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Triplet versus Singlet Photoreaction Mechanism in the Barrelene Di-π-methane Rearrangement

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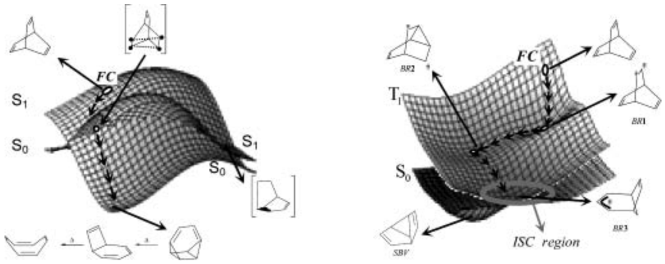
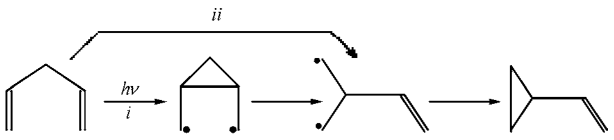
ABSTRACT



A detailed study of the potential energy surfaces involved in the di-π-methane rearrangement (singlet and triplet states) reveals the factors that modulate the mechanisms (pathways) and reactivity in strained di-π-methane systems such as bicyclo[2.2.2]octa-2,5,7-triene (barrelene).

Since 1966, when Zimmerman and Grunewald reported this reaction in bicyclo[2.2.2]octa-2,5,7-triene (barrelene),[1] the di-π-methane rearrangement (DPMR) had become an important topic in organic photochemistry, which today still continues to be an active field of research.[2] Typically, DPMR takes place when a molecule with two vinyl groups or equivalent π-moieties (i.e., aryl groups) linked to the same sp^3 carbon atom is irradiated to yield a vinylcyclopropane (Figure 1). Two possible mechanisms have been described for the di-π-methane rearrangement (Figure 1). In the present communication, we advance the results of a theoretical study on the photoreactivity of barrelene by direct as well as triplet-sensitized irradiation. Different reaction mechanisms as well as their relative probabilities, and some of the factors controlling them, are discussed.

The irradiation of barrelene in the presence of a triplet sensitizer leads to the formation of the di-π-methane rearrangement product with a high yield,[3a] while the direct photolysis of the molecule follows a different path (see below).



BR**2** BR**3**

Figure 1. (i) Zimmerman mechanism[1,3] and (ii) Bernardi and Robb mechanism[4,5] for the di-π-methane rearrangement in 1,3-pentadiene. The 1,4- (BR**2**) and 1,3-biradicals (BR**3**) are reaction intermediate species in the Zimmerman mechanism. BR**3** is the biradical on S$_0$ formed in the nonadiabatic reaction involving a tetraradicaloid (S$_1$/S$_0$) conical intersection in the Bernardi and Robb mechanism.

The mechanism proposed by Zimmerman,[1,3] in which a biradical species (BR2) is an intermediate of the reaction, is

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[1] Zimmerman, H. E.; Grunewald, G. L. *J. Am. Chem. Soc.* **1966**, *88*, 183−184.

[2] For a recent review see: Zimmerman, H. E.; Armesto, D. *Chem. Rev.* **1996**, *96*, 3065−3112.

[3] (a) Zimmerman, H. E.; Binklet, R. W.; Givens, R. S.; Sherwin, M. A. *J. Am. Chem. Soc.* **1967**, *98*, 393. (b) Zimmerman, H. E.; Mariano, P. S. *J. Am. Chem. Soc.* **1969**, *91*, 1718. (c) Zimmerman, H. E. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: London, 1980; Vol. 3, p 131.

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strongly supported by theoretical results presented here, based on the detailed study of the SEPs of electronic states involved in the reaction[6] at the CASSCF(8,8)/6-31g*[7] and CASPT2(8,8)/6-31g*[8] levels of theory. The reaction takes place in four steps (Figure 2).

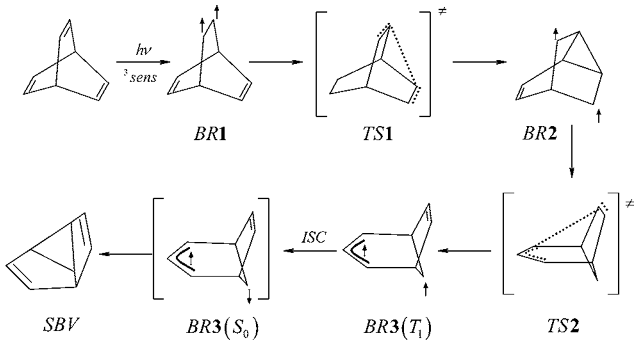

Figure 2. Photoreaction of barrelene by triplet-sensitized irradiation, leading to the di-π-methane rearrangement (species in brackets are not minima in the PES).

In the first step, after the triplet-sensitized excitation, the barrelene on T_1 yields the 1,2-biradical (BR**1**). This BR**1** (minimum on T_1) does not bear the orthogonal *p* orbitals present in analogous compounds without the structural restrictions of barrelene. An intersystem crossing (ISC) point T_1/S_0[9a] corresponding to this situation is located 39 kcal/mol above the BR**1** in the PES.[9b] Hence, because of its instability; this ISC is not an effective channel of deactivation to the ground state, which, on the other hand, will recover barrelene.

After the formation of BR**1**, and since any biradical species would tend to adopt a structure that minimizes electron repulsion, the molecule evolves in a first step, to the 1,3-biradical (BR**2**), and afterward to an 1-allyl,3-biradical (BR**3**), the most stable of all of them. These two biradicals were also identified as minima in the PES of naphtho-barrelenes.[10] As the system enters the 1,3-biradical region, the energy of T_1 and S_0 becomes very close, giving rise to a quasidegenerated situation (Figure 3).

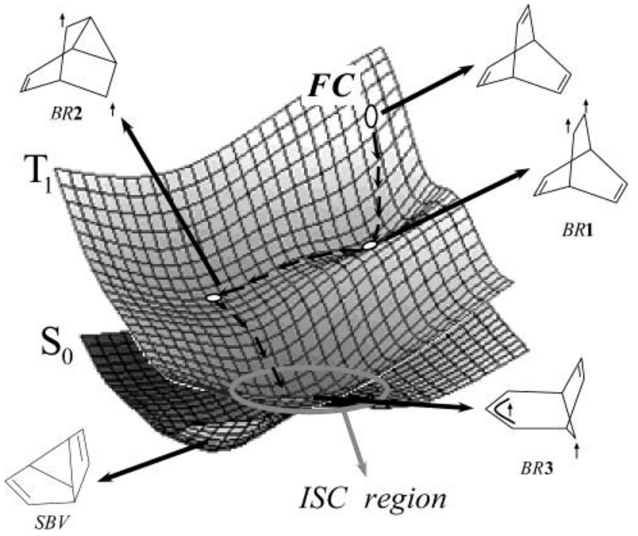

Figure 3. Schematic potential energy surface regions of T_1 and S_0 involved in the sensitized di-π-methane reaction. The most stable biradical (BR**3**) and the intersystem crossing (ISC) region are also indicated, as well as the semibullvalene (SBV) photoproduct.

The two-half-filled orbitals containing the unpaired electrons in BR**3** are nearly perpendicular, while those in BR**2** are parallel. This could result in a much higher ISC rate for BR**3** than for BR**2**, due to the angular dependence of the spin−orbit coupling (SOC) energy $\langle T_1|H_{SO}|S_0\rangle$, as illustrated by the case of the trimethylene biradical,[11] and more recently for barrelene derivatives in a DPMR.[10] Therefore, the surface crossing to the ground state would be clearly much more efficient at the BR**3** region, not only because this is the most stable species, but also because of the enhanced SOC. Since the biradical BR**3** is not a stable intermediate on the S_0 surface (Figure 3), the fast pairing of the two electrons finally yields semibullvalene (SBV) as the only reaction product.

On the other hand, direct irradiation of barrelene into the first absorption band at 239 nm[12] populates the $1^1E''$ electronic state, which presents a multiconfigurational wave function corresponding essentially to the HOMO → LUMO monoexcitation, as calculated at the CASPT2(8,8)/6-31-g* level of theory,[8] being the calculated transition energy ($1^1A'_1 \rightarrow 1^1E''$) 242 nm.

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(4) Reguero, M.; Bernardi, F.; Jones, H.; Olivucci, M.; Ragazos, I. N.; Robb, M. A. *J. Am. Chem. Soc.* **1993**, *115*, 2073−2074.

(5) Zimmerman has also noted that BR**2** and BR**3** are not necessarily minima on the PES; see for example: Zimmerman, H. E.; Sulzbach, H. M.; Tollefson, M. B. *J. Am. Chem. Soc.* **1993**, *115*, 6548.

(6) Analytical frecuencies, minimum energy paths, and stationary point optimizations were carried out with Gaussian 98, revision A.7 (see ref 7). Single-point calculations were carried out with MOLCAS 5.0 (see ref 8)

(7) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(8) CASPT2 calculations were made with: *MOLCAS*, version 5; Andersson, K.; Blomberg, M. R. A.; Fülscher, M. P.; Karlström, G.; Lindh, R.; Malmqvist, P.-Å.; Neogrády, P.; Olsen, J.; Roos, B. O.; Sadlej, A. J.; Schütz, M.; Seijo, L.; Serrano-Andrés, L.; Siegbahn, P. E. M.; Widmark, P.-O.; Lund University: Lund, Sweden, 1999.

(9) (a) This ISC topology is responsible for the cis−trans isomerization in acyclic compounds. (b) An algorithm developed by our laboratory for locating minima in the intersystem crossing region working in conjunction with energy gradient calculated with Gaussian 98 (see ref 7) was used to locate minima on the T_1/S_0 crossing subspace.

(10) Zimmerman, H. E.; Kutateladze, A. G.; Maekawa, Y.; Mangette, E. *J. Am. Chem. Soc.* **1994**, *116*, 9795.

(11) Carlacci, L.; Doubleday: C.; Furlany, T. R.; King, H. F.; McIver, J. W. *J. Am. Chem. Soc.* **1987**, *109*, 5323.

(12) Gedanken, A.; Meijere, A. de *J. Chem. Phys.* **1988**, *88*, 4153−4157.

After the Franck−Condon (FC) excitation, the system relaxes vibrationally, reaching a conical intersection region (CoInR), rather than a conical intersection point (CoIn), corresponding to the [2 + 2] cycloaddition CoIn topology.[13] No intermediate is reached in the relaxation on S_1, and the $S_1 \rightarrow S_0$ radiationless transition occurs via a CoIn in the time scale of a few molecular vibrations, supporting the ultrafast character of this reaction. Passing the CoInR, the system evolves on the ground state through several intermediates (Figure 4) to yield 1,3,5,7-cyclooctatetraene (COT).

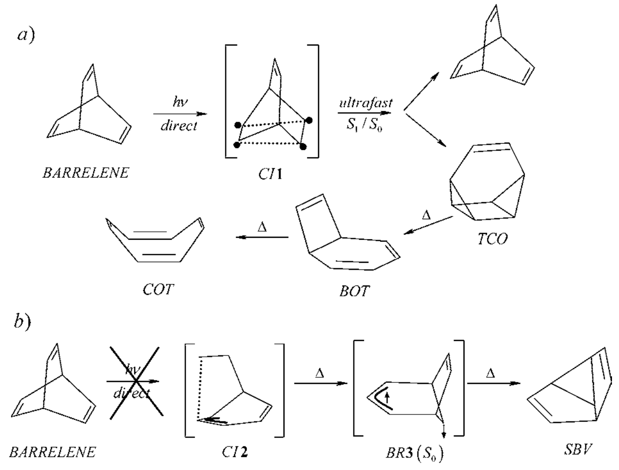

Figure 4. Photochemistry of barrelene after direct irradiation. (a) Mechanism allowed by [2 + 2] cycloaddition and (b) forbidden di-π-methane rearrangement mechanism (species in brackets are not minima on the PES). (BOT = bicyclo[4.2.0]octa-2,4,7-triene, TCO = tetracyclo[4.2.0.0.^{2,8}0^{5,7}]octene.)

In the case of molecular systems free of the barrelene structural restrictions (usually acyclic compounds), it has been proposed from theoretical arguments that the DPMR must involve decay to ground state via a CoIn.[4] This CoIn, the most stable one, corresponds to an ethylenic rearrangement that yields the DPMR product.[4] The same type of CoIn is found in the barrelene potential energy surface (PES), and in fact, it is the most stable CoIn (in 19 kcal/mol). This CoIn would yield the di-π-methane rearrangement product, in a concerted process (SBV). This CoIn, however, cannot be reached from the FC region on S_1, despite its stability, and the [2 + 2] cycloaddition CoInR would be the preferred crossing (S_1/S_0) space, followed by the relaxation of the system to the ground state.

Comparison of the results described with those of ref 4 points out the similar relative stability of the CoIns in systems as different as 1,4-pentadiene and barrelene, due to the large structural and electronic similarity between the CoIns in both compounds. Therefore, despite the structural differences existing between the two (di-π-methane) molecular systems, the photochemical reactivity by direct irradiation cannot be explained on the basis of the differences in the CoIn stability.

On the contrary, the reactivity will be controlled by the CoIn region that can be accessed after the FC transition. In this way, if the molecule in the ground state presents two neighbor ethylene groups, after the FC transition the system would most probably reach the [2 + 2] cycloaddition CoInR. On the other hand, if the system presents conformational flexibility in such a way that the molecule in the ground-state preserves the separation of the two ethylene bonds, the di-π-methane or the cis−trans isomerization CoInR could be accessible. Hence, the photochemical reactivity by direct irradiation must be controlled mainly by the properties of S_0, and not by those of the excited state (S_1), because the conformational stability on the ground state would determine the CoInR reached after the FC transition, and consequently, the photoproducts obtained. Therefore, it should be possible to control the photoproducts by designing, for example, the substituents of a di-π-methane system in order to optimize, in the S_0 state, the desired conformation.

In conclusion, our theoretical study supports the Zimmerman mechanism for the sensitized reaction of barrelene. This mechanism must be common to many di-π-methane rearrangements in molecules with structural restrictions such as barrelene, in which the cis−trans isomerism is hindered and, therefore, cannot be an effective mechanism for relaxation to the ground state. The photoproducts are controlled by the stability of the biradical species with the higher SOC, the BR**3**, and it is not expected to depend on the FC transition region. In contrast, for the direct photoreaction, the photoproducts must be determined by the FC transition region, and the stability of the CoIns should not play any important role.

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(13) (a) Gerhartz, W.; Poshusta, R. D.; Michl, J. *J. Am. Chem. Soc.* **1977**, *99*, 4263. (b) Olivucci, M.; Ragazos, I. N.; Bernardi, F.; Robb, M. A. *J. Am. Chem. Soc.* **1993**, *115*, 3710. (c) Olivucci, M.; Bernardi, F.; Ottani, S.; Robb, M. A. *J. Am. Chem. Soc.* **1994**, *116*, 2034.