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Highly Aromatic Planar *all-cis*-[10]Annulene Derivatives

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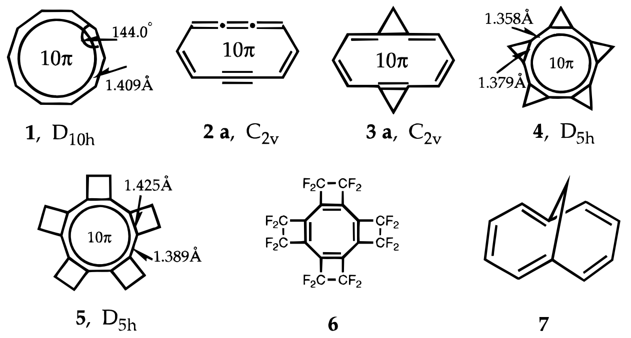
Ring strain precludes D_{10h} symmetry for the parent [10]-annulene (**1**).[2] The considerable 10π electron aromaticity of **1** is overwhelmed by the energy required to deform the CCC angles to 144°. We now describe strategies which take advantage of strain to overcome the planarity problem in simple *all-cis* derivatives of **1**. Our *ab initio* explorations have located and characterized several promising planar 10-membered-ring systems **2**−**5** (Scheme 1). Not only the theoretical structures and energies but also the computed magnetic properties demonstrate the considerable aromaticity in these "next higher" analogs of benzene.

Sworski[3] and Sondheimer[4] discussed the hypothetical 1,6-didehydro[10]annulene (**2**) as an attractive conjugated 10-membered-ring candidate.[2d] Sondheimer described **2** as a "substance formally derived from benzene by elongating two opposite bonds by the introduction of acetylene groupings". He favored a D_{2h} (**2**), rather than a classical, Kekulé structure formulation (**2a**, C_{2v}). The synthesis of **2** has been achieved recently.[4b,c] "The ^{1}H NMR chemical shifts show clear evidence of a diamagnetic ring current, supporting the notion that [compound **2**] is an 'aromatic' compound...."[4b] Unfortunately, **2** cyclizes rapidly at temperatures above 60 °C. We now report the structure of **2**, and characterize **3**−**5**, computationally.

While the angle strain in **2** is negligible, the "triple bonds" have several undesirable features. They are prone to side reactions, do not conjugate well, and in **2** result in unfavorable in-plane transannular p-orbital overlap[4] that causes a deviation (8°) of the acetylenic CCC angles from 180° (Figure 1).

These disadvantages can be overcome if cyclopropenes, instead of acetylene "spacers", are used for the benzene elongation. The HC═C bond angle in cyclopropene (ca. 151°) is not far from the 144° in **1**. Indeed, we find that the simple [10]annulene derivative **3** prefers a planar geometry. While the double bonds might also adopt the Kekulé cyclodecapentaene form (**3a**), the D_{2h} structure (**3**, Figure 1) is the only energy minimum.

Scheme 1. Planar *all-cis*[10]Annulene Derivatives **1**−**5**[a] as Well as Perfluorocyclobutano-Annulated Planar Cyclooctatetraene **6** and Vogel's 1,6-Methano[10]annulene **7**



[a] MP2(fc)/DZd geometry for **1** and Becke3LYP/DZd geometries for **4** and **5** are given.

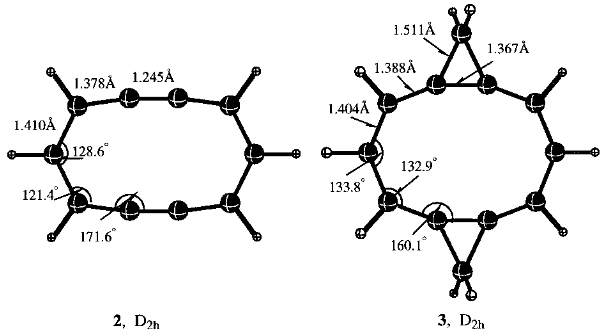


Figure 1. Bond lengths and bond angles for 1,6-didehydro[10]annulene **2** (D_{2h}) and 1,6-biscyclopropa[10]annulene **3** (D_{2h}) at Becke3LYP/DZd.

The design of our other candidates, **4**, and **5**, is apparent from the foregoing. The HC═C grouping in cyclobutene also is "splayed out" to 134°. Consequently, if five cyclopropene or cyclobutene rings are incorporated, the CCC angle strain in the [10]annulene ring is reduced and **4** and **5** are computed to be planar minima with D_{5h} symmetry (4-fold perfluorocyclobutano annulation results in a stable, planar cyclooctatetraene **6**).[5]

The most common criteria of aromaticity are structure and energy,[6] but the current ability to compute the diamagnetic susceptibility enhancement and the magnetic anisotropy facilitate their application as indicators for aromaticity.[7] Consequently, we have investigated the structures, energies, and magnetic properties of compounds **2**−**5** to probe their aromaticity. Density functional theory (Becke3LYP/DZd) as implemented in Gaussian94 was employed for full geometry optimizations and frequency calculations (**2**−**5** are minima, see supporting information).[8] We used Huzinaga's double-ζ (DZ) basis set in Dunning's contraction appended with a set of five d polarization functions ($\alpha_d = 0.75$, DZd).[9] While MP2 tends to overestimate and HF underestimates aromatic stabilization,[10] DFT gives more satisfactory results.[11] The magnetic properties were computed

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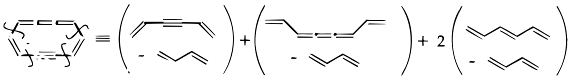
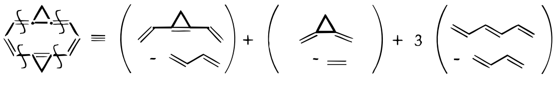
with a DZ basis set using Kutzelnigg's IGLO program[12] and with GIAO-SCF/6-31G* using Gaussian94.[8]

Both **2** and **3** have D_{2h}-symmetry minima. Except for the "triple" bonds in **2** (1.245 Å) and the three-ring CC bonds in **3** (1.367 Å), all CC lengths are between 1.378 and 1.410 Å, close to the CC bond length of 1.40 Å in benzene. Not only the geometrical but also the energetic criteria of aromaticity are met. The aromatic stabilization energies (ASE) correspond to the energy lowerings defined by homodesmotic reactions involving conjugated polyenes (eqs 1−4). To compute the strain in **2**−**5**, the polyene reference species also were computed at Becke3LYP/DZd with fixed angles corresponding to those in structures **2**−**5** (all the other parameters were optimized). The strain-corrected ASEs derived in this manner are 7.4 kcal/mol for **2** (eq 1) and 13.9 kcal/mol for **3** (eq 2).



2a

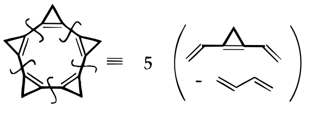
(1)



3a

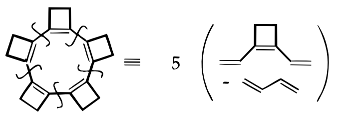
(2)

The aromaticities of **4** and of **5** are indicated by the 10-ring CC bond lengths: 1.358 and 1.379 Å in **4** as well as 1.389 and 1.425 Å in **5** (Scheme 1). Both of the lengths in **4** are remarkably short, and their alternation is small. The aromaticity of **4** and **5** also is manifested energetically. The strain-corrected ASEs are 18.5 kcal/mol for **4** and 23.0 kcal/mol for **5**. To compensate for the strain, the cyclobutene and cyclopropene reference molecules used to evaluate the ASE (eqs 3 and 4) were constrained to have the 144° C−C═angles as in **4** and **5**.



4

(3)



5

(4)

The aromaticity of **2**−**5** is also revealed by the large exaltation of the magnetic susceptibilities (Λ, the benzene value is −13.4[13]) and their anisotropies (χ_{anis}, the benzene value is −62.9).[14] Like the ASEs, eqs 1−4 can be employed to evaluate Λ for **2**−**5**. Table 1 also lists the total magnetic susceptibility (χ_{tot}) and its anisotropy.

Table 1. Calculated Total Magnetic Susceptibilities (χ_{tot}, ppm cgs), Anisotropies (χ_{anis}, ppm cgs), Exaltations (Λ, ppm cgs), Li^+ and the Nucleus Independent Chemical Shifts (NICS) at the Ring Centers (ppm), and the Aromatic Stabilization Energies (ASE, kcal/mol) of **1**−**5**, as Well as the Benzene Values for Comparison

	1[d]	**2**	**3**	**4**	**5**	benzene[e]
χ_{tot}[a]	−182.6	−163.7	−197.3	−216.1	−283.0	−68.1
χ_{anis}[a]	−215.9	−171.5	−207.2	−199.4	−161.8	−62.9
Λ[a]	−80.1	−52.7	−64.4	−38.1	−61.0	−13.4
δ Li^+ [a]	−18.9	−31.5	−24.1	−16.3	−14.2	−6.6
NICS[b]	−15.9	−17.3	−14.9	−10.8	−15.0	−11.5
ASE[c]	26.1	7.4	13.9	18.5	23.0	21.7

[a] At IGLO/DZ//Becke3LYP/DZd. [b] At GIAO-SCF/6-31G*//Becke3LYP/DZd. [c] At Becke3LYP/DZd. [d] Using the MP2(fc)/DZd geometry. [e] References 7c and 13.

The magnetic susceptibility exaltations of **2**−**5** (Table 1) are almost as large as that of the strongly aromatic hypothetical parent compound **1** (computed in D_{10h} symmetry) and exceed the Λ's for bicyclic 10 π electron systems: naphthalene (−28.2 ppm cgs) and Vogel's 1,6-methano[10]annulene (−46.0 ppm cgs, **7**).[15] The susceptibility anisotropies of **2**−**5** (Table 1) also are comparable to that of **1**.[2a]

Chemical shifts can be probed, e.g., by computing the chemical shifts of Li^+ placed on the center of **1**−**5**.[16] δ Li^+ are −18.9 ppm (**1**), −31.5 ppm (**2**), −24.1 ppm (**3**), −16.3 ppm (**4**), and −14.2 ppm (**5**). Such high-field shifts of nuclei in the middle of ring systems are typical for aromatic systems.[17] The nucleus independent chemical shifts (NICS) also can be evaluated by computing the magnetic shieldings at points in the center of the **1**−**5** rings (Table 1). Together with the diamagnetic susceptibility exaltation and the magnetic anisotropy, these data show that **2**−**5** fulfill all the magnetic criteria of aromaticity.

Although **2** is very unstable,[4b] **3**, **4**, and **5** are highly attractive candidates for experimental investigation. The synthesis of perfluorotetracyclobutacyclooctatetraene **6**, a stable planar molecule,[5] shows that systems like **4** and **5** should be experimentally accessible. Unlike **4** and **5**, **3** offers CH positions for studying the aromatic substitution chemistry.

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Supporting Information Available: Tables with absolute energies and zero-point energies of compounds **1**−**5** and of the reference compounds in eqs 1−4 which were used to evaluate the strain-corrected ASEs (1 page). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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