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Theoretical Studies on Structures and Aromaticity of Finite-Length Armchair Carbon Nanotubes

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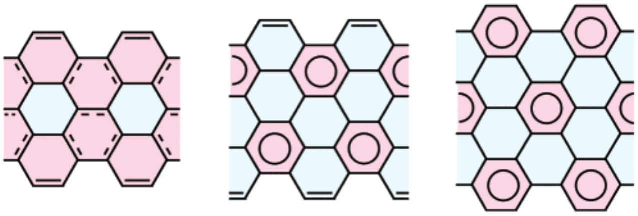
ABSTRACT



Depending on the exact length of the tube, the chemical structure of finite-length armchair [n,n] single-wall carbon nanotube ($n = 5$ and 6) falls into three different classes that may be referred to as Kekulé, incomplete Clar, and complete Clar networks. The C–C bond lengths, nucleus-independent chemical shift analysis, and orbital energies suggest that the chemical reactivities of the finite-length tube change periodically as the tube length is elongated by one-by-one layering of cyclic carbon array.

Chemical modification of a single-wall carbon nanotube (CNT) is an important current subject of nanoscience.[1] However, the first step of CNT functionalization that involves modification of the CNT π-conjugated system has not yet reached the level of accuracy and precision that has been achieved in the fullerene chemical modification.[2] In modern chemistry, accurate information on the chemical structure of the molecule in question is essential for studies of chemical reactivities; however, such information is lacking in the CNT research. There has been no experimental structural data sufficiently accurate to discuss the C−C bond lengths, bond alternation, aromaticity, and chemical reactivities of CNTs. Theoreticians working on CNTs generally rely on "ideal graphite" structures (i.e., equal C−C length)[3] and seldom[3f,3g] tried structure optimization. In the present study, we obtained optimized structures of a series of finite-length [5,5]- and [6,6]CNTs by starting with the shortest model **1** up to its 200 carbon homologue and analyzed their chemical and electronic structures as well as the aromaticity of the ring structures with the aid of nucleus-independent chemical shift (NICS) analysis.[4,5] We report that the structure and the local aromaticity oscillate periodically to generate three structures, a Kekulé network,[6] a p-phenylene network flanked by peripheral double bonds (denoted as incomplete Clar network),[6] and an array of p-phenylene network that covers the

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whole tube structure (complete Clar), as the tube is elongated by one-by-one layering of a cyclic carbon array. A reasonable conclusion that has been drawn from this finding is that the chemical reactivities of a finite-length CNT will depend on the exact tube length.

We recently synthesized the first hoop-shaped aromatic, [10]cyclophenacene **2**, by selective detraction of π-conjugation of [60]fullerene (Figure 1) and determined its single-crystal structure (±0.01 Å error).[7] The compound is a ground-state singlet, luminescent, and hence has a finite HOMO/LUMO gap. This molecule represents the shortest [5,5]CNT, and the study therefore provided the first high-precision structural information of the CNT class of compounds, setting the first experimental basis to which the accuracy of theoretical calculations has been testified. Thus, hybrid density functional (B3LYP/6-31G*) and semiempirical (PM3) methods were found to reproduce well the experimental geometry of **2** (e.g., C−C bond lengths matching within 1.4%).[7] The calculated geometry of a simple model of **1** also agrees well with the experimental geometry (e.g., C−C bond length matching within 1.5%), indicating in turn that these theoretical methods provide a reliable protocol for the studies of the structures of finite-length armchair CNTs. Note that previous structure studies on CNTs relied on the STM measurement, which is inherently incapable of giving high precision C−C bond lengths.

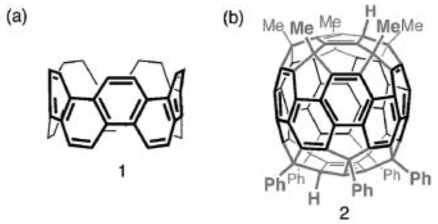

Figure 1. Shortest CNTs. (a) Hydrogen-terminated model [5,5]CNT, $C_{40}H_{20}$. (b) Capped [5,5]CNT recently synthesized $C_{60}Me_5Ph_5H_2$.

With this structural information in hand, we decided to study the optimized structures of [*n*,*n*]CNTs for a series of the homologues of **1**, $C_{10j}H_{20}$ (j = 4−20), under D_{5d} symmetry for j = even numbers or under D_{5h} symmetry for j = odd numbers (similarly, D_{6d} or D_{6h} symmetry was assumed for [6,6]CNTs) by the use of the B3LYP/6-31G* and the PM3 methods. Local aromaticity of polycondensed aromatics can be evaluated by the NICS calculations (GIAO-SCF/6-31G*//HF/6-31G*).[4] NICS values more negative than a certain threshold (e.g., −4.5) suggest the character of the six-membered ring in question to be aromatic, and those close to zero suggest nonaromatic character. Bond lengths of the optimized structures are shown in Table 1, and schematic structures with color coding of NICS values are shown in Figure 2.

Table 1. Bond Lengths (Å) of B3LYP/6-31G* Optimized Structures of Finite-Length [5,5]CNTs. See Supporting Information for Data of Longer CNTs

	a	b	c	d	e	f	g	h	i
$C_{40}H_{20}$	1.366	1.435	1.452	1.415					
$C_{50}H_{20}$	1.361	1.445	1.422	1.426	1.444				
$C_{60}H_{20}$	1.384	1.418	1.468	1.416	1.428	1.441			
$C_{70}H_{20}$	1.372	1.432	1.451	1.416	1.438	1.434	1.409		
$C_{80}H_{20}$	1.366	1.441	1.435	1.422	1.441	1.428	1.413	1.437	
$C_{90}H_{20}$	1.381	1.421	1.465	1.417	1.435	1.438	1.424	1.418	1.446

As the [5,5]CNT is elongated layer-by-layer of 10 carbon atoms, three different structures, Kekulé and two types of Clar *p*-phenylene networks, emerge periodically (Table 1, Figure 2). As discussed previously,[7] $C_{40}H_{20}$ can be regarded as a Kekulé structure (Figure 2i) or, more precisely, as a hybrid of 125 canonical resonance structures.[8]

Addition of one layer of 10 carbon atoms to $C_{40}H_{20}$ creates $C_{50}H_{20}$ (Figure 2ii), where a cyclic array of Clar structure can be identified (bond c ≃ d) and the edge double bonds are isolated from the Clar network and are quite short (a = 1.361 Å). It is notable that the geometry of $C_{50}H_{20}$ is similar to that of the equatorial belt region of [70]fullerene (X-ray: a = 1.378 Å; b = 1.447 Å; c = 1.426 Å; d = 1.414 Å; e = 1.462 Å).[9] We can thus regard [70]fullerene as the second shortest [5,5]CNT capped by two 10-carbon half-spheres (note that [60]fullerene, from which we created the C_{40}-hoop conjugation, consists only of the two 10-carbon half-spheres and contains no structural features of CNT). Further addition of 10 carbon atoms afforded $C_{60}H_{20}$ that comprises two rows of Clar network (b ≃ d ≃ e; bond a is rather short because it bears hydrogen atoms). A recently identified football-shape isomer of C_{80} corresponds to $C_{60}H_{20}$, but experimental structural data is yet to be obtained.[10] Progression from $C_{40}H_{20}$ to $C_{60}H_{20}$ completes the first period of the structural oscillation.

In the next series, $C_{70}H_{20}$ comprises two rows of the Kekulé network (Figure 2iv). Similarly, $C_{80}H_{20}$ has two rows of Clar array flanked by peripheral double bonds (Figure 2v), and $C_{90}H_{20}$ has three rows of Clar array (Figure 2vi). We have confirmed the periodicity until $C_{200}H_{20}$ (data are shown in Supporting Information). The observed structural oscillation arises because of the match/mismatch of the periodicity made out of the array of the Clar benzene structure and the one-dimensionality of the CNTs: We can draw as many as possible Clar structures in the series $C_{60}H_{20}$, $C_{90}H_{20}$, etc. (matched), but in the next series, shorter by one C_{10}-layer ($C_{50}H_{20}$, $C_{80}H_{20}$, etc.), we are left with the one row of isolated olefins in the two edges flanking the Clar structure

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(6) Kekulé structure infers a 1,3,5-cyclohexatriene-type cyclic conjugate system, and the Clar structure represents a benzene structure with equivalent C−C bond lengths.

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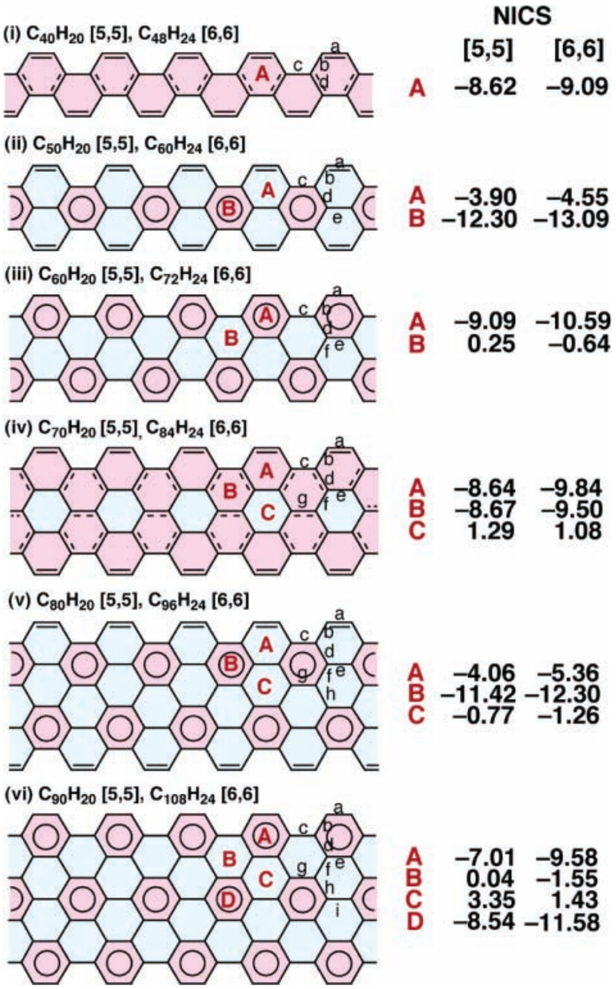

Figure 2. Schematic structures and color-coded NICS maps of finite-length $[n,n]$CNTs ($n = 5$ and 6). Hydrogen atoms are omitted for clarity. Chemical bonds are schematically represented by using single-bond (solid single line; bond length > 1.43 Å), double-bond (solid double line; bond length < 1.38 Å), single-bond halfway to double-bond (solid-dashed line; 1.43 Å > bond length > 1.38 Å), and Clar structures (i.e., ideal benzene). NICS coding: red, aromatic < -4.5; blue, nonaromatic > -4.5. See Supporting Information for data of longer CNTs.

in the center. In the third series ($C_{40}H_{20}$, $C_{70}H_{20}$, etc.), we cannot draw Clar structures any more and are left with the Kekulé arrays.

Geometry-optimized structures of [6,6]CNTs $C_{12j}H_{24}$ ($j = 4-9$) also exhibited the same trend of oscillation of the structure (bond lengths in Supporting Information) and aromaticity (Figure 2). Three characteristic structures similarly emerge by addition of one-by-one layers of 12 carbon atoms, suggesting that this is a general trend among armchair CNTs. One small difference between the [5,5]- and the [6,6]CNTs is that the latter shows larger negative values likely because of increased planarity and hence better π-overlaps.

As the structure oscillates, the energy of the frontier orbitals and the HOMO/LUMO gap also oscillate (Figure 3).[3b−e,g] As a whole, the HOMO energy tends to increase and the LUMO energy decreases within each period. Thus, within one period, the Kekulé structure shows a larger HOMO/LUMO gap than the other two, and the complete Clar network has the smallest gap. (One may expect that the gap eventually will disappear at a certain tube length, where the present level of theory cannot be applied any more to the system.) The HOMO/LUMO contour surface pattern also oscillates (data not shown).[3b,c] However, the orbital coefficients of carbons atoms are very small and not localized in particular areas of the tube and hence give little information on the area dependence of the chemical reactivities of CNTs.

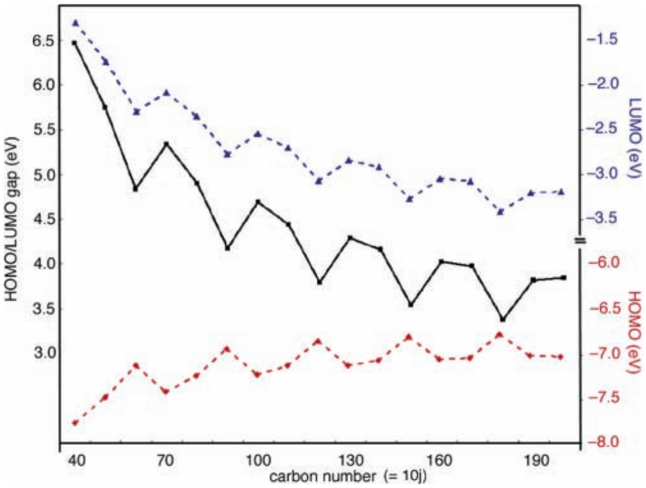

Figure 3. HOMO/LUMO levels and band gap oscillation of the finite-length [5,5]CNTs ($C_{10j}H_{20}$). The values were determined by PM3 level calculations, and the trend parallels the one observed in the B3LYP/6-31G* calculations (for $C_{40}H_{20}$ till $C_{120}H_{20}$) (see Supporting Information).

In summary, the geometry-optimized structures, NICS values, and molecular orbital studies on the finite length armchair CNTs indicated that the chemical and electronic structures oscillate as the tube is elongated. The oscillation occurs due to match/mismatch of the Clar benzene structure and the one-dimensionality of the CNTs, generating Kekulé and incomplete and complete Clar networks in this sequence, possibly until the HOMO/LUMO gap disappears.

Since aromaticity and frontier molecular orbital energies represent certain measures of thermodynamic and kinetic stabilities, we expect that the chemical properties of finite-length CNTs of different lengths will depend critically on the exact length of the tube. Following the Fukui theory,[11] we would expect that the reactivities of CNTs toward both nucleophilic and electrophilic attacks will be the highest for the tubes with the complete Clar network (e.g., $C_{60}H_{20}$, $C_{90}H_{20}$, $C_{120}H_{20}$, etc., in the [5,5]CNT series possessing high HOMO and low LUMO values). The present studies did not give any direct clue to predict the site selectivity in the chemical modification of CNTs.[12] The lack of discernible MO-coefficient localization along the tube axis suggests, however, that the reactions may take place more easily on the flexible open end of the tube, where hybridization change of the carbon atoms must be much easier than in the center where a rigid sp^2 carbon network exists. If this is indeed true, a defect-free finite-length CNT will chemically degrade preferentially at its edges rather than randomly in the center. Recently reported AFM images of PNA/DNA-functionalized short CNTs, where the PNA/DNA side chains are attached only on the edge regions of the CNTs,[13] might support this idea. Experimental verification of the statement in this paragraph, however, awaits the discovery of the size-controlled synthesis of a series of finite-length CNTs and of their selective chemical transformations as well as determination of their precise structures.

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Supporting Information Available: Computational details and Cartesian coordinates of optimized geometries of CNTs. This material is available free of charge via the Internet at http://pubs.acs.org.

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