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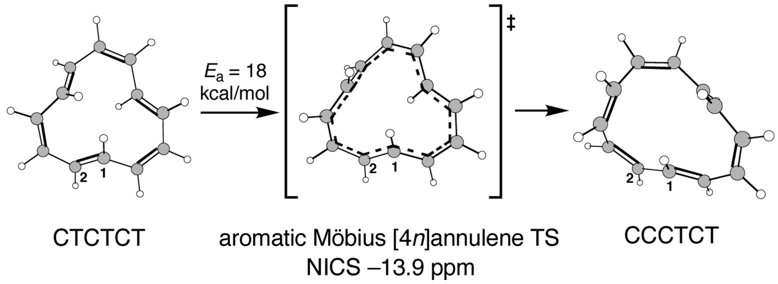

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Mŏbius Aromaticity in [12]Annulene: Cis−Trans Isomerization via Twist-Coupled Bond Shifting

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The study of annulenes and the dynamic processes that they undergo has led to many fascinating discoveries.[1] Bond shifting in cyclobutadiene is now believed to proceed via heavy-atom tunneling.[2] Ring inversion and bond shifting in cyclooctatetraene (COT) have been extensively investigated;[3] the latter process occurs via a singlet, diradical transition state that violates Hund's rule.[3b] Comparisons of theory and experiment for [10]annulene provided critical insights regarding the validity of different methods for computation of annulenes.[4,5] Recent work by Wannere et al. revealed that [14]- and [18]annulene are *not* bond-equalized; rather, both exhibit pronounced C−C bond-length alternation, with the implication being that bond shifting *is* relevant to these [4n + 2]-annulenes.[5] In all of these cases ([4]-, [8]-, [10]-, [14]-, and [18]-annulene), bond shifting is believed to occur via a planar or nearly planar structure.

In contrast with the planar annulenes mentioned above, there is a resurgence of interest in potential aromaticity in Möbius [4n]annulenes,[6−10] exemplified by the synthesis of a Möbius [16]-annulene derivative,[8] though later work argues it is nonaromatic.[9] The preparation of a stable, neutral, clearly aromatic Möbius annulene remains elusive. Here, we present the first evidence that neutral, highly aromatic, Möbius annulenes play a critical role in the known chemistry of [4n]annulenes. We show, using density functional and coupled cluster calculations,[11−13] that bond shifting in [12]annulene can take place via such species, and that this provides a mechanism for the thermal cis−trans isomerization proposed by Oth and Schröder over 30 years ago.[18] The work described herein unites three fundamental concepts: thermal cis−trans isomerization, bond shifting in annulenes, and Möbius aromaticity.

After characterizing tri-*trans*-[12]annulene **1a** by low-temperature NMR, Oth and Schröder found that upon warming to −40 °C, the bicyclic product **3** was formed, presumably via electrocyclization of the transient di-*trans* isomer **2** (Scheme 1).[18a] Because **2** was never observed, the determined barrier of 17.4 ± 0.1 kcal/mol effectively pertains to the isomerization **1a** → **2**. For comparison, similar configuration change in [16]annulene was found to have a barrier of ca. 10 kcal/mol.[18b] Both of these barriers are much lower than those for thermal cis−trans isomerization (via diradicals) in acyclic systems of similar size (E_a > 28 kcal/mol),[19] suggesting that cis−trans isomerization in annulenes occurs via a different mechanism than in acyclic systems. We find that this is indeed the case for [12]annulene.

Given an appropriate starting conformation of **1**, bond shifting can effectively result in cis−trans isomerization to **2**.[20] Assuming that bond shifting proceeds via a bond-equalized transition state, the solution to finding the appropriate conformation lies in Heilbronner's idea that for [4n]annulenes, distortions from planar to Möbius topology[10] could occur without loss of π-electron energy, assuming that angle strain is not prohibitive.[6a] On the basis of our prior computational work on conformational automerization in **1**,[21] the lowest-energy conformer of **1** (**1a**, Scheme 1, Figure S1)[22] can undergo slight bond rotation with minimal energy cost (<1 kcal/mol) to form the Möbius, *nonaromatic*, conformation **1b** (Figure 1).

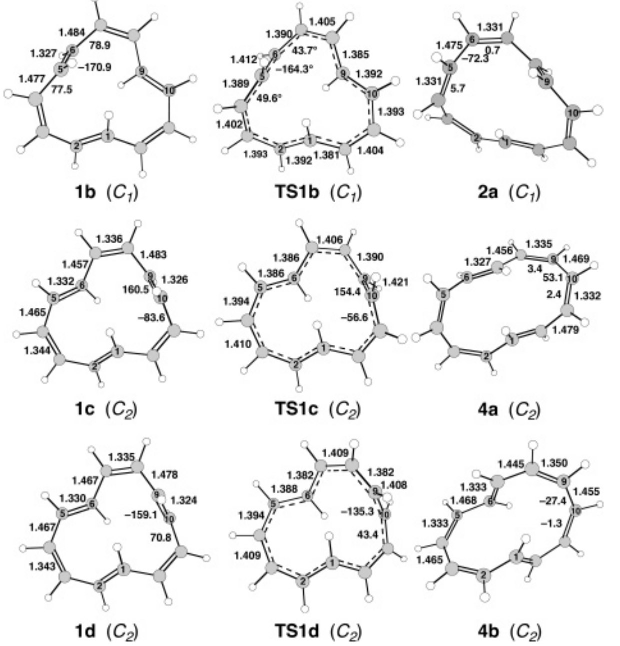
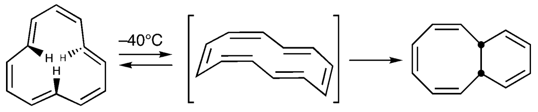


Figure 1. BH&HLYP/6-311+G** optimized geometries of three Möbius conformations of tri-*trans*-[12]annulene **1** (left), transition states for bond shifting from each (middle), and bond-shifting products (right). Selected C−C distances (Å) and CCCC dihedral angles (°) are shown.

Scheme 1



1a *CTCTCT*   **2** *CCCTCT*   **3**

From this latter conformation, twisting of the C4−C5, C5−C6, and C6−C7 bonds, coupled with bond-length equalization of all C−C bonds, leads to a highly delocalized transition state for bond shifting (**TS1b**, Figure 1). We refer to this process as "twist-coupled bond shifting". IRC calculations indicate that **TS1b** connects **1b** to di-*trans* isomer **2a**, which can readily undergo conformational change to **2b** (Figure S2), followed by thermal electrocyclization to **3** (E_a = 13.8 kcal/mol).[22] Figure 2 summarizes the energetics of the entire process at the CCSD(T)/cc-pVDZ//BH&HLYP/6-311+G** level. The computed overall barrier of 18.0 kcal/mol for the **1a** → **3** process (bond shifting being the rate-determining step) agrees well with the experimental barrier of ca. 17.4 kcal/mol.[18a]

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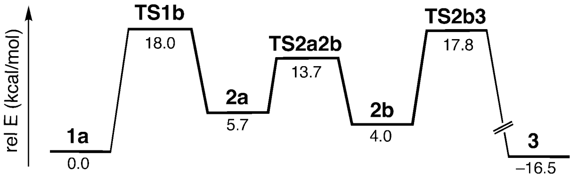

Figure 2. CCSD(T)/cc-pVDZ//BH&HLYP/6-311+G** potential energy curve for the conversion of tri-*trans*-[12]annulene **1a** to di-*trans* isomer **2a** and ultimately to *cis*-bicyclo[6.4.0]dodeca-2,4,6,9,11-pentaene (**3**).

Table 1. Relative Energies (kcal/mol) and Aromaticity Indicators of [12]Annulene Stationary Points and Related Species[a]

species	sym	config	BHH rel *E*	CC rel *E*	Δr	NICS	Λ
1a	C_1	CTCTCT	0.0	0.0	0.147	1.3	10.6
1b	C_1	CTCTCT	0.8	0.7	0.156	−1.6	0.4
TS1b	C_1		20.2	18.0	0.031	−13.9	−43.8
2a	C_1	CCCTCT	5.4	5.7	0.150		
TS2a2b	C_1	CCCTCT	13.9	13.7			
2b	C_s	CCCTCT	2.8	4.0			
TS2b3	C_s		19.3	17.8			
3	C_1		−15.2	−16.5			
1c	C_2	CTCTCT	4.7	4.5	0.157	−0.3	6.0
TS1c	C_2		27.8	25.5	0.035	−13.4	−43.8
4a	C_2	CCTCCT	0.5	0.9	0.152		
1d	C_2	CTCTCT	8.3	7.9	0.154	0.5	5.9
TS1d	C_2		26.8	25.8	0.027	−15.3	−46.7
4b	C_2	CCTCCT	5.7	6.3	0.135		

[a] Config = cis−trans configuration. BHH = BH&HLYP/6-311+G**. CC = CCSD(T)/cc-pVDZ//BH&HLYP/6-311+G**. Relative energies (kcal/mol) are corrected for differences in ZPE. Δr = difference, in Å, between the longest and shortest C−C bonds in the annulene ring. NICS and Λ computed at the B3LYP/6-311+G**//BH&HLYP/6-311+G** level. NICS = nucleus-independent chemical shift, in ppm, computed at the ring center using the GIAO method. Λ = magnetic susceptibility exaltation (MSE, in cgs-ppm), computed using the CSGT method and the increment method. Details can be found in Supporting Information.

TS1b is a clear example of a Möbius aromatic species. Moreover, it is the first example of a Möbius aromatic transition state that does not involve breaking or forming σ bonds.[6b,23] As expected for a bond-shifting transition state, **TS1b** exhibits a small Δr value of 0.031 Å. Its large negative NICS value[24] (−13.9 ppm) and magnetic susceptibility exaltation[25] (Λ) (−43.8 cgs-ppm) reveal that **TS1b** is highly aromatic (Table 1). Thus, the transformation of **1** → **2** via **TS1b** suggests that Oth and Schröder prepared a Möbius aromatic [4*n*]annulene, albeit in the form of a transition state, over 30 years ago.[26]

Two other conformations of **1** (**1c** and **1d**, Figure 1)[27] can undergo twist-coupled bond shifting via Möbius aromatic transition states, though these barriers are higher than that for **1b** (Table 1). Analogous to **TS1b**, the transition states **TS1c** and **TS1d** (Figure 1) exhibit strong aromatic character, based on the large negative NICS and Λ values (Table 1). Bond shifting via **TS1c** or **TS1d** leads to two different conformations of di-*trans*-[12]annulene **4** (**4a** and **4b**, respectively, Figure 1), an isomer previously studied.[7c,28,29]

Whereas planar bond shifting interconverts degenerate species, twist-coupled bond shifting produces configuration change. This new mechanism (i) suggests that neutral, highly aromatic, Möbius geometries serve as the transition states for cis−trans isomerization in the case of [12]annulene, and (ii) probably explains the numerous known examples of facile cis−trans isomerization in [4*n*]annulenes ($n \geq 3$).[1,18b]

Acknowledgment. Dedicated to the memory of Orville Chapman. This work was supported in part by a grant from the University of San Francisco Faculty Development Fund.

Supporting Information Available: Computational details, Figures S1−S3, absolute energies, thermal corrections, and Cartesian coordinates for all optimized structures, and complete ref 11. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) In tracing the π system along one face of the ring, a return to the starting point on the same face indicates Hückel topology, whereas a return on the opposite face indicates Möbius topology.
(11) All calculations were performed with Gaussian 98: Frisch, M. J. et al. *Gaussian 98*, revision A.11.3; Gaussian, Inc.: Pittsburgh, PA, 2002.
(12) Geometry optimizations and vibrational analyses were performed at the BH&HLYP/6-311+G** level.[14,15] BH&HLYP performs much better than B3LYP in computing the relative energy ordering of bond-equalized versus bond-alternating isomers of [10]-, [14]-, [18]-, and [22]annulene.[5]
(13) Single-point energies were computed at the CCSD(T)/cc-pVDZ//BH&HLYP/6-311+G** level[16,17] and were corrected for differences in unscaled zero-point energies. The success of the CCSD(T) method for the problematic case of [10]annulene is described in ref 4.
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(26) Despite extensive searching, we failed to locate a diradical mechanism for cis−trans isomerization of **1** to **2**.
(27) These conformations have been described in ref 21. Despite appearances, species **1c** and **1d** are neither equivalent nor enantiomeric. H1 and H10 are syn to each other in **1c** and **TS1c**, whereas they are anti in **1d** and **TS1d**.
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(29) We have also found a Möbius bond-shifting transition state connecting **4a** to a mono-trans isomer via a 12.7 kcal/mol barrier (Figure S3, Table S2).

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