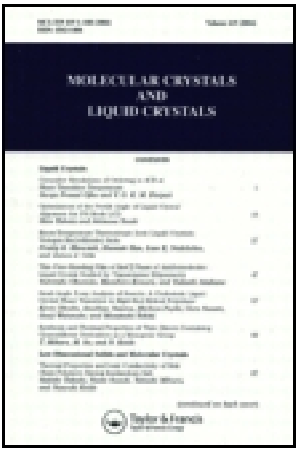

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Interpretation of Anomalous Absorption Spectra. A Theoretical Study of the Geometric, Electronic and Optical Properties of Poly[3-(4-Octylphenyl)-Thiophene]

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Version of record first published: 04 Oct 2006.

To cite this article: Magnus Boman & Sven Stafström (1994): Interpretation of Anomalous Absorption Spectra. A Theoretical Study of the Geometric, Electronic and Optical Properties of Poly[3-(4-Octylphenyl)-Thiophene], Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 256:1, 705-710

To link to this article: http://dx.doi.org/10.1080/10587259408039313

Mol. Cryst. Liq. Cryst. 1994, Vol. 256, pp. 705–710
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INTERPRETATION OF ANOMALOUS ABSORPTION SPECTRA. A THEORETICAL STUDY OF THE GEOMETRIC, ELECTRONIC AND OPTICAL PROPERTIES OF POLY[3–(4–OCTYLPHENYL)–THIOPHENE].

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Abstract The geometric, electronic, and optical properties of poly–[3–(4–octylphenyl)–thiophene] are studied. The effect of the side groups as well as doping is analyzed. Band structures, oscillator strengths and optical absorption spectra are calculated. Absorption spectra reported for the doped polymer show up to four peaks below the band–gap energy.

INTRODUCTION

Polythiophene (PT) is a prototype for non–degenerate ground state conjugated polymers. Side groups are however often substituted on the thiophene unit in order to get a soluble polymer. This type of polymers have already been used to fabricate LED, FET and other electronic devices. The side groups have normally no effect on the electronic and optical properties of the polymer. However, recently optical absorption spectra were reported for poly[3–(4–octylphenyl)–thiophene][1] (POPT), a polymer with a phenyl ring together with an alkyl chain as a side group on each thiophene ring (Figure 1). Absorption spectra for the doped sample have up to four peaks below the band–gap energy. This differ significantly from absorption spectra reported for polythiophene, which normally shows only two peaks. The unusual spectroscopical features of POPT were interpreted as spectroscopic evidence for asymmetric polaron states. This raises questions about the influence of the side group on the properties of POPT. The phenyl part of the side group has a delocalized π–electron system and might therefor affect the polymer to a larger extent and in a different way compared to the influence of, for instance, side groups with saturated hydrocarbons only.

The work reported here includes a theoretical study of the geometric, electronic and optical properties of POPT. The effect on the geometry due to the side groups as well as charge injection doping are calculated. Band structures, oscillator strengths and optical absorption spectra are calculated for both neutral and doped systems.

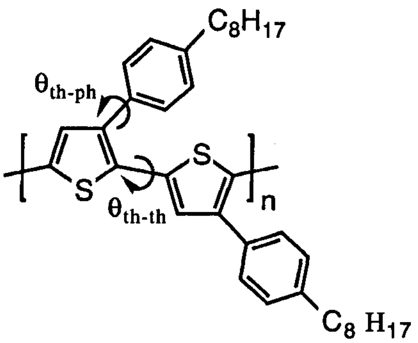

FIGURE 1 The unit cell of POPT.

METHODOLOGY

The scope of this work is to investigate the importance of side groups with a delocalized π–electron system, therefore the saturated alkyl side chain of POPT is left out from our model system which consequently is referred to as PPT. The geometry of different systems has been determined by energy minimization of oligomers that consist of up to eight monomers. We have used an optimization procedure that combines the semi–empirical methods AM1[2] and MNDO[3]. It is found that AM1 gives more reliable torsion angles between neighboring rings, while MNDO results have a dimerization that shows larger agreement with *ab initio* calculations[4] than AM1.

The band structure is calculated using the Valence Effective Hamiltonian[5] (VEH) for a polymer chain with periodic boundary conditions. The band states $\phi_n(k)$ and band energies $E_n(k)$ are obtained by solving the eigenvalue problem

$$H\phi_n(k) = E_n(k)\phi_n(k), \qquad (1)$$

where H is the hamiltonian, n band index, and k the wave vector. The primitive unit cell of the neutral system is always chosen to consist of two monomers in order to allow for arbitrary torsion angles between neighboring thiophene rings. Doped systems are also assumed to be periodic but with larger unit cells.

The optical properties of POPT are studied by calculating absorption spectra based on the oscillator strengths for different inter band transitions. The dipole approximation is used and only direct transitions are considered. The absorption cross section coefficient σ(E) is then given by

$$\sigma(E) = \frac{4\pi^2}{3}\alpha \times$$
$$\sum_k \sum_{m,n} \eta_{m,n}(E_m(k) - E_n(k))| < \phi_m(k)|r|\phi_n(k) > |^2 \delta(E - [E_m(k) - E_n(k)]), \qquad (2)$$

where m and n are the band index of the final and initial state respectively, and α is the fine structure constant. The factor $\eta_{m,n} \in \{0,1,2\}$ counts the number of possible transitions allowed by the occupancy of the two states. The summations are carried out over the whole Brillouin zone and all band indices. Eq. (2) is the result obtained after averaging over all possible orientations of the polymer relative to polarization direction of the incident probe light. To simulate lifetime broadening as well as other effects the delta function in Eq. (2) has been replaced by a Gaussian with a full width at half maximum of 0.1 eV.

RESULTS AND DISCUSSION

Geometry

The substitution of every second hydrogen atom in PT with a phenyl side group, i.e. going from PT to PPT leads to an increased departure from planarity of the thiophene backbone. The torsion angle between to neighboring thiophene rings, θ_{th-th}, is around or greater than 30° in the neutral system (0° corresponds to the planar conformation shown in Figure 1). Variation of θ_{th-th} in the interval 30°– 60° gives only small changes in the total energy of the oligomer. It is more likely that this angle is determined by inter chain interactions, since small changes of the angle cause large changes of the position of the outer atoms of the long side group of POPT. To find a specific value of θ_{th-th} we are guided by the experimental results[1] where the optical gap is found to be 2.1 eV. By tuning the band gap against this value we have found θ_{th-th} to be 40°. It is also found that θ_{th-th} is by far the most important geometrical parameter for the band gap. The band gap is found to increase from 1.7 eV to 3.4 eV as θ_{th-th} goes from 0° to 90°. The substitution of hydrogen atoms with phenyl groups without any relaxations in thiophene backbone, yields a decrease of the band gap on the order of 0.1 eV. The substitution is accompanied with a small increase in the dimerization, on average 0.006 Å, which is estimated to increase the band gap by about 0.05 eV. Thus, the net effect of these changes for the band gap is at least one order of magnitude less than the effect of changes in θ_{th-th}.

The optimized torsion angle between a thiophene ring and its phenyl side group, θ_{th-ph}, is found to be 60°. Small values of the angle (coplanar conformation) are very energetically unfavorable. The band gap of PPT decreases only 0.1 eV as θ_{th-ph} is varied from 0° to 90°, keeping θ_{th-th} fixed, which shows that the electronic mixing between orbitals of the phenyl ring and the thiophene system is weak for energies close to the band gap. This is partially due to the fact that the bond that connects the phenyl group to the thiophene ring has a length of 1.48 Å, i.e. a weak single bond, a value which is almost unchanged for different torsion angles and upon doping.

Doping and the formation of bipolarons yields two significant changes in the geometry of PPT. Firstly, the dimerization of the thiophene backbone changes sign where the injected charges are located, this dip of the bond length alternation function resemble very much what is seen in PT[6]. Secondly, the torsion angles θ_{th-th} tend to go to zero, i.e. a planar conformation around the doping charges. Whether this change in θ_{th-th} is possible in a POPT sample depend upon the inter chain interactions.

Band structure

The evolution of the band structure when going from PT to PPT is shown in Figure 2a and b. The two bands just above and below the Fermi level are almost unchanged, with their states completely located to the thiophene backbone. The two dispersionless bands in PT, however, mix with π–orbitals of the phenyl rings and form four flat bands in PPT.

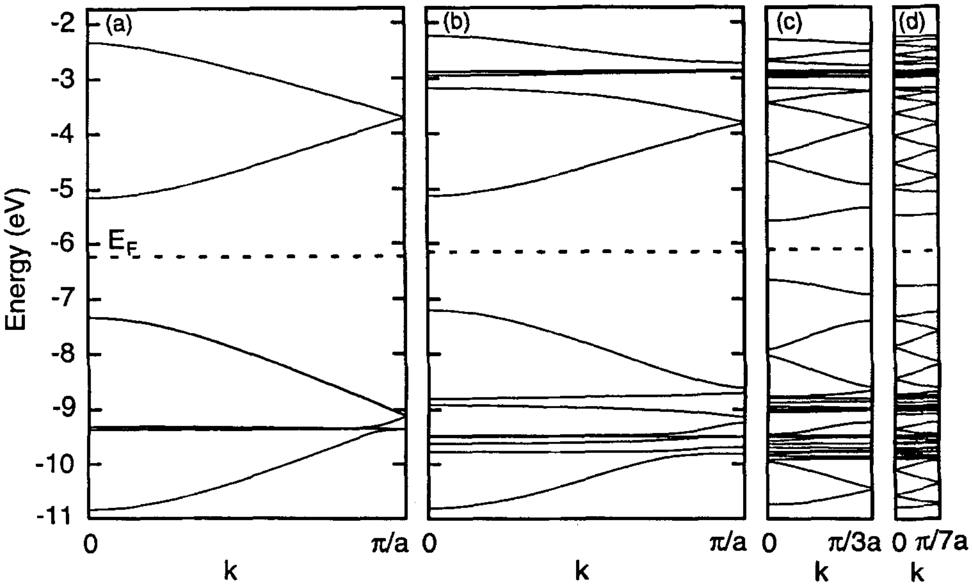

FIGURE 2 Band structure of: (a) PT; (b) PPT with a unit cell of length L=a, i.e. two monomers; (c) bipolaron lattice in PPT, L=3a ; (d) bipolaron lattice in PPT, L=7a.

The band structure of doped PPT is shown in Figure 2c and d. Two different bipolaron lattices are considered. The unit cell in Figure 2c is of the same size as the bipolaron width, estimated to be 6 monomers[6]. In Figure 2d contains the unit cell 14 monomers. In both cases two bipolaron bands appear at energies that correspond to the band gap of the undoped polymer. The states in these bands are localized with no significant contribution from the phenyl rings. The bipolarons interact in the first lattice and form dispersive bands, while they are non–interacting in the second lattice. The bipolaron states are symmetrically placed in the band gap. In the case of non–interacting bipolarons the bipolaron bands appear 0.49 eV above the top of the valence band and 0.44 eV below the bottom of the conduction band, respectively. Thus, the asymmetry is too small to explain the four peaks in the absorption spectra[1].

Optical absorption

The calculated absorption spectra for the two bipolaron lattices in PPT are shown in Figure 3a and b. For comparison are the absorption spectra obtained when the phenyl side groups of are substituted with hydrogen atoms, keeping the geometry of the thiophene backbone fixed, shown in Figure 3c and d. The small difference between spectra for PT and PPT shows that the substitution of the side groups alone gives no significant changes in the

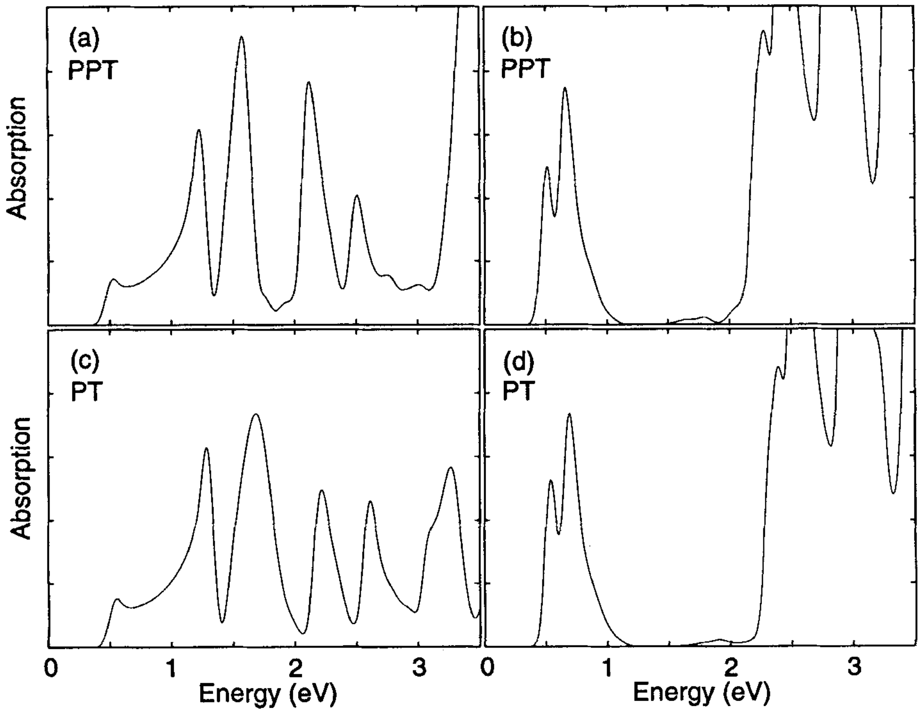

FIGURE 3 Absorption spectra for bipolaron lattice in PPT and PT. The unit cell contains: (a) 6; (b) 14; (c) 6; (d) 14 monomers.

absorption spectra for photon energies below the band–gap energy. The importance of the flat bands of PPT around –9 eV is only a minor contribution to the peak at 2.1 eV in Figure 3a. Thus, the large differences observed between PT and POPT spectra[1] can only be explained in terms of geometrical modifications in the thiophene backbone.

The spectrum for interacting bipolarons in Figure 3a has four peaks below the onset at 2.5 eV for transitions not involving bipolaron states. The position of the peaks agree well with those observed experimentally[1], the intensities also agree apart from the peak at 0.5 eV which has too low intensity. For the case of non–interacting bipolarons (Figure 3b), the absorption spectrum approaches that of a single bipolaron[7]. Transitions to the lower bipolaron band have merged, almost into a single peak around 0.6 eV. There is also absorption around 1.7 eV in Figure 3b but with very low intensity due to weak oscillator strengths for transitions to the upper bipolaron band in this lattice.

From geometry optimizations of the doped system we observe that the angle θ_{th-th} is reduced in the center of the bipolaron. Since it is plausible to assume that the long side groups will reduce the ability of POPT to change this angle, the bipolarons will accumulate in the segments with small angle and interact with each other, while the concentration is much smaller in the segments with large angles. The two types of lattices will coexist and the measured absorption spectra will be a superposition.

CONCLUSIONS

Absorption spectra are almost unaltered below the band–gap energy when the phenyl side groups of POPT are replaced with hydrogen atoms. Differences in spectra of POPT and PT is likely to be due to differences in the inter chain interactions, in particular the effect on the torsion angle θ_{th-th}. Bipolaron states are symmetrically placed in the band gap. It is possible to obtain absorption spectra with four peaks below the band–gap energy in the framework of bipolaron excitations, which are known to be stable in these type of polymers.

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