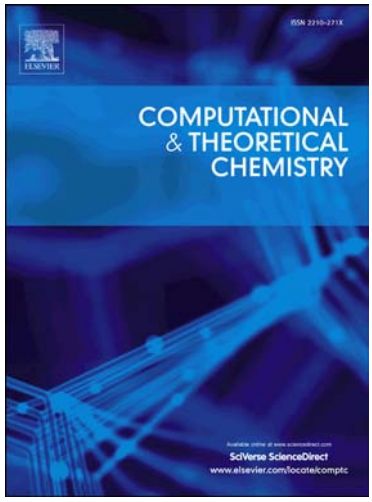

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Resonance assisted electron transport in olygophenyl conductors

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Abstract

High electron delocalization is responsible of the unusual electric conductance displayed by some πconjugated olygophenyl chains. Recently, it has been observed that oligophenyl chains connected via methylene linkers to gold electrodes are significantly better conductors than equivalent chains with a direct ring-metal contact. In recent theoretical studies it has been shown how a simple resonance model may explain the different conductance of these chains, connecting this electric response property with chemical concepts such as aromaticity and bond order. In this work, we validate the previous qualitative model by analysing the effect of an external electric perturbation over domain averaged Fermi hole (DAFH) densities, bond orders and atomic charges obtained with the Hirshfeld iterative atomic partitioning of the molecular electron densities. The variations in the DAFH plots reflect perfectly the role played by resonance on the electrode-electrode electron transfer. Whereas charge transfer is mainly due to πelectrons in oligophenyl chains connected through methylene linkers, following a resonance assisted mechanism, it occurs via σelectrons with a direct ring-metal contact and π electrons polarize in counter-field direction. Calculation of the variations experienced by the bond orders and atomic charges in the molecular junction upon the external electric perturbation confirms the bonding reorganization predicted by the resonance model.