Photorearrangements

DOI: 10.1002/ange.201208002

The Triplet Surface of the Zimmerman Di-π-Methane Rearrangement of Dibenzobarrelene**

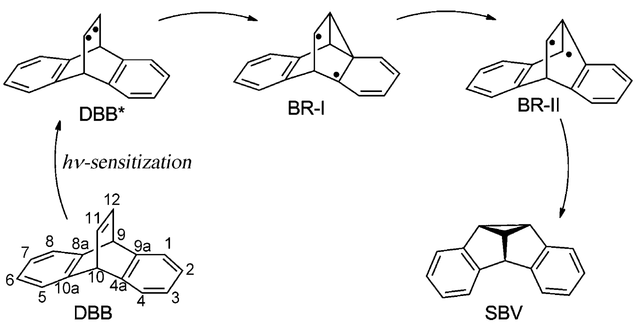
*Ricardo A. Matute and Kendall N. Houk**

In memory of Howard Zimmerman

The Zimmerman di-π-methane (DPM) photorearrangement is a magnificent example of the novel transformations that can be achieved photochemically. Since the first studies by Zimmerman,[1,2] the reaction has captivated attention of mechanistic photochemists. The reaction is formally a $[\pi^2+\sigma^2]$ rearrangement of 1,4-dienes. In acyclic dienes, upon photoexcitation, the reaction mainly occurs through a singlet pathway in the excited state (S_1). The vinylcyclopropane product is formed after coupling of the excited and the ground state through a conical intersection, which affords a fast and effective decay channel to reach the ground state.[3,4] The reaction via a triplet state is ineffective in acyclic molecules, since it does not effectively compete with a *cis–trans* photoisomerization of the double bond in the triplet state.[5]

In polycyclic molecules, the DPM rearrangement occurs via a triplet state. Zimmerman pioneered the studies of the rearrangement in bicyclic molecules, especially barrelene and various benzo derivatives.[1,2] Barrelenes form cyclooctatetraenes and derivatives from the excited singlet state and semibullvalenes from the triplet state. The mechanism of this reaction involves two biradical intermediates on the excited triplet state (T_1), namely BR-I and BR-II (Scheme 1 and Figure 1). Zimmerman studied the aryl–vinyl DPM rearrangement, using a cyanodibenzobarrelene, and showed that the preferred product is the one that arises from formation of the most stable substituted BR-I. This is consistent with a mechanism in which the transition states leading to isomeric triplet biradicals of BR-I determine the regioselectivity of the reaction.[6] However, a mechanism skipping the BR-I intermediate has been suggested invoking a direct 1,2-aryl shift[6–10] (dashed line in Scheme 1).

We have characterized by quantum chemical computations the mechanism of the triplet-sensitized DPM rearrangement of dibenzobarrelene, especially exploring the role played by the BR-I intermediate and determining that a reaction mechanism that skips such an intermediate is also possible.



Scheme 1. Reaction mechanism for the DPM rearrangement of dibenzobarrelene. Upon sensitization, two possible pathways are depicted from DBB*: two-step or one-step (dashed arrow) pathways.

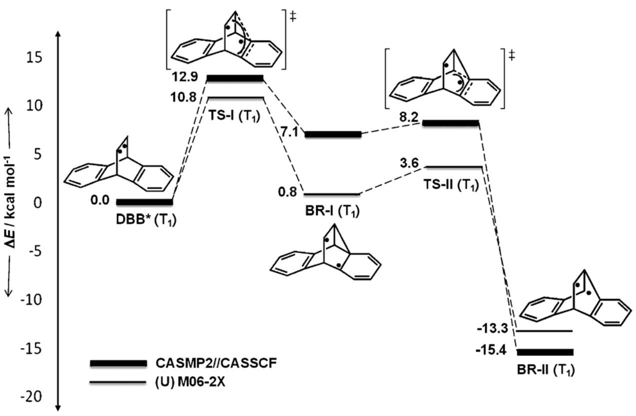


Figure 1. Electronic energy profile for the DPM rearrangement of dibenzobarrelene in the triplet state. Thin line: (U) M06-2X/6-31G(d). Thick Line: CASMP2/6-31G(d)//CAS(10,10)/6-31G(d).

The electronic energies were calculated using unrestricted density functional theory (DFT) with the (U)M06-2X/6-31G(d)[11] functional. An ab initio multiconfigurational CASSCF method[12] was also used, with calculations performed at a CAS(10,10)/6-31G(d) level of theory. Dynamic correlation effects were included with the CASMP2 method[13] (CASMP2(10,10)/6-31G(d)). A smaller active space of CAS(6,6) was used to localize the intersystem crossing structure (ISC). The topology of the potential-energy

---

[*] Dr. R. A. Matute, Prof. Dr. K. N. Houk
Department of Chemistry and Biochemistry
University of California, Los Angeles
607 Charles E. Young Drive East, Los Angeles, CA 90095 (USA)
E-mail: houk@chem.ucla.edu

[**] We are grateful to the National Science Foundation (grant number CHE-0548209) for financial support of this research. This work used the Extreme Science and Engineering Discovery Environment (XSEDE), which is supported by the National Science Foundation grant number OCI-1053575. Computer time was also provided by the UCLA Institute for Digital Research and Education (IDRE). R.A.M. acknowledges the financial support from CONICYT and BECAS CHILE.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201208002.

surface (PES) describing the mechanism along the triplet hypersurface was obtained by a grid of full optimized structures imposing constraints on the distances between the atoms involved in the formation and cleavage of the cyclopropane intermediate (BR-I), respectively, using the unrestricted (U)M06-2X functional with the 6-31G(d) basis set (relaxed scan protocol). The energy profile including another DFT functional, (U)B3LYP/6-31G(d),[14a,b] was obtained for comparison (see the Supporting Information). All calculations were performed with the Gaussian 09 package,[15] and the PES plot shown later was obtained with data smoothing upon cubic interpolation using the Matlab software.[16]

DBB* is the optimized structure of the triplet excited state. There is a barrier associated with transition state TS-I, where bond formation occurs to give the first 1,4-biradical intermediate BR-I. For aryl–vinyl DPM rearrangements, one radical center is benzylic. The energies from DFT are improved by the use of higher level calculations (CASMP2//CASSCF) (Figure 1). According to those values, the barrier TS-II is only 1–3 kcal mol^{-1} higher than the shallow intermediate. BR-II has a 1,3-biradical character with delocalization of one of the radical centers as in BR-I. The transition states TS-I and TS-II involve bond formation and bond cleavage respectively, but once the intermediate BR-II is reached, the diradical undergoes intersystem crossing (ISC) via a radiationless decay channel to the ground state to form the dibenzosemibullvalene (SBV) product. The structure associated with the crossing (ISC in Figure 2) shows the shortening of the distance between the atoms that will eventually form the last bond to give the SBV product (from 2.44 Å to 1.99 Å). According to Salem's rules for ISC of biradicals,[17] the occurrence of the ISC mechanism is relatively facile, since the nonbonding orbitals in BR-II have the best orbital orientation to induce spin–orbit coupling (perpendicular with respect to one another) in agreement with the computational study for the case of barrelene by Frutos et al.[7] BR-II is a deep well in energy, and the excited triplet will visit the crossing repeatedly until eventually the spin flip occurs and the decay to the ground state proceeds, giving SBV formation.

The spin density distributions for the species participating in the DPM are shown in Figure 3. In DBB*, the twisted alkene has two orthogonal radical centers. In TS-I, BR-I, and TS-II, one of the radicals is delocalized into one of the benzo groups. The spin distribution suggests that the stabilizing effect observed by Zimmerman[6] with cyano as substituent on one of the benzenes stabilizes BR-I and simultaneously TS-I and TS-II.

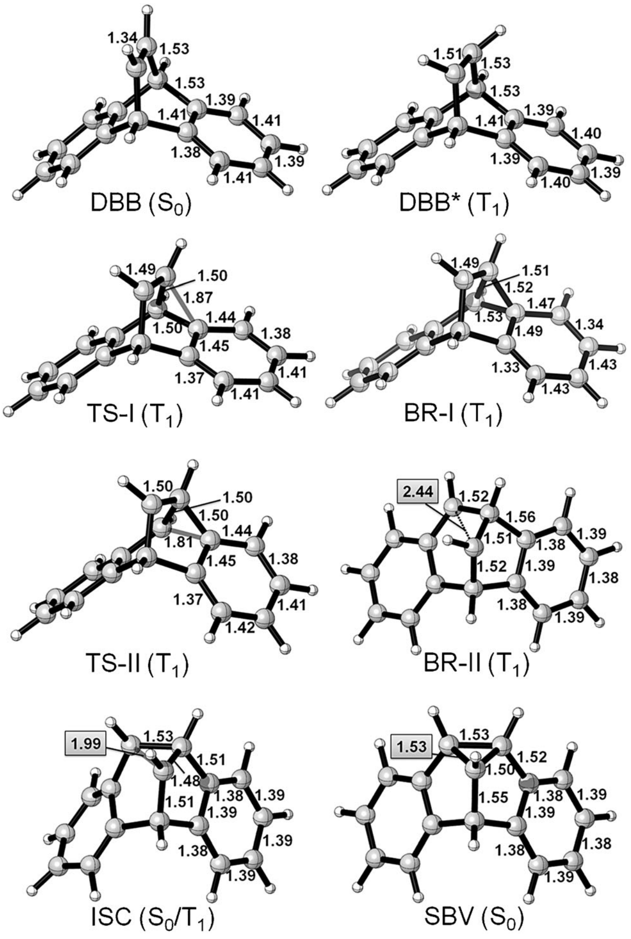


Figure 2. Structures involved in the mechanism for the DPM rearrangement of dibenzobarrelene. Bond lengths are shown in Ångström for representative bonds. The highlighted values show the change in distance between the radical centers in the intersystem crossing (CASSCF geometries).

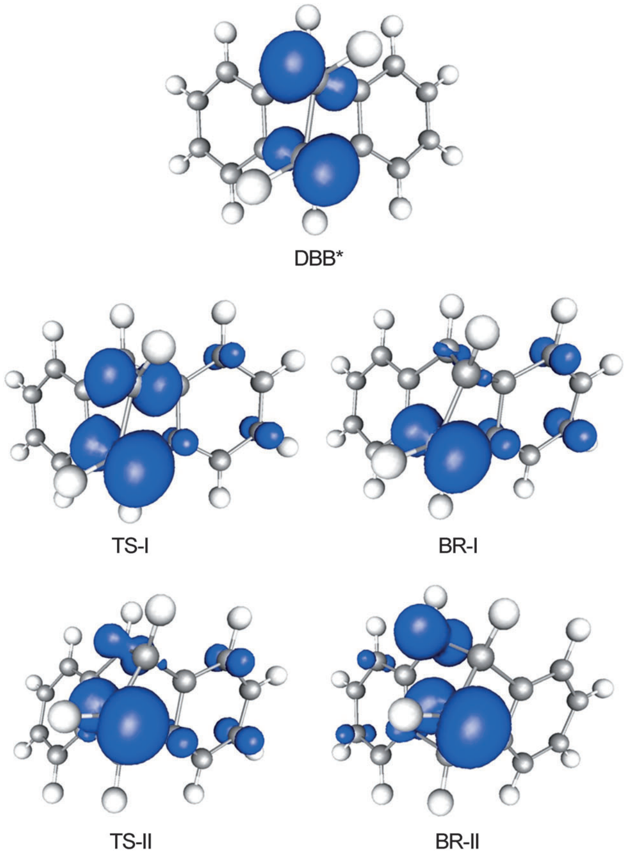


Figure 3. Spin density distribution of triplet biradical intermediates and transition states for the DPM rearrangement of dibenzobarrelene ((U) M06-2X/6-31G(d)).

Frutos et al. suggested the BR-II determines the photoproduct formation.[7] Indeed, BR-II is the region of the surface where ISC occurs, but BR-II is low in energy and will not revert to BR-I or DBB*. The photoproduct formation rate (and regioselectivity for DBB derivatives) is determined by the highest barrier along the reaction pathway, the transition state TS-I. In DBB derivatives, different substituents can influence the relative heights of the barriers.

The topology of the energy profile is the key to the mechanism of this reaction. Figure 4 shows two representations of the triplet surface. Access to this surface occurs in the proximity of DBB*, upon sensitization. Alternatively, intersystem crossing from the excited singlet S_1 to the triplet T_1 can compete with the [2+2] cycloaddition conical intersection[7] that leads to the cyclooctatetraene product. From DBB*, there is no direct 1,2-aryl shift pathway via a concerted transition state (single first-order saddle-point connecting DBB* and BR-I). However, immediately after the reaction coordinate passes TS-I, the PES becomes flat. This flat region can lead to trajectories traversing a pathway represented by the dashed arrow. Hence, despite the energetic preference for the stepwise pathway (solid arrows), that after passing the entrance high-energy barrier (TS-I), many trajectories will have sufficient energy to pass directly to the final deepest well corresponding to BR-II, bypassing in that way the shallow well of the biradical BR-I (dashed arrow). This topology is known to cause nonstatistical behavior in organic reaction dynamics. In particular, Carpenter has shown in a related ground state diradical that the shallow intermediate may be bypassed all together[18] and that even quite energetically stable intermediates can be skipped.[19,20] We have explored such a situation for a 1,3-shift on a caldera and related reactions.[21–26] Singleton has uncovered several such examples for typical organic reactions.[27–29]

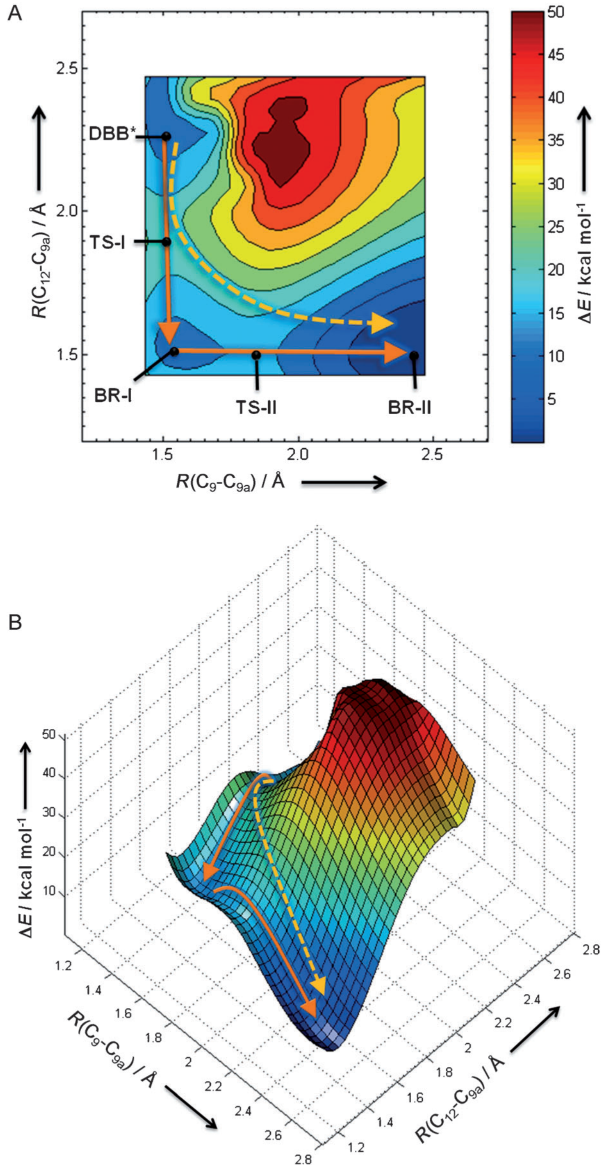


Figure 4. PES of the triplet state for the DPM rearrangement of dibenzobarrelene. A) Contour plot of the PES. The critical points on the reaction pathways are shown. B) 3D representation of the PES. The stepwise reaction pathway (solid arrows) and a direct reaction pathway that might occur dynamically (dashed arrow) are shown. Relative energies with respect to the lowest triplet intermediate energy.

In summary, the DPM rearrangement of dibenzobarrelene proceeds via a triplet state, with decay to the ground state via ISC only after BR-II is formed. The minimum energy reaction pathway involves two barriers on the corresponding triplet state. After overcoming the first barrier, the biradical can proceed directly to the second biradical intermediate BR-II, avoiding the formation of the first biradical intermediate BR-I. The photoproduct formation is determined only by the first transition state TS-I. Most importantly, the occurrence of a shortcut on the potential-energy surface bypassing BR-I suggests that the reaction can occur by competing one-step and two-step mechanisms on the triplet surface.

Received: October 4, 2012

Keywords: density functional calculations · nonstatistical dynamics · potential-energy surfaces · rearrangements

---

[1] H. E. Zimmerman, G. L. Grunewald, *J. Am. Chem. Soc.* **1966**, *88*, 183–184.
[2] H. E. Zimmerman, R. W. Binkley, R. S. Givens, M. A. Sherwin, *J. Am. Chem. Soc.* **1967**, *89*, 3932–3933.
[3] S. S. Hixson, P. S. Mariano, H. E. Zimmerman, *Chem. Rev.* **1973**, *73*, 531–551.
[4] M. Reguero, F. Bernardi, H. Jones, M. Olivucci, I. N. Ragazos, M. A. Robb, *J. Am. Chem. Soc.* **1993**, *115*, 2073–2074.
[5] K. N. Houk, *Chem. Rev.* **1976**, *76*, 1–74.
[6] H. E. Zimmerman, H. M. Sulzbach, M. B. Tollefson, *J. Am. Chem. Soc.* **1993**, *115*, 6548–6556.
[7] L. M. Frutos, U. Sancho, O. Castaño, *Org. Lett.* **2004**, *6*, 1229–1231.
[8] W. Adam, M. Dörr, J. Kron, R. J. Rosenthal, *J. Am. Chem. Soc.* **1987**, *109*, 7074–7081.
[9] W. Adam, O. DeLucchi, M. Dörr, *J. Am. Chem. Soc.* **1989**, *111*, 5209–5213.
[10] Y. Mori, K. Takano, *J. Photochem. Photobiol. A* **2011**, *219*, 278–284.

[11] Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **2008**, *120*, 215–241.
[12] B. O. Roos, *Adv. Chem. Phys.* **1987**, *69*, 399–446.
[13] J. J. McDouall, K. Peasley, M. A. Robb, *Chem. Phys. Lett.* **1988**, *148*, 183–189.
[14] a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652; b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789.
[15] Gaussian 09, Revision A.1, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, **2009**.
[16] *MATLAB* version 7.6.0, 2008, computer software, The MathWorks Inc., Natick, Massachusetts.
[17] L. Salem, C. Rowland, *Angew. Chem.* **1972**, *84*, 86–106; *Angew. Chem. Int. Ed. Engl.* **1972**, *11*, 92–111.
[18] M. B. Reyes, B. K. Carpenter, *J. Am. Chem. Soc.* **2000**, *122*, 10163–10176.
[19] J. A. Nummela, B. K. Carpenter, *J. Am. Chem. Soc.* **2002**, *124*, 8512–8513.
[20] S. L. Debbert, B. K. Carpenter, D. A. Hrovat, W. T. Borden, *J. Am. Chem. Soc.* **2002**, *124*, 7896–7897.
[21] C. P. Suhrada, K. N. Houk, *J. Am. Chem. Soc.* **2002**, *124*, 8796–8797.
[22] C. Doubleday, C. P. Suhrada, K. N. Houk, *J. Am. Chem. Soc.* **2006**, *128*, 90–94.
[23] C. P. Suhrada, C. Selcuki, M. Nendel, C. Cannizzaro, K. N. Houk, P. J. Rissing, D. Baumann, D. Hasselmann, *Angew. Chem.* **2005**, *117*, 3614–3618; *Angew. Chem. Int. Ed.* **2005**, *44*, 3548–3552.
[24] Y. L. Zhao, C. P. Suhrada, M. E. Jung, K. N. Houk, *J. Am. Chem. Soc.* **2006**, *128*, 11106–11113.
[25] K. S. Khuong, W. H. Jones, W. A. Pryor, K. N. Houk, *J. Am. Chem. Soc.* **2005**, *127*, 1265–1277.
[26] B. H. Northrop, K. N. Houk, *J. Org. Chem.* **2006**, *71*, 3–13.
[27] T. Bekele, C. F. Christian, M. A. Lipton, D. A. Singleton, *J. Am. Chem. Soc.* **2005**, *127*, 9216–9223.
[28] J. B. Thomas, J. R. Waas, M. Harmata, D. A. Singleton, *J. Am. Chem. Soc.* **2008**, *130*, 14544–14555.
[29] X. S. Bogle, D. A. Singleton, *Org. Lett.* **2012**, *14*, 2528–2531.