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J. Am. Chem. Soc., **2005**, 127 (8), 2425-2432• DOI: 10.1021/ja0458165 • Publication Date (Web): 04 February 2005

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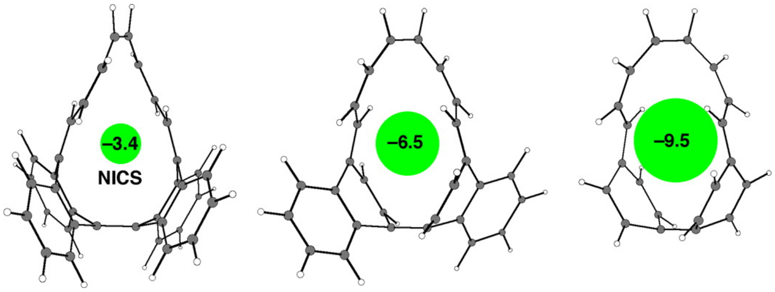

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Published on Web 02/04/2005

Investigation of a Putative Möbius Aromatic Hydrocarbon. The Effect of Benzannelation on Möbius [4*n*]Annulene Aromaticity

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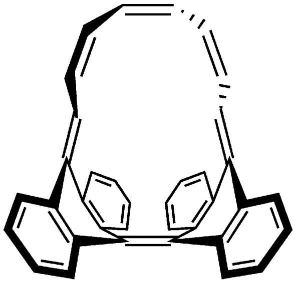
Abstract: The first experimental example of a [4*n*]annulene derivative with one Möbius twist, **1**, was synthesized recently [Ajami, D.; Oeckler, O.; Simon, A.; Herges, R. *Nature* **2003**, *426*, 819] and was purported to possess aromatic character. However, critical analysis of the published crystallographic data indicates that the Möbius [16]annulene core of **1** shows large bond alternation (Δr up to 0.157 Å). Delocalization in this core is inhibited by large dihedral angles, which hinders effective π overlap. This conclusion is supported by computational results (B3LYP/6-311+G**) on **1** and several less benzannelated derivatives, based on geometric (Δr, Δr_m, Julg A, HOMA) and magnetic (NICS, magnetic susceptibility exaltation) criteria of aromaticity. That benzannelation results in bond localization in the [16]annulene core is shown by additional computations on benzannelated derivatives of other Möbius aromatic species. Additionally, the aromatic stabilization energy (ASE) of **1** has been reinvestigated using two different procedures. Evaluation of uncorrected ISE$_{II}$ values of just the polyene bridge portion of **1** and its Hückel counterpart suggests that stabilization of **1** relative to its Hückel isomer is confined to the polyene bridge and is not due to a delocalized π circuit. Furthermore, application of s-cis/s-trans corrections lowers the ISE$_{II}$ value of **1** from 4.0 kcal/mol to 0.6 kcal/mol, suggesting that **1** is nonaromatic.

Introduction

The recent synthesis[1] of neutral hydrocarbon **1** having a Möbius [4*n*]annulene topology (enforced by the presence of a bianthroquinodimethane unit) has received well deserved attention.[2] This species provided the first opportunity to test Heilbronner's original prediction[3] on neutral [4*n*]annulenes experimentally.[4] Möbius [4*n*]annulenes should be aromatic if they are large enough to accommodate the small dihedral angle "twists" going from one carbon p orbital to the next around the annulene cycle. Small twists ensure that most of the π overlap is retained. Heilbronner suggested that [20]annulene might be the smallest [4*n*]annulene to be able to adopt a Möbius topology without a large attendant increase in bond angle strain.

Interestingly, **1** has a [16]annulene core and was characterized as being "moderately aromatic,"[1] thus apparently verifying Heilbronner's 40-year old prediction.[3] This conclusion was based primarily on two observations: the modest bond equalization through the polyene bridge ($\Delta r = 0.095$ Å, B3LYP/6-31G*) and the difference in the computed aromatic stabilization energies between **1** and a Hückel isomer, which was also isolated. Using the indene−isoindene isomerization energy (ISE$_{II}$)[5] method, Herges et al. determined that **1** was stabilized



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(4) (a) The first example of serendipitous preparation of a Möbius system, the cation $C_9H_9^+$, was not recognized originally by authors. The characterization of $C_9H_9^+$ as a Möbius aromatic was computationally revealed by Schleyer and co-workers.[4b] (b) Mauksch, M.; Gogonea, V.; Jiao, H.; Schleyer, P. v. R. *Angew. Chem., Int. Ed.* **1998**, *37*, 2395.

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by 4 kcal/mol, while the Hückel isomer was destabilized by 2 kcal/mol. Having explored the Möbius concept in related systems computationally,[6] we now subject the structure, bonding, and possible aromatic character of **1** and closely related systems to more extensive scrutiny.

Aromaticity is enjoying a renaissance.[7] This concept is being applied ever more widely, e.g., to inorganic and metallic element rings and clusters, which also possess "systems of delocalized electrons in closed circuits."[8] Akin to many key concepts in chemistry that cannot be measured directly or defined uniquely quantitatively, "aromaticity" is assessed best by invoking several criteria. This is especially true in cases for which the various "aromaticity criteria", geometric, energetic, and magnetic, do not agree and may be responding to different influences.[9] For example, a recent and especially pertinent study evaluated the computed geometries, energetics, and magnetic properties of Hückel $[4n+2]$- and $[4n]$-π electron annulenes to judge their aromaticity.[5,10] Changes in geometry from equalized to alternating C−C bond lengths only affected the energy to a minor extent but influenced the magnetic properties enormously.[5,10,11] Moreover, it is now recognized that a moderate degree of C−C bond length alternation does not preclude aromaticity.[11]

These results undermine, at least to some extent, traditional geometric criteria, such as the Julg parameter A[12] and the HOMA index,[13] which are used here to quantify aromaticity based on the degree of bond length equalization. In addition, Δr (the largest difference between single- and double-bond lengths) and Δr_{m} (the maximum deviation from the mean C−C bond length) still provide very useful indicators of the degree of aromaticity in systems such as **1**.

Aromatic stabilization energies are difficult to evaluate especially in strained systems, although effective strategies have been proposed recently. Schleyer and co-workers have developed "isomerization methods" (ISE and ISE$_{\mathrm{II}}$),[5,10,14] which give consistent stabilization energies and overcome the inadequacies and uncertainties of prior treatments when studying planar or nearly planar systems.[15] However, these methods have not been applied systematically to highly nonplanar systems, making it difficult to assess their validity when evaluating aromaticity for molecules with Möbius topology.

Arguably, magnetic properties based on the effects of induced "ring currents" are the most closely related to the essence of aromaticity. These criteria include magnetic susceptibility exaltations (MSE, Λ),[16] nucleus-independent chemical shifts (NICS),[17] ^{1}H NMR chemical shifts, and induced ring current density maps.[9b,11bc] However, all these methods have some drawbacks and interferences. For example, recently there has been a discussion on how accurately the chemical shifts of arene protons mirror the degree of aromaticity of the rings to which they are attached.[18]

Aromaticity of hypothetical neutral Möbius [4*n*]annulenes[6,19,20] and of the Möbius aromatic cation $C_9H_9^+$, for which there is experimental evidence,[4] has been assessed employing various criteria. Interestingly, the greater aromaticity of a Möbius $[4n]$-π electron system does not necessarily ensure that it will be more stable than its Hückel-topology counterparts.[6,19−21] Energies are very sensitive to bond angle strain, while magnetic criteria (NICS, Λ, proton NMR chemical shifts) are more sensitive to delocalization arising from ring current effects.

Because the structure of **1** contains multiple benzene rings fused to a [16]annulene core, it is reasonable to ask how benzannelation influences the aromatic character of the core. Clar's concept of the "aromatic sextet"[22] has been known since 1972. Based on extensive studies of polycyclic benzenoid hydrocarbons, Clar concluded that π electrons that are part of an aromatic sextet in a benzene ring should not be viewed as being easily shared with adjacent fused rings or as contributing to aromaticity in those fused rings. This concept was further developed by Cremer and Günther.[23] While Clar's focus was on benzenoid hydrocarbons, results for systems with benzenes fused to larger annulenes are consistent with Clar's conclusions.[24−28]

We have augmented the experimental data for **1**[1] with density functional theory[29] (DFT) computations of the geometric and magnetic properties of **1**. While these aromaticity criteria have been applied extensively to isolated systems with Hückel topology, this study will be the first application of these criteria to an *experimentally isolated* compound containing a Möbius [4*n*]annulene. In addition, a number of species related to **1** are included in order to elucidate their aromaticity. In particular,

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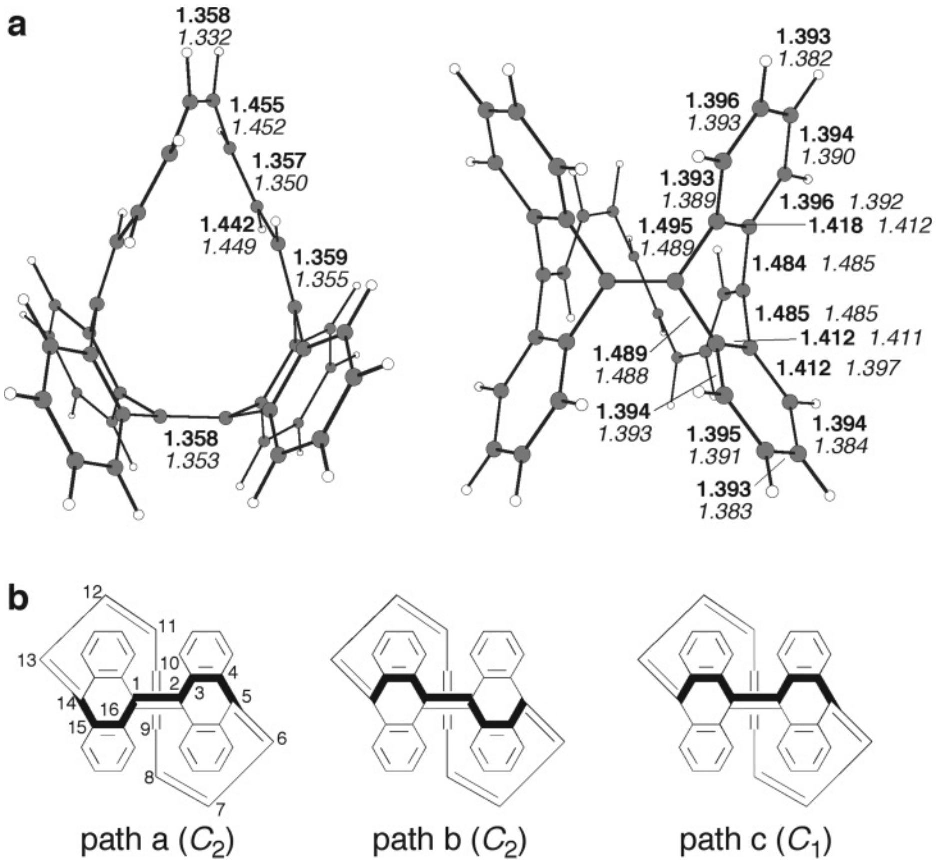

Figure 1. (a) Structure of the Möbius hydrocarbon **1** synthesized by Herges and co-workers.[1] B3LYP/6-311+G** optimized C−C bond lengths (bold) in Å. Bond lengths from the X-ray crystal structure of **1**[1] are in italics. (b) Possible paths through the bianthroquinodimethane section of **1**.

we have studied how benzannelation affects the degree of aromatic character in these Möbius [4*n*]annulenes. Finally, we have critically evaluated the use of the $\mathrm{ISE_{II}}$ method to obtain aromatic stabilization energies for **1**.

Computational Methods

All calculations were performed using the Gaussian 98 program.[30] Geometries were optimized using the B3LYP DFT method,[31,32] in conjunction with both the 6-31G* and 6-311+G** basis sets.[33] The structures reported here were obtained with the latter basis set, which includes one set of diffuse functions on carbon and one set of polarization functions on both carbon and hydrogen. Vibrational analyses were carried out at the B3LYP/6-31G* level using the B3LYP/6-31G* geometries. Unscaled zero-point energy corrections (ZPE), based on the B3LYP/6-31G* vibrational frequencies, were applied to the B3LYP/6-311+G** energies. Magnetic susceptibilities, χ_M, were computed at the CSGT[34]-B3LYP/6-311+G**//B3LYP/6-311+G** level. The magnetic susceptibility exaltations, Λ, were determined by subtracting χ'_M (derived from increment values[35]) from χ_M (computed for the system of interest). See Table 2 for details of derivation of increment values. Nucleus-independent chemical shift (NICS) values were computed at the GIAO[36]-B3LYP/6-311+G**//B3LYP/6-311+G** level. These were determined at the geometric center of the carbons forming the Möbius cycle and are referred to as NICS(0).

Results and Discussion

Structure 1. Figure 1a compares our B3LYP/6-311+G** optimized geometry of **1** with the C−C bond lengths determined from X-ray crystallography.[1] Based on B3LYP/6-31G* computations, Herges et al.[1] reported a 0.095 Å difference between the longest and shortest bond lengths (Δr) of the polyene bridge segment (C5−C14; see Figure 1b for numbering) and claimed that this supported the aromaticity of **1**. We obtain a $\Delta r = 0.098$ Å at B3LYP/6-311+G** for the polyene bridge. However, if the crystallographic data is used, the Δr value increases to 0.120 Å. Note that all three Δr values are larger than the $\Delta r = 0.078$ Å computed for the interior of a long chain conjugated linear polyene, $\mathrm{R{-}(CH{=}CH)_n{-}R}$.[5]

Rather than focusing on the polyene bridge, a more relevant way to assess aromaticity is to consider the *entire* [16]annulene circuit in **1**. There are three possible [16]annulene paths in **1** with Möbius topology, shown in Figure 1b: two with C_2

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Table 1. B3LYP/6-311+G** Analysis of the Geometries of **1**−**12**[a]

species	sym	NI[b]	rel E[c]	Δr[d]	Δr_m[e]	Julg A[f]	HOMA[g]
1							
path a	C_2	0		0.135	0.074	0.68	−0.02
path b				0.132	0.069	0.69	0.02
path c				0.135	0.075	0.68	0.02
path a	exptl			0.157[h]	0.085[h]	0.63[h]	−0.06[h]
[16]annulenes							
2a	C_2	1	28.3	0.131	0.066	0.68	0.20
2b	C_2	1	21.3	0.139	0.070	0.58	−0.04
2c	C_1	0	20.8	0.143	0.078	0.63	0.09
3	C_2	0	15.2	0.011	0.011	0.997	0.95
4	S_4	0	0.0	0.100	0.052	0.75	0.37
	exptl			0.158	0.081	0.57	0.03
derivatives of **2a** and **2b**							
5a	C_2	1	3.5	0.147	0.079	0.66	0.02
5b	C_2	0	0.0	0.152	0.079	0.61	−0.10
6a	C_2	0	1.6	0.118	0.069	0.70	0.21
6b	C_2	0	0.0	0.135	0.070	0.68	0.15
7	C_2	0		0.115	0.059	0.78	0.39
other species							
8	C_1	0		0.105	0.060	0.84	0.52
9	C_2	0		0.116	0.058	0.77	0.28
10	C_2	0		0.043	0.022	0.97	0.89
11	C_1	0		0.153	0.079	0.81	0.42
12a	C_2	0		0.152	0.092	0.67	−0.11
12b	C_2	0		0.112	0.077	0.89	0.43

[a] All structures were optimized using the B3LYP/6-311+G** method unless otherwise noted. [b] NI = number of imaginary frequencies, based on B3LYP/6-31G*//B3LYP/6-31G* vibrational analysis. [c] Rel E = relative energy, in kcal/mol, using B3LYP/6-311+G**//B3LYP/6-311+G** energies, and corrected for differences in B3LYP/6-31G* zero-point energies. [d] Δr = difference (in Å) between the longest and shortest C−C bonds. [e] Δr_m = maximum difference (Å) between the mean C−C bond length and either the longest or shortest C−C bond. [f] Computed by the method in ref 12. [g] Computed by the method in ref 13, using R_{opt} = 1.388. [h] Based on crystallographic data for **1** in the Supporting Information of ref 1.

symmetry (paths a and b) and one with C_1 symmetry (path c). The geometric indices for all three paths are virtually identical (Table 1), and thus we will restrict our discussion to results derived for path a. Earlier DFT calculations on numerous Möbius [4*n*]annulenes revealed that those with clear aromatic character, based on magnetic criteria, exhibited $\Delta r < 0.080$ Å, as well as Julg $A > 0.90$ and HOMA > 0.70.[6] However, at the B3LYP/6-311+G** level, the bond length alternation in the [16]annulene core of **1** (via path a) is large ($\Delta r = 0.135$ Å, $\Delta r_m = 0.074$ Å) while the *A* value (0.68) and HOMA index (−0.02) are small, suggesting that **1** does not possess a delocalized core.

Crystallographic data for path a also support a strong bond-localized structure. The Δr value here of 0.157 Å is very similar to that for the known [16]annulene **4**, (0.158 Å, Figure 2)[37] and for the methoxycarbonyl derivative of anti bismethano[14]-annulene (0.16 Å).[38] Neither of these reference compounds is considered to be aromatic. The crystallographic data for path a also yield a Julg *A* value of 0.63 and a HOMA value of −0.06.[39] Thus, these various geometric criteria do not support delocalization in the [16]annulene moiety of **1**.

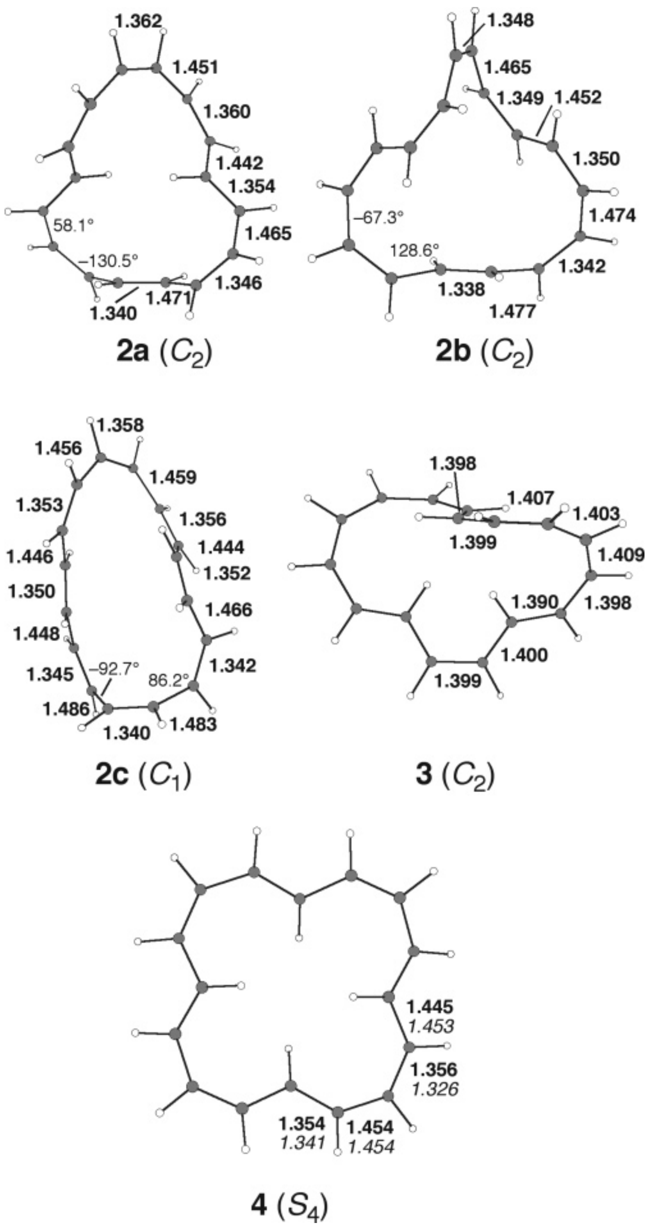

Figure 2. B3LYP/6-311+G** optimized geometries of three possible [16]-annulene cores, **2a**, **2b**, and **2c**, Möbius aromatic [16]annulene **3**,[6a] and the experimentally known S_4-symmetry [16]annulene, **4**. C−C bond lengths in Å. Selected CCCC dihedral angles are given for **2a**−**c**. Average C−C distances from the X-ray crystal structure of **4** are shown in italics.[37]

We have also investigated magnetic criteria to further probe aromaticity in this system. The computed NICS(0) value for **1**, −3.4 ppm (Table 2), is much smaller than −14.9 ppm obtained for the hypothetical Möbius [16]annulene **3**[6a] (Figure 2, vide infra) at the same level of theory (Table 2). While **3** is a hypothetical compound, it serves as a useful reference species, since it exhibits strong aromatic character according to a variety of criteria. In addition, the magnetic susceptibility exaltation (MSE, Λ) of **1**, calculated using an incremental approach,[35] is −30.0 cgs ppm, which, after corrections for the four benzene rings, is a large positive value (Λ_{corr}) of +19.6 cgs ppm. Granting the difficulties in evaluating the MSEs of molecules with this degree of complexity, this result provides no evidence for delocalization of the central annulene ring. Thus, the

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(37) Johnson, S. M.; Paul, I. C.; King, G. S. D. *J. Chem. Soc. B* **1970**, 643.
(38) Gramaccioli, C. M.; Mimun, A. S.; Mugnoli, A.; Simonetta, M. *J. Am. Chem. Soc.* **1973**, *95*, 3149.
(39) This HOMA value is much smaller than that (0.35) reported in ref 1, which evidently was based on B3LYP/6-31G* calculations using an R_{opt} value of 1.400 Å, rather than 1.388 Å as specified in ref 13. In addition, the reported HOMA value of 0.35[1] apparently was computed for the *entire* molecule (including all the benzene bonds) and not just the [16]annulene core.

Table 2. B3LYP/6-311+G** Computed Magnetic Properties for Species **1**−**12**[a]

species	NICS(0)[b]	$\chi_M{}'$[c]	χ_M[c]	Λ[d]	Λ_{corr}[e]
1	−3.4[f]	−230.5	−260.5	−30.0	+19.6
			[16]annulenes		
2a	−3.7	−106.5	−117.9	−11.4	−11.4
2b	−2.6	−107.5	−107.7	−0.2	−0.2
2c	−2.5	−107.5	−101.9	+5.6	+5.6
3	−14.9	−107.0	−177.5	−70.5	−70.5
4	+10.4	−106.0	−19.8	+86.2	+86.2
			derivatives of **2a** and **2b**		
5a	−2.4	−156.3	−172.0	−15.7	+9.1
5b	−2.8	−157.3	−174.9	−17.6	+7.2
6a	−6.5[g]	−180.7	−206.9	−26.2	−1.4
6b	−5.0[g]	−180.7	−201.8	−21.1	+3.7
7	−9.5[h]	−130.9	−155.2	−24.3	−24.3
			other species		
8	−8.3	−131.9	−172.2	−40.3	−27.9
9	−5.3	−156.8	−187.9	−31.1	−6.3
10	−11.5	−52.8	−70.0	−17.2	−17.2
11	−0.3	−77.7	−86.5	−8.8	+3.6
12a	+1.7	−102.6	−114.4	−11.8	+13.0
12b	+0.9	−102.6	−119.6	−17.0	+7.8

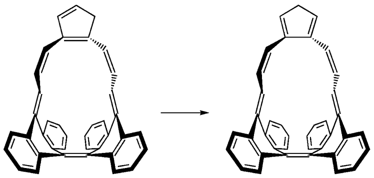
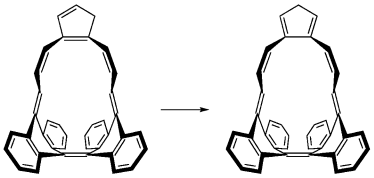
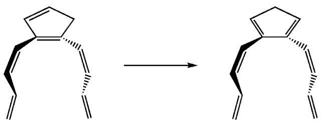
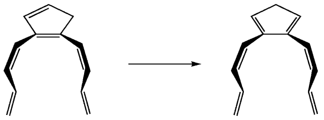
[a] All calculations were performed on B3LYP/6-311+G** optimized geometries. [b] NICS(0) values were computed at the center of the [16]annulene ring for species **1**−**9** and at the center of the nine-membered ring for **10**−**12**. For **1**, **5**, **6**, and **7**, the point used was the average of the coordinates for a C_2-symmetric 16-carbon pathway around the core. NICS calculations employed the GIAO method. [c] Magnetic susceptibilities were computed with the CSGT method. χ' values were determined using increments derived from reference species as follows: CH_3, −12.2 cgs-ppm, from ethane; *cis*-HC=CH, −13.5, from *cis*-2-butene − 2(CH_3); *trans*-HC=CH, −13.0, from *trans*-2-butene − 2(CH_3); trisubstituted >C=CH-, −12.5, from 2-methyl-2-butene − 3(CH_3); tetrasubstituted >C=C<, −11.4, from 2,3-dimethyl-2-butene − 4(CH_3); and CH^+, +1.2, from 2-propyl cation − 2(CH_3). [d] $\Lambda = \chi_M - \chi'_M$. [e] Λ_{corr} values were obtained using the formula $\Lambda_{corr} = \Lambda - n\Lambda(\text{benzene})$, where Λ(benzene) is the B3LYP/6-311+G** value for benzene (−12.4 cgs-ppm), and *n* is the number of fused benzenes in the system of interest. [f] For **1**, the NICS(0) value was computed at the center of path **a** (see Figure 1b). [g] Obtained using the 16-carbon path that avoids the benzene rings. [h] Obtained using the 16-carbon path analogous to path a in Figure 1b.

magnetic criteria, combined with the geometric data, do not support any significant delocalization in **1**.

As mentioned earlier, a comprehensive study evaluating the various ASE methods for Möbius systems (or *any* nonplanar systems) is lacking. Herges et al. reported an uncorrected ISE_{II} value (4.04 kcal/mol) for **1** and further indicated that this value is greater than that obtained for the Hückel isomer (−2.22 kcal/mol). The ASE of **1** computed by the ISE_{II} method (Table 3, entry 1) indeed matches the reported value of 4 kcal/mol. If this number reflects aromatic stabilization through the [16]-annulene core, then the ASE of 4.0 kcal/mol for **1** would correspond to only 0.25 kcal/mol per carbon in a 16-membered ring. This value is much smaller than the ca. 1.5 kcal/mol ASE per carbon, obtained via the same method, for aromatic annulene rings of similar size.[5,10]

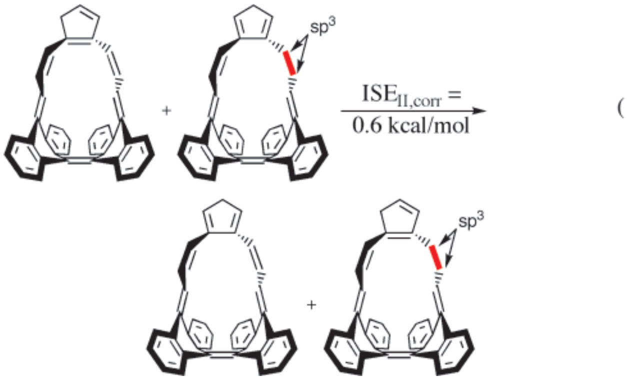
Interestingly, application of the ISE_{II} method to “Möbius” and “Hückel” *acyclic* models of the polyene bridge gave energies (Table 3, entries 3 and 4) comparable to those for the full systems (entries 1 and 2). Thus, it is difficult to conclude that the difference in isomerization stabilization energies between **1** and its Hückel isomer arises from aromatic stabilization. Rather, the difference in ISE_{II} values can be attributed to effects confined *within the polyene bridge* and not to the full cyclic π system.

Table 3. B3LYP/6-31G* ISE_{II} Values (kcal/mol) for **1** and Related Systems[a]

entry	topology	reaction	ΔE
1[b]	Möbius		4.0
2[b]	Hückel		–2.1
3[c]	Möbius		4.4
4[d]	Hückel		–2.9

[a] Energies are reported at the B3LYP/6-31G* level and are uncorrected for differences in zero-point energy. They are also not corrected for differences in s-cis and s-trans units, due to the nonplanar nature of the systems. [b] Structures were fully optimized at the B3LYP/6-31G* level. [c] Structures were partially optimized at the B3LYP/6-31G* level; within the main 10-atom polyene unit, all CCC angles and CCCC dihedral angles were frozen at the values of the corresponding parameters in the B3LYP/6-31G* optimized structure of **1**. [d] Structures were partially optimized at the B3LYP/6-31G* level; within the main 10-atom polyene unit, all CCC angles and CCCC dihedral angles were frozen at the values of the corresponding parameters in the B3LYP/6-31G* optimized structure of the Hückel isomer of **1**.

Moreover, Schleyer et al. have shown that the ISE_{II} values for planar [4*n*]annulenes usually decrease significantly when s-cis/s-trans corrections are applied.[5] These are needed since s-trans dienes are several kcal/mol more stable than s-cis conformations. When such corrections are applied to the ISE_{II} evaluation, (eq 1), the stabilization energy (B3LYP/6-31G*) of **1** decreases to 0.6 kcal/mol. A small ASE indicates that **1** is neither stabilized nor destabilized.



(1)

Why is **1** not aromatic, despite having Möbius topology? There are two simple answers. The first is that the overly large CCCC dihedral angles of **1** lead to poor overlap of the π system and thereby prevent effective delocalization. Both the computed and X-ray structures support this. For example, the computed structure exhibits dihedral angles of −109.0° (C1−C2−C3−C4; see Figure 1b) and 129.3° (C3−C4−C5−C6), while the corresponding values in the crystal structure are −107.7° and 131.3°, respectively. These deviate by ca. 70° and 50°, respectively, from the ideal ±180° value. These deviations are much greater than the largest deviation in **3** (ca. 30°).[6a] Despite the offsetting slight pyramidalization at C2 and C5, effective delocalization through these segments appears unlikely.

As expected, the fused benzene rings also contribute significantly to the nonaromatic character of the [16]annulene core of **1**, in accordance with Clar/Günther principles.[22,23] Clar showed that in polybenzenoid aromatics, the bond length alternation of an adjacent fused ring is increased when the aromatic sextet is retained in the first ring.[22] This effect, as well as a decrease in aromaticity (e.g., based on proton chemical shifts), has also been observed in benzo derivatives of higher [4*n*+2]annulenes.[24] Relevant examples include benzo[18]annulene,[25] benzo[14]-annulene,[26] benzo-dehydropyrenes,[27] and benzo-octadehydro-[14]annulenes.[28] Alternatively, the benzannelation effect might be rationalized in terms of the larger circuit. When a benzene is fused with an annulene ring, the "aromatic circuit" can then go around the entire enlarged outer perimeter. For computed [4*n*+2] Hückel (i.e., planar) systems, the ASE per carbon gets smaller when annulene rings increase in size;[10] it is more favorable energetically to "localize" six electrons in a benzene ring.[26] Hence, benzannelation diminishes the aromaticity of a larger annulene ring. These effects also should operate in Möbius systems. By inducing bond localization, benzannelation in Möbius systems could result in larger dihedral angles and further reduce the π overlap or the larger aromatic circuit might simply diminish the ASE per carbon.

[16]Annulenes 2−4. To assess the influence of benzannelation, we removed the sets of benzene substituents from **1** and evaluated the degree of aromaticity of the resulting species (Table 1). The three Möbius [16]annulenes (**2a, 2b, 2c**) are based on the possible paths (shown in Figure 1b) through the bianthroquinodimethane bridge. The computed structures are given in Figure 2, along with the highly aromatic, but experimentally unknown, Möbius [16]annulene **3**[6a] and the experimentally characterized Hückel [16]annulene **4**.[37]

The Δr values of the [16]annulene isomers (**2a−c**) in Table 1 reflect the same considerable degree of bond alternation as that in **1**. All the HOMA indices are small. The bond localization arises, in part, from the poor π overlap in the lower half of the molecules as shown in Figure 2. For example, the C1−C2 and C3−C4 bonds are very short, the C2−C3 bond is very long, and the C1−C2−C3−C4 and C3−C4−C5−C6 dihedrals deviate by at least 50° from ideal planar arrangement (see Figure 1b for the numbering key). In addition, while **2a** and **2b** clearly have Möbius topology, **2c** has two CCCC dihedrals that are very close to 90°, indicating that the latter has neither a Möbius nor a Hückel topology. Since the Δr and Δr_m values are also the largest for **2c** and its derivatives, these structures were excluded from further study.

The magnetic properties of **2a** and **2b** (Table 2), in general, support the geometric data. Although **2a** might appear to have some degree of aromaticity based on magnetic criteria (NICS-(0) = −3.7 ppm, and $\Lambda = -11.4$ cgs ppm), these values are inconsequential compared with those obtained for the highly aromatic Möbius [16]annulene **3** (NICS(0) = −14.9 ppm, $\Lambda = -70.0$ cgs ppm).

Neither **2a** nor **2b** are minima; both have one imaginary vibrational frequency[40] (Table 1) and are over 20 kcal/mol higher in energy than the known **4** (Hückel topology). They also are 6−12 kcal/mol higher in energy than the previously reported hypothetical Möbius **3**.[6a] These results suggest that the [16]annulene core of **1** does not prefer the Möbius twist inherently; this topology is adopted due to the constraints applied. As has been shown,[6,19] imposing Möbius topology on [4*n*]annulenes does not guarantee aromaticity.

Structures 5−7. We next consider several of the possible species intermediate between the [16]annulene cores **2** and the full system **1**. These include the benzannelated derivatives **5**, systems in which the polyene bridge is spanned by a bis-(benzocyclohexadiene) unit (**6**), and the biquinodimethane bridged species **7** (Figure 3).[41] The structural and magnetic aromaticity indices are given in Tables 1 and 2, respectively.

The bond lengths in **5a** and **5b** are similar to those in **2a** and **2b**, except that the C−C bonds adjacent to the benzenes in **5** are even longer than their counterparts in **2**, since the effect of the benzenes is to increase the adjacent dihedral angles. The geometric indices in Table 1 and the small NICS(0) values for **5a** (−2.4 ppm) and **5b** (−2.8 ppm) are characteristic of nonaromatic species. The corrected Λ values for **5a** (+9.1 cgs ppm) and **5b** (+7.2 cgs ppm) reinforce the conclusion that both are nonaromatic.

Incorporation of two ethylene bridges into **5a,b** leads to **6a,b**. Although **6** has benzene substituents, cyclic delocalization is now possible via the ethene bridges. While the localization effect due to benzannelation can, in principle, be avoided, our computational results show that this does not occur. The pyramidalization at the bottom two carbons in **6a,b** (as depicted in Figure 3) increases their separation to over 1.36 Å, i.e., by ca. 0.025 Å relative to **5a,b** (Figure 3). This increase does not necessarily imply greater delocalization, since the adjacent bonds toward the ethylene bridges remain long: 1.48 Å in both **6a** and **6b**. Neither the geometric parameters of **6a** and **6b** (Table 1) nor the corrected MSEs (−1.4 and +3.7 cgs ppm, respectively) suggest aromatic character. The modest NICS(0) values for these species (**6a**, −6.5 ppm; **6b**, −5.0 ppm) may be attributed to local effects, since the π orbitals of the C5−C6 and C13−C14 bonds point directly toward the ring center.

Finally, it is significant that **7**, which has no benzenes fused to its core, is the only structure derived from **1** that displays some aromatic character: **7** has the highest Julg and HOMA values (0.78 and 0.39) and a nontrivial MSE (−24.3 cgs ppm), as well as substantially negative NICS(0) (−9.5 ppm) and NICS-(1) values (−7.2 ppm, at a point 1.0 Å outward from the ring center[17b]). The two pyramidalized carbons (shown at the bottom of **7** in Figure 3) may allow enough overlap to sustain a modest ring current.

The overall aromaticity of species with bis(quinodimethane) bridges (**1**, **6**, and **7**) diminishes with the increase in the number

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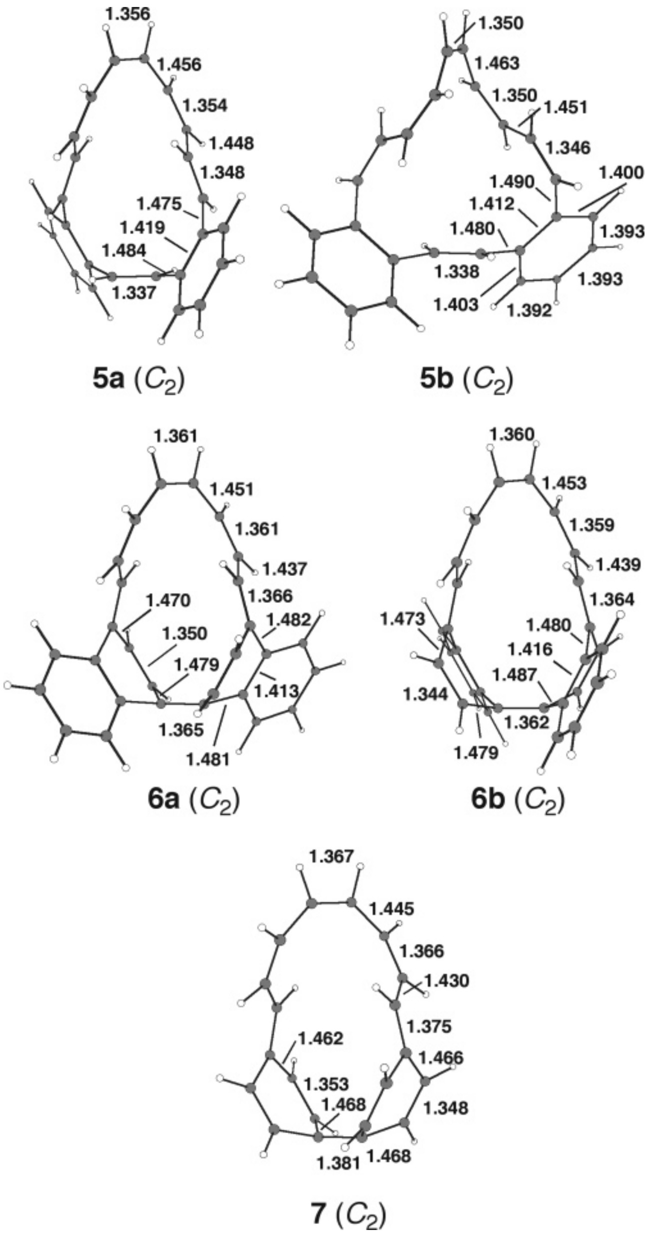
(40) The imaginary mode corresponds to rotation of the trans C1−C2 bond into the plane of the page. For **2a**, following the imaginary mode and reoptimizing yields a C_1 structure ca. 19 kcal/mol lower in energy. For **2b**, similar reoptimization affords a C_1 structure ca. 7 kcal/mol lower. These structures showed little evidence for aromaticity and were not pursued further.

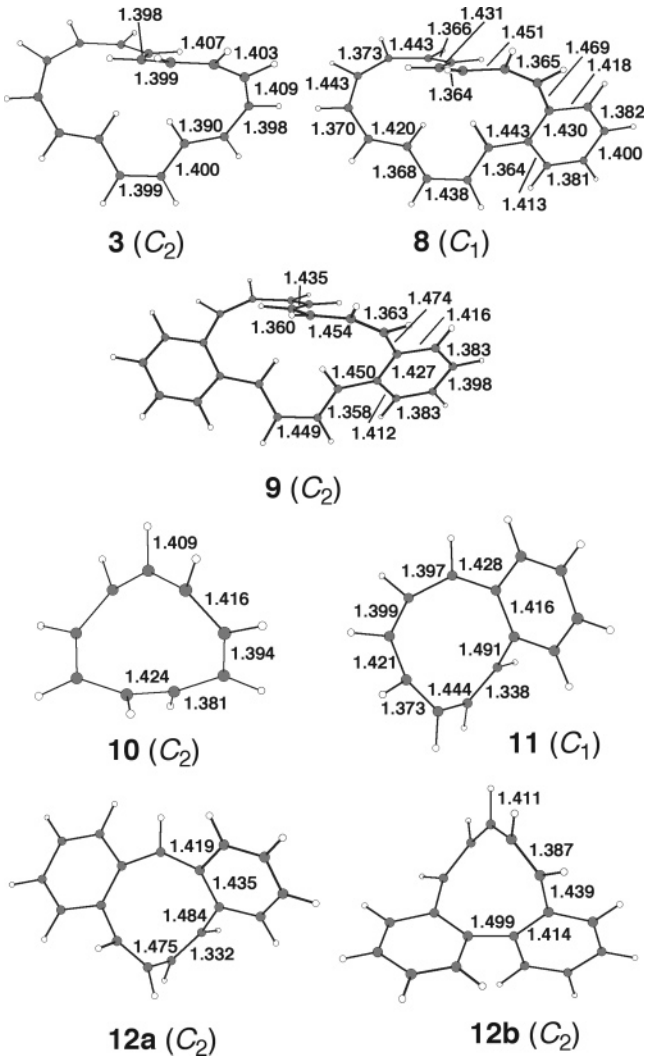


5a (C_2) **5b** (C_2)

6a (C_2) **6b** (C_2)

7 (C_2)

Figure 3. B3LYP/6-311+G** optimized structures of benzannelated and bridged derivatives of core structures **2a** and **2b**. C−C distances in Å.



3 (C_2) **8** (C_1)

9 (C_2)

10 (C_2) **11** (C_1)

12a (C_2) **12b** (C_2)

Figure 4. B3LYP/6-311+G** optimized structures of Möbius aromatic species **3** and **10** and their benzo-derivatives. C−C distances in Å.

of benzene rings fused to the core. These results are consistent with the explanation provided by "Clar effect".

Benzannelation of Möbius Aromatic [16]Annulene 3 and $C_9H_9^+$. To further probe the Clar effect on Möbius systems, we chose two Möbius structures, **3** and **10** (Figure 4), whose aromaticity has been established.[4b,6] The aromatic character decreases with increasing the number of benzene rings fused to **3**, as shown by both structural and magnetic indices (Figure 4, Tables 1 and 2).[42] The annelation of one benzene ring (as in **8**) increases overall bond alternation 10-fold, from 0.01 Å (for **3**) to 0.1 Å. The bond alternation effect, however, is more prominent on the side with the benzene attached ($\Delta r = 0.105$ Å) than on the opposite side (0.077 Å). The bond alternation of the benzene ring itself increases to 0.049 Å. The introduction of two benzene rings (as in **9**) further increases bond localization while concurrently reducing ring current effects. The 16-membered ring of **9** is essentially nonaromatic.

The effect of benzannelation is more dramatic in $C_9H_9^+$ (**10**), which, due to its charge, is delocalized to a considerable degree.[4b,6b] Fusion of a single benzene to various positions on **10** yields only a single monobenzo species, ion **11**, upon optimization (Figure 4). The loss of aromaticity in the nine-membered ring of **11** is shown by the pronounced bond-length alternation near the benzene ring and by both the NICS(0) (−0.3 ppm) and Λ_{corr} (+3.6 cgs ppm) values. The two representative dibenzo derivatives **12a** and **12b** also are nonaromatic. In all the derivatives of **10**, it is difficult to distinguish between Clar-type localization and the effect of benzannelation on dihedrals. While **12b** retains a Möbius topology, **12a** prefers a Hückel topology, and **11** is borderline.

Based on the behavior of the benzo derivatives of **3** and **10**, as well as other work on Hückel systems,[24−28] we conclude that benzannelation of Möbius aromatic annulenes largely destroys the aromatic character of the parent system **1**. Our only exception, **8**, still suffers a 50% reduction in aromatic character

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(41) For computational efficiency, we confined this part of the study to species with C_2 symmetry.

(42) Benzenes were placed at positions where the HCCH dihedrals in the parent system were close to 0° to ensure that any loss of delocalization was due to the "Clar effect" rather than to changes in the dihedral angles.

(based on magnetic criteria) due to the presence of only a single fused benzene ring.

Conclusions

There have been numerous examples in the extensive investigations of Hückel [4n+2]annulene systems[43] where the properties of an experimentally realized species (e.g., [10]-annulene) revealed that it was not aromatic. The achievement of Herges and co-workers in synthesizing **1**, a neutral [4n]-annulene derivative with Möbius topology through its [16]-annulene core, is an important milestone in the study of aromaticity. Unfortunately, our detailed investigation of this core using geometric, magnetic, and energetic criteria casts serious doubt on the aromaticity of **1**. Specifically, all geometric criteria employed here (Δr, Δr_{m}, Julg A, HOMA) point to a bond-localized structure, regardless of whether the crystallographic or the computed geometry is used. The presence of very large CCCC dihedral angles (e.g., −107.7° and 131.3°) minimizes effective π delocalization. In addition, this core by itself (without benzannelation) is not a minimum. Finally, computations on other Möbius systems (**3** and **10**) show that benzannelation clearly reduces the degree of bond-length equalization: sextet delocalization in the benzene rings dominates. This demonstrates that the "Clar effect" is applicable not only to Hückel but also to Möbius systems.

The magnetic properties of **1** and its derivatives give results consistent with the geometry evaluations. The small negative NICS values and negligible MSE do not indicate the presence of a significant ring current in the [16]annulene core of **1**. Calculations on less highly benzannelated derivatives of **1** afford similar results. The magnetic properties of **3** and **10** also show a dramatic decline in aromaticity upon benzannelation.

Because standard methods to determine aromatic stabilization energies have been confined to Hückel-type systems, it is difficult to evaluate the aromaticity of the nonplanar Möbius systems using existing energetic methods. However, our detailed analysis of the ISE$_{\mathrm{II}}$ results for **1** suggests that energy differences found between **1** and its reference Hückel isomer are due largely to variations in the polyene bridges. Moreover, the small *corrected* ISE$_{\mathrm{II}}$ value of 0.6 kcal/mol for **1** indicates that this molecule is devoid of any energetic stabilization.

Based on these results, taken collectively, we conclude that the [16]annulene core of **1** is nonaromatic and that any aromatic character of **1** is confined to the benzene rings. The goal of preparing an unambiguously aromatic neutral Möbius [4n]-annulene remains to be realized.

Acknowledgment. This paper is dedicated to the memory of Orville L. Chapman. This work was supported in part by National Science Foundation Grant CHE-0209857. C.C. and W.L.K. are grateful to the University of San Francisco Faculty Development Fund for financial support.

Supporting Information Available: Cartesian coordinates and computed energies for all optimized structures. This material is available free of charge via the Internet at http://pubs.acs.org.

JA0458165

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(43) Balaban, A. T.; Banciu, M.; Ciorba, V. *Annulenes, Benzo-, Hetero-, Homo-Derivatives, and Their Valence Isomers*; CRC Press: Boca Raton, FL, 1987; Vols. 1−3.