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Electronic structure of highly conducting poly-(p-phenylene) chains: An *ab initio* Hartree-Fock study

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Ab initio self-consistent-field—linear combination of atomic orbitals—molecular-orbitals calculations on undoped and lithium-doped p-quaterphenyl, a model chain for poly-(p-phenylene), demonstrate dramatic changes in geometrical and electronic structures upon doping. For a charge transfer of less than $0.1e$ per carbon atom, p-quaterphenyl becomes nearly coplanar and the rings adopt a strong quinoidal character, resulting in an important decrease of the band gap. This stresses the need for taking proper account of such modifications in order to comprehend the physics of the insulator-metal transition in the whole class of highly conducting organic polymers. Possible bipolaron defects in highly doped poly-(p-phenylene) are shown to extend over about four rings.

Among the new class of highly conducting doped organic polymers, poly-(p-phenylene) (PPP) appears very attractive for many reasons. High conductivities can be achieved, e.g., of the order of 500 S/cm upon doping with AsF_5.[1] Formation of rechargeable batteries based on doped PPP has been demonstrated.[2] AsF_5 doping of PPP oligomers single crystals (p-terphenyl, p-quaterphenyl, p-sexiphenyl) provides a new solid-state polymerization process and also leads to highly conducting complexes.[3] Experimental[4] and theoretical[5] studies have suggested the fascinating possibility of the presence of bipolarons on the chain in the highly doped regime.

However, polyacetylene (PA) has been so far the most-studied compound in the field. A reason for this is that all-trans PA is very unique in possessing a degenerate ground state. This degeneracy leads to possible soliton excitations and related lattice structural deformations. Theoretical works on the soliton model,[6] as well as on highly-lithium-doped PA,[7] have clearly demonstrated the inadequacy of rigid-band models in order to explain the soliton-based physics of the insulator-metal transition in all-trans PA. On the other hand, PPP does not possess any degenerate ground state and the same is true for the other polymers forming highly conducting complexes. Recent theoretical work on PA and PPP suggested the appearance of doping-induced geometrical and electronic changes also in PPP.[5] However, that work was based on a crude model (Hückel theory) unable to make quantitative predictions and neglecting the presence of dopants. Therefore, in this Communication, we investigate very precisely through *ab initio* self-consistent-field—linear combination of atomic orbitals—molecular-orbitals (SCF-LCAO-MO) geometry optimizations, the changes in electronic and geometrical structures that are induced upon the lithium doping of a model p-phenylene chain, p-quaterphenyl (PQP).

The key results of our calculations are that, for a charge transfer of less than $0.1e$ per carbon atom, the chain becomes nearly coplanar, the rings adopt a strong quinoidal character, and the band gap is significantly decreased.

Calculations are performed in the framework of the restricted-Hartree-Fock (RHF) SCF-LCAO-MO *ab initio* technique, at minimal Slater-type-orbital—three-Gaussians (STO-3G) basis set level. This method is known in quantum chemistry to afford good ground-state properties. Standard Slater exponents are used for carbon and hydrogen. For lithium, we adopt a basis set tested in calculations on cation-ligand interactions[8]: The $1s$ shell, with exponent $\zeta = 2.69$, is represented by six Gaussians (6G expansion); the $2s$ orbital, represented by a 3G expansion, has an optimized exponent $\zeta = 0.95$; and the $2p$ orbitals are suppressed. Note that in all calculations, the carbon-hydrogen bond length is set at 1.08 Å. For undoped PQP, $C_{24}H_{18}$, we optimize seven parameters under D_2 symmetry: the torsion angle between two consecutive rings; the C—C bonds between rings; within rings, the C—C bonds "parallel" to the chain axis and the bonds "inclined" with respect to it; the bond angles between an inclined bond and, respectively, another inclined bond, a parallel bond, and a C—H bond. The optimized geometry and the charges on C atoms obtained from a Mulliken population analysis are given in Fig. 1.

Optimized bond lengths and bond angles are in close agreement with x-ray and neutron-diffraction data on PQP and p-terphenyl.[9–11] The slight quinoid structure we obtain within the rings is supported by

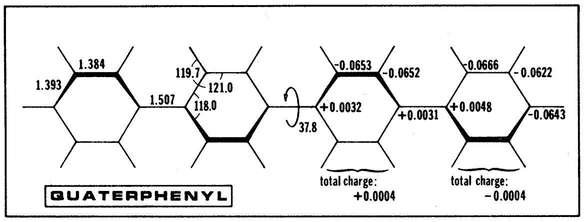

FIG. 1. p-quaterphenyl, $C_{24}H_{18}$ (D_2 symmetry): STO-3G RHF optimized geometry (bond lengths in Å, bond angles in degrees) and carbon atomic charges (in e).

the neutron-diffraction experiments on p-terphenyl.[11] The very large 37.8° torsion angle agrees very well with the 42° value determined from diffraction data on gaseous biphenyl.[12] Note that the maximum difference in C—C bond lengths along the chain is 0.123 Å, i.e., larger than the estimate in PA ($\sim$0.1 Å).[13] Charges on C atoms connected to H atoms are of the order of 0.06e, due to the slight polarization of the C—H bond. Total charges per ring are, however, negligibly small. Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) orbital energies are, respectively, equal to -0.2228 and $+0.2003$ a.u.

In the doped case, we add two lithium atoms to PQP. This formally corresponds to a per monomer 50% doping level, as is usually achieved in n-doped PPP.[1] Each lithium is located at a fixed 1.85-Å distance above the middle of an inner ring and is therefore positioned almost equidistant from the atoms of the ring. This structure is in complete analogy with what is found in the lithium intercalated graphite compound.[14] We optimize the same parameters as before, but allow for different relaxations of bond angles and lengths within rings, between the inner and outer rings. We are than in a position to determine the extent of the influence of the lithium atoms. Results are presented in Fig. 2.

The calculations predict a charge transfer toward the chain of the order of 0.64e per lithium atom. As is deduced from the total charges per ring, most of the charge is transferred to the inner rings, only 22.4% of the charge going to the outer rings. It can therefore be expected that in longer chains, the charge transferred to (and the influence on) next-nearest-neighbor rings will be very small. Since in these calculations we take into account charge transfer from two close lithium atoms, this actually mimics the situation where bipolarons are possibly present on the chain. As discussed in Ref. 5, bipolarons correspond to doubly charged spatially localized defects. Our results imply then that bipolarons extend over about four rings.

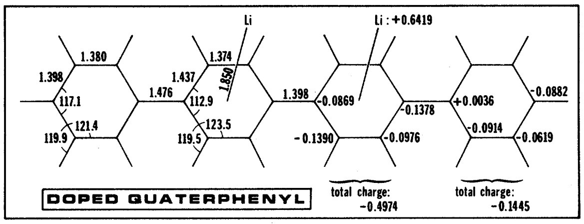

FIG. 2. Lithium-doped p-quaterphenyl, $C_{24}H_{18}Li_2$ (C_2 symmetry): STO-3G RHF optimized geometry (bond lengths in Å, bond angles in degrees) and lithium and carbon atomic changes (in e). A different relaxation is allowed for inner and outer rings. Distance of a lithium atom from the middle of the ring over which it is centered is fixed at 1.85 Å. Optimized torsion angle between two consecutive rings is 2.0°.

Charge transfer causes drastic modifications of PQP geometry. The system becomes nearly coplanar since the torsion angle evolves from 37.8° to 2.0°. As a result of the difference in charge transfer between the inner and outer rings, evolution of the geometrical parameters in the two types of rings are quite different. In the inner rings, the C—C bond between rings is markedly reduced by 0.109 to 1.398 Å. Parallel bonds in the rings acquire a slightly more pronounced double-bond character, decreasing by 0.010 Å. Inclined bonds increase significantly by 0.044 Å. The maximum C—C bond length difference in the inner rings becomes 0.063 Å, i.e., one-half of what is found in the undoped case. These changes contribute to give the inner rings a very strong quinoid character. The same is true for the outer rings, however by a smaller degree: Bonds within rings change by less than 0.005 Å, bonds between rings decrease by 0.031 Å.

As a consequence of the decrease in maximum C—C bond-lengths difference and the achievement of a nearly coplanar conformation leading to a much larger overlap between atomic π orbitals, the first optical transition energy is expected to be reduced. As a matter of fact, the HOMO-LUMO separation decreases from 0.4231 to 0.1769 a.u., the HOMO orbital energy being strongly pushed up in energy, in agreement with the transfer of electrons towards the chain. HOMO-LUMO separations are, however, known to bear little quantitative meaning at the RHF level. Therefore, we have performed calculations using the valence effective Hamiltonian (VEH) *ab initio* technique that has been shown to properly predict band gaps in hydrocarbon polymer chains.[15] We have computed the band structures of a PPP chain with the RHF optimized coordinates from undoped PQP (except for the torsion angle set at the 22.7° solid-state value) and a neutral polyquinoid chain with the coordinates of the inner rings from lithium-doped PQP. We obtain for PPP a 3.5-eV band-gap value (in close agreement with the 3.4-eV experimental estimate[16]). For the polyquinoid chain, the band gap is reduced by one-half, decreasing to 1.7 eV. This suggests that upon strong doping of PPP, bipolaron states should appear in the gap at roughly 0.9

$[\simeq(3.5-1.7)/2]$ eV above the valence-band edge and below the conduction-band edge. Broadening of these states can lead to the formation of bands and conduction through bipolarons that carry no spin. Such a conduction mechanism through spinless carriers is supported by the absence of any significant Pauli susceptibility in the metallic regime of SbF_5 doped PPP.[4]

In summary, we have performed RHF *ab initio* calculations on undoped and lithium-doped poly-(*p*-phenylene) model chains. The calculations demonstrate that charge transfer provokes dramatic changes in the geometrical and electronic structures of PPP. These modifications are to play a key role in the physics of the insulator-metal transition in PPP and all the other highly conducting organic polymers and not only in systems possessing a degenerate ground state. The calculations indicate that doubly charged spinless defects (bipolarons) possibly formed in highly doped PPP extend over about four rings.

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