



New cyclic oligothiophenes and their co-oligomers derivatives of molecular engineering interest



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ABSTRACT

The electronic properties of several series of bridged oligomers and their co-oligomers derivatives of five-membered biheterocycles (bithiophene, bipyrrole, bifuran bridged by CO or CS group) in their linear and cyclic structures (planar rings and crowns), have been studied using Density Functional Theory (DFT) calculations. The stability of ring forms of bridged oligo(6)biheterocycles is evidenced. Moreover, when replacing the CO bridging group by the CS one, in all oligomers the HOMO–LUMO energy gap is reduced, due mainly to the strongest stabilization of the LUMO. This energy gap is further reduced with the introduction of bridged bithiophene or bridged bifuran in the cyclic chain of bridged bipyrrole, thus suggesting an improvement of the conductivity properties of such species. The CS bridged co-oligo(3)(bithiophene-bipyrrole) and CS bridged co-oligo(3)(bifuran-bipyrrole) seems to be promising candidates for molecular engineering applications.

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1. Introduction

Polyheterocycles, such as polypyrrole, polythiophene, polyaniline and their derivatives, have attracted considerable attention since they can lead to conducting polymer materials. Their conductivity after adequate doping, their good mechanical property and their stability made these compounds candidates for applications in microelectronics and also in various domains of nanotechnology [1,2]. New materials based on functionalized heterocycles are actively researched. Experimentally, the synthesis of polyheterocyclic species after functionalization of the monomer or after fusing or bridging monomer units [2–4] constitute a way to access to new polyheterocyclic polymers with enhanced properties. For instance, different polyalkylthiophenes [5] and polybithiophenes exhibiting a low electronic band gap (1.10–1.20 eV) have been obtained by fusing a benzene and a thiophene ring or by fixing electro-attracting groups on bithiophenes bridged by a substituted sp^2 carbon atom [6]. Fusing of different heterocyclic monomers by electrochemical copolymerization was also developed [7–15] in the case of oxidation potentials close to each other. Thus, different copolymers were synthesized electrochemically: pyrrole with bithiophene

[9] pyrrole with furan [10] pyrrole with methyl-pyrrole [11,12], pyrrole with thiophene [13], pyrrole with N-phenyl substituted pyrrole [14]. The electrochemical copolymerization of furan with 3-methylthiophene [15] and with 3-chlorothiophene [16] was also performed: the measurement of the spectro-electrochemical properties of the obtained copolymers shows that they are intermediate between those of their corresponding homopolymers. Moreover the band gap of polyfuran is reduced by incorporation of substituted thiophene units in the polymeric chain. It is also worth noting the synthesis and characterization of new light-emitting copolymers containing 3,4-dialkoxythiophenes [17], and of fluorescent polyheteroaromatic oxadiazoles with alternating electron-donating thiophene and electron-withdrawing oxadiazole units [18]. To our knowledge, the idea of bridging electron-donating and electron-withdrawing groups along a conjugated chain has been initiated by Havinga et al. [19].

The design and synthesis of conjugated copolymers with donor–acceptor architectures for potential applications in micro-electronic devices, photovoltaic cells, electrochromics [20–22] are in continuous development as well as the synthesis and characterization of low-bandgap materials based on benzodithiophene and benzodifuran units [20a] on cyclopentadithiophene (CPDT) [20b], or based on cyclopentathiophene (CPT) as donors and diazole derivatives or triazole derivatives as acceptors [20c].

Moreover, since the discovery of fullerenes and carbon nanotubes [23], great interest is focused on systems exhibiting cyclic or tubular structures for which interesting optical, electronic,

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conducting properties are expected. Mishra et al. [24] describe the synthesis, characterization and properties of mixed macrocycles based on thiophenes and other unsaturated units. Other works highlight interesting electronic and optoelectronic properties of such species [25–30] and of cyclo(n)pyrrole [31]. On the theoretical side, various results have been obtained; in 2012, Shuang Huang et al., using DFT/MPWB95/6-31G* computations studied the ring size effect on properties of macrocyclic thiophene and pyrrole derivatives [32a]. Then, these authors carried out a ZINDO computational study of the electronic structures, UV–vis spectra and static second-order nonlinear optical susceptibilities of macrocyclic (trithiophene-diacetylene) $_n$ ($n=2,5$) that showed that macrocyclic thiophene derivatives compounds potentially exhibit large static second-order nonlinear optical susceptibilities [32b]. A previous work focused on 2D-macrocyclo(8)thiophenes [33] which brought to light that there exists a noticeable interaction between π -orbitals of individual macrocycles in tubular aggregates leading to a decrease of the band gap with the number of units in neutral aggregates. Moreover, oxidized 2D macrocyclic oligothiophenes are able to form tubular aggregates because of π - π stacking between macrocycles. In the same way, Manuel Garcia et al. [34] investigated theoretically the geometrical and electronic structures as well as electronic properties of donor–acceptor tubular nanoaggregates of cyclic oligocyclo(8)thiophenes and cyclo(8)(3,4-dicyanothiophene); they concluded that donor–acceptor tubular aggregates could be a promising new class of photovoltaic materials due to a small and adjustable band gap, strong charge separation in the excited state, and high possible mobility of the charge carriers due to their low relaxation energies. Otherwise, cyclic oligothiophenes [35a] have been studied theoretically at the B3LYP/6-31G(d) level of theory; the results show that HOMO–LUMO gap of cyclooligothiophene is lower than those of corresponding linear oligothiophene. Thus, cyclic oligoheterocycles seem to be promising candidates for applications in electronics, optoelectronics, photovoltaic cells [35b,c].

For our part, we plan to study new co-oligomers of bridged five-membered heterocycles in their linear structure and macrocyclic structures that we expect to be interesting for technological applications. To our knowledge, the sole reported calculations on this kind of species are the ones of Bakhshi and co-workers [36] who studied the electronic properties and conduction properties of copolymers based on furan and thiophene. The latter studies considered only linear structures, the calculations using *ab initio* Hartree–Fock crystal orbital method. In a previous work [37], we applied standard B3LYP/6-31G(d) computations to study the structure and electronic properties of linear oligomers based on bithiophene bridged by a sp^2 carbon bearing a chalcogen atom (O, S, Se and Te), and of their oligobifuran and oligobipyrrole analogues. An important reduction of the HOMO–LUMO gap was observed for the whole series of biheterocyclic compounds when substituting the extracyclic oxygen atom by a chalcogen atom of higher atomic number. In the present work, several novel series of co-oligo five-membered heterocycles, where every biheterocycle (bithiophene, bipyrrole and bifuran) is bridged by CO or by CS groups, will be considered. The most stable combination of these heterocyclic species, considering different linear and cyclic architectures, will be first studied; then we shall investigate if their electronic and optoelectronic properties are adequate for potential technological applications. Our preliminary design will be based on standard DFT computations.

2. Method of calculation and systems under consideration

Density Functional Theory (DFT) [38] calculations have been carried out using the B3LYP functional [39] and the standard 6-31G(d)

basis set. Another double zeta basis set, namely the LANL2DZ one, also supplemented by polarization functions on heavy atoms, has also been used, because 6-31G(d) is not available for heavy elements. The DFT calculations were carried out using the Gaussian 09 package [40]. The geometry optimizations were followed by vibration frequencies calculations. The calculations have been carried out without any constraint of symmetry.

The structures of the considered unbridged and bridged oligo(6)biheterocycles and co-oligo(3)biheterocycles (X and $X' = \text{NH, O, S}$ and $Y = \text{S, O}$) in linear and cyclic chains, are given in Fig. 1. We have considered the energetically favoured α - α' linkage for all linear and cyclic chains. The linear unbridged oligo(6)biheterocyclic model that we considered, is based on a unit constituted by two planar rings, α - α' linked in such a way that the X heteroatoms are in trans position (Fig. 1a). The same linkage was considered between two bridged biheterocycles in linear bridged oligo(6)biheterocycles and closed bridged oligo(6)biheterocycles (Fig. 1b, b', c, and c'). The planar cyclic unbridged and bridged oligo(6)biheterocyclic and co-oligo(3)biheterocyclic models we have considered, are constituted by two units in such a way that the heteroatoms are in a cis position (Fig. 1a', b', c'). These cyclic planar structures have been our starting point for the geometry optimization of each of the closed oligomers. We found that the optimized final structures could either remain in a planar conformation (a', b', c') or take a tubular conformation (a'', b'', c''). The a'' one is a tubular structure where the X heteroatoms are in trans position whereas b'' and c'' refer to different relative positions of the bridged biheterocyclic units. The structural and electronic properties of each studied oligomer are calculated considering the most stable optimized conformation. The used abbreviation for linear and cyclic unbridged oligo(6)biheterocycle with 12 rings is 6(H-H) where H = (T, F, P) for respectively thiophene, furan and pyrrole; the L or C prefix indicates if the structure is respectively linear or cyclic. The denominations for the bridged linear (b) and cyclic (b', b'') bridged oligo(6)biheterocycle are respectively L6(HYH) and C6(HYH) where Y = (O or S). For the co-oligomers (c), (c') and (c'') the denomination is L3(HYH)(H'YH') and C3(HYH)(H'YH') where $H \neq H'$ = (pyrrole or thiophene or furan) and Y = (O, S).

For the sake of consistency, the values $n=6$ for 1a, 1a', 1a'', 1b, 1b' and 1b'' and $n=3$ for 1c, 1c' and 1c'', n being the number of units in the oligomeric chains, have been chosen.

3. Results and discussion

3.1. Unbridged linear and cyclic of oligo(6)bithiophene, of oligo(6)bipyrrole, and of oligo(6)bifuran

First, in order to assess the validity of our approach, the structural and electronic properties of well known oligomers of bithiophene, bipyrrole and bifuran, and more specifically oligo(6)biheterocycles in linear (open) and cyclic (ring) chains, have been studied. The optimized values of relevant geometrical parameters are reported in Table 1 as well as the drawings of the obtained cyclic structures. All structures have been checked to be ground state ones considering their normal modes of vibration (no imaginary frequency). The optimization of closed structures of cyclic oligo(6)bifuran and cyclic oligo(6)bipyrrole, starting from a planar cisoid ring (Fig. 1a'), led to cyclic transoid conformers of tubular (crown) forms (Fig. 1a'') (dihedral angles O10–C9–C4–O3 equal to 143° and N11–C10–C4–N3 equal to 129°) whereas the optimized geometries of cyclic oligo(6)bithiophene remain cisoid planar (dihedral angles equal to 0.0 or $\sim 180^\circ$). The optimized structures (Table 1) in the three cases exhibit only small bond lengths alternation: for example for C6(F-F), the distances C6–C5, C5–C4 and C4–C9 are respectively equal to ca. 1.43, 1.38 and 1.44 Å.

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