

## Hole Transfer in Open Cumulenenic and Polyynic Carbyne Chains

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### ABSTRACT

We studied in [Simserides \(2020a\)](#) and [Simserides \(2020b\)](#) hole transfer in open atomic, cumulenenic and polyynic, carbon nanowires ([Cretu \(2013\)](#), [Milani \(2017\)](#)), employing Real-Time Time-Dependent Density Functional Theory (RT-TDDFT) and Tight-Binding (TB). The end-sites contain 1 or 2 or 3 hydrogen atoms. For DFT, CDFT, RT-TDDFT, we use the basis sets 3-21G, 6-31G\*, cc-pVDZ, cc-pVTZ, cc-pVQZ and mainly the functional B3LYP. For TB, we try the following wire models: one simplistic with all sites equivalent and transfer integrals given by the Harrison  $pp\pi$  expression (TBI), one with modified initial and final sites (TBI<sub>mod</sub>) to include the presence of 1 or 2 or 3 hydrogen atoms at the edge-sites [this achieves similar site occupations in cumulenes with those obtained by converged RT-TDDFT], and one with TBI<sub>mod</sub> transfer integrals multiplied by a factor of four (TBI<sub>mod</sub>4times) [this achieves also similar frequency content of charge and dipole moment oscillations and similar coherent transfer rates]. Full geometry optimization shows that in cumulenes the bond length alternation (BLA) is not zero and is not constant, although it is symmetrical relative to the molecule center. BLA in cumulenes is much smaller than in polyynes. Vibrational analysis shows which molecule conformations are stable. In [Simserides \(2020a\)](#) and [Simserides \(2020b\)](#) we discuss the DFT ground state energy of neutral molecules, the CDFT “ground state energy” of molecules with a hole at one end group, energy spectra, density of states, energy gap, charge and dipole moment oscillations, mean site occupations, coherent transfer rates, frequency content. Here we present a few aspects of those results.

### 1. INTRODUCTION

We live in the era of nanoelectronics, where in a laptop or in a smartphone, in an area of approximately 3 cm x 3 cm,  $10^9$  nanotransistors coexist, each covering approximately 1  $\mu\text{m}$  x 1  $\mu\text{m}$ . The channel length has been diminished below 10 nm. For usual semiconductor materials, that would mean approximately 20 atoms in a row. Since the dogma “The smaller you make it, the more you can pack into a single chip” governs our efforts, considering the above magnitudes, we could easily imagine using instead of semiconducting structures, just polymers or oligomers or plain molecules. A channel length around or below 10 nm means also that the electron mean free path is greater than the channel length, hence transport is now ballistic and semiclassical approaches,

as the Boltzmann equation ones, have to be abandoned. However, these molecules, oligomers and polymers, to be used as channels, have to be stiff enough so that they can be placed between source and drain, i.e., serve as channels. The persistence length,  $\ell_p$ , quantifies a polymer's stiffness. If the length of the polymer  $L$  is such that  $L < \ell_p$ , then it will behave as a flexible elastic beam, however, if  $L \gg \ell_p$ , then it is likely to bend, and therefore, it is not useful for a channel.  $\ell_p$  in carbynes is around 14 nm, which means around 100 carbon atoms in a row, given the approximate length of the bonds between carbon atoms. Hence, carbynes are promising candidates for channels and so it is interesting to study their electronic structure and their charge transfer and transport properties.

The difference between charge transfer and transport is explained in Fig. 1. Transfer [left panel] means that a carrier is created at a site by oxidation (hole) or reduction (electron) and then moves, time-passing, to more favorable sites, depending on the relevant on-site energies and transfer integrals. Transport [right panel] implies the application of external bias between electrodes.

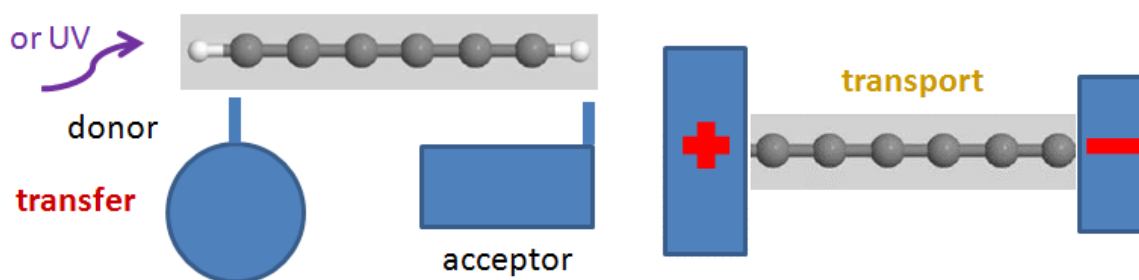


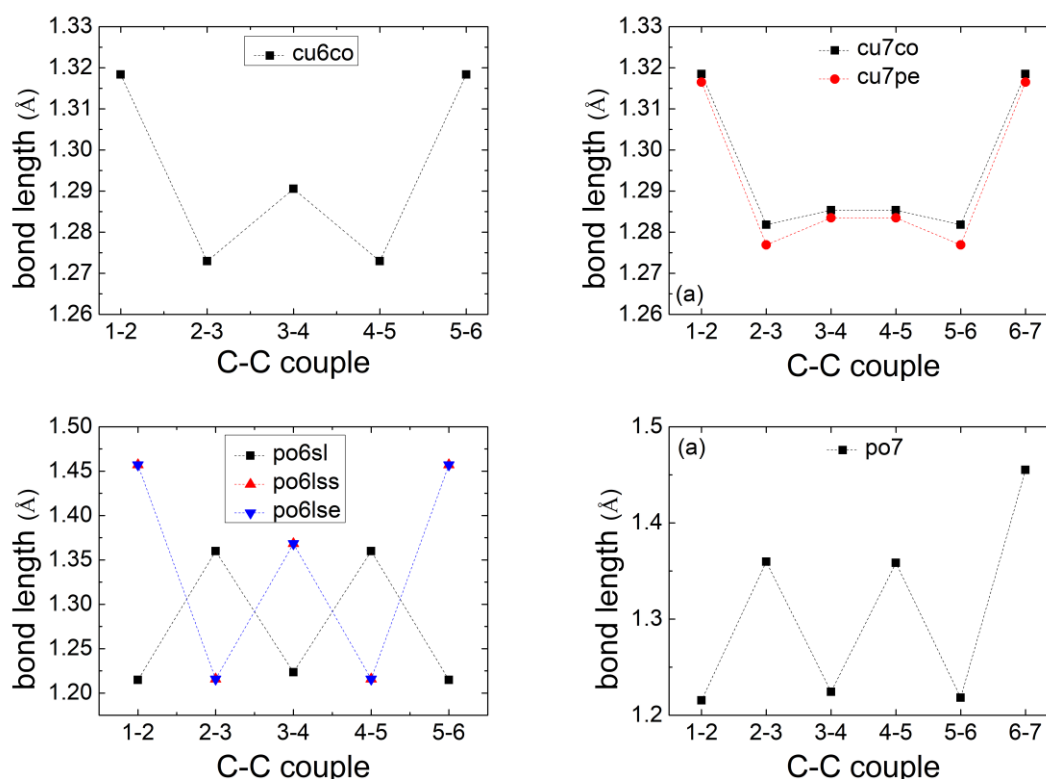
Fig. 1 The difference between charge transfer (left) and transport (right).

In this proceedings article we will briefly describe the methods that we use, and we will show some results concerning the bond length and the hole transfer rates. Details in [Simserides \(2020a\)](#) and [Simserides \(2020b\)](#). In Section 2 we discuss bond length and the division into cumulenes and polyynes and in Section 3 we discuss hole transfer rates. In Section 4 we briefly state our conclusions from our work, up to now, in carbynes.

## 2. BOND LENGTH

Carbynes, i.e., atomic carbon wires, have bond lengths crudely around 130 pm. They represent the ultimate nanowire since they are atomically thick. They are conceptually divided into cumulenic with equidistant carbon atoms and polyynic with alternating shorter and longer distances between carbon atoms. These distances are roughly around 128 pm for cumulenic cases, although they are not strictly equal and in the range 120 pm to 150 pm for polyynic cases depending on the end-groups involved. In cumulenes, the end-groups are  $\text{CH}_2$ , but in polyynes they are either  $\text{CH}_3$  or  $\text{CH}$  depending on the parity of C atoms and on whether the molecule starts with short or long bond. Details can be found in [Simserides \(2020b\)](#). Some examples are shown in Fig. 2

at the B3LYP/6-31G\* level of theory, using Density Functional Theory (DFT) via NWChem, cf. [Valiev \(2010\)](#).



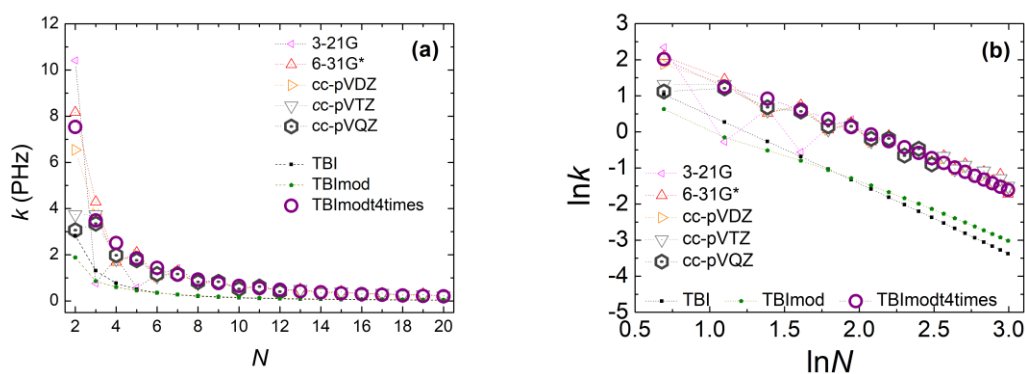
**Fig. 2** Bond lengths of cumulenenic (co) and polyynic (po) molecules with 6 and 7 carbon atoms: co (pe) denotes cumulenenic molecule with coplanar (perpendicular) methylene groups, sl (ls) means polyynic molecule with bond alternation short, long,... (long, short,...). Moreover, lss and lse denote polyynic molecules with staggered and eclipsed methyl end-groups, respectively. Geometry optimization at the B3LYP/6-31G\* level of theory, without any constraint on the position of atoms.

## 2. CHARGE TRANSFER

Conceptually, we discriminate two types of mechanisms for charge transfer: *incoherent* or *thermal* transfer between nearest neighbors or more distant sites, and *coherent* transfer or *tunneling* or *superexchange*. Here we deal with coherent transfer. Tunneling implies quantum mechanical tunneling, while superexchange emanates from distant interaction. In the coherent regime, all sites contribute with finite occupation probabilities, although those with adequate on-site energies, for the initial placement of the carrier in the sequence, are more favored. Coherent transfer is expected to dominate at low temperatures and short distances. To study charge transfer in carbynes, we use analytical and numerical Tight Binding (TB) as well as Real-Time Time-Dependent Density Functional Theory (RT-TDDFT) that is integrated in NWChem computational package, cf. [Lopata \(2011\)](#).

For TB, we obtain the time evolution of a carrier placed initially at a particular site (usually at one of the end-sites) via a system of TB coupled differential equations, which we solve via the eigenvalue method, analytically (in easier cases), numerically, or both. We employ variants of the TB Wire Model, choosing carefully the relevant on-site energies and transfer integrals. We analyze the molecular wave function into site wave functions, with coefficients  $C_j(t)$ ;  $\langle |C_j(t)|^2 \rangle$  gives the probability to find the carrier at site  $j$ . The time evolution of  $C_j(t)$  satisfies the system of differential equations, which, to be solved, need a wise choice of the on-site energies of sites and of the transfer integrals between sites. Details in [Simserides \(2020a\)](#) and [Simserides \(2020b\)](#).

For ab initio calculations the procedure we follow can be divided into various steps: 0. Initial Geometry, e.g., from some external source or from own Molecular Dynamics simulation, 1. Geometry Optimization via NWChem, 2. Ground State DFT via NWChem (usually with Löwdin population analysis), 3. Vibrational Analysis via NWChem (however, now we proceed with phonons taken into account to construct, via Monte Carlo, a number of microstates according to Bose-Einstein distribution of eigenmodes), 4. CDFT (constrained DFT) to create a carrier at a particular site (usually a hole) and RT-TDDFT via NWChem, Löwdin population analysis, and 5. Own post-processing to obtain the charge of each site, the total dipole moment and its components, transfer rates, frequency content, site occupations and so on. Details can be found in [Simserides \(2020a\)](#) and [Simserides \(2020b\)](#).



**Fig. 3** Hole transfer rates  $k$  along open cumulenic carbynes with  $N$  carbon atoms, obtained by RT-TDDFT with different basis sets and functional B3LYP, for coplanar methylene groups. We also present results obtained by three different TB wire models: TBI (black squares) is a simplistic model with equivalent sites, TBI mod (olive pentagons) differs from TBI in that the end-sites are considered different. TBI mod 4 times (purple circles) takes into account three different paths for charge transfer. (a)  $k(N)$ , (b)  $\ln k(N)$ .

In [Fig. 3](#) we display hole transfer rates  $k$  along open cumulenic carbynes with  $N$  carbon atoms, obtained by RT-TDDFT with different basis sets (3-21G, 6-31G\*, cc-pVDZ, cc-pVTZ, cc-pVQZ) and the functional B3LYP, for coplanar methylene groups as well as results obtained by three different TB wire models variants. TBI is a simplistic model with equivalent sites. TBI mod differs from TBI in that the end-sites are considered different because they hold also one or two or three hydrogen atoms. TBI mod 4 times takes into account the three different paths for charge transfer (one  $\sigma$  and two  $\pi$  paths). Details can be found in [Simserides \(2020a\)](#) and [Simserides \(2020 b\)](#). A fit of the type  $k(d) = k_0$

$\exp(-\beta d)$ , where  $d$  is the distance, gives approximately  $\beta \approx 0.25 \text{ \AA}^{-1}$ , in accordance with experiments in longer polyene and polyene bridges, where  $\beta \approx 0.2 - 0.6 \text{ \AA}^{-1}$  were obtained, cf. Tour (1996), Grosshenny (1996), Sachs (1997).

### 3. CONCLUSIONS

We have studied the electronic structure and the hole transfer in open cumulenic and polyynic carbynes, using DFT, CDFT, RT-TDDFT and TB variants. Clearly converging results at the 3-21G, 6-31G\*, cc-pVDZ, cc-pVTZ, cc-pVQZ / B3LYP levels of theory, in terms of all the studied physical properties, have been obtained (including the ground-state energy, the energy gap between occupied and empty states, the site occupations, the coherent transfer rates, the charge and dipole moment oscillations and the frequency content). We have tried three TB wire models. TBI is a simplistic wire model where all sites are equivalent and the transfer integrals are given by the Harrison  $pp\pi$  expression. In TBI<sub>mod</sub> the on-site energies of the end-sites have been modified to take into account the fact that they contain, apart from one carbon atom, one or two or three hydrogen atoms; however we have used the same transfer integrals as in TBI. With TBI<sub>mod</sub> we obtain similar occupation probabilities as with RT-TDDFT, but the transfer rates and the frequency content are much lower. To achieve similar frequency content of charge and dipole moment oscillations and similar coherent transfer rates, the TBI, TBI<sub>mod</sub> transfer integrals have to be multiplied by a factor of four, which is done in TBI<sub>mod</sub>4times. The explanation is the following: in CDFT the hole is created at the first site and not at a specific orbital of the first site, hence, there are approximately three channels for charge transfer: one  $sp$   $sp$   $\sigma$  channel and two  $pp\pi$  channels perpendicular to the molecule growth axis. When the different coupling strengths of these channels, are correctly taken into account, we obtain a factor of approximately four times greater than by using only one  $pp\pi$  channel. Hence, we have agreement of the TBI<sub>mod</sub>4times results with the RT-TDDFT converged results.

We also studied the bond length with full geometry optimization at the 6-31G\*/B3LYP level of theory. In cumulenes, bond length alternation (difference between the bond length of consecutive bonds, BLA) is not strictly zero and is not constant, although it is symmetrical relative to the molecule center. In cumulenes, BLA is much smaller than in polyynic cases, so, although not strictly, the separation to cumulenes and polyynes, holds. Cumulenes have longer C–C bonds at the ends. In cumulenes with  $N$  odd, molecules with perpendicular methylene end-groups have shorter bond lengths than molecules with coplanar methylene groups, which is another manifestation that their ground state energy is lower. Polyynes with  $N$  odd have one possible geometry, but polyynes with  $N$  even have three possible geometries,  $sl$ ,  $lss$  and  $lse$ ;  $lss$  and  $lse$  denote staggered and eclipsed methyl end-groups, respectively, with negligible difference in their ground state energies.

Vibrational analysis has confirmed that for  $N$  even all cumulenes with coplanar methylene end-groups are stable, for  $N$  odd all cumulenes with perpendicular methylene end-groups are stable, and the number of hydrogen atoms at the end groups is clearly seen in all cumulenic and polyynic cases as higher frequencies.



Finally, we mention that DFT shows that cumulenes also have an energy gap between occupied and empty states, albeit smaller than polyynes. At the limit of large  $N$ , the energy gap approaches 0.3 eV for cumulenes and 0.9 eV for polyynes.

## ACKNOWLEDGEMENT

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