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[14]Annulene: Cis/Trans Isomerization via Two-Twist and Nondegenerate Planar Bond Shifting and Möbius Conformational Minima

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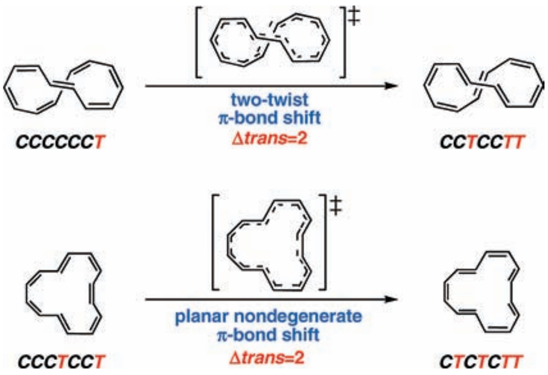
ABSTRACT



Mechanisms linking dihydrooctalenes and the corresponding [14]annulene isomers have been investigated computationally. CCSD(T)/cc-pVDZ//BHLYP/6-31G* calculations suggest that the cis/trans isomerization steps required by these mechanisms can occur with reasonable activation barriers by π-bond shifting, in some cases with two-twist topology, and in others in a planar but nondegenerate fashion. In addition, numerous Möbius conformational minima were located for [14]annulene isomers directly related to the mechanisms studied.

It is well established that different synthetic routes, which would be expected to yield different configurations of a given size annulene, typically produce the same configuration.[1] The syntheses of [16]annulene exemplify this.[2] Mechanisms involving π-bond shifting via Möbius-topology conformations have been proposed to explain known or postulated interconversions of configurations of [16]-, [14]-, and [12]annulene.[3] To date, however, viable mechanisms for configuration change that involve other topologies have not been presented. Here we show that bond shifting via planar and two-twist (figure-eight) conformations can also play a role in proposed interconversions of [14]annulene isomers.

Upon methylation of the dianion of octalene, Vogel and Müllen observed 1,8-dimethyl[14]annulene (Scheme 1).[4] While the major isomer has four trans double bonds (CTCTCTT, **1**), a small amount of the tritrans isomer (CCTCTCT, **2**) could not be excluded based on the observed

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(1) Oth, J. F. M. *Pure Appl. Chem.* **1971**, *25*, 573.

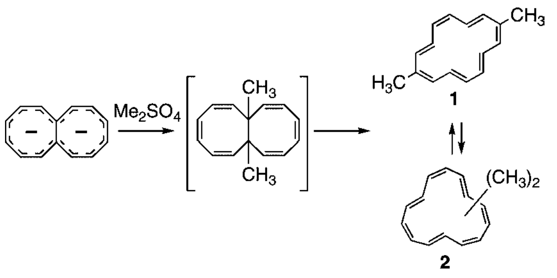
(2) (a) Sondheimer, F.; Gaoni, Y. *J. Am. Chem. Soc.* **1961**, *83*, 4863. (b) Schröder, G.; Oth, J. F. M. *Tetrahedron Lett.* **1966**, 4083.

(3) (a) Pemberton, R. P.; McShane, C. M.; Castro, C.; Karney, W. L. *J. Am. Chem. Soc.* **2006**, *128*, 16692. (b) Moll, J. F.; Pemberton, R. P.; Gutierrez, M. G.; Castro, C.; Karney, W. L. *J. Am. Chem. Soc.* **2007**, *129*, 274. (c) Castro, C.; Karney, W. L.; Valencia, M. A.; Vu, C. M. H.; Pemberton, R. P. *J. Am. Chem. Soc.* **2005**, *127*, 9704..

(4) Vogel, E.; Engels, H.-W.; Huber, W.; Lex, J.; Müllen, K. *J. Am. Chem. Soc.* **1982**, *104*, 3729.

10.1021/ol100025j

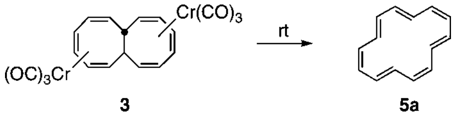
Scheme 1



NMR spectrum. The appearance of an equilibrium between these two isomers in solution is analogous to what is observed in the parent system.[1]

Vogel and Müllen were unable to determine whether the *cis*- or *trans*-dimethyldihydrooctalene system had been formed upon methylation. Nonetheless, thermal ring-opening of either isomer would yield an initial product that would have to undergo configuration change (cis/trans isomerization) to reach **1** or **2**.

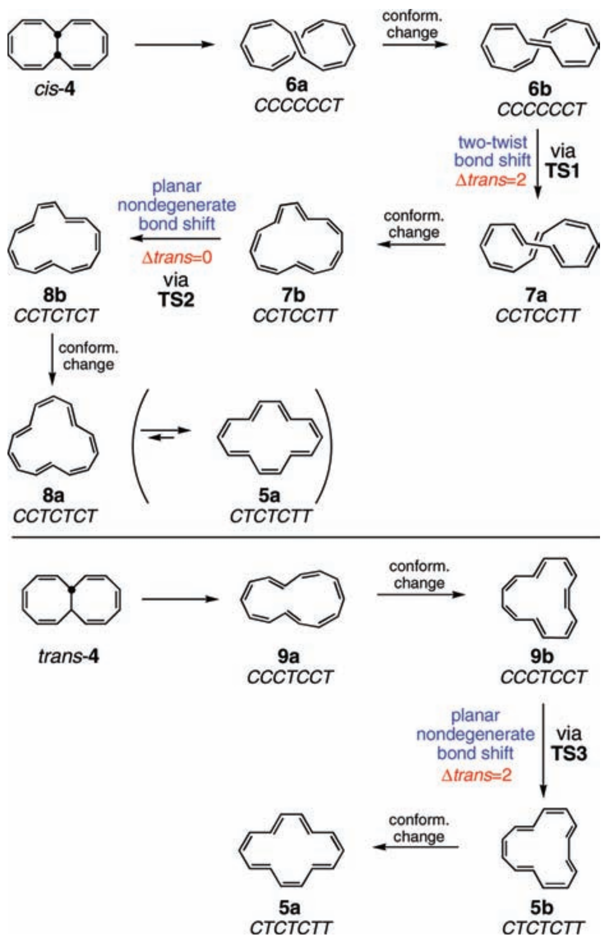
Scheme 2



In a similar vein, Sondheimer and co-workers reported the synthesis of hexacarbonyl-*trans*-6a,12a-dihydrooctalene-dichromium(0) (**3**) and its subsequent thermal reversion to [14]annulene **5a** in various solvents at room temperature (Scheme 2).[5] X-ray crystallography indicated a trans ring juncture in **3**. If both chromiums dissociate before ring-opening, *trans*-dihydrooctalene (*trans*-**4**) would be the precursor to [14]annulene.[6] This suggests that the dimethyldihydrooctalene in Scheme 1 also has a trans configuration.

We now report the results of density functional (BHLYP[7]) and CCSD(T) calculations on possible mechanisms for the conversion of the initial ring-opened products of **4** to either **5a** or **8a**, the unsubstituted analogues of **1** and **2**.[8,9] Unless otherwise stated, energies are reported at the CCSD(T)/cc-pVDZ//BHLYP/6-31G* + ZPE level of theory.[10]

Scheme 3



Scheme 3 depicts the most likely pathways from *cis*- and *trans*-**4** to **5a**.[11] Electrocyclic ring-opening of *cis*-**4** yields monotrans, two-twist isomer **6a**, which has been studied computationally by Rzepa.[12] In addition to necessary conformation change steps, key steps then include two-twist bond shifting (**6b** → **7a**, via **TS1**) and planar *nondegenerate* bond shifting (**7b** → **8b**, via **TS2**) (Scheme 3, upper). Transition states **TS1** and **TS2** (shown in Figure 1) are ca. 15 and 12 kcal/mol, respectively, higher in energy than *cis*-**4** (Table 1).

Beginning instead from *trans*-dihydrooctalene (*trans*-**4**), ring-opening produces ditrans [14]annulene isomer **9a** (Scheme

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(5) Stöckel, K.; Sondheimer, F.; Clarke, T. A.; Guss, M.; Mason, R. *J. Am. Chem. Soc.* **1971**, *93*, 2571.

(6) It is conceivable that ring opening occurs after only one chromium has dissociated. Due to the more complicated nature of the calculations, we have not explored this possibility.

(7) We here use "BHLYP" to denote the BHandHLYP method: (a) Becke, A. D. *J. Chem. Phys.* **1992**, *98*, 1372. (b) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200.

(8) Geometry optimizations and vibrational frequencies were performed at the BHLYP/6-31G* level. Single point energies were computed at these geometries using the CCSD(T)/cc-pVDZ method. All energies are corrected for differences in zero point energies. Nucleus-independent chemical shifts (NICS) were computed at the GIAO-B3LYP/6-311+G**//BHLYP/6-31G* level. All calculations were carried out with Gaussian 03: Frisch, M. J.; et al. *Gaussian 03*, Revision D.01; Gaussian, Inc.: Wallingford, CT, 2004.

(9) That **5a** and **8a** are in equilibrium in solution was established by Oth using NMR.[1] A detailed mechanism connecting these two isomers has been proposed.[3b] So, either species can serve as the "target" for mechanistic studies.

(10) The advantages of the BHLYP method for geometry optimizations of neutral annulenes has been demonstrated.[3] See also: (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.

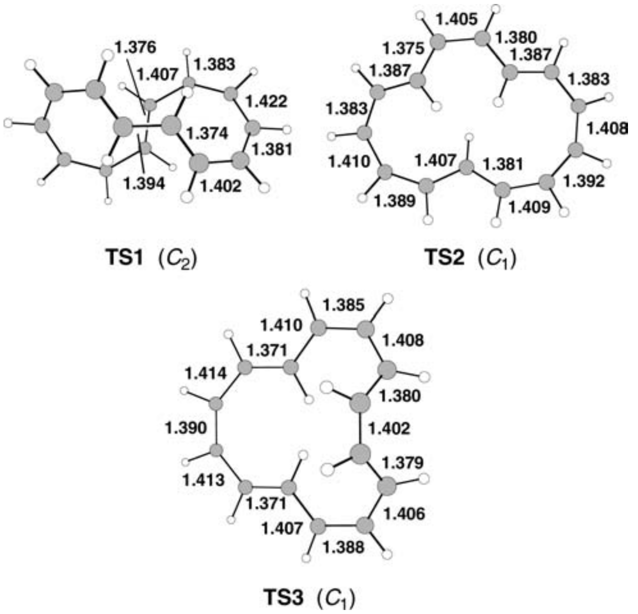
(11) Numerous possible pathways connecting **4** to **5** or **8** were explored. Only the most energetically favorable are presented here. See Supporting Informationfor details of alternate pathways.

(12) Rzepa, H. S. *Org. Lett.* **2005**, *7*, 4637. Isomer **6a** is predicted to have a bond-equalized structure and to be highly aromatic. It has not previously been linked to any known experimental result.

Table 1. Relative Energies (kcal/mol) of $C_{14}H_{14}$ Stationary Points[a]

species	sym	config	BHLYPrel E	CCSD(T)rel E
cis-**4**	C_1	–	7.4	3.0
5a	C_s	CTCTCTT	0.0	0.0
6a	D_2	CCCCCCT	13.8	10.8
6b	C_2	CCCCCCT	13.4	10.3
TS1	C_2	–	21.2	18.0
7a	C_2	CCTCCTT	20.7	17.5
7c[b]	C_2	CCTCCTT	18.0	15.8
7b	C_1	CCTCCTT	14.2	15.6
TS2	C_1	–	13.6	14.7
8b	C_1	CCTCTCT	12.1	12.9
8e[b]	C_1	CCTCTCT	10.0	8.3
8a	C_1	CCTCTCT	0.5	1.6
trans-**4**	C_i	–	2.9	−1.9
9a	C_1	CCCTCCT	15.2	12.8
9b	C_1	CCCTCCT	10.9	9.1
TS3	C_1	–	22.4	21.0
5b	C_1	CTCTCTT	20.8	18.9

[a] BHLYP = BHLYP/6-31G*//. CCSD(T) = CCSD(T)/cc-pVDZ//BHLYP/6-31G*. All energies corrected for BHLYP/6-31G* ZPE differences. [b] Species **7c** and **8e** are conformational minima not shown in Scheme 3. See text for explanation.



TS1 (C_2) **TS2** (C_1)

TS3 (C_1)

Figure 1. BHLYP/6-31G* structures of transition states for two-twist and planar nondegenerate bond shifting. Selected C−C distances (Å) are shown.

3, lower). According to the bond-shift rule,[3b] conversion to tetra-trans isomer **5** could involve a single π-bond shift step (with Δtrans=2)[13] via a Hückel-topology conformation. Indeed, bond shifting from nearly planar conformer **9b**, via **TS3**, leads directly to the desired configuration with an overall barrier of 23 kcal/mol from *trans*-**4**. The barriers represented by **TS1**, **TS2**, and **TS3** are comparable to barriers for cis/trans isomerization in other annulenes, such as the Möbius π-bond shifting that connects **8a** to **5a**.[3] These results suggest that energetically feasible paths exist from either *cis*-**4** or *trans*-**4** to **5**.[14]

Figure 1 displays the geometries of the key transition states. These illustrate that bond shifting via nearly planar and two-twist conformations can play a role in mechanisms of configuration change in annulenes. This concept was first mentioned by Oth[1] (for nearly planar cases), but has not received support until now. Also noteworthy is the potential involvement of two-twist isomer **6a**,[12] which until now has been a purely hypothetical species unconnected to experimental observations.

In the process of exploring possible mechanisms, we located numerous conformational minima with Möbius topology (Figure 2), some of which lie directly on the pathways investigated here. For example, conformer **7c** is an intermediate connecting **7a** and **7b**, and **8e** is an intermediate between **8b** and **8a**. The other Möbius minima are located on spurs off the *cis*-**4** pathway shown in Scheme 3. Though the presence of such minima has been established computationally for [16]annulene,[3a] this is the first report of Möbius minima for a [4n+2]annulene. The geometries of these species reveal that the worst torsional angle in some is 70−80° (**8c**, **8e**), but in others it is only 44−52° (**7c**, **7d**, **8d**). As a result of these torsional angles, these minima exhibit significantly greater bond-length alternation (Δr = 0.131 − 0.146 Å) than their Hückel counterparts such as **5a** and **6a** (Δr = 0.011−0.098 Å, Table 2). The lack of optimal overlap is also reflected in the nucleus-independent chemical shift[15] (NICS) values of these species (Table 2), which suggest that they are essentially nonaromatic.

Contrary to occasional statements in the literature that annulenes will "avoid" conformations associated with antiaromaticity, these [14]annulene Möbius minima emphasize the concept that, other factors such as angle strain and sterics being equal, modest π-overlap around the ring is better than interrupted overlap. (This is analogous to the presence of nearly planar minima for [4n]annulenes such as [16]annulene, which is well established.[16]) Even though the π-overlap is not strong enough to induce a significant ring current (see NICS values in Table 2), it is apparently enough to make these species minima on the potential energy surface. Moreover, four of these Möbius species are computed to lie within 6−9 kcal/mol of **5a** (the global minimum), and are predicted to be more stable than some of the Hückel isomers such as **6a**, **6b**, and **7a**. Three of these Möbius species—**8c**, **8d**, and **8e**—have the same configuration as **8a** (and are presumably in equilibrium with it), which is believed to be in equilibrium with **5a** in solution.

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(13) Δtrans = the change in number of trans C═C bonds.

(14) Interestingly, *trans*-**4** is computed to be lower in energy than **5a** at our highest level of theory, by ca. 2 kcal/mol. This suggests that [14]annulene **5a** would *not* predominate in an equilibrium mixture of these. However, analogous calculations pertinent to the case of Vogel and Müllen's system place dimethyl[14]annulene **1** ca. 12 kcal/mol lower than *trans*-dimethyldihydrooctalene. See Supporting Information for energies.

(15) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. v. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317.

(16) Johnson, S. M.; Paul, I. C. *J. Am. Chem. Soc.* **1968**, *90*, 643.

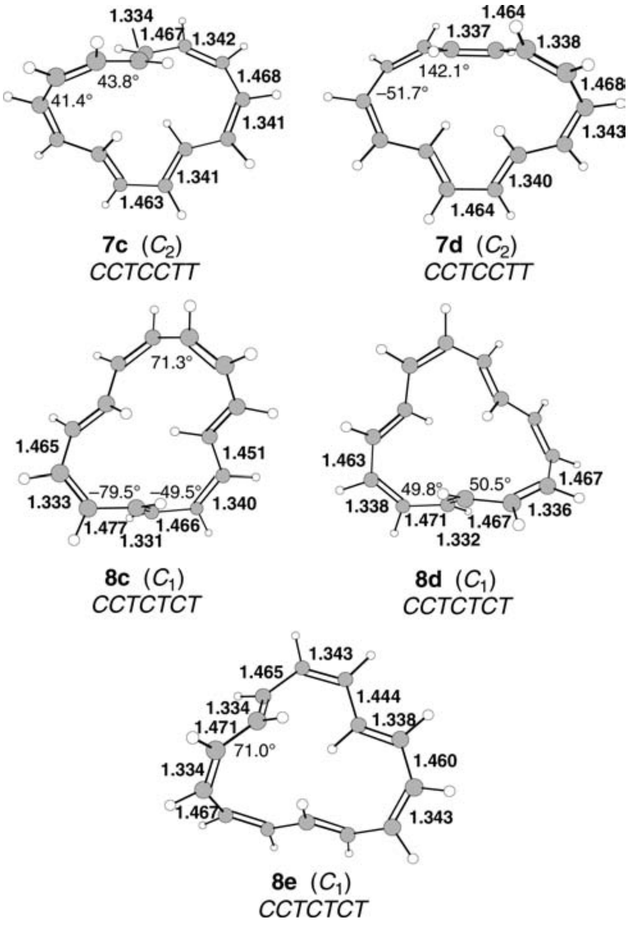

Figure 2. BHLYP/6-31G* structures of Möbius $C_{14}H_{14}$ conformational minima. Selected C−C distances (Å) and CCCC dihedral angles (deg) are shown.

Table 2. Relative Energies (kcal/mol) and Aromaticity Data for Selected Planar, Two-Twist, and Möbius [14]Annulenes[a]

species	sym	topology	CCSD(T)rel E	Δr	NICS(0)
5a	C_s	planar	0.0	0.098	−8.1
8a	C_1	planar	1.6	0.109	−5.5
6a	D_2	two-twist	10.8	0.011	−20.1
6b	C_2	two-twist	10.3	0.118	−9.9
7a	C_2	two-twist	17.5	0.114	−11.1
7c	C_2	Möbius	15.8	0.134	1.0
7d	C_2	Möbius	6.7	0.131	−0.6
8c	C_1	Möbius	8.3	0.146	−1.0
8d	C_1	Möbius	6.6	0.139	1.8
8e	C_1	Möbius	8.3	0.137	0.1

[a] All data obtained using BHLYP/6-31G* geometries. Relative energies computed with the cc-pVDZ basis set. Δr = difference between longest and shortest CC bond length (Å). NICS values computed at the GIAO-B3LYP/6-311+G** level.

In summary, the previously observed conversions of dihydrooctalene systems to the corresponding CTCTCTT-[14]annulenes must involve one or more thermal configuration change steps. These steps occur according to the bond-shift rule, and can take place via either two-twist or nearly planar conformations. At the CCSD(T)/cc-pVDZ//BHLYP/6-31G* level, the key bond-shift transition states studied here are 14−21 kcal/mol above the global minimum, resulting in activation energies comparable to those for other annulene configuration change reactions. Thus, in addition to π-bond shifting via Möbius conformations, planar and two-twist topologies are also likely involved in annulene cis/trans isomerizations. The proposed mechanisms include a role for the hitherto purely hypothetical CCCCCCT-[14]annulene with figure-eight topology (**6a**). Finally, several Möbius [14]annulene conformational minima are predicted to lie on or near the mechanistic paths presented, and within 6−9 kcal/mol of the global minimum **5a**, indicating that Möbius *minima* are relevant not only to [4n]annulenes, but also to the known chemistry of the [4n+2]annulenes.

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Supporting Information Available: Absolute energies and optimized Cartesian coordinates for all stationary points reported, details of other pathways explored, and full citation for ref 8. This material is available free of charge via the Internet at http://pubs.acs.org.

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