

## The Role of Lone Pairs in Heteroatomic Chemistry. Graphical Analysis and *Ab Initio* Calculations of Oxirane and Aziridine Ring Opening

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Received March 6, 1984

The »overlap graph«, where vertices represent atomic orbitals and edges, their in-phase or out-of-phase overlaps, suggests that, in the thermal electrocyclic opening of oxirane, the second oxygen lone pair has little effect on the allowed conrotatory mode but lowers the activation energy of the forbidden disrotatory mode. This effect does not exist in the electrocyclic opening of aziridine, which is one reason why the energy gap between the allowed and forbidden processes should remain substantial. In the course of an aziridine ring opening, the nitrogen's hydrogen may remain in the plane of the heavy atoms or may move out into either of the two half-spaces defined by this plane. Three different disrotatory pathways are thus conceivable. They are compared by a perturbational treatment using simple Hückel theory. Localization of the transition states on these three reaction paths — *i. e.* determination of their »early« or »late« character, as measured by the magnitude of the rotation of the two methylene groups, for example — can be made with the help of »natural correlation diagrams«. This provides a simple criterion for predicting the breakdown of the perturbational treatment, when pathways of similar energies are compared: if one transition state is much earlier (later) than the other(s), no safe conclusion can be reached. These qualitative arguments are fully supported by *ab initio* calculations (STO-3G + (3 × 3) CI and 4-31G + extensive CI). Substituent effects and possible cases of violation of orbital symmetry requirements are discussed.

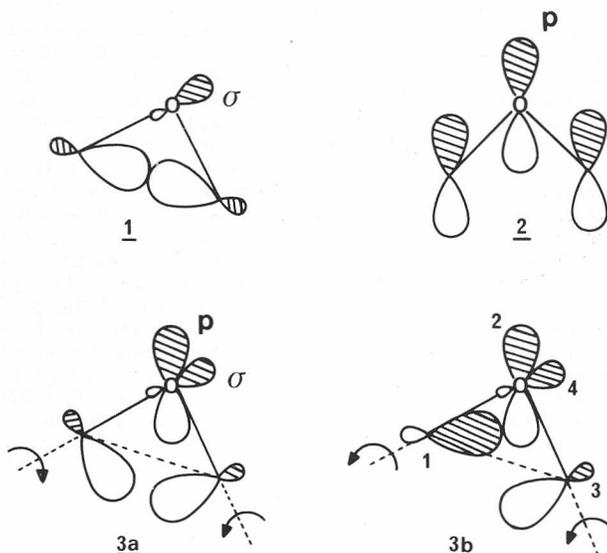
### INTRODUCTION

There is nowadays a large choice of quantum chemical programs of all degrees of sophistication and every chemist can easily have access to powerful, high-speed electronic computers. Theoretical calculations can therefore be routinely performed. However, »to transform calculation into understanding, we need sharpened analytical tools with which we may extract the essential physical features which made a calculation come out the way it indeed did.«<sup>2</sup> In this paper, we wish to show that natural correlation diagrams, which hitherto have been mostly employed for the study of photochemical reactions<sup>3</sup>, can also be useful for the study of thermal reactions, and that the *overlap graph* can give valuable insights, especially in the perturbational analysis of systems in which one atom makes use of two or more atomic orbitals.

I. THERMAL ELECTROCYCLIC OPENINGS OF OXIRANES AND AZIRIDINES.  
 A QUALITATIVE TREATMENT

Huisgen and his co-workers<sup>4</sup> have found that while the thermal opening of aziridines is conrotatory, that of oxiranes may give a mixture of products resulting formally from both the conrotatory and disrotatory processes. This difference in behaviour has been attributed to the higher electronegativity of the oxygen atom which reduces the energy gap between the allowed and forbidden processes and lowers the barrier for carbonyl ylid isomerization\*. The electronegativity change is certainly an important factor, but one may wonder if it is the only one. In particular, cannot the second lone pair of oxygen also play a role?

As a matter of fact, it is usual to consider the carbonyl ylid (or azomethine ylid) to be isoconjugate with the allyl anion. Applying the Woodward-Hoffmann rules, it is then predicted that the thermal ring opening should be conrotatory. This approach is not entirely correct. In the initial compound oxirane **1**, the carbon atomic orbitals overlap with the  $\sigma$  oxygen lone pair. In the product (carbonyl ylid **2**), they interact with the  $p$  lone pair. In consequence, there is no reason why one should single out one lone pair and completely neglect the other. Furthermore, it is obvious that in the transition state (**3a** or **3b**)\*\*, whose energy is rate-determining, both lone pairs overlap with the carbon AO's.



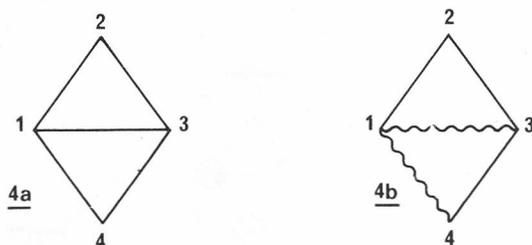
## A. »Overlap Graph«

It is also clear that if both lone pairs are taken into account, the Woodward-Hoffmann rules are not directly applicable, the oxygen atom contributing two AO's and 4 electrons<sup>7</sup>. The transition state is a 6 electron system, but the

\* *Ab initio* calculations indicate that there is indeed a reduction of the activation energy gap ( $\sim 11$  kcal/mol for oxirane<sup>5</sup> vs.  $\sim 18$  kcal/mol for aziridine, *vide infra*). According to the same calculations, however, the loss of stereospecificity in oxirane is due to the rapid isomerization of carbonyl ylid.

\*\* Strictly speaking, the highest point on the symmetry-forbidden reaction path is *not* a transition state, but a hilltop<sup>5,6</sup>.

reaction will not be disrotatory. We have found that »overlap graphs«\* can be of great help in the qualitative analysis of those problems in which at least one atom makes use of more than one atomic orbital. In these graphs, vertices represent atomic orbitals and edges connect overlapping AO's. If in the basis set two AO's overlap in phase (out of phase), the corresponding vertices are linked by a straight-line (wavy) edge. Thus **4a** and **4b** are the graphs corresponding to **3a** and **3b**, with the AO numbering shown in **3b**\*\*



In the first approximation, all four AO's may be considered as equivalent: **4a** and **4b** result then from the union of AO 4 with a Hückel and a Möbius

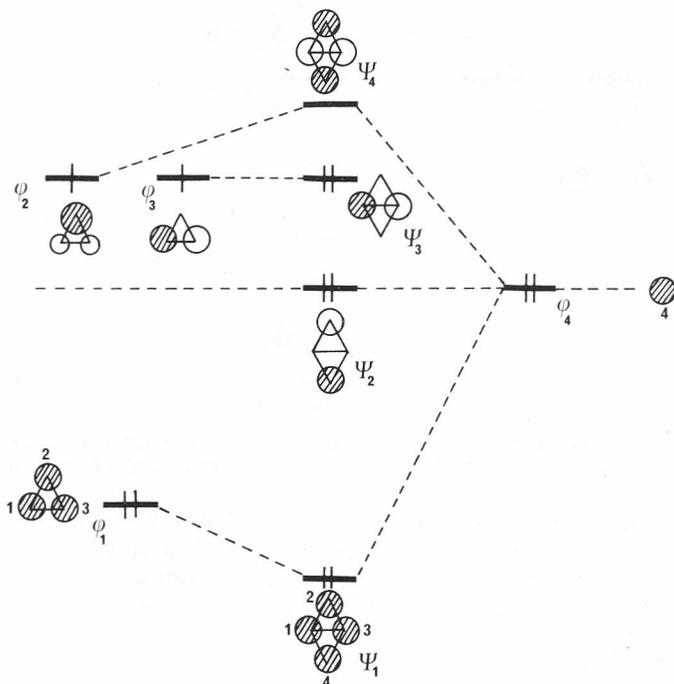


Figure 1. Interaction diagram showing the effect of the second lone pair of oxygen in the disrotatory opening of oxirane. The diagram also indicates the qualitative construction of the MO's of **4a**.

\* This neologism has been introduced in order to distinguish these graphs from the usual chemical graphs (molecular graphs, Hückel graphs<sup>8</sup>) in which vertices represents atoms.

\*\* The choice of the AO phases in the basis set is completely arbitrary. A different graph may correspond to each choice but this does not change the chemical conclusions.

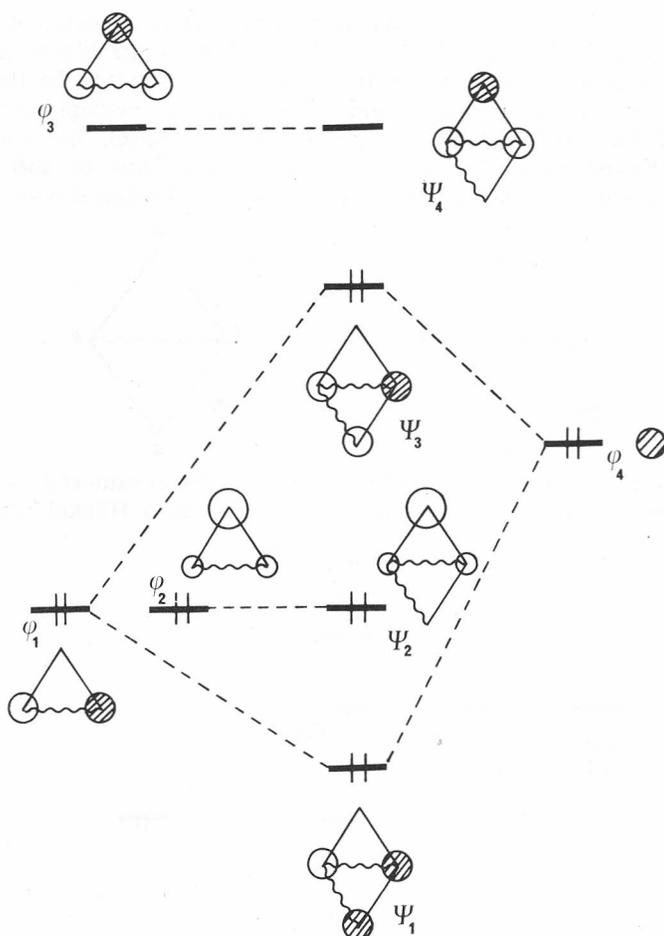


Figure 2. Interaction diagram showing the effect of the oxygen  $\sigma$  lone pair in the conrotatory opening of oxirane. Qualitative construction of the MO's of **4b**.

3-annulene respectively. The union is such that AO 4 overlaps in phase with both AO's 1 and 3 in **4a**; it overlaps in phase with 3 and out of phase with 1 in **4b**. The MO's may then be constructed by perturbation, as shown in Figures 1 and 2. Let us analyse these interaction diagrams in some details.

### B. The Role of the Second Oxygen Lone Pair

Note first that the 3-annulene fragment (left part of Figures 1 and 2) corresponds to the usual approximation in which one lone pair is neglected. It follows that Figures 1 and 2 may be considered as showing either the perturbative construction of the MO's of **4a** and **4b** or as showing the effect of the second lone pair in the disrotatory and conrotatory processes. In the diagram of Figure 1, for symmetry reasons,  $\varphi_4$  can interact only with  $\varphi_1$  and  $\varphi_2$ . At the simple Hückel level of approximation,  $\varphi_2$  is raised ( $\varphi_2 \rightarrow \psi_4$ ),  $\varphi_1$  is lowered ( $\varphi_1 \rightarrow \psi_1$ ) and the two interactions ( $\varphi_1, \varphi_4$ ) and ( $\varphi_2, \varphi_4$ ) are equal in

magnitude: the energy gap between  $\varphi_1$  and  $\varphi_4$  is bigger but this is compensated by the larger  $S_{14}$  overlap. Therefore,  $\varphi_4$  remains at the same non-bonding level ( $\varphi_4 \rightarrow \psi_2$ ). Naturally,  $\varphi_3$  is transformed, unperturbed, into  $\psi_3$ . Thus, *intervention of the  $\sigma$  oxygen lone pair lowers the activation energy of the forbidden disrotatory process*: two electrons, initially occupying  $\varphi_1$ , are stabilized, whereas the other four electrons remain unchanged.

In the conrotatory process (Figure 2),  $\varphi_4$  can interact only with  $\varphi_1$  (remember that in **4b**, the overlap between AO's 1 and 4 is out of phase). Both orbitals being occupied, what is gained by the stabilization of  $\varphi_1$  is exactly compensated by the destabilization of  $\varphi_4$ : in the first approximation, *the effect of the  $\sigma$  oxygen lone pair on the energy of the allowed conrotatory transition state is nil*.

The basis sets and AO numbering being as indicated in **3a** and **3b**, the MO's of these transition state models can be easily deduced from Figures 1 and 2. Figure 3 shows the »translation« of the MO's of Figure 1 into their conventional three-dimensional representations.

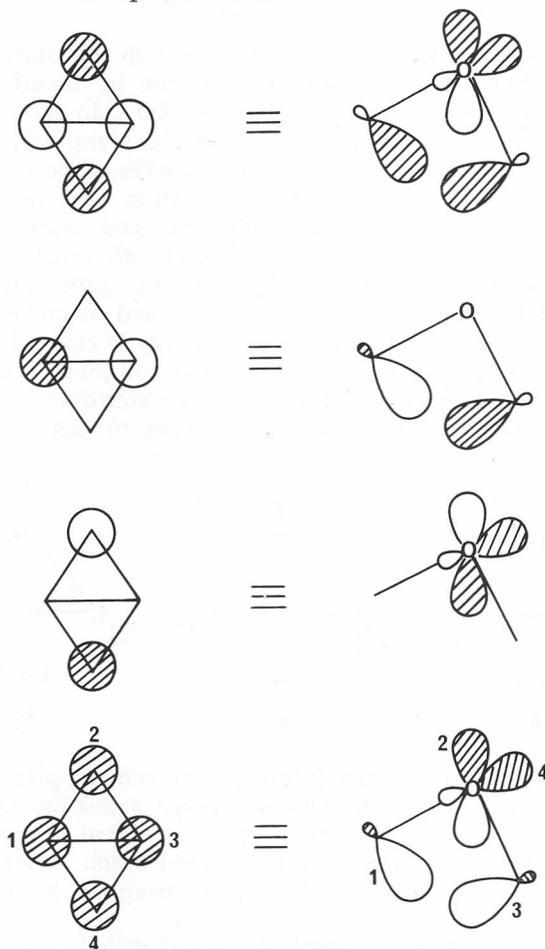
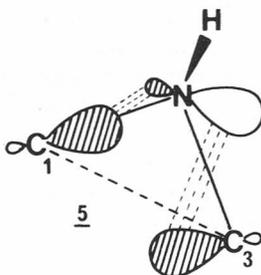


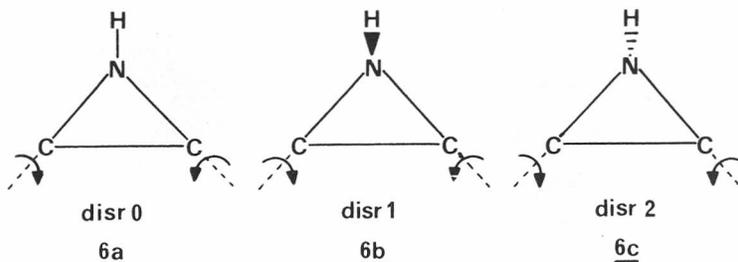
Figure 3. The MO's of **4a** in their graphical forms and the corresponding usual three-dimensional representations.

### C. The Lone Pair in Aziridines

Let us now turn to the aziridine ring opening. No second lone pair\* can intervene here to lower the forbidden pathway, and taking into account also the fact that nitrogen is not highly electronegative, it is expected that the energy gap between the conrotatory and disrotatory modes should remain substantial.



Although the direct influence of the NH bond on the course of the reaction is negligible, this bond can play an indirect role by modifying the overlap between the nitrogen lone pair and the carbon AO's. In the conrotatory mode (cf. 5), moving the hydrogen atom out of the CNC plane will slightly increase one overlap ( $\langle N | C_1 \rangle$ ) and more sharply decrease the other overlap ( $\langle N | C_3 \rangle$ ). It may then be presumed that the nitrogen atom will remain planar in a conrotatory ring opening, provided that the enhanced »aromatic stabilization« overrides the nitrogen inversion barrier. Indeed, *ab initio* calculations (*vide infra*) indicate that in the optimized conrotatory path, the nitrogen atom remains planar. If the hydrogen atom is constrained to move out of the CNC plane by an angle of  $60^\circ$ , the transition state energy is raised by  $\sim 10$  kcal/mol. This implies that when N is substituted by a donor (halide, alkoxy or amino) group, as the inversion barrier is then high<sup>9</sup>, the conrotatory process becomes less easy than for aziridine itself. We shall return to this point later.



For the disrotatory mode, the N atom may remain planar or may pyramidalize either »upward« or »downward«. These 3 possibilities are shown in **6a**, **6b** and **6c**. Now the transition state for an aziridine disrotatory opening is isoconjugate with the antiaromatic cyclopropenyl anion, whose Hückel energy is  $2\beta$ . Assuming that  $\beta$  is proportional to the overlap ( $S$ ), increasing  $S$  will sta-

\* The N—H bond may be neglected, its corresponding  $\sigma$  and  $\sigma^*$  orbitals lying too low or too high to interact efficiently with the carbon AO's.

bilize the transition state. With respect to mode DISR.0 represented in **6a**, all other geometrical parameters being the same, the N—C overlap is diminished in mode DISR.1 and augmented in mode DISR.2. In other words, the decreasing order of preference for a disrotatory aziridine opening should be:

$$\text{DISR.2} > \text{DISR.0} > \text{DISR.1}$$

The above argument is based on a model of the transition state. It is interesting to compare its conclusions to those reached by a perturbational treatment of the initial stages of the ring-opening (ring-closure) reaction. The MO's undergoing a major change in the electrocyclic interconversion are shown in Figure 5. Their symmetry is defined with respect to the plane orthogonal to the ring. In the cyclic structures for DISR.1 and DISR.2 (left-hand side in Figures 5a and 5b), the  $\sigma$  and  $\sigma^*$  orbitals associated with the CC bond and the nitrogen lone pair  $n$  are involved. Due to the out-of-plane position of the central hydrogen atom, the  $\sigma$  and  $n$  orbitals, both of  $S$  symmetry, can interact leading to an in-phase  $\sigma + n$  and an out-of-phase  $n - \sigma$  combination (**7a** and **7b**). In the azomethine ylids (right hand side in Figure 5a and 5b) the usual allylic  $\pi$  orbitals are involved.



**7a** bonding  $\sigma + n$  interaction

**7b** antibonding  $n - \sigma$  interaction

In the ring opening process, the energy change of the  $\sigma + n$  combination favors DISR.2 rather than DISR.1. For the  $n - \sigma$  combination, the situation is reversed. Thus, no definite conclusion can be reached by perturbation arguments alone. *Ab initio* calculations suggest a steeper initial slope for DISR.2 (Figure 7). In the ring closure reaction, the HOMO  $\pi_2$  is the same for the three DISR. modes. The only discrimination comes from the lowest MO  $\pi_1$ , whose stabilization is largest for DISR.2 intermediate for DISR.0 and smallest for DISR.1.

Thus, predictions based on an antiaromatic transition state model agree with the initial slopes of the ring-closure pathways but not with the initial slopes of the ring-opening pathways (Figure 7). A possible explanation of this discrepancy is given in Figure 4. Let us consider two competitive reactions having comparable activation energies. If the two transition states are reached at about the same value of the reaction coordinate (Figure 4b), or if the earlier transition state corresponds to the pathway with the smoother initial slope (Figure 4a), then perturbation treatment of the direct or reverse reaction should give exactly the same results: one pathway always lies below the other one. However, the perturbational treatment breaks down if the earlier transition state belongs to the pathway with the steepest initial slope (Figure 4c): the two pathways will cross and predictions for the direct reaction will differ from those for the reverse reaction. Furthermore, higher activation

energy may correspond to the pathway with the smoother initial slope if the transition state is late enough.

To check that the DISR.0, DISR.1 and DISR.2 paths for aziridine ring opening cross as in Figure 4c, we must be able to localize correctly the relative positions of the three transition states on the reaction paths. This, fortunately, can be done without extensive calculations, with the help of »natural correlation diagrams«<sup>3</sup>.

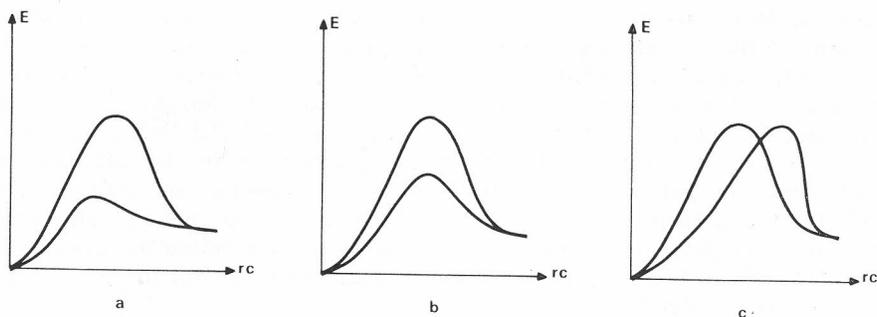


Figure 4. Relative positions of competitive transition states and failure of the perturbational treatment. a) The pathway with the smoother initial slope has earlier transition state. b) Both transition states are reached for about the same value of the reaction coordinate. c) The earlier transition state belongs to the pathway with the steepest initial slope. A crossing occurs and the perturbational treatment breaks down.

#### D. Natural Correlation Diagrams for Disrotatory Ring Openings of Aziridines

While the usual Woodward-Hoffmann correlation diagrams are identical for the three disrotatory processes described above, a striking feature arises from a more detailed analysis based on natural correlation diagrams.

Figure 5 shows these diagrams for the DISR.1 and DISR.2 processes. In both diagrams, the antisymmetric  $\sigma^*$  orbital correlates with  $\pi_2$  in a straightforward manner. Correlation of symmetric orbitals is a little more complex. In the DISR.2 mode, the phase relations in  $\sigma + n$  and  $n - \sigma$  are such that the lowest symmetric orbital  $\sigma + n$  correlates directly with the lowest orbital  $\pi_1$  of the azomethine ylid, the remaining  $n - \sigma$  orbital correlating then with  $\pi_3$ . In the DISR.1 mode, however, the phase relations in  $\sigma + n$  and  $n - \sigma$  lead to »natural« correlations  $(\sigma + n) \leftrightarrow \pi_3$  and  $(n - \sigma) \leftrightarrow \pi_1$  (dotted lines in Figure 5a). Since these orbitals are both symmetric, an avoided crossing occurs. Therefore, at the beginning of the reaction,  $\sigma + n$  is destabilized while  $n - \sigma$  is stabilized. The crossing between the A and the higher S levels is thus displaced towards the reaction product in DISR.1. Now, assuming that the highest point on the potential energy surface corresponds roughly to the crossing of the frontier orbitals (diradical structure), one can conclude from the Figure 5 diagrams that the transition state for DISR.1 occurs at a larger methylenic rotation angle than that found for DISR.2. In other words, a later transition state is expected for DISR.1, while the transition state for DISR.2 should be earlier. The transition state for DISR.0 is located somewhere in the middle (white circles in Figure 5).

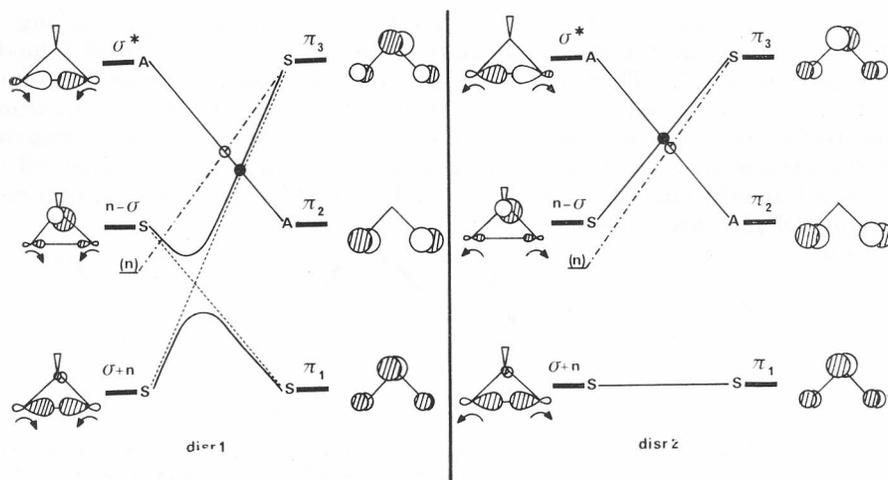


Figure 5. Natural correlation diagrams for the DISR.1 and DISR.2 modes of the aziridine ring opening. The black circle indicates the approximate localization of the DISR.1 or DISR.2 transition state and the white circle that of the DISR.0 transition state.

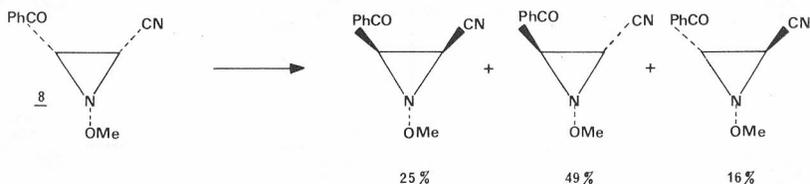
### E. Substituent Effects

The foregoing discussion has shown that it is difficult to give with certainty a preferential order for the three modes DISR.0, DISR.1 and DISR.2. One simple way for modifying this situation is to try substituent effects.

Substituting the carbon atom will affect essentially the CC bond breaking. It is expected that the effect on the three DISR. modes will be approximately the same. Substituting the nitrogen atom appears more promising. If the N hydrogen atom of aziridine is replaced by an electron attracting substituent, say, a *p*-NO<sub>2</sub>Ph group, conjugation will enforce the N planarity and favor the DISR.0 mode with respect to its rivals. The activation energy should diminish slightly: the interaction with the substituent lowers the lone pair energy level and increases the apparent electronegativity of N. However, as the conrotatory mode is also facilitated by the planarity of the N atom (cf. I. C.), the CONR.-DISR. energy gap is not reduced.

If the H atom is replaced by an electron-releasing group, N tends to pyramidalize and the DISR.0 mode is disfavored. The lone pair is raised, which is equivalent to a decrease of the nitrogen apparent electronegativity: the activation energy should be augmented for DISR.1 and DISR.2. This is expected, however, to be a rather small effect, the N pyramidalization reducing the repulsive overlap between the lone pair and the substituent. On the other hand, it has already been mentioned that this same pyramidalization would increase the activation energy for the CONR. mode by about 10 kcal/mol. This is still not sufficient to render the DISR. mode competitive with the CONR. mode. However, if we can introduce in the system another effect which disfavors the CONR. mode and/or favors the DISR. mode, then orbital symmetry requirements may be violated. It follows that a particularly interesting case is the one in which the electron donor substituent is at the same time a strongly electronegative atom like O or X. In such a case, the  $\sigma_{\text{NO}^*}$  (or  $\sigma_{\text{NX}^*}$ ) orbital is sufficiently low to interact appreciably with the  $\sigma_{\text{CC}}$  orbital to stabilize

the disrotatory transition state. This effect does occur and is so strong in N-chloroaziridines that these compounds actually react in the DISR.1 mode, with expulsion of  $\text{Cl}^-$ .<sup>10</sup> These reactions however are conducted under solvolytic conditions and are usually considered as 2e electrocyclic reactions, analogous to the DePuy reactions of cyclopropane derivatives<sup>11</sup>. More directly connected with the present discussion is an unquestionable 4e isomerization observed by Grée and Carrié<sup>12</sup>: heating **8** for 5 h in refluxing toluene gives quantitatively a mixture of the three other isomers:



Although the loss of stereochemistry may be due to a non-concerted mechanism, or, more likely, to a rapid isomerization of the azomethine ylid<sup>6,13</sup>, a competitive »forbidden« disrotatory process may not be excluded in this particular case.

## II. AB INITIO CALCULATIONS

### A. Method

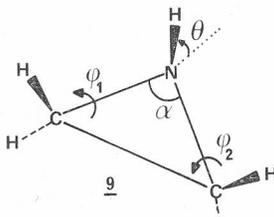
It has been pointed out previously that, because of the high diradical character of some structures encountered on the potential surface, simple SCF calculations cannot yield reliable results. However, a limited  $3 \times 3$  CI involving the three lowest singlet configurations built from the two frontier orbitals, has been shown to give *qualitatively* correct main features<sup>14</sup>. Therefore calculations were undertaken in the following manner:

1) The potential surface was first explored with the STO-3G basis set and  $3 \times 3$  CI, using the Gaussian 70 programs<sup>15</sup> (open shell RHF calculations).

2) The various possible pathways shown by this surface were then recalculated with the split-valence 4-31G basis set (Monstergauss program<sup>16</sup>), the (open shell RHF) SCF calculations being followed by extensive CI using the CIPSI algorithm<sup>17</sup>. A variational zeroth order wave function is built by including all the determinants with coefficients larger than .03. All the other determinants, generated by single and double excitations from the main ones, are taken into account through a second-order perturbation treatment. Test calculations have shown that lowering the threshold does not notably change the calculated energy.

### B. Geometries

In all calculations, except for aziridine, the methylene groups were held trigonal ( $\text{CH} = 1.08 \text{ \AA}$ ,  $\angle \text{NCH} = 120^\circ$ ). The NH bond was fixed at 1.01 Å.



In the first series of calculations, the xNH angle ( $\theta$ , cf. 9) was kept at fixed values whereas the CNC angle ( $\alpha$ ) and the rotations of methylene groups ( $\varphi_1$  and  $\varphi_2$ ) were treated as independent variables. For the disrotatory ( $\varphi_1 = -\varphi_2$ ) and conrotatory ( $\varphi_1 = \varphi_2$ ) motions, a grid of points was calculated, with  $\alpha$  varying from  $90^\circ$  to  $150^\circ$  by steps of  $10^\circ$  and  $\varphi$  from  $0^\circ$  to  $90^\circ$  by steps of  $15^\circ$  ( $\varphi = 0$  and  $\varphi = 90^\circ$  corresponding respectively to the aziridine and azomethine ylids). At each point, the NC distance was optimized. From the three potential surfaces  $E(\alpha, \varphi)$  calculated with  $\theta = 0$ ,  $\theta = 60^\circ$  and  $\theta = -60^\circ$ , five pathways were selected: CONR.0, CONR.60, DISR.0, DISR.61 and DISR.62. The notation DISR.61 (resp. DISR.62) means that this pathway corresponds to the DISR.1 mode **6b** (DISR.2 mode **6c**) with the xNH angle kept at  $60^\circ$  ( $-60^\circ$ ). Four of these pathways are shown in Figure 6, and the last one, DISR.0, is shown in Figure 7.

Then the constraint on  $\theta$  was relaxed and  $\theta$  was varied from  $-80^\circ$  to  $80^\circ$  by steps of  $20^\circ$ . A grid of points was thus obtained for the four-dimension surface  $E(\alpha, \varphi, \theta)$  and a comparison of the  $E(\alpha, \varphi)$  and  $E(\theta, \varphi)$  sections allows determination of the non-constrained DISR. and CONR. pathways.

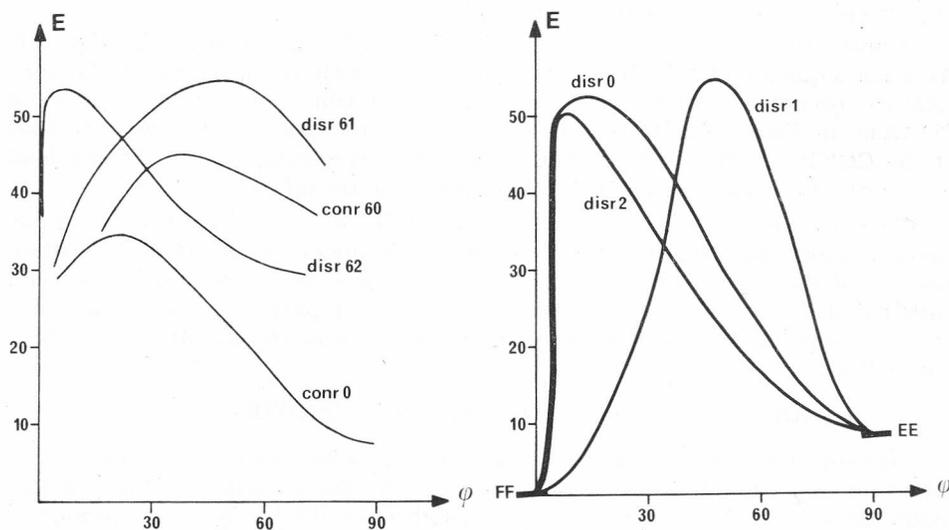


Figure 6. The conrotatory pathway with the nitrogen kept planar (CONR.0) and the three pathways with the nitrogen pyramidalized at  $60^\circ$ . Energies are in kcal/mol. See text for further details.

Figure 7. The two »non-constrained« disrotatory pathways and, for comparison, the DISR.0 pathway where the nitrogen atom is maintained planar. Energies are in kcal/mol. See text for further details.

### C. Results

*Initial and final products.* — Aziridine was calculated with the geometry obtained by Lathan *et al.*<sup>18</sup>. The ground state wave function is essentially the ground configuration and the total energy is  $-133.11938$  a.u.

The azomethine ylid has been optimized (STO-3G +  $3 \times 3$  CI): NC = 1.367 Å,  $\alpha = 130^\circ$ ,  $\theta = 0$ ,  $E = -133.10778$  a.u. The ground state wave function is  $\psi = 0.925 (\dots \pi_1^2 \pi_2^2) - 0.365 (\dots \pi_1^2 \pi_3^2) + \dots$

This strong mixing of configurations indicates a rather high diradical character for this ylid. Note that, due to the electronegativity of oxygen, the diradical character in the carbonyl ylid is even higher:  $\psi = 0.886 (\dots \pi_1^2 \pi_2^2) - 0.455 (\dots \pi_1^2 \pi_3^2) +$ . This trend is maintained in the transition states, the conrotatory wave functions being (STO 3G + 3 × 3 CI):

oxirane:  $0.854 (\dots \pi_1^2 \pi_2^2) - 0.521 (\dots \pi_1^2 \pi_3^2) + \dots$

aziridine:  $0.899 (\dots \pi_1^2 \pi_2^2) - 0.439 (\dots \pi_1^2 \pi_3^2) + \dots$

The stronger configuration mixing in the carbonyl ylid may be attributed to higher electronegativity of oxygen, which reduces the energy gap between  $\pi_2$  and  $\pi_3$ .

*Constrained  $\theta = 0^\circ$  pathways.* — The H<sub>N</sub> atom is constrained to lie in the CNC plane. The corresponding pathways are shown in Figures 6. (CONR.0) and 7 (DISR.0). The difference in activation energy is calculated to be 18.1 kcal/mol (cf. Table) in favor of the conrotatory mode. This is significantly higher than the difference in the oxirane case (10.9 kcal/mol, calculated by the same method and using the same geometrical assumptions).

*Constrained  $\theta = \pm 60^\circ$  pathways.* — The results are reported in Figure 6. As a consequence of the C<sub>2</sub> axis of symmetry which is conserved in the conrotatory process, there is only one constrained conrotatory motion (marked CONR.60 in Figure 6). Its transition state lies 10.6 kcal/mol higher than that of the CONR.0 motion. This is due to the reduced overlap of the nitrogen lone pair with the carbon AO's in the CONR.60 motion (cf. 5).

The two disrotatory »transition states« DISR 61 and DISR 62 have similar energy, lying respectively 2.1 and 0.2 kcal/mol above the DISR.0 »transition state«, but quite different geometries (Table). These agree well with the trend anticipated from natural correlation diagrams. In particular, assuming that  $\varphi = \varphi_1 = -\varphi_2$  is the main component of the reaction coordinate, it is indeed found that:

$$\varphi (\text{DISR.61}) = 47^\circ 5 > \varphi (\text{DISR.0}) = 15^\circ > \varphi (\text{DISR.62}) = 4^\circ 5$$

*Non-constrained pathways.* — The non-constrained pathway for the conrotatory mode is found to be CONR.0 (Figure 6). As a matter of fact, in this mode, as soon as the  $\alpha$  angle is large enough ( $\alpha > 100^\circ$ ) only one minimum is found with  $\theta = 0$ , for all values of  $\varphi$ .

On the contrary, two different non-constrained pathways (DISR.1 and DISR.2, Figure 7) exist for the disrotatory mode. The corresponding »transition states« are very close in energy and in structure to those of the DISR.61 and DISR.62 pathways (Table). The DISR.2 »transition state« is earlier than that of DISR.0, which in turn is earlier than that of DISR.1:

$$\varphi (\text{DISR.1}) = 48^\circ > \varphi (\text{DISR.0}) = 15^\circ > \varphi (\text{DISR.2}) = 8^\circ$$

As shown in Figure 7 and in the Table, the DISR.1 »transition state« is 1.6 kcal/mol higher than the DISR.0 one, which in turn is 2.1 kcal/mol higher than the DISR.2 »transition state«. It may seem surprising that the transition state for the non-constrained DISR.1 path is higher than that for the constrained DISR.0 path. The reason is that the highest point on a symmetry-forbidden path does not have the structure of a transition state<sup>5,6</sup>, there being

at least two negative force constants. Moving out of the path at this point may either raise or lower the energy.

TABLE  
Activation Energies and »Transition State« Geometries for Seven Representative Pathways

	CN bond Å	$\alpha$ deg	$\phi$ /deg	$\theta$ /deg	$E_a$ kcal mol
CONR.0	1.401	98	21	0	27.1
CONR.60	1.451	103	47.5	60	37.7
DISR.0	1.423	114	15	0	45.2
DISR.61	1.469	111.5	47.5	60	47.3
DISR.62	1.460	117	4.5	-60	45.4
DISR.1	1.465	114	48	58	46.8
DISR.2	1.446	120	8	-53	43.1

### III. CONCLUSIONS

The first conclusion of this study is that in the chemistry of compounds containing elements from columns VI and VII of the Periodic Table, more than one AO per atom may intervene and modify sensibly the course of the reaction. Quite often, the »extraneous« AO is a lone pair. A typical example, besides the reactions examined in this paper, is the gas phase syn-elimination of HCl from  $\text{CH}_3\text{—CH}_2\text{Cl}$  through a cyclic transition state. This reaction is rendered possible by the intervention of a chlorine lone pair<sup>19</sup>.

The second conclusion is that the perturbation treatment may fail if the two competitive pathways have similar activation energies and if one transition state is much earlier than the other. In favorable cases, it is possible to localize the relative positions of the two transition states with the help of natural correlation diagrams. In general, these diagrams may be quite useful in studying the modifications resulting from geometrical deformations (*e. g.* the nitrogen pyramidalization in aziridine ring opening). On the other hand they offer little information on the role of the second lone pair of oxygen in the electrocyclic transformation of oxirane: this lone pair correlates with itself in the disrotatory process and apparently plays no role. We have found that for this type of problems, where one atom makes use of more than one AO in the course of the reaction, »overlap graphs« may give valuable indications. These graphs introduce no new principles. Their interest resides in the elimination of all irrelevant features (three-dimensional drawings, representation of 2 or 4 lobes for a *p* or *d* orbital) and in allowing the attention to focus on the essential, *i. e.* the interactions between the most important AO's.

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#### SAŽETAK

#### Uloga osamljenih parova kod heterocatonskih molekula. Analiza otvaranja oksiranskih i aziridinskih prstena s pomoću *ab initio* računa i grafova prekrivanja

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Uveden je pojam grafa prekrivanja koji je i primijenjen na analizu barijera termalnih elektrocikličkih reakcija otvaranja prstena oksirana i aziridina kao i njihovih derivata. Utvrđeno je da osamljeni parovi atoma kisika i dušika potpuno različito utječu na veličinu energije aktivacije. Kvalitativni zaključci potkrijepljeni su *ab-initio* računima s bazama STO-3G i 4-31G, uzevši eksplicitno u obzir učinak korelacije elektrona metodom konfiguracijskih interakcija.