J|A|C|S
COMMUNICATIONS

Configuration Change in [14]Annulene Requires Möbius Antiaromatic Bond Shifting

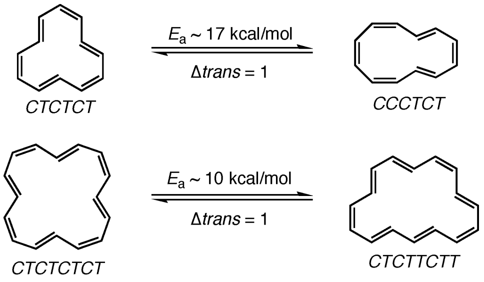
Joseph F. Moll, Ryan P. Pemberton, M. Gertrude Gutierrez, Claire Castro,* and William L. Karney*

Department of Chemistry, University of San Francisco, 2130 Fulton Street, San Francisco, California 94117-1080

Received November 2, 2006; E-mail: castroc@usfca.edu; karney@usfca.edu

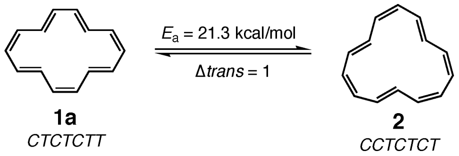
The study of annulenes continues to be a vibrant area of research.[1] The desire to synthesize novel topologies[2,3] and to probe the concept of aromaticity[4] has further propelled interest in Möbius annulenes.[5,6] The observation[7,8] that medium and large annulenes readily undergo cis/trans isomerization in solution renders it difficult to study these species, but simultaneously raises intriguing mechanistic questions, especially since the barriers are much lower than those measured for cis/trans isomerization of acyclic polyenes of similar π-conjugation length.[9] Recent computational work suggests that facile thermal configuration change in [12]- and [16]annulene[7,8] proceeds via Möbius aromatic π-bond shifting.[10,11] We now argue that configuration change in these systems *requires* such bond-shifting transition states. It follows that configuration change in [14]annulene must involve a Möbius *antiaromatic* transition state[12]—the first example of a concerted reaction that proceeds through such a transition state. Computational results support this prediction.

π-Bond shifting in annulenes converts s-cis single bonds to cis double bonds and s-trans single bonds to trans double bonds. For Hückel-topology[13] annulenes, the number of s-trans single bonds is either equal to the number of trans double bonds or differs by an even number. Thus, bond shifting via a Hückel conformation either will be degenerate, or will produce a new configuration with Δtrans = 0, 2, 4, etc., where Δtrans is the difference in the number of trans double bonds between the starting material and product (see Supporting Information for examples). In contrast, in Möbius-topology annulenes[13] the number of s-trans single bonds differs from the number of trans double bonds by an odd number. Thus, bond shifting via a Möbius conformation necessarily produces a new configuration with Δtrans = 1, 3, 5, etc. This bond-shifting rule means that for a process with Δtrans = 1, the mechanism *requires* a Möbius bond-shifting step. Two examples of this are the aforementioned [12]- and [16]annulene, which undergo facile thermal cis/trans isomerization:[7,8]



Computed barriers for Möbius bond shifting in these cases are consistent with experimental values.[10,11] Because these are [4*n*]-annulenes, the bond-equalized transition states are closed-shell and highly aromatic.

[14]Annulene is also known to isomerize (Δtrans = 1) in solution, with a barrier of only 21.3 kcal/mol:[8]



Application of the above rule means that the mechanism for **1a** → **2** also requires a Möbius bond-shifting step, but since [14]-annulene is a $4n + 2$ π-electron system, the necessary bond-equalized transition state must be antiaromatic.

Using UBH&HLYP calculations,[14,15] we located four different bond-shifting transition states that accomplish the desired configuration change CTCTCTT → CCTCTCT. All have Möbius topology and singlet diradical character. The transition state of lowest energy, **TS1**, is shown in Figure 1. As expected for a bond-shifting transition state, **TS1** is strongly bond-equalized (Δr = 0.040 Å). The largest CCCC torsional angles are ca. 39°, allowing for cyclic π overlap.

The full mechanism connecting **1a** to **2** involves two conformation change steps, followed by Möbius bond shifting (Figure 2). Because UDFT actually yields "50:50" wave functions for open-shell singlets,[18] the UDFT energies for these species are not reliable. We therefore computed energies at the CASPT2(14,14)/cc-pVDZ//(U)BH&HLYP/6-311+G** level.[19] Figure 2 summarizes these energetics. The computed barrier of 19.3 kcal/mol agrees well with 21 kcal/mol from experiment. Analogous calculations using (U)-B3LYP geometries gave a barrier of ca. 25 kcal/mol.

The wave function for **TS1** has considerable open-shell character ($\langle S^2 \rangle$ value of 1.48) at UBH&HLYP/6-311+G**. From CASSCF-(14,14)/cc-pVDZ calculations, the occupation numbers for the HOMO (1.57e) and LUMO (0.44e), as well as the ratio of the two highest configuration weights (c_1^2/c_2^2 = 6.7), also reflect the significant singlet diradical character.[20] However, this diradical is fundamentally different from the type involved in thermal cis/trans isomerization in acyclic polyenes.

The disjoint nature[21] of the UDFT singly occupied MOs (SOMOs, Figure 3) rationalizes why this transition state becomes

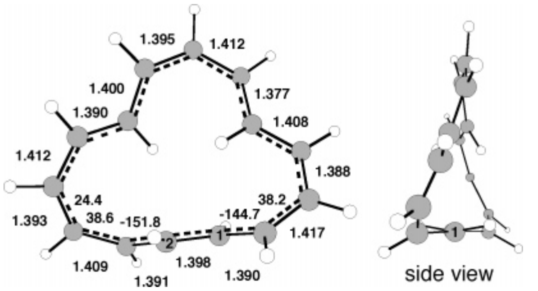


Figure 1. BS-UBH&HLYP/6-311+G** optimized structure of the lowest-energy Möbius bond-shifting transition state (**TS1**) connecting **1a** and **2**. Distances (Å) and selected CCCC dihedral angles (deg) are shown.

10.1021/ja0678469 CCC: $37.00

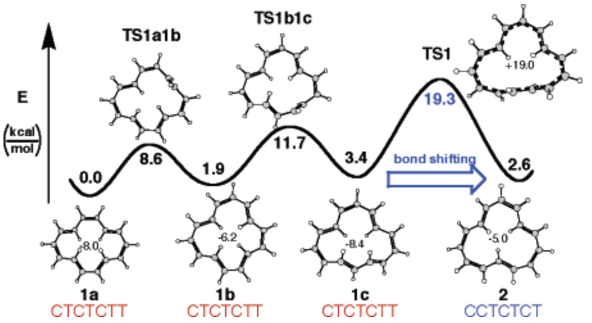


Figure 2. CASPT2(14,14)/cc-pVDZ//(U)BH&HLYP/6-311+G** energetics of conformation change followed by thermal configuration change connecting **1** and **2**. NICS(0) (ppm) values are given at ring centers.

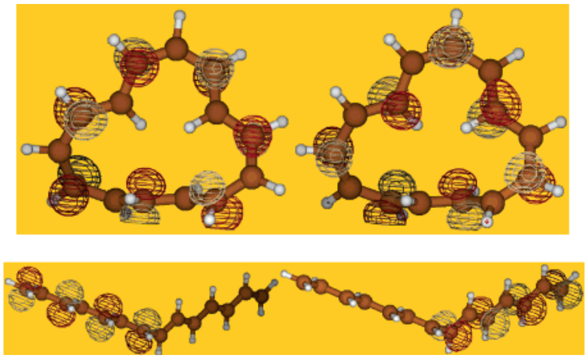


Figure 3. (Top) UBH&HLYP SOMOs for **TS1** and (bottom) UBH&YLYP SOMOs for the cis/trans isomerization transition state for 1,3,5,7,9,11,13-tetradecaheptaene.

more energetically accessible relative to a comparable acyclic singlet diradical mechanism that focuses on a single π bond to effect configuration change.[9] In **TS1**, the two nonbonding electrons reside on different sets of seven carbons (Figure 3, top). For a comparable acyclic polyene, the analogous MOs are confined to four carbons each (Figure 3, bottom). If CASSCF MOs are used, the HOMO and LUMO of **TS1** allow the density from the two highest-energy electrons to be distributed over all 14 carbons of the ring. In contrast, the CASSCF symmetry-adapted HOMO and LUMO for the acyclic polyene transition state are both confined to the same group of eight carbons (see Supporting Information).

The fact that **TS1** is not a pure singlet diradical (unlike the bond-shifting transition state in cyclooctatetraene, COT[22]) is presumably due to its lack of symmetry, which removes the degeneracy of the two nonbonding MOs. Of the two sets of seven alternating C−C bonds in **TS1**, one set has only one CCCC torsional angle greater than 30°, and the CASSCF HOMO has π-bonding interactions across these bonds. The other set of bonds has two such torsional angles, and the CASSCF LUMO has π-bonding interactions across these bonds.

The antiaromatic character in **TS1** is evident from the computed NICS(0) value (+19.0 ppm),[23] the computed chemical shifts of the two inner protons (26.4 and 26.7 ppm), and the large negative NICS (−14.0) for the vertical triplet of **TS1**.[12,24]

There are many examples of concerted reactions that involve Hückel or Möbius aromatic transition states.[25,26] Processes that involve antiaromatic transition states are comparatively scarce. Bond shifting in COT—perhaps the best-studied example[22]—involves a Hückel antiaromatic transition state. To our knowledge, the bond-shifting mechanism for configuration change in [14]annulene provides the first example of a concerted reaction that can only occur via a Möbius antiaromatic transition state. Moreover, the bond-shifting rule outlined here requires a Möbius transition state for this system and for other known cases of configuration change in annulenes.

Acknowledgment. We thank Prof. Phil Warner for sharing results prior to publication. The authors gratefully acknowledge financial support from the National Science Foundation (Grant CHE-0553402) and the Petroleum Research Fund.

Supporting Information Available: Computational details, examples of the bond-shifting rule, pictures of CASSCF nonbonding MOs, absolute energies, optimized Cartesians for all stationary points, and complete citations for refs 16 and 17. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Spitler, E. L.; Johnson, C. A.; Haley, M. M. *Chem. Rev.* **2006**, *106*, 5344. (b) Kennedy, R. D.; Lloyd, D.; McNab, H. *J. Chem. Soc., Perkin Trans. 1* **2002**, 1601.
(2) Tahara, K.; Tobe, Y. *Chem. Rev.* **2006**, *106*, 5274.
(3) (a) Ajami, D.; Hess, K.; Köhler, F.; Näther, C.; Oeckler, O.; Simon, A.; Yamamoto, C.; Okamoto, Y.; Herges, R. *Chem.—Eur. J.* **2006**, *12*, 5434. (b) Castro, C.; Chen, Z.; Wannere, C. S.; Jiao, H.; Karney, W. L.; Mauksch, M.; Puchta, R.; Hommes, N. J. R. v. E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **2005**, *127*, 2425.
(4) (a) Schleyer, P. v. R., Ed. *Chem. Rev.* **2001**, *101*, May issue. (b) Schleyer, P. v. R., Ed. *Chem. Rev.* **2005**, *105*, October issue.
(5) Heilbronner, E. *Tetrahedron Lett.* **1964**, 1923.
(6) Rzepa, H. S. *Chem. Rev.* **2005**, *105*, 3697.
(7) (a) Oth, J. F. M.; Röttele, H.; Schröder, G. *Tetrahedron Lett.* **1970**, 61. (b) Oth, J. F. M.; Gilles, J.-M.; Schröder, G. *Tetrahedron Lett.* **1970**, 67.
(8) Oth, J. F. M. *Pure Appl. Chem.* **1971**, *25*, 573.
(9) Doering, W. v. E.; Kitagawa, T. *J. Am. Chem. Soc.* **1991**, *113*, 4288.
(10) Castro, C.; Karney, W. L.; Valencia, M. A.; Vu, C. M. H.; Pemberton, R. P. *J. Am. Chem. Soc.* **2005**, *127*, 9704.
(11) Pemberton, R. P.; McShane, C. M.; Castro, C.; Karney, W. L. *J. Am. Chem. Soc.*, published online Dec. 6, 2006, http://dx.doi.org/10.1021/ja066152x.
(12) For recent work on Möbius antiaromatic species see: Warner, P. M. *J. Org. Chem.* **2006**, *71*, 9271−9282.
(13) "Hückel-topology" annulenes have an even number of CCCC dihedral angles (ω) with $180° \geq |\omega| > 90°$. This includes "two-twist" annulenes. "Möbius-topology" annulenes have an odd number of such dihedrals.
(14) For validation of the BH&HLYP method (and reasons not to use B3LYP) when studying annulenes, see: (a) Wannere, C. S.; Sattelmeyer, K. W.; Schaefer, H. F.; Schleyer, P. v. R. *Angew. Chem., Int. Ed.* **2004**, *43*, 4200. (b) Castro, C.; Karney, W. L.; Vu, C. M. H.; Burkhardt, S. E.; Valencia, M. A. *J. Org. Chem.* **2005**, *70*, 3602.
(15) Geometries were optimized with the 6-311+G** basis set, using broken spin symmetry for Möbius bond-shifting transition states. CASPT2(14,14)/cc-pVDZ single point energies were computed at the optimized geometries. Calculations were carried out with Gaussian 98,[16a] Gaussian 03,[16b] and MOLCAS.[17]
(16) (a) Frisch, M. J.; et al. *Gaussian 98*, revision A.11.3; Gaussian, Inc.: Pittsburgh, PA, 2002. (b) Frisch, M. J.; et al. *Gaussian 03*, revision D.01; Gaussian, Inc.: Wallingford, CT, 2004.
(17) Andersson, K.; et al. *MOLCAS 6.2*, University of Lund: Lund, Sweden, 2003.
(18) Cramer, C. J. *Essentials of Computational Chemistry: Theories and Models*, 2nd ed.; Wiley: New York, 2004; pp 504−507.
(19) Includes corrections based on CASSCF(2,2)/6-31G*//(U)BH&HLYP/6-311+G** ZPEs (see Supporting Information for details).
(20) For comparison, the corresponding ratios in the benzynes, using CASSCF-(8,8)/3-21G, are: para, 1.7; meta, 4.3; ortho, 11.1. Wierschke, S. G.; Nash, J. J.; Squires, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 11958.
(21) (a) Borden, W. T. *J. Am. Chem. Soc.* **1975**, *97*, 5968. (b) Borden, W. T. In *Diradicals*; Borden, W. T., Ed.; Wiley: New York, 1982; pp 1−72. (c) See also: Hammons, J. H.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1991**, *113*, 4500.
(22) Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1992**, *114*, 5879.
(23) NICS values were computed at the GIAO-(U)B3LYP/6-311+G**//(U)-BH&HLYP/6-311+G** level. NICS(1) for **TS1**: +15.4 to +16.0 ppm.
(24) (a) Baird, N. C. *J. Am. Chem. Soc.* **1972**, *94*, 4941. (b) Gogonea, V.; Schleyer, P. v. R.; Schreiner, P. R. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1945.
(25) Zimmerman, H. E. *Acc. Chem. Res.* **1972**, *4*, 272.
(26) Sakai, S. *J. Phys. Chem. A* **2006**, *110*, 6339 and references therein.

JA0678469