

DFT study of zigzag (n, 0) single-walled carbon nanotubes: ^{13}C NMR chemical shifts



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ABSTRACT

^{13}C NMR chemical shifts of selected finite-size models of pristine zigzag single walled carbon nanotubes (SWCNTs) with a diameter of ~ 0.4 – 0.8 nm and length up to 2.2 nm were studied theoretically. Results for finite SWCNTs models containing 1, 4 and 10 adjacent bamboo-type units were compared with data obtained for infinite tubes in order to estimate the reliability of small finite models in predicting magnetic properties of real-size nanotubes and to assess their tube-length dependence. SWCNTs were fully optimized using unrestricted density functional theory (DFT-UB3LYP/6-31G*). Cyclacenes, as the shortest models of open-ended zigzag SWCNTs, with systematically varying diameter were calculated as well. GIAO NMR calculations on the SWCNT and cyclacene models were performed using the BHandH density functional combined with relatively small STO-3G_{mag} basis set, developed by Leszczyński and coworkers for accurate description of magnetic properties. Regular changes of carbon ^{13}C chemical shifts along the tube axis of real size (6, 0) and (9, 0) zigzag carbon nanotubes were shown. The ^{13}C NMR shifts according to increasing diameter calculated for zigzag (n, 0, n = 5–10) cyclacenes followed the trends observed for zigzag (n, 0) SWCNTs. The results for 4-units long SWCNTs match reasonably well with the data obtained for infinite zigzag (n, 0) SWCNTs, especially to those with bigger diameter (n = 8–15). The presence of rim hydrogens obviously affects theoretical ^{13}C chemical shieldings and shifts in cyclacenes and thus cyclacenes can provide only approximate estimation of ^{13}C NMR parameters of real-size SWCNTs. The NMR properties predicted for the longest 10-units long models of SWCNTs reliably correspond to results obtained for infinite nanotubes. They were thus able to accurately predict also recently reported experimental chemical shift of chiral (6, 5) SWCNT.

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1. Introduction

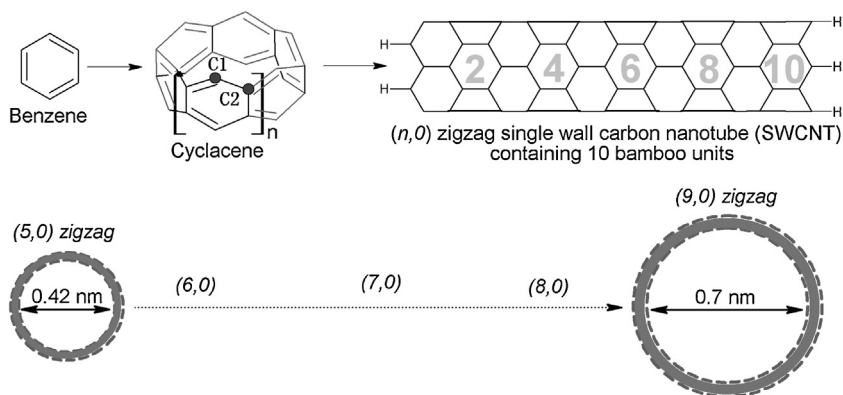
Fullerenes [1], carbon nanotubes (CNTs [2–4]) and recently graphenes [5] have paved their way to basic and applied science in recent twenty five years of nanoscience development. These ordered carbon allotropes are considered promising materials for many applications ranging from hybrid or future quantum electronics to a rational development of intelligent composites [4]. Thus, pristine CNTs, as well as functionalized tubes, are used in several fields of research and industry [4,6,7]. For example, the CNTs can serve as reactors for nanoscale chemical reactions due to their favorable tubular morphology [8]. Open-ended SWCNTs have been a subject of many model studies in nanocarbon

chemistry. For example, encapsulation of simple molecules inside the carbon nanotube has attracted the attention of scientists resulting to numerous studies on interaction of small molecules or atoms with interior, as well as exterior of the tube or proton transfer studies [9–13].

Carbon nanotubes could be viewed as a graphene sheet (or a flat set of conjugated benzene rings forming a honey comb pattern) rolled along a chiral vector \mathbf{C}_h into a tube [4]. The chiral vector $\mathbf{C}_h = n\mathbf{a}_1 + m\mathbf{a}_2$ depends on the lattice vectors \mathbf{a}_1 , \mathbf{a}_2 . Typically, a short notation (n, m) is used to describe zigzag (n, 0), armchair (n, n) and chiral (n, m) types of single wall carbon nanotubes. Originally, the (n, m) tubes with newly defined parameter $\lambda = \text{mod}(n - m, 3) = 0$ were considered as metallic [14], however, due to the curvature effects and s-p hybridization in SWCNTs with extremely small diameters, the rule is broken and e.g. (5, 0) SWCNT is considered metallic according to theoretical predictions [15].

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Scheme 1. Schematic structures of selected zigzag $(n, 0)$ cyclacenes ($n=4-16$) and $(n, 0)$ zigzag SWCNTs used in calculations ($n=5-9$, with diameter in nm).

Nevertheless, dividing SWCNTs to families according to their λ value is still reasonable and will be used in this work.

Unfortunately, SWCNTs are produced as mixtures of tubes, difficult to separate and characterize [4]. Commercial SWCNTs are produced in diameters ranging from a fraction of nanometer (~ 0.3 nm) to tens of nanometers. In addition, the ultra-thin SWCNTs [16] were reported inside the zeolite structural channels [17], aluminum oxide [18] and inside larger multi-walled carbon nanotubes [19]. Although experimental characterization of commercial samples is essential in nanotechnology, no simple method is available so far. Instead, a combination of several spectroscopic and microscopic techniques is used in characterization of technical SWCNTs. Therefore, a highly challenging structural and spectroscopic characterization of SWCNTs is usually performed employing several techniques. Raman spectroscopy is widely used to support X-ray and microscopic determination of SWCNTs diameter since the Raman active radial breathing mode vibration (RBM) frequency is inversely proportional to the tube diameter [19–21]. Also a number of experimental and theoretical NMR works on SWCNTs and closely related fullerenes has been published [22–24] [25–31]. Recently, we reported on the impact of $-OH$ and $-COOH$ end substituents on structural changes, RBM, ^{13}C NMR chemical shifts (δ) and HOMO-LUMO gaps of ultra-thin $(4, 0)$ zigzag, $(5, 5)$ armchair and $(8, 2)$ chiral SWCNTs [32–36].

Due to growing demand for well-characterized nanomaterials and insufficient use of spectroscopic techniques for their characterization (e.g. NMR) we propose in this study theoretical modeling of NMR parameters for finite SWCNT models of a size near to real SWCNTs to support their experimental analysis [22–24,26,28–30]. The main goal of the present study is an accurate theoretical modeling of ^{13}C NMR chemical shifts of selected finite models of zigzag SWCNTs of diameters common in commercial samples using density functional theory (DFT). Obtained results will be critically compared with available experimental data or with previously reported calculations on infinite SWCNTs.

The idea of using finite models is also driven by future aims at NMR studies on one-end functionalized SWCNTs, where the use of periodic calculations on infinite SWCNTs is limited. The finite models could also be utilized for modeling of properties of chiral SWCNTs that is still often computationally expensive procedure if the periodic calculations on infinite models are employed. Enormous computational demands of calculations on infinite chiral tubes are caused due to large unit crystal cells containing often several hundreds of heavy atoms. Standard calculations with the usual periodic boundary conditions (PBC) are not easily compatible with helical symmetry so far. An algorithm comprising infinitely propagated helicity compatible with commonly used Molecular Dynamic software was developed in our group [37]. Nevertheless, we are

not aware of any helical symmetry propagating PBC code working at QM level and plane waves. Thus, suitable finite models can be a relatively cheap alternative providing results with a precision described in this work. Note, that the size of our finite models is considerably wider than reported before [26–30,36,38] (up to $n=15$) and this should also enable better observations of convergence patterns of SWCNTs' parameters in accordance with their diameter. The current study should also make possible a better interpretation of observed experimental ^{13}C NMR chemical shifts of SWCNTs.

2. Computational methodology

Three distinct model systems were chosen—zigzag type cyclacenes and open-end finite zigzag SWCNTs consisting of 4 or 10 “bamboo” units [36,39–42] (Scheme 1). These models were constructed by increasing their diameter from 0.4 to 0.8 nm (10-units SWCNTs), and even up to 1.3 nm for 4-units SWCNTs and cyclacenes. The length of models range from 0.3 nm for cyclacenes to 0.9 nm for 4-units SWCNTs or even 2.2 nm for 10-units SWCNTs.

All structural calculations were performed using Gaussian 09 program [43] and the unrestricted wavefunction approximation of the Becke three-parameter Lee-Yang-Parr exchange-correlation functional (UB3LYP [44–46]) combined with the 6-31G* basis set. The method together with unrestricted approach was suggested earlier for better description of open-shell singlet states in polyaromatic systems [47–49]. This approach was successfully applied in our previous studies on polyaromatic molecules [15,50]. Besides, we applied loose symmetry and tight SCF and optimization thresholds with a very fine computational grid (GRID = 150,590) during the optimization [43]. The calculations of vibrational frequencies were performed for optimized geometries to ensure the minimum on the potential energy surface for the studied systems [40].

The gauge including atomic orbital [51,52] (GIAO) calculations of nuclear isotropic shieldings for optimized UB3LYP/6-31G* geometries were performed using the BHandH [43,44] functional and the STO-3G_{mag} basis set [53]. The BHandH [44] density functional and a modified basis set were successful in calculating carbon nuclear shieldings (and chemical shifts) in earlier studies on hydrocarbons, small molecules or nanocarbons [15,36,50,54–57].

The STO-3G_{mag} basis set was developed for accurate description of magnetic properties with a reasonable effort. Leszczyński and coworkers' idea of STO-3G_{mag} basis set arises from an extension of standard STO-3G basis set by functions obtained from analytical first-order corrections using the Green's function [53]. This modified STO-3G basis set shows a very good accuracy, comparable to Jensen's pcS-2 basis set [58], dedicated to accurate prediction of nuclear shieldings, while being half the size of the latter [50]. Benzene nuclear isotropic shielding (σ_0), calculated at the same level

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