fragments and just one of the π and π* pairs in the C≡CH and C≡C⁻ fragments. This simplification in presentation does not, however, affect the rigor of our argument.

(20) A similar argument has been presented by R. F. Hudson, O. Eisenstein, and N. T. Anh, *Tetrahedron*, **31**, 751 (1975).

(21) The dominance of the interaction π_Me···π_A* over π_A···π_Me* is consistent with both conventional experimental evidence concerning hyperconjugative interaction of a methyl group with unsaturated centers and with the theoretically derived charge distribution.

(22) This result is readily demonstrated by a simple PMO argument.

(23) Experiments carried out in part to test this prediction have indeed confirmed the result: R. T. McIver, paper PHYS-093, 175th National Meeting of the American Chemical Society, Anaheim, Calif., March 1978.

(24) P. Kebarle, *Annu. Rev. Phys. Chem.*, **28**, 445 (1977).

(25) Since this manuscript was submitted, an interesting related article dealing with the n-donor bases CH₃O⁻, CH₃NH⁻, and CH₃S⁻ has appeared: D. J. De Frees, J. E. Bartmess, J. K. Kim, R. T. McIver, and W. J. Hehre, *J. Am. Chem. Soc.*, **99**, 6451 (1977).

Theoretical ab Initio SCF Investigation of the Photochemical Behavior of Three-Membered Rings. 1. Diazirine

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Abstract: Ab initio SCF CI methods (minimal basis STO-3G and limited CI) are used to calculate the potential energy surfaces of the ground and low-lying excited states of the diazirine-diazomethane system when various distorsions are simulated: (1) the continuous "out of plane" bending of linear diazomethane followed by its closure into diazirine; (2) the "in-plane" bending of linear diazomethane and the breaking of the N–C bond; (3) the elongation of the N–C linkage in linear or bent diazomethane and the concerted two-bond scission in diazirine.

In a previous paper[3] we have investigated the successive and concerted scissions of the pair of NH bonds in *cis*-diimide. This molecule is the simplest acyclic system which contains the –N=N– chromophore which, however, can also appear in cyclic species. Such is diazirine **3**. In the present study we will simulate theoretically the major processes occurring in the photochemistry of this three-membered ring[4] and related species such as linear[5] **1** or bent diazomethane **2** and **4**.

Substituted diazomethane and diazirine are known to cleave, whether thermally or photochemically, into a carbene fragment and a nitrogen molecule.[6] The intimate mechanism of this fragmentation remains somewhat obscure. On the other hand, substituted diazomethane and the primary products of diazirine decomposition exhibit 1,3-dipolar cycloadditions with various dipolarophiles.[7] It is therefore interesting to obtain some information pertaining to all these species and their interconversions.

The reactions we will consider are summarized in Figure 1. To facilitate their discussion we will choose linear diazomethane **1** as the starting point of our investigations.

The first distortion (path a) is the bending of diazomethane **1** which results in its closure into diazirine **3**, that is, the continuous decrease of the NNC angle from 180° (its value in linear diazomethane **1**) to 110° (in the corresponding bent form **2**) and finally to 64.8° (in diazirine **2**). The bisecting plane of the CH₂ group is the only symmetry element of the whole molecule conserved throughout this first process. Note here that the reverse process **3** → **2** should be qualitatively similar to the breaking of a single NH bond in *cis*-diimide, minor quantitative differences arising from the fact that (a) NC bonds (bond energy 78 kcal/mol) are now concerned instead of nh bonds (bond energy 92 ± 2 kcal/mol) and (b) a cyclic molecule is now considered which releases its ring strain energy (15–20 kcal/mol). Starting with species **1**, **2**, and **3** the elongation of the NC bond(s) will finally result in the complete breaking of the molecule into its constituent fragments: methylene and a nitrogen molecule (paths b, c, and d, respectively). Note again that, with similar quantitative restrictions, path d should be somewhat reminiscent of the concerted scis-

sion of *cis*-diimide into hydrogen and nitrogen molecules.

The second distortion is the in-plane bending of diazomethane (e) followed by the dissociation of the corresponding bent species **4** (path f). (This is now the plane of the CH₂ group which is the only symmetry element conserved during the bending.)

Methods of Calculations

From a technical point of view, the calculation of all these ground- and excited-state potential energy curves (PECs) requires two steps. The first is the familiar SCF part which will provide us with adequate MOs. This part was carried out with the usual GAUSS 70 series of program[8] in its STO-3G minimal basis version. Two different calculations were, however, done at each point. The first, using Roothaan's closed-shell formalism,[10] gives the best MOs in the reactant (closed-shell) regions of the reaction paths while the second, Nesbet brand[11] of open-shell treatments is more suited for regions where the dissociation of a bond is already well underway. Using these two approaches and their respective MO manifolds, we have then carried out the CI part of the treatment by allowing the mixing of all singly and doubly excited configurations obtained from the ground-state configuration by varying the population of the five highest occupied and the two (or three) low-lying empty MOs.[12] For each state, and at each point, Roothaan and Nesbet MOs give two different results. The lower in energy was conserved to draw the various PECs displayed in the figures. It will be obvious to the reader that this procedure is already more than adequate to obtain the qualitative features of these PECs. The quantitative information (activation energies) must be considered with care. They could be improved by (a) adding a diffuse basis set of atomic orbitals for the description of nπ* singlet states (though these states do not play a prominent role in our analysis), (b) extending the scope of our CI step to include triply excited configurations, and (c) minimizing the molecular geometries at each point of a reaction path and for each state. Still the vertical excitation energies tabulated below agree fairly well with both experimental results[13] and SCF theoretical determinations[14] already published
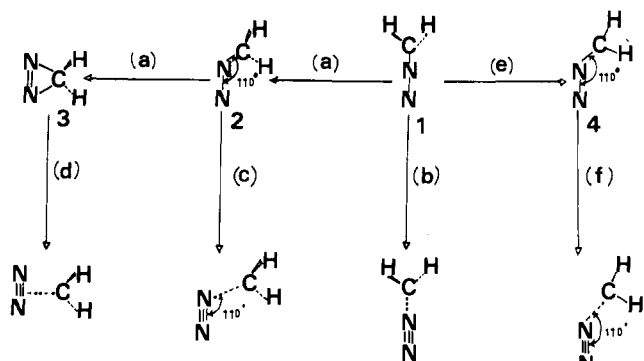
Figure 1. Scheme presenting the different reaction paths of the system diazirine–diazomethane presently studied.
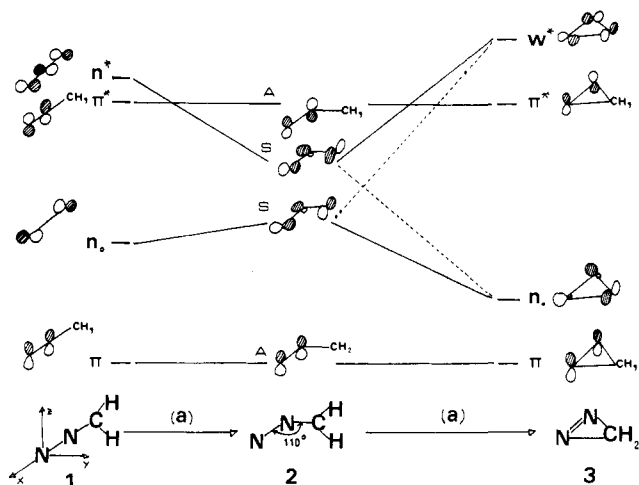

Figure 2. MO correlation diagram in the distortion of diazomethane 1, first to the bent intermediate 2, and then to diazirine 3 (path a). The symmetry symbol S or A refers to the symmetry plane conserved in the process, as in Figure 3.

Figure 3. State correlation diagram in the distortion of diazomethane (path a).

for diazomethane and diazirine. We thus believe that the PECs obtained by this method are semiquantitatively realistic and that their analysis will be of chemical significance.

Reaction Path a

Let us first consider the behavior of the molecular orbitals when linear diazomethane 1 is distorted, first to an intermediate bent form 2 and then to the three-membered ring diazirine 3 (Figure 2). The π and π^* MOs are not appreciably affected during this process which takes place in their nodal plane (xy). On the contrary, the pair of in-plane allylic type MOs, the nonbonding n_0 and its antibonding partner n*, are strongly perturbed. Owing to the increase of the 1-3 antibonding character, the first is more and more destabilized and would naturally intend to correlate with the antisymmetric antibonding Walsh MO (W*) of the cyclopropane-like ring 3. On the other hand, both the decrease of the C–N (central) antibonding character and the reinforcement of the C–N (terminal) bonding quality contribute to the continuous stabilization of n* which would finally correlate with the n_ MO of diazirine.[15a] The intended crossing (near $\theta = 110°$) of these two orbitals of similar symmetry (dotted lines in Figure 2) is avoided and taken into account at the SCF stage of the calculations (full lines).

Let us then turn our attention toward the states. The nature of the states of bent diazomethane $(\theta = 120°)$ deserves some comments. The lowest singlet–triplet pair of states exhibits $D_{\sigma\sigma}$ (homosymmetric) diradical character. That is, the triplet member is a "pure" diradical whose wave function is simply the $n_0{\rightarrow}n^*$ triplet configuration. The singlet counterpart is
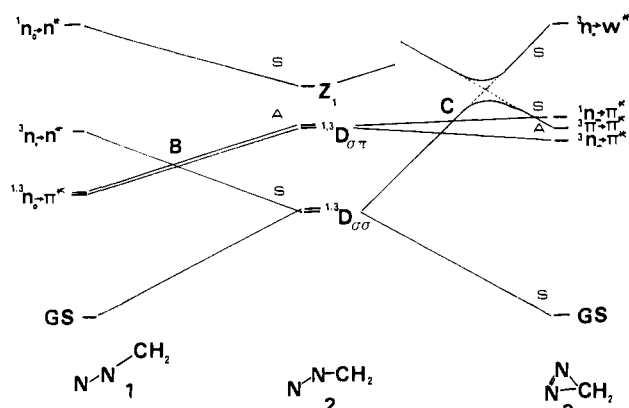
somewhat contaminated by ionic character. Its wave function thus conserves some memory of the intended crossing of the n_0 and n* MOs and is a mixture of the n_0^2 (80%) and $(n_0{\rightarrow}n^*)^2$ (20%) singlet configurations. One has then to keep in mind that this ionic character would undoubtedly be increased by appropriate substitution. The next pair of states results from the $n_0{\rightarrow}\pi^*$ excitation. Both singlet and triplet states have pure (heterosymmetric) $\sigma\pi$ diradical character. Finally one finds, still higher in energy, the $n_0{\rightarrow}n^*$ singlet state, the first to possess zwitterionic or charge transfer character.

The state correlation diagram for the first half of the bending motion (1 → 2) is straightforward (Figure 3). The ground and $^{1,3}n_0\pi^*$ states of diazomethane are destabilized in a parallel fashion and correlate with the $D_{\sigma\sigma}$ singlet and the $^{1,3}D_{\sigma\pi}$ states, respectively. On the contrary, both singlet and triplet $n_0{\rightarrow}n^*$ states are stabilized and correlate with the zwitterionic Z_1 state and the triplet $D_{\sigma\sigma}$ diradical. Note that in these first stages of the bending the nature of the states is not sensibly altered since it is known that diazomethane in its ground state is a diradical[14h] (the two radical centers at the terminal N and C atoms being coupled via the central nitrogen atom) while the $n_0{\rightarrow}n^*$ singlet shows charge separation.[14a]

We will not comment on the second half of the bending motion 2 → 3 itself (in which the closure is completed) but rather the reverse process. The ground state of diazirine is destabilized and correlates with the singlet $D_{\sigma\sigma}$ diradical while, at the same time, the pair of $n_-\pi^*$ states do so with the duo of $D_{\sigma\pi}$ wave functions. The n_W* triplet plays, in this bond scission, the same role as the n_0n^* triplet in the bending of diazomethane. This state is continuously stabilized and intends to correlated with the $D_{\sigma\sigma}$ triplet. However, and this is a new feature which differentiates the two reaction paths (1 → 2) and (3 → 2), the familiar $\pi\pi^*$ state of diazirine now appears below the n_W* triplet. Indeed it falls just between the pair of n_π^* states. This triplet is destabilized and, as a result, would cross the n_W* triplet. This crossing is symmetry forbidden. The mixing of the two configurations in the CI part of the calculations forces the $\pi\pi^*$ triplet state to correlate with the lowest $D_{\sigma\sigma}$ triplet of bent diazomethane 2. Its potential energy curve should thus exhibit a maximum which is the remnant of the natural (or intended) behavior.

Figure 4 represents the calculated potential energy curves for the ground and low-lying excited states of the diazomethane–diazirine system. Note first that they completely confirm our analysis of the state correlation diagrams (Figures 2 and 3) and, second, the similarity between the right-hand part of this figure with that obtained in our study of the one-bond breaking in *cis*-diimide (Figure 2 in ref 3). These curves allow us to review the various possibilities resulting in the opening of diazirine. The "naturally" dissociative state is the n_W*
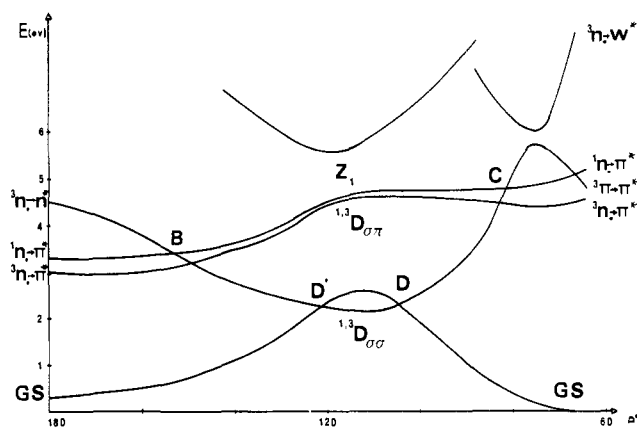
Figure 4. Calculated potential energy curves in the distortion of diazomethane **1** ($\theta = 180°$) first to the bent form **2** ($\theta = 110°$) and then to diazirine ($\theta = 64.8°$).

Table I. Comparative Values of the Different Studied Systems

	state	present work	other calculations		expt
diazomethane	GS	$-146.010\ 95^a$			
		$(-145.918\ 48)$			
	$^3A_2$	2.72^b	2.65^c		
	$^1A_2$	3.10	2.93		3.14^e
	$^3A_1$	4.30	3.		
	$^1A_1$	7.74	5.90		5.70^e
diazirine	GS	$-146.025\ 17^a$			
		$(-145.946\ 48)$			
	$^3A_2$	4.51^b	3.19^f	3.54^g	
	$^3B_2$	4.72	5.03	5.08	
	$^1A_2$	5.15	4.17	4.28	3.86^d
	$^1B_2$	11.30	10.42	9.19	
open form **2**	GS	$-145.933\ 45^a$			
		$(-145.655\ 20)$			
open form **4**	GS	$-145.936\ 02^a$			
		$(-145.772\ 40)$			
methylene^h	$^3B_1$	$-38.440\ 64^a$			
		$(-38.417\ 30)$			
	$^1A_1$	0.63^b			
	$^1B_1$	2.85			
nitrogen N_2	GS	$-107.599\ 45$			
		$(-107.496\ 50)$			

^{a} Value in atomic units; in parentheses is the value before CI. ^{b} Value in eV above the ground state. ^{c} From ref 14a. ^{d} L. C. Robertson and J. A. Merritt, *J. Mol. Spectrosc.*, **17**, 48 (1965). ^{e} G. Herzberg, "Molecular Spectra and Molecular Structures. III. Electronic Spectra and Electronic Structure of Polyatomic Molecules", Van Nostrand, Princeton, N.J., 1966, p 530. ^{f} From ref 14c. ^{g} From ref 14f. ^{h} Calculations achieved for a 117° HCH angle (see text).

triplet state. This state cannot be easily populated. Two low-lying excited states may act as "reservoirs" for the population of this reactive state in the course of its natural (but interrupted) descent toward the $D_{\sigma\sigma}$ triplet of bent diazomethane **2**.

The first is the $\pi\pi^*$ triplet which can be, for example, generated by sensitization. Such a triplet state would need to acquire an activation energy of 1 eV to overcome the barrier which results from the $^3\pi\pi^*/^3n_-W^*$ avoided crossing. This theoretical value is an upper limit. If one recalls that a triplet state lives long enough to acquire between 14 and 18 kcal/mol of vibrational energy before it phosphoresces,[15b] it is reasonable to assume that this $\pi\pi^*$ state may, in some cases, induce the rupture of the CN linkage.

The second is the $n_-\pi^*$ singlet state. This state intersects the dissociative curve at C where efficient intersystem crossing
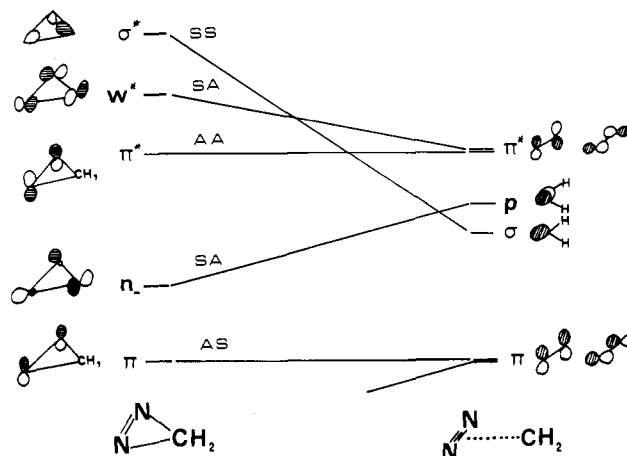

Figure 5. MO correlation diagram of the extrusion of carbene CH_2 from diazirine **3** via the simultaneous two-bond scission (path d). The symmetry symbol refers first to the plane of the molecule and second to the perpendicular one.
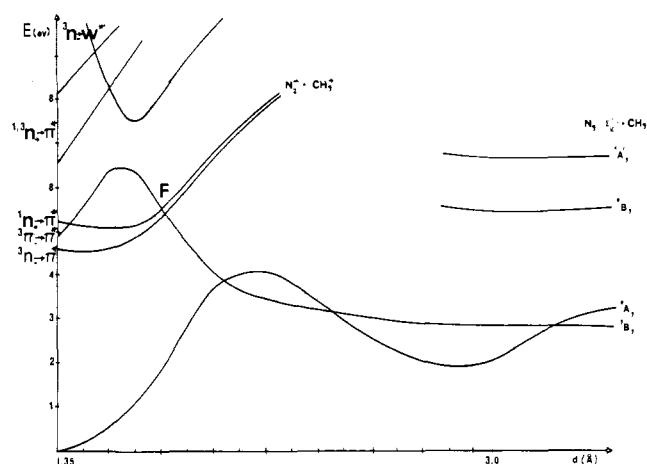

Figure 6. Calculated potential energy curves of the extrusion of carbene from diazirine (path d).

may occur[16] since the flipping of the electron spin is counterbalanced by a 90° rotation of the electron location in space (from n_- to π). If the molecule switches surfaces, again the breaking occurs. If not, the $n_-\pi^*$ is endowed with sufficient energy to be able to populate the $^{1,3}n_0\pi^*$ states of linear diazomethane (and even the n_0n^* triplet).

When the breaking intervenes the molecule usually ends up as a $^3D_{\sigma\sigma}$ bent diazomethane. This species can intersystem cross to the singlet ground state surface of diazirine (point D) or linear diazomethane (D') or else, as will be shown later, can dissociate to give triplet methylene and a nitrogen molecule.

Of course it is not possible, at the present time, to evaluate the relative efficiency of all these competing processes. We are only in position to list them.

Path d

The MO correlation diagram for methylene extrusion in diazirine (Figure 5) exhibits a typical Woodward-Hoffmann situation: the n_- MO—the HOMO—is destabilized since it loses N-C bonding character and intersects the empty cyclopropane-like σ^* antibonding MO which is strongly stabilized when the methylene fragment escapes. This MO crossing is allowed and induces, at the state level, an avoided crossing between the diazirine ground state and the doubly excited $(n_- \rightarrow \sigma^*)^2$ state. The ground state of diazirine finally dissociates into nitrogen ($^1\Sigma_g^+$) and methylene in its lowest A_1 singlet state.[17] The maximum in its potential energy curve
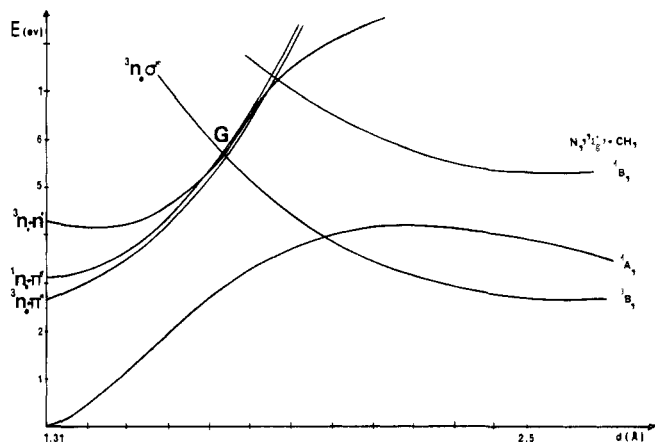
Figure 7. Calculated potential energy curves of the CN rupture of linear diazomethane **1** (path b). *d* is the CN distance.

Figure 8. Calculated potential energy curves in the CN rupture of the bent diazomethane **2** (path c).

serves as a witness of the "natural" correlations (Figure 6). The pair of $n-\pi^*$ states now intends to correlate with high-lying CH_2^+ and N_2^- charge-transfer states and is continuously destabilized. Finally the maximum in the $\pi\pi^*$ triplet curve again results from a symmetry-forbidden crossing. This triplet would "naturally" correlate with a high-lying state of the products: CH_2 ($^1A_1'$) + N_2 ($\pi \rightarrow \pi^*$). Its potential energy curve crosses that of the $n-\sigma^*$ triplet state, the dissociative state, which correlates with the ground state of the fragments, that is, CH_2 ($^3B_1$) + N_2 ($^1\Sigma_g^+$).

Figure 6 shows a strong similarity with that obtained in the concerted dissociation of *cis*-diimide into hydrogen and nitrogen molecules (Figure 1 in ref 3), but presents also an additional and unexpected feature: in the final stages of the process the lowest singlet state of the system (N_2 + CH_2 ($^1A_1$)) drops 1 eV below the lowest triplet (N_2 + CH_2 ($^3B_1$)). It then increases in energy to finally end up above the triplet, that is, to give the expected energy ordering of the methylene states. This behavior could possibly result from imperfections in our calculations. A first explanation might be found in the dependence of the relative energy of the $^1A_1$ and $^3B_1$ states of methylene as a function of the HCH angle. The optimum angle of the B_1 triplet is 136°, that of the A_1 singlet 105°,[18] whereas this angle has been kept constant in our procedure and equal to its value in diazirine itself (117°). To check this possibility we have minimized the energy of both states with respect to the new variable. The triplet state surface is a rather flat minimum between 115 and 130° while the A_1 singlet is even more stabilized below its partner (2 eV) upon decrease of the HCH angle to 105°. This first rationalization then fails. So does a second possibility suggested by well-documented importance of the correlation terms in methylene states. Indeed, the correlation energy is 15 kcal/mol larger in $^1A_1$ than in $^3B_1$.[19] Finally we investigated the relative excited energies of methylene itself (HCH angle = 117°). Using the theoretical procedure outlined at the beginning of this paper, we have found that the methylene ground state is the $^3B_1$ triplet. The first singlet state ($^1A_1$) appears 0.63 eV (15 kcal/mol) above this ground state. (The B_1 singlet and second $^1A_1'$ singlet vertical excitation energies are 2.85 and 6.05 eV, respectively.)

It appears therefore that the potential well in the lowest singlet state of the system is of chemical significance: when an incoming methylene fragment approaches a nitrogen molecule a stable intermediate is formed between the first (excited) singlet of CH_2 and the ground-state nitrogen species. This complex is the ground state of the whole system for separation of the two fragments ranging between 2.5 and 3.0 Å. We cannot at the present time offer any convincing and clear-cut rationale for the existence of this complex.
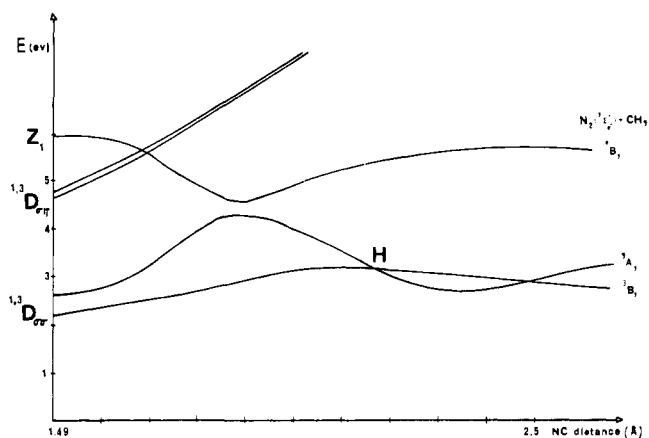
Paths b and c

Let us now consider the scission of the N–C bond in linear and bent diazomethane. In the dissociation of the linear form the MO correlation diagram again involves the allowed crossing between an occupied MO and an empty partner: the HOMO—the nonbonding allylic wave function n_0—is slowly destabilized and correlates with the pure P_{CH_2} orbital which is perpendicular to the methylene plane. The empty counterpart is a high-lying N(central)–C antibonding MO which correlates with the familiar σ_{CH_2} sp_2 hybrid pointing away from the CH_2 fragment. The ground state of linear diazomethane dissociates into a nitrogen molecule in its $^1\Sigma_g^+$ ground state plus methylene in its lowest A_1 singlet. The scission is very endothermic (3 eV) but it is interesting to note that the reverse process should be facile since its (calculated) activation energy is only 12 kcal/mol (Figure 7). The low-lying excited states of diazomethane—$^{1,3}n_0\pi^*$ and $^3n_0n^*$—all correlate with high-lying charge-transfer, or excited states of the pair of fragments. On the contrary the $n_0\sigma^*$ triplet (again the dissociative state) is strongly stabilized and correlates with the triplet ground state of the products, that is, N_2 ($^1\Sigma_g^+$) + CH_2 ($^3B_1$). The various crossings which result from these conflicting behaviors all involve states of different symmetries and are allowed.

Photodissociation originating at the singlet and triplet $n_0\pi^*$ states of diazomethane would demand an activation energy of 2.5 eV, at the n_0n^* triplet 1.5 eV. These energies appear much too large for these states to acquire them in a time compatible with their lifetimes. On the other hand, predissociation occurs in the two singlet states but its low efficiency is difficult to assess.

The bending of diazomethane perturbs this description in two ways (Figure 8). First the relative energies of the states are strongly modified. As we have already mentioned the stabilization of n^* upon bending and the more subdued destabilization of n_0 result in the lowering of the n_0n^* triplet and the concomitant destabilization of the ground state. Both states become quasi-degenerate ($^{1,3}D_{\sigma\sigma}$) for large NNC angles (110°). The second factor is the collapse of the overall symmetry from C_{2v} to C_s. Crossings which were allowed in the linear scission become forbidden. Prominent among them is that which involves the n_0n^* and $n_0\sigma^*$ triplets (point G in Figure 7). As a consequence there is a smooth pathway which is readily available for bent $^3D_{\sigma\sigma}$ diazomethane to dissociate into N_2 ($^1\Sigma_g^+$) + CH_2 ($^3B_1$). The calculated activation energy for this trajectory is still of the order of 1 eV but a molecule originally excited in the $n_0\pi^*$ state would be endowed with such an energy. On the other hand, the $^1D_{\sigma\sigma}$ state correlates with the $^1A_1$ state of methylene (and N_2 ($^1\Sigma_g^+$)). This correlation, however, presents two additional features. The first is a po-
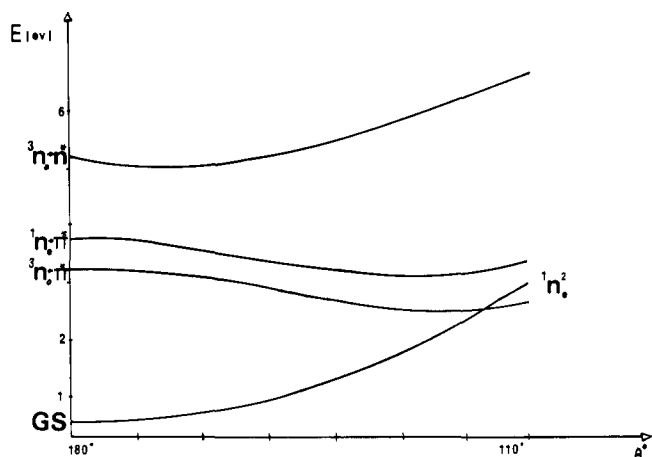
Figure 9. Calculated potential energy curves in the in-plane bending of linear diazomethane **1** to the intermediate bent form **4** ($\theta = 110°$).
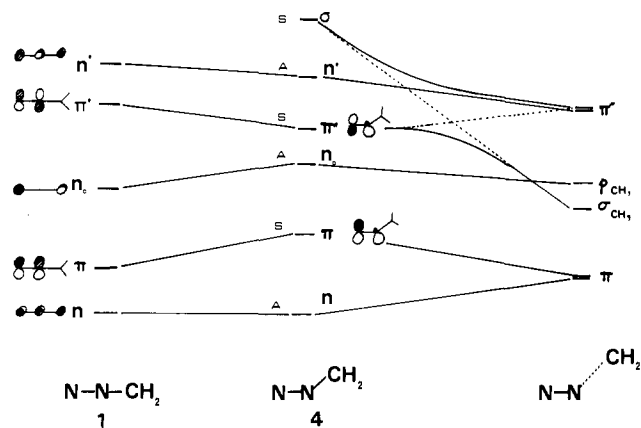

Figure 10. MO correlation diagram of the formation of nitrogen and carbene from linear diazomethane **1** by first in-plane bending and then elongation of the CN bond. The symmetry symbol refers to the symmetry plane conserved along the whole process.

tential maximum (activation energy of 1.5 eV) which results from an avoided crossing between the $^1D_{\sigma\sigma}$ PEC (which would correlate with the second $^1A_1'$ singlet state of methylene) and the zwitterionic Z_1 state (or, in other words, the n_0n^* singlet of linear diazomethane) which would like to end up as the lowest methylene $^1B_1$ state. (In fact the situation is more complex since it involves three states of the same symmetry, namely, those which correlate with N_2 ($^1\Sigma_g^+$) and methylene ($^1A_1$, $^1A_1'$, and $^1B_1$, respectively).) The second is that, here again, the lowest A_1 singlet drops below the lowest B_1 triplet (but now the energy difference is only 0.25 eV). There is therefore a continuous modification of the relative energy of these two states (for large values of the dissociation coordinate): in diazirine itself $^1A_1$ drops as much as 1 eV below $^3B_1$; in bent diazomethane this effect is smaller (0.25 eV) and entirely disappears for linear diazomethane.

Paths e and f

Let us investigate finally the in-plane bending of linear diazomethane. Figure 9 represents the behavior of the three lowest states as a function of the NNC angle. The ground state is continuously destabilized with increasing bending while the pair of singlet and triplet $n_0\pi^*$ states is slowly stabilized. The reasons for these contrasting tendencies are to be found in the molecular orbitals. The π and π^* MOs of diazomethane are destabilized and stabilized, respectively, because of the rehybridization (from a pure p to sp^2 lobe) which takes place at the central N atom, thus decreasing the bonding (in π) or antibonding (in π^*) characters. On the other hand, the in-plane nonbonding n_0 MO is also destabilized since the 1–3 antibonding nature increases.

This in-plane motion has been arbitrarily stopped at a (realistic) value of 110° for the NNC angle. At this point we started to elongate the N(central)–C bond. Figure 10 displays the corresponding MO correlation diagram in which the central feature is a new symmetry-avoided crossing involving the π^* and the N(central)–C antibonding σ^* MOs. The first would intend to correlate with the corresponding π^* orbital of the nitrogen molecule whereas the second is efficiently stabilized by the elongation and would naturally end up as the σ_{CH_2} MO of methylene (dotted lines in Figure 10). This avoided crossing is taken into account at the SCF stage of the calculation and, as a result, π^* and σ^* correlate finally with σ_{CH_2} and $\pi^*_{N_2}$, respectively (full lines in Figure 10).

The calculated PECs for the three lowest states of the system are represented in Figure 11. The singlet and triplet $n_0\pi^*$ states correlate with the N_2 ($^1\Sigma_g^+$) + CH_2 ($^{1,3}B_1$) states of the fragments. On the other hand, the "ground state" $^1n_0^2$ PEC exhibits a maximum which is the memory of an avoided
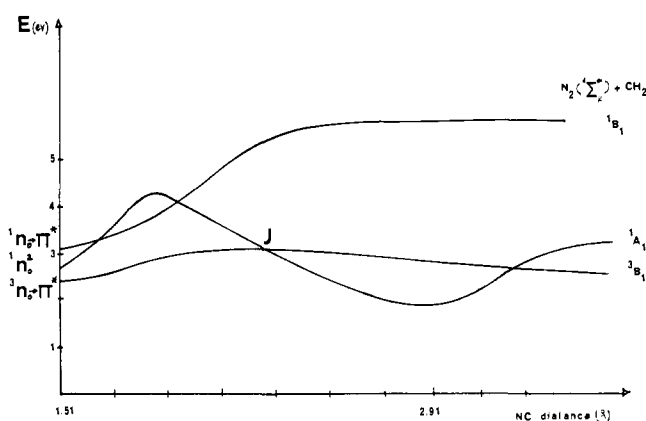

Figure 11. Calculated potential energy curves in the CN rupture of the bent form **4** of diazomethane.

crossing involving (a) the ground state of diazomethane which intends to give the N_2 ($^1\Sigma_g^+$) + CH_2 ($^1A_1'$) states of the products (in which the methylene P_{CH_2} orbital is doubly occupied) and (b) the doubly excited $(n_0\sigma^*)^2$ state of bent diazomethane which dissociates readily to give the N_2 ($^1\Sigma_g^+$) + CH_2 ($^1A_1$) lowest singlet state of the products (now the methylene σ_{CH_2} is doubly occupied).

Conclusion

It has been shown experimentally that excited diazirine can isomerize into diazomethane or break to give methylene and a nitrogen molecule. Two different reaction paths have been postulated. In the first an excited diazirine forms directly excited diazomethane[6e] which then (1) loses its excitation energy via radiationless processes and thus gives ground-state diazomethane or (2) breaks into the familiar fragments (CH_2 and N_2). In the second, the primary process is the breaking of excited diazirine into, again, CH_2 and N_2. In a subsequent step these species recombine and ground-state diazomethane is formed.[6a]

The theoretical PECs we have discussed suggest that these sequences are both realistic.

Let us start with diazirine in its singlet $n_-\pi^*$ state. We have already emphasized in our discussion of Figure 4 the importance of point C where the excited system may jump from the $^1n_-\pi^*$ surface to the dissociative state (which starts as the n_-W^* triplet and would naturally correlate with $^3D_{\sigma\sigma}$ but for its avoided crossing with the $\pi\pi^*$ triplet).

If the excited system does not intersystem cross and remains on the $^1n_-\pi^*$ curve no dissociation will occur (Figures 6–8 all show that, whatever the bending angle, the breaking is ener-

getically very difficult). The $n_0\pi^*$ singlet state of diazomethane will then be populated and may decay to the ground state. A second alternative is intersystem crossing at point B (Figure 4). The switch of the excited molecule from the singlet to the n_0n^* triplet drives the molecule to the $^3D_{\sigma\sigma}$ diradical which, in turn, may dissociate (vide infra).

If intersystem crossing does occur at C the excited species ends up at the bottom of the $^3D_{\sigma\sigma}$ potential well. It is then apparent (Figure 8) that the breaking of the second NC bond in this triplet intermediate can occur in two ways. The first possibility is that the system remains on the triplet PEC. Complete separation of N_2 ($^1\Sigma_g^+$) and CH_2 ($^3B_1$) develops (activation energy ~ 1 eV). However a second possibility cannot be overlooked, that is, intersystem crossing at H (Figure 8) will populate the well in the singlet $D_{\sigma\sigma}$ potential energy curve. In this second case the breaking is not complete. A complex is obtained in which N_2 ($^1\Sigma_g^+$) and singlet methylene ($^1A_1$) are loosely held together at a distance of 3 Å. For $r_{CN} \sim 3$ Å and varying bending angles the potential energy surface is rather flat. The species will explore it without any difficulty and will eventually reach regions where it has a quasi-linear geometry. Figure 7 shows that, in this case, a small activation (12 kcal/mol) is required for the fragments to recombine into linear diazomethane.

Let us now consider linear diazomethane. It is clearly apparent that the $^{1,3}n_0\pi^*$ excited states are not endowed with sufficient energy to populate directly diazirine excited states. Direct breaking of the N–C linkage in this linear geometry is also very endoenergetic (Figure 7). To achieve such a rupture, it is first necessary to bend the molecule.

The first bending distortion conserves the bisecting plane of the CH_2 end as the unique plane of symmetry (Figure 4). The molecule in its $^1n_0\pi^*$ state may intersystem cross at B (Figure 4), reach the $n_0\sigma^*$ triplet curve, and end up as the $D_{\sigma\sigma}$ triplet diradical which, as explained above, dissociates.

A second alternative exists in which the bending occurs in the plane of the molecule, in other words, the plane of the CH_2 group is now the symmetry element conserved throughout the distortion. Figure 9 shows that the pair of $^{1,3}n_0\pi^*$ states remains unaffected (at least for realistic bending angles which prevent any strong interaction between the two ends of the molecule). The bent molecule may then dissociate. It is obvious in Figure 11 than the singlet $n_0\pi^*$ state, which correlates with a high-lying excited state of the products (N_2 ($^1\Sigma_g^+$) + CH_2 ($^1B_1$)), cannot be the reactive state. On the contrary its triplet partner readily breaks (activation energy 13 kcal/mol). There again it may remain on the triplet surface and give two independent species (a nitrogen molecule and a triplet methylene) or switch (point J in Figure 11) to the neighboring singlet ("$^1n_0^2$") surface to form a loose complex between a ground-state nitrogen molecule and methylene in its A_1 singlet state. These results in turn suggest that the spin multiplicity of the products and the stability of the singlet complex might be strongly medium dependent since solvation (and even substitution) is likely to stabilize one form (independent triplet methylene) or the other (loose singlet complex). Experiments should be imagined to check the existence of this "exciplex" and, if its formation is confirmed, to understand how the in plane or out of plane $D_{\sigma\sigma}$ triplet diradicals decide which way to go.

References and Notes

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(2) This laboratory is associated with CNRS (ERA no. 549).
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