

Packing Structure of Poly(3-hexylthiophene) Crystal: Ab Initio and Molecular Dynamics Studies

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We present a theoretical study of the stacking properties of poly(3-hexylthiophene) (P3HT) and its effect on the electronic and transport properties. Our study is based on ab initio density functional calculations including van der Waals interactions and molecular dynamics simulations. Our calculations provide detailed information of the atomic structures and the formation mechanisms of the particular stacking structures. We found the most stable stacking structure produces a relatively small hole effective mass in the stacking direction, which allows large interchain mobility.

Poly(3-hexylthiophene) (P3HT) is arguably the most-used conjugated polymer in organic electronic applications.^{1,2} A single P3HT is made up of a π -conjugated thiophene backbone and alkyl side chains (Figure 1a). The regioregular P3HT (all the side chains pointing in the same orientation) is the most used variant due to its superior packing capability.^{3,4} The morphology and stacking properties of P3HT play a critical role in its electronic and transport properties. It is well-known that the regioregular P3HT tends to form stacking plates, which then form lamellar structures between stacking plates (stacks).^{4,5} It is essential to understand the atomic structures inside the stacks and their consequences for electronic properties.

In the early 1990s, the stacking structure of P3HT was studied extensively by several experimental groups^{6–8} based on X-ray diffraction (XRD) data. These experiments have shown half-unit shifting of neighboring thiophene chains, lack of interdigitation between the stacks, tilting of the alkyl side chains, and parallel or zigzag lamellar structure between P3HT stacks. Recently, there have been a few scanning tunneling microscopy (STM) experiments directly imaging the thiophene chain structures on planar substrates.^{9,10} Unfortunately, they cannot be used directly to measure P3HT stacking. From the earlier XRD measurements, one can get the information on the stacking unit cell, but it is difficult to get the detailed atomic structures. Besides, there are debates⁸ about the lamellar structure between the P3HT stacks. Very often, different structures can fit equally well to the measured XRD data. As computer power increases, it is now possible to tackle this problem from the ab initio calculation point of view.¹¹ But previous calculations have investigated only the simplest stacking structure and relied only on total energy minimum (i.e., zero temperature). As shown previously,⁸ the temperature effects might change the stacking structure significantly. Furthermore, previous ab initio calculations were based on the density functional theory (DFT) without the long-range van der Waals (vdW) interaction. We have thus carried out ab initio calculations including the long-range vdW interactions. We have also performed molecular dynamics simulations to study the thermodynamic properties of the system. Our study not only confirmed many of the earlier experimental results but also provided detailed atomic structures, modified

structure parameters, and a different lamellar structure. We have also analyzed the underlying formation mechanism of the calculated stacking structure.

We use the generalized gradient approximation (GGA) of the DFT.^{12,13} Projector-augmented wave (PAW) pseudopotentials were used for C, S, and H atoms.¹⁴ An energy cutoff for plane waves up to 450 eV and a fine Monkhorst–Pack¹⁵ k -point sampling were used. We have added a truncated vdW attraction term: $E_{\text{vdW}} = -\sum f_d(R)C_6R^{-6}$ to the GGA total energy. Here $f_d(R)$ is a damping function that goes to zero at small distance R .¹⁶ The summation is carried out only for atom pairs between different P3HT chains. Although this is an ad hoc approach, it has been shown that such a GGA+vdW Hamiltonian describes well the binding energy of thiophene oligomers¹⁷ and the stacking interactions in π -conjugated organic molecular crystals.¹⁸ Our own test, discussed below, also shows that this GGA+vdW approach agrees well with the results of previous MP2 calculations.¹⁹

The relaxed geometry of a single isolated P3HT chain is shown in Figure 1a, and optimized chain length in a period along the y direction is found to be 7.81 Å, which is comparable with the experimental result of 7.7 Å.⁶ In this geometry, the alkyl side chains are in planar positions (i.e., the side chains and the backbone chain form a plane). We have also calculated the energy barrier of rotating the torsion angle C1–C2–C3–C4 around the bond connecting the thiophene ring and the alkyl chain (Figure 1b). There are two local minima at 0° and 85° with only 0.1 eV energy difference.

We have used a 2×2 supercell that contains four P3HT chains (Figure 1c,d). We used a conjugated-gradient (CG) method to optimize both the atomic positions and the unit cell parameters. The binding energy (per single chain) among the P3HT chains is defined as $E_s = E_{2 \times 2}/4 - E_{\text{chain}}$, where $E_{2 \times 2}$ is the 2×2 GGA+vdW supercell energy and E_{chain} is the energy of an isolated chain. Thus a negative binding energy means the stacking is stable against separated P3HT chains. We started with the aligned stacking in which the thiophene rings are aligned and on top of each other between upper and lower P3HT chains (Figure 1c). The binding energy E_s for the aligned structure is -0.335 eV. The lattice parameters a , b , and c are shown in Table 1.

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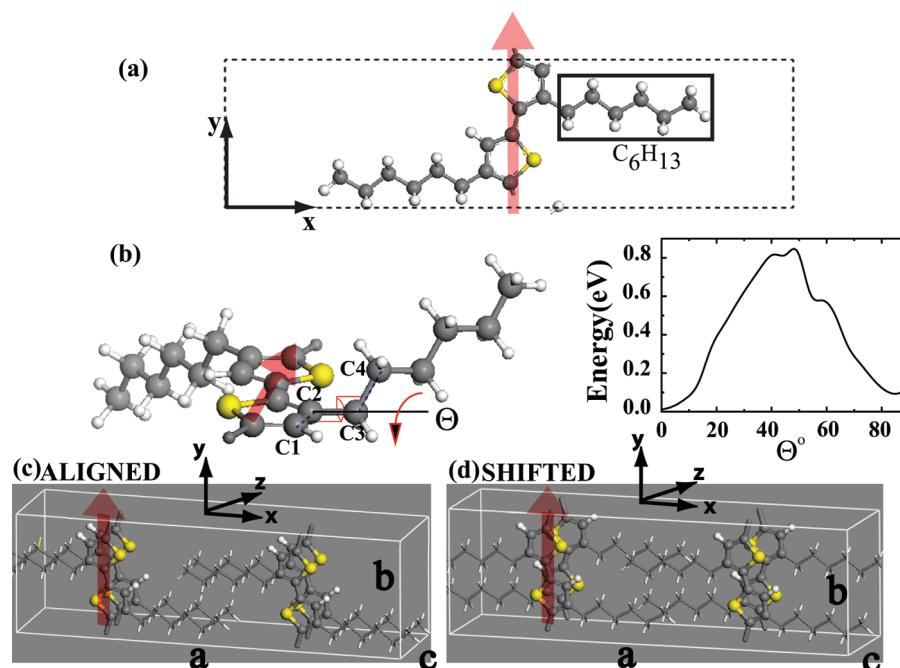


Figure 1. (a) Molecular structure of single P3HT chain. (b) Change in total energy of single chain with respect to torsional angle of C–C linkage between thiophene and alkyl chain. (c, d) Schematic model showing the hierarchical organization of the (c) aligned and (d) shifted structures.

TABLE 1: Calculated and Experimental Crystal Lattice Parameters and Binding Energies

parameters	aligned	shifted	tilted	exp ⁶
a/2 (Å)	16.0	16.0	16.76	16.80
b (Å)	7.81	7.81	7.81	7.70
c (Å)	8.2	7.85	7.70	7.66
E _s (eV/chain)	-0.335	-0.388	-0.630	

We next study the shifted structure. This corresponds to a shift of one of the two thiophene layers along the thiophene chain direction (y direction) by one thiophene–thiophene distance (*b*/2). This will make the alkyl side chains from adjacent layers be staggered, and thus sterically less contentious. Figure 1d shows the optimized structure of the shifted stacks. This shifted structure is also a planar structure with alkyl side chain perpendicular to the axis of the thiophene chain. The binding energy per chain for this shifted structure is −0.388 eV, which is −0.05 eV lower than the aligned structure, thus more stable.

As shown in Figure 1b, there is another local minimum for the torsional angle rotation of the alkyl side chain for an isolated single P3HT chain. Besides, previous XRD experiments also indicate the tilting of the alkyl side chains. In a P3HT stack, such a rotation (tilting) of the alkyl side chain can alter the relative positions between adjacent alkyl chains, thus changing their electrostatic and vdW interactions. We have thus calculated the tilted structure. This is a shifted structure but in addition with all alkyl side chains rotated around the torsion angle. We then relax the atomic positions to yield a local minimum structure. Figure 2a shows top and side views of the optimized structure. The binding energy and lattice parameters are given in Table 1. The binding energy is −0.630 eV, which is the lowest energy stack we found according to GGA+vdW calculations. The calculated lattice constants for this structure (Table 1) agree excellently with the experimental results obtained from XRD.⁶ We also found that the torsion angle θ is 97.6°, which is slightly larger than the 85° in the isolated single P3HT chain.

So far, our above structures are obtained purely on the basis of ab initio total energy calculations. The energy differences

among the structures can be as small as a few times *kT*. It is thus critical to find out whether the structures are thermodynamically stable. To test that, we have carried out molecular dynamics (MD) simulation using the class II force field, which is well adopted for thiophene rings¹⁶ with Coulomb and Lennard-Jones potentials as its nonbonded interactions. This force field gives the same energy order for the above three stacking structures as the ab initio results. We then simulated systems of 36 P3HT chains with 6 unit cell lengths. As an initial configuration, we started with the planar shifted stacking structure without alkyl side-chain tilting. After MD simulation for about 1.1 ns at 300 K and then quenching the system to a local minimum, we found that the system has become the tilted structure, as shown in Figure 2b. The overall tilted structure agrees quite well with the ab initio calculated tilted structure. We have also started with the aligned structure at 300 K and found that it is unstable. The system reached a disorder structure after 100 ps of MD simulation. For an open boundary condition (instead of a periodic boundary condition), if the system started with the aligned structure, the individual P3HT chains will fly away. On the other hand, if it starts with the planar shifted structure, the stacking will be maintained and the side chain will be tilted. These simulations indicate that the aligned and shifted stackings, although they correspond to local energy minima, are thermodynamically unstable at room temperature. Thus, it is unlikely they will be observed experimentally at room temperature. By use of the atomic structures we obtained, the XRD spectrum can be calculated,²¹ which is shown in Figure 3 in comparison with recent experimental results. We see that, among the three structures we found, the tilted structure agrees best with the experimental results.

For the tilted structure, the ends of the alkyl chains from neighboring stacks just touch each other. Thus there is no interdigitation, in agreement with the experiments.^{6,22} On the other hand, both the aligned and shifted structures have significant interdigitation, as shown in Figure 1a,d. This interdigitation is not an artifact due to local minima in our atomic relaxation. We have directly calculated the energy as a function

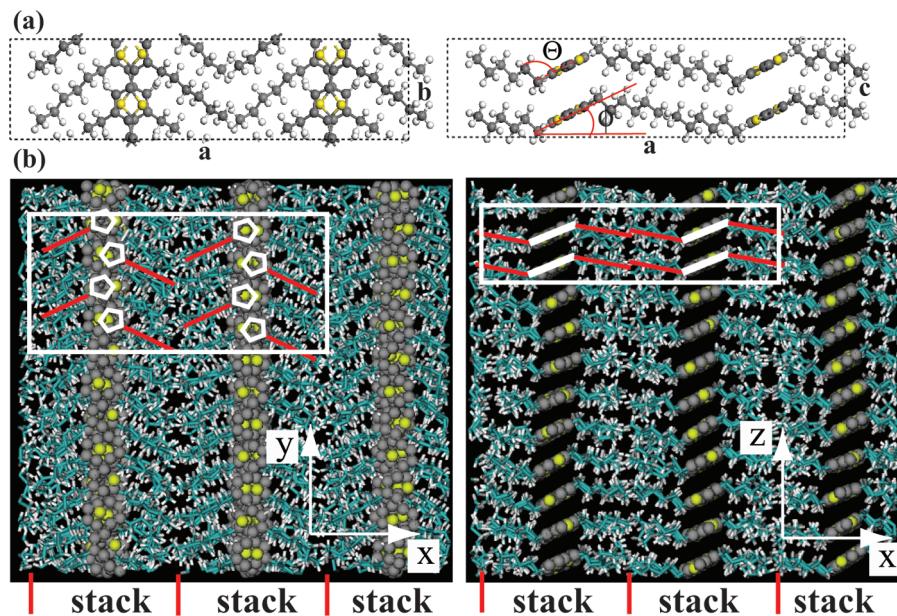


Figure 2. (a) Top and side view of the schematic representation of optimized tilted structure. (b) MD simulation results: snapshot of the system with 36 P3HT chains. Thiophene layers are highlighted with balls. Both top and side views are shown. $T = 300$ K.

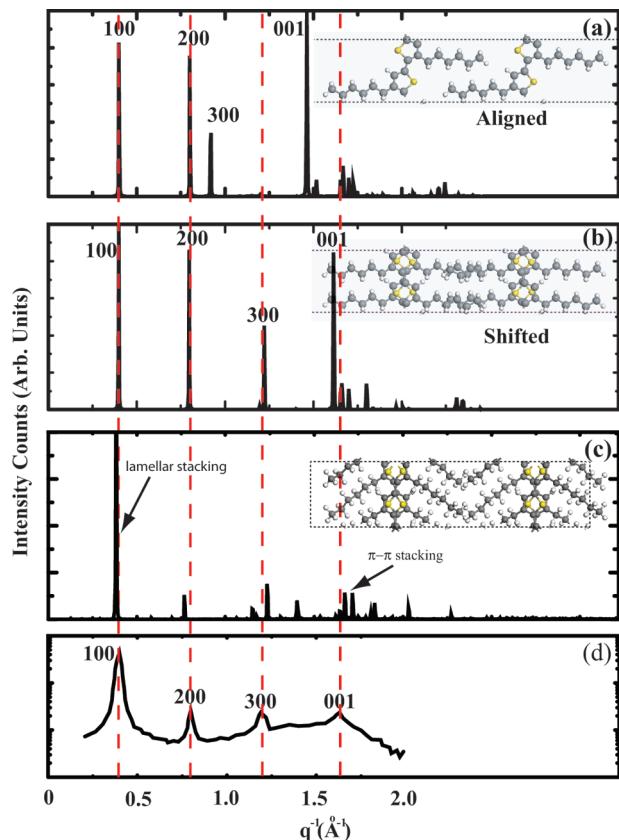


Figure 3. Theoretical X-ray diffraction pattern for (a) aligned, (b) shifted, and (c) tilted stacked P3HT crystals. (d) Experimental X-ray diffraction pattern from ref 20.

of *a* and *c*, and lattice constants reported in Table 1 are obtained from the minimum of this two-dimensional energy function. It is interesting to realize that the lack of interdigitation in the tilted structure is due to a geometric effect (see Figure 2a), where interdigitation is impossible due to nonparallel alignment between neighboring side chains. On the other hand, in planar structures, despite the small space, interdigitation does happen.

In our simulation, we do not find the zigzag lamellar structure among the P3HT stacks.⁶ Instead the alkyl side chains from

adjacent P3HT stacks are parallel to each other (to be called parallel lamellar structure). The zigzag lamellar structure was proposed by Prosa et al.⁶ However, on the basis of similar XRD experiments, Tashiro et al.⁸ later argued that one cannot discard the possible parallel lamellar structure. Prosa et al.²³ have also reported the possibility of parallel structures for P3DDT and P3OT. In our simulation, the MD started with the shifted planar structure. Thus, it has the potential to change to parallel or zigzag structures (or a mixture of them). But we always find the parallel lamellar structure. This indicates that, from the simulation, the parallel lamellar structure is more stable. Note that, as discussed by Tashiro et al.,⁸ the parallel and zigzag structures both fit the experimental XRD data well. As shown in Figure 3, our parallel structure fits the recent X-ray diffraction data well. Our alkyl side-chain rotation angle (Figure 1b) of 97.6° is slightly larger than the 89° reported in ref 6. Another important difference is the angle Φ between the plane of the thiophene ring and the plane of the stacking as defined in Figure 2a. Our result of 29.2° is significantly larger than the 5° reported in ref 6. Since there are significant uncertainties in determining the structure solely on the basis of XRD data, our simulation provides valuable data points to this P3HT stacking problem.

To understand the underlying reason for the tilted structure, we first analyzed the interaction between two isolated thiophene rings. Tsuzuki et al.¹⁹ have studied the $\pi-\pi$ interactions using MP2/6-311G** calculations. They found that the two parallel stacked thiophene rings prefer to have 180° rotated orientations with 3.33 \AA stacking distance and a 1.93 \AA upper thiophene ring in-plane displacement (along the *x* direction of Figure 1a). Our GGA+vdW approach reproduces their MP2 results very well. The GGA+vdW stacking distance is 3.40 \AA , and the thiophene in-plane displacement is 1.65 \AA . Note, this thiophene-thiophene arrangement is much like in the tilted P3HT structure shown in Figure 2a. There, the stacking distance is 3.45 \AA and the displacement in the *x* direction is 1.4 \AA . On the basis of these lines of evidence, it is tempting to claim that the tilted structure is driven by the thiophene-thiophene backbone interaction, although the following investigation shows that the situation is more complicated.

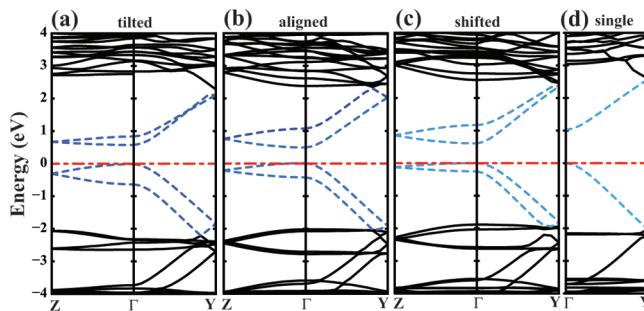


Figure 4. Electronic band structure of (a) tilted, (b) aligned, and (c) shifted stacked structures; (d) single P3HT structures along high-symmetry directions. Fermi level is set to be zero. Blue dashed lines show highest occupied and lowest unoccupied molecular orbital (HOMO and LUMO) levels.

We next calculated the interaction energies among the backbone thiophene chains. From each of the stacking structures, we removed alkyl side chains (and added H atoms to passivate the broken bonds), leaving only the thiophene chain backbones. It turns out that the aligned backbone thiophene chain has the lowest GGA+vdW calculated energy, while the shifted structure is 0.28 eV higher and the tilted structure is 0.49 eV higher. This is in contrary with the above thiophene–thiophene ring dimer result. This difference might come from the thiophene–thiophene interaction between neighboring thiophene rings not on top of each other from adjacent layers. But it might also be due to the fact that the atomic positions are extracted from the stacking structure without relaxations. We thus have relaxed the atomic positions in thiophene backbone stacking, and indeed we found that, after the relaxation, the energy order is changed: the shifted one has the lowest energy, followed by the tilted and then the aligned structure, thus similar to the dimer situation. Finally, we calculated the interaction energies among the alkyl side chains. Here, we removed thiophene chain backbones from the three stacking structures and added one H atom to passivate the broken bond. The atomic positions are kept as they are without further relaxations. The tilted structure has the lowest energy, followed by the shifted structure (0.73 eV higher) and then the aligned structure (0.83 eV higher). Thus, it is clear that the main driving force for the tilted structure is the alkyl side-chain interactions. Although this by itself is hardly news, the fact that the side-chain interaction can pull the backbone chains out of their optimal stacking positions is interesting. This means that the side chains not only determine the lamellar structures between stacks but also affect the backbone alignments within a stack.

Figure 4 shows the GGA-calculated electronic band structures for the three stacking structures, along with the band structure of a single P3HT chain. Although the GGA does not give the correct band gap, the band structures and splitting within the valence band can still be trusted. The calculated effective masses along the chain direction (*y*) and the stacking direction (*z*) are listed in Table 2. We can see that the hole effective mass in the *z*-direction is about $1.8m_e$, which is similar to the hole effective mass in many inorganic semiconductors. Thus, there should be

TABLE 2: EFFECTIVE MASSES IN UNITS OF THE FREE ELECTRON MASS

	aligned		shifted		tilted	
	HOMO	LUMO	HOMO	LUMO	HOMO	LUMO
\hat{y}	0.17	0.20	0.20	0.18	0.19	0.19
\hat{z}	1.97	1.81	4.10	2.28	1.84	5.95

high-mobility transport in both the intrachain and interchain directions within one P3HT stack. Note that the stacking structure can change the electronic structure significantly. For the shifted structure, the hole effective mass is $4.1m_e$.

In conclusion, our theoretical investigation shows that the low energy and thermodynamically stable P3HT stacking structure is a tilted structure. This structure is mostly caused by the alkyl–alkyl side chain interactions (at the cost of the thiophene–thiophene backbone interactions). Different stacking structures can alter their electronic structures significantly, change the hole effective mass from $4.1m_e$ to $1.8m_e$. For the tilted stacking structure, the interchain direction hole effective mass is $1.8m_e$, similar to inorganic crystals; thus it should have efficient hole transport, which should contribute to its overall large hole mobility.

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