Density Functional Theory Study on Global Aromaticity of Carbon Nanobelts

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Many types of carbon nanobelts, of which structures can be formed from one-dimensional carbon nanotubes (CNTs), have attracted much attention due to their potential of structural diversity with highly π-conjugated electronic structures, although most of them have not yet been synthetically realized. In particular, the bottom-up synthesis of an isomer of [12]cyclophenacene was successfully demonstrated and inspired theoretical investigation for a variety of carbon nanobelt (CNB) structures [1]. The electronic structures of CNB can also provide an opportunity for in-depth study on the structure-property relation related to global aromaticity. Herein, we performed computational study based on density functional theory (DFT) to investigate the structural stability and aromaticity-related electronic properties of six types of CNB structures, such as (i) cyclacenes and (ii) benzocyclacenes derived from zigzag CNTs, and (iii) cycloparaphenylenes, (iv) cyclophenacenes, (v) Vögtle-type belts, and (vi) recently synthesized isomeric forms of cyclophenacenes derived from arm-chair CNTs, depending on their size (see Figure 1). We considered the size of molecules within ~1 nm of molecular diameter. The global aromaticity of their ionized species (q = -2, -1, 0, +1, +2) were extensively also elucidated. Anisotropy of the Induced Current Density (AICD) and Nucleus-Independent Chemical Shifts (NICS) techniques were used to investigate the relationship between chemical shift and ring current (see Figure 2).

Our results suggest that their aromaticity is mostly related to the spatial distribution of frontier molecular orbitals (HOMO and LOMO).
We believe that our study can contribute to better understanding the structure-property relation for the aromaticity of CNBs.

References

[1] G. Povie, Y. Segawa, T. Nishihara, Y. Miyauchi, and K. Itami, Science. 2017, 356, 172–175.

Figures

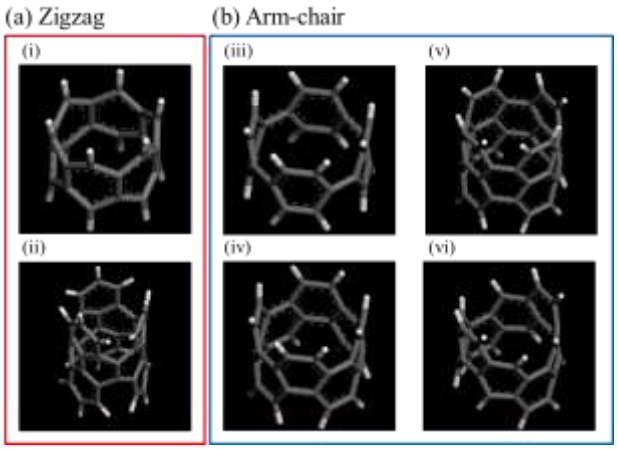

Figure 1: Six-types of carbon nanobelts (CNBs).

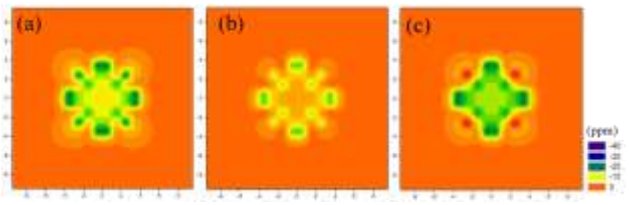

Figure 2: NICS distribution of (a) neutral, (b) cationic (q = +1), and (c) anionic (q = –1) species of benzocyclacene (n = 4).