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PHOTOCHEMICAL RING OPENING PATHS OF AZIRINE — AN AB INITIO GVB ENERGY GRADIENT APPROACH

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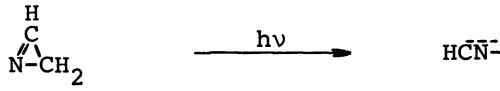
The energy gradient method with the ab initio GVB wavefunction has been used to trace reaction paths of the photochemical ring opening of azirine. All the geometrical parameters have been optimized as functions of the CNC angle for the four low-lying electronic states. Based on the results, a new reaction mechanism has been suggested.

Theoretical interpretation of the mechanism of photochemical reactions requires knowledge of several potential energy surfaces including those for diradical and zwitterionic states.[1,2,3] To describe these surfaces, a theoretical method beyond a single-determinant Hartree-Fock method is necessary because the electron correlation is essential in such states. In the present paper, we have calculated reaction paths for photochemical ring opening, Eq. 1, of azirine by the use of the generalized



(1)

valence bond (GVB)[4] energy gradient method. The few existing molecular orbital (MO) calculations for this system use assumed or partially optimized geometries.[2,5,6] Since electronic states of different nature are involved in photochemical reactions, it is particularly important to optimize geometry for each state. For this purpose, the recently developed energy gradient method with correlated wavefunctions is most appropriate.[7] To our knowledge the present work is the first application of this method to a complex photochemical reaction.

It is sufficient to consider the four low-lying states, $1^1A'$, $1^3A'$, $1^1A''$ and $1^3A''$, in the C_s nuclear framework, to investigate the reaction (1).[2] In constructing the GVB wavefunctions for these states, we have chosen six active orbitals (7a'~10a', 3a'' and 4a'') and assigned six electrons to them. The eight lower orbitals were kept doubly occupied throughout. For example, the GVB wavefunctions for $1^1A'$ and $1^1A''$ are expressed, respectively, as follows:

$$|(1a')^2(2a')^2\cdots(6a')^2(1a'')^2(2a'')^2\{C_1^2(7a')^2-C_1^{*2}(9a')^2\}\{C_2^2(8a')-C_2^{*2}(10a')\}^2 \times \{C_3^2(3a'')^2-C_3^{*2}(4a'')^2\}| \quad (2)$$

$$|(1a')^2(2a')^2\cdots(6a')^2(1a'')^2(2a'')^2\{C_1^2(7a')^2-C_1^{*2}(9a')^2\}\{C_2^2(3a'')^2-C_2^{*2}(10a')^2\} \times (8a')(4a'')\frac{1}{\sqrt{2}}(\alpha\beta-\beta\alpha)| \quad (3)$$

The basis set used was the split valence 4-31G. In Fig.1, the geometrical parameters describing the system are shown. We optimized all seven parameters for a given C_1NC_2 angle, θ, under the assumption of the C_s symmetry. The potential energy curves for four electronic states as functions of θ are plotted in Fig.2. The geometries of stationary points on the surfaces (equilibrium or saddle points) are shown in Table I.

The ring opening on the ground state surface ($1^1A'$) has a large potential barrier of 46 kcal/mol (the saddle point B in Fig.2), which is considerably lower

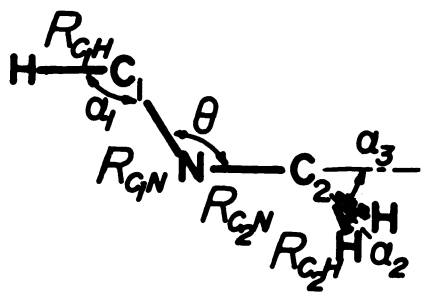


Fig.1 Geometrical parameters used. C_s assumed.

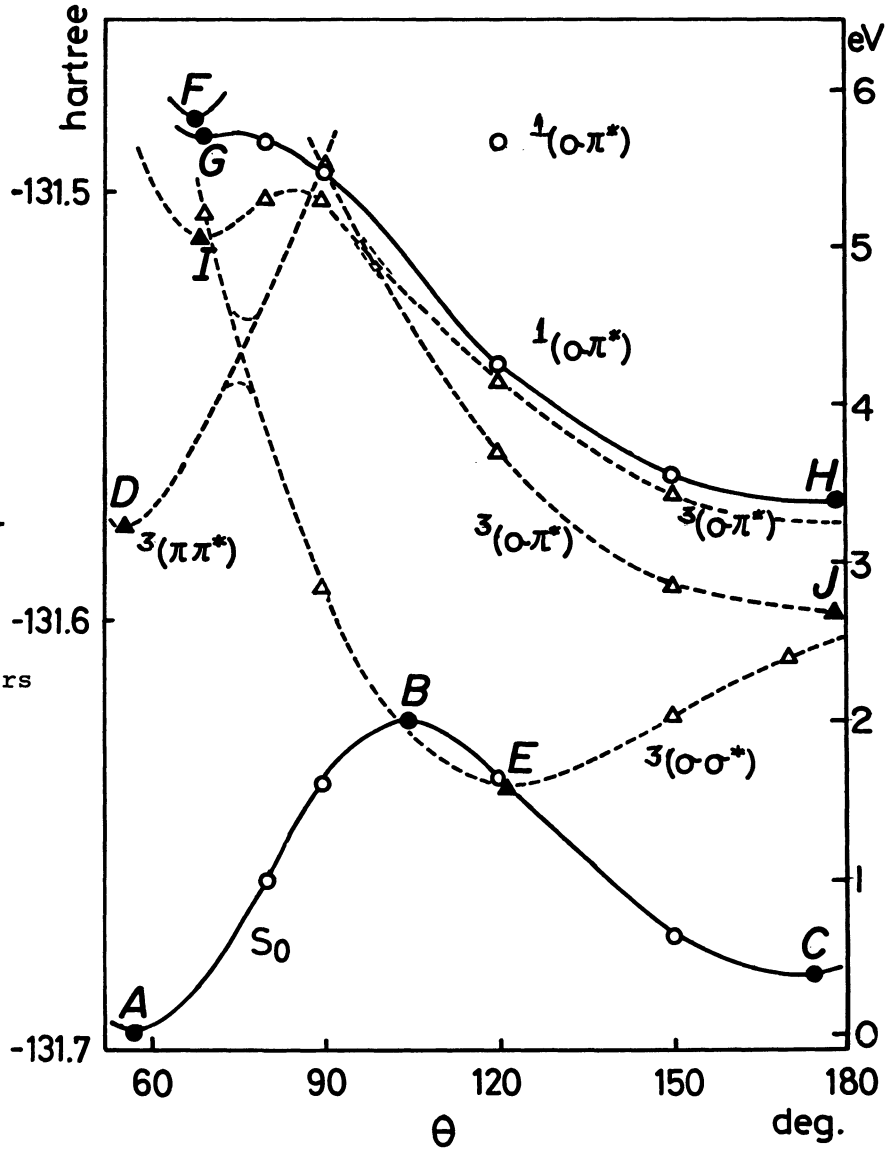
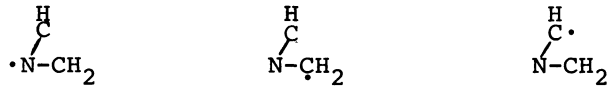


Fig.2 Energies of various states as functions of θ, with all other parameters optimized for each state. Solid and dashed lines are for singlet and triplet, respectively. Symbols correspond to those in Table I.

than ~80 kcal/mol of previous calculations.[2,5] As the ring opens, the "crossing" between the CC boning and antibonding orbital makes the ground state a diradical; the diradical nature becomes maximum at θ~110°, where the coefficients of CC bonding and antibonding orbital, C_1^2 and C_1^{*2} in Eq.2, are equal. The $^3(\pi\pi^*)$ state, the lowest $^3A'$ state near the reactant D, increases its energy with the increase of θ. At θ~75°, the $^3(\pi\pi^*)$ surface crosses with the $^3(\sigma\sigma^*)$ surface; they form an avoided crossing in the real surfaces. As seen in Fig.2, the $^3(\sigma\sigma^*)$ state comes below the ground state for 100°<θ<120°. Considering that the $^3(\sigma\sigma^*)$ has a minimum E at θ~120° and that its geometry in this region is very similar to that of the ground singlet state (Table I), the intersystem crossing between them is expected to be a very efficient process.

For the A" state, we can consider three different types of electronic configurations classified by the position of the σ odd electron. Experimentally



(I) (II) (III)

the photochemical ring opening reaction is initiated by the excitation to the $^1(n\pi^*)$ state F, type (I). The calculated excitation energy is 5.7 eV, which is to be compared with the experimental value for aromatic substituted azirine, 5.2 eV.[8] As seen in Fig.2, there is another equilibrium point G at θ~70°, correspoinding to the type (II) electronic configuration. Although these two points lie on the same adiabatic surface, they are independent equilibrium points as their geometries and electronic configurations are very different from each other. The type (II) $^1A"$ state is correlated to the open form of $^1(\sigma\pi^*)$ state H and its energy decreases rapidly with an increase of θ, possibly after a slight potential barrier at θ~80°. For the $^3A"$ state, only one equilibrium point I ($^3(n\pi^*)$, type (I)) was obtained near the reactant geometry. In this case, the electronic configuration changes

Table I. Optimized Stationary Points and Some of Their Geometrical Parameters[a]

Symbol[b]		R_{C_2N}	R_{C_1N}	θ	α_1	α_3
A	Azirine (S_0)	1.70	1.27	57	137	37
B	Saddle Point on S_0	1.50	1.26	105	131	20
C	Open Form (S_0)	1.29	1.23	174	117	0
D	$^3(\pi\pi^*)$	1.60	1.52	55	139	41
E	$^3(\sigma\sigma^*)$	1.45	1.25	122	128	27
F	$^1(n\pi^*)$	1.46	1.37	69	149	25
G	$^1(\sigma\pi^*)$ type (II)	1.70	1.30	70	166	29
H	$^1(\sigma\pi^*)$ Open Form	1.39	1.21	178	180	5
I	$^3(n\pi^*)$	1.45	1.35	69	148	25
J	$^3(\sigma\pi^*)$ Open Form	1.25	1.36	178	125	0

a) Bond distances are in Å and angles are in degrees.

b) Symbols correspond to those in Fig.2.

smoothly from the type (I) to the type (II) along the ring opening path. This potential energy curve is nearly parallel to the type (II) $^1(\sigma\pi^*)$ curve in the region of $\theta>90°$. The $^3(\sigma\pi^*)$ type (III) configuration becomes lower in energy than the type (II) for $\theta\gtrsim100°$ and the energy separation between $^3(\sigma\sigma^*)$ and $^3(\sigma\pi^*)$ becomes small at $\theta\sim180°$. The corresponding singlet state type (III) was optimized at $\theta=120°$, but its energy is much higher than the type II singlet.

Compared with the previous calculations, new observations obtained from the present calculation are as follows. (1) The $^1A''$ state is strongly downhill along the ring opening path, contrary to a very flat curve of previous calculations. This suggests that the $^1(n\pi^*)$ state may have a very short lifetime if the barrier between the type (I) and the type (II) singlet state is not high. (2) There is a new triplet state belonging to the type (III), which was not known previously. These new findings are due to extensive optimization of excited state geometries. Since many electronic configurations of different nature are involved and their preferred geometries are different from each other, assumed geometries could give misleading results. We have found an intimate interplay between the ring opening angle θ, the C_1N and C_2N distances and the CH_2 distortion angles for each type of state. Details of findings will be published elsewhere.

In the previous studies the reaction mechanism has been interpreted as the intersystem crossing from the $^1(n\pi^*)$ to the $^3A'$ state, followed by another intersystem crossing from $^3A'$ to the ground state near the minimum of the $^3A'$ state. This mechanism would be operational if the lifetime of $^1(n\pi^*)$ state is long. From the results of present calculation, we can suggest an alternative route of reaction through the open form of the $^1A''$ state. The reaction system initiated at the vertically excited $^1(n\pi^*)$ state can directly travel in the region of F or G and ride downhill on the $1^1A''$ surface, to produce the open form of the $^1A''$ state H. This process would be efficient since it involves no intersystem crossing. Once formed, H can be converted easily to the ground state either by internal conversion or by intersystem crossing through the $^3(\sigma\sigma^*)$ state.

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