FORMATION OF POLARON BANDS IN OXIDIZED 3,4-ETHYLENEDIOXYTHIOPHENE OLIGOMER

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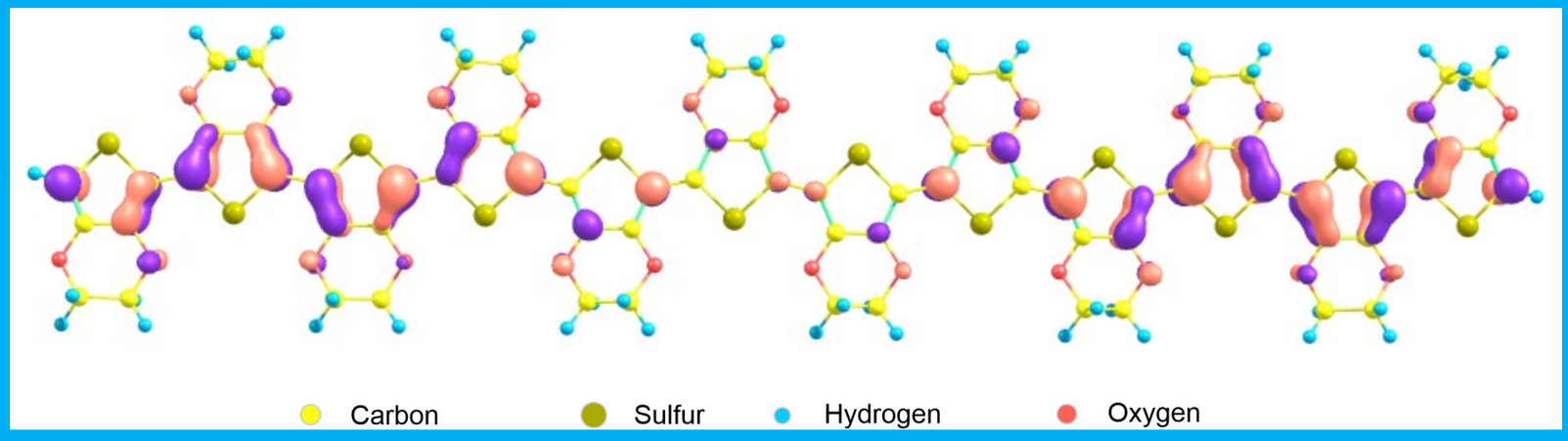
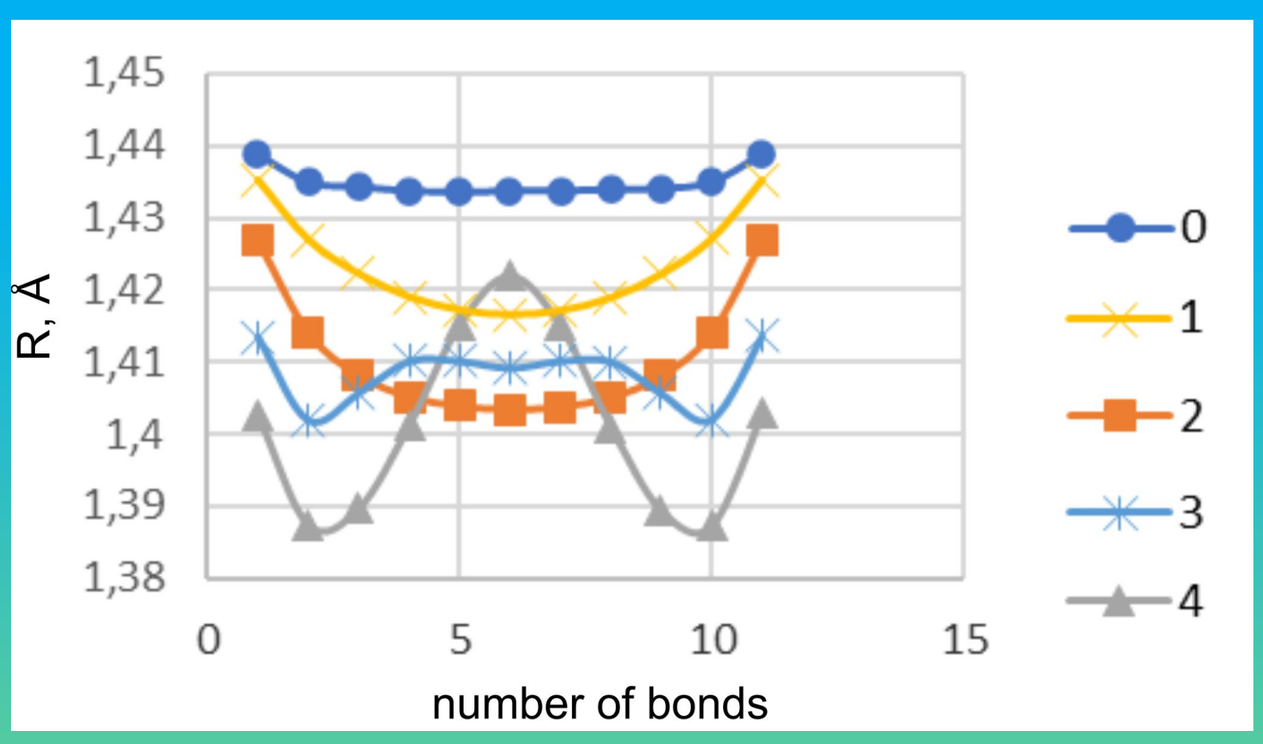
Derivatives of polythiophene, including poly 3,4-ethylenedioxythiophene, are the most studied among conductive polymers. However, even for this polymer, there are conflicting opinions about the nature of charge carriers and its dependence on the length of the polymer chain.

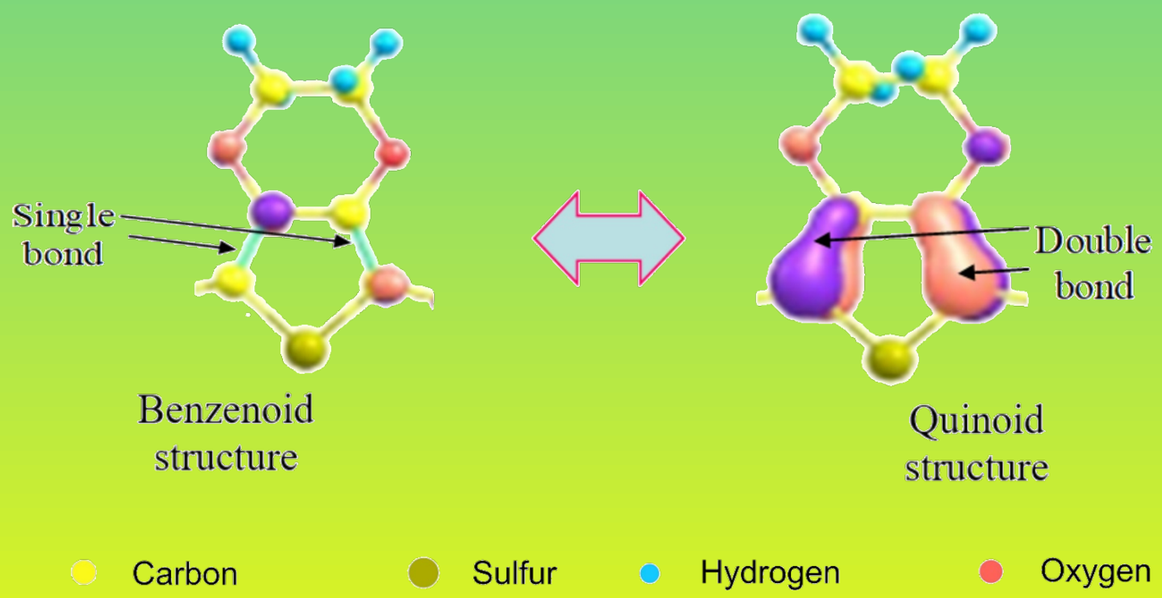


Structure of the molecular orbital localized at the lowest polaron level in the gap between the HOMO and LUMO energies of the $E12^{4+}$ oligomer.

For the electroneutral state of the E12 oligomer, the calculated C–C bond lengths between adjacent monomer units are 1.433 Å, which is typical of the benzenoid phase



Dependence of the length of C–C bonds between monomeric units on the charge state of the E12 oligomer. Bond numbering begins with the bond between the first and second monomer units.

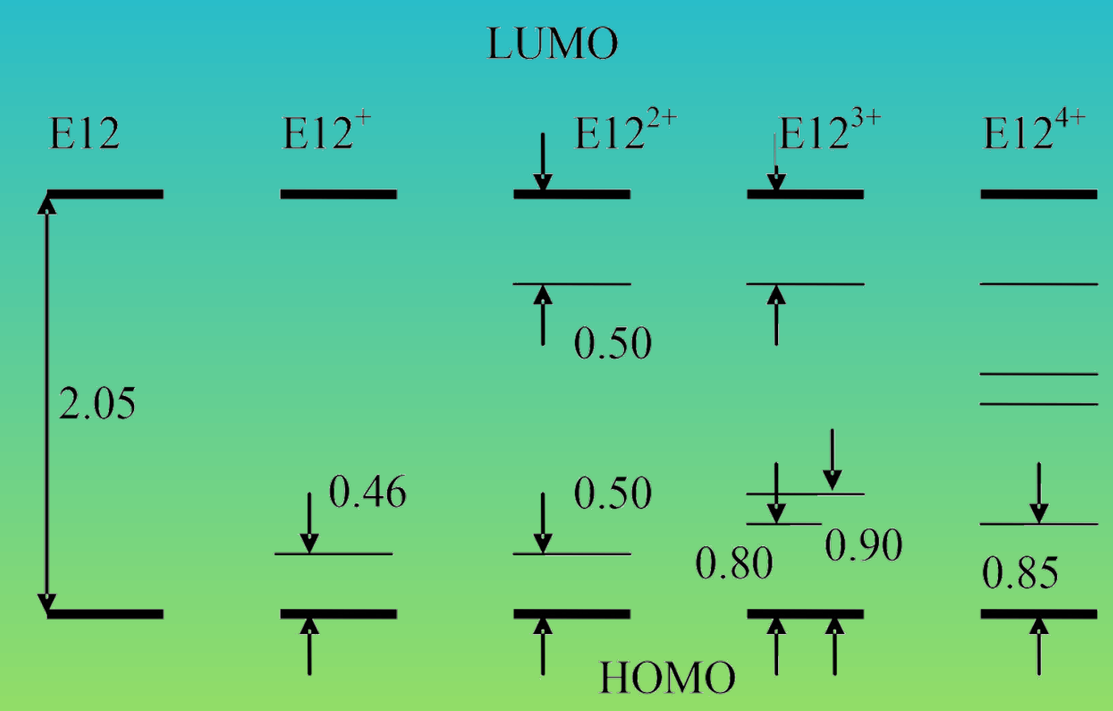


Benzoic and quinoid structures of the monomer units of the $E12^{4+}$ cation

Calculation methods and models

The results of a study of the electronic and spatial structure obtained by the density functional theory method with exchange-correlation functional B3LYP 6-31 G**. An increasing in charge is simulates an increase in the degree of doping. An unrestricted approach was used (UB3LYP functional) for calculations in charge states +1 and +2.

When a positive charge appears in the E12 oligomer, a polaron "hole" level appears in the gap between the energies of the upper occupied molecular orbital (HOMO) and the lower unoccupied molecular orbital (LUMO) of the E121+ cation, which is 0.46 eV away from the top of the valence band



Formation of the polaron band (eV) depending on the charge state of the E12 oligomer.

Thus, the obtained results allow us to conclude that in the oxidized 3,4-ethylenedioxythiophene oligomer containing 12 monomer units, at a high degree of doping, the conductivity is provided by the formation of two polarons at the ends of the chain. For oligomers with a different number of units and 3,4-ethylenedioxythiophene, more complex polaron structures can be charge carriers.