Molecular ordering in bis(phenylenyl)bithiophenes†

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The crystal structure of phenylene–bithiophene oligomers (PTTP) has been investigated by powder X-ray diffraction measurements and *ab initio* Monte Carlo modelling. Two new hydroxyl-terminated PTTP powders, 5,5'-bis-4-(6-hydroxyhexyloxy)-phenyl-2,2'-bithiophene and the shorter alkyl chain substituted oligomer 5,5'-bis(4-hydroxyphenyl)-2,2'-bithiophene, are compared to single crystals of 5,5'-bis(4-ethylphenyl)-2,2'-bithiophene. The new molecules are characterized by a close packed, distorted hexagonal array with tilted short axes in a herringbone-type structure. Neighbouring molecules within layers are displaced along the long axis. Modelling the electrostatic potential surface suggests that electrostatic interactions are responsible for the observed herringbone-like ordering. Alkyl chains facilitate a partial mixing through interdigitation of aromatic and aliphatic moieties.

Introduction

Characterizing and modelling the structure of molecular ordering is central to understanding conduction mechanisms in organic electronics. Substituted phenylene-thiophene molecules are interesting candidates for organic electronics, based on their stability, solubility, general high field effect mobility, and surface chemical reactivity.¹⁻⁴ Phenylene-thiophene oligomers uniquely combine field effect mobility of the order of $0.01-0.1 \text{ cm}^2 \text{ V s}^{-1}$, resistance to oxidative doping and therefore higher on/off ratios relative to zero gate voltage than all-thiophene oligomers, and the possibility of solution processing that is relatively rare for molecular solids.^{1,2} Their syntheses are facile enough to allow the attachment of polar end groups, such as the hydroxyalkyl described here. Such groups enable further surface modification after film deposition, and controlled interactions with a variety of overlying substances. The addition of hexyl end groups on

phenlyene-thiophene aromatic cores has been shown to enhance long-range molecular ordering and thus increase organic transistor field effect mobility.^{2,3,5} For this class of molecules, it is important to determine the crystal structure in order to determine the effect of adding peripheral substituents to a core molecule. In general, long-chain oligothiophenes order in a herringbone arrangement with triclinic (P1, $P\overline{1}$), monoclinic $P2_1$, $P2_1/c$, $P2_1/a$ or orthorhombic $P2_12_12_1$, or *Pbca* symmetry.^{6–9} However, the structural implications of extensive alkyl and/or polar end group functionalization have not yet been uncovered, due to the difficulty involved in preparing single crystals. Structure analysis is difficult because unlike smaller unsubstituted molecules, which readily crystallize and can be analyzed by single crystal X-ray diffraction, longer molecules require powder X-ray diffraction and a more complex analysis. Therefore, we utilize powder X-ray methods to solve the crystal structure of longer molecules not available as single crystals. To understand the influence of polar and alkoxy termini on molecular ordering, we have combined synchrotron powder X-ray diffraction measurements and ab initio Monte Carlo modelling to determine the ordering of two new hydroxyl-terminated phenylene-bithiophene powderform oligomers, 5,5'-bis(4-hydroxyphenyl)-2,2'-bithiophene (HOPTTPOH) and 5,5'-bis-4-(6-hydroxyhexyloxy)-phenyl-2,2'-bithiophene (HOC6PTTPC6OH), and compared them with a simplified single crystal of 5,5'-bis(4-ethylphenyl)-2,2'-bithiophene (2PTTP2).

Experimental

Synthesis

5,5'-Bis(4-ethylphenyl)-2,2'-bithiophene was synthesized from 5,5'-bis(tributylstannyl)-2,2'-bithiophene and 1-bromo-4-ethylbenzene, using the Stille-coupling procedure described by Mushrush *et al.* for a hexylphenyl analog.³ Single crystals were grown by physical vapor transport.

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[†] Electronic supplementary information (ESI) available: Powder diffraction data for 5,5'-bis(4-ethylphenyl)-2,2'-bithiophene (2PTTP2) at 120 and 300 K, 5,5'-bis(4-hydroxyphenyl)-2,2'-bithiophene (HOPTTPOH), 5,5'-bis-4-(6-hydroxyhexyloxy)-phenyl-2,2'-bithiophene (HOC6PTTPC6OH). See DOI: 10.1039/b701035d

5,5'-Bis(4-hydroxyphenyl)-2,2'-bithiophene was synthesized using the Stille-coupling procedure with 1-bromo-4-(tert-butyldimethylsilyloxy) benzene. The starting material was prepared by stirring 4-bromophenol (6 g), tert-butyldimethylsilyl chloride (5.3 g), imidazole (2.4 g) and dimethylformamide (50 mL)overnight at room temperature, and partitioning the reaction mixture between ethyl ether and aqueous sodium carbonate. The deprotection of the tert-butyldimethylsilyl-protected four ring compound (purity verified by NMR after solidifying from the reaction mixture upon cooling to room temperature) was as follows: the protected compound (105 mg) was stirred with methylene chloride (50 mL), acetic acid (0.2 mL), and tetrabutylammonium fluoride (150 mg) for two days under nitrogen. The dihydroxy compound was then collected as a vellow-green solid (60 mg). The compound is susceptible to surface oxidation in air, evident by the powder colour changing to green. Infrared absorption spectroscopy of aged-in-air KBr pellet samples shows loss of peaks at 1570, 1420, and 1030 cm⁻¹ and a gain of intensity at 1360 cm^{-1} (not shown). However, many other peaks are the same in both fresh and aged samples. Aging does not lead to any increased signal within the 1620- 1800 cm^{-1} range, which would have been indicative of quinoid formation. The sharpness of the powder diffraction peaks shows that crystallinity is well preserved in the aged sample.

5,5'-Bis-4-(6-hydroxyhexyloxy)phenyl-2,2'-bithiophene was synthesized using the Stille-coupling procedure with 1-bromo-4-(6-hydroxyhexyloxy)benzene. This starting material was prepared by heating 4-bromophenol (9.3 g), 6-bromohexanol (9.8 g), potassium *tert*-butoxide (6.1 g) and dimethylformamide (50 mL) for four hours at 70 °C, partitioning between ethyl ether and water, and purifying the concentrated organic fraction on a 100 g silica gel column. Purification by recrystallization from 30–40 mL of dimethylformamide per gram of crude solid was performed.

Single-crystal diffraction

A single crystal of 2PTTP2 is used as a reference material since ethyl is the shortest alkyl chain possible. The structure was determined using a conventional single-crystal Oxford Diffraction Xcalibur 2 CCD-equipped diffractometer and analyzed, using the CRYSTALS program.¹⁰ Crystal growth of 2PTTP2 usually resulted in small, very thin platelets, with thicknesses of less than 1 μ m. Therefore, weak sample scattering will affect the crystal structure determination. Two data sets were collected on a 2.5 μ m-thick sample, one at room temperature and the other at 120 K. The 120 K data set gives an improved refinement over the room temperature data. However, the number of observed reflections is still severely limited by the size of the crystal.

Powder diffraction

The HOPTTPOH and HOC6PTTPC6OH powder diffraction data were collected at the Brookhaven National Laboratories National Synchrotron Light Source (NSLS), with beamline X22A and a wavelength of $\lambda = 1.2084$ Å, using a four-circle goniometer at room temperature. The powder sample was in pellet form and was mounted on a glass coverslip. Diffraction data acquired at different beam intensities and exposure times

verify that the beam does not damage the sample. Powder averaging was achieved by *in situ* 4° theta rotation of the sample while each two-theta data point was collected.

Structual modelling analysis

The powder data were analyzed by the CMPR¹¹ and Crysfire¹² sub-algorithms to determine the unit-cell. Chekcell¹³ then examined the Crysfire solutions and the space groups were identified. PowderCell¹⁴ was used for manual trials of calculating the diffraction pattern for different unit-cell decorations and space groups. An *ab initio* reverse Monte Carlo structure determination program developed by Favre-Nicolin and Cerny (Fox software)¹⁵ was used to identify the molecular conformations and unit-cell decorations by real-space simulations. The initial minimum energy molecular shapes of fully planar molecules and other structural parameters of molecules were determined by Ghemical.¹⁶ The Mercury program was used to generate real-space images.

Results and discussion

The crystal structures of 2PTTP2, HOPTTPOH and HOC6PTTPC6OH were determined by single-crystal X-ray diffraction and powder X-ray diffraction, respectively, using synchrotron powder X-ray diffraction and ab initio Monte Carlo modelling. The 2PTTP2 molecule crystallizes in a monoclinic unit-cell with a symmetry $P2_1/a$ and unit-cell parameters a = 9.345Å, b = 5.782Å, c = 18.393Å, and $\beta =$ 99.97°. The conjugated backbone phenylene-bithiophenephenylene is flat, and the alkyl chain has its terminal methyl group oriented almost perpendicular to the PTTP unit (torsion angle of 103.57°). The PTTP backbone is flat in contrast to the PTTP system in diisopropyl-PTTP, where the phenylene rings are tilted by 32.2° against the bithiophene motif.⁴ The molecules pack in a herringbone-type arrangement, with the molecules aligned approximately along the *c*-axis, with a herringbone angle of 53.41°, thus forming 2-dimensional layers with pseudo-hexagonal packing. This type of ordering is defined as crystalline-H in liquid crystals.¹⁷ The cross-sectional area per molecule is about 23 Å². A similar hexagonal packing was observed in the thin film structure of 5,5'-bis(4-hexylphenyl)-2,2'-bithiophene (6PTTP6).²

The structure of 2PTTP2 can be explained by electrostatic and steric interactions. The electrostatic potential surface¹⁶ at the van der Waals distance, as shown in Fig. 1(a), displays the most electropositive and electronegative parts of the molecule, indicated in red and blue colours, respectively. In the crystalline phase, electrostatic attraction would favour placing the most electronegative part of the molecule (the centre of the phenyl rings) near the most electropositive part of the neighbouring molecule (between the hydrogen atoms of the thiophene and the phenyl rings). The only solution that will satisfy this condition for every single molecule is the herringbone structure shown in Fig. 1(b). Steric interactions, set by the aromatic groups, determine the orientation and ordering, while the short alkyl chains determine the herringbone-type layer spacing.

The crystalline structure of HOPTTPOH was determined by *ab initio* powder data analysis, yielding an orthorhombic



Fig. 1 Energy-minimized configuration of the 2PTTP2 molecule and value of the electrostatic potential at the van der Waals distance or electrostatic potential surface (a) and crystal structure of 2PTTP2 determined from single-crystal X-ray diffraction (b).

unit-cell in a $P2_12_12_1$ group symmetry with a = 5.558Å, b =7.665Å, c = 37.188Å, and cell volume = 1584.29Å³. Figs. 2(b) and (c) show the molecular structure in the unit-cell and the ab initio diffraction data fit for rigid planar molecules as determined by Ghemical.¹⁶ The long axis of the molecule is slightly tilted towards the centre of the distorted hexagonal packing. This type of ordering is defined as crystalline-K in liquid crystals.¹⁷ This structure can also be understood in terms of electrostatic interactions. As shown in Fig. 2(a), electropositive and electronegative sections of the molecule extend over a much larger area along the long axis of the molecule compared with 2PTTP2. Close examination of the structure confirms that every molecule is coordinated to maximize this electrostatic interaction. Without the alkyl spacer chains, molecules pack closer to each other as evidenced by a small $\sim 19.5 \text{ Å}^2$ per molecule cross-sectional area.

For a rigid HOPTTPOH molecular shape, the tilt to the (101) plane is about 28° or 56° between the neighbouring molecular short axes, whereas the long axes are inclined by 4.23° to the <001> direction. The shortest distances between neighbouring molecules are S-H = 2.44 Å, C-S = 3.36 Å, and O-O = 2.24 Å, which are shorter than observed in 2PTTP2, S–H = 3.07Å, and C–S = 3.86Å (the van der Waals values for these distances are S-H = 3.05Å, C-S = 3.55Å, and O-O = 2.80Å). This indicates that there are strong orbital interactions between the HOPTTPOH molecules. The unusually short O-O contact distance may indicate the presence of H-bonds between the molecules. Dimerization is unlikely, due to the atomic contact values falling within expected bonding distance. Fits allowing all degrees of freedom between the core rings determine the thiophene rings to be planar, while phenyl rings are slightly rotated and translated. Although these refinements were found not to alter the unusually short intermolecular distances, the exact magnitude of these slight displacements cannot be determined reproducibly.

The HOC6PTTPC6OH structure is similarly identified by powder data analysis as a monoclinic unit-cell with



Fig. 2 Energy-minimized configuration of the HOPTTPOH molecule and value of the electrostatic potential at the van der Waals distance or electrostatic potential surface (a), real-space crystal structure (b), and *ab initio* powder pattern fit of HOPTTPOH (c).

a = 33.056Å, b = 7.486Å, c = 5.876Å, and $\beta = 96.161^{\circ}$ with figure of merit values of M(20) = 9.0, and F(20) = 14.9.^{12,18,19} This cell assignment correctly predicts weak peaks at (1,1,1), $(5,0,\overline{1}), (4,0,1), (0,2,1)$ and $(10,0,\overline{1})$ that were originally omitted. The cross-sectional area per molecule is approximately 20Å². The short axis of the molecule is tilted from the (101) plane by about 38.5° or about 77° between neighbouring molecule short axes that is characteristic of the crystalline-K phase.¹⁷ The experimental and calculated diffraction patterns in P2₁ symmetry are shown in Fig. 3. In the $P2_1/n$, $P2_1/a$ space group symmetries with doubled unit-cell a = 66.112Å, b =7.486Å, c = 5.876Å, and $\beta = 96.161^{\circ}$ fits improve slightly, indicating that one of these space group symmetries may be the correct one. Here, the shortest distances between neighbouring molecules are H-S = 2.18Å, H-C = 2.67Å, and C-S = 3.25Å, indicating the possible presence of H-bonds between the molecules. Another PTTP analogue with shorter alkylterminated end-units, 5,5'-bis(4-isopropylphenyl)-2,2'-bithiophene has been determined as $P2_1/a$, (a = 8.387, b = 9.634, c = 13.368, and $\beta = 96.43^{\circ}$), with a similar layered, herringbonetype arrangement of molecules tilted along the long and the short axes.4





Fig. 3 Energy-minimized geometry of the HOC6PTTPC6OH molecule and value of the electrostatic potential at the van der Waals or electrostatic potential surface (a). Crystal structure of HOC6PTTPC6OH determined by *ab initio* Monte Carlo calculations, using a rigid PTTP core and a single torsional motion on alkyls (b) and the corresponding powder data fit (c).

To verify the uniqueness of the HOC6PTTPC6OH solution, we have systematically evaluated the results obtained from multiple repeat calculations, using different initial conditions, molecular conformations, unit-cell decorations, and space group symmetries. We find that overall a herringbone packing structure is readily reproduced even in fully rigid molecules. The main findings: molecules are aligned near the *a*-axis, neighbouring molecules are shifted along the molecular long axis, and tilted both along the short axis in opposite directions with respect to each other forming a herringbone-type structure. If, however, all of the atoms in the molecule are unrestrained and allowed to move simultaneously (within bond length and angle limits), the global optimization leads to similar solutions for different conformations of the alkyl chains. This is not surprising, since some degree of alkyl chain tail disorder should exist. Existing data on similar molecules have consistently identified a rigid alkyl chain in the trans configuration. This observation was the basis for our assumption made in Fig. 3. This assumption has little effect on the overall quality of the fits, indicating that our molecular ordering model is accurate.

In the case of torsional freedom of four distinct rings of the core, we find that the aliphatic tails again align parallel to the (101) plane, the bithiophene rings remain planar [39° to the (101) plane], but one of the phenyl rings goes through a slight rotation [26.5° to the (101) plane]. The corresponding calculated pattern of this conformation and the measured data are shown in Fig. 4, along with the difference data and the expanded range inset that shows that the observed differences are mainly due to peak profile shapes. The data exhibit a non-uniform peak broadening, indicating the presence of some characteristic defects. For instance, the (020) peak at 18.576° is significantly broader than predicted, suggesting a specific defect that disrupts the long-range order along this axis.

The structure of HOC6PTTPC6OH consists of layers whose spacing is defined by the tilted molecular length. Layering is induced by the aromatic/aliphatic separation of the neighbouring molecules. Within the layers near the (100) plane, molecules are close packed in a distorted hexagonal array. For a perfect hexagonal array, $b/c = 3\frac{1}{2} = 1.732$. In our case, b/c = 1.39 in the plane perpendicular to cores. Molecules in neighbouring (101) planes are shifted along the long axis of the molecule such that one of the thiophene rings of molecules in one layer is approximately aligned with one of the phenyl rings of the neighbouring layers as shown in Fig. 3(b). Molecules within the layer have alternating offsets along the long molecule axis such that a phenyl ring aligns with a thiophene ring. The alternative arrangement produces the interdigitation of the alkyl chains. Molecules in the (101) planes are all tilted in one direction with respect to molecules in neighbouring planes that are tilted in the opposite direction. The magnitude of the tilt is about 38.5° to the (101) plane, for molecules modelled by rigid aromatic cores and flexible aliphatic tails.

The HOC6PTTPC6OH structure appears to be interdigitated, with partial mixing of the aliphatic and aromatic parts of the neighbouring molecules. The calculated electrostatic potential of a planar molecule, as shown in Fig. 3(a), finds a charge distribution on the aromatic part similar to that of 2PTTP2. In the *ab initio* calculated structure, some of the most



Fig. 4 Globally optimized Monte Carlo structure determination of HOC6PTTPC6OH, where six rigid groups, two alkyls and four rings model the molecule. The bottom curve shows the difference data. The inset shows the details of the fit. Observed differences are attributed to dissimilar functional forms of the peak profiles.

electronegative phenyls are aligned with the hydrogen atoms of the neighbouring thiophenes, strongly suggesting that the most electropositive part is now shifted towards the thiophene rings. This can be explained by the separation of phenyl hydrogen atoms from the plane of the thiophene hydrogen atoms, or a rotation of the phenyl rings. Since we have fixed the aromatic core to be rigid in our *ab initio* and potential surface models, we would not be sensitive to such effects. A driving force for interdigitation would be purely steric, diluting the high mass density core regions with the extra space of the aliphatic regions.

These findings are similar to the case of the mesomorphic smectic phase of liquid crystals, where long-range ordering is governed by the interaction of aromatic and aliphatic parts of the molecule and steric effects. The strength of the aromatic core interactions plays a major role in determining the range of smectic phases in thermotropic liquid crystals. For strong core interactions, layered phases will be stable at all temperatures and will not disorder into nematic phases. Within the layers, the molecules are typically close packed in an hexagonal array. In liquid crystals, smectic-E phase molecules become ordered in a herringbone arrangement within the plane, while remaining perpendicular to the layer. At low temperatures, all hindered motions of the molecules gradually disappear, long-range order sets in, and the molecules crystallize. If the molecules become tilted with respect to the layers in the crystalline phase, the two generalized tilt directions (perpendicular to a side or towards a corner of the hexagonal in-plane underlying structure, respectively) define the crystalline-H and K phases.¹⁷ For the HOC6PTTPC6OH case, the only observable phase is crystalline, suggesting that aromatic interactions are very strong. As the aliphatic tails appear to be frozen, it is improbable that highly conformable aliphatic tails would display perfect long-range order. In fact, the frozen disorder of the alkyl chains may be responsible for our broad diffraction peaks. In support of this, the HOPTTPOH (identical molecule without aliphatic tails) structure reveals a highly ordered crystalline structure, with well-defined Bragg peaks. While Monte Carlo calculations treat the alkyl chains as fully crystalline, in essence the optimized atomic coordinates of the tails are weighted average positions. The fact that these alkyl-substituted bis(phenylenyl)bithiophenes are planar facilitates the pi-bond overlap. Moreover, the electrostatic interactions help reduce the intermolecular distance. Therefore, these molecules are promising for use as organic semiconductors. The methods presented for evaluating the structure of alkyl-substituted PTTP compounds, which cannot easily form single crystals, will allow further investigation of compounds whose alkyl substitution would provide advantageous properties, such as low surface energies, surface sensitivity, or orderenhancing properties.4

Conclusions

The molecular structure orderings of phenylene–bithiophene (PTTP) oligomers have been studied with different end groups. The structure of 2PTTP2 is determined by single-crystal diffraction to be layered, with an in-plane herringbone-type packing. The molecules are tilted with respect to the layer

surface in analogy to the crystalline-H phase of liquid crystals. The crystal structures of HOPTTPOH and HOC6PTTPC6OH powders are determined by synchrotron X-ray powder diffraction (XRD) to be analogues of crystalline-K phase of liquid crystals.¹⁷ In all cases, crystalline structures are found with layer spacing defined by the tilted long axes of the molecules whose common bis(phenylenyl)bithiophene cores have a similar tendency to be flat as well as similar ordering. The molecules are close packed in a distorted hexagonal array with their tilted short axes forming a herringbone-type structure, while neighbouring molecules within the layers are displaced along the long axis with respect to each other. In the case of HOC6PTTPC6OH, alkyl chains appear to facilitate a partial mixing of the aromatic and aliphatic parts by interdigitation. Electrostatic interactions alone can account for the interdigitation of the herringbone-type ordering in this novel class of molecular compounds. With its hydroxyl (polar) termination, thin films of HOC6PTTPC6OH deposited with vacuum sublimation are being considered and currently studied with infrared absorption spectroscopy as a useful platform for attaching biomolecules and for the investigation of its gas sensing properties using organic field effect transistors.

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