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[10]Annulene: Bond Shifting and Conformational Mechanisms for Automerization

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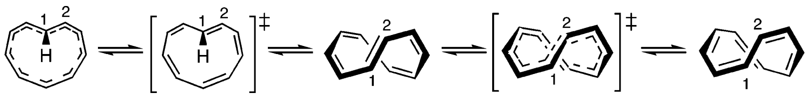

We report density-functional and coupled-cluster calculations on conformation change and degenerate bond shifting in [10]annulene isomers **1**−**5**. At the CCSD(T)/cc-pVDZ//CCSD/6-31G level, conversion of the twist (**1**) to the heart (**2**) has a barrier of 10.1 kcal/mol, compared to $E_a = 16.2$ kcal/mol for degenerate "two-twist" bond shifting in **1**. Pseudorotation in the all-cis boat isomer (**3**) proceeds with a negligible barrier. The naphthalene-like isomer **4** has a 3.9 kcal/mol barrier to degenerate bond shifting. The azulene-like isomer **5** is the only species for which the nature of the bond-equalized form (**5-eq**) depends on the method. At the CCSD(T)/cc-pVDZ//CCSD/6-31G level, **5-eq** is 1.2 kcal/mol more stable than the bond-alternating form **5-alt**. Conversion of **5-eq** to **4** has a barrier of 12.6 kcal/mol. Despite being significantly nonplanar, both **5-eq** and the transition state for bond shifting in **4** are highly aromatic based on magnetic susceptibility exaltations. On the basis of a detailed consideration of these mechanisms and barriers, we can now, with greater confidence, rule out **4** and **5** as candidates to explain the NMR spectra observed by Masamune. Our results support Masamune's original assignments for both isolated isomers.

Introduction

The rich history of [10]annulene reflects the keen interest chemists have had over the years in testing Hückel's [4*n*+2] rule.[1] This is the smallest [4*n*+2]annulene that can adopt a variety of conformational and configurational isomers. Its synthesis and characterization have been complicated by the fact that numerous dynamic processes are available to it in solution even at low temperatures: bond shifting, conformational change, and valence isomerization to bicyclic compounds.

The early synthesis of [10]annulene by van Tamelen[2] was expanded by Masamune, who isolated two crystalline isomers at low temperature.[3] One of these isomers exhibited five peaks in both the ^{1}H and ^{13}C NMR spectra at −160 °C and only one peak at higher temperature (−40 °C). Masamune assigned this isomer to mono-*trans*-**1** and suggested that it interconverts with the nearly planar **2**. These are currently referred to as the "twist" and "heart", respectively. Bond shifting through the heart conformation, followed by conformational change, would eventually render all carbons and hydrogens magnetically equivalent. The other isomer exhibited only a single NMR peak from −160 to −40 °C and was assigned to **3**. Masamune proposed that **3** undergoes a facile pseudorotation, rendering all CH groups equivalent.

Since that work, numerous computational studies have appeared assessing the validity of these assignments.[4−6] In addition, [10]annulene has become a sensitive test case for the

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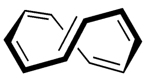
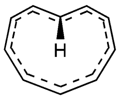
10.1021/jo0521450 CCC: $33.50


1 (C_2)
twist
CCCCT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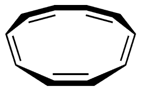
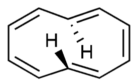
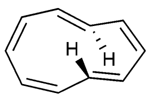
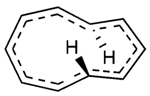
heart
CCCCT


3 (C_s/C_1)
boat
CCCCC


4 (C_2)
naphthalene-like
CCTCT


5-alt (C_1)
azulene-like
CCTCT


5-eq (C_2)
azulene-like
(bond equalized)

ability of theoretical methods to accurately predict the degree of π-delocalization as well as the relative stabilities of bond-equalized vs bond-alternating annulenes.[5b−e,6−9] Stanton and Schaefer showed that both MP2 and B3LYP overestimate delocalization in [10]annulene and hence erroneously predict the nearly bond-equalized (and hence aromatic) heart **2** to be more stable than the bond-localized twist **1**.[5d,e] In that work, the more computationally intensive CCSD(T)//CCSD(T) calculations revealed that **1** was the most stable, followed by the "naphthalene-like" structure **4** (rel $E = 1.40$ kcal/mol) and **2** (rel $E = 4.24$ kcal/mol).[10]

Both Wannere et al. and Orlova and Goddard have shown that the use of DFT methods with a larger HF component (such as BH&HLYP and KMLYP) provides [10]annulene relative energies that are largely consistent with those obtained by CCSD(T) methods.[7,8] Moreover, these methods provide geometries for [4n+2]annulenes that more accurately reflect ^{1}H NMR data (e.g., vs B3LYP geometries).[8,11] Finally, Price and Stanton simulated the ^{13}C NMR of **1**, **2**, and **4** at the CCSD(T) level of theory.[6] Analysis of these three isomers indicated that the twist form **1** matched most closely the observed five-peak NMR spectrum. Stanton drew no conclusions regarding Masamune's other isomer, noting only that its identity "remains a mystery".

Although the above studies probed minima on the [10]annulene potential energy surface (PES), none have explicitly addressed how these minima are connected. Alternative mechanisms that might account for the experimental NMR spectra have not been explored. In particular, we sought to determine (i) the detailed mechanism and barrier for interconversion of **1** and **2**, (ii) if nonplanar bond shifting might be a competitive process for automerization of **1**, and (iii) whether it would be possible for the naphthalene-like **4** or azulene-like **5** to play a role in the dynamic processes of [10]annulene in a manner consistent with the experimental results.

Computational Methods

Geometries were optimized at the BH&HLYP/6-311+G**[12,13] and CCSD/6-31G[14] levels. For all systems studied here, the CCSD/6-31G method predicts C−C bond lengths that are 0.02−0.03 Å longer than those computed with the BH&HLYP/6-311+G** method. For the bond-alternating species **1** and **4**, our CCSD/6-31G bond lengths for the short C−C bonds are within ±0.003 Å of the CCSD(T)/DZd distances reported by King et al.,[5e] and the bond lengths for the long C−C bonds are ca. 0.010 Å longer than the corresponding CCSD(T)/DZd distances, presumably because of the lack of polarization functions on carbon in the 6-31G basis set (Supporting Information, Figure S1). For the bond-equalized heart (**2**), the CCSD/6-31G C−C bond lengths are all within ±0.003 Å of their CCSD(T)/DZd counterparts.[5e] As a check on the influence of polarization functions, we also optimized **1** at the CCSD/6-31G* level. On the basis of deviations in C−C bond lengths, the CCSD/6-31G geometry of **1** is closer to the CCSD(T)/DZd geometry than is the CCSD/6-31G* structure (Supporting Information, Figure S1). Finally, CCSD(T)/cc-pVDZ single-point energies on BH&HLYP/6-311+G**, B3LYP/6-311+G**, and CCSD/6-31G geometries (and the CCSD/6-31G* geometry of **1**) reveal that the lowest absolute energies are obtained with the CCSD/6-31G geometries. Thus, of the methods that are feasible for these systems, we consider the CCSD/6-31G geometries to be the most reliable for determining relative energies and aromaticity assessment.

Because of limited resources, vibrational analyses were not performed for the CCSD geometries. Rather, vibrational frequencies were computed at the BH&HLYP/6-311+G** level on the BH&HLYP geometries. Single-point energies were computed at the BH&HLYP and CCSD geometries using the CCSD(T) method[14] with the cc-pVDZ basis set.[15] In these latter calculations, all T1 diagnostic values were less than 0.02, indicating that the single-configuration reference wave functions were adequate. Aromaticity assessment was done using magnetic susceptibility exaltation (MSE, Λ)[16,17] and Δr (difference between longest and shortest C−C bond). Magnetic susceptibilities (χ_M) were computed using the CSGT method[18] at the B3LYP[19]/6-311+G** level using both sets of geometries. Exaltations were taken as the difference between χ_M for a given species and that computed for **1**. All calculations were performed using Gaussian 98[20a] and Gaussian 03M.[20b] Structures were visualized with MacMolPlt,[21] and vibrational modes were visualized with Molden.[22] Unless otherwise noted, all energies reported in the text are those calculated at the CCSD(T)/cc-pVDZ//CCSD/6-31G + ZPE (BH&HLYP) level of theory.

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(11) Although the BH&HLYP method yields annulene geometries in which all C−C bonds are too short (e.g., compared to CCSD(T) geometries for [10]annulenes[5e]), it nevertheless does reasonably well at estimating the degree of delocalization in these systems (e.g., as manifested in Δr). For this reason, BH&HLYP is more reliable than B3LYP when the geometries obtained are to be evaluated for magnetic properties and aromaticity.

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TABLE 1. Relative Energies (kcal/mol) and Magnetic Susceptibility Exaltations (cgs-ppm) for [10]Annulene Stationary Points[a]

			BHH[b]			CCSD[c]		CCSD(T)//BHH[b,d]	CCSD(T)//CCSD[c,d]	BHH[b]	CCSD[c]
species	symmetry	config[e]	NI[f]	rel *E*	Δ*r*[g]	rel *E*	Δ*r*[g]	rel *E*	rel *E*	MSE[h]	MSE[h]
1	C_2	CCCCT	0	0.0	0.152	0.0	0.145	0.0	0.0	0.0	0.0
2	C_S	CCCCT	0	1.0	0.045	15.4	0.047	4.8	5.0	−47.9	−48.3
TS2ri	C_{2v}	CCCCT	1	1.2	0.047	16.2	0.051	5.1	5.4	−49.7	−50.6
TS12	C_1	CCCCT	1	9.3	0.145	16.1	0.134	11.7	10.1	−7.8	−30.4
TS1bs	D_2	CCCCT	1	19.0	0.015	26.6	0.013	16.1	16.2	−12.0	−11.2
3	C_2	CCCCC	0	2.7	0.154	4.1	0.148	5.8	5.4	+1.4	+1.9
TS3cf	C_S	CCCCC	1	2.7	0.149	4.2	0.146	5.8	5.4	+1.3	+2.0
4	C_2	CCTCT	0	1.3	0.136	3.3	0.140	0.9	1.7	−6.3	−2.0
TS4bs	C_{2h}	CCTCT	1	6.0	0.024	16.9	0.023	5.3	5.6	−32.6	−32.3
5-alt	C_1	CCTCT	0	5.0	0.117	8.9	0.157	5.3	7.5	−18.1	−0.7
5-eq	C_2	CCTCT	1	5.6	0.029	17.4	0.031	5.9	6.3	−33.1	−33.5
TS5cf	C_S	CCTCT	1	8.7	0.141	8.6	0.146	8.8	9.0	−7.8	0.0
TS45	C_1	CCTCT	1	17.7	0.119	22.7	0.154	18.0	18.9	−22.2	+2.4

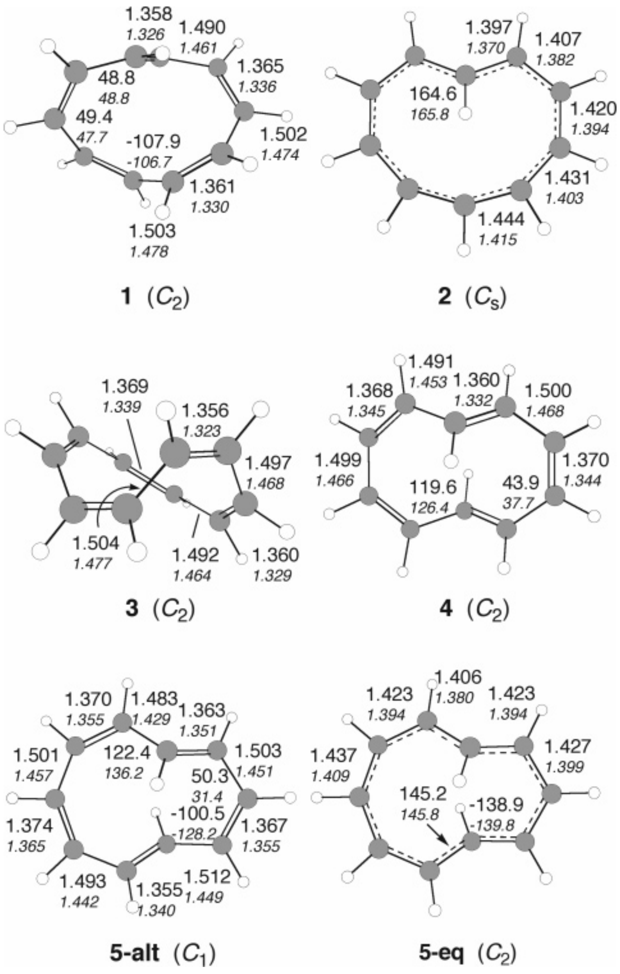
[a] In numbering of transition states for degenerate processes, ri = ring inversion, cf = conformation change, bs = bond shifting. All relative energies are corrected for differences in unscaled BH&HLYP/6-311+G** zero-point energies. [b] BHH = BH&HLYP/6-311+G**. [c] CCSD = CCSD/6-31G. [d] CCSD(T) = CCSD(T)/cc-pVDZ relative energy (kcal/mol) at the indicated geometry, ZPE corrected as described above. [e] config = configuration (C = cis, T = trans). [f] NI = number of imaginary vibrational frequencies based on BH&HLYP/6-311+G** vibrational analysis. [g] Δ*r* = difference, in Å, between the longest and shortest C−C bond. [h] MSE = magnetic susceptibility exaltation (Λ, cgs-ppm), relative to the magnetic susceptibility (χ_M) of **1**. Magnetic susceptibilities were computed with the CSGT method at the B3LYP/6-311+G** level, using the geometries indicated.

Results and Discussion

Table 1 gives relative energies of all stationary points. Figure 1 shows geometries of **1**−**5**, and Figure 2 shows geometries of the most important transition states. Structures not shown in Figures 1 and 2 are available in the Supporting Information.

To compare alternative mechanisms with those proposed by Masamune, it was first necessary to compute all barriers for the interconversions initially proposed. The transition state connecting the twist and heart isomers (**TS12**) is shown in Figure 2. Our calculations (Table 1) indicate that, although the heart **2** is quite bond equalized (Δ*r* = 0.047 Å), this conformational change proceeds via a bond-alternating transition state. Compared to the BH&HLYP geometry, the CCSD geometry for **TS12** has much smaller CCCC torsion angles and less bond alternation (Figure 2) and consequently sustains a moderate ring current based on the computed MSE (Table 1). Despite these geometric differences, the CCSD(T) barrier does not depend strongly on which of these geometries is used. The 10.1 kcal/mol barrier for **1** → **2** (and effectively for **1** → **1′**), i.e., for rendering all carbons equivalent, is consistent with the temperature dependence of the NMR spectrum found by Masamune. The energetics of this process are summarized in Figure 3.

Despite being only 5.0 kcal/mol above **1**, the heart **2** lies in a substantial potential well, with a 5.1 kcal/mol barrier to reversion to the twist. Thus, this mechanism (bond shifting in **1** via **2** as an intermediate) runs counter to the popular notion that bond shifting in annulenes occurs via a bond-equalized transition state rather than via a bond-equalized aromatic intermediate.[5,8,23] In addition, the completely planar heart isomer (**TS2ri**, Table 1, Supporting Information Figure S2) serves as a transition state for ring inversion (E_a = 0.4 kcal/mol), in agreement with earlier findings of Sulzbach et al.[5b]



1 (C_2) **2** (C_s) **3** (C_2) **4** (C_2) **5-alt** (C_1) **5-eq** (C_2)

FIGURE 1. Optimized structures of [10]annulene isomers **1**−**5**. CCSD/6-31G values (plain) and BH&HLYP/6-311+G** values (italics) of C−C distances (Å) and selected CCCC dihedral angles (°) are shown. The dihedral angles given are those that deviate most from planarity.

Although the above mechanism is consistent with the experimental data, we wished to explore an alternative. Following recent results on Möbius bond shifting in [12]annulene,[24] the possibility of a two-twist bond-shifting mechanism to rationalize the observed NMR behavior of **1** seemed attractive.[25,26] The transition state for this two-twist bond shifting

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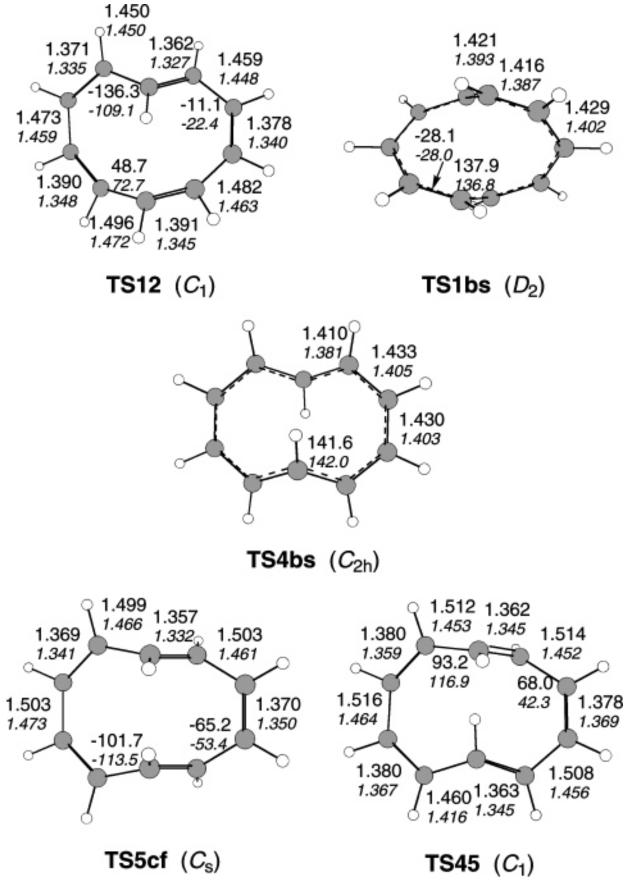

TS12 (C_1) **TS1bs** (D_2)

TS4bs (C_{2h})

TS5cf (C_s) **TS45** (C_1)

FIGURE 2. Optimized structures of transition states for bond shifting and conformational change in [10]annulenes. CCSD/6-31G values (plain) and BH&HLYP/6-311+G** values (italics) of C−C distances (Å) and selected CCCC dihedral angles (°) are shown. The dihedral angles given are those that deviate most from planarity. bs = transition state for degenerate bond shifting. cf = transition state for degenerate conformation change.

(**TS1bs**, Figure 2) connects degenerate forms of **1** with a barrier of 16.2 kcal/mol (Table 1, Figure 3). At our best level of theory, the barrier for two-twist bond shifting is 6.1 kcal/mol higher than that for the Masamune mechanism (**1** → **2** → **1′**). Thus, although not competitive in this case, our results suggest that (1) two-twist bond shifting is possible and may be competitive in more substituted systems which raise the barrier to the heart[25] and (2) two-twist bond shifting might be possible in other [4*n*+2]annulenes.[26]

Furthermore, the two-twist bond-shifting transition state **TS1bs** is unique: although very nonplanar, it still retains Hückel topology (zero sign inversions) and is potentially aromatic. Although Δr is small (0.013 Å), the MSE is also small (−11.2 cgs-ppm), indicating at best a modest ring current. Although the two largest CCCC torsion angles (ca. 42°) clearly diminish overlap in the π system, there are certainly other examples of clearly aromatic annulenes with torsion angles of this magnitude (vide infra).[24,27] The computed NICS(0) of −5.3 ppm is also small and may likely be due to local effects (e.g., the two π bonds pointing toward the ring center).[17,28] This appears to be the first example of a parent [4*n*+2]annulene with Hückel topology that is bond-equalized yet *not* highly aromatic. Inspection of the geometry of **TS1bs** provides no evidence for pyramidalization at the carbons; the sum of the three bond angles around any carbon is within 0.3° of 360.0°.

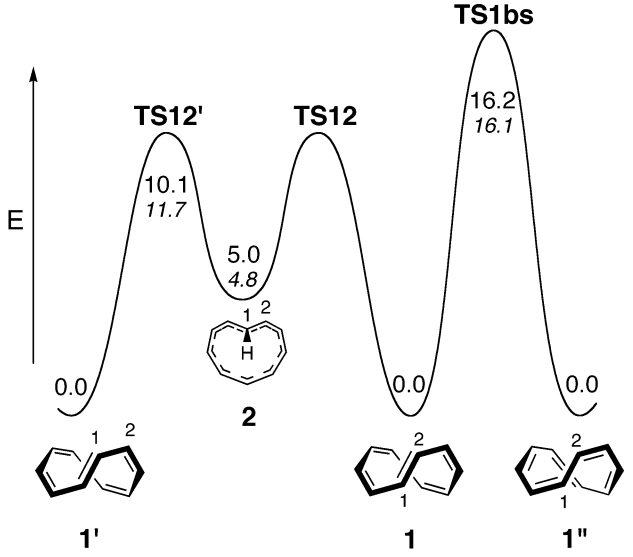

FIGURE 3. Potential energy curve (kcal/mol) for interconversion of the twist (**1**) and heart (**2**) isomers as well as for degenerate two-twist bond shifting in the twist isomer (via **TS1bs**). CCSD(T)/cc-pVDZ//CCSD/6-31G (plain) and CCSD(T)/cc-pVDZ//BH&HLYP/6-311+G** (italics) values are given.

In agreement with Masamune's proposal, the computed barrier for the pseudorotation in **3** (via **TS3cf**) is indeed negligible (Table 1). We find the minimum-energy structure to have C_2 symmetry (in contrast to earlier claims of C_S or C_1 symmetry;[4,5,8] see Figure 1), although both the C_2 and C_S forms are essentially isoenergetic.[29] The very flat energy surface clearly supports the idea that the nuclei in **3** can attain magnetic equivalence with no energetic cost.

Intrigued by alternative mechanisms that might account for the observed NMR data, we focused our attention on the energetically low-lying isomers **4** and **5**.[30] Assuming the minima corresponding to **4** and **5** are bond-alternating species, each of these can conceivably undergo degenerate bond shifting and possibly interconvert with each other via conformational change. In addition, **5** could undergo degenerate conformational change (Scheme 1). With appropriate barrier heights for these processes, **5** could be consistent with the NMR data assigned to **1** or **3**.

For example, in its bond-alternating form, **5** has ten unique CH units. However, if degenerate conformational change in **5** (Scheme 1) is fast on the NMR time scale, this would be reflected in only five ^{1}H or ^{13}C signals. In addition, if bond shifting in **5** has a somewhat higher barrier than conformational change, the combination of these two processes would render

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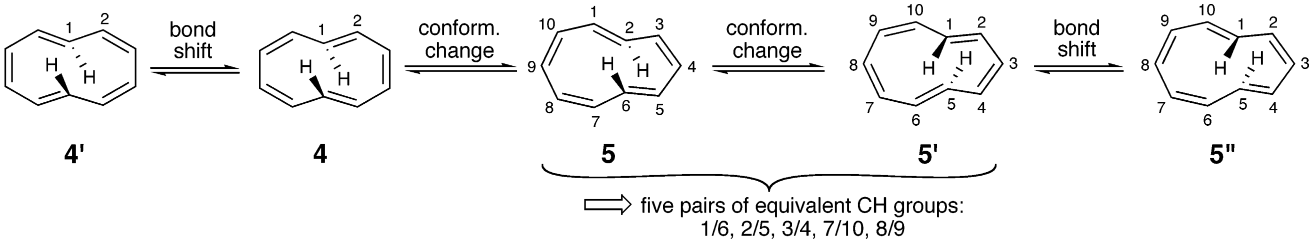
[28] NICS computed at the CSGT-B3LYP/6-311+G**//BH&HLYP/6-311+G** level.

[29] The flatness of the PES is also reflected by the low magnitude of the imaginary frequency for the C_S isomer (26.2i cm^{-1}) and the lowest vibrational frequency for the C_2 form (26.0 cm^{-1}).

[30] Masamune ruled out the possibility of **4** accounting for the magnetic equivalence of all nuclei on the basis of the belief that the processes involved would be highly unlikely. Instead, **4** would prefer to undergo permanent isomerization to a bicyclic compound.[3b]

SCHEME 1



all ten CH groups magnetically equivalent (Supporting Information, Scheme S1), resulting in a single NMR peak at higher temperature.[31] This temperature-dependent NMR would then suggest that **5**, *not* **1**, is responsible for the NMR spectra observed by Masamune. Alternatively, if both bond shifting and degenerate conformation change in **5** are especially facile, then the NMR results for **5** would be equivalent to those observed for **3**.

Both BH&HLYP and CCSD predict a strongly bond-alternating structure for the naphthalene-like isomer **4**, in agreement with the CCSD(T) results of King et al.[5e] The barrier to bond shifting via **TS4bs** is only 3.9 kcal/mol. Although the structure of **4** (C_2 symmetry) is qualitatively consistent with the observation of five NMR peaks at very low temperature, rapid bond shifting at higher temperatures would result in only three peaks. This is inconsistent with the observation of only one peak at the higher temperatures of the Masamune study; therefore, **4** can be ruled out.

Like [14]annulene and [18]annulene, the azulene-like isomer **5** is predicted to be bond equalized (**5-eq**) at the B3LYP and MP2 levels[5b] but bond alternating (**5-alt**) at the BH&HLYP level.[8] Using the BH&HLYP geometries, the CCSD(T) barrier to bond shifting in **5-alt** is only 0.6 kcal/mol (Table 1). Interestingly, at the CCSD/6-31G level, **5** is once again predicted to be bond equalized. With the CCSD/6-31G geometries, **5-eq** (Figure 1) is computed to be 1.2 kcal/mol *lower* in energy than **5-alt** (Figure 1, Table 1).

Conformational automerization of **5-eq**, via **TS5cf**, has a barrier of 2.7 kcal/mol. As mentioned above, this process renders all ten CH groups equivalent. Thus, the barrier to obtain magnetic equivalence for the nuclei in **5** is less than the 5 kcal/mol cutoff that Masamune reported would be necessary to explain the magnetic equivalence. Even at -160 °C, only one peak would be present in the NMR. This suggests that **5** might be responsible for the spectra Masamune attributed to **3**. Further probing of the [10]annulene PES, however, revealed that conformational conversion of **5** to **4** (via **TS45**, $E_a = 12.6$ kcal/mol) would be possible at the higher temperature (-40 °C) of the Masamune study. At temperatures that allow **4** and **5** to equilibrate, **4** would predominate. Again, rapid bond shifting in **4** would result in only three NMR peaks. This was not observed. As an additional argument against the involvement of **5**, our preliminary calculations indicate that **TS5cf** is extremely labile with respect to thermal electrocyclic ring closure, suggesting that irreversible ring closure would occur readily. Therefore, both **4** and **5** can be effectively ruled out as candidates for both of Masamune's isomers. Figure 4 summarizes the energetics for the relevant dynamic processes of **4** and **5-eq**.

The bond-equalized structures **TS4bs** and **5-eq** provide points of comparison for **TS1bs** in terms of aromatic character. Both **TS4bs** and **5-eq** are clearly aromatic based on Δr and MSE, despite having two or more torsion angles of ca. 40°. This degree of nonplanarity is comparable to that observed crystallographically by Scott et al. for an aromatic, bond-equalized homoazulene derivative[27] and further supports the idea that distortions up to this magnitude do not preclude strong diamagnetic ring currents.[32] In contrast, **TS1bs** is *not* strongly aromatic, despite having comparable torsion angles. However, for both **TS4bs** and **5-eq**, pyramidalization of two carbons (the two carbons bearing the inner hydrogens) is clearly evident on the basis of summation of bond angles. This pyramidalization facilitates greater p-orbital overlap than would be expected from considering only CCCC torsion angles. In the case of **TS1bs**, which is moderately aromatic at best, summation of bond angles indicates little or no pyramidalization, so the CCCC torsion angles accurately reflect the misalignment of p-orbitals.

Conclusions

We have used CCSD(T)/cc-pVDZ//CCSD/6-31G and CCSD(T)/cc-pVDZ//BH&HLYP/6-311+G** calculations to study the mechanisms of dynamic processes in several isomers of [10]annulene. For the most part, both of these methods give comparable energetic results, despite significant differences in geometries for particular species.

The computed barrier for conformational conversion of **1** to **2** is ca. 10 kcal/mol. This is consistent with Masamune's

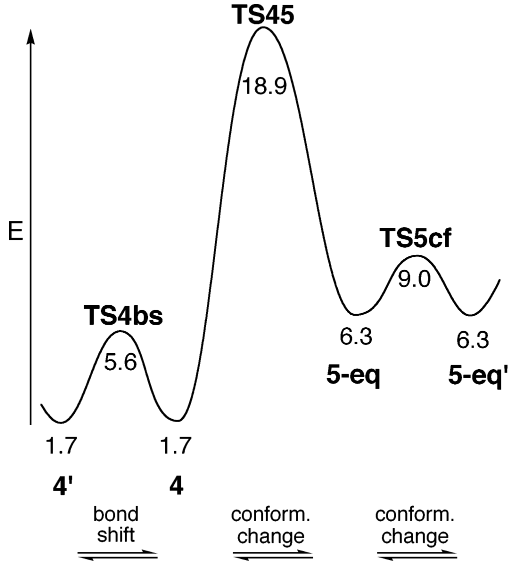


FIGURE 4. CCSD(T)/cc-pVDZ//CCSD/6-31G potential energy curve (kcal/mol) for bond shifting and conformational interconversions of **4** and **5**. Energies are given relative to the twist isomer, **1**.

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[31] For a detailed discussion of this type of analysis on other annulenes, see ref 23.

interpretation of early variable-temperature NMR spectra of [10]annulene. In addition, **1** can undergo two-twist bond shifting via a barrier ca. 6 kcal/mol higher than that for conversion to **2**, opening up the possibility that this latter mechanism might operate in substituted [4*n*+2]annulenes in which conformational barriers are raised. Interestingly, the transition state for the two-twist bond shifting was found not to be strongly aromatic, although it has a small Δr value and torsional angles comparable to other nonplanar aromatic annulenes.

Our results also indicate that bond shifting in naphthalene-like **4** is quite facile (E_a = 3.9 kcal/mol) and proceeds via an aromatic bond-shifting transition state, whereas azulene-like **5** is already bond equalized and aromatic according to CCSD(T)//CCSD data. Degenerate conformational change in **5-eq** is possible via a barrier of ca. 3 kcal/mol, making **5-eq** qualitatively consistent with the earlier NMR spectra assigned to **1**. However, had **5** been present in the earlier experiments, the conversion of **5-eq** to **4** (E_a = 12.6 kcal/mol) would have been observable under the experimental conditions. Because a three-peak NMR spectrum (corresponding to a rapidly bond-shifting **4**) was not observed in the early experiments, we can now, with greater confidence, rule out both **4** and **5** as candidates to explain the spectra observed by Masamune. These computational results support Masamune's original assignments for both **1** and **3**.

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Supporting Information Available: Scheme S1, Figures S1 and S2, absolute energies, computed magnetic susceptibilities, optimized Cartesian coordinates for all stationary points, and complete citation for ref 20. This material is available free of charge via the Internet at http://pubs.acs.org.

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(32) See also ref 24 for other highly aromatic bond-shifting transition states with large torsion angles.