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Electronic Structure of the Pentacene Single Crystal: Relation to Transport Properties

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The field of molecular organic semiconductors is being revolutionized by the availability of ultrahigh purity single crystals that have allowed the demonstration of phenomena long thought to be restricted to inorganic semiconductors. Batlogg and coworkers have recently demonstrated in single crystals of tetracene and pentacene: the appearance of electron and hole mobilities on the order of 10^4-10^5 cm^2/V^{-1} s^{-1} at very low temperature;[1,2] the observation of the fractional quantum Hall effect[1] and superconductivity;[3] the fabrication of a solid-state injection laser.[4] These truly extraordinary developments trigger a renewed interest in understanding the transport properties of molecular organic materials, since the stage is now set for theoretical calculations to be directly confronted to experimental data that are not hampered by structural defects and impurities.[5] Recently, we have exploited a theoretical approach based on the semiempirical Hartree−Fock INDO (intermediate neglect of differential overlap) Hamiltonian where calculations performed on clusters extracted from the single-crystal structures allow us:[6] (i) to determine the preferential directions for charge transport, (ii) to estimate the relative mobilities of electrons and holes, and (iii) to provide reasonable estimates for the intermolecular transfer integrals t for holes and electrons (based on the splitting of the HOMO and LUMO levels upon interaction, respectively[7]); these transfer integrals can then be used as input into macroscopic models based for instance on polaron transport.[8] It is important to point out that the reliability of the INDO method to describe intermolecular processes in organic assemblies has been recognized in earlier theoretical works.[9] An advantage of the cluster approach with respect to full band−structure calculations is that the INDO Hamiltonian can also be coupled to a configuration interaction (CI) scheme in order to characterize the optical absorption and emission properties of the single crystals.[6]

In this communication, we focus on the electronic structure of the single crystal of pentacene since this is one of the most promising materials for the fabrication of highly efficient field-effect transistors as well as more complex circuit architectures.[2,10] In agreement with recent experimental data, our calculations demonstrate that: (i) electrons can be as mobile as holes in organic solids in the absence of impurities and defects, in contradiction to conventional wisdom and the results of earlier mobility measurements pointing most often to a dominant hole transport,[5] and (ii) the valence and conduction bandwidths in such molecular crystals can be much larger than the usual expectations of at most 100 me.[11]

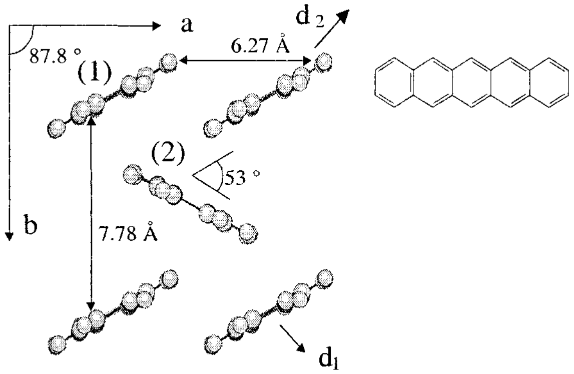

Figure 1. Lattice parameters within the *ab* layer of the single crystal of pentacene. Labels 1 and 2 refer to the two inequivalent molecules in the layer; axes *d*1 and *d*2 are those that connect these inequivalent molecules.

Figure 1 illustrates the herringbone packing of the pentacene molecules within the *ab* layer of the crystal (triniclic space group P-1[12]). There are two inequivalent molecules within the layers (labeled 1 and 2 in Figure 1), which have slightly different geometries, a feature that cannot be simply attributed to statistical fluctuations during the X-ray measurements;[13] this leads to a significant difference in the INDO-calculated HOMO andLUMO level energies of the two molecules (61 and 70 meV, respectively).

We find that significant electronic splittings are obtained only along the *a* axis and the *d*1 and *d*2 axes. Interactions between molecules located in adjacent layers (along *c*) are negligible. Thus, it can be concluded that charge transport in pentacene has a dominant two-dimensional character and takes place within the layers in directions that are nearly perpendicular to the long molecular axes. The same behavior has been established in the α-sexithienyl (6T) single crystal which presents a similar herringbone packing;[6,14] this contrasts, however, with the situation in self-organized films of poly-3-hexylthiophene chains where charge transport efficiently takes place along the long chain axes.[15] Interestingly, a one-dimensional transport perpendicular to the chain axes has been predicted in the bis-dithienothiophene (BDT) single crystal[6] where one finds a nearly cofacial packing of the molecules within the layers.[16]

Figure 2 gives the evolution of the width of the HOMO and LUMO bands as a function of the number of pentacene molecules considered in interaction and stacked along the *a* axis. The interchain transfer integrals t_a (estimated as half the electronic splitting in the dimer) are very similar for electrons and holes, on the order of 47 meV. Note that the calculated bandwidths evolve linearly as a function of $\cos(\pi/N + 1)$, with N being the number of molecules; this implies that the intermolecular interac-

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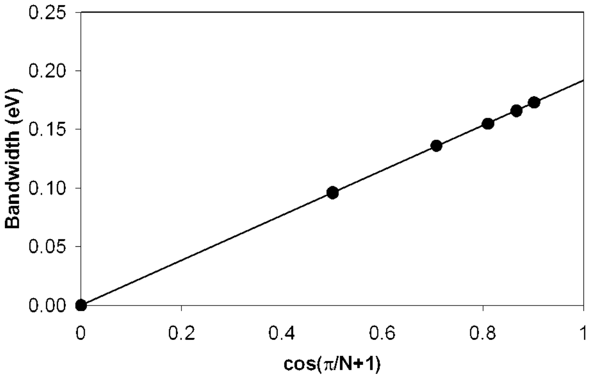

Figure 2. Evolution of the INDO-calculated bandwidths formed by the HOMO levels of pentacene molecules as a function of $\cos(\pi/N + 1)$, with N being the number of interacting units along the a axis; nearly identical values are obtained for the LUMO levels.

tions in pentacene can easily be cast into a tight-binding (Hückel) model, as was also observed for 6T and BDT.[6]

The evolution of the HOMO and LUMO bandwidths formed by pentacene molecules stacked along the $d1$ and $d2$ axes does not match the classical cosine relationship due to the fact that the total HOMO and LUMO splittings result from both the interaction processes and the offset of the frontier levels of the inequivalent units that was described above. Since the evolutions obtained for the equivalent molecules along the a axis follow a tight-binding model, we have extracted the effective transfer integrals t' along the $d1$ and $d2$ axes from the exact expression of the total splitting for a dimer within the tight-binding formalism, which is given by:[17]

$$2t' = \sqrt{4t^2 - (E_1 - E_2)^2} \tag{1}$$

where t' and t are the effective and total interchain transfer integrals, respectively, and $E_1 - E_2$ the energy offset between the HOMO or LUMO levels. Application of eq 1 to the INDO results leads to values of t'_{d1} [t'_{d2}] equal to 80 and 59 meV [72 and 88 meV] for the HOMO and LUMO levels, respectively. The total valence and conduction bandwidths can then be estimated in the context of a tight-binding approach, in terms of the effective transfer integrals, as the energy difference between the most bonding and antibonding interchain patterns for a herringbone packing of the interacting units. When t_a is smaller than t'_{d1} and t'_{d2}, as is the case in the pentacene crystal, the total bandwidth is then found to be equal to $4t'_{d1} + 4t'_{d2}$.[18] This leads to very large values of 608 and 588 meV for the valence and conduction bandwidths, respectively. These large calculated bandwidths are fully consistent with recent experimental estimates on the order of 500 meV[1]. These values constitute a considerable improvement with respect to earlier extended-Hückel calculations[1] and validate the use of the INDO Hamiltonian to describe intermolecular interactions.

It is most interesting to point out that the experimental and theoretical estimates of the conduction and valence bandwidths in the single crystal of pentacene have the same order of magnitude as the conduction bandwidth characteristic of the widely studied TTF−TCNQ (tetrathiafulvalene−tetracyanoquinodimethane) organic charge-transfer salt and its derivatives.[19] In the TTF−TCNQ case, a 0.59 |e| charge transfer takes place in the ground state between the donor and acceptor molecules that are located in adjacent segregated stacks; this leads to one-dimensional metallic channels in each of the stacks due to the appearance of a partly filled conduction band. The bandwidths are estimated to be on the order of 500 meV, from various sets of experimental measurements.[19] However, that the bandwidths are very comparable in the TTF−TCNQ and pentacene crystals is a priori unexpected in view of the large overlap and short interchain separation (∼3.8 Å) along TTF or TCNQ stacks and the apparent weak overlap between the inequivalent molecules in the herringbone pentacene single crystal (see Figure 1). This demonstrates that the electronic splitting of the HOMO/LUMO levels results from a very subtle interplay between the distribution of the electronic density over the molecule and the relative positions of the interacting units. Thus, estimates of the relative HOMO and LUMO splittings in molecular crystals are hardly predictable from a simple examination of the crystal packing and require detailed calculations (except for a few simple cases[20]).

The similar splittings calculated for the HOMO and LUMO levels are consistent with recent experimental data,[2] indicating that electrons and holes have very similar mobilities, whatever the transport mechanism (hopping or band-like motion). At very low temperature where a band-like picture prevails (and thus the total bandwidth governs the mobilities), the hole mobility in the pentacene single crystal is expected to be much higher than in the 6T and BDT crystals since the total valence bandwidth estimated at the INDO level for the two materials is much smaller than in pentacene (240 and 328 meV for the low- and high-temperature phases of 6T, respectively, and 344 meV in BDT[6]). However, at room temperature, where hopping processes occur and where the individual interchain transfer integrals between adjacent neighbors are the critical parameters to be considered, the highest hole mobilities are not expected to be observed for the pentacene single crystal for which the largest value, t'_{d1}, is 80 meV; the largest interchain transfer integrals for holes among the three compounds are calculated in the BDT single crystal (on the order of 170 meV [6]).

To summarize, we have shown that INDO semiempirical quantum-chemical calculations on aggregates can be exploited to obtain good estimates of important parameters governing the transport properties of technologically relevant organic molecular single crystals. Excellent agreement with experiment is obtained for the pentacene single crystal.

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