# Modeling zigzag CNT: dependence of structural and electronic properties on the length and application to the encapsulation of HCN and HCCH

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## INTRODUCTION

Recently, carbon nanotubes (CNT) have been the focus of a lot of research efforts because their physical properties and potential applications. The first theoretical works on CNT used only one C=C bond length. When different C=C distances are considered the a most stable CNT is predicted[1,2]. Experimental crystallographic results[3] for zigzag CNT indicate that longitudinal C=C (CCL) bond lengths are shorter than tangential (CCT) ones. In this work we have performed B3LYP calculations in order to determine the minimal length of zigzag single wall CNT that reproduce the experimental C=C bond behavior and evaluated the effect of the model size on the encapasulation of the isoelectronic molecules HCCH and HCN.

## METHODS

The set of calculated zigzag CNTs have chiral index of 6 to 9 and lengths of two (×2), three (×3) or four (×4) times the unit cell of repetition. The geometries were fully optimized with the B3LYP/6-31G(d) method using the Gaussian 09 program. The encapsulation energies (ΔE) were calculated according to the supermolecule approach corrected by the BSSE counterpoise method. All atomic charges were evaluated with the Natural Bond Orbital (NBO) partition. The effect of dispersion corrections on these systems was studied with the two parameters Grimme's empirical dispersion correction (GD2).

## RESULTS AND DISCUSSION

We observed that C=C bond are larger at the CNT borders and decrease as approach to the center and when CNT length ($L_t$) reaches twice its diameter ($d_t$) the CCL < CCT experimental observation is fulfilled. The atomic charges that assume values close to zero at nanotube's center and negative values at the border due its saturation with hydrogen atoms. Based in this observations we can define an useful region of CNT where the computational model behaviors as expected for the real system (see Figure 1 to the (7,0)x4 CNT).

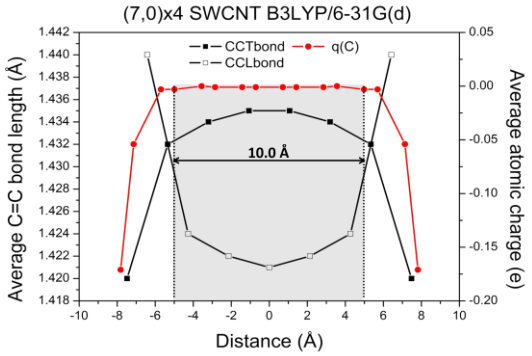


**Figure 1**. In black, average CCL (open squares) and CCT (filled squares), in Å. In red, average carbon charge, in electrons. Grey area refers to the CNT useful region.

The ΔE values are sensitive to the change of C=C bond pattern of CNT getting smaller as the tube length grows. Both ΔE and charge transfer, from CNT to dopants, decrease with the increase of tube diameter. The dispersion energy stabilize the supermolecule and shortens the C=C bonds.

## CONCLUSIONS

CNT's with $L_t/d_t > 2$ reproduce, at its center, the experimental pattern of C=C bonds which affect the ΔE, stabilizing it, being an important parameter to model interacting system with CNT.

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