

Theoretical Conclusions. If antiaromaticity is absolute, its domain must be the limited one of C_3^- and C_4 (in the monocyclic series). Even here the support is tenuous, at best. The present preponderance of evidence suggests that C_3^- and C_4 , in fact, have small positive cyclic conjugation energies. This same evidence suggests that C_3^- , C_4 , and C_5^+ are antiaromatic in the relative sense, but that Möbius C_6 , C_7^- , C_8 and all other $4n$ monocycles are possibly not antiaromatic even in this limited sense.

Conclusions

The concept of antiaromaticity articulated by Breslow is an original and highly significant one, and well worth our critical attention. The brilliant experimental sallies of the Breslow group validate beyond reasonable doubt the relative antiaromaticity of C_3^- , C_4 , and probably C_5^+ . The attempt to demonstrate absolute antiaromaticity may well be one of the most difficult experimental proofs ever undertaken in chemistry. The upshot of the present paper is that the latter extreme form of antiaromaticity is demanded neither by experiment nor theory. Indeed, the weight of the evidence of both kinds would appear to negate the proposal of absolute antiaromaticity, even for C_3^- and C_4 . Nevertheless it is evident that the conjugation energies of these latter species are unusually small.

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Theoretical ab Initio SCF Investigation of the Photochemical Behavior of Three-Membered Rings. 2. Azirine¹

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Abstract: Ab initio SCF CI methods have been used to calculate the different potential energy curves corresponding to the ground and low-lying states of the azirine system when various reaction paths are simulated. On one hand, the ring openings, either by CN or CC bond rupture, are examined. On the other hand, the different fragmentation processes into a cyanide molecule HCN and a methylene entity CH_2 are studied. The two-step processes (the CH_2 departure following the ring opening) are compared to the direct simultaneous two-bond scission. These theoretical results afford a rationale for the understanding of the experimental facts and confirm that the preferential photochemical path is the ring opening via the CC bond rupture while the thermal one is the ring opening via CN bond rupture. The substituent influence, as shown, can reverse this order.

For 10 years a constant interest has been devoted to the derivatives of the three-membered heterocyclic ring 1-azirine **1**. The high energy strain locked in this structure renders it particularly suitable to be a precursor for easy fragmentation and further reactions. These compounds are indeed useful intermediates in the synthesis of larger heterocyclic rings.³ The most frequently occurring reaction is the photochemical ring cleavage resulting in a rupture of the CC bond to yield reactive nitrile ylides.⁴ These 1,3-dipolar species can be trapped by a variety of dipolarophiles to form five-membered rings⁵ or can also undergo photochemical (but not thermal) reclosure, regenerating the starting molecule.⁶

Other reactive processes are also documented, depending on the reaction conditions or on the cycle substituents. For example, the thermal reaction of 1-azirine derivatives can in-

volve both a CN⁷ and a CC cleavage,⁸ according to the location of the aromatic substituents on carbon 2 or 3. In all cases, the intermediate formed can lead in a second step to the formation of a carbenic species plus a nitrile molecule.^{8,9} At any rate, the products obtained by thermal cleavage are different from those resulting from a photochemical process.

It was therefore interesting to get theoretical information about all these reaction paths and to try a rationalization of the main tendencies governing this complex reactive pattern.

In this perspective we have simulated by calculation the chart of Figure 1. Path a, CN bond rupture, and path b, CC bond rupture, correspond to the primary ring openings, and lead respectively to the formation of the intermediates **2** and **3**. These two can, in a second step, cleave into a carbenic

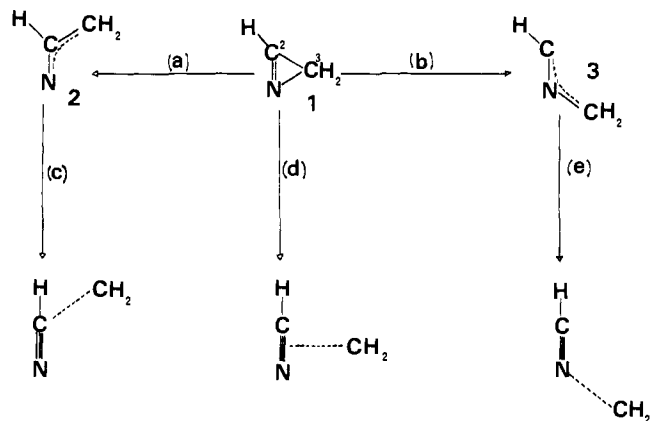


Figure 1. Scheme illustrating the different reaction paths simulated in this work.

moiety, CH_2 , and a cyanid acid molecule, HCN , via paths c and e. The same two fragments can also be obtained by a simultaneous two-bond scission (path d).

All the ab initio calculation of the potential energy curves (PECs) of the ground state (GS) and low-lying excited states have been achieved following a method described elsewhere,¹ with the series of GAUSS70 programs,^{10a} in the minimal basis STO-3G option.^{10b} The CI segment of our calculation involves the single and double excited configurations obtained by promoting one or two electrons from the six highest occupied to the four lowest unoccupied molecular orbitals (MOs).

Azirine 1 and the Open Forms 2 and 3. Various calculations dealing with the ground state of 1-azirine have been already reported^{5c,11} in the literature. In this study we have adopted the geometrical parameters described by Pople et al.^{11b} They are in good agreement with the experimental results and are confirmed by a recent study on the prototype itself.¹²

Little is known about 1-azirine spectroscopy and most of the available data come from aromatic substituted structures. Two main absorption bands are found¹³ near 300 and 240 nm, attributed respectively to the $^1n\pi^*$ and $^1\pi\pi^*$ excitations of the $\text{C}=\text{N}$ chromophore.

Another way to get information about these transitions is to consider the closely related open structures containing the same $\text{C}=\text{N}$ chromophore without aromatic substituents. The $^1n\pi^*$ absorption occurs around 240 nm and $^1\pi\pi^*$ around 180 nm.^{5c} The presently calculated values (183 nm for $^1n\pi^*$ and 100 nm for $^1\pi\pi^*$) constitute only a rough estimate, especially for the singlet $^1\pi\pi^*$. To improve our results it would be necessary to use a larger basis in the SCF calculation, including polarization functions. The triplet states are better described by our method and they appear closer to the expected values (234 nm for $^3\pi\pi^*$ and 214 nm for $^3n\pi^*$). Note that the first triplet state has $\pi\pi^*$ character and that the $^3n\pi^*$ state appears 10 kcal/mol higher in energy.

The choice of a geometry for the final open intermediates 2 or 3 is a delicate problem. Indeed, as pointed out by Salem¹⁵ in a study of the CC bond rupture, various resonance structures, related to different electronic configurations, can intervene in 2. The weight of each one, in a particular electronic state, depends strongly on the geometry. It is therefore clear that as the reaction goes on, small changes in bond lengths and angles would induce important charge, energy, and state variations. These variations are strongly dependent on the nature of the reaction medium; they will, in consequence, govern the regioselectivity exhibited by the intermediates in subsequent reactions.^{5d,15,16}

For all these reasons we have adopted the following procedure. The geometries of the intermediates have been optimized in the ground state with respect to all geometrical parameters,

except for the bond angle (CNC or NCC, respectively, for 2 and 3).^{17a-c} This angle was arbitrary fixed at a realistic value of 120° .^{17d} Salem's work¹⁵ has shown that, for the CC rupture, the breaking is then terminated and that the further opening to 180° only concerns the electronic reorganization of the intermediate. A linear variation of all parameters was then assumed from the initial structure 1 to the open form 2 or 3. This procedure appears reliable to get qualitative informations on the PECs of the different states during the reaction. It is obvious that refined quantitative information such as activation energies is beyond the scope of this study since we have used a minimal basis set.¹⁸ Other calculations^{1,19} of the same type allow us, however, to believe that the PECs obtained by this method are semiquantitatively realistic and that their analysis is of chemical significance.

It is noteworthy that azirine is isoelectronic with the cation C_3H_5^+ , whose most stable isomer is the planar allylic structure as shown by Pople et al.²⁰ Consequently the rotation of the methylene group in 2 and 3 leading to the corresponding planar intermediates 2' and 3' has been examined and will be discussed in a following paragraph.

Ring Opening of Azirine 1, Paths a and b. We will first consider the transformations of the MOs when azirine transforms itself into 2 via path a, or 3 via path b, undergoing a σ -bond rupture. In both cases a symmetry plane containing the carbons and nitrogen atoms is conserved along the whole reaction, and it will be used as a reference for the states symmetries.

Examination of the MO Correlations. The π_{CN} and π^*_{CN} MOs are not directly involved in the rupture and consequently they are preserved all along the reaction coordinates, in both cases, as can be seen in Figure 2, right and left parts. The in-plane (s) orbitals of the intermediate 2 or 3 differ in relative position. In 2 the in-phase combination p_+ of the terminal lobes, as expected, appears at lower energy than the out of phase combination p_- . It is the reverse in 3 because the n lone pair centered on the nitrogen atom, and at higher energy than its analogue in 2, the σ_{CH} MO, is allowed to mix significantly, in an antibonding fashion, with p_+ , pulling this MO above p_- , which remains unaffected.

In paths a and b, σ_{N} tends to correlate naturally with p_+ and σ^* with p_- . The very simple MO correlation diagram of the right part of Figure 2 follows for path a. In path b, there is an avoided crossing between occupied and empty levels resulting from the exchange of the relative positions of p_+ and p_- , as precedently justified (left part of Figure 2).

Examination of the State Correlations. In the starting molecule the excited states ($^1,3\pi\pi^*$, $^1,3\sigma_{\text{N}}\pi^*$, $^1,3\sigma_{\text{N}}\sigma^*$) are clearly described by the labeling of the MOs they are built on. The situation is more complex for the open forms since two quasi-degenerate MOs are involved, p_+ and p_- , suitable to describe a classical homosymmetric diradical,²¹ whose relevant states are the following.

Appearing at low energy is the singlet-triplet pair called here $D_{\sigma\sigma}$ to recall that the electrons are located in the plane of the former σ bond. The triplet has the electronic configuration $^3(p_+^1p_-^1)$. In this covalent form, the two electrons of parallel spin are located on the extremities of the open moiety, in the lobes coming from the σ bond. The singlet possesses as main contribution $[(p_+)^2 - (p_-)^2]$. In 2, this character is dominant and the corresponding state is mainly covalent, but in 3 it is contaminated by a noticeable participation of the state $^1(p_+^1p_-^1)$, which brings some ionic character to $^1D_{\sigma\sigma}$. The amount of ionic forms will be increased if aromatic substituents are present.²³

Next we find the first ionic state Z_1 , with the electronic configuration $^1(p_+^1p_-^1)$, and at still higher energy the second ionic state Z_2 , whose electronic configuration is $(p_+)^2 + (p_-)^2$.

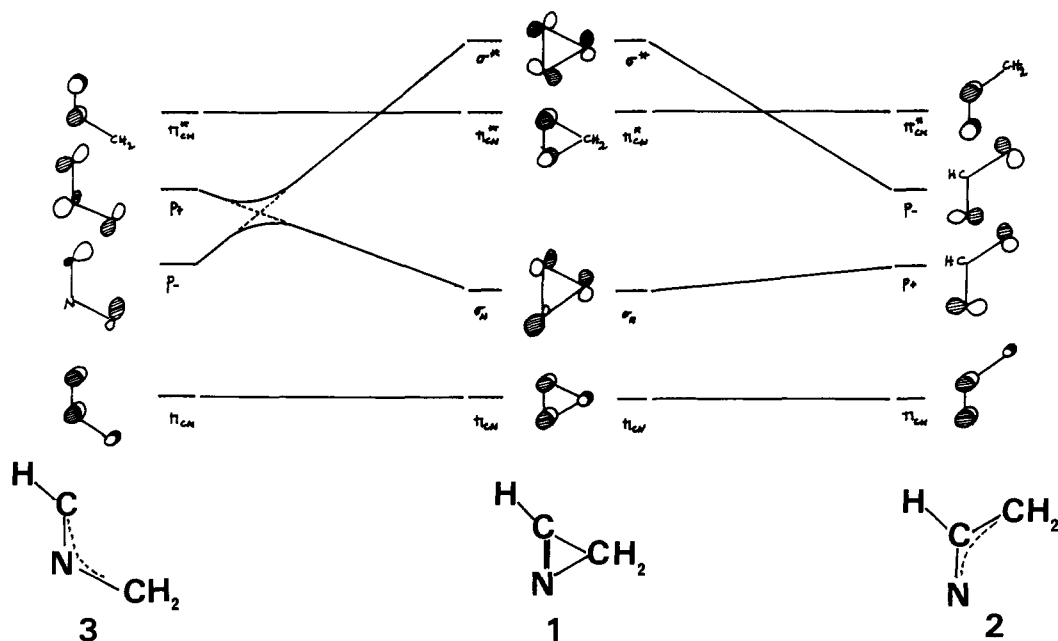


Figure 2. MO correlation diagrams corresponding to path b (left) and path a (right) of the ring opening.

Of interest are also the $^1,^3D_{\sigma\pi}$ states, of different symmetry, corresponding to the location of one electron in the symmetry plane MO, and the other in the π^* MO. These states are at somewhat higher energy than the $^1,^3D_{\sigma\sigma}$ couple.

The state correlation diagrams of Figures 3 and 4 follow. We will first consider the correlations corresponding to path a (Figure 3). As inferred at the MO level, the GS of azirine **1** is directly linked to the diradical form $^1D_{\sigma\sigma}$ of the intermediate. The $^1,^3\pi\pi^*$ states intend to correlate with the corresponding states of **2** at high energy. Doing so they would cross $^1\sigma_N\sigma^*$ and $^3\sigma_N\sigma^*$ which respectively tend to correlate with Z_1 and the low-lying $^3D_{\sigma\sigma}$ diradical. Because they have the same symmetry, the resulting crossings are avoided and finally we get the full-line correlations.

Let us now examine Figure 4 corresponding to path b. The behavior of the $\pi\pi^*$ states is identical with that of the preceding case and also results in avoided crossings with the $\sigma_N\sigma^*$ states. The ground state of the initial molecule **1** is again directly linked to $^1D_{\sigma\sigma}$, but owing to the crossing at the MO level, an energy barrier exists on the potential curve.²⁴ This barrier is a remnant of the fact that, without the MO avoided crossing, the GS would correlate with Z_2 . The $^1,^3\sigma_N\pi^*$ couple of states correlate, as previously, with $^1,^3D_{\sigma\pi}$ but here again there appears energy barriers that are memories of the avoided crossings found at the MO level.

The calculated PECs of Figures 5 and 6 are drawn for the reactive processes, that is to say, path a + c and path b + e. One must remark that we have in fact to consider, in both figures, two distinct reaction coordinates; the first corresponds to the ring opening, up to a value of 120° , and the second, independently, represents the departure of the CH_2 group in the open intermediate. In a first step we will only examine those parts of the drawings dealing with paths a and b. The calculated curves nicely confirm the preceding state correlations.

Thermally, the CC bond rupture (activation energy of around 80 kcal/mol) is more difficult than the CN bond one (35 kcal/mol). In the latter case, no extremum appears on the GS PEC, and no barrier prevents the intermediate **2** to reclose. In the former case, as already seen, the $^1D_{\sigma\sigma}$ state of the intermediate **3** is contaminated by a nonnegligible ionic character; from this fact it can be stabilized by appropriate substitution and really exist as a metastable species.

Photochemically, in both paths, the dissociative state is the

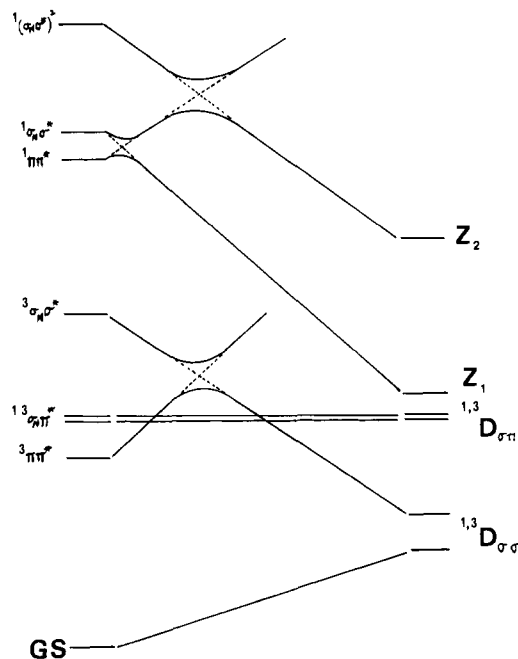


Figure 3. State correlation diagram corresponding to path a.

descending $^3\sigma_N\sigma^*$ PEC, which, by an avoided crossing, proceeds from $^3\pi\pi^*$. This last state acts as a reservoir of low-energy excitations. The reactive PEC can be populated in different ways. The first one is by sensitization or internal conversion from $^3\sigma_N\pi^*$, but along the two paths, the avoided crossings generate important energy barriers (16 and 25 kcal/mol for path a and b, respectively), thus preventing $^3\pi\pi^*$ from reacting during its lifetime.²⁴ The second manner consists in populating $^1\sigma_N\pi^*$ by direct irradiation. The corresponding PECs are ascending in path a and slightly descending in path b, before reaching a minimum for a θ value of 69° . Then two different possibilities arise.

(1) In path a, if the small barrier of 5 kcal/mol can be cleared during the singlet lifetime, we can reach the open form $^1D_{\sigma\pi}$, which is a very hot species.

(2) In path b, around the minimum on the $^1\sigma_N\pi^*$ PEC, the

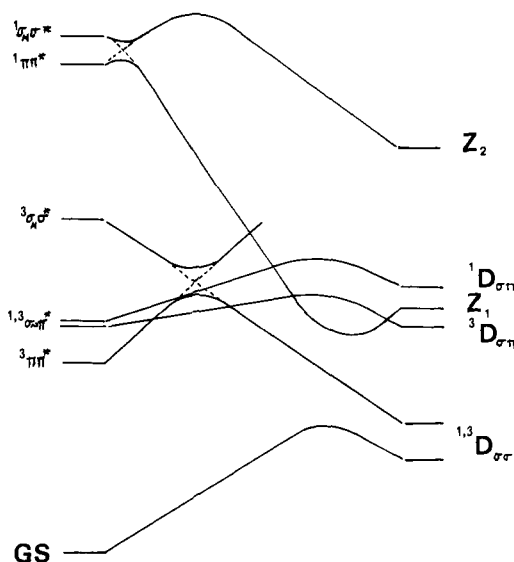


Figure 4. State correlation diagram corresponding to path b.

triplet dissociative state is in a situation of “near touching”.²⁵ To reach the triplet state, an intersystem crossing (point A) is possible. Here the change of multiplicity is compensated by a simultaneous change of symmetry,²⁶ thus allowing a favorable exchange. Once the transformation is carried out, the system has two quasi-equal possibilities: to go back to the azirine in its $^3\pi\pi^*$ state or to transform without any further activation energy into the stable $^3D_{\sigma\sigma}$ open diradical.

In path a there is nothing comparable since the energy gap between the $^1\sigma_N\pi^*$ and $^3\pi\pi^*$ PECs is more than 1 eV in the intersystem crossing region. This clearly illustrates the striking difference between the photochemical reactivity of the CC and CN bonds, the dichotomy coming from the positions of the avoided crossings which exchange $^3\sigma_N\sigma^*$ and $^3\pi\pi^*$.

The fact that the CC bond is stronger than the CN one is equally reflected on the GS PEC and the $^3\pi\pi^*$ PEC, since in both cases there is no depopulation of bonding MO or population of antibonding MO, concerning the broken bond. Note that the initial slopes of the two PEC are near parallel. Consequently the avoided crossing $^3\sigma_N\sigma^* \leftrightarrow ^3\pi\pi^*$ is pushed up to higher energy in path b than in path a and the maximum on the $^3\pi\pi^*$ PEC can reach a near touching situation with the $^1\sigma_N\pi^*$ PEC which facilitates the internal conversion.

An ultimate possibility is to populate $^3\sigma_N\pi^*$, essentially by intersystem crossing from $^1\sigma_N\pi^*$. The corresponding PEC

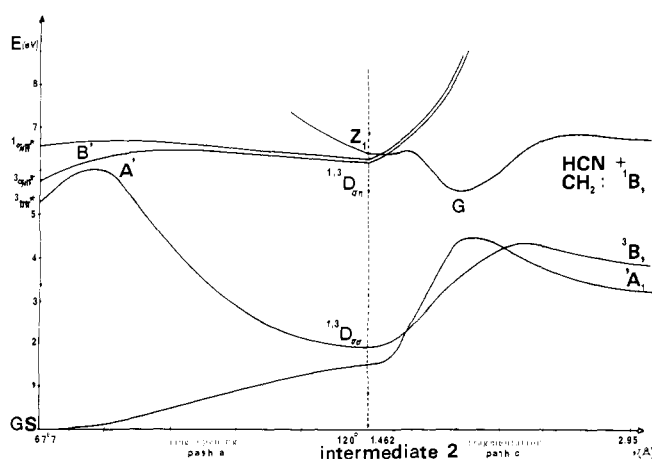


Figure 5. Calculated potential energy curves (PEC) corresponding to the ring opening (path a) of azirine (left side of the figure) and to the subsequent fragmentation (path c) (right side of the figure).

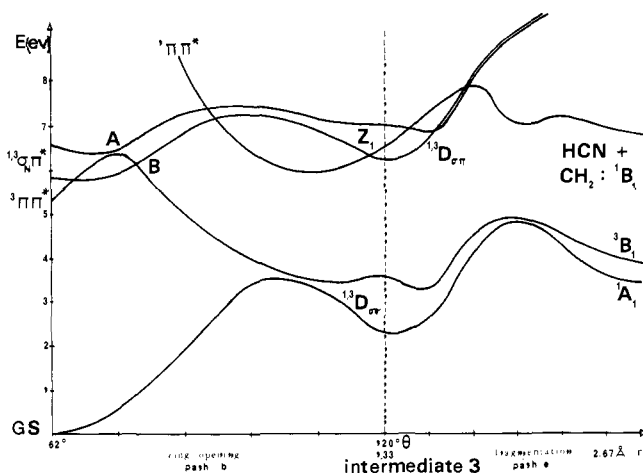


Figure 6. Calculated potential energy curves (PEC) corresponding to the ring opening (path b) of azirine (left side of the figure) and to the subsequent fragmentation (path e) (right side of the figure).

crosses the dissociative state in B' (path a) or B (path b); there an internal conversion can take place, implying barriers of 6 and 10 kcal/mol for paths a and b, respectively. These energetic values lie in the energy range compatible with a triplet lifetime.²⁴

In this study as well as in Salem's work,¹⁵ the $^3D_{\sigma\sigma}$ PEC presents an energy minimum near $\theta = 110\text{--}115^\circ$. At this point the system can “fall” on $^1D_{\sigma\sigma}$, of lower energy, or undergo a further fragmentation as will be seen later.

As was already mentioned, the $^1D_{\sigma\sigma}$ state ($\theta = 120^\circ$) contains nonnegligible ionic character which can be reinforced by suitable substitution. The consequent stabilization will increase the energy barrier (30 kcal/mol) for reclosure of the intermediate 3 to azirine 1. In this case 3 will be a thermally stable intermediate and the only way to reclose will be to photochemically populate the $^3D_{\sigma\sigma}$ state, the PEC of which comes in near touching with that of GS- $^1D_{\sigma\sigma}$. By decay in the region $\theta = 103^\circ$ the system can yield either azirine 1 or intermediate 3, $^1D_{\sigma\sigma}$.

Now let us examine the influence, on these reaction schemes, of methylene rotation in 2 and 3, yielding the species 2' and 3'.

During the rotation processes, important changes occur in the p_+ , p_- couple of MOs. In both cases, it is split into a localized lone pair, (centered on the carbon atom in 3' and on the nitrogen atom in 2'), and into the familiar nonbonding allylic MO which is common to both moieties 2' and 3'.

At state level, the two species behave similarly: the three $^3D_{\sigma\sigma}$, $^1D_{\sigma\pi}$, and Z_1 states are stabilized while the $^1D_{\sigma\sigma}$ state is destabilized. For the $2 \rightarrow 2'$ transformation, the stabilization energies are respectively 0.96, 2.8, and 2.0 eV. For the corresponding $3 \rightarrow 3'$ transformation, they are respectively 1.3, 1.5, and 2.5 eV. The destabilization energy is 0.13 eV for $2 \rightarrow 2'$ and 0.83 eV for $3 \rightarrow 3'$. All the PECs corresponding to the rotation processes are monotonous. The bulk result is that the first singlets are more stable in 2 and 3 than in 2' and 3', the contrary being observed for the first triplet states.

Consequently the only important change brought by the methylene rotation concerns the $^1\sigma\pi^* \leftrightarrow ^1D_{\sigma\pi}$ PEC in the CN bond rupture (path a). The resulting stabilization of $^1D_{\sigma\pi}$ may greatly increase the feasibility of this transformation.

Fragmentation of Azirine 1. There are three ways to fragment azirine 1 into a carbene moiety and a cyanide acid molecule. The first one is the simultaneous two-bond scission (path d); the second (path a + path c) and third (path b + path e) ones are two-step reactions with CH_2 departure following ring opening. In these two cases, we will examine first the rupture

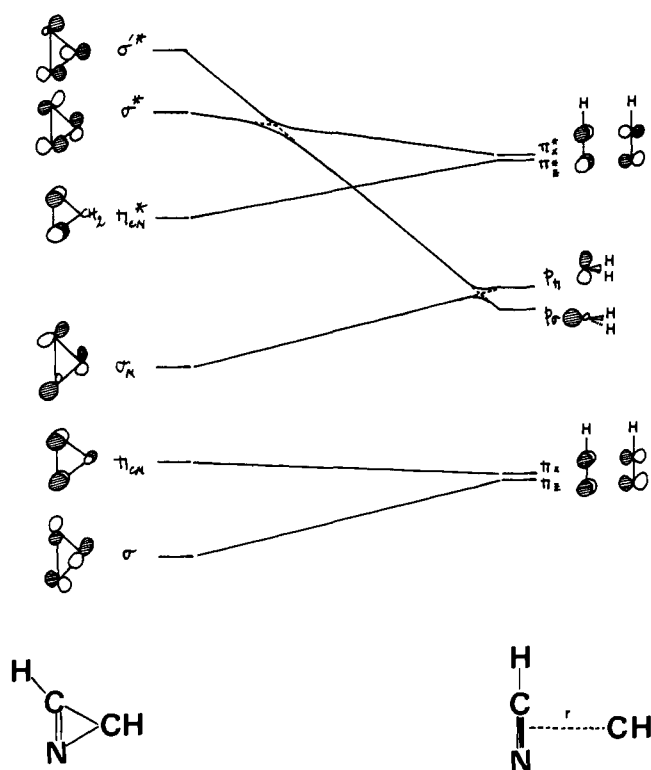


Figure 7. MO correlation diagram corresponding to path d (two-bond scission). The distance r is the reaction coordinate.

from **2** and **3** and next consider the modifications involved in the corresponding processes starting from the related **2'** and **3'**.

Let us first consider path d. The MO correlation diagram of this synchronous rupture of the CC and CN bonds is described in Figure 7. The main feature is an avoided crossing between unoccupied and occupied MO. The dashed lines correspond to the "natural" correlations and the full lines to the calculated ones.

This scheme is very similar to other simultaneous two-bond scissions already studied^{1,24} and is closely related to the "four

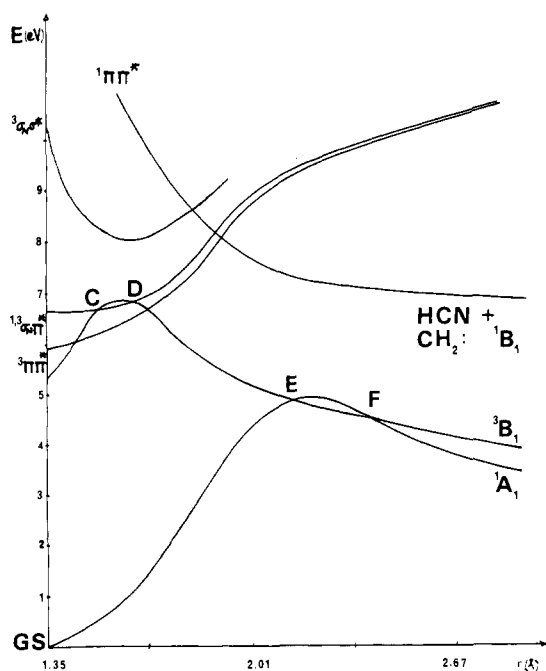


Figure 8. Calculated potential energy curves (PEC) corresponding to the simultaneous two-bond scission (path d).

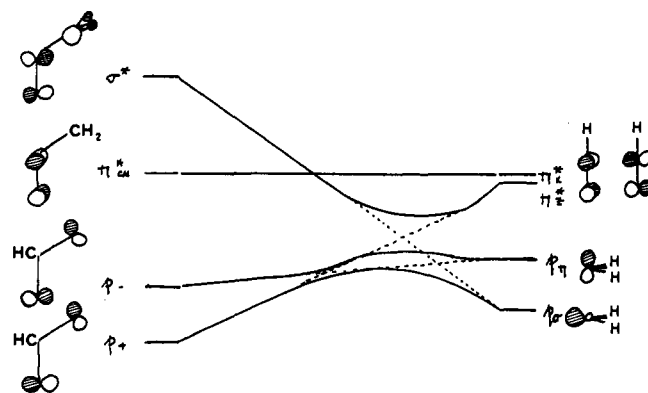


Figure 9. MO correlation diagram corresponding to path c.

electrons forbidden process",²⁷ The resulting PECs (Figure 8) confirm completely this analysis.

The very high energy barrier (115 kcal/mol) on the GS PEC results from the strongly MO avoided crossing and prevents a thermal simultaneous two-bond scission here again. Photochemically, the easiest reactive channel consists in populating the $^1\sigma_N\pi^*$ and following its PEC to reach points C or D, where an intersystem crossing with the dissociative state $^3\pi\pi^*$ can take place, leading either to the initial azirine **1** (from point C) or to HCN ($^1\Sigma$) and CH₂ (3B_1) (from point D). The energy barrier (5 kcal/mol) seems compatible with this hypothesis. Note that for a r distance of the order of 2.3 Å, the GS PEC and the $^3\pi\pi^*$ PEC cross each other (points E and F) and that a new intersystem crossing can occur leading to GS azirine **1** or to HCN ($^1\Sigma$) and CH₂ (1A_1).

We will now consider the other two possibilities, and first the MO correlation diagrams of paths c and e. As in path d, the π_z orbitals (antisymmetric according to the molecular plane) are not involved in the process and are directly linked to their counterpart in the final system. For the symmetric MO, the natural correlations are the same in path c and path e. This way, p_+ intends to correlate to π_x^* , p_- to the p_π MO of the CH₂ fragment and a high σ^* to p_σ . These correlations induce several avoided crossings that are described in Figures 9 and 10. The essential and common features are the strongly avoided crossings between unoccupied and occupied MO which are reflected in the corresponding PECs (Figures 5 and 6) by the presence of appreciable energy barriers.

One must note that the total barriers from GS azirine to HCN ($^1\Sigma$) + CH₂ (1A_1) are in the same range whatever the process under consideration: 104 kcal/mol for path a + c, 110 kcal/mol for path b + e, 115 kcal/mole for path d.

Then the barriers from the $^1D_{\sigma\sigma}$ state of the intermediates **2** and **3** are such that, in the two cases, the reclosure process (0 and 30 kcal/mol, respectively) is more favorable than the

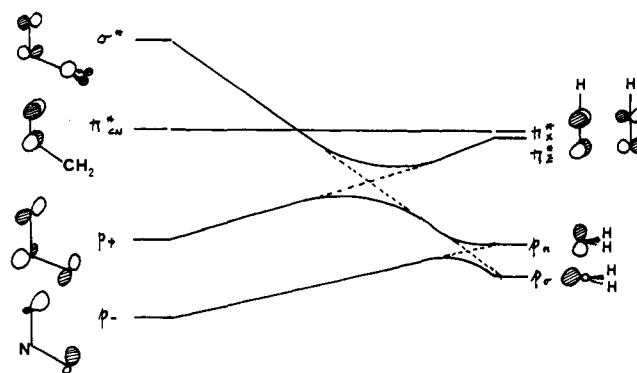


Figure 10. MO correlation diagram corresponding to path e.

expulsion of a carbene species (70 and 57 kcal/mol, respectively).

In the $^3D_{\sigma\sigma}$ states of **2** and **3**, the barriers are again high to reach a carbene species (51 and 32 kcal/mol, respectively), but they can be passed if we consider that, during the ring opening, the molecule has gained an important internal energy that it has no time to dissipate in totality.

The ultimate possible way to obtain fragmentation is, in the case of path a + c, to populate the Z_1 state, for example, by internal conversion from $^1\sigma_N\pi^*$ in the region where $\theta \simeq 120^\circ$. The system can then reach a deep minimum, point G, and decay to the lower singlet PEC where it can go either to azirine **1** (GS) or to HCN + CH₂ (1A_1).

The calculations reveal that the planar open forms **2'** and **3'** lead to a reactivity which is similar to that of **2** and **3**. Both first singlet states remain quite unreactive (high energy barriers). For the triplet states, no evident changes occur on the PECs shapes and no noticeable reactivity modification may be predicted.

Conclusion

The two main experimentally well documented reactions of azirine derivatives are the photochemically induced CC bond rupture⁴ and the thermally induced CN bond rupture.⁷ In the first case the primary product is a stable intermediate (nitrile ylide) while in the second it has not been trapped till now. The stable intermediate can reclose by photochemical excitation. Moreover, recently it was shown that CC bond rupture can also occur thermally, but leading to different products from those obtained by photochemical reaction.⁸

At least, the carbene formation appears clearly established in the case of the thermal^{7,8} and the photochemical⁴ reactions of some particular substituted azirine derivatives.

The calculated PEC we have discussed confirm fully and explain these different processes.

Photochemically, the only realistic reactive state appears to be the $^1\sigma_N\pi^*$. Its easiest reaction path is the opening of the ring by CC bond rupture which calls into play the internal conversion between the $^1\sigma_N\pi^*$ and $^3\pi\pi^*$ PECs (Figure 6, point A). It leads, by CC bond rupture, to the formation of intermediate **3** which can either decay from its $^3D_{\sigma\sigma}$ state to the $^1D_{\sigma\sigma}$ one, or more difficultly pursue its evolution by breaking the second bond to form HCN ($^1\Sigma$) and CH₂ (3B_1). One must note that once on the $^3\pi\pi^*$ potential surface leading to $^3D_{\sigma\sigma}$ there is sufficient internal energy to overcome the activation barriers of the second steps (CH₂ departure).

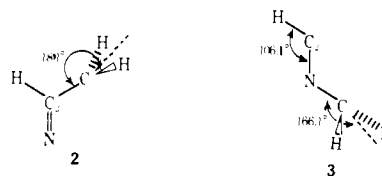
Two less probable, but feasible, reactive processes, from the $^1\sigma_N\pi^*$ state, are the two-bond scission and the CC bond rupture. The first one involves an intersystem crossing after overcoming a barrier of 5 kcal/mol (point D, Figure 8). The second one is the direct transformation of the $^1\sigma_N\pi^*$ of azirine **1** into the $^1D_{\sigma\sigma}$ state of the intermediate **2**, staying on a single PEC. Here again the barrier is feeble ($\simeq 5$ kcal/mol) (Figure 5). The intermediate **2** can then either react in this state or fragment into HCN ($^1\Sigma$) and CH₂ (1A_1) after conversion to the near-degenerate Z_1 state and jump to the lowest singlet state PEC. Thermally it is clear that CN rupture is easier than CC rupture but it is not necessarily a reactive path. Indeed it is easy to imagine that intermediate **2** in its $^1D_{\sigma\sigma}$ state can have no competing reactive path other than the reclosure to azirine since there is no energy barrier in this process. Inversely the thermal CC rupture is much more difficult but, if it is achieved, the intermediate **3** has certainly a longer lifetime than the intermediate **2**. This fact explains clearly the effect of the substitution encountered in the thermal reactivity.

If the stabilizing substituent is on carbon 3, the open product **2** or **3** is always stabilized and the easiest reaction will be CN rupture. If the stabilizing substituent is on carbon 2, only the open product **3** is stabilized. This fact, without any doubt, reduces the barrier to reach **3** from azirine **1** (Figure 6, GS PEC) and permits the formation of **3**. The formation of **2** remains the easiest energetically, but intermediate **2** has no other competing reaction path than to reclose.

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