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Open-Shell Singlet Character of Cyclacenes and Short Zigzag Nanotubes

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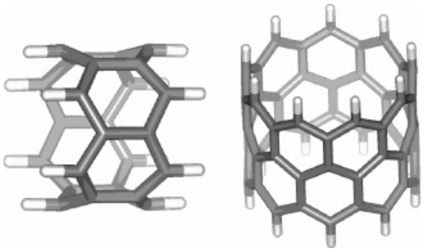
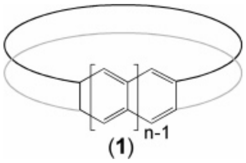
ABSTRACT



The electronic ground states of [*n*]cyclacenes, as well as short-zigzag nanotubes, computed at unrestricted broken spin-symmetry density functional theory (UBS-DFT), were found to be open-shell singlets, rather than triplets. Computations for [6]cyclacene at complete active space self-consistent field (CASSCF) and multireference perturbation theory (MRMP2) levels support this conclusion. Along with strain, the radical character of the open-shell singlet with antiferromagnetically coupled electron spins may contribute to the difficulties in synthesizing [*n*]cyclacenes.

First imagined by Edgar Heilbronner more than 50 years ago,[1] [*n*]cyclacenes (**1**) have remained one of the most fascinating but, as yet, unrealized preparative targets.[2] Despite the optimistic prognosis announced in 1998, “it is now all but certain that we are closing in on the synthesis of the first cyclacene”,[3] cyclacenes (**1**) are still elusive experimentally.[4−7]



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There have been several notable attempts to prepare these “molecular belts”;[8] Stoddart and co-workers’ efforts to synthesize [12]cyclacene realized a hydrogenated derivative, but its dehydrogenation did not yield the cyclacene.[5] Cory et al. attempted to synthesize [8]cyclacene by a stereospecific

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(1) Heilbronner, E. *Helv. Chim. Acta* **1954**, *37*, 921.

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double Diels−Alder macroannulation.[6] A belt of eight fused six-membered rings was obtained, but further reaction to produce [8]cyclacene did not succeed. Tahara and Tobe[2] pointed out that many other attempts failed even at the precursor stage.

Consequently, the current knowledge of cyclacene properties stems from several density functional theory (DFT) and semi-empirical investigations.[9] The DFT studies have focused on their energies, structures, and aromaticity (for example, by means of nucleus-independent chemical shifts computations).[9a] According to these computational investigations, cyclacenes consist of two fully delocalized polyene (trannulene)[10] ribbons connected by long C−C bonds.[9] Furthermore, larger cyclacenes were predicted to possess triplet electronic ground states.[9] However, an analysis of the published DFT data suggests that the results[9] were based on a spin-restricted ansatz for the singlet states.[11] In contrast, our present investigation achieves a lower-energy singlet description by employing an unrestricted broken spin-symmetry (UBS) wavefunction. This approach, already used for the linear oligoacene cousins,[12] gives energies in agreement with multiconfiguration computations[12,13] and results in dramatically different energetic properties and significantly modified geometries of $[n]$cyclacenes ($n = 6$ and higher).

More reliable theoretical descriptions of cyclacenes also are important for carbon nanotube (CNT) research since cyclacenes, the shortest zigzag CNT, have been used as finite-length tube models in simulations.[14] While the total synthesis of CNTs is another unsolved problem,[15] short tubes were recently obtained by cutting long single-walled CNTs.[16] Although the structures and electronic properties of finite-length models of armchair CNTs[17] are well studied, knowledge of short zigzag analogues[18] is still scarce.

We now present DFT and ab inito computational evidence that the ground states of [6]- and higher cyclacenes as well as short zigzag nanotubes are open-shell (OS) singlets, similar to the electronic structures of long linear polyacenes,[12] rather than triplets as previously reported.[9]

Cyclacene geometries were optimized at B3LYP/6-31G*; [6]cyclacene was also optimized at the complete active space self-consistent field (CASSCF) level, and its energy was further refined using second-order multireference perturbation theory (MRMP2).[19] All CASSCF and MRMP2 calculations employed GAMESS-US,[20] while the Gaussian 03 program was used for all DFT computations.[21]

Two possible electronic ground states were investigated: triplet and singlet. The latter was described with "open-shell (OS)" UBS theory, rather than by the restricted "closed-shell" (CS) B3LYP approach.

At the CASSCF(8,8)/6-31G* and the MRMP2/6-31G*//CASSCF(8,8)/6-31G* levels, the triplet state of [6]cyclacene is 14.9 and 7.4 kcal/mol higher in energy, respectively, than the $^1A_{1g}$ ground state. The natural orbital occupation numbers for the CASSCF wavefunction, 1.98, 1.93, 1.87, 1.46, 0.54, 0.14, 0.07, and 0.01, clearly indicate the significant multiconfiguration character of the singlet state.

These CASSCF and MRMP2 results are *not reproduced* at the spin-restricted (CS) B3LYP/6-31G* level. Just as in previous investigations at such inadequate levels,[9a,c] the triplet

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state is favored erroneously (by 1.2 kcal/mol) over the spurious [6]cyclacene CS singlet state (Figure 1, S-Tables 1 and 2 in SI). However, the restricted wave function has a triplet instability, and a UBS ansatz[22] gives a lower energy (OS) solution. After reoptimization at the UBS-B3LYP/6-31G* level, the singlet is favored by 6.8 kcal/mol over the triplet, in very good agreement with the MRMP2 result (7.4 kcal/mol).

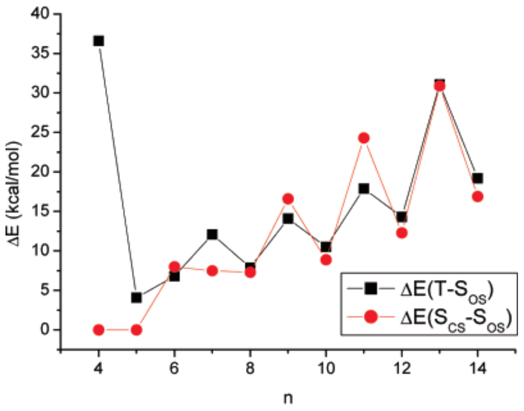

Figure 1. Relative energies of triplet [$\Delta E(\mathrm{T} - \mathrm{S}_{\mathrm{OS}})$] and restricted closed-shell (CS) singlet states [$\Delta E(\mathrm{S}_{\mathrm{CS}} - \mathrm{S}_{\mathrm{OS}})$] to the UBS open-shell (OS) singets of [*n*]cyclacenes at the B3LYP/6-31G* level of theory.

Figure 1 plots the changes in energies of the triplet and the CS singlet (relative to that of the OS singlet) with the number of fused benzene rings in [*n*]cyclacenes. Clearly the ground state is the OS singlet when *n* is greater than 5. When *n* is 4 or 5, the OS singlet relaxes to the CS singlet ground state. For $n = 3$, the D_{3h} cyclacene structure is unstable (geometry optimization gives a different structure, which is not a local minimum; see S-Figure 1 in SI).

Figure 1 also shows that the relative energy of the OS singlet to the CS singlet fluctuates when *n* is greater than 8. This behavior is caused by the fact that even [*n*]cyclacenes are more stable than the odd [*n*]cyclacenes for the CS singlets (see S-Figure 2 in SI for the atomization energy per benzene ring for the OS and CS singlets, which indicates the stability of an [*n*]cyclacene).

The [*n*]cyclacene OS singlets display nearly D_{nh} symmetry (see S-Table 3 in SI), and have shorter transannular C−C bonds (S-Table 3 in SI), in particular for the odd *n* [*n*]cyclacenes. The transannular CC and the edge $\mathrm{CC_H}$ bond lengths, where $\mathrm{C_H}$ designates a carbon atom bound to hydrogen, converge toward 1.46 and 1.41 Å, respectively, with increasing *n*. This practically eliminates the transannular C−C bond length alternation, discussed previously in the context of $4k + 2$ and $4k$ electron aromaticity and antiaromaticity.[9c] Nonetheless, the significant bond length alternation (BLA) in each individual benzene ring reported previously[9a,c] persists here (0.05 Å) as does the unusual fully delocalized polyacetylene nature of the ribbons.

More insights can be obtained by examining the isosurfaces for the spin magnetization density ($\rho_\alpha - \rho_\beta$). For example, the α-spin electrons for [10]cyclacene are mainly localized on the upper edge, while *β*-spin electrons are on the lower edge (Figure 2). Moreover, minor *β*-spin electrons appear in between α-spin upper edge carbon atoms (those connected to hydrogen). The antiferromagnetic (AFM) coupling observed here originates from the two zigzag edges and the two sublattices in cyclacenes (one sublattice α-spin, the other *β*-spin). Zigzag-edged graphene nanoribbons,[23] higher acenes,[12,13] and rectangular polycyclic aromatic hydrocarbons[24] have been shown to share this AFM coupling. The localized spins at the zigzag edges behave chemically as partial radicals, as previously shown by the reaction energetics with other common radicals.[23b] Mulliken population analysis yields a local spin moment of $\pm 0.32\ \mu_{\mathrm{B}}$ on zigzag edge carbon atoms for [10]cyclacene, supporting the partial radical concept. The open-shell ground state character is also apparent in the singly occupied frontier molecular orbitals (S-Figure 3 in SI). The singly occupied frontier orbitals reside on the two edges. Note that polyradical character is already apparent for [6]cyclacene. This resembles well the oligoacenes larger than hexacene.[12,13] We also find that the number of unpaired α-spins (by integrating over the space where spin magnetization density is positive) increases with *n* for the OS singlets of [*n*]cyclacenes which, as expected, leads to increased spin contamination for the OS singlets (for $\langle S^2 \rangle = 1.2$ for [6]cyclacence and $\langle S^2 \rangle = 2.8$ for [14]cyclacence; see S-Table 2 in SI).

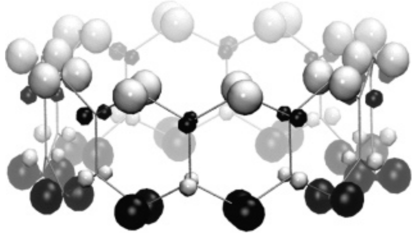

Figure 2. Isosurfaces of spin magnetization density for the open-shell singlet of [10]cyclacene. Isosurface values are at 0.1 e/Å^3 and −0.1 e/Å^3 for the light and dark surfaces, respectively.

Because of their radical character, the open-shell singlets should be highly reactive and unstable.[25] Along with strain, this may help explain why previous attempts to prepare [8]-

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and [12]cyclacenes did not succeed.[5,6] Unfortunately, smaller cyclacenes with closed-shell singlet ground states are too highly strained[18d] to be good targets for synthesis. The belt structure of [5]cyclacene (Figure 3) results in ca. 70 kcal/mol strain.[18d] Although [4]cyclacene also has a CS singlet ground state, its strain (ca. 120 kcal/mol)[18d] is even larger (see S-Figure 2 in SI).

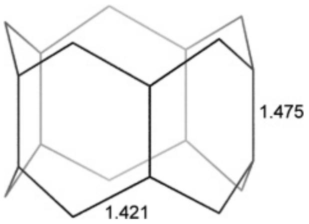

Figure 3. B3LYP/6-31G* optimized geometry for [5]cyclacene. $C-C_H$ and $C-C$ bond lengths are shown.

While [*n*]cyclacenes can be regarded as the shortest H-terminated (four-layered) (*n*,0) zigzag carbon nanotube models, our computations show that cyclacenes with more than five fused benzene rings have open-shell singlet ground states. Is this also the case for short zigzag nanotubes with more layers?

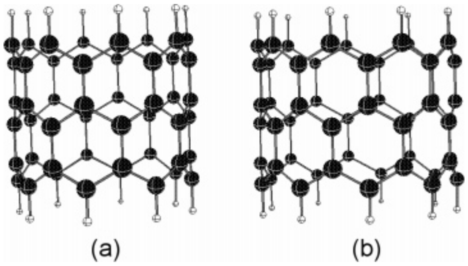

Figure 4. Six-layered zigzag carbon nanotube models: (a) (8,0) tube, and (b) (9,0) tube.

We find that the open-shell singlet states of the six-layered models (Figure 4) of zigzag (8,0) and (9,0) tubes (S-Table 4 in SI) are 20.3 and 36.8 kcal/mol lower in energy, respectively, than the restricted closed-shell descriptions at B3LYP/6-31G*.[11] Consequently, the singlets are lower in energy than the triplets for very short CNT models by sizable amounts. The computed restricted and UBS DFT energy difference for the singlet states is larger for six-layered than for four-layered models, suggesting enhanced radicaloid character of the longer tubes. The open-shell singlet character is clearly seen in the singly occupied frontier molecular orbitals (S-Figure 4 in SI). This result is also consistent with previous findings of antiferromagnetic coupling for zigzag-edged graphene systems.[23,24]

In summary, we have shown that [*n*]cyclacenes, where *n* is 6 or larger, as well as short zigzag (*n*,0) tubes have open-shell singlet ground states. This refines previous investigations of [*n*]cyclacenes, which were based on inadequate restricted B3LYP descriptions of the singlet states.[9,11] However, our UBS-B3LYP computations give an energetic preference of open-shell singlet over triplet states with increasing [*n*]cyclacene size. This is contrary to the expectation (based on the decreasing singlet−triplet energy splitting for the linear [*n*]acenes[12,13] and the indistinguishability of [*n*]acenes and [*n*]cyclacenes at infinity) that the singlet−triplet energy difference should converge to a small finite value.[12,13,26] Further computational investigations are required for establishing an understanding of the electronic structure of polyacenes and cyclacenes. The expected high reactivity of the radicaloid singlet ground states and the strain energies complicate cyclacene synthesis. We are hopeful that suitable kinetically stabilized members of this series of fascinating hydrocarbons can be achieved.

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Supporting Information Available: B3LYP/6-31G* total energies, energy differences between different electronic states, key geometry parameters, building unit energies of [*n*]cyclacenes, the singly occupied frontier orbitals of [6]-cyclacene and 6-layered (8,0) zigzag nanotube model, the B3LYP/6-31G* Gaussian 03 archive files, Cartesian coordinates, and complete ref 21. This material is available free of charge via the Internet at http://pubs.acs.org.

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