

[14]- AND [16] ANNULENE STRUCTURES

Castro and Karney¹ previously predicted a Möbius aromatic transition state for the π -bond shift in [12]annulene (see Chapter 2.4.3.1), a process they termed “twist-couple bond shifting”. In late 2006 they turned their attention to the conformational surface of [16]annulene, searching again for Möbius aromatic ground or transition states.²

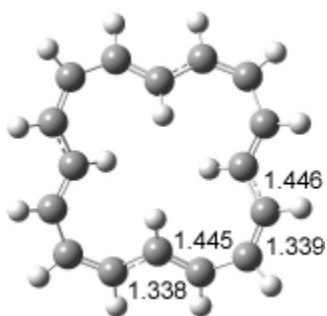
Oth synthesized [16]annulene by the photolysis of cyclooctatetraene dimer. He observed two isomers **1a** and **2a** in a 83:17 ratio³ at -140 °C, with a barrier⁴ of 10.3 kcal mol⁻¹ separating them. The ¹H NMR spectrum at -30 °C shows only one signal. The equivalence of all of the protons implicates rapid conformational changes and bond shifting, as suggested in Scheme 1. Also noted was that these conversions, including the configuration change from **1** to **2**, have barriers much lower than for the electrocyclization of Reaction 1 of about 22 kcal mol⁻¹.⁵

Following on the results from their [12]annulene study, Castro and Karney optimized geometries at BH&HLYP/6-311+G(d,p).

Since, as we discussed in Chapter 2.4.3.1, relative energies of annulene conformations are very sensitive to the computational method and basis set, they determined estimated CCSD(T)/cc-pVDZ energies, which I will call E_{est} , according to a prescription proposed by Bally and MacMahon,⁶ namely

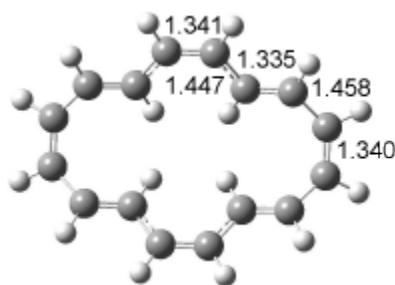
$$E_{\text{est}} = E(\text{HF}/\text{cc-pVDZ}) + \frac{E_{\text{corr}}(\text{MP2}/\text{cc-pVDZ})}{E_{\text{corr}}(\text{MP2}/6-31\text{G(d)})} E_{\text{corr}}(\text{CCSD(T)}/6-31\text{G(d)})$$

The optimized structures of **1a** and **2a** are drawn in Figure 1. Both molecules are not planar, their bond lengths are clearly alternating, and their NICS(0) values are +6.4 ppm (**1a**) and +7.3 ppm (**2a**), all evidence that neither molecule is aromatic. **1a** is predicted to be 0.8 kcal mol⁻¹ lower in energy than **2a**, consistent with experiment.



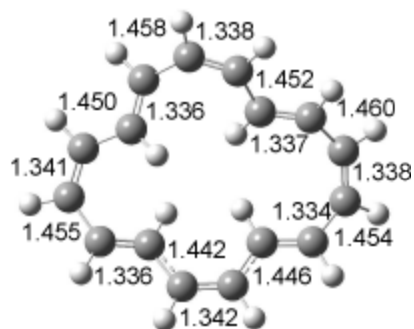
1a (0.0)

[xyz file](#)



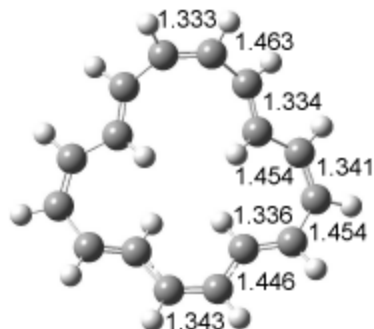
1b (5.6)

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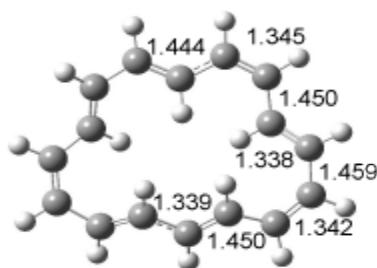
1c (5.4)

xyz file



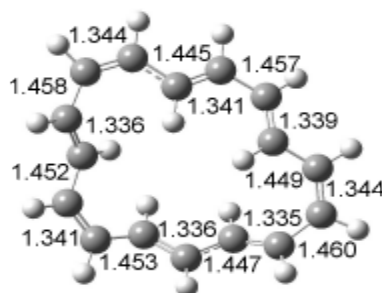
1d (7.7)

xyz file



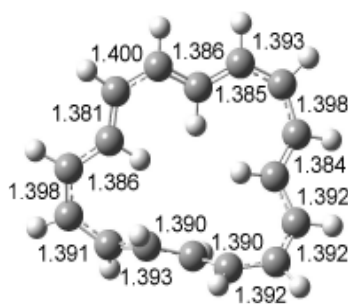
2a (0.8)

xyz file



2b (4.1)

xyz file



TS-1c2b (13.7)

xyz file

Figure 1. BH&HLYP/6-311+G(d,p) optimized geometries and relative energies (kcal mol⁻¹) based on E_{est} .²

The conformational change **1a** → **1a'** is a multi-step process. This is in contrast to [12]annulene where this change occurs via a concerted mechanism. So, **1a** first converts to **1c** through a barrier of 7.9 kcal mol⁻¹. The path now splits; **1b** can next be formed with a barrier of 9.4 kcal mol⁻¹ to give **1c'** or **1d** can be formed through a barrier of 7.7 kcal mol⁻¹ to produce **1c'**. **1c'** converts to **1a'** with a barrier of 7.9 kcal mol⁻¹. The structures of the intermediates and their relative energies are shown in Figure 1.

The conversion of **1** to **2** takes place through the transition state **TS-1c2b** that actually connects isomer **1c** to **2b**. This structure, shown in Figure 1, exhibits little bond alternation and has a NICS(0) value of -14.2, both strongly suggestive of Möbius aromatic character. Aromaticity should also imply energetic stabilization; **TS-1c2b** lies only 13.7 kcal mol⁻¹ above **1a**. This barrier is less than that predicted for the twist-coupled bond shift in either [10]annulene or [12]annulene.

The highest barrier for the various interconversions indicated in Scheme 1 is the barrier associated with **TS-1c2b**. This barrier (13.7 kcal mol⁻¹) is significantly *lower* than the activation energy for Reaction 1 (22 kcal mol⁻¹). These

computations confirm that the scrambling of the protons of [16]annulene is due to the rapid rearrangements of Scheme 1. Furthermore, the computations demonstrate that the key step is a twist-coupled bond shift that is facilitated by the Möbius aromatic character of its transition state.

Since the configuration change in [12]- and [16]annulene proceeds with a bond-shifting Möbius aromatic bond shifting transition state, might not the configuration change of [14]annulene proceed through a Möbius antiaromatic bond shifting transition state? In 2007, Castro and Karney⁷ answered this question in the affirmative.

Consistent with their previous studies, geometries were optimized at UBH&HLYP/6-311+G**. The unrestricted method is necessary since the expected antiaromatic transition state will have singlet radical character. In order to obtain reasonable energies, CASPT2(14,14)/cc-pVDZ single-point computations were employed.

[14]annulene must undergo two conformational changes (**3a-c**) before the bond shift/configuration change can occur through transition state **4** to give **5**.

Note that this process changes the number of *cis* and *trans* double bonds. This overall process is shown in Figure 2. The optimized structures of **3c**, **4**, and **5** are shown in Figure 3.

Figure 2. CASPT2(14,14)/cc-pVDZ// UBH&HLYP/6-311+G** relative energies of stable structures along the pathway for configuration change of [14]annulene.

The computed barrier for the configuration change (through **4**) is computed to be 19.3 kcal mol⁻¹, in very reasonable agreement with the experimental value⁴ of 21.3 kcal mol⁻¹.

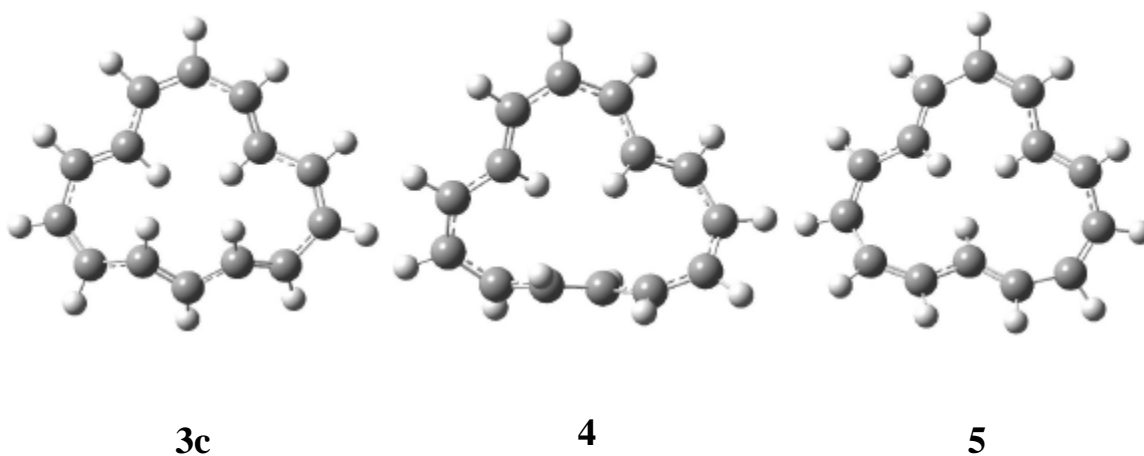


Figure 3. UBH&HLYP/6-311+G** optimized geometries of **3c**, **4**, and **5**.⁷

Based on its magnetic properties, transition state **4** has decided antiaromatic character. Its computed NICS(0) value is +19.0 ppm. Compare this to the NICS(0) values for **3a** and **5** of -8.0 and -5.0 ppm, respectively. In addition, the computed chemical shifts of the two interior protons are very downfield, 26.4 and 26.7 ppm.

Source: <http://comporgchem.com/blog/?p=16>