

Force field modelling of oligothiophenes

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We present molecular dynamics simulations of tetrathiophene thin films on a graphite surface, and the results of a subsequent re-parametrization of an improved force field for this and other oligothiophenes.

The tetrathiophene/graphite simulations[1] employed the CFF91 force field of the Materials Studio/Discover package, with the interring torsion potential parametrized on the basis of high-level (MP2/aug-cc-pVTZ) calculations on bithiophene.[2] We find that the molecules on the first layer are relatively planar and packed against the underlying surface, while those outside it are not arranged in well-defined layers and are more conformationally disordered. On the time scale of the simulations, the molecules do not crystallize but rather achieve a liquid-crystalline-like state, with their average director parallel to the surface (see Figure 1). However, the same simulations highlighted the need to develop an improved force field, since CFF91 fails to describe correctly the observed crystal structures.

A thorough test and development of a force field for crystalline oligothiophenes has been recently completed by us.[3] Starting from the MM3 forcefield of Allinger and coworkers, different methods for the representation of electrostatic interactions were investigated. Atomic charges and distributed multipoles were obtained from ab initio calculations (see Figure 2). Using these models, lattice parameters and molecular geometries of the polymorphs of tetra- and hexathiophene and of tetrahexilsexithiophene were optimized. We find that the point charge method is at least as good as the multipole method, and was thus adopted for molecular dynamics simulations of the crystals. The Lennard-Jones interactions parameters were also adjusted in order to reproduce the experimental densities, in room-temperature simulations. This forcefield was used to compute the surface energies of the two polymorphs of tetrathiophene, to be presented in the poster by Campione et al. Molecular dynamics simulations of crystal surface reconstructions, diffusion of deposited molecules etc., are currently under way.

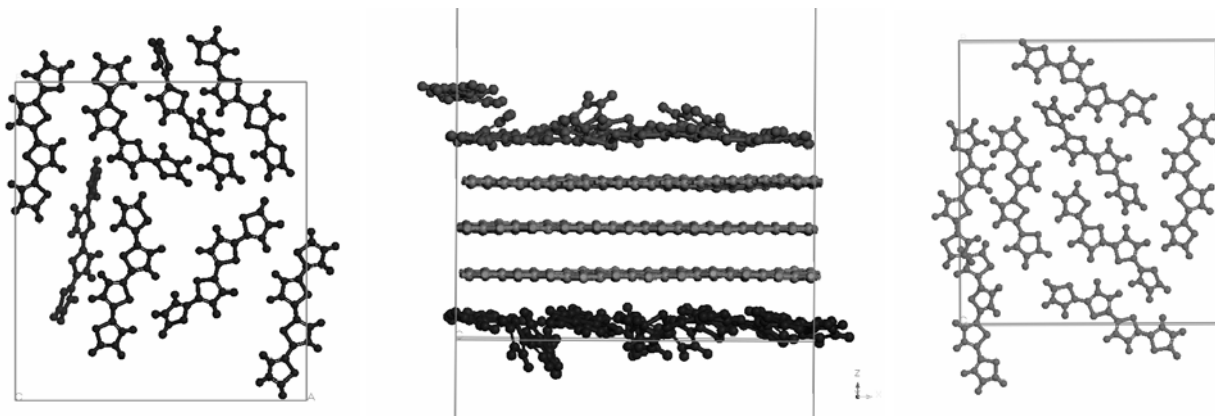


Figure 1: Side view (center) and top views (left and right) of the final configuration in a molecular dynamics simulation of tetrathiophene on graphite, at 300 K. There are 8 molecules on each side of the graphite slab, which has a surface area of 806 \AA^2 .

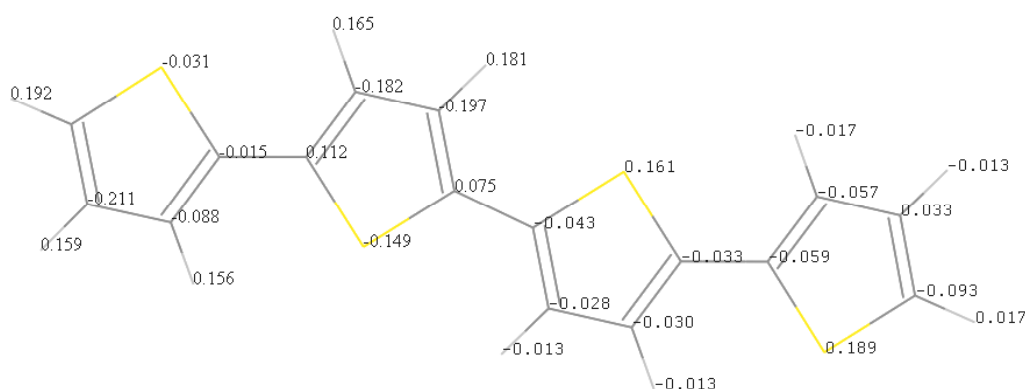


Figure 2: Comparison of the atomic charges of tetrathiophene, obtained by fitting the electrostatic potential (left-hand side) and by a distributed multipole analysis (right-hand side) of B3LYP/6-31G** electron densities. Note the fair degree of transferability of these quantities, so that “chemically similar” sites bear similar charges.

References

- [1] V. Marcon, G. Raos and G. Allegra, *Macromol. Theory Simul.*, in press.
- [2] G. Raos, A. Famulari and V. Marcon, *Chem. Phys. Lett.* **379**, 364 (2003).
- [3] G. Raos and V. Marcon, manuscript in preparation.