An ab Initio Study of the Photochemical Decomposition of 3,3-Dimethyldiazirine

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Photochemical decomposition of 3,3-dimethyldiazirine (DMD) has been computationally investigated by using high-level ab initio calculations in conjunction with the 6-31G* and cc-pvdz basis sets. The geometries of minima and transition states, as well as conical intersection points in the seam of crossing of two surfaces, have been optimized with the complete active space self-consistent field (CAS-SCF) method, and their energies, recalculated with second-order multireference perturbation (CAS/MP2) theory. The reaction path starting at the excited n-π* state of DMD is predicted to occur via a nonadiabatic mechanism, giving carbene and molecular dinitrogen (both in their singlet ground states) as the main products; the computed barrier height (1.0 kcal mol^{-1}) agrees well with the experimental estimate of the activation energy in the singlet excited state (0.0−1.5 kcal mol^{-1}). Ground state of dimethylcarbene is the only species where a 1,2-hydrogen shift takes place, being the only source of propene. The calculated potential energy barrier height for dimethylcarbene to propene isomerization (2.6 kcal mol^{-1}) agrees well with the observed activation energy (2.56 kcal mol^{-1}). No evidence for rearrangement in the first singlet excited state of DMD has been found; such a process would lead to a higher activation energy than the observed one. Consequently, 1,2-hydrogen migration concurrent with N_2 extrusion in the excited state has been ruled out.

Introduction

The photochemically relevant orbitals of 3,3-dimethyldiazirine (DMD) are sketched in Figure 1. It is assumed that the photochemistry of diazirines involves the first singlet excited state,[1−9] which results from the electronic n → π* transition. This state is of diradical nature, having one unpaired electron in a σ-like orbital, and the other one occupies a π-like orbital, so that it is denoted as a $D_{\sigma\pi}$ state. The second excited state is of diradical nature as well and corresponds to an electronic n → σ* promotion, being denoted as a $D_{\sigma\sigma}$ state.

There are, in principle, several possible decay pathways from the excited n-π* state of a diazirine (Scheme 1): (1) fluorescence, (2) intersystem crossing with the production of triplet dimethylcarbene, (3) formation of a diradical excited state followed by internal conversion and production of singlet carbene with N_2 extrusion, (4) adiabatic and subsequent internal conversion to diazoalkane isomer, and (5) α-hydrogen migration and alkene formation concurrent with nitrogen extrusion.

Photochemical decomposition of 3,3-dimethyldiazirine (DMD) in pentane has been studied by Platz and coworkers[5−7] using spectroscopic and laser flash photolysis (LFP) techniques. Upon decomposition the excited state of dimethyldiazirine yields a 40/60 mixture of dimethylcarbene and propylene, respectively.[4,6] The results of LFP studies on 3,3-dimethyldiazirine indicate the formation of short-lived singlet carbenes which can be trapped with pyridine. Under these experimental conditions, the presence of diazoalkane isomers that are observed during the photolysis of other diazirine derivatives such as isopropylchlorodiazirine[10a] or adamantyldiazirine[10b] could not be detected by LFP. It must be noted that only a weak infrared band at 2050 cm^{-1} upon very low temperature photolysis of DMD in methylpentane is detected. This absorption frequency is typically assigned to diazo compounds. However, diazo formation is not important at room temperature because LFP of DMD fails to produce transient absorption in the 250 nm region where dialkyl diazo compounds absorb significantly. Platz also reports a temperature dependence of the fluorescence intensity of 3,3-dimethyldiazirine.[6] The data show a decrease in intensity as the temperature is increased. This loss in fluorescence intensity is associated with an activation energy barrier that ranges from 0.02 to 1.50 kcal mol^{-1}. A similar study on the dependence of the fluorescence intensity by isotopic substitution was carried out as well. According to the experimental data, 3,3-dimethyldiazirine-d_6 shows a fluorescence intensity about 50% greater than that of 3,3-dimethyldiazirine-h_6. In principle, it seems unlikely that isotopic substitution that is remote from the diazirine chromophore will increase the rate

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(1) Seburg R. A., McMahon R. J. *J. Am. Chem. Soc.* **1992**, *114*, 7183.

(2) Ammann, J. F., Subramanian, R., Sheridan, R. S. *J. Am. Chem. Soc.* **1992**, *114*, 7592.

(3) Chen, N.; Jones, M., Jr.; Platz, M. S. *J. Am. Chem. Soc.* **1991**, *113*, 4981.

(4) Modarelli, D. A.; Platz, M. S. *J. Am. Chem. Soc.* **1993**, *115*, 470.

(5) Modarelli, D. A.; Platz, M. S. *J. Am. Chem. Soc.* **1991**, *113*, 8985.

(6) Modarelli, D. A.; Morgan, S.; Platz, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 7034.

(7) Ford, F.; Yuzawa, T.; Platz, M. S.; Matzinger, S.; Fülscher, M. *J. Am. Chem. Soc.* **1998**, *120*, 4430.

(8) O'Gara, J. E.; Dailey, W. P. *J. Am. Chem. Soc.* **1992**, *114*, 3581.

(9) Michl, J.; Bonacic-Koutecky, V. *Electronic Aspects of Organic Photochemistry*; John Wiley & Sons: New York, 1990.

(10) (a) Liu, M. T. H.; Bonneau, R. *J. Am. Chem. Soc.* **1996**, *118*, 7229. (b) Buterbaugh, J. S.; Toscano, J. P.; Weaver, W. L.; Gord, J. R.; Hadad, C. M.; Gustafson, T. L.; Platz, M. S. *J. Am. Chem. Soc.* **1997**, *119*, 3580.

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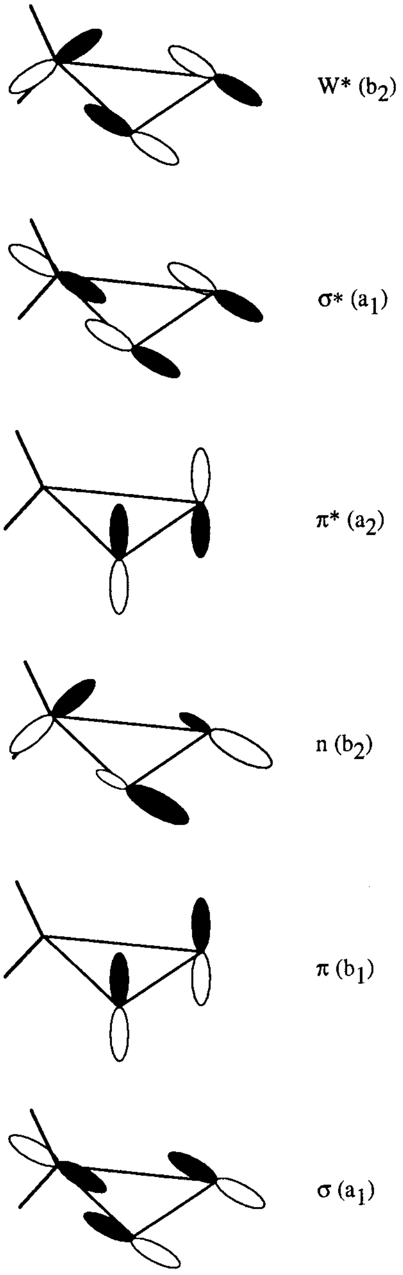

Figure 1. Photochemically important orbitals in 3,3-dimethyldiazirine, from top to bottom: Walsh-type antibonding, σ^*-(C−N) antibonding, π^*(N−N) antibonding, σ-type nonbonding, π(N−N) bonding, σ(C−N) bonding orbitals.

constant of fluorescence or decrease the rate constant of other nonradiative processes. A proof for this hypothesis[6] is based on the phosphorescence lifetimes of the triplet n-π^* states of acetophenone and benzophenone.[11] Isotopic substitution of these compounds does not change their phosphorescence lifetimes. However, the same is not true for acetone-d_6, which certainly is more similar to DMD and which shows a phosphorescence time of life in the gas phase at 25 °C 50% greater than that of acetone-h_6.[11] Therefore, the interpretation of the fluorescence studies was that deuteration reduces the yield of chemical reaction of the excited state. This was taken as evidence for 1,2 hydrogen migration concurrent with nitrogen extrusion in the diazirine excited state. Moreover, the distributions of products formed on thermolysis and photolysis of alkyldiazirines are different (ref 4 and references therein). The mixture of products formed on photolysis is less regioselective than the mixture of products formed upon pyrolysis. These observations, in conjunction with the fluorescence studies, were interpreted according to a rearrangement of alkyldiazirines in the excited singlet state. Direct photochemical formation of alkene from an excited state of alkyldiazirine was first proposed by Frey in 1965.[12]

On the other hand, the role of triplet states in dimethyldiazirine photochemistry has been also investigated.[6] There is no evidence for intersystem crossing ($S_1 \rightarrow T_1$) in the excited state at room temperature. The yield of ylide, formed in the reaction of dimethylcarbene with pyridine, is not decreased upon LFP of DMD in the presence of 1.0 M isoprene,[13] at constant pyridine concentration. This observation was considered as an evidence that dimethylcarbene is not generated by decomposition of the excited triplet state of dimethyldiazirine. The involvement of triplet state in photochemistry of carbenes has been ruled out by other authors[1,2] and more recently by transient grating spectroscopy.[14]

Theoretical methods are the only techniques for determining the behavior of the various excited state potential energy surfaces. However, to our knowledge, works on the photochemical decomposition of diazirines are scarce. The only attempts to rationalize the photochemical decomposition mechanism of diazirines have been the SINDO1 study of Müller-Remmers and Jug,[15] the CIS/STO-3G computations of Devaquet et al.,[16] and more recently, the CASSCF/6-31G* calculations carried out by ourselves.[17] All of these investigations dealt with the smallest member in the diazirine compound family (CH_2N_2), where the only two possible reactions are (1) decomposition to give $^{1,3}CH_2 + N_2$, and (2) isomerization to diazomethane. Therefore, we have chosen 3,3-dimethyldiazirine as a model to study computationally the chemistry in the excited state of diazirine derivatives. Despite many experimental suggestions indicating this class of reaction takes place on the excited potential energy surface, we do not find evidence for such a mechanism in 3,3-dimethyldiazirine. The only reaction path that has been found on the n-π^* potential energy surface involves a nonradiative relaxation through a $D_{\sigma\pi}$ conical intersection, from which diazirine → diazo isomerization and dimethylcarbene formation take place, respectively. Thus, our calculations indicate that propene is formed via rearrangement of dimethylcarbene in its singlet ground state.

Computational Details

The CAS-SCF calculations have been performed with the MC-SCF program released in GAUSSIAN 94[18] using the 6-31G*[19] and cc-pvdz basis sets.[20] Due to the diversity of reactions involved in the global process, it is impossible at all to maintain the same active space along the whole reaction

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[11] Miller, J. C.; Borkman, R. F. *J. Chem. Phys.* **1972**, *56*, 3727.

[12] Frey, H. M.; Stevens, I. D. R. *J. Chem. Soc.* **1965**, 1700.

[13] Isoprene is a diffusion-controlled quencher of triplet excited states with triplet energies in excess of 60 kcal mol^{-1}. (a) Murov, S. L. *Handbook of Photochemistry*; Dekker: New York, 1973. (b) Kellog, R. E.; Simpson, W. T. *J. Am. Chem. Soc.* **1965**, *87*, 4320.

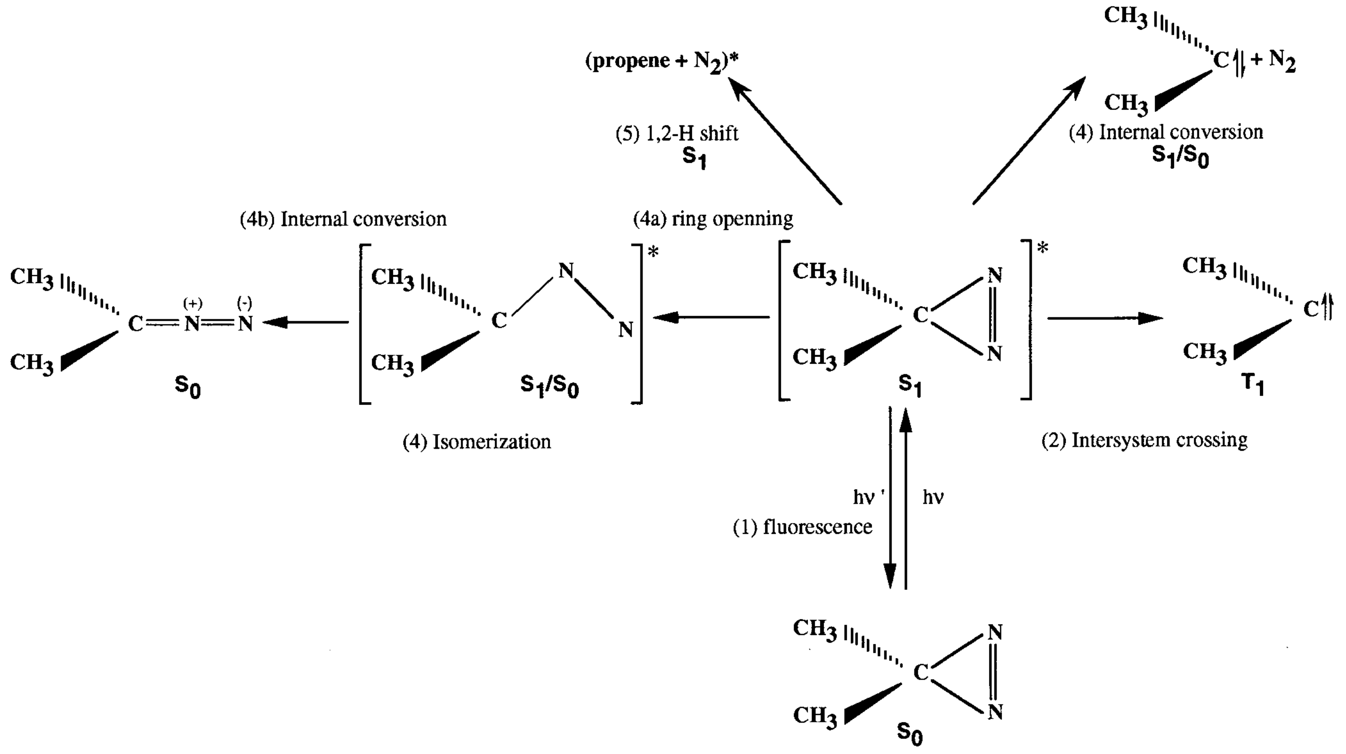
[14] Toscano, J. P.; Platz, M. S. *J. Am. Chem. Soc.* **1996**, *118*, 3527.

[15] Müller-Remmers, P. L.; Jug, K. *J. Am. Chem. Soc.* **1985**, *107*, 7275.

[16] Bigot, B.; Ponec, R.; Sevin, A.; Devaquet, A. *J. Am. Chem. Soc.* **1978**, *100*, 6575.

[17] Yamamoto, N.; Bernardi, F.; Bottoni, A.; Olivucci, M.; Robb, M. A.; Wilsey, S. *J. Am. Chem. Soc.* **1994**, *116*, 2064.

Scheme 1



coordinate. Thus, we shall describe the active space used in each reaction step.

The active space chosen to describe (1) diazirine → diazo rearrangement, and (2) carbene production from 3,3-dimethyldiazirine, is composed by six electrons distributed in six orbitals, and four orbitals from N_2 plus the p_σ and p_π orbitals of the $(CH_3)_2C$ moiety. These orbitals represent, in 3,3-dimethyldiazirine minimum, two σ(C−N), two σ^*(C−N), and the π(N−N) and π^*(N−N) bonds, respectively. Within this active space, the bonding between the $(CH_3)_2C$ and N_2 fragments in the ground and excited states can be described for all possible orientations of both fragments.

The active space for describing the 1,2-H migration comprises eight electrons in eight orbitals, i.e., the six orbitals used in the previous paragraph plus the $\sigma(C-H_\alpha)$ and $\sigma^*(C-H_\alpha)$ orbitals. Consequently, this active space must be flexible enough to describe the N_2 extrusion concurrent with α-H migration in both the ground and excited states.

Dimethylcarbene to propene isomerization has been studied with a four electron−four orbital active space. These orbitals represent, in dimethylcarbene minimum, the p_σ and p_π orbitals on the carbenoid center plus the $\sigma(C-H_\alpha)$ and $\sigma^*(C-H_\alpha)$ bonds, respectively.

To correct the energetics for dynamic electron correlation, we have used the multireference Møller−Plesset (CAS/MP2) algorithm[21] as implemented in the program package GAUSSIAN 94.

Every stationary point has been characterized by its harmonic frequencies computed analytically at the CAS-SCF level. For each transition state, an IRC (CAS-SCF) calculation[22] has been performed as well. Thus, the products and reagents connected by the respective transition states have been unambiguously localized.

Localization of the minima, transition states, conical intersection minima, and mapping of the intrinsic reaction coordinates have been performed in Cartesian coordinates; therefore, the results are independent of any specific choice of the internal variables.

For the optimization of the lowest energy points on the seam of crossing of two surfaces, we have used the algorithm[23] implemented in GAUSSIAN 94, (see ref 24 for more details). For all the computations of surfaces crossing, state-average orbitals[25] have been used; therefore, the energies of the surface crossings are quoted to 0.001 hartrees.

Results and Discussion

In this section we shall discuss the main features of the excited and ground-state singlet surfaces related to the photochemical decomposition of 3,3-dimethyldiazirine. The energetic data for all the critical points found on these surfaces are collected in Table 1. The optimized

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(18) Gaussian 94, Revision E.2, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, Gaussian, Inc.; Pittsburgh, PA, 1995.

(19) (a) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971** *54*, 724. (b) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972** *56*, 2257. (c) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973** *28*, 213.

(20) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.

(21) McDouall, J. J. W.; Peasley, K.; Robb, M. A. *Chem. Phys. Lett.* **1988**, *148*, 183.

(22) (a) Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys.* **1989**, *90*, 2154. (b) Gonzalez, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5523.

(23) Ragazos, I. N.; Robb, M. A.; Bernardi, F.; Olivucci, M. *Chem. Phys. Lett.* **1992**, *197*, 217.

(24) (a) Bernardi, F.; Olivucci, M.; Ragazos, I. N.; Robb, M. A. *J. Am. Chem. Soc.* **1992**, *114*, 2752. (b) Bernardi, F.; Olivucci, M.; Robb, M. A.; Tonachini, G. *J. Am. Chem. Soc.* **1992**, *114*, 5805. (c) Bernardi, F.; Olivucci, M.; Ragazos, I. N.; Robb, M. A. *J. Am. Chem. Soc.* **1992**, *114*, 8211. (d) Palmer, I.; Bernardi, F.; Olivucci, M.; Robb, M. A. *J. Org. Chem.* **1992**, *57*, 5081. (e) Palmer, I.; Ragazos, I. N.; Bernardi, F.; Olivucci, M.; Robb, M. A. *J. Am. Chem. Soc.* **1993**, *115*, 673. (f) Reguero, M.; Bernardi, F.; Jones, H.; Olivucci, M.; Robb, M. A. *J. Am. Chem. Soc.* **1993**, *115*, 2073. (g) Olivucci, M.; Ragazos, I. N.; Bernardi, F.; Robb, M. A. *J. Am. Chem. Soc.* **1993**, *115*, 5, 3710.

(25) (a) Werner, H.; Meyer, W. *J. Chem. Phys.* **1981**, *74*, 5794. (b) Hinze, J. *J. Chem. Phys.* **1973**, *59*, 6424. (c) Lengsfield, B. H. *J. Chem. Phys.* **1982**, *77*, 4073. (d) Diffenderfer, R. N.; Yarkony, D. R. *J. Phys. Chem.* **1982**, *86*, 5098.

Table 1. Ground and Excited State Structures and Energetics for the Potential Energy Surfaces of 3,3-Dimethyldiazirine and 2-Diazopropane

geometry	CAS[a]	CAS/MP2[b]	ΔE[c]	CAS[d]	CAS/MP2[e]	ΔE[f]
ground state DMD (Figure 1a)	−226.021 66	−226.593 68	0.0	−226.040 15	−226.632 01	0.0
ground state DMD[g]	−226.037 92	−226.583 58	0.0[g]	−226.056 20	−226.620 07	0.0[g]
1n-π^* vertical excitation DMD	−225.846 71	−226.450 89	89.6	−225.865 29	−226.489 25	89.6
DMD S_1 minimum (Figure 1b)	−225.857 33	−226.449 79	90.3	−225.876 00	−226.488 24	90.2
DMD S_1 minimum[g]	−225.873 89	−226.439 81	90.2[g]	−225.892 36	−226.475 88	90.5[g]
DMD/DAZ S_1 transition state (Figure 1c)	−225.853 52	−226.446 39	92.4	−225.872 54	−226.486 63	91.2
ground state DAZ (Figure 1d)	−226.034 46	−226.635 44	−26.2	−226.054 30	−226.676 20	−27.7
1n-π^* vertical excitation DAZ	−225.912 52	−226.507 60	54.0	−225.973 89	−226.545 02	54.6
$D_{\sigma\pi}$ S_0/S_1 conical intersection (Figure 1e)	−225.953 91	−226.553 66	25.1	−225.972 52	−226.593 44	24.2
N_2 extrusion S_0 transition state (Figure 1f)	−225.972 17	−226.538 46	34.7	−225.993 18	−226.582 57	31.0
1,2-H migration S_1 transition state[g] (Figure 1g)	−225.782 66	−226.351 64	145.5[g]	−225.805 96	−226.393 90	141.9[g]
1,2-H migration S_0 transition state[g] (Figure 1h)	−225.883 07	−226.427 35	98.0[g]	−225.907 13	−226.466 53	96.3[g]
ground state DMC[h] (Figure 7a)	−117.006 20	−117.368 99	0.0[h]	−117.018 89	−117.391 72	0.0[h]
DMC → propene transition state[h] (Figure 7b)	−116.977 84	−117.346 13	14.3[h]	−116.994 47	−117.387 57	2.6[h]
ground state propene[h] (Figure 7c)	−117.117 74	−117.483 63	−71.9[h]	−117.127 78	−117.513 63	−76.5[h]

[a] CASSCF/6-31G* energy in hartrees. [b] CASSCF/MP2/6-31G* energy in hartrees. [c] CASSCF/MP2/6-31G* relative energy in kcal mol^{-1}. [d] CASSCF/cc-pvdz energy in hartrees. [e] CASSCF/MP2/cc-pvdz energy in hartrees. [f] CASSCF/MP2/cc-pvdz relative energy in kcal mol^{-1}. [g] Energetics corresponding to an eight electron−eight orbital active space. [h] Energetics corresponding to a four electron−four orbital active space.

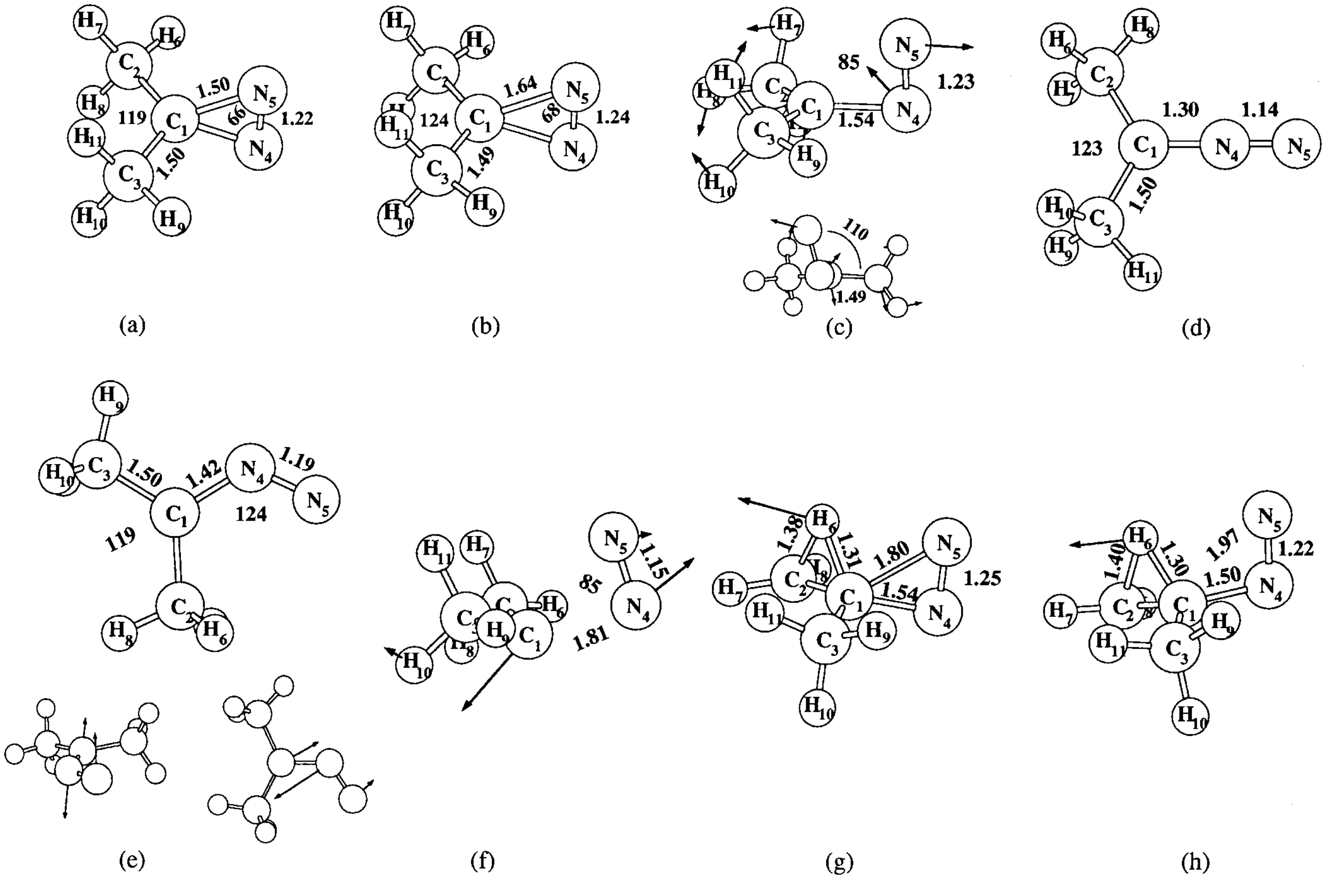

Figure 2. Optimized structures, at the CASSCF/cc-pvdz level, on S_0 and S_1 surfaces: (a) ground state 3,3-dimethyldiazirine; (b) S_1 minimum (^{1}n-π^*) of DMD; (c) two views of the S_1 transition state (^{1}n-π^*) for diazirine−diazo isomerization, the arrows on the structures correspond to the direction of the transition vector; (d) ground state 2-diazopropane; (e) S_0/S_1 (^{1}n-π^*) $D_{\sigma\pi}$ conical intersection, the two drawings at the bottom of the figure correspond to the directions of the nonadiabatic coupling (left) and gradient difference (right) vectors; (f) S_0 transition state for dimethylcarbene formation, the arrows on the structure correspond to the transition vector; (g) S_1 transition state (^{1}n-π^*) for 1,2-hydrogen migration, the transition vector is shown as in f; (h) S_0 transition state for 1,2-hydrogen migration, the transition vector is shown as in f.

structures are displayed in Figure 2. This section is structured in four subsections: (i) First, we address the question of the isomerization of 3,3-dimethyldiazirine (DMD) to 2-diazopropane (DAZ). (ii) In the second subsection we deal with the carbene formation from both the excited and ground states of 3,3-dimethyldiazirine. (iii) The third subsection is devoted to 1,2-hydrogen migration in the excited state of DMD. (iv) The dimethylcarbene to propene rearrangement is studied.

(i) Isomerization of 3,3-Dimethyldiazirine to 2-Diazopropane. The calculated n-π^* vertical excitation energy (3.88 eV), at the CAS/MP2/cc-pvdz level, compares

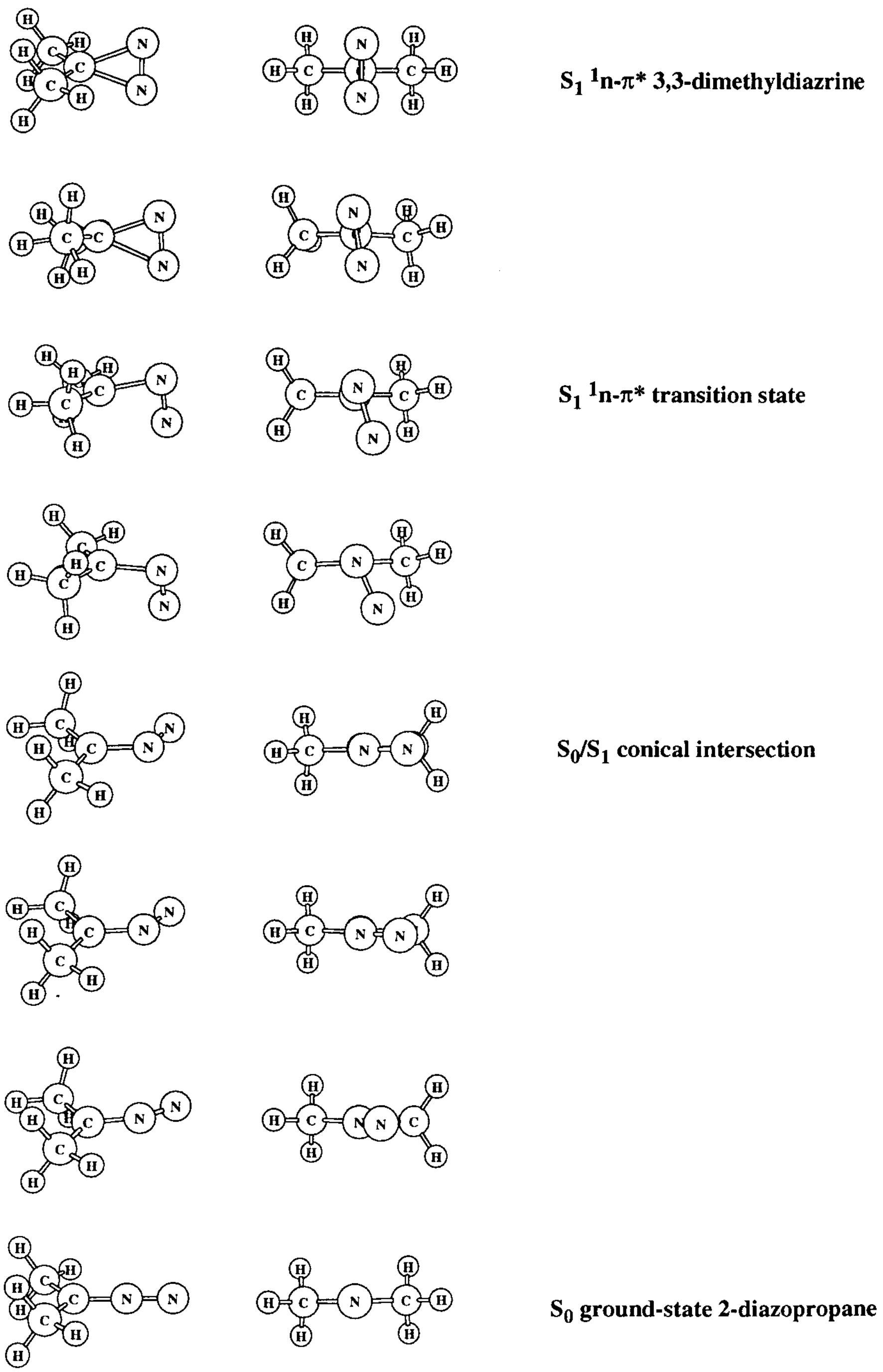

Figure 3. IRC (CAS/6-31G*) from the S_1 diazirine−diazomethane (^{1}n-π*) transition state to the S_0/S_1 (^{1}n-π*) $D_{\sigma\pi}$ conical intersection and continued on the ground state.

well with the experimental value (3.86 eV) of diazirine.[26] The absorption spectrum of DMD in pentane[6] shows several bands in the region between 270 and 364 nm (4.44−3.41 eV). The optimized structures for ground-state diazirine and 2-diazopropane are given in Figure 2a,b; both minima belong to C_{2v} symmetry. The calculated geometries for the ground state of DMD and DAZ agree well with the B3-LYP/cc-pvdz values. For example, the N−N distances in DMD and DAZ are 1.22 and 1.14 Å, respectively, which compares with the DFT values of 1.23 and 1.15 Å. The S_1 minimum of 3,3-dimethyldiazirine (Figure 2c) lies in a very shallow minimum; there is a transition state (TS1, Figure 2d) only 1.0 kcal mol^{-1} above the S_1 minimum. As it was pointed out in the Introduction, an activation energy barrier was experimentally found on the excited singlet surface ranging from 0.02 to 1.50 kcal mol^{-1}. The normal coordinate corresponding to the imaginary frequency (355 i cm^{-1}) involves torsion of the N_2 fragment. An IRC from this transition state (Figure 3) terminates at a S_0/S_1 conical intersection (the lowest energy point on this conical intersection of C_s symmetry is shown in Figure 2e). Restarting the IRC on the ground state leads to 2-diazopropane, as shown in Figure 3.

A plot of the surface energies in the immediate vicinity of the crossing point has the form of a double cone[24] (Scheme 2). The directions of the nonadiabatic coupling

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(26) Roberston, L. C.; Merrit, J. A. *J. Mol. Spectrosc.* **1965**, *17*, 48.

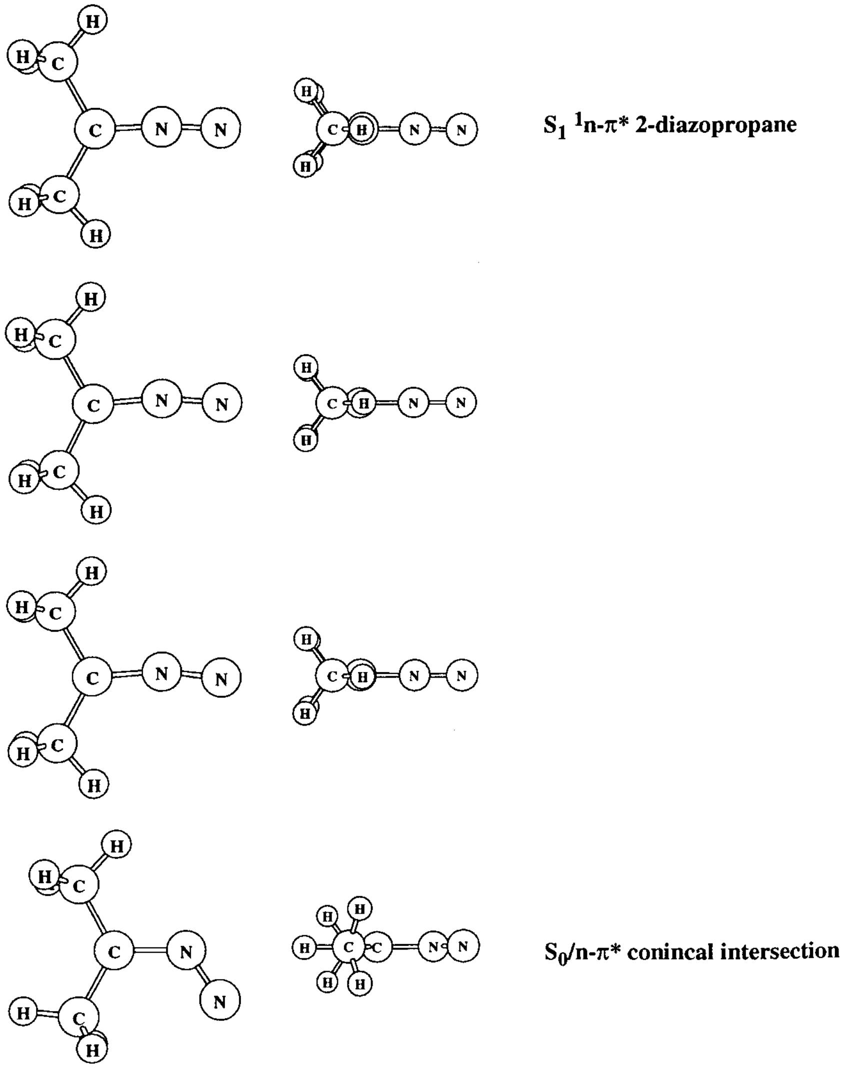
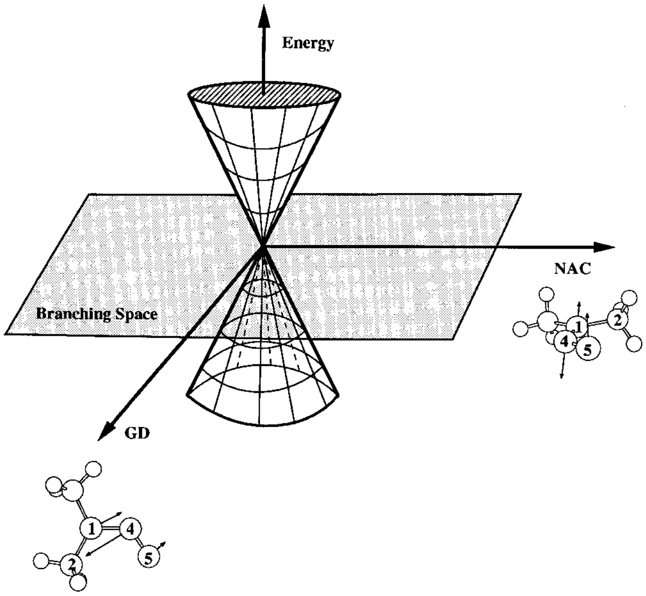


Figure 4. IRC (CAS/6-31G*) from the (^{1}n-π^*) vertical excitation region of 2-diazopropane leading to S_0/S_1 (^{1}n-π^*) $D_{\sigma\pi}$ conical intersection.

Scheme 2



(NAC) and gradient difference (GD) vectors, which are also plotted in Figure 2e, define a plane in the space of nuclear motions. Motion in this plane (the branching space) lifts the degeneracy, while the energy has been minimized in the remaining (n − 2)-dimensional space. These two special directions correspond to bending in plane (GD) and bending out-of-plane (NAC) of the N_2 moiety, with respect to the plane defined by the $C_2-C_1-N_4-N_5$ atoms. The GD is totally symmetric, while NAC is nontotally symmetric. The S_0/S_1 conical intersection corresponds to the global minimum of the 3,3-dimethyldiazirine/2-diazopropane n-π^* excited-state surface. However, while the energy is minimized, the structure shown in Figure 2e is a conical intersection rather than a true minimum as the energy gradient does not go to zero. Furthermore, an IRC (Figure 4) beginning at the 2-diazopropane S_1 (n-π^*) Franck−Condon region terminates at the same conical intersection. Thus, essentially, photoexcitation of diazoalkanes and diazirines follow the same decay pattern.

Nonradiative relaxation in both diazirine and diazo compounds involves the path through a conical intersection; this fact has very important dynamic implications. For the passage from one potential energy surface to another, the nuclear and electronic motion must be coupled, the magnitude of the nonadiabatic coupling controlling this process. After a surface hop, the trajectories of the molecules will follow the direction of the GD vector only if they pass exactly through the tip of the cone.[27] However, most of the trajectories will miss the cone tip; in this case, the preferential direction to follow on the ground state surface will be the NAC vector. Because trajectories that miss the cone tip and go near it only in the two-dimensional branching space have some probability of staying on the upper surface and continuing to be guided by its curvature, there is some probability of performing a jump onto the lower surface and being afterward guided by it. However, in this latter case, an amount of energy equal to the height of the jump is converted into a component of motion in a direction given by the NAC vector,[27] which is the direction of the maximum mixing of the adiabatic wave functions. In $D_{\sigma\pi}$-like conical intersections of diazirine derivatives, the direction of the NAC vector points to diazirine minimum. Therefore, a diazo → diazirine isomerization mechanism must exist, being more efficient than the reverse one. For example, photolysis of diazoethane yields appreciable amounts of 3-methyldiazirine, whereas photolysis of 3-methyldiazirine gives only traces of diazoethane.[2]

(ii) Production of Singlet Dimethylcarbene with N_2 Extrusion. In 3*H*-diazirine[17] (CH_2N_2), a route for direct photochemical production of singlet carbene was proposed involving the path through the lowest energy point in the seam of crossing of the ground and excited n-σ^* surfaces (Figure 5a, $D_{\sigma\sigma}$ conical intersection). However, it was not possible to find the reaction path connecting this conical intersection with the S_1 minimum of 3*H*-diazirine. The only reaction path found on the singlet surface was the one analogous to that described in the above subsection, i.e., $S_1 \rightarrow TS1 \rightarrow D_{\sigma\pi}$ conical intersection → diazomethane (Figure 3). Consequently, it was postulated that a bifurcation occurred in the reaction path connecting diazirine S_1 minimum with the $D_{\sigma\pi}$ diazomethane conical intersection (structure shown in Figure 5b), which would lead to the $D_{\sigma\sigma}$ conical intersection via vibrational leakage.

The behavior of the potential energy surfaces of 3,3-dimethyldiazirine is somewhat different. We are not able to find a $D_{\sigma\sigma}$-like conical intersection in DMD. As a probe of the reliability of our calculations, we have searched for this class of conical intersection in another related system, 3-methyldiazirine. In this molecule such a critical point exists, and its structure is plotted in Figure 5c. Therefore, we are confident with our results with 3,3-dimethyldiazirine. Hence, a most economical interpretation of the data is in accordance with carbene production in the ground state. As it was pointed out in the above subsection, there must be a reaction path for radiationless decay from the S_1 excited state to the region of DMD minimum, through the $D_{\sigma\pi}$ S_0/S_1 conical intersection. 3,3-Dimethyldiazirine is generated in this reaction path as a highly vibrationally excited species. Consequently, it has the necessary internal energy to surmount the potential energy barrier which leads to dimethylcarbene + N_2 formation. In fact, a transition state on the ground-state potential energy surface, 31.0 kcal mol^{-1} above S_0 DMD minimum, has been localized (Figure 2f). An IRC starting at this critical point leads to dimethylcarbene production via N_2 extrusion in a stepwise mechanism, as it was proposed by Liu and Toriyama.[28] When the opposite direction of the transition vector is followed, the minimum of 3,3-dimethyldiazirine is reached (Figure 6).

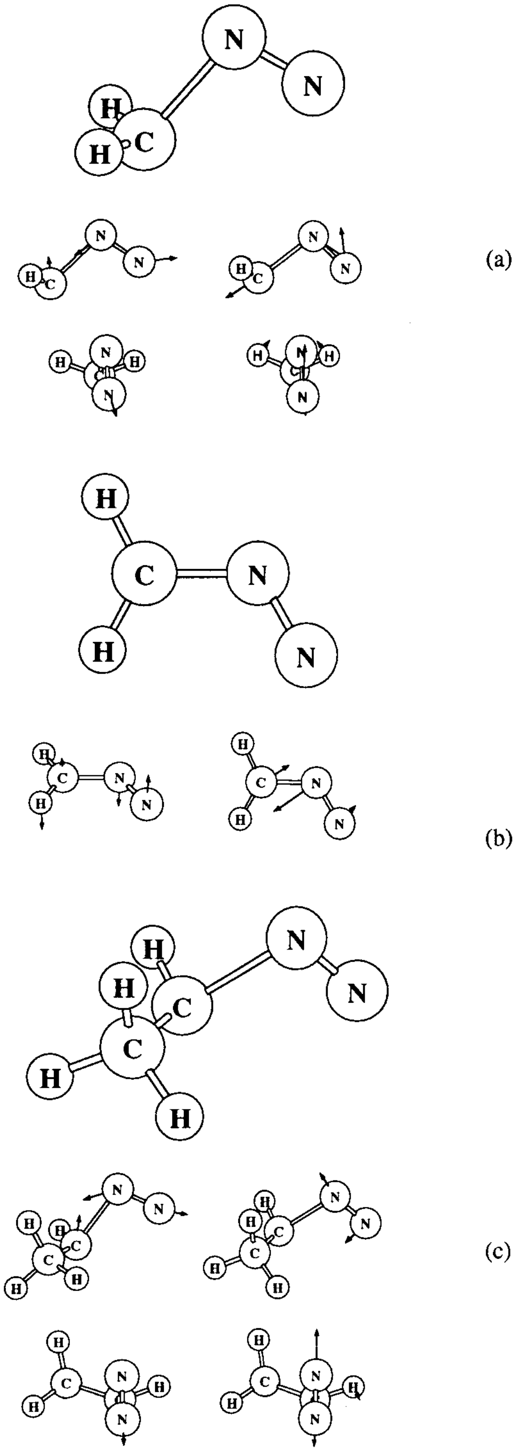


Figure 5. Optimized structures at the CAS/6-31G* level: (a) S_0/S_1 $D_{\sigma\sigma}$ conical intersection of 3*H*-diazirine, the structures at the bottom of the figure correspond to the nonadiabatic coupling (left) and gradient difference (right) vectors; (b) S_0/S_1 $D_{\sigma\pi}$ conical intersection of 3*H*-diazirine, nonadiabatic and gradient difference vectors are shown as in a; S_0/S_1 $D_{\sigma\sigma}$ conical intersection in 3-methyldiazirine, nonadiabatic and gradient difference vectors are shown as in a.

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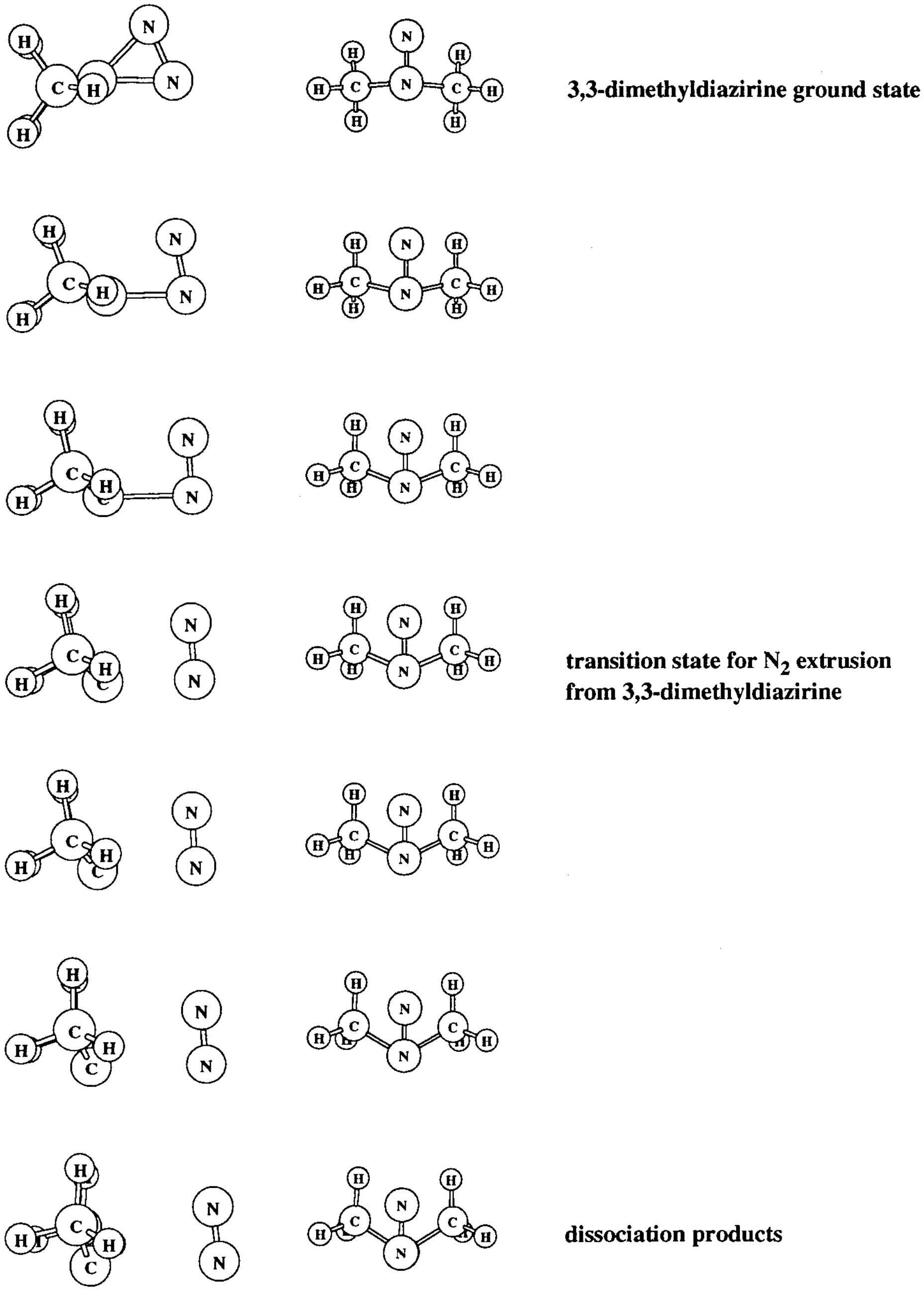
(27) Klessinger, M.; Michl, J.; *Excited States and Photochemistry of Organic Molecules*; WCH Publishers: New York, 1995.

(28) Liu, M. T. H.; Toriyama, K. *Can. J. Chem.* **1972**, *50*, 3009.



3,3-dimethyldiazirine ground state

transition state for N_2 extrusion from 3,3-dimethyldiazirine

dissociation products

Figure 6. IRC (CAS/6-31G*) from the S_0 transition state which corresponds to dimethylcarbene formation.

The experimental activation energy[29] for the thermal decomposition of DMD in the gas phase is 33.17 kcal mol^{-1}; the experimentally observed reaction products are only propene and N_2.

(iii) 1,2-Hydrogen Migration. To explain propene formation in the photolysis of DMD, it has been suggested that 1,2-hydrogen shift concurrent with nitrogen extrusion takes place on the excited-state surface.[6] Therefore, we have undertaken the study of this possible reaction in the excited state of 3,3-dimethyldiazirine. The only transition state found on the excited surface, corresponding to hydrogen migration, is plotted in Figure 2g. This structure is almost 51.7 kcal mol^{-1} above the S_1 minimum of DMD, at the CAS/MP2/cc-pvdz level. All attempts to find a transition state for hydrogen migration in the excited state always converged on the structure shown in Figure 2g. Because the energy barrier height is quite large, the reaction path through this transition state cannot be a competitive mechanism in the photolysis of DMD. An analogous conclusion is recently reached by Platz and co-workers[30] when they studied the photochemical decomposition of a diazoester derivative using the LFP technique. They expected a rearrangement (a Wolff reaction concurrent with N_2 extrusion) in the excited state of the diazo compound, but it is found that such a process takes place from a spin-equilibrated carbene[31] which is generated in a previous step via N_2 extrusion. The same finding is obtained by Wang et al.[32] using time-resolved infrared spectroscopy.

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[29] Frey, H. M.; Stevens, I. D. R. *J. Chem. Soc.* **1962**, 3865.

[30] Wang, J.-L.; Likhotvorik, I.; Platz, M. S. *J. Am. Chem. Soc.* **1999**, *121*, 2883.

[31] Zhu, Z.; Bally, T.; Stracener L. L.; McMahon, R. J. *J. Am. Chem. Soc.* **1999**, *121*, 2863.

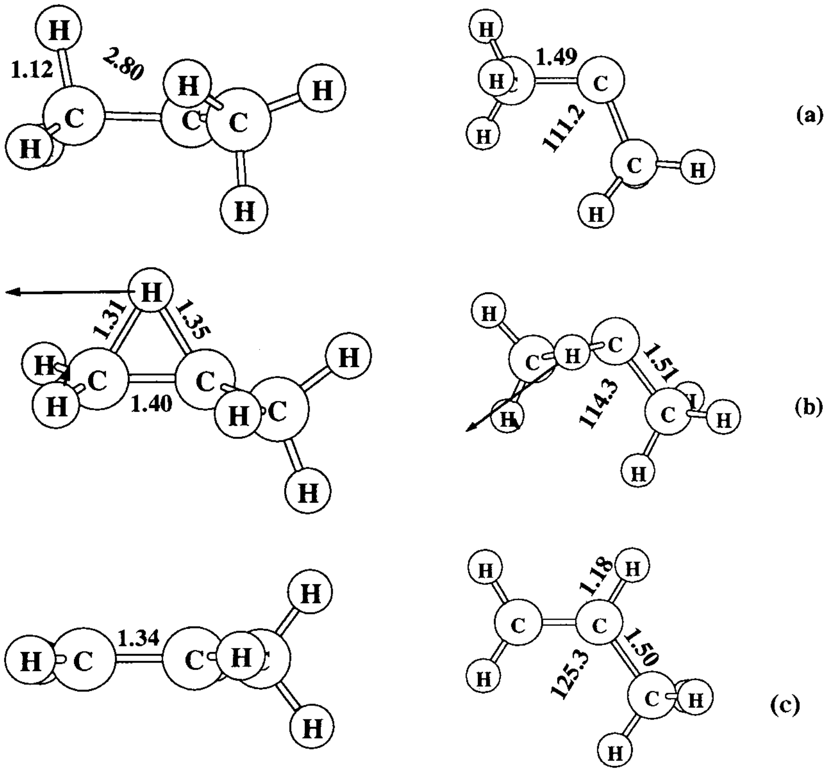

Figure 7. Two orthogonal views of the optimized structures, at the CASSCF/cc-pvdz level, on the S_0 surface: ground-state dimethylcarbene (DMC); (b) transition state for DMC → propene isomerization, the arrows correspond to the direction of the transition vector; (c) ground-state propene.

It is well established by experimentalists[6] and theoreticians[33,34] that the 1,2-H shift in the ground state of diazirine derivatives is not an important pathway. However, to complete our study, the reaction path for hydrogen migration on the ground-state surface has been studied. The obtained result was a very similar structure (Figure 2h) to that one found on the excited singlet surface. This transition state is 96.3 kcal mol^{-1} above the S_0 minimum of DMD. Thus, a 1,2-hydrogen shift concerted with nitrogen formation in the ground state has been ruled out again.

(iv) Dimethylcarbene to Propene Isomerization. Provided that hydrogen migration concurrent with nitrogen extrusion is not an effective reaction mechanism, and that the only nonradiative decay pathway is through the S_0/n-π^* conical intersection, dimethylcarbene has to be generated on the ground state surface from a vibrationally excited species. High level ab initio calculations[35-37] predict that dimethylcarbene have a singlet ground state, and the best estimate of the singlet–triplet energy gap[36] is 1.5 kcal mol^{-1}. The rearrangement of dimethylcarbene to propene on the singlet-state surface has been investigated previously by Evanseck and Houk[38] and more recently by Ford et al.[7] These latter authors have performed a combined experimental and theoretical study. The calculated energy barrier height for the 1,2-H shift is 7.4 kcal mol^{-1} at the CCSD(T)/ANO+ZPVE level of theory, whereas the observed activation energy is 2.56 kcal mol^{-1} in perfluorohexane. The energy difference between the calculated and experimental values, in conection with the observed isotope effects ($\Delta E_a^D - \Delta E_a^H = 3.07$ kcal mol^{-1}, $A_D/A_H = 158$), was taken as evidence for the involvement of quantum mechanical tunneling in the isomerization of dimethylcarbene.

In ref 7, the electronic energy is computed on structures optimized at the MP2/RHF level of theory. In this work, we have studied the carbene to alkene rearrangement optimizing all critical points at the CAS-SCF level. The energetic data are collected in Table 1, and the geometries are shown in Figure 6. The S_0 minimum of DMC is of C_2 symmetry (Figure 7a). At only 2.60 kcal mol^{-1} above this minimum there is a transition state (Figure 7b) which connects DMC with propene (Figure 7c). The IRC (Figure 8) following both directions of the transition vector leads to dimethylcarbene and propene, respectively. It must be noted that the calculated energy barrier compares nicely with the experimental activation energy. Consequently, on the basis of the computed energy barrier only, it cannot be said that quantum mechanical tunneling is involved in the isomerization reaction.

Conclusions

No evidence for a concerted N_2 extrusion concurrent with the 1,2-H shift, on both the excited and ground state surfaces, has been found for 3,3-dimethyldiazirine. Our

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[32] Wang, Y.; Yuzawa, T.; Hamaguchi, H.; Toscano, J. P. *J. Am. Chem. Soc.* **1999**, *121*, 2875.

[33] Miller, D. M.; Schreiner, P. R.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1995**, *117*, 4137.

[34] Keating, A. E.; García-Garibay, M. A.; Houk, K. N. *J. Am. Chem. Soc.* **1997**, *119*, 10805.

[35] Richards, C. A. J.; Kim, S.-J.; Yamaguchi, Y.; Schaefer III, H. F. *J. Am. Chem. Soc.* **1995**, *117*, 10104.

[36] Matzinger, S.; Fülscher, M. P. *J. Phys. Chem.* **1995**, *99*, 10747.

[37] Bally, T.; Matzinger, S.; Truttmann, L.; Platz, M. S.; Morgan, S. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1964.

[38] Evanseck, J. D.; Houk, K. N. *J. Am. Chem. Soc.* **1990**, *112*, 9148.

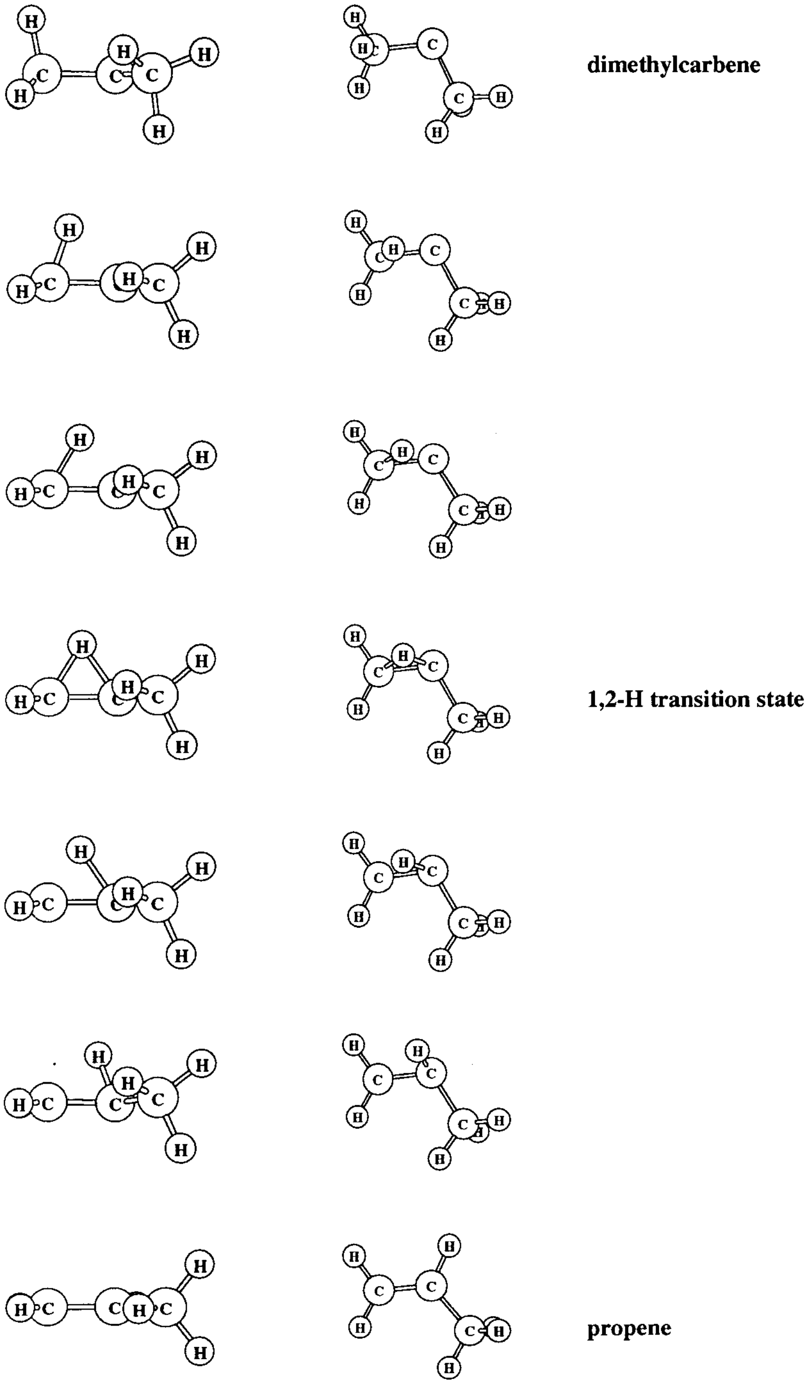

Figure 8. Two orthogonal views of the IRC (CAS/6-31G*) showing the DMC → propene isomerization.

calculations have shown that the only reaction path, on the singlet excited n-π^* surface, is a nonadiabatic mechanism; the calculated barrier energy height to start such a process (1.0 kcal mol^{-1}) is in accordance with the experimental estimate of the activation energy,[6] which ranges from 0.0 to 1.50 kcal mol^{-1}. Thus, the decay pathway starts at the transition state shown in Figure 2d, leading to an S_0/S_1 conical intersection (Figure 2e). After the $S_1 \rightarrow S_0$ surface hop has taken place, the region of the potential energy well dominated by the S_0 DMD minimum is populated. Therefore, if the internal energy stored in the photoexcitation process is not released to the surrounding medium, the molecule decomposes to give dimethylcarbene and molecular dinitrogen, both in their electronic ground states (Figure 5, stepwise mechanism), again the computed barrier energy for this process (31.0 kcal mol^{-1}) agrees satisfactorily with the activation energy of the thermolysis (33.17 kcal mol^{-1}).[29] Another reaction path from the S_0/S_1 conical intersection, which certainly is not important, involves the diazirine → diazo isomerization.

On the other hand, due to the energy barrier for 1,2-H migration in the ground state of dimethylcarbene is very low (2.56 kcal mol^{-1}),[7] this rearrangement takes place easily, giving the most thermodynamically stable propene as the final product of the global reaction. The calculations predict a barrier height for the carbene isomerization of 2.6 kcal mol^{-1}; therefore, the tunneling effect in the 1,2-H isomerization of 3,3-dimethylcarbene must be questioned.

To finish, we must stress that our main objective in this work was to elucidate qualitatively the reaction mechanism with a reliable method of calculation. The computation of the activation energies is a valuable tool for such an objective. Therefore, the trustiness of the computed values plays a crucial role. It is certainly possible that the very good agreement between calculated and experimental energies is the product of an error cancelation. However, we must point out that the used methodology yields very good predicted energy barriers for other systems (see, for example, refs 39 and 40).

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(39) Arenas, J. F.; Marcos, J. I.; Otero, J. C.; Sánchez-Gálvez, A.; Soto J. *J. Chem Phys.* **1999**, *111*, 551.

(40) Arenas, J. F.; Marcos, J. I.; Otero, J. C.; López-Tocón, I.; Soto J. *J. Chem Phys.* **2000**, *113*, 2282.