Photochemical Conversion of 1-Amino-2-cyanoethylene to Imidazole: An ab Initio SCF–CI Study

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In order to test the mechanistic hypothesis suggested by available experimental results on the photochemical isomerization of enaminonitriles to imidazoles derivatives, ab initio SCF–CI calculations of potential energy surfaces relative to various low-lying electronic states have been performed. The reaction paths considered were a nitrile–isonitrile isomerization and the formation of either azirine or azetine intermediates. The present analysis shows that the formation of an azirine intermediate represents the most favorable reaction path and that the overall isomerization of enaminonitriles to imidazoles is a sequence of two photochemical reactions.

In 1966, the remarkable photochemical rearrangement of 1,2-diamino-1,2-dicyanoethylene to 4-amino-5-cyano-imidazole was reported by Ferris and Orgel.[2] This unusual reaction involves the replacement of the initial sequence of atoms NCCCN by NCCNC. Since its discovery, the scope of this photochemical isomerization to imidazole derivatives has been extended to various enaminonitriles.[2-5] This photochemical rearrangement is important because it represents a key step in one of the pathways proposed for the prebiological synthesis of purine from hydrogen cyanide in aqueous solution.[6]

The experimental studies have clearly established that the reaction requires a cis orientation of the nitrile and amino functions[4,7] and an N–H bond of the amino group.[5] Furthermore, the reaction is intramolecular[3,7] and involves a singlet $\pi\pi^*$ state excitation.[3]

Various proposals have been considered to describe the intimate mechanism of the NCCCN–NCCNC reorganization of the molecular skeleton. On the one hand, Ferris and Orgel suggested, in their first paper,[2] the formation of intermediates containing either three- or four-membered rings (azirine or azetine derivatives, respectively), but they ruled out the possible involvement of five-membered rings (pyrazole). The last assertion has been recently confirmed.[4,9] On the other hand, Becker et al.[8] have assigned the yellow color observed at low temperature to the formation of carbenic intermediates. This assignment was later rejected.[5] The direct or indirect conversion of nitrile to isonitrile has also been suggested,[4] but an experiment designed to observe the indirect conversion was unsuccessful.[3]

Thus, the two main hypotheses compatible with the experimental results concern the intervention of an azirine or azetine intermediate, should any be involved in the reaction.

A priori, the intervention of an azirine intermediate would require a two-photon process for the enaminonitrile–imidazole rearrangement to occur. Azirines with structures similar to those considered here (Scheme III) are thermally stable at room temperature,[10] while they easily experience CC bond breaking under photonic excitation.[11]

The observation that the efficiency of the enaminonitrile photoreaction is independent of light intensity[7] but dependent on wavelength[8] is not inconsistent with the photochemical rearrangement of an intermediate[7] such as an azirine, although this assertion has been denied.[4]

Ferris and co-workers[3-5] put forward the following arguments for azetine as a possible intermediate. The IR

Scheme I. Nitrile–Isonitrile Rearrangement (Path a) and Related Reaction Paths
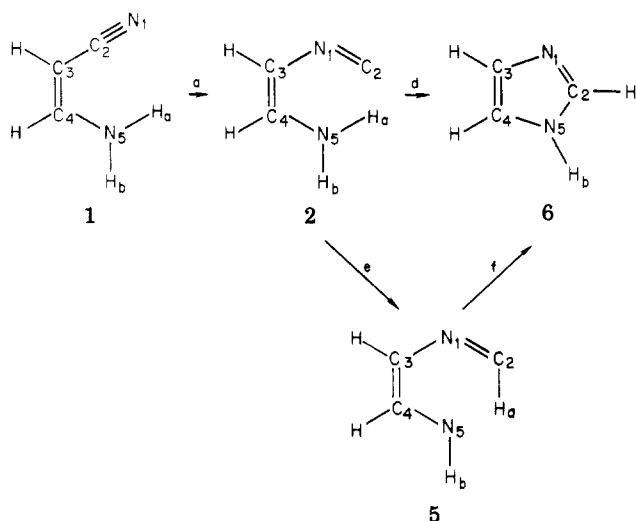
bands at 2000–2020 cm^{-1} observed at low temperature are characteristic of a ketenimine chromophore.[4] The transformation of ketenimine to azetine would correspond to a concerted thermal cyclization of the butadienic part of the ketenimine.[12] Oxetenes, compounds similar to azetine derivatives, have been estimated to be thermally unstable;[14] as a matter of fact, a case of thermal rearrangement of an azetine to an imidazole derivative has been reported.[15] However, this fact is not fully convincing for the present problem since the suggested mechanism[15] (intervention of a β-hydrogen atom) is incompatible with the

(1) This laboratory is also part of CNRS (ERA No. 549).

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(12) It is worth noting that such behavior looks unusual since, in the case of the isoelectronic conjugated ketene–cyclobutene system, the reaction proceeds mainly in the opposite direction,[13a,b] except for the specifically substituted system.[13c]

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Table I. Energies[a] of the Low-Lying Electronic States of the Various Stable Molecular Structures Involved in Schemes I-III

	S_0	S_1	S_2	T_1	T_2
1-amino-2-cyanoethylene (1)	−6039.80	−6030.10	−6030.08	−6034.40	−6031.31 (−6030.85, T_3)
imidazole (6)	−6040.61	−6031.72		−6034.70	−6032.93
azetine (8)	−6036.86	−6030.19		−6032.99	−6030.74
pyrazole (12)	−6039.54	−6031.49		−6033.51	−6032.44
azirine (13)	−6037.01	−6030.38	−6029.58	−6032.52 (−6030.48, T_3)	−6031.64 (−6030.38, T_4)

[a] All the energies are in eV.

Scheme II. Reaction Paths Initiated by a *N*-Hydrogen Abstraction (Path b)
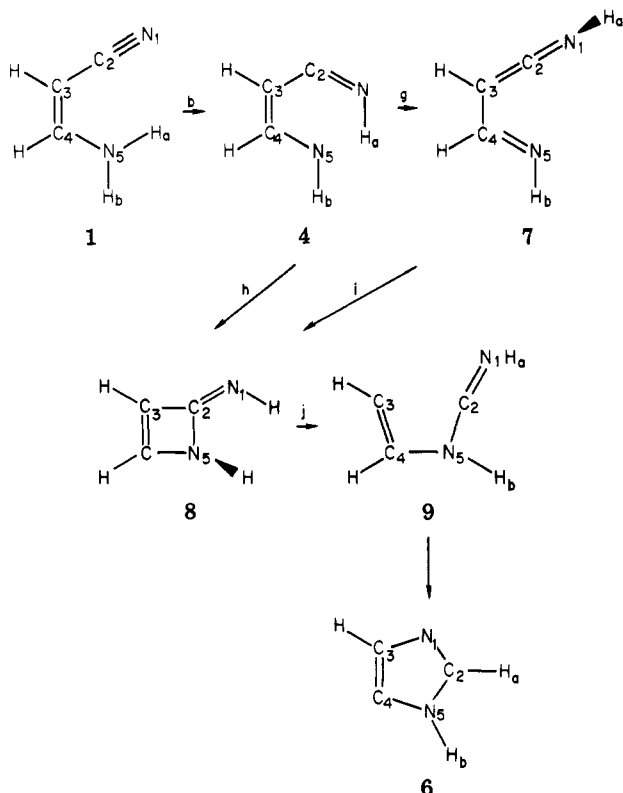
Scheme III. Reaction Paths Initiated by a *C*-Hydrogen Abstraction (Path c)
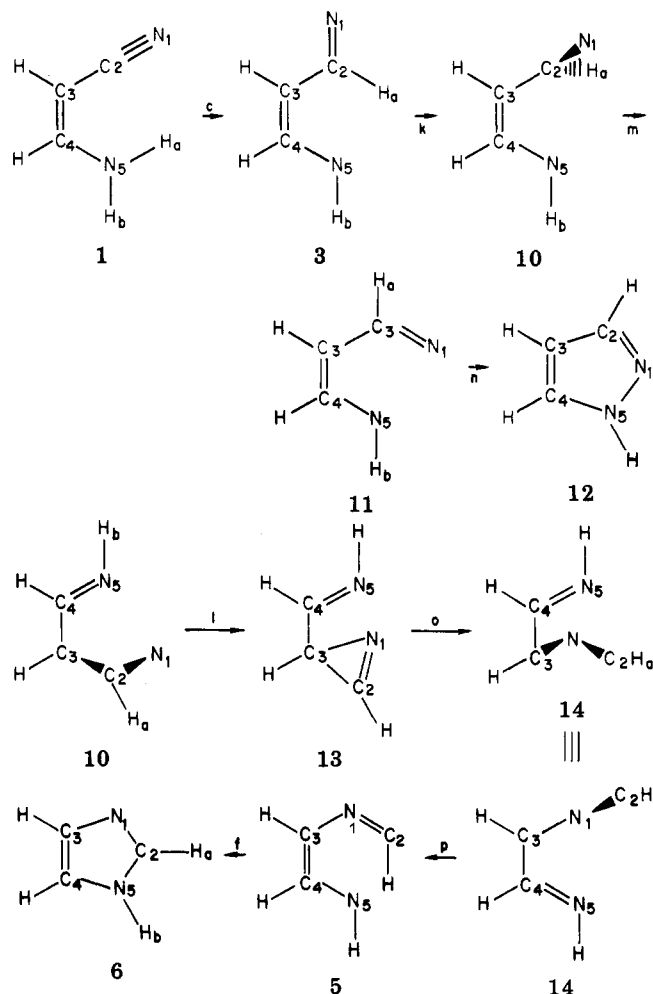
structure of the azetine which would correspond to the hypothetical intermediates in the experimentally observed enaminonitrile to imidazole rearrangement.

Thus, despite the number of proposals presented for the mechanism of this conversion, none is convincingly in agreement with the experimental results presently available.

The understanding of this intramolecular reaction presents an interesting challenge for theoretical chemistry. The simplest structure experimentally known as reactive,[3] 1-amino-2-cyanoethylene, is accessible to computational ab initio calculations (minimal STO-3G basis set,[16] limited interactions of configuration[17] whose conclusions were shown to be of chemical significance in the study of the photochemistry of similar systems.[18] Let us recall that in this method of study, the reactivity of a unimolecular

process is represented by observing the motion of a "system point" on potential energy surfaces. Here we shall focus our attention mainly on the topographic features of the surfaces (energy barrier, potential well, monotonous descent).

The determination of the complete surfaces of the ground state and lowest excited states of the considered molecular system (see Table I for energies of these states) is out of the range of the ab initio method presently used. We have therefore limited ourself to the study of selected reaction paths which are depicted in Schemes I-III.

Three primary reaction paths have been considered for 1. The first, path a, involves a nitrile–isonitrile rearrangement and leads to the formation of intermediate 2. The other two represent the abstraction of a hydrogen of the amino group either by the nitrogen atom (path b, intermediate 4) or by the carbon atom (path c, intermediate 3) of the nitrile group. The further rearrangements of the intermediates 2–4 will be described in full detail

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(17) The interaction of configuration involves the single and double excitated configurations obtained from the six highest occupied MO's to the four lowest unoccupied MO's. The SCF part of the calculations used the Gaussian 70 series of programs: Hehre, W. J.; Lathan, W. A.; Ditchfield, R.; Newton, M. D.; Pople, J. A., "Quantum Chemistry Program Exchange"; QCPE no. 236, Indiana University: Bloomington, IN.

(18) See, for example: Bigot, B.; Devaquet, A.; Sevin, A. *J. Org. Chem.* **1980**, 45, 97 and preceding papers in the series. For a description of the method, see: Bigot, B.; Sevin, A.; Devaquet, A. *J. Am. Chem. Soc.* **1978**, 100, 2639, 6924.
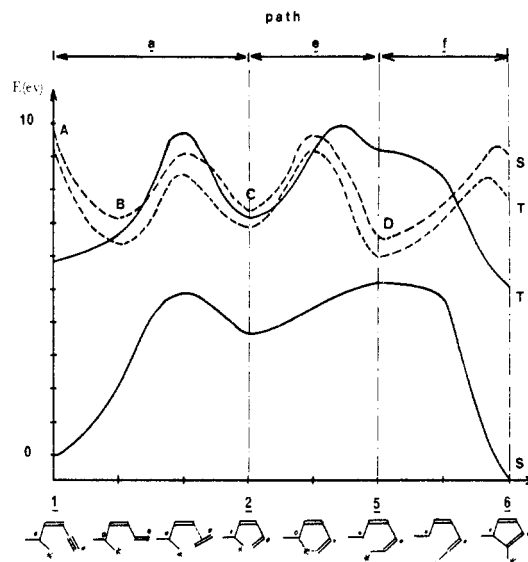
after analysis of the primary processes. Before focusing on the reactivity of the enaminonitrile 1, let us first consider its geometrical and electronic characteristics.

1-Amino-2-cyanoethylene. The geometry of *cis*-1-amino-2-cyanoethylene in its ground state has been optimized at the simple SCF level. The structure has been checked to be planar. The main parameters are N_5C_4 = 1.39 Å, C_4C_3 = 1.34 Å, C_3C_2 = 1.45 Å, C_2N_1 = 1.16 Å, and $H_aN_5H_b$ = 122.0°; the other bond angles do not significantly deviate from their standard values (120.0° and 180.0°). The atomic indices refer to Schemes I–III. The first nonrelaxed excited states presently calculated correspond to various electronic occupations of the highest occupied (π_{CN},π_3) and lowest unoccupied (π_4,π^*_{CN}) molecular orbitals of the system. The orbitals π_{CN} and π^*_{CN} relative to the nitrile chromophore lie in the symmetry plane of the molecule 1. The first excited states are the triplet states $^3\pi_3\pi_4$ (5.4 eV), $^3\pi_{CN}\pi^*_{CN}$ (8.5 eV), $^3\pi_{CN}\pi_4$ (8.9 eV), and $^3\pi_3\pi^*_{CN}$ (9.7 eV) and the singlet states $^1\pi_3\pi_4$ (9.7 eV), $^1\pi_{CN}\pi_4$ (9.7 eV), $^1\pi_3\pi^*_{CN}$ (10.1 eV), and $^1\pi_{CN}\pi^*_{CN}$ (11.5 eV). These values are undoubtedly overestimated since the diffuse functions which would be necessary for an accurate description of these states were not included in the starting basis set. It must be kept in mind that this poor estimation is mainly marked for the singlet states.[19]

Nitrile–Isonitrile Rearrangement (Path a) and Related Reaction Paths. The nitrile–isonitrile rearrangement (RCN → RNC) has been experimentally observed under various conditions when R was either a hydrogen atom[20] or a saturated alkyl group.[21] Some theoretical studies have been devoted to the subject.[22] They illustrate that the reaction cannot proceed thermally at room temperature. A photochemically induced reaction path has been described.[22d] However, to the best of our knowledge, such an isomerization with a conjugated unsaturated R group has not been reported in the literature.

The in-plane rearrangement of the nitrile structure 1 to isonitrile 2 can be defined to a first approximation by the variations of two geometrical parameters, i.e., the C_3C_2 distance (1.45–2.60 Å) and the $C_3C_2N_1$ angle (180–0°). In a first step, a simultaneous variation of both parameters has been assumed. The resulting potential energy curves relative to the lowest electronic states clearly show that the only states which could be considered as possible channels for the reaction to occur are the singlet and triplet antisymmetrical states $^{1,3}\pi_{CN}\pi_4$. In a second step, the best reaction paths were determined by calculating several points on the energy surfaces $E = f(C_3C_2, C_3C_2N_1)$ relative to these antisymmetrical states. For each point, the geometrical parameters other than C_3C_2 and $C_3C_2N_1$ were optimized at the SCF–CI level.

By following the reaction path of steepest descent on the surfaces, we obtained the energy profiles of Figure 1. The respective variations of the two main parameters for this reaction path (Figure 2) show that the reaction begins by an important relaxation of the angle $C_3C_2N_1$ without significant change of the C_3C_2 distance. This motion leads the system to a deep potential well (point B, –2.6 eV from the initial point A). From this potential well, the system can either decay to the lowest energy surfaces or go on

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Figure 1. Calculated potential energy curves relative to the isomerization of enaminonitrile 1 to imidazole 6 via an isonitrile intermediate, 2. The left part of the figure is relative to the nitrile–isonitrile rearrangement (path a), the central part is relative to the hydrogen abstraction by the carbon atom of the isonitrile intermediate (path e), and the right part is relative to the ring closure of imidazole (path f). The letters S or T refer to the spin multiplicity. The dashed lines correspond to the antisymmetric tates and the full lines to the symmetric states.
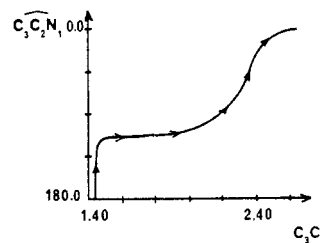
Figure 2. Diagram depicting the variations of the distance C_3–C_2 and of the angle C_3–C_2–N_1 along the reaction path a.

toward the isomerization to isonitrile via the overcoming of a large energy barrier (2.5 eV from the bottom of the potential well). In the first case, the starting molecular system is formed again. Indeed, the vertical decay from point B reaches the lowest surfaces in an area from where the system can only rearrange back to the initial molecule. The whole process represents an inefficient energy leakage.

In the second case, in the present state of our study it is difficult to estimate the feasibility of the reaction which yields the isonitrile intermediate 2. If we consider the irrealistic hypothesis of the total conservation of the internal energy accumulated in the first step, the barrier could be overcome. On the contrary, if we consider that there is an even partial dissipation of the vibrational energy of the excited system depicted by the point B before it could undergo the second step, the height of the barrier makes the isomerization impossible. The results for the present nitrile to isonitrile isomerization are at variance with those determined for the similar rearrangement of hydrogen cyanide where no barrier exists in the excited state $^1A'$.[22d] The results relative to the HCN–HNC process have been checked with our methods of calculation, which proved without any ambiguity that the influence of the conjugation is determinant on the feasibility of the nitrile to isonitrile rearrangement.

Nevertheless, if one assumes that the nitrile–isonitrile isomerization (path a) can take place, the chemical transformation of the intermediate 2 to imidazole 6 will

proceed in two ways. The first involves a direct insertion of the carbon atom C_2 into the N_5H amino bond (path d). The second one is a two-step process. In the first step, the formation of intermediate **5** via abstraction of a hydrogen of the amino group is required (path e). Then, in the second step, **5** yields imidazole by ring reclosure (path f). For the sake of simplicity, only the second process has been analyzed numerically.
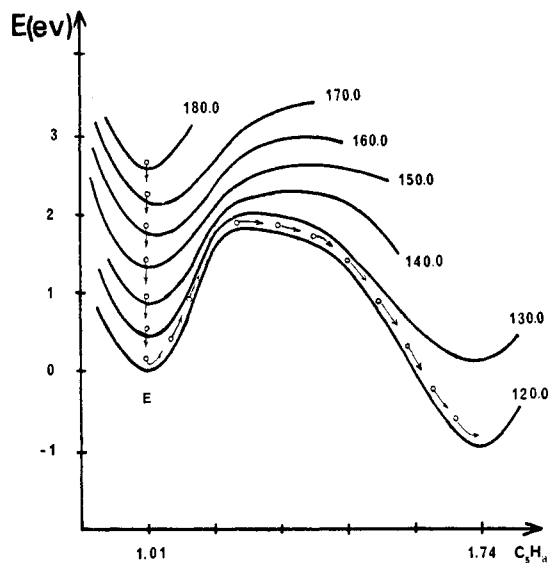
In order to study the reaction path e, we optimized the structure **5** by assuming all the angles to be 120° and the structure to be planar. The results are as follows: C_2N_1 = 1.26 Å, N_1C_3 = 1.32 Å, C_3C_4 = 1.33 Å, C_4N_5 = 1.31 Å. A linear variation of all the geometrical parameters of structure **2** was performed to calculate the potential energy curves relative to the transformation **2** → **5**. The curves are plotted in Figure 1 (central part) and show that, for all the lowest electronic states of intermediate **2**, the hydrogen transfer (path e) requires the overcoming of a large barrier: ca. 1.7 eV on the symmetric singlet surface and 2.3 eV on the antisymmetric singlet or triplet surfaces.

The ring closure of the intermediate **5** to imidazole **6** was also analyzed in the same conditions as in path e, i.e., linear variation of the geometrical parameters between the initial and final structures. Imidazole **6**, which has the geometry determined by Del Bene et al.,[23] was found to be 0.82 eV below the energy level of the initial structure **1** by our calculations. The calculated curves for reaction path f are plotted in Figure 1 (right part). They show that the formation of imidazole from the intermediate **5** does not require any expenditure of energy in the first symmetric singlet or triplet states but that in the antisymmetric singlet or triplet states, a large energy barrier (2.5 eV) must be overcome.

The calculated potential energy curves for the whole process **1** → **6** (Figure 1) show that there is no really favorable way for the reaction to occur. All the possible channels would require the overcoming of a large energy barrier on the surfaces of the excited states. This situation prevents the sequence of reaction paths a, e, and f to be considered as a plausible hypothesis to explain the easy photochemical conversion of **1** into the imidazole **6**. This conclusion is in agreement with the available experimental results.[3]

Reaction Paths Initiated by an *N*-Hydrogen Abstraction (Path b). This second primary process concerns a hydrogen exchange between both nitrogen atoms of structure **1** (path b). As already mentioned, a symmetry plane is preserved all along the reaction path which is defined by the variation of two main parameters, the distance N_5H_a and the angle $C_3C_2N_1$. The structure of intermediate **4** was optimized in its first antisymmetric triplet state. All the bond angles were assumed to have a value of 120°. The following bond lengths were determined: N_5C_4 = 1.28 Å, C_4C_3 = 1.46 Å, C_3C_2 = 1.49 Å, C_2N_1 = 1.23 Å, N_1H_a = N_5H_b = 1.01 Å. The lowest electronic states of this intermediate are a singlet symmetric state and a triplet–singlet pair of antisymmetric states (5.5, 5.8, and 6.0 eV with respect to the ground state of structure **1**, respectively).

In order to determine the nature of the potentially reactive states for the *N*-hydrogen abstraction, the natural correlation method previously described[24] was used. It clearly showed that as in the nitrile–isonitrile isomerization (path a), the only channels to be considered for the reaction

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(24) Devaquet, A.; Sevin, A.; Bigot, B. *J. Am. Chem. Soc.* **1978**, *100*, 2009. Bigot, B.; Devaquet, A.; Turro, N. *J. Am. Chem. Soc.* **1981**, *103*, 6.

Figure 3. Calculated potential energy surfaces relative to reaction path b in the first antisymmetric singlet state. The surface is represented in the form of a series of cuts for constant value of the angle $C_3-C_2-N_1$. The path of steepest descent is indicated by a sequence of arrows.

to occur involve the potential energy surfaces relative to the antisymmetric states.

The profile of these surfaces was determined in terms of both parameters N_5H_a and $C_3C_2N_1$. At each point of the surface (35 points), the molecular structure was partially optimized. The results for the singlet surface are depicted in Figure 3 in the form of a series of cuts for constant values of the $C_3C_2N_1$ angle. The surface for the triplet antisymmetric state is similar to the singlet surface. The diagram in Figure 3 shows that the path of steepest descent corresponds to an initial relaxation of the $C_3C_2N_1$ angle from 180° to 120° before the so-called hydrogen transfer will begin. This relaxation leads to the formation of a deep potential well E (2.6 eV below the energetic position of the excited state of the initial linear structure **1**). From point E, the hydrogen transfer requires the overcoming of an energy barrier of 1.8 eV. The feasibility of the complete reaction (path b) depends on the same factors as were emphasized for the nitrile–isonitrile isomerization, i.e., the factors which govern the competition between the decay to the lowest electronic surface, the dissipation of the internal energy accumulated during the relaxation step, and the overcoming of the barrier relative to the hydrogen transfer.

Strictly speaking, the reaction is possible, since the initial excited state has an energy higher than the energy of the barrier. However, the consideration of the various dissipative channels of this highly energetic system should greatly reduce its effectiveness.

Nevertheless, let us suppose that the excited molecule **1** undergoes isomerization to structure **4**. This intermediate should further rearrange either into ketenimine **7** or azetine **8**.

The geometrical structures of compounds **7** and **8** were optimized in their ground state. The bond lengths of ketenimine are N_1C_2 = 1.23 Å, C_2C_3 = 1.31 Å, C_3C_4 = 1.49 Å, and C_4N_5 = 1.28 Å; all the angles were assumed to have their standard values. The bond lengths of azetine are N_1C_2 = 1.25 Å, C_2C_3 = 1.49 Å, C_3C_4 = 1.39 Å, and C_4N_5 = 1.48 Å; the values of some representative angles are $H_aN_1C_2$ = 135.0°, $N_1C_2C_3$ = 137.0°, $C_2C_3C_4$ = 95.0°, $C_3C_4N_5$ = 91.0°, $C_4N_5C_2$ = 95.0°, and $N_5C_2C_3$ = 79.0°; all the atoms lie in the same plane except the hydrogen H_b. The NH_b
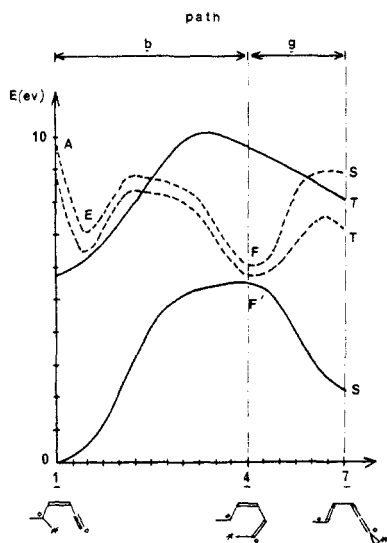
Figure 4. Calculated potential energy curves relative to the rearrangement of enaminonitrile 1 to ketenimine 7. The left part of the figure depicts the *N*-hydrogen abstraction (path b) according to the reaction path determined in Figure 3. The right part is relative to reaction path g.

Figure 5. Calculated potential energy curves relative to the rearrangement of enaminonitrile 1 to azetine 8. The left part of the figure depicts the formation of azetine via an n hydrogen abstraction (paths b and h). The right part is relative to the CC ring opening of azetine (path j).

bond makes a dihedral angle of 59.0° with the plane of the molecule. Ketenimine 7 and azetine 8 were found to be 2.18 and 2.40 eV above the ground state of structure 1, respectively.

Linear variations of the geometrical parameters have been assumed in order to study the reaction paths g and h which link the structures 4 and 7 on the one hand and 4 and 8 on the other hand.

Let us first consider the reaction path g. The calculated potential energy curves of the lowest electronic states along this path are plotted on Figure 4 (right part). The left part of Figure 4 represents the profile of the potential energy curves relative to the most favorable reaction path b previously described.

From point F which corresponds to the intermediate 4 possibly formed according to the reaction path b, the easiest channel to yield ketenimine 7 involves a decay from the antisymmetric surfaces to the lower symmetric surface (point F'). Then, the energy of the system is continuously descending to the ground state of the ketenimine or of the starting structure 1. Thus the key step in the formation of ketenimine is the *N*-hydrogen abstraction.

The calculated curves relative to the reaction path h are depicted in Figure 5 (central part).

As in the reaction path g, the most favorable channel from point F to azetine involves a decay from the antisymmetric surfaces to the lowest symmetric singlet surface (point F'). Once this jump is carried out, the reaction proceeds to completion by a constant decrease of the electronic energy of the system.

The above analysis of reaction paths g and h shows that the formations of ketenimine 7 and azetine 8 from intermediate 4 are similar quasi-spontaneous processes which will compete with each other.

Another possible way to obtain azetine from intermediate 4 is a two-step process via the ketenimine (path g plus path i). Indeed, ketenimine could yield azetine, a four-membered unsaturated ring analogous to cyclobutene, by a concerted cyclization of its butadienic skeleton. The whole reaction path i has not been studied numerically. The previous experimental[25] and theoretical[26] studies on
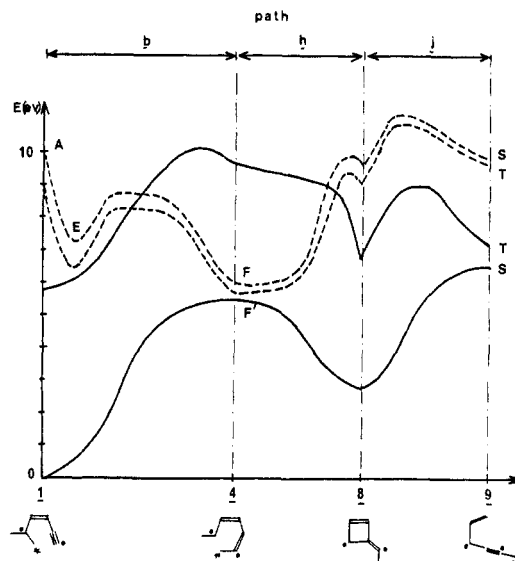
the isoelectronic butadiene–cyclobutene cyclization have shown that the thermal reaction requires the overcoming of an energetic barrier whose height was at least 1.5 eV. This result was confirmed by a preliminary calculation carried out for the midpoint on the reaction path linking ketenimine to azetine. The ketenimine–azetine reaction 7 → 8 could only proceed under the experimental conditions (room temperature) if we consider that the ketenimine molecule 7 formed according to reaction paths b and g has retained a sufficient part of the initial energy of structure 1. From the previous analysis, it would appear that the easiest way to form azetine follows the sequence of reaction paths b and h.

The rearrangement of azetine to imidazole (6) requires the rupture of the CC single bond of the cycle, the migration of a hydrogen atom from the nitrogen N_1 to the carbon atom C_2, and the formation of a new bond between the carbon atom C_3 and the nitrogen atom N_1.

It is very difficult to select a realistic reaction path for such a rearrangement among the numerous degrees of freedom that the molecular structure would have. In an exploratory step, the azetine ring was opened to yield an arbitrarily selected intermediate, 9, with the standard geometrical parameters $N_1C_2 = 1.32$ Å, $C_2N_5 = 1.33$ Å, $N_5C_4 = 1.40$ Å, and $C_4C_3 = 1.34$ Å; the values of all the angles were assumed to be 120.0° except for $N_1C_2N_5$ which was 180°. The calculated curves for the low-lying electronic states (Figure 5, right part) showed that no state was favorable to such an opening. Indeed, each curve exhibited a maximum whose position was about 3 eV above the corresponding state of the azetine structure. This unfavorable situation is enhanced when we compare the calculated curves relative to the CN bond breaking to those relative to the CC bond breaking previously described (reverse of path h).

Thus this superficial analysis of azetine reactivity suggests that, either thermally or photochemically, the azetine ring opens preferentially along the CN bond rather the CC bond. Due to the difficulty of exploring the surfaces

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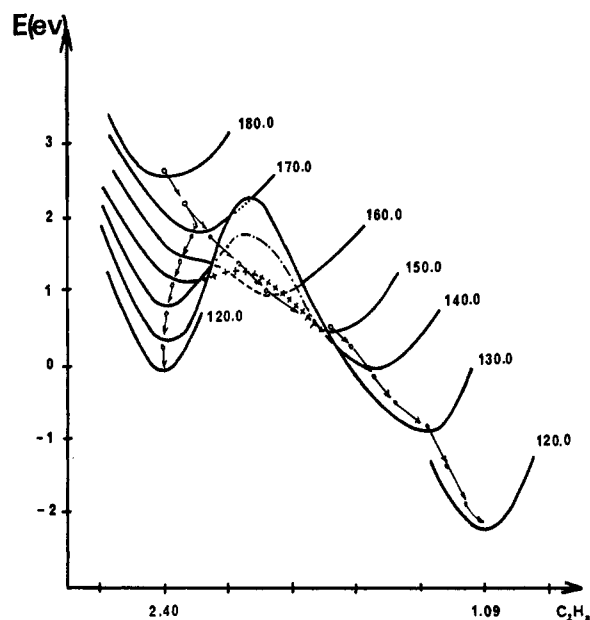
Figure 6. Calculated potential energy surface relative to the reaction path c in the first antisymmetric singlet state. The surface is represented in the form of a series of cuts for constant values of the angle C_3-C_2-N_1. The paths of steepest descent are indicated by arrows. The first one yields intermediate **3** and the second corresponds to an angular relaxation of the structure **1** in its antisymmetric singlet state.

Figure 7. Calculated potential energy curves relative to the enaminonitrile–imidazole rearrangement via an azirine intermediate **13**. The diagram is relative to the sequence of reaction paths c, k, l, o, p, and f from left to right. The curves corresponding to reaction path c depict the behavior of the lowest electronic states according to the reaction path determined in Figure 6.

connecting azetine **8** to imidazole **6**, no further calculations were performed.

Keeping in mind the limitations of the analysis relative to the azetine species, it is possible to conclude that the route which would yield imidazole **6** from **1** via the formation of an azetine intermediate is incompatible with the experimental conditions which favor the occurrence of the reaction.

Reactions Paths Initiated by a *C*-Hydrogen Abstraction (Path c). The third primary process which was considered involves the abstraction of one hydrogen of the amino group by the carbon atom of the nitrile (path c). As in the two primary processes previously studied, a symmetric plane is preserved all along the reaction path. The structure of the intermediate formed here was optimized in its first antisymmetric and symmetric singlet states. All the angles were assumed to be 120.0°. The bond lengths in both states are, respectively, $N_1C_2 = 1.30$ and 1.42 Å, $C_2C_3 = 1.47$ and 1.34 Å, $C_3C_4 = 1.38$ and 1.46 Å, and $C_4N_5 = 1.29$ and 1.28 Å. The low-lying electronic states of intermediate **3** are a singlet–triplet pair of antisymmetric states (4.4 and 3.8 eV, respectively, with respect to the ground state of the initial structure **1**). A symmetric singlet state (4.8 eV) comes after.

As with the N abstraction, the natural correlation method was used in order to permit potentially reactive states to be distinguished from nonreactive states. This method showed that as in both primary processes previously studied, the reactive states were the antisymmetric ones. The profiles of these states have been determined in terms of two parameters, N_5H_a and $C_3C_2N_1$. At each point of the surfaces (35 points), the molecular structure was partially optimized.

The results for the singlet surfaces are depicted in Figure 6 in the form of a series of cuts for constant values of the $C_3C_2N_1$ angle. As in the case of N abstraction, the triplet surface is parallel to the singlet one. The surface exhibits two valleys. The first one is relative to the angular relaxation of the CCN linkage. The second yields the intermediate **3** directly. The study of the surface shows that
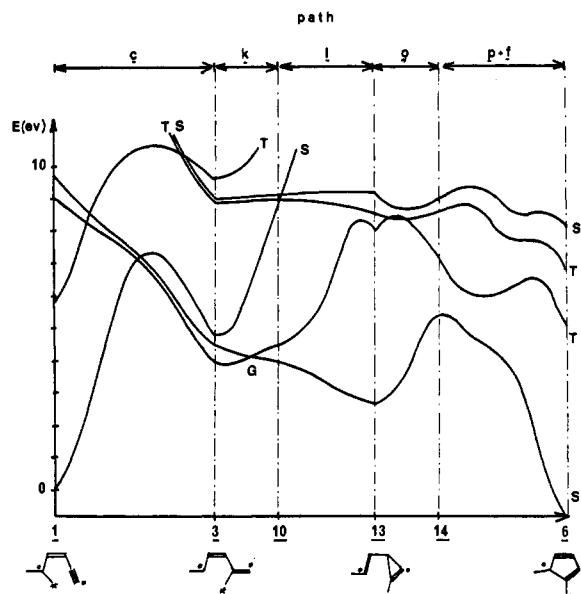
the reaction path of minimum energy follows the bottom of the second valley and involves a continuously descending pathway toward **3**. This fact distinguishes this primary process from those previously analyzed (paths a and b). Indeed, the deep valley relative to the angular relaxation of the CCN linkage remains, but in this case it is not a required passage on the reaction path considered.

The potential energy curves relative to the section of the surfaces along the most favorable reaction path c are depicted in Figure 7 (left part).

From the intermediate **3**, two reaction paths were considered. The first involves a rotation of the terminal $N_1C_2H_a$ group about the C_2C_3 bond. This rotation can be defined by the variation of the dihedral angle between the $C_2C_3C_4$ and $N_1C_2H_a$ planes. A rotation of 90° yields the intermediate **10** and a rotation of 180° yields the intermediate **11**. The second reaction path corresponds to a migration of the $N_1C_2H_a$ fragments in the plane of symmetry of **1** in order to yield the imidazole structure **6** directly.

Let us first consider the reaction path which begins by the rotation of the $N_1C_2H_a$ group (path k). The optimized structure of the intermediate **10** in its first triplet state is $N_1C_2 = 1.28$ Å, $C_2C_3 = 1.50$ Å, $C_3C_4 = 1.42$ Å, and $C_4N_5 = 1.30$ Å. The calculated curves relative to the linear deformation of the structure **3** to produce **10** are plotted on the central part of Figure 7. They show that the rotation of 90° stabilizes the lowest singlet state slightly and continuously (−0.5 eV) while destabilizing the corresponding triplet state by the same amount. The intermediate **10** may be considered as resulting from a CN ring opening in the azirine **13**. This reaction path was previously studied by the presently used method.[27] The calculations carried out on the actual structure **13**[27a] are consistent with the previous analysis[27b] and show that **13** is easily formed from the intermediate **3** either from the

(27) (a) The intermediate **13** has been optimized in its ground state. Its geometrical structure is as follows: $N_1C_2 = 1.27$ Å, $N_1C_3 = 1.53$ Å, $C_3C_4 = 1.54$ Å, $C_4N_5 = 1.32$ Å, $N_1C_3C_2 = 62.0°$, $HC_3C_4 = 115.0°$ $N_1C_5H_b = 146.1°$, $C_3C_4N_5 = 120.0°$. (b) Bigot, B.; Sevin, A.; Devaquet, A. *J. Am. Chem. Soc.* **1978**, *100*, 6924.
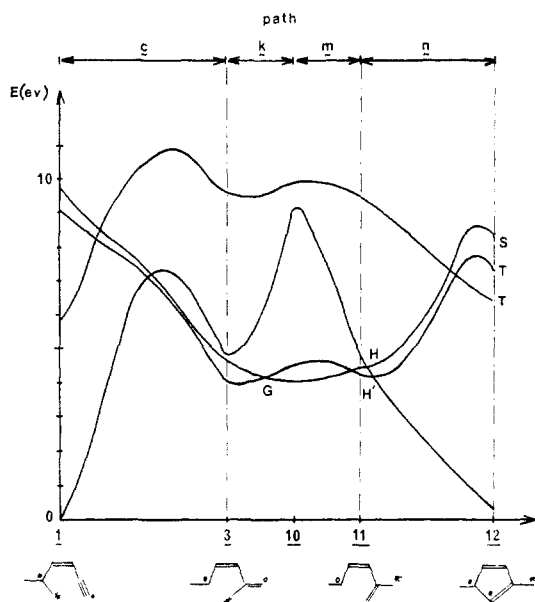
path

Figure 8. Calculated potential energy curves relative to the enaminonitrile–pyrazole rearrangement. The left part of the figure corresponds to the previously mentioned hydrogen abstraction by the carbon atom of the nitrile group (path c). The central part is relative to the rotation of the fragment $N_1C_2H_a$ about the bond C_2-C_3 (paths k and m). The right part corresponds to the ring closure of pyrazole (path n).

lowest singlet surface (no energy barrier prevents the formation of the three-membered ring) or from the lowest triplet state by intersystem crossing to the singlet surface at point G. If we assume that the intermediate 10 does not yield the azirine derivative 13 under the conditions previously described, the rotation of the $N_1C_2H_a$ fragment around the C_2C_3 bond could go on to yield the planar intermediate 11 (which was assumed to have the same bond lengths as intermediate 3). The calculated potential energy curves (Figure 8, central part) show that the lowest singlet state is slightly destabilized continuously along the reaction path (+0.5 eV) while the lowest triplet state is stabilized in the same conditions (-0.3 eV). The intermediate 11 is an obvious precursor of pyrazole 12. The calculated curves relative to the ring closure were determined by a linear variation of the geometrical parameters between both structures[28] (Figure 8, right part). They show that the most favorable channel for the reaction n involves intersystem crossing or internal conversion from the antisymmetric surfaces to the symmetric singlet surface which yields 12 directly.

The last pathway considered from intermediate 3 concerns the in-plane migration of the fragment $N_1C_2H_a$ from its initial position to that which it occupies in imidazole 6. This possibility which is similar to the nitrile–isonitrile isomerization (path a) was tested since Schaeffer et al.[29] have shown that the cationic species H_2CN^+ rearranged directly to $HCNH^+$ and that the lowest symmetric singlet state of intermediate 3 had a nonnegligible contribution (50%) of the valence structure $^-HN(5)$—$C(4)H$—$C(3)H$—$C(2)H=N(1)^+$. Various reaction paths relative to the in-plane rearrangement of the intermediate 3 to imidazole (path o) were tested. In the most favorable case, the re-

action path involved a barrier of around 3.2 eV from the lowest states of intermediate 3.

The comparison of the three reaction paths initiated from the intermediate 3 clearly shows that the formation of an azirine derivative is undoubtly the most likely to occur, although the pyrazole formation is energetically accessible.

It is well established that primary photochemical reaction of azirine derivatives occurring most frequently is the ring opening by CC bond cleavage, while their thermal reactions involve both CC and CN cleavages according to the location and nature of the substituents.[30]

Let us first consider the case where the azirine 13 is photonically excited. The comparison of the calculated potential energy curves for the CC and the CN ring openings shows that the CN opening is the more likely reaction, as it was previously discussed.[27] It involves the population of excited singlet or triplet nπ states localized on the CN chromophore of the cycle and decay to the lowest triplet surface which yields the intermediate 14 directly (Figure 7, central part).

A variation of the dihedral angle of the planes $C_3N_1C_2$ and C_3C_4H between the values 90° and 0° leads to the formation of 6 (paths p and f). The calculated curves relative to this path show that the most favorable channel involves a decay from the triplet surface to the lowest singlet surface which is continuously descending to the ground state of imidazole 6 (Figure 7, right part).

Let us now consider the case of thermal reactions of azirine derivatives 13. With respect to the unsubstituted azirine, the unsaturated ketimine substituent could intervene in the thermal reactivity of the cycle in two ways. On the one hand, it could stabilize the open intermediates 10 and 14 in their first singlet state by conjugation with the adjacent radicalar center. One may estimate that such a stabilization would be of equal importance in both intermediates due to the location of the substituents. On the other hand, the ketimine group could allow the concerted formation of either a pyrazole or an imidazole by a simultaneous CN or CC ring opening of the azirine coupled with the cyclization of a five-membered ring. These reaction paths could be defined as a [1,3] sigmatropic shift relative to the ketimine double bond. The calculated curves relative to these processes in the first singlet state showed no significant change from the three-step processes (paths l–n or o, p, f). Indeed, as it was established for various other three-membered rings,[31] the opening of the cycle begins by the lengthening of a bond of the cycle before the rotation of the substituents could proceed. The position of the transition states relative to the formation of pyrazole and imidazole is 1.4 and 2.5 eV above the ground state of azirine 13, respectively.[34] These values prevent a thermal ring opening either by CN or CC bond rupture and require the consideration of rearrangement of azirine 13 to imidazole 6 as a photochemical reaction.

The above analysis suggests that the primary step of the photorearrangement of enaminonitrile to imidazole proceeds via the singlet or triplet antisymmetric excited states $\pi_{CN}\pi_4$. However, if one takes into account that the position of the singlet symmetric state $\pi_3\pi_4$ is poorly estimated, as it was previously mentioned, the potential energy curves relative to this state must be shifted down. They will therefore cross the curves relative to the antisymmetric

(28) Pyrazole has been assumed to have the structure mentioned in: "Molecular Structures and Dimensions, A₁, Organic and Organometallic Crystal Structures"; Crystallographic Data Center: Pittsburgh, PA, 1970; p 181.

(29) Conrad, M. P.; Schaeffer, H. F., III. *Nature (London)* 1978, *274*, 456. Schaeffer, H. F., III. *Acc. Chem. Res.* 1979, *12*, 288.
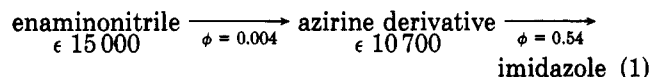
(30) Wendling, W. A.; Bergman, R. G. *J. Am. Chem. Soc.* 1974, *96*, 308 and references therein.

(31) Chapuisat, X.; Jean, Y. *J. Am. Chem. Soc.* 1975, *97*, 6325. See also ref 18.

states. At the crossing, an internal conversion or inter-system crossing could occur and permit the system to jump to the antisymmetrical surfaces previously considered as reactive. Such a description of the primary process would be in agreement with the available experimental results which show that the reactive state is a singlet $\pi\pi^*$ state.

Discussion

The above analysis suggests the existence of a thermally stable azirine intermediate which rearranges photochemically to imidazole. This conclusion could, at first sight, appear to be inconsistent with the fact that the various experiments so far reported have not been able to detect any stable intermediate. Various data, however, support the idea that, indeed, there is no inconsistency between the experimental results and the above-mentioned theoretical conclusions. Padwa et al.[11] reported that 2-(phenylimino)-3-phenyl-2*H*-azirine gives 1,2-diphenylimidazole as the exclusive photoproduct (ϕ = 0.54) when irradiated at 243 nm (ϵ 10 700), while it gives 1,3-diphenylpyrazole when it is heated for 15 h at 140 °C. Various other vinyl-substituted 2*H*-azirines have similar behavior.[11] These facts confirm our results: the azirine derivative **13** cannot lead to imidazole thermally under the experimental conditions (25 °C) of the enaminonitrile–imidazole photochemical rearrangement (the reaction occurs even at –77 °C).[4] The comparison of the extinction coefficients of enaminonitrile (ϵ 15000, λ = 243 nm) and 2-imino-2*H*-azirine derivatives (ϵ 10700, λ = 257 nm) on the one hand and of the quantum yields for the enaminonitrile–imidazole (ϕ = 0.0034)[7] and azirine derivative–imidazole (ϕ = 0.54) photochemical rearrangements on the other hand shows that in the overall enaminonitrile–imidazole isomerization, the ratio of the concentration of azirine to the concentration of enaminonitrile must be small all along the reaction path. According to the kinetic scheme expressed in eq 1, the maximum value for the ratio is 8.4 ×

$$\underset{\epsilon\,15\,000}{\text{enaminonitrile}} \xrightarrow[\phi\,=\,0.004]{} \underset{\epsilon\,10\,700}{\text{azirine derivative}} \xrightarrow[\phi\,=\,0.54]{} \text{imidazole} \quad (1)$$

10^{-3}. If the above value of the ratio between the concentrations of the reagent and the intermediate is considered as independent of temperature, it is understandable that it would be rather difficult to detect such an intermediate even at low temperature.

Conclusions

The present study of the reaction paths relative to three different primary photochemical processes of 1-amino-2-cyanoethylene shows that the most probable reaction is the abstraction of a hydrogen atom of the amino group by the carbon atom of the nitrile group. This primary step yields an azirine derivative directly. The rearrangement of this intermediate to imidazole requires a photonic excitation. Therefore, the isomerization of the enaminonitriles to imidazole derivatives must be a two-photon process. This study suggests the existence of a thermally stable azirine intermediate which has not yet been experimentally identified. The intervention of such an intermediate has already been suggested in a parent reaction involving the five-membered rings isoxazole and oxazole.[32,33]

A possible explanation of the nondetection of this intermediate despite the various attempts using IR or UV techniques could be related to the fact that the enaminonitrile and the azirine intermediate absorb in the same region of the spectrum but that the intermediate reaction has a much greater quantum yield than that of the reactant. It would result that the concentration of the intermediate would be very small all along the reaction path.

The formation of ketinimine or azetine structures as suggested by Ferris et al.[3-5] could not be definitively ruled out, although the primary process involved in their formation looks less favorable than the previously mentioned C abstraction (path c). If these compounds were formed, they should not be involved in the isomerization to imidazole since, neither thermally nor photochemically, the azetine derivative undergoes CC bond breaking preferentially.

(32) Singh, B.; Zweig, A.; Gallivan, J. B. *J. Am. Chem. Soc.* **1972**, *94*, 1199.

(33) Tanaka, H.; Osamura, Y.; Natsushita, T.; Nishimoto, K. 3rd Congress in Quantum Chemistry, Kyoto, Japan, 1979. Also private communication.

(34) It has been checked that a quasi-concerted azirine ring opening–imidazole ring closure is energetically less favorable than the reaction pathway depicted in this paper.