

POLARON STATES OF 3,4-ETHYLENEDIOXYTHIOPHENE OLIGOMERS

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*The electronic and spatial structure of 3,4-ethylenedioxythiophene oligomer containing 12 units (E12) in 0, +1, +2, +3, and +4 charge states has been calculated by the method of density functional theory (B3LYP 6-31 G**). It is shown that electron conductivity in the oxidized oligomer E12⁴⁺ is provided by two bipolarons at the ends of the chain.*

Keywords: 3,4-ethylenedioxythiophene, polaron, bipolaron, conductive polymers, oxidation state, benzoid structure, quinoid structure.

Conductive polymers (CP) belong to a class of “synthetic metals”, which are polymers with a conjugated carbon chain. They have electrical, electronic, magnetic, and optical properties of metals while retaining the plasticity of ordinary polymers, which facilitates their processing and further use. Their conductivity is significantly increased when small amounts of dopants are introduced into the matrix of original polyconjugated polymers with typical conductivity from 10^{-10} to 10^{-5} S·cm⁻¹ reaching the conductivity of semiconductors or even metals from 1 to 10^5 S·cm⁻¹. Doping is performed by chemical or electrochemical oxidation (*p*-doping) or reduction (*n*-doping) of a polymer. In this case, polymer chains acquire a positive or negative charge, which is compensated by the formation of intermolecular complexes of the polymer matrix with polyions of the opposite sign in an electrolyte solution. By adjusting the doping level, it is possible to change the CP electrical conductivity in a wide range [1,2].

The main CP issue that needs to be solved to promote its practical use, is the establishment of the nature and characteristics of charge carriers. According to the literature data [3-5], polarons and/or bipolarons with or without spin can be the charge carriers, ensuring CP conductivity. Therefore, this study aims at solving the issue of charge carriers in 3,4-ethylenedioxythiophene oligomers (the structural formula of a monomer is shown in Fig. 1). The solution may be useful in the development of new materials with improved CP-based properties for their use in molecular electronics. In contrast to [3-5], higher oxidation states (+3 and +4) were considered in the work, promoting the study of more complex polaron structures.

Polythiophene derivatives, in particular poly-3,4-ethylenedioxythiophene, are the most studied among CPs. However, there are different opinions about the nature of charge carriers and their dependence on the length of a polymer chain even for this polymer.

CALCULATION METHODS AND MODELS

The work presents the results of the study of the electronic and spatial structure of 3,4-ethylenedioxythiophene oligomer containing 12 units (E12) in charge states 0, +1, +2, +3, and +4, obtained by the density functional theory method [6,

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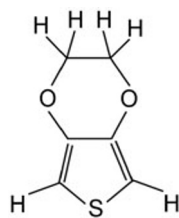


Fig. 1. Structural formula of 3,4-ethylenedioxythiophene monomer.

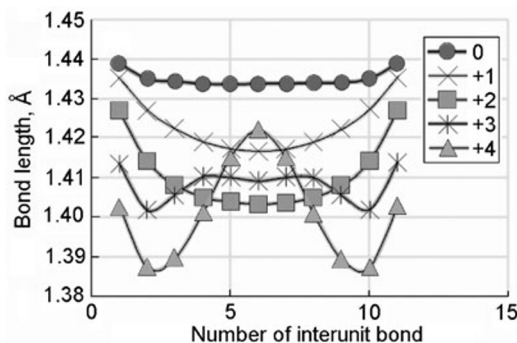


Fig. 2. Dependence of the length of carbon–carbon bonds between monomer units on their position (number) in the oligomeric chain for different charge states of the E12 oligomer.

7] containing B3LYP exchange–correlation functional [8, 9] and 6-31 G** basis set while using a software module [10]. An increase in charge simulates an increase in the doping degree. An unlimited approach, namely, UB3LYP functional, was used in the calculations of +1 and +3 charge states.

RESULTS AND DISCUSSION

The calculated C–C bond lengths between adjacent monomer units are 1.433 Å for the electroneutral state of an E12 oligomer, which is typical for the benzoid phase (Fig. 2).

However, the lengths of these bonds monotonically decrease from the ends of the chain to its center for an E12⁺ cation even at an insignificant degree of doping; reaching a minimum value of 1.417 Å at bond 6 (central), which is typical for the quinoid phase of the studied system. A similar dependence of bond lengths between monomer units is also observed for an E12²⁺ dication. They are considerably shorter compared to similar bond lengths in the E12⁺ cation, which determines the increase in the contribution of the quinoid phase. This indicates the presence of delocalized polaronic (for E12⁺ cation) and bipolaronic (for E12²⁺ dication) states. Typical minima appear on the corresponding curves of dependence of the interunit bond length on its number for higher oxidation states (+3 and +4). The minima are observed in the regions of bonds 2, 3, 6, 9, and 10 in the case of an E12³⁺ oligomer, which indicates a further increase in the contribution of the quinoid phase and the formation of three separated polarons at the ends and the center of the oligomer chain. The local minimum localized in the center of the chain (for E12³⁺) is rather smooth. However, it should be noted that the state with +3 oxidation state is characterized by three polarons considering the presence of three polaron levels on the energy level diagram (Fig. 3). The minima in the regions of bonds 2, 3, 9, and 10 correspond to two separated bipolarons at the ends of the chain for an E12⁴⁺ oligomer. Similar dependences were obtained for charged pyrrole oligomers [4, 11].

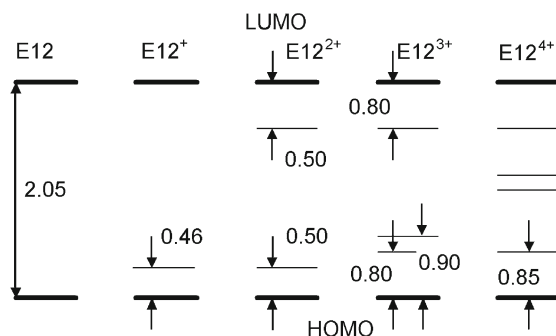


Fig. 3. Formation of the polaron region depending on the charge state of the E12 oligomer.

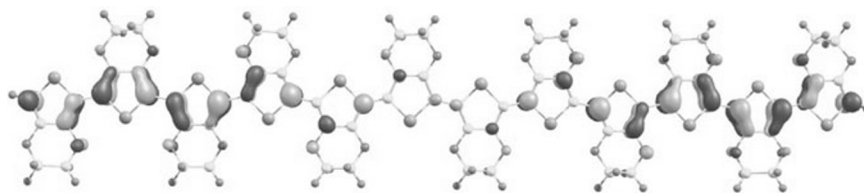


Fig. 4. The structure of the molecular orbital localized at the lowest polaronic level in the gap between the HOMO and LUMO energies of the E12⁴⁺ oligomer.

When a positive charge appears in the E12 oligomer, there is a polaron hole level, which is 0.46 eV away from the upper level of the valence band, in the gap between energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the E12⁺ cation. Since an electron is removed from the HOMO level of the E12 oligomer during the formation of the E12⁺ cation, the level corresponding to the formation of a hole will be located above the HOMO level. It is similar to the process when one electron is removed from a doubly occupied molecular orbital of a typical molecule. The width of this gap is 2.05 eV for the neutral E12 oligomer. Fig. 3 shows the energy diagram of frontal MO and polaron levels between them. According to the article, the HOMO level will be identified at the upper level of the valence band, while the LUMO level will be identified at the bottom of the conduction band.

Two polaron hole levels appear in the E12²⁺ dication with a further increase in the doping degree; which are 0.50 eV away from the upper level of the valence band and the bottom of the conduction band. There are three such levels in the E12³⁺ cation; two of which are 0.80 eV away from the upper level of the valence band and the bottom of the conduction band, while one is located 0.90 eV higher than the upper level of the valence band. Four such hole levels are formed for the E12⁴⁺ cation during quadruple ionization of the E12 oligomer; thus promoting in pairs the formation of a polaron region in the energy gap between the HOMO and LUMO levels. The structure of a molecular orbital corresponding to the lowest polaron level, located at a distance of 0.85 eV from the HOMO level, is shown in Fig. 4. It demonstrates the formation of two bipolarons at the ends of the E12 oligomer. According to the appropriate interpretation, the experimental data can confirm the formation of two polarons [11-14].

Fig. 4 shows that the quinoid phase of the studied molecular orbital of the E12⁴⁺ cation is localized at the ends of the chain in two regions, each of which covers four monomer units. This indicates that the vacancies (holes) are not delocalized throughout the oligomer chain, as it follows from the band theory of solids. Localization of holes occurs on two marginal four-unit sections of the E12⁴⁺ cation; namely, a pair of bipolarons with a charge of +2|e| appears at the ends of the oligomeric chain. It causes a structural deformation of the carbon skeleton of an oligomer (the transition from the benzenoid phase to the quinoid phase). The positive charges of two bipolarons exert a Coulomb effect on each other. Both polarons and bipolarons under the action of an electric field can move along the polymer chain, leading to rearrangement of double and single bonds of the conjugated system (Fig. 5).

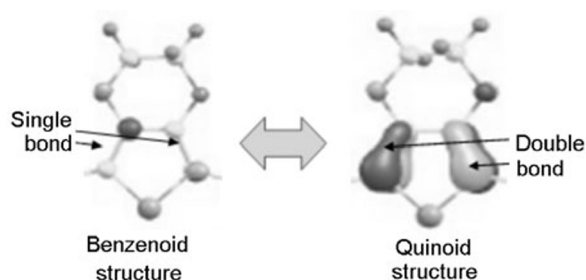


Fig. 5. The benzenoid and quinoid structure of monomer units of the $E12^{4+}$ cation.

Therefore, the obtained results indicate that conductivity in the highly oxidized (heavily doped) 3,4-ethylenedioxythiophene oligomer $E12^{4+}$ is provided by the formation of two bipolarons at the ends of the chain. On the one hand, bipolaron states become more stable than states with separated polarons when the chain is shortened [4, 5, 11]; on the other hand, an increase in the oxidation state under other conditions is equivalent to chain shortening (the degree of doping increases in both cases). Therefore, it can be expected that further oxidation of 3,4-ethylenedioxythiophene oligomers will result in the increased susceptibility of such materials to bipolaron conductivity. It can also be assumed that more complex polaron structures can act as charge carriers for oligomers with other number of 3,4-ethylenedioxythiophene units.

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