Intrinsically Competitive Photoinduced Polycyclization and Double-Bond Shift through a Boatlike Conical Intersection**

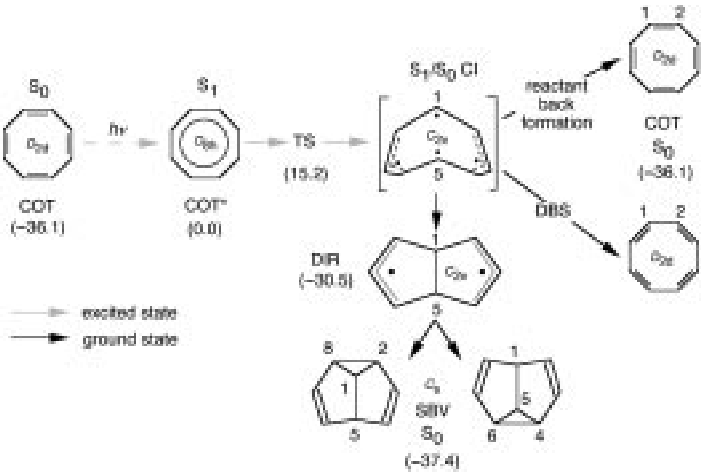
Marco Garavelli,* Fernando Bernardi,
Vicente Moliner, and Massimo Olivucci*

The production of polycyclic carbon backbones through the direct irradiation of simple conjugated hydrocarbons is a remarkably simple way of forming complex molecular architectures.[1] Examples of these processes are the production of bicyclobutanes from butadienes,[2] tetrahedranes from cyclobutadienes,[3] benzvalenes from benzenes,[4] and semibullvalenes from cyclooctatetraenes.[5] We have demonstrated[6] that the photogeneration of 1,2-di-*tert*-butylbicyclobutane and benzvalene involves the deactivation at different types of S_1/S_0 conical intersections, which prompts a concerted (simultaneous formation of two new σ bonds)[6a] or stepwise (initial formation of the prefulvene diradical)[6b] mechanism, respectively. Herein, we discuss our investigations into the mechanisms of the photochemical production of polycyclic hydrocarbons, specifically the conversion of cycloocta-1,3,5,7-tetraene (COT) into semibullvalene (SBV). We show that a novel type of conical intersection is involved in this process.

Although SBV was first isolated after the sensitized irradiation of barrelene,[5a] it can also be synthesized by the direct irradiation of COT.[5b,c] In particular, direct irradiation in solution[5b] affords SBV and benzene (as a by-product), whereas vapor-phase UV irradiation is of preparative value.[5c] Experimental evidence was obtained for the direct formation of SBV,[5b] and a two-photon mechanism for SBV photogeneration was proposed.[5b] According to this model, the first photon is absorbed by the stable (*cis*,*cis*,*cis*,*cis*) configuration of COT, thus leading to the production of the strained *trans*,*cis*,*cis*,*cis* isomer, which then absorbs a second photon to produce SBV. The SBV is produced more rapidly than the strained isomer.

Double-bond shifting (DBS) is an alternative process that occurs in antiaromatic [4*n*] systems such as COT. It has been established that the reversible interconversion between DBS isomers (a π-skeletal rearrangement) may be induced either thermally or photochemically.[7–9] Although DBS is of no practical interest for the parent COT, it may be used to turn on and off the conjugation between π substituents located at the vicinal position. The DBS reaction may thus be exploited to design photochemically driven switches.[9]

We have found computational evidence that SBV and DBS originate from the same (excited-state) reaction path. In particular, the calculated S_1 path[10] (Scheme 1; light lines) goes through a novel type of boatlike S_1/S_0 conical intersection (CI), which provides the locus for decay and branching[11] by means of three independent S_0 paths (dark lines).



Scheme 1. Schematic representation of the reaction paths of COT*. Symmetry labels and relative CASPT2 energies (kcal mol^{-1} in parenthesis) are also reported for each calculated structure.

S_1 COT is a planar D_{8h}-symmetric minimum (COT*). This structure (Figure 1) corresponds to the expected (aromatic) geometry, which characterizes the S_1 state of an antiaromatic system.[7] The S_1-S_0 energy gap in COT* is relatively large (20 kcal mol^{-1}), and deformation towards a C_{2v} boat conformation causes a progressive decrease in the gap. This change leads to the C_{2v} S_1/S_0 conical intersection point (CI; see structure in Figure 1). Access to the CI is controlled by a C_{2v} transition structure (TS) that is located 15.2 kcal mol^{-1} above COT* (CASPT2 and ZPE-corrected value)[12] and is structurally close to CI. The reactive mode (i.e. the transition vector) is shown on the CI structure. Although higher energy conical intersections exist on the S_1 surface, these do not provide competitive reaction channels and are not discussed herein.[12]

The analysis of the molecular and electronic structure shows that the CI has tetraradical character, with two unpaired electrons located at opposite centers (atoms C1 and C5) and another two electrons residing on the allyl moieties C2-C3-C4 and C6-C7-C8. S_1 motion towards the CI promotes the approach of the unpaired electrons (the C1−C5 distance decreases from 3.68 Å in COT* to 2.89 Å in CI), to form a diradical intermediate with a C1−C5 transannular bond. The S_0 path that corresponds to this process has been located at a distance of 5 au from the conical intersection (see Figure 1). The calculated C_{2v} bicyclo[3.3.0]octadienyl diradical (DIR) corresponds to the structure suggested by Iwamura and Morio[13] and by Martin et al.[14] as an intermediate in the thermal valence tautomerization of COT to SBV. Although DIR is a flat S_0 energy minimum at the CASSCF level, the inclusion of dynamic correlation energy (CASPT2 level)

---

[*] Dr. M. Garavelli, Prof. F. Bernardi
Dipartimento di Chimica “G. Ciamician”, Università di Bologna
Via Selmi 2, 40126 Bologna (Italy)
Fax: (+39) 051-2099456
E-mail: mgara@ciam.unibo.it
Prof. M. Olivucci
Dipartimento di Chimica, Università di Siena
Via Aldo Moro, 53100 Siena (Italy)
Fax: (+39) 0577-234278
E-mail: olivucci@unisi.it
Prof. V. Moliner
Dpt. De Ciències Experimentals, Universitad de Jume I
Campus Riu Sec, 12071, Castelló de la Plana (Spain)

[**] This work was supported by the Università di Siena (P.A.R. 99/00), the Università di Bologna (MURST ex-60 %), NATO (CRG 950748), and HFSP (RG 0229/2000-M).

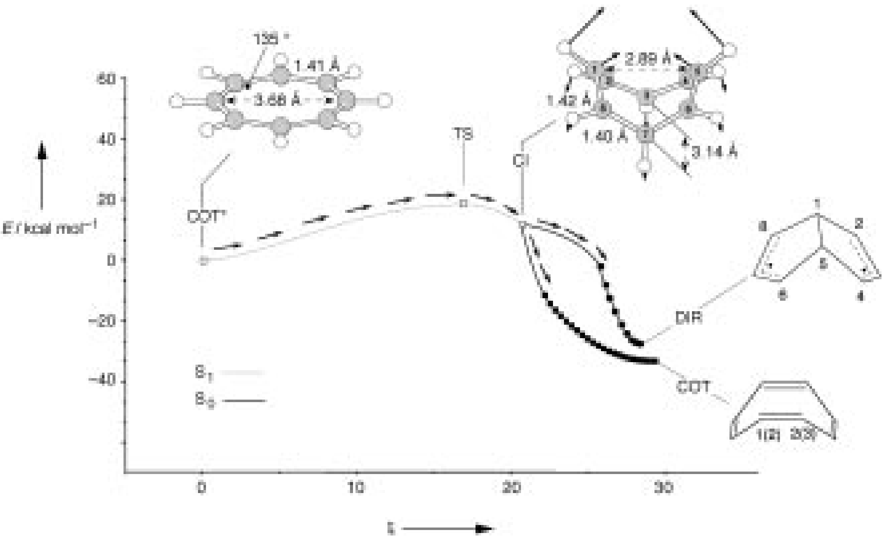


Figure 1. CASPT2-scaled energy profiles along the reaction coordinate ξ [bohr (amu)$^{1/2}$] describing the evolution of COT*. The geometries of COT* and of the conical intersection (CI) document the progression along the path (open squares). The arrows illustrate the S_1 reactive mode. The two S_0 relaxation paths (full squares and full circles) terminate at COT (or its DBS isomer), or at the DIR transition state. The inclusion of ZPE correction lowers the excited-state barrier from 18 to 15.2 kcal mol^{-1}.

shows that this structure is unstable along the symmetry-breaking deformation that leads to SBV (see Scheme 1). Thus, DIR is the transition state in the Cope rearrangement of SBV, as previously proposed by Jiao et al.[15b] and more recently by Castano et al.[16]

The SBV relaxation path discussed above is a continuation of the S_1 path, through the CI and DIR structures. We have been able to locate two additional (degenerate) relaxation paths (Scheme 1 and Figure 1), which start closer (1.5 au distance) to the CI and develop along a steeper region of the S_0 energy surface (Figure 1). One path leads back to the reactant, whereas the other leads to its DBS isomer. The associated relaxation coordinates indicate that a drastic change in direction of "motion" from the S_1 path is needed to access these channels.

The above results do not provide evidence for the formation of the previously proposed[5b] *trans,cis,cis,cis*-COT as an intermediate in the two-photon formation of SBV.[17] On the other hand, the documented paths provide a computational model for predicting the products of "vibrationally hot" or "vibrationally cold" photochemistry.[5b,c] When the S_1 vibrational excess energy is low, COT* would either decay radiatively/non-radiatively at its equilibrium structure, or be displaced towards the CI with a small momentum along the reactive mode, thus populating only the closer and steeper S_0 relaxation paths.[18] In both cases, the decay would yield COT together with its DBS isomer only. On the other hand, in the presence of a vibrationally excited reactant, part of the S_1 population would be channeled along the transition vector, with enough momentum to be displaced towards the SBV path. As a consequence, the photolysis of COT would yield a mixture of SBV and double-bond shifted COT photoproducts. This model provides an explanation for the fact that SBV can be produced efficiently by the gas-phase (vibrationally hot) photolysis of COT,[5c] as well as for the low reactivity of 1,3,5,7-tetramethyl-COT,[5b] which does not lead to a detectable production of 1,3,5,7-tetramethyl-SBV (i.e. inertia and steric effects imposed by the substituents restrain DIR formation). Finally, the production of bicyclo[4.2.0]octa-2,4,6-triene, as a precursor of benzene (and acetylene),[5b] may occur from the CI through an additional relaxation path, which leads to C2–C7 transannular bond formation (currently under investigation).[12]

In conclusion, we have investigated the S_1 potential-energy surface of the prototype antiaromatic hydrocarbon COT. The results show that the photochemical behavior of COT is controlled by the conical intersection, which features a tetraradical structure that has never been found in aromatic (e.g. benzene) or open-chain (e.g. butadiene) conjugated hydrocarbons. In Figure 2a we show that in the CI, the weak interactions of the four singly occupied orbitals adopt a tetrahedral pattern (see dashed lines). In the previously reported bicyclobutane[6a] and benzvalene[6b] conical intersection structures (Figures 2b and 2c, respectively), the interactions of the four singly occupied orbitals adopt different patterns (rhomboid (Figure 2b) and triangular (Figure 2c)). In the past, the same interaction patterns have been documented for the conical intersections of H_4 clusters.[19] Thus our results support the conjecture by Michl and coworkers[19] that the structure of the conical intersections of conjugated hydrocarbons conforms to the conical intersections of elementary systems.

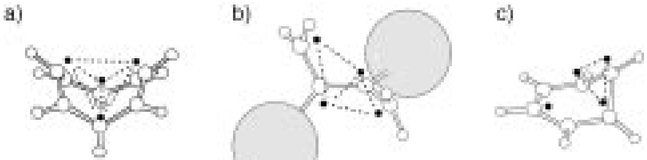


Figure 2. Prototype tetraradical conical intersections found in conjugated hydrocarbons: a) SBV; b) bicyclobutane; c) benzvalene photogeneration.

The main "chemical" result reported above is that the production of SBV and DBS are bound processes. However DBS dominates only under conditions of low vibrational excess energy (for instance in solution or in a matrix). This feature should be considered when designing DBS-based molecular switches.

Received: December 4, 2000 [Z16214]

---

[1] A. Gilbert in *CRC Handbook of Organic Photochemistry and Photobiology* (Eds.: W. M. Horspool, P.-S. Song), CRC Press, Boca Raton, FL, **1995**, pp. 229–236.

[2] H. Hopf, H. Lipka, M. Traetteberg, *Angew. Chem.* **1994**, *106*, 232–233; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 204–205.

[3] G. Maier, *Angew. Chem.* **1988**, *100*, 317–341; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 309–335.

[4] D. Bryce-Smith, A. Gilbert, *Tetrahedron* **1976**, *32*, 1309.

[5] a) H. E. Zimmermann, G. L Grunewald, *J. Am. Chem. Soc.* **1966**, *88*, 183–186; b) no evidence for the accumulation of any intermediate could be found in low-temperature irradiation experiments: H. E. Zimmermann, H. Iwamura, *J. Am. Chem. Soc.* **1970**, *92*, 2015–2022; c) N. J. Turro, J.-M. Liu, H. E. Zimmermann, R. E. Factor, *J. Org. Chem.* **1980**, *45*, 3511–3513.

[6] a) M. Garavelli, B. Frabboni, M. Fato, P. Celani, F. Bernardi, M. A. Robb, M. Olivucci, *J. Am. Chem. Soc.* **1999**, *121*, 1537–1545; b) I. J. Palmer, I. N. Ragazos, F. Bernardi, M. Olivucci, M. A. Robb, *J. Am. Chem. Soc.* **1993**, *115*, 673–682.

[7] a) D. A. Hrovat, W. T. Borden, *J. Am. Chem. Soc.* **1992**, *114*, 5879–5881, and references therein; b) P. G. Wenthold, D. A. Hrovat, W. T. Borden, W. C. Lineberger, *Science* **1996**, *272*, 1456–1459, and references therein; c) C. D. Stevenson, E. C. Brown, D. A. Hrovat, W. T. Borden, *J. Am. Chem. Soc.* **1998**, *120*, 8864–8867, and references therein.

[8] L. A. Paquette, *Acc. Chem. Res.* **1993**, *26*, 57–62, and references therein.

[9] A. A. S. Briquet, P. Uebelhart, H.-J. Hansen, *Helv. Chim. Acta* **1996**, *79*, 2282–2315, and references therein.

[10] A CASSCF/6-31G(d) approach (with an active space of eight electrons in eight π orbitals) has been used for minimum-energy path mapping (including transition state, frequency, and reaction/relaxation path computations) and for conical intersection optimization. These computations were carried out by using the Gaussian98 package: Gaussian98, Revision A.7, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Lui, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1998**). Relaxation path calculations require the preliminary evaluation of the "initial relaxation directions," which determine the direction of the steepest descent paths departing from the lower tip of a conical intersection. These calculations were performed by means of the IRD method (see P. Celani, M. A. Robb, M. Garavelli, F. Bernardi, M. Olivucci, *Chem. Phys. Lett.* **1995**, *243*, 1–8); to improve the energetics by including the dynamic correlation contribution, we performed single-point CASPT2 computations for all the relevant structures by using the MOLCAS-4 package: K. Andersson, M. R. A. Blomberg, M. P. Fülscher, G. Karlström, R. Lindh, P.-Å. Malmqvist, P. Neogrády, J. Olsen, B. O. Roos, A. J. Sadlej, M. Schütz, L. Seijo, L. Serrano-Andrés, P. E. M. Siegbahn, P.-O. Widmark, MOLCAS, Version 4, Lund University, Sweden, **1997**. All CASPT2 computations give a balanced weight (0.76) of the zeroth-order wavefunction. The CASPT2 absolute energy calculated for COT* is -308.48067 Hartree particle^{-1}. Zero-point-energy (ZPE) corrections were included in the evaluation of the excited-state barriers. We found that CASPT2 correction shifts the position of the conical intersection towards COT*. We do not discuss this effect in the present mechanistic investigation.

[11] a) F. Bernardi, M. Olivucci, M. A. Robb, *Chem. Soc. Rev.* **1996**, *25*, 321–328; b) M. A. Robb, M. Olivucci, M. Garavelli, F. Bernardi in *Reviews in Computational Chemistry, Vol. 15* (Eds.: K. B. Lipkowitz, D. B. Boyd), Wiley-VCH, Weinheim, **2000**, pp. 87–146.

[12] A complete report that documents the full network of COT S_1 and S_0 paths (including the photochemical versus thermal processes, etc.) is in preparation: M. Garavelli, F. Bernardi, and M. Olivucci, unpublished results.

[13] H. Iwamura, K. Morio, *Bull. Chem. Soc. Jpn.* **1972**, *45*, 3599–3603.

[14] H. D. Martin, T. Urbanek, R. Walsh, *J. Am. Chem. Soc.* **1985**, *107*, 5532–5534.

[15] a) H. Jiao, P. von R. Schleyer, *Angew. Chem.* **1993**, *105*, 1830–1833; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1760–1763; b) H. Jiao, R. Negelkerke, H. A. Kurtz, R. V. Williams, W. T. Borden, P. von R. Schleyer, *J. Am. Chem. Soc.* **1997**, *119*, 5921–5929.

[16] O. Castano, L. M. Frutos, R. Palmeiro, R. Notario, J. L. Andrés, R. Gomperts, L. Blancafort, M. A. Robb, *Angew. Chem.* **2000**, *112*, 2168–2170; *Angew. Chem. Int. Ed.* **2000**, *39*, 2095–2097.

[17] This intermediate could be produced by a conical intersection that is too high in energy to provide a competitive deactivation funnel; see ref. [12].

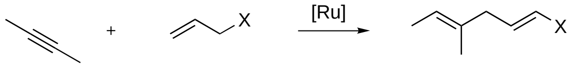
[18] Semiclassical trajectory computations, starting near the higher tip (S_1 state) of a conical intersection and with no initial kinetic energy, show that S_0 relaxation mainly occurs along the channels departing closer to the conical intersection. See: M. Garavelli, P. Celani, M. Fato, M. Olivucci, M. A. Robb, *J. Phys. Chem.* A **1997**, *101*, 2023–2032.

[19] W. Gerhartz, R. D. Poshusta, J. Michl, *J. Am. Chem. Soc.* **1977**, *99*, 4263–4271.

An Atom-Economic Three-Carbon Chain Extension to Give Enamides[**]

Barry M. Trost[*] and Jean-Philippe Surivet

Enamides represent a significant class of compounds because of their versatility as building blocks—a result of the enhanced nucleophilicity of the double bond—and as precursors to saturated amines.[1–3] Normally, such compounds are prepared by additions to aldehydes via imines or other equivalent intermediates.[2] As a continuation of our development of metal-catalyzed additions of alkenes and alkynes,[4] we have been interested in chain-extension reactions by means of additions catalyzed by ruthenium complexes [Eq. (1)]. Our recent discovery of the effectiveness of $[(\eta^5\text{-}C_5H_5)Ru(N{\equiv}CCH_3)_3]PF_6$ (**1**) [5, 6] suggested the prospect of expanding the scope of such additions. If X was an amide function, this chain-extension method would directly create an enamide. A significant issue in such a reaction is the



(1)

---

[*] Prof. B. M. Trost, Dr. J.-P. Surivet
Department of Chemistry
Stanford University
Stanford, CA 94305-5080 (USA)
Fax: (+1) 650-725-0002
E-mail: bmtrost@leland.stanford.edu

[**] We thank the National Science Foundation and the National Institutes of Health, General Medical Sciences, for their generous support of our programs and Rhône–Poulenc for partial financial support for J.P.S. Mass spectra were provided by the Mass Spectrometry Facility of the University of California, San Francisco, supported by the NIH Division of Research Resources.

Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.