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Photochemical Electrocyclic Reaction Mechanism of Methyleneamine *N*-Oxide to Form Oxaziridine. MINDO/3 CI Study

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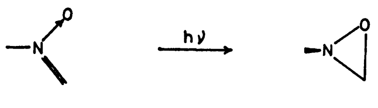
The photochemical electrocyclic reaction mechanism of methyleneamine *N*-oxide to form oxaziridine was explored on the basis of the potential energy surfaces obtained by the MINDO/3 CI calculation. The strong interaction between the ground state and the doubly-excited state, which appears in the disrotatory cyclization process of the corresponding hydrocarbon system, was not observed. Instead, a deep potential well, which can be a leakage channel from the excited state to the ground state, was found in the S_1 surface. The predicted reaction path is characteristic of hetero-atom conjugated systems, and an important participation of the oxygen σ lone-pair electrons is expected in this reaction path.

Photochemical isomerization reactions of methyleneamine *N*-oxide, **1**, are quite common;[1–3] they undergo *cis-trans* isomerization reaction and electrocyclic reaction to form oxaziridines, **2**. Although the thermal (ground state) *cis-trans* isomerization reaction of **1**[4] and the photo-isomerization of **2** into amides[5] have been studied theoretically, little attention has been paid to the electron behavior and reaction paths for the photochemical electrocyclic **1**→**2** reaction. From the orbital symmetry arguments,[6,7] the allyl anion is expected to cyclize photochemically by disrotatory rotation of the methylene groups. The formal electrocyclic **1**→**2** reaction may be considered to proceed by means of a mechanism similar to that of the **3**→**4** reaction.[2] However, there are two essential differences between the **1**→**2** and **3**→**4** reactions. The first is the mode of rotation of the methylene groups. In the conjugated hydrocarbon system, **3**→**4**, the disrotatory and conrotatory modes give potential curves of very different shapes, while there is no distinction between these two rotation modes in the **1**→**2** reaction, since only one methylene group is involved in methyleneamine *N*-oxide. The second difference is the existence of the lone-pair electrons of the terminal oxygen atom of methyleneamine *N*-oxide. Since the lone-pair electrons distribute on the σ framework where the new σ bond is being formed, the lone-pair electrons should participate in the electrocyclic reaction mechanism of the **1**→**2** reaction, even if the photochemical reaction proceeds from the $\pi\to\pi^*$ excited state. Because of these essential differences, the mechanism of the **1**→**2** reaction cannot be understood sufficiently well by analogy with the **3**→**4** reaction; therefore it is worthwhile to investigate the reaction process of the **1**→**2** reaction and to compare the reaction mechanism with that of the all-hydrocarbon conjugated system, **3**→**4**. In the present study, the reaction paths of the **1**→**2** reaction will be explored on the basis of the potential energy surfaces obtained by means of the semi-empirical MINDO/3[9] CI calculation.



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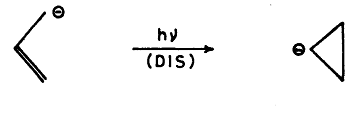

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Method and Results

The structures of the compounds **1** and **2** were optimized by the SCF MINDO/3 (without CI) calculation. They are shown in Fig. 1. The potential energy surfaces for the **1**→**2** reaction are a function of many geometrical variables. In the present study, the potential energy surfaces were calculated with respect to two independent variables. One of these is the rotation angle, θ, of the methylene group. All the other geometrical variables were allowed to vary simultaneously from their initial to final values. This variation is expressed by the second parameter, d, which varies from 0.0 (initial) to 1.0 (final). In the CI calculation, 40 and 39 configuration functions were selected from the singly- and doubly-excited configurations for the singlet and triplet states respectively. The potential energy surfaces of four lower singlet states are shown in Fig. 2. The symbols W and H correspond to local minimum and maximum points on the potential surfaces respectively. The broken line in Fig. 2-a indicates the concerted path in which all the geometrical variables vary simultaneously. The potential energy curves along this concerted path are shown in Fig. 3. The S_1 and S_2 states of methyleneamine *N*-oxide consist of the $n_0\to\pi^*$ and $\pi\to\sigma^*$ excited configurations. The $\pi\to\pi^*$ configuration is involved in the S_3 and S_5 excited states. The T_1 state is the $\pi\to\pi^*$ triplet state and the T_3 state is the $n_0\to\pi^*$ triplet state.

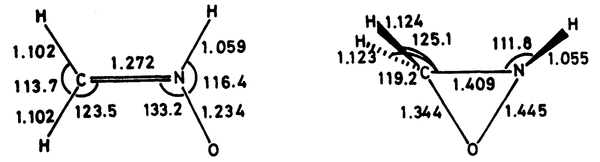


Fig. 1. Molecular structures of methyleneamine *N*-oxide and the oxaziridine optimized by the MINDO/3 method. Bond lengths are in Å and bond angles are in degrees.

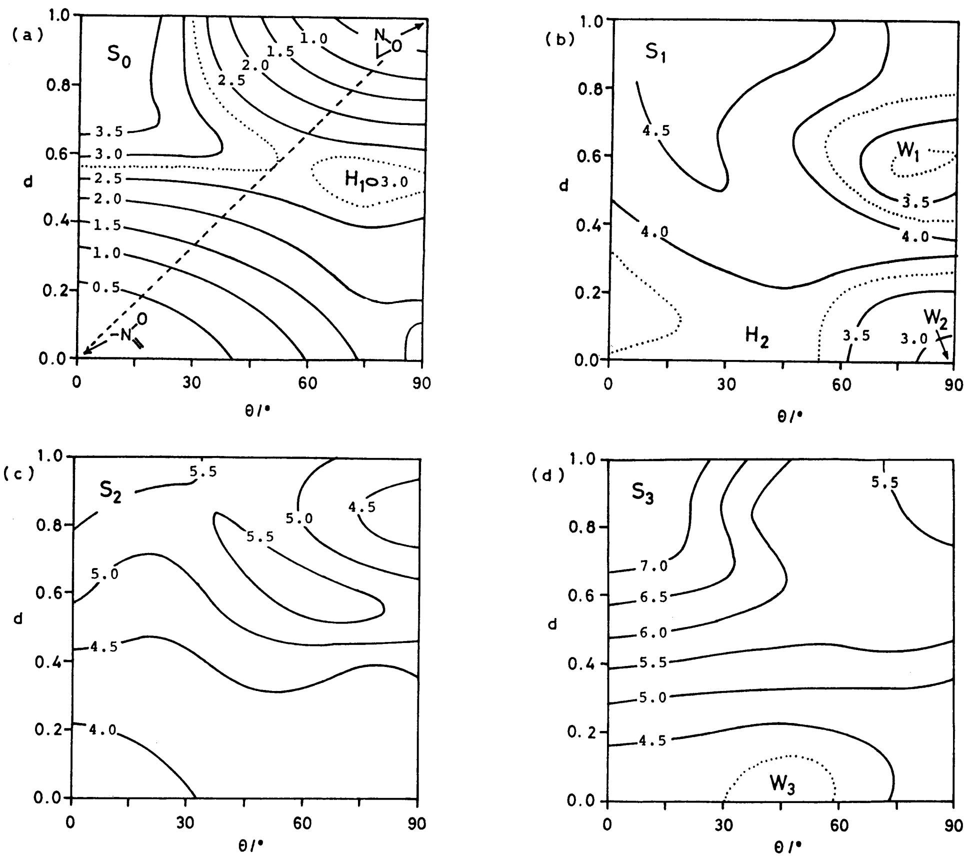


Fig. 2. Two-dimensional potential energy surfaces of (a) S_0, (b) S_1, (c) S_2, and (d) S_3 states of the methyleneamine *N*-oxide–oxaziridine system. The energies (eV) are relative values with respect to the ground state of methylenimine *N*-oxide.

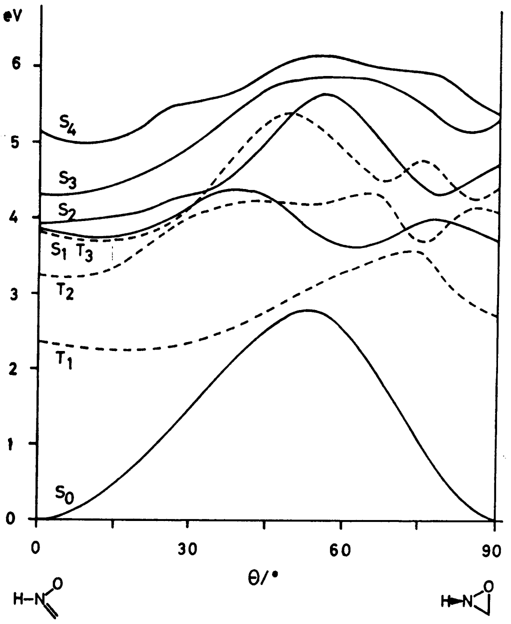


Fig. 3. Potential energy curves for the methyleneamine *N*-oxide–oxaziridine system along the concerted path. All the geometrical variables are varied simultaneously between the optimized structures of methyleneamine *N*-oxide and the oxaziridine.

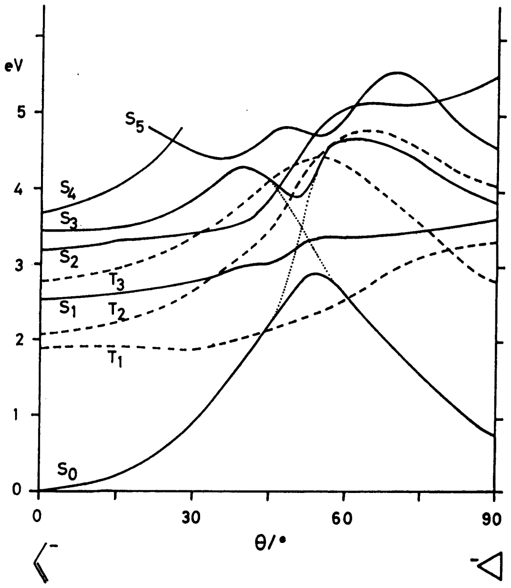


Fig. 4. Potential energy curves along the disrotatory mode of cyclization of the allyl anion into the cyclopropyl anion. All the geometrical variables are varied simultaneously between the two species.

The potential curves for the disrotatory cyclization of the allyl anion along the concerted path are shown in Fig. 4. The S_1 and S_2 states are the $\pi\rightarrow\sigma^*$ singlet states. The S_4 state is the $\pi\rightarrow\pi^*$ singlet state. The $\pi\rightarrow\pi^*$ doubly-excited configuration is involved in the S_5 state. The T_1 state is the $\pi\rightarrow\pi^*$ triplet state. The π_2 and π_3 MO's of the allyl anion cross during the cyclization; avoided crossing at the middle stage of the cyclization involves the ground state and $\pi_2\rightarrow\pi_3$ doubly-excited configurations. The true crossing which involves the $\pi\rightarrow\pi^*$ singly-excited state and its doubly-excited counterpart occurs between the S_4 and S_5 curves at the begining of cyclization. This crossing point lies higher (1 eV) than the S_4 state of the allyl anion; it is expected that the photochemical cyclization of the allyl anion from its $\pi\rightarrow\pi^*$ singlet state is inefficient.

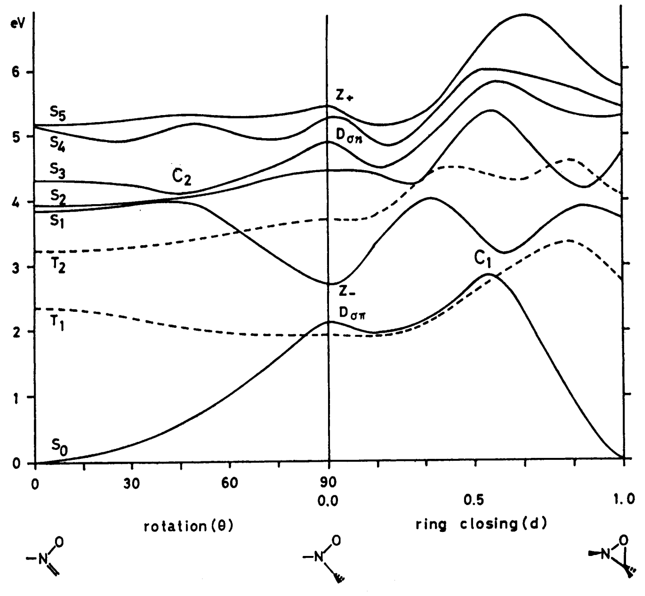
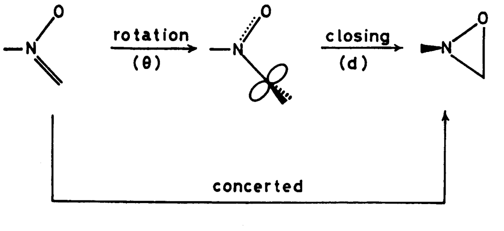
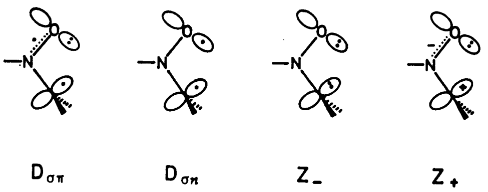


Fig. 5. Potential energy curves for the step-by-step path of the methyleneamine *N*-oxide–oxaziridine system. θ is the rotation angle (degree) of the terminal methylene and d represents the simultaneous change of all the geometrical variables other than θ.

It has been pointed out that the step-by-step path in which the methylene rotation is followed by ring closure may exist in the photochemical electrocyclic reaction of hetero-atom conjugated systems.[8,10] The potential curves along this path are shown in Fig. 5. The vertical line at the center of Fig. 5 corresponds to the twisted structure of methyleneamine *N*-oxide. The D and Z states of the twisted structure have the following electron configurations. In the twisted structure, the $D_{\sigma\pi}$ diradical state has a symmetry property different from that of the Z_-, $D_{\sigma\pi}$, and Z_+ states. The C_1 avoided crossing is caused by pyramidalization of the nitrogen atom during the ring closing.





Discussion

During the photochemical electrocyclic reaction of the allyl anion, the symmetry-allowed crossing occurs between the highest occupied π_2 orbital and the unoccupied π_3 orbital. In this crossing region, strong coupling exists between the ground and the $\pi_2\rightarrow\pi_3$ doubly-excited configurations, and it gives the avoided crossing between the S_0 and S_2 potential energy curves shown in Fig. 4; this is the "C" type of avoided crossing in Salem's classification.[11] In the case of the cyclization of methyleneamine *N*-oxide, the strong coupling between the ground and the doubly-excited configurations does not exist due to the non-symmetric property of the system with respect to the vertical plane; no crossing occurs between π_2 and π_3 orbitals of methyleneamine *N*-oxide. The interaction between the S_0 and S_1 states observed in Fig. 3 is a different kind of avoided crossing. As may be seen from Figs. 2-a and 2-b, the S_0-S_1 interaction observed in Fig. 3 originates from the S_0-S_1 interaction at the W_1 region in the two-dimensional surfaces. Since the θ value at this region is large (80°), this crossing can be understood from the state correlation diagram between the 90°-twisted structure and its cyclization product (Fig. 6). The ground $D_{\sigma\pi}$ state correlates with the $\pi\sigma^*$ excited state of the cyclic product, while the Z_+ (or $D_{\sigma\pi}$) excited state correlates with the ground state of the cyclic product. If the symmetry property with respect to the CN(H)O molecular framework is preserved during the cyclization, the $D_{\sigma\pi}$-Z_+ crossing

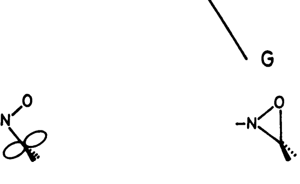
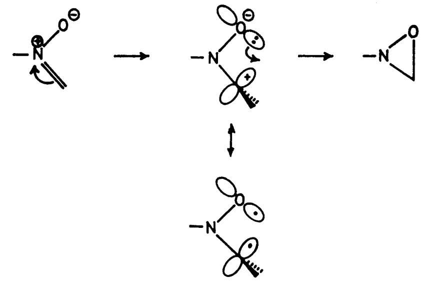


Fig. 6. State correlation diagram between the twisted structure of methyleneamine *N*-oxide and its cyclic structure.

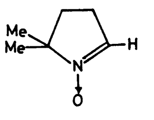
is allowed symmetrically as shown in the correlation diagram. In reality, however, the N–H hydrogen atom moves out of the plane during the cyclization, and the two states mix. The avoided crossing appeared in Figs. 2-a and 2-b is caused by this geometrical change; this is the "A" type of avoided crossing in Salem's classification.[11)]

The clear difference between the potential energy curves of the **1**→**2** and **3**→**4** reactions indicates that the photochemical electrocyclic reaction of **1** proceeds by means of a mechanism different from that of its corresponding all-hydrocarbon system, **3**. The W_1 well in the S_1 surface can be a leakage channel from the excited state to the ground state, and the photochemical formation of the oxaziridine is expected to proceed through the non-adiabatic transition from the W_1 well to the S_0 surface; the reaction mechanism can be expressed by the following scheme.

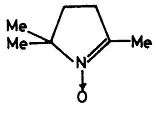


In this mechanism, the oxygen lone-pair electrons on the CNO plane play a key role. The important role of the lone-pair electrons on the terminal hetero atom in the photochemical electrocyclic reaction of hetero-atom conjugated systems has been pointed out in our previous studies on the acrylaldehyde–oxetene system.[8,10)]

The calculated potential surfaces (Fig. 2) indicate a strong interaction between the S_3 and S_1 surfaces at the W_3 region. The $\pi\rightarrow\pi^*$ excited state (S_3) of methyleneamine *N*-oxide will have high chance to access the W_1 well and to form the oxaziridine through the $W_3\rightarrow H_2$ transition. On the other hand, the formation of the twisted Z_- state (W_2 well in Fig. 2) from the $\pi\rightarrow\pi^*$ excited state results in reproduction of methyleneamine *N*-oxide; this is the *cis-trans* isomerization process. As may be seen from Fig. 2-b, the formation of oxaziridine (the $H_2\rightarrow W_1$ path) competes with the *cis-trans* isomerization (the $H_2\rightarrow W_2$ path). It is expected that the methyleneamine *N*-oxides having a lower W_1 well and a higher W_2 well undergo cyclization to form oxaziridines preferably than the *cis-trans* isomerization. Since the electronic structure at W_1 involves the Z_+ character and that at W_2 is of the Z_- type, the electron-donating substituents at the carbon atom increases the formation of the oxaziridine, while the electron-donating substituents at the nitrogen atom decreases it. The oxaziridine formation (%) from the above three compounds[12,13)] is parallel to this prediction.



(11%)



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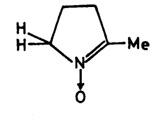
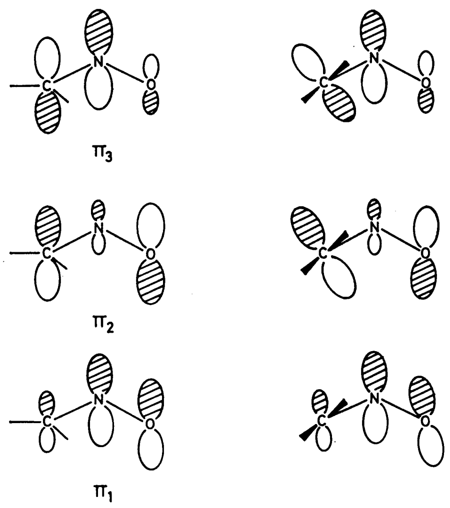


(50%)

Since only one methylene group is involved in methyleneamine *N*-oxide, there is no distinction between the conrotatory and disrotatory modes of methylene rotation. However, it may be interesting to illustrate the change in the orbital shape on the oxygen atom, which is induced by the rotation of the terminal methylene group. When the terminal methylene group is rotated, the π_1 orbital fragment on the oxygen atom rotates in the conratatory manner, while other π orbitals remain unchanged.



Planar 30° rotation

References

1) G. G. Spence, E. C. Taylor, and O. Buchardt, *Chem. Rev.*, **70**, 231 (1970).

2) N. J. Turro, "Modern Molecular Photochemistry," Benjamin/Cummings, Menlo Park, Calif. (1978), p. 510.

3) A. Lablache-Combier, "Photochemistry of Heterocyclic Compounds," ed by O. Buchardt, John Wiley and Sons, New York (1976), p. 207.

4) W. B. Jennings, D. R. Boyd, and L. C. Waring, *J. Chem. Soc., Perkin Trans. 2*, **1976**, 610; W. B. Jennings and S. D. Warley, *Tetrahedron Lett.*, **1977**, 1435.

5) E. Oliveros, M. Riviere, J. P. Malrieu, and Ch. Teichteil, *J. Am. Chem. Soc.*, **101**, 318 (1976).

6) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965).

7) K. Fukui, *Bull. Chem. Soc. Jpn.*, **39**, 498 (1966).

8) O. Kikuchi, H. Kubota, and K. Suzuki, *Bull. Chem. Soc. Jpn.*, **54**, 1126 (1981).

9) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97**, 1285 (1975).

10) O. Kikuchi, *Tetrahedron Lett.*, **22**, 859 (1981).

11) L. Salem, *J. Am. Chem. Soc.*, **96**, 3486 (1974).

12) L. S. Kaminsky and M. Lamchan, *J. Chem. Soc., C*, **1966**, 2295; **1967**, 2128.

13) R. Bonnett, V. M. Clark, and A. Todd, *J. Chem. Soc.*, **1959**, 2102.