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Theoretical Analysis of $[5.7]_n$Cyclacenes: Closed-Shell Cyclacene Isomers

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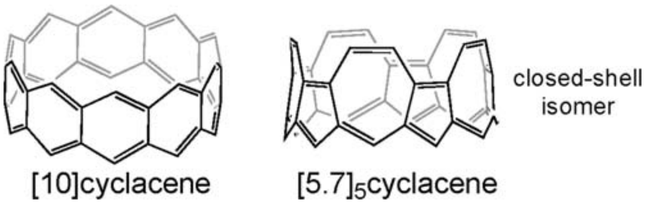
ABSTRACT



The $[5.7]_n$cyclacenes represent a novel class of all sp^2-hybridized carbon structures. In contrast to the isomeric [*n*]cyclacenes, $[5.7]_n$cyclacenes are predicted at the B3LYP/6-31G* level of theory to have stable, closed-shell singlet ground state configurations. Predicted geometries, electronic structures, band gaps, nucleus-independent chemical shift (NICS) values, and strain energies for this new family of cyclic conjugated molecules are presented.

Since Kekulé's description of benzene in 1865,[1] cyclic conjugated molecules have captivated the interests of chemists.[2] In particular, structures such as [*n*]cyclocarbons,[3] [*n*]cycloparaphenylacetylenes,[4] [*n*]cycloparaphenylenes,[5] [*n*]cyclophenacenes,[6] and [*n*]cyclacenes[7] with inwardly oriented π-systems[8] have extensively been explored theoretically and, in some cases, synthesized successfully. These unique structures have served as platforms to study aromaticity, magnetism, electron delocalization, and host–guest interactions.[9] In addition, these structures represent highly strained molecular targets that challenge existing synthetic methodologies.

More recently, many of these long sought after structures are finding renewed interest as subunits of carbon nanotubes (CNTs).[10] For instance, the [*n*]cycloparaphenylenes can be envisioned as subunits of armchair CNTs (Figure 1a) and

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the [*n*]cyclacenes as subunits of zigzag CNTs (Figure 1b). These two distinct types of carbon nanotubes have vastly different properties with zigzag CNTs behaving as semiconductors and armchair CNTs having metallic character.[11] Our research group is developing syntheses of these subunits of CNTs (e.g., cycloparaphenylenes) as a first step toward the rational, bottom-up synthesis of single-chirality CNTs.[5f,10]

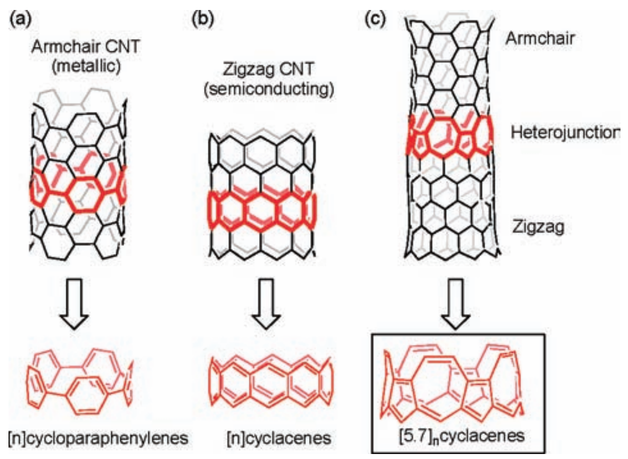

Figure 1. [*n*]Cycloparaphenylenes, [*n*]cyclacenes, and [5.7]$_n$cyclacenes are substructures of distinct types of CNTs.

With the bottom-up synthesis of CNTs serving as inspiration, we have become interested in a novel family of [*n*]cyclacene isomers—the [5.7]$_n$cyclacenes (Figure 1c). The nomenclature presented herein is as follows: "*n*" for [*n*]cyclacenes refers to the number of fused benzene rings, whereas "*n*" for [5.7]$_n$cyclacenes refers to the number of fused azulene ring systems. As illustrated in Figure 1, the [5.7]$_n$cyclacene structures represent seamless junctions bridging semiconducting and metallic CNTs and therefore are of significant interest.[12] Although "7,5 defects" are often observed in CNT structures, their rational preparation is an unsolved problem. In addition to their role as CNT junctions, we were drawn to these cyclacene isomers in that although azulenes are well studied isomeric structures of naphthalenes,[13] we were unaware of any studies related to the [5.7]$_n$cyclacenes.[14] In this Letter, we report several theoretically predicted properties of this new family of molecules using Density Functional Theory with the B3LYP functional and the 6-31G* basis set.

We modeled our approach to the theoretical analysis of the [5.7]$_n$cyclacenes after that by Houk and co-workers for the [*n*]cyclacenes.[7c] All geometries were optimized at the B3LYP/6-31G* level of theory using the Gaussian 03 program.[15] Singlet geometries were optimized with both restricted and unrestricted broken spin-symmetry (UBS) wave functions. In addition, band gaps were calculated with TD-DFT method[16] and magnetic susceptibilities were determined using the CSGT method. π-Orbital axis vector (POAV) angles were extracted from the minimized geometries using the Mol2Mol package.[17]

Based on our calculations, the electronic ground states of [5.7]$_n$cyclacenes ($n = 3-7$) are closed-shell singlets.[18] For all sizes investigated, the open-shell (OS) singlet relaxes back to the closed-shell (CS) singlet ground state. This result stands in sharp contrast to the [*n*]cyclacenes in which structures with $n > 5$ all have open-shell singlet ground states.[7c] Figure 2a illustrates the singlet–triplet energy gap for the [5.7]$_n$cyclacenes. In general, as *n* increases, the singlet–triplet gap narrows. Anomalously, the [5.7]$_3$cyclacene has a smaller singlet–triplet gap than [5.7]$_4$cyclacene. The closed-shell ground state of the [5.7]$_n$cyclacenes suggests these molecules may be more synthetically tractable than their isomeric cousins, which, despite numerous attempts, have yet to succumb to total synthesis.[7d−h]

The [*n*]cyclacenes have been described as two fully delocalized *trans* annulene systems linked by longer single bonds.[7b,c] We were curious as to whether the [5.7]$_n$cyclacenes would illustrate similar behavior—in this case, a *trans* annulene linked to a *cis* annulene. The [5.7]$_n$cyclacene optimized geometries show C_{nV} symmetry. Figure 2b illustrates the minimized geometry for [5.7]$_3$cyclacene with corresponding bond lengths.[18] The bond lengths along the bottom *trans* annulene portion of the molecule are virtually identical (1.42 Å) suggesting extensive delocalization of the π-system. The top edge (or *cis* annulene portion) of the molecule shows almost no delocalization. Alternating bond lengths of 1.38 and 1.34 Å suggest isolated alkenes. As the [5.7]$_n$cyclacenes increase in size, the bond length alternation along the top edge decreases suggesting greater delocalization of the π-system with increasing size.

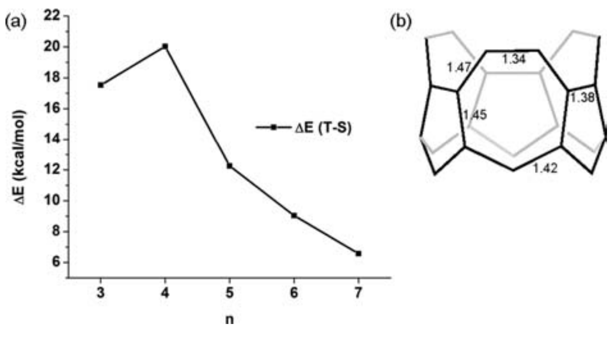

Figure 2. (a) Difference in energy between the triplet state and singlet closed-shell ground state of the [5.7]$_n$cyclacenes and (b) minimized geometry of [5.7]$_3$cyclacene (bond lengths in Å).

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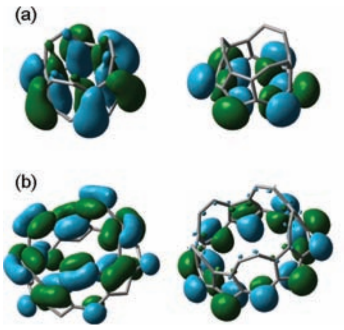
Interestingly, when considered as isolated annulenes or together, the [5.7]$_n$cyclacenes contain a 4n number of π-electrons (antiaromatic). In order to probe the aromaticity of these structures, NICS values[19] were calculated at the geometric center of the molecule and the center of the bottom trannulene (Figure 3). For n = 3, the NICS values are close to zero, indicating the molecule is nonaromatic. For $n \geq 4$, the NICS values become more negative with increasing size. We hypothesized that the lack of antiaromatic behavior is due to coupling of the trans annulene system to the isolated alkenes along the top rim. To support this hypothesis, we evaluated the NICS values of a similar structure wherein the upper rim was saturated (Supporting Information Figure S7).[17] Accordingly, the NICS value for this structure was found to be +72 ppm indicating strong antiaromaticity.

n	NICS, middle	NICS, bottom
3	3.01	8.44
4	-4.13	-0.56
5	-11.32	-9.73
6	-14.32	-13.39
7	-14.40	-14.31

Figure 3. NICS values for [5.7]$_n$cyclacenes.

Figure 4 depicts localization of the frontier molecular orbitals.[17] The LUMO for all [5.7]$_n$cyclacenes is localized along the *trans* annulene portion of the molecule. Interestingly, for sizes n = 3 or 4, the HOMO is localized vertically along the single bonds, with the larger coefficient lying along the bottom rim (*trans* annulene). For larger sizes where $n \geq 5$, the localization of the HOMO is along the *cis* annulene portion of the molecule. Distinct localization of the HOMOs and LUMOs may allow for the site selective derivatization of these molecules.

Figure 4c presents predicted band gaps for the [5.7]$_n$cyclacenes. The [5.7]$_n$cyclacenes have band gaps that classify them as organic semiconductors. As n increases from 3 to 7, the band gap decreases from 2.2 to 1.12 eV. For comparison, the band gap of hexacene is approximately 1.8 eV but is unstable due to its open-shell ground state.[20] [5.7]$_4$cyclacene is calculated to have a similar band gap (1.93 eV), but a closed-shell ground state.



(c)

n	band gap, eV
3	2.20
4	1.93
5	1.51
6	1.31
7	1.12

Figure 4. HOMO (left) and LUMO (right) localization for (a) [5.7]$_3$cyclacene and (b) [5.7]$_5$cyclacene, and (c) band gaps for [5.7]$_n$cyclacenes.

The strain energy (SE) of bent sp^2-hybridized molecules such as the [5.7]$_n$cyclacenes is a significant challenge to their synthesis. We explored the strain energy of these structures using two different methods: (1) homodesmotic reactions[21] and (2) π-orbital axis vector angles (POAV)[22]

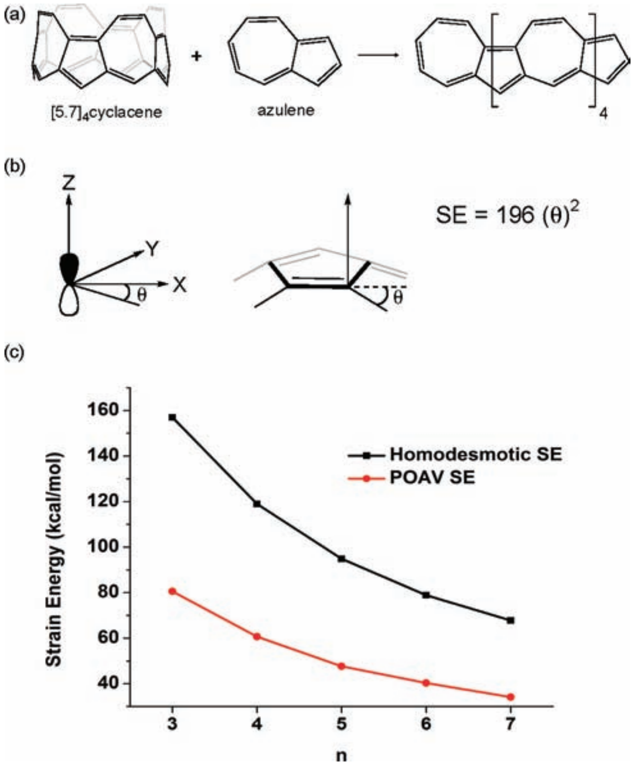


Figure 5. (a) Representative homodemosmotic reaction, (b) method of POAV analysis, and (c) strain energies of the [5.7]$_n$cyclacenes.

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(17) This program is available for download at http://www.gunda.hu/mol2mol/index.html.

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analysis (Figure 5). Both methods have been utilized to assess strain energies for other bent sp^2-hybridized structures. Following the approach used for the [*n*]cycloparaphenylenes,[23] we formulated homodesmotic reactions that conserved the number and types of each bond and atom found in the $[5.7]_n$cyclacenes (Figure 5a). For POAV analysis, we estimated the strain energy resulting from pyramidalization using the equation shown in Figure 5b, where θ is the distortion of the σ-framework from its ideal sp^2-hybridized geometry. The calculated strain energies for both methods are shown in Figure 5c. Not surprisingly, the $[5.7]_n$cyclacenes become less strained with increasing *n*. In all cases, the homodesmotic reaction approach leads to higher strain energies than POAV analysis. $[5.7]_3$cyclacene has the highest POAV distortion of 12.4°.[17] For comparison, the degree of pyramidalization of $[5.7]_3$cyclacene (12.4°) is similar to that found in tetraindenocorranulene (12.6°), a highly bent sp^2-hybridized molecule that has been recently synthesized.[24,25]

In summary, we have computationally investigated a novel class of all sp^2-hybridized carbon macrocycles—the $[5.7]_n$cyclacenes. In contrast to [*n*]cyclacenes, the $[5.7]_n$-cyclacenes are predicted to be stable with closed-shell singlet ground states.[26] Predicted band gaps suggest that these molecules are promising new organic semiconductors. Furthermore, the $[5.7]_n$cyclacenes represent a substructure of CNTs capable of connecting a metallic and semiconducting CNT to form an organic molecular diode.[12] As such, we believe the $[5.7]_n$cyclacenes warrant further theoretical and experimental investigation. Studies toward their synthesis are currently underway in our laboratory.

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Supporting Information Available. Cartesian coordinates and B3LYP/6-31G* total energies of all molecules, singlet–triplet gaps, HOMO/LUMO images, bond lengths, POAV angles, and complete ref 15. This material is available free of charge via the Internet at http://pubs.acs.org.

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(26) This conclusion is based on computational methods modeled after ref 7c. Other methods may lead to different results.