

SIMULATION OF ELECTRON TRANSPORT IN HELICENES

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Abstract

Helicenes attract attention as simple models for screw-shaped biomolecules, such as proteins and nucleic acids. Recently, they have been recognized as potential building blocks in nanomaterial sciences and the interest in their chemistry and physico-chemical properties has remarkably increased. Thus, helicenes represent an attractive objective for further research in various branches of chemistry and nanoscience. For mechanical and electrical simulation of helicenes we used Atomistix ToolKit licensed by QuantumWise. It is combining DFT and NEGF for ab initio and semi-empirical calculations of structure and electron transport. We simulated molecular mechanics and basic electronic properties of [49] helicene structure in standalone and two electrode configuration. Electron density and electron transmisivities of this structure has been analyzed.

Keywords: Helicene, carbon nanostructure, transmisivity

1. INTRODUCTION

Helicenes are polycyclic aromatic compounds comprised of ortho-fused benzene rings. The chemistry of helicenes has attracted persistent attention due to their unique structural, spectral and optical features. Steric repulsion of the terminal benzene rings forces the molecule to adopt a helical non-planar shape. Thus helicenes are inherently chiral, while lacking chiral centres. The non-superimposable clockwise and counterclockwise helices represent an example of helical chirality. Their twisted shape offers applications in nanoscale molecular machinery as 'springs' or 'pawls'. [1] Further applications of helicenes can be found in the fields of non-linear optics and circularly polarized luminescence [2]. The unique structure of functionalized helicenes make them very stable towards acids, bases as well as being stable at high temperature. These type of molecules are considered as potentially useful in new materials such as discotic liquid crystals [3] or conjugated polymers [4]. Study of helical compounds is an active field of research in supramolecular chemistry due to their self-assembly and physicochemical properties [5]. During the last two decades, enormous advancement has been accomplished in understanding of the helicenes chemistry, which have been tremendously exploited in a variety of domains. Today, helical core effectively forms a design element in the development of chiroptical materials [6], photochromic materials [7], sensors [8], molecular level devices [9], organic electronics [10], NLO materials [11] etc. The most astounding feature is that helicenes (by virtue of their inherent chirality) are obvious choices for eliciting certain biological activities. In particular, investigation of the interactions of nucleic acids with small molecules is an active area of research insofar as the drug design in anticancer therapy is concerned [12, 13]. Moreover helicenes possessing inherent chirality have attracted attention owing to their extraordinary electronic and optical properties [14]. Directional electron transport properties of helicenes and potential charge-trapping properties make them ideal molecular components for nano-scale electronic materials. Recently, the theoretical formalisms that help in understanding, at an atomistic level, the role of the intermolecular forces in electron transport mechanism and in nonlinear optical response of π -conjugated organic systems under various packing densities and different external field conditions have been revisited by several authors [15, 16].

2. MODEL AND METHOD

We were approaching by the same way as in our previous articles. [17] We used the Atomistix ToolKit simulation software with Virtual NanoLab user environment from QuantumWise [18, 19, 20]. We selected the

proper structure, placed the carbon atoms in the original positions and passivated all the free bonds with hydrogen atoms. In order to reach thermodynamical equilibrium of the system, optimized atom positions are computed by molecular mechanics technique. We used embedded Brenner's quick optimizer to optimize geometry of the chemical bonds so as the maximal component of interatomic forces was less than 10^{-5} eV/Å after the optimization. For electrical properties calculation we used semi-empirical Extended Hückel self consistent field (EH-SCF) method for nanoscale devices [21] in two terminal device mode. The simulated system is divided in two electrodes (source and drain) and the central region. Due to the used method, we need to extend the electrodes into the structure. In order to consider the electrodes as a bulk region, there is also a need to have enough space in the central region for both electrode extensions. In order to shorten simulation time, we used only [49]helicene structure shown on **Fig. 1** (which is not periodic over assumed distance) while the first three and last three turns are considered as a part of respective (source, drain) electrodes. We also requested symmetrical structure of central region for invariant analysis. Considering periodicity of electrodes this makes two turns ([13]helicene) for effective central region (channel). The terminal two hydrogen atoms on both ends are, for purposes of periodic elongation of electrodes, removed after molecular mechanics optimization.

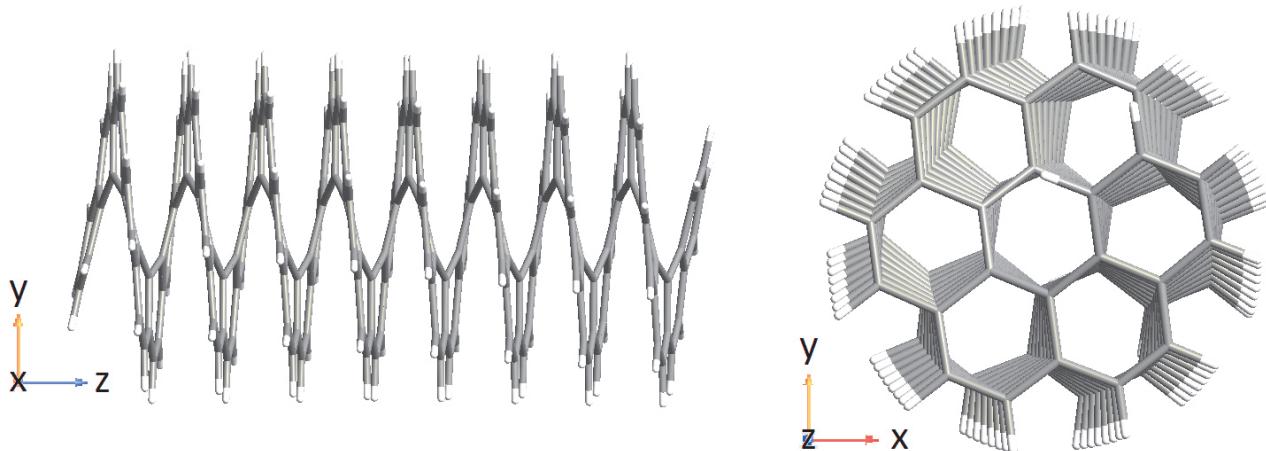


Fig. 1 Stick model of [49]helicene used as channel with two periodically extended electrodes. Figure is depicting result of Brenner's molecular mechanics optimization to maximal energy of interatomic forces of 10^{-5} eV/Å

3. NUMERICAL RESULTS

The set of results for molecular mechanics (**Fig. 1**) gives us a chiral structure with constant interpitch distance of 2 Å. This value may be disputed because neutral $[n]$ helicene molecule should have interpitch distance around 3.75 Å. However, the overall molecular mechanics calculation by these means is giving us a rough picture about [49]helicene molecule. While in center are forces pressing atoms closer to each other, on edges there are steric repulsive forces pulling ends of molecule out. The complex interaction leads to twisting and to fact that single turns do not overlap with each other.

As for the electronic transport properties, we analyzed electron density (**Fig. 2**) and transmission spectra (**Fig. 3**). The electron density analysis shows that electron density is highest around central helix, formed by energy levels associated with inner carbon atoms, and is decreasing as a function of distance from center of the structure while shape of isosurfaces follows the shape of helix. The transmission spectra shows high transmission peak around Fermi energy level if zero bias voltage applied. For small bias voltage applied (**Fig. 3** right) there is decrease of transmisivity around Fermi energy level and peak splits in two which roughly follow energy levels corresponding to applied bias voltage.

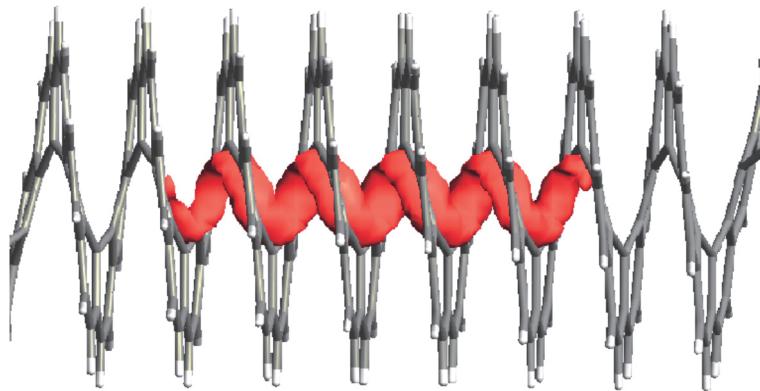


Fig. 2 Electron density isosurface for value 0.79 [-]

The transmission spectrum is disturbed by fact that for simulated 2 Å interpitch distance is presumably stronger interaction between particular turns and it creates higher total energy of system. This can be taken as a case where helicene molecule is forced to be compressed (e. g. by electrostatic forces or mechanical means) in a sensor. The electron density may change during this process and create measurable changes in channel (e. g change in current flowing through).

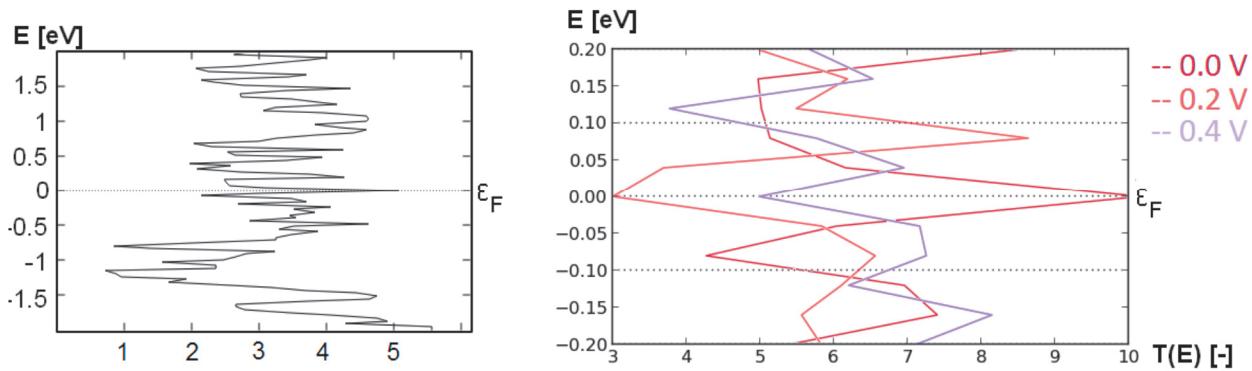


Fig. 3 Transmission spectra. Left: Zero bias. Right: Detail for 0, 0.2 and 0.4 V bias voltage

4. CONCLUSIONS

Based on our results, van der Waals force between particular turns of helicene need to be taken into account by more appropriate molecular mechanics method (e. g. DFT-D, dispersion corrected DFT) performed to give more reliable values of interpitch distance. Even though the simulated structure contains only 299 atoms, the visible tendency of these larger structures is to have roughly the same stability as smaller helicenes. The electronic transport properties exhibit possible dirac point near fermi level similar to 2D graphene structures. This implies possible utilization for inter-layer vias to connect different layers of (e. g.) graphene sheets with specified electronic transport properties (e. g. spin polarization). Moreover, electron density is periodic by nature of helicene molecule and therefore it can be used for compilation of oscillators for HF applications. The fact that electrons are with high probability localized in helical shape at the center of molecule is also interesting considering that there are benzene aromatic rings delocalizing electrons along the whole molecule. The combination of de-localized and localized electrons may imply use in quantum computing applications as well.

Although this work is only a brief insight into helicene structure and electrical transport properties it shows that these molecules are stable and can form greater structures usable in electronics and other branches. This implies future use of these structures (e. g. as very sensitive sensors of mechanical strain or acceleration). Most important stays to say that there are already developed methods for these structures to be prepared by growth from chemical precursors which implies possible study by experimental means.

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