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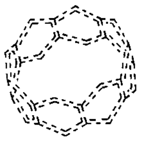
Structures, Magnetic Properties, and Aromaticity of Cyclacenes[**]

Hyuk Soon Choi and Kwang S. Kim[*]

The quest to design novel molecular architectures that are intellectually appealing and possess exciting physical and chemical properties has attracted the attention of a number of experimental[1] and theoretical chemists.[2] This has led to the postulation of a number of belt-shaped structures made up of laterally fused benzoid hydrocarbons such as cyclacenes (**1**), collarenes (**2**), and beltenes (**3**). While collarenes have been synthesized, the synthetic approaches to cyclacenes proposed by Vögtle[3] have stalled at the stage of their precursors.[4]



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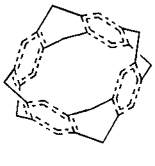

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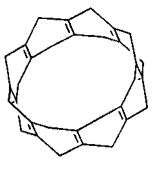

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Cyclacenes are of interest because of their remarkable structural similarity to carbon nanotubes and the possible utility of their cylindrical cavities in host–guest chemistry.[4] Hence, a detailed investigation of their physical and chemical properties could be a useful aid in the broader field of chemistry. The present theoretical study of [*n*]cyclacenes (where *n* refers to the number of fused benzene rings) reveals unusual electronic and magnetic properties, which can be associated with the peripheral rings of the structures being similar to two fused [2*n*]trannulenes (where *n* refers to the number of carbon atoms in the ring). This is in contrast to the original hypothesis of [*n*]cyclacenes having completely aromatic carbon skeletons.

Schleyer and co-workers have recently reported some interesting properties of [*n*]trannulenes (Figure 1a and b).[5] For $n = 4k+2$ (k = integer), [*n*]trannulenes favor aromatic singlet states of D_{nd} symmetry in which all C–C bond lengths are equivalent. On the other hand, for $n = 4k$, singlet states of D_n symmetry are antiaromatic and display C–C bond length alternation. These singlet states are only 5–7 kcal mol^{-1} lower in energy than the corresponding triplet states, which are stabilized by aromaticity. On a similar note, three possible valence isomers of D_{nh}, C_n, and D_n symmetry for [*n*]cyclacenes (Figure 1c–e) existing in either the singlet or triplet state can be considered.

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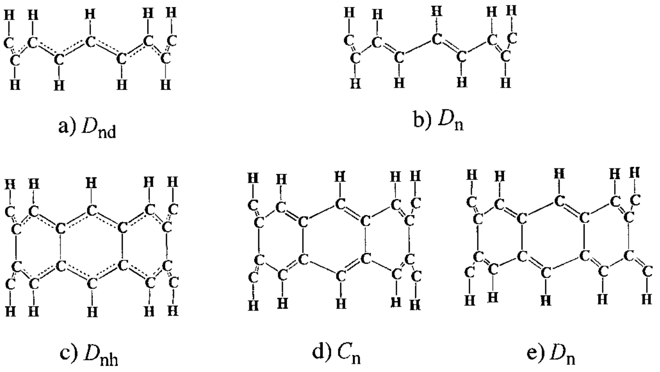

a) D_{nd} b) D_n c) D_{nh} d) C_n e) D_n

Figure 1. Possible valence isomers of [2n]trannulenes (a, b) and [n]cyclacenes (c–e).

We carried out unrestricted density functional calculations employing Becke's three parameters with Lee–Yang–Parr functionals (UB3LYP) and a 6-31G* basis set[6] for [n]cyclacenes ($n \leq 14$). The fully optimized geometries with minimum energy were confirmed to have D_{nh} symmetry by vibrational frequency analysis. The structures of the singlet and triplet states of [n]cyclacenes are very similar; the differences are within 0.01 Å in the bond lengths and 0.5° in the bond angles. Two C–C bond lengths, $r(CC_H)$ and $r(CC)$ (where C denotes a carbon atom bonded to other three C atoms, and C_H denotes a carbon atom linked to an H atom), show somewhat different values ($r(CC_H) = 1.40-1.42$ Å, $r(CC) = 1.45-1.47$ Å). The significant bond length alternation (BLA: 0.3–0.6 Å) in the benzene moiety indicates that the aromaticity of original building unit is broken due to the structural strain in the [n]cyclacenes. Since all values of $r(CC_H)$ are equal and very close to the C–C bond length of benzene, one can infer that the [2n]trannulene moieties in [n]cyclacenes show aromaticity, while the n C–C bonds are single-bond-like. Hence, these bonds seem to play a simple role as linkages connecting two [2n]trannulene moieties.

The properties of [n]cyclacenes described by the plots in Figure 2 show clear distinction between the cases of odd n ($=2k+1$) and even n ($=2k$) for integer k. [n]Cyclacenes with even values of n show greater stability in terms of building unit energy (E/n), shorter r(CC), smaller BLA, and much more negative magnetic property values (magnetic susceptibility (χ), magnetic susceptibility exaltation (Λ), and nucleus-independent chemical shift (NICS);[5, 7] see Table 1) along with distinctive patterns for the singlet–triplet energy gap (ΔE_{S-T}) and the HOMO–LUMO energy gap (ΔE_{gap}). As n increases, odd values of n favor triplet states more, while even values favor singlet states more. For [n]cyclacenes with even values of n, the ΔE_{S-T} is very small (≈ 1 kcal mol^{-1}), implying interesting magnetic properties. In addition, it is expected that at higher values of odd n the ΔE_{gap} quickly drops from about 2 eV (insulatorlike character for $n = 5$, 7) toward zero (metallike character for large n) with an intermediate value of around 0.6 eV (semiconductor character for $n = 13$). Meanwhile, at higher values of even n, the ΔE_{gap} decreases very slowly (semiconductor character of ca. 1 eV for $n = 6-14$).

Comparison of the calculated magnetic values of [n]cyclacenes and [2n]trannulenes[5] reveals that [2k+1]cyclacenes are almost nonaromatic: the aromaticity of two [4k+2]trannulene moieties is almost cancelled out. On the other hand, the triplet [2k]cyclacenes have aromaticity similar to the triplet [4k]trannulenes as well as similar magnetic property values. The singlet [2k]cyclacenes have nearly twice the aromaticity of the triplet [4k]trannulenes—the aromaticity of the two [4k]tran-

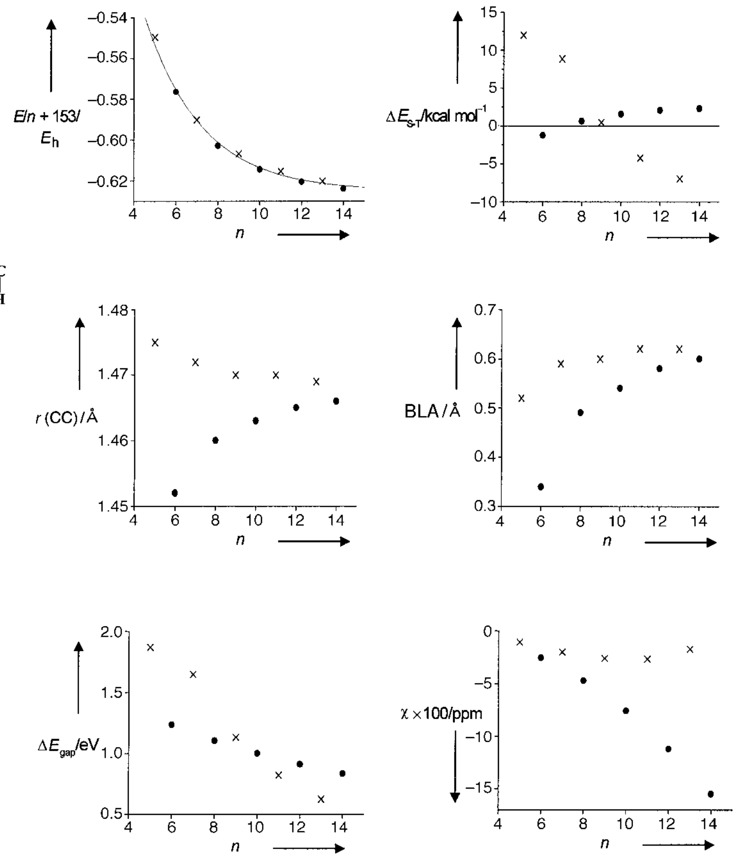

Figure 2. Building unit energy E/n (in hartree, E_h), ΔE_{S-T}, r(CC), BLA, ΔE_{gap}, and χ of [n]cyclacenes: odd n (×), even n(●).

Table 1. Values predicted (UB3LYP/6-31G*) for magnetic properties of [n]cyclacenes.[a]

n	χ[b]	Λ[b]	NICS[c]	δ^1H[d]
singlet				
5	−104	−12	−9.6	2.6
7	−199	−35	−10.4	1.7
9	−258	−47	−6.4	1.7
11	−265	−7	−2.3	1.3
13	−172	133	−1.7	−1.3
singlet				
6	−253	−113	−32.1	2.5
8	−469	−282	−31.8	1.2
10	−757	−523	−30.0	0.6
12	−1119	−837	−27.7	0.4
14	−1550	−1222	−25.4	0.4
triplet				
6	−177	−37	−16.1	4.5
8	−319	−132	−17.0	3.4
10	−506	−272	−16.7	2.8
12	−736	−455	−15.8	2.5
14	−1002	−675	−4.6	2.3

[a] The data of [n]cyclacene should be compared with those of [2n]trannulenes of Schleyer and co-workers.[5] [b] Units are in ppm. [c] NICS at the molecular center. [d] Relative to the signal for tetramethylsilane (σ^1H = 31.0).

nulene moieties is concerted—whereas the singlet [4*k*]trannulenes are antiaromatic. The aromaticity of the singlet [2*k*]cyclacenes is also evidenced from the small calculated δ^1H chemical shift (0.4–2.6 ppm upfield), which arises from the perpendicular orientation of the hydrogens in the diatropically shielded region over the ring faces of the [4*k*]trannulene moieties.

According to the Hückel rule, 4*k* π-carbon rings like [4*k*]trannulenes tend to have two singly occupied molecular orbitals (SOMOs), so the singlet states are nonaromatic and unstable. Thus, in [2*k*]cyclacenes, two [4*k*]trannulene moieties tend to be coupled strongly through 2*k* bonds, as seen from somewhat short r(CC) values. Then, the two SOMOs of one [4*k*]trannulene moiety couple with the two SOMOs of the other. These four SOMOs are split into two occupied and two unoccupied MOs, which include the HOMO and LUMO, and are separated by ΔE_{gap}. The HOMO and LUMO, which have *k* nodal planes on each [4*k*]trannulene unit, are distinguished by one nodal plane between the two [4*k*]trannulenes (Figure 3). Since the coupling of two [4*k*]trannulene moieties by 2*k* single-bond-like C–C bonds is somewhat weak, the ΔE_{gap} of [2*k*]cyclacenes is moderately small (≈ 1 eV), resulting in a very small $\Delta E_{\text{S-T}}$ value (≈ 1 kcal mol^{-1}). Thus, [2*k*]cyclacenes that are stabilized by strong aromaticity have interesting magnetic properties and behave as organic semiconductors.

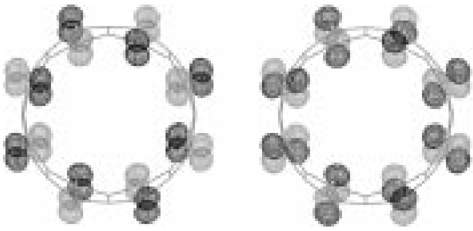

Figure 3. HOMO (left) and LUMO (right) of [8]cyclacene.

We thus find that the cyclacene family invites experimental exploration. Potential applications include utilization as ionophores, receptors, organic semiconductors, organic magnetic materials, and molecular electronic devices. Owing to well-defined cavities or rims (radius $= 0.3875n + 0.0664$ Å), [*n*]cyclacenes with even values of *n* are suitable to capture cationic guests through cation–π interactions.[2a, 8] An understanding of the electronic structure and magnetic properties of [*n*]cyclacenes, the simplest building units of (*n*,0) carbon nanotubes, may be useful in designing short carbon nanotubes and investigating their growth mechanisms.

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Total Synthesis of the Marine Natural Product 7-Deoxy-okadaic Acid: A Potent Inhibitor of Serine/Threonine-Specific Protein Phosphatases**

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Steven F. Sabes, and Craig J. Forsyth*

The naturally occurring marine toxin okadaic acid (**1**)[1] and its congeners present a widely recognized human health hazard due to their accumulation in edible shellfish.[2] Paradoxically, okadaic acid has also become an extremely valuable biomedical tool as the original member of a structurally diverse class of natural products that potently inhibit the serine/threonine-specific protein phosphatases 1 and 2A

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