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Modeling the Polymorphism of Pentacene
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Abstract: Thin films of pentacene are known to crystallize in at least four different polymorphs. All polymorphs are layered structures that are characterized by their interlayer spacing d(001). We develop a model that rationalizes the size of the interlayer spacing in terms of intralayer shifts of the pentacene molecules along their long molecular axes. It explains the wide variety of interlayer spacings, without distorting the herringbone pattern that is characteristic of many acenes. Using two simple theoretical models, we attempt to relate the intralayer shifts with the dominant, although weak, interatomic interactions (van der Waals, weak electrostatic, and covalent). For two polymorphs, a consistent picture is found. A full understanding of the other two, substrate-induced, polymorphs probably requires consideration of interlayer interactions.

1. Introduction

Band formation in molecular organic conductors is of enormous scientific and applied interest, because it is prerequisite for achieving high values of electronic mobility. In molecular organic charge-transfer salts, band formation and high mobilities can be achieved, leading to a wealth of physical properties such as superconductivity, quantum Hall effect, etc. recently, it was shown that these high electronic mobilities can be observed also in single-crystal organic materials, such as C60. 

1. Introduction

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2. Structures of the Polymorphs

In planar aromatic hydrocarbons, two different, important intermolecular interactions can be discerned: C–H, between a carbon of the aromatic system and a hydrogen at a ring edge, and C–C, between the aromatic groups. Gavezzotti et al. have performed a database study for this class of molecular systems. They find that all crystallize in layered structures. The intralayer structure depends on the relative abundance of C–H bonds.

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and C–C interactions. If the C–H interactions dominate, a herringbone structure is generally found. With an increasing relative number of C–C interactions, the structure becomes more graphitelike, progressing from a sandwiched herringbone, via a γ-structure, to a β-structure. In these structures, the b axis becomes increasingly longer, and the a axis becomes shorter. In the β-structure, the a axis is very short; it closely resembles a graphic arrangement of the molecules.

All of the acenes, benzene through pentacene17–19 (and several oligothiophenes20–23 and oligophenlenes24), crystallize in a herringbone structure (Figure 1 depicts the herringbone structure for pentacene). This is consistent with the observations by Gavezzotti et al. as the acenes possess a relatively large number of H atoms. In view of the rather generic nature of this structure, we will try to explain the thin film polymorphs as a variation on the herringbone motif. To do so, we have to analyze the similarities and differences between the structures of all of the acenes. As the benzene molecule has a much higher symmetry than the other molecules in the series of acenes, it is omitted from the discussion.

Naphtalene,25–27 anthracene,19,28,29 tetracene,30,31 and pentacene12,31,32 have two molecules in the unit cell. The angle between the molecules (i.e., the angle between the vectors normal to the molecular planes) is remarkably similar: 52.3°, 51.1°, 51.3°, and 51.9°, respectively.

Differences are also apparent. The shorter acenes naphthalene and anthracene are monoclinic, whereas tetracene and pentacene have a lower symmetry and crystallize in a triclinic structure. In the shorter acenes, one molecule can be transformed into the other via a screw axis. In tetracene and pentacene, both molecules are crystallographically inequivalent. Only inversion symmetry is left. The inversion centers are located at the molecular centers. In the longer acenes, the long molecular axes (LMAs) have practically the same direction: for tetracene, they differ not more than 2.5°, and for pentacene, they differ not more than 1.5°. For the shorter acenes, these angles are significant: ~22° for naphthalene and for anthracene.

The LMA in all four acenes is not oriented along the c*-axis, but is rotated [see, e.g., Figure 1a]. For pentacene, the molecules are rotated such that they are almost parallel to the [1,1,~1] axis. This rotation is most easily characterized by relative shifts of neighboring molecules within a layer along the LMA. For the pentacene single-crystal structure, this is illustrated in Figure 2. Neighboring molecules in the direction a – b (see Figure 1b) exhibit almost no shift. However, neighboring molecules in the direction a + b are shifted considerably. These shifts are most conveniently expressed in units of one aromatic ring: d002 = 2.43 Å. We obtain 0.05 and 0.89 for d002, respectively. These shifts lead to a pattern of steps within the molecular layers, as depicted in Figure 3a. The values for tetracene, 0.2 and 0.8 for d002, respectively, are slightly different. For naphthalene and anthracene, the characterization is less exact, because the LMAs are not parallel. Nevertheless, a step pattern can be recognized. As is evident from Figure 3b, the step pattern for anthracene is qualitatively very different.

From the preceding results, we conclude that the longer acenes behave very similar. We may consider the intermolecular angle as fixed at 51.9°. The LMAs of both molecules have the same direction. Also, the lateral distances between the molecules in the molecular layers are very similar in tetracene and pentacene. Clearly, these are fixed by the C–H and C–C interactions. The only intralayer degrees of freedom left are the

relative shifts of the molecules along the LMAs. We will use these degrees of freedom to model the structure of the thin film polymorphs and thus determine \( d(001) \). The specific values of these shifts are fixed by experimental data on the thin film polymorphs. In section 3, we will rationalize these shifts from a careful consideration of the intermolecular interactions within the layers. First, the shift-model will be derived from the single-crystal structure, and its parameters will be defined. The model will then be used to describe the thin film polymorphs.

Figure 1c shows the result of a projection of a pentacene layer along the LMA. All distances and angles in this figure are fixed by the single-crystal data. The only parameters are the shifts of the molecules perpendicular to the plane of view. The lattice, and therefore the slant in the molecular layer, is uniquely determined by the shifts of the molecules at \( a \) and \( b \), denoted by \( \lambda_a \) and \( \lambda_b \), respectively, relative to the molecule at \((0,0,0)\). If inversion symmetry is present, the shift of the inequivalent molecule at \((1/2,1/2,0)\) is \( \lambda_{\bar{a}} = (\lambda_a + \lambda_b)/2 \). For the single-crystal polymorph, the LMA is close to \([1,1,-1]\). We approximate the shift along the LMA by a shift along \([1,1,-1]\). This implies that the unit cell volume is independent of \( \lambda_a \) and \( \lambda_b \) and therefore always equals the single-crystal unit cell volume. However, \( d(001) \) is a function of \( \lambda_a \) and \( \lambda_b \). (In section 3.2.3, we follow a slightly more sophisticated route to determine \( d(001) \).

If we take \( \lambda_a = \lambda_b = 0 \), all of the molecules stand upright at 90° angles, and the layer—layer distance (i.e., periodicity) \( d(001) \approx 16.2 \text{ Å} \). [Note that 16.2 Å equals the length of the molecule (13.8 Å) plus twice the van der Waals radius of the hydrogen atom (1.2 Å).] The single-crystal structure, with \( d(001) = 14.1 \text{ Å} \), is obtained for \( \lambda_a = -0.84 d_0 \) and \( \lambda_b = -0.94 d_0 \).

As noted above, polymorphism in pentacene is well documented. Four thin film polymorphs are presently known. They can be classified by the molecular layer thickness \( d(001) \): 14.1, 14.4, 15.0, and 15.4 Å. The experimental values of the lattice parameters of the four different polymorphs are summarized in Table 1. The 14.1 and 15.0 Å polymorphs grow on Kapton, whereas the 14.4 and 15.5 Å polymorphs grow on \( \alpha-\text{SiO}_2 \). As the thin film 14.1 Å polymorph has the same \( a^* \), \( b^* \), and \( c^* \) values as the single crystal, it is assumed to be isostructural with the single crystal. For the 14.4 Å polymorph, powder X-ray diffraction (PXD) data are available. These data are sufficient to determine the cell. For the 15.0 Å (XRD1) and 15.4 Å (XRD2) polymorphs, only \( d(001) \) could be determined from X-ray diffraction.

Additional data on the polymorphs are available from electron diffraction (ED). The substrate is a carbon covered copper grid, that is, different from the substrates used for the X-ray diffraction measurements. Four measurements (four different spots on one sample) of \( a^* \) and \( b^* \) (or \( c^* \)) have been carried out (ED1, ED2, ED3, ED4). However (apart from ED2), direct assignment to a specific \( d(001) \) is not possible, as \( c^* \) could not be measured. Four different polymorphs are apparent, see Table 1. This additional data from ED can be used to characterize the thin film polymorphs. For more details, we refer to ref 5.

As two independent parameters have to be constrained, assignment of the powder X-ray data (P-XRD) and the electron diffraction experiments ED3 and ED4 is possible. \( \lambda_a \) and \( \lambda_b \) are determined by the values of \( a^* \) and \( b^* \) and listed in Table 2.

For the powder X-ray data, the shift-model accurately predicts \( c^* \) and \( d(001) \). The predicted angles \( \alpha^* \), \( \beta^* \), and \( \gamma^* \) are all off by a few degrees, although the relative sizes are well predicted. For ED3, the predicted value of \( \gamma^* \) is close to the experimental value; for ED4, the discrepancy is a bit larger. All deviations are acceptable. Moreover, small deviations in these angles hardly affect \( d(001) \). For ED3, we predict \( d(001) = 15.1 \text{ Å} \), and for ED4, \( d(001) = 15.9 \text{ Å} \). ED3 is readily assigned to the film that

### Table 1. The Reciprocal Lattice Parameters of Pentacene as Observed in Several Experiments

<table>
<thead>
<tr>
<th></th>
<th>( a )</th>
<th>( b )</th>
<th>( c )</th>
<th>( a^* )</th>
<th>( b^* )</th>
<th>( \gamma^* )</th>
<th>( d(001) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>SXD</td>
<td>0.1603</td>
<td>0.1328</td>
<td>0.0708</td>
<td>103.374</td>
<td>91.1114</td>
<td>94.91</td>
<td>14.12</td>
</tr>
<tr>
<td>ED1</td>
<td>0.1610</td>
<td>0.1319</td>
<td>0.0708</td>
<td>103.374</td>
<td>91.1114</td>
<td>94.91</td>
<td>14.12</td>
</tr>
<tr>
<td>PXD</td>
<td>0.1563</td>
<td>0.1399</td>
<td>0.0696</td>
<td>102.25</td>
<td>92.37</td>
<td>98.4</td>
<td>14.37</td>
</tr>
<tr>
<td>ED2</td>
<td></td>
<td></td>
<td></td>
<td>0.0694</td>
<td></td>
<td></td>
<td>14.4</td>
</tr>
<tr>
<td>ED3</td>
<td>0.173</td>
<td>0.134</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>15.0</td>
</tr>
<tr>
<td>ED4</td>
<td>0.180</td>
<td>0.140</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>15.4</td>
</tr>
<tr>
<td>XRD1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>XRD2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* The values of \( a^* \), \( b^* \), and \( c^* \) are in Å\(^{-1}\), \( \alpha^* \), \( \beta^* \), and \( \gamma^* \) are in degrees, and \( d(001) \) values are in Å. All data are from ref 5. Each line lists an experiment, performed on different samples or different parts of a sample. SXD is single-crystal X-ray diffraction, XRD is X-ray diffraction, PXD is powder X-ray diffraction, and ED means electron diffraction.
Only intralayer interactions are considered. The interlayer we have a simple, albeit approximate, description of all possibly interactions: the van der Waals and electrostatic forces. Thus, pentacene will not be strong. In a second approach (section 3.2), molecule. Covalent overlap in a molecular crystal such as HOMO simple model and consider the overlap of the HOMO (and close, both in energy and spatially. In section 3.1, we use this interaction. The HOMO of the pentacene Molecule. Density functional theory (DFT) in the generalized gradient approximation (GGA, using Perdew–Wang ‘91)34 was used to describe the electronic states of the molecule and to calculate the electron density of the LUMO, HOMO, and HOMO−1 (the level just below the HOMO) of pentacene. The Vienna ab initio simulation program (VASP) was employed,35–38 using the projector augmented wave method.39,40 The wave functions of the valence electrons were expanded in plane waves. The kinetic energy cutoff was 500 eV. The molecule was placed in a periodically

3. Rationalization of the Structures

Here we investigate whether it is possible to understand the proposed shifts on the basis of the intermolecular interactions. Because of their size, systems such as pentacene are outside the realm of sophisticated quantum chemical calculations. We aim to model the important interactions with as simple means as possible.

From simple geometry [e.g., Figure 1], it is evident that the most important interactions occur along a + b and a − b. Here the hydrogens of one molecule point toward the π systems of the carbon atoms on the other, crystallographically inequivalent molecule. In the a direction, the hydrogen atoms of the molecules interact with other hydrogens of the periodic images.

Table 2. The Unit Cell Parameters (Å and Å−1) of the Thin Film Polymorphs, Calculated from Their a* and b* Values

<table>
<thead>
<tr>
<th></th>
<th>d_{A}(001)</th>
<th>d_{B}(001)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SXD</td>
<td>0.403</td>
<td>0.410</td>
</tr>
<tr>
<td>PXD</td>
<td>0.403</td>
<td>0.410</td>
</tr>
<tr>
<td>ED 3</td>
<td>0.403</td>
<td>0.410</td>
</tr>
<tr>
<td>ED 4</td>
<td>0.403</td>
<td>0.410</td>
</tr>
</tbody>
</table>

“λ_a and λ_b are the shifts in units of d_{A}, that were used to construct unit cells with the specific a* and b* values. d_{A}(001) is the d(001) value of the thin film polymorph to which the model structure is assigned. All d(001) values are in Å.

![Figure 4](https://example.com/figure4.png)

3.1. Overlap Model. We take the overlap between empty and filled states as a measure for the strength of the covalent interaction. The HOMO of the π system is the highest filled state. We seek empty states on the other (neighboring) molecule, that are close in energy, but also have a sizable overlap. Considering the interatomic C−H distances, the hydrogens along the a + b or a − b direction lie closest to the π system. Therefore, we take H functions, which are not fully filled. The H 1s state lies closest in energy to the HOMO. However, also hydrogen p orbitals are part of the LUMO and the orbitals directly above the LUMO.35 It is difficult to exactly separate the contributions of the 1s, 2s, and 2p states to the density of states. Therefore, we take all of the hydrogen 1s, 2s, and 2p states and consider their overlap with the HOMO separately. As the HOMO−1 is only 1.1 eV below the HOMO, it is also included in the discussion.

Along the a direction, the adjacent molecules also lie in rather close proximity. Yet here we expect a HOMO−LUMO overlap involving the hydrogen atoms at the ends of the molecules. It should, therefore, be much weaker. Therefore, we will neglect the overlap in the a direction.

The overlap integral S is calculated as a function of one (or part of one) molecule relative to a neighboring molecule. We start with the overlap of one hydrogen atom (on one molecule) with the HOMO (of the other molecule) toward which it points. We then extend the model to the overlap of five hydrogen atoms (one edge of a molecule). The relative positions of the molecules are fixed to those of the single crystal. The only coordinate is the shift along the LMA relative to the neighboring molecule. Within the structural model for the polymorphs, it can be identified with (λ_a + λ_b)/2 = λ_{a+b}/2 or (λ_a − λ_b)/2 = λ_{a−b}/2. Of course, this assignment implies inversion symmetry.

3.1.1. Electron Density and Wave Functions of the Pentacene Molecule. Density functional theory (DFT) in the generalized gradient approximation (GGA, using Perdew–Wang ‘91)34 was used to describe the electronic states of the molecule and to calculate the electron density of the LUMO, HOMO, and HOMO−1 (the level just below the HOMO) of pentacene. The Vienna ab initio simulation program (VASP) was employed,35–38 using the projector augmented wave method.39,40 The wave functions of the valence electrons were expanded in plane waves. The kinetic energy cutoff was 500 eV. The molecule was placed in a periodically.

repeated box (20 × 12 × 10 Å³) with the LMA along the long axis of the box and the π system pointing along the short axis. The box was chosen so large that the molecule does not “feel” the presence of its periodic image; that is, effectively the charge density of a single pentacene molecule was calculated. In Figure 5, the calculated electron densities for the LUMO, HOMO, and HOMO−1 of pentacene are shown. The plane of the molecule is a nodal plane, so the electron density is shown for a plane just above the molecule. The different parts of the orbital, which are separated by nodal planes, have alternating signs. The 1s orbital of hydrogen is incorrectly calculated by DFT-GGA.

Figure 5. The calculated electron density for a pentacene molecule in a plane above the nodal plane. On top, LUMO; middle, HOMO; and bottom, HOMO−1. The large and small black circles indicate the position of the C-atoms and H-atoms, respectively. The lines are on a logarithmic scale. The lines lie at 0.0001 × 10^n e/Å², n ≥ 1. (n should be counted from the outermost lines. Note that the number of lines enclosing a C atom differs.)

3.1.2. Results. First, the overlap of one 1s hydrogen orbital with the HOMO was calculated. Figure 6a shows the overlap S as a function of the relative shift d of the H atom. Zero shift corresponds to the situation where the H-orbital is pointing at the middle ring. Other maxima are observed for shifts of slightly more than 1 or 2 d₀.

The results for the overlap of five hydrogens with the HOMO can be seen in Figure 6b. The dotted line was drawn, assuming that the hydrogen orbitals do not have mutual interaction. Therefore, the phase (±) of each hydrogen orbital can adapt to the phase of the π system, and the overlap is positive for all shifts. The solid line assumes that all hydrogen orbitals of a molecule have the same sign. The dashed line is the overlap calculated, assuming that all adjacent hydrogen orbitals have alternating signs. This pattern is similar to the sign alternation of the LUMO. From the graph (dashed line), it is evident that the extrema (i.e., maximal overlap) lie at zero and almost integer multiples of d₀. For large shifts, they shift to values a bit larger than the integer numbers. This can be understood from the electron density of the HOMO (Figure 5). Here the positions with a high electron density are shifted a little toward the ends of the molecule. Minimal overlap occurs for shifts of approximately 0.5, 1.5, 2.5, … × d₀. This corresponds with the nodes in the electron density of the HOMO.

Figure 6c,d depicts the overlap of the 1s H-orbital with the HOMO−1. Although the curves are different, the extrema are at approximately the same positions.

The overlap integral was also calculated for a 2s and 2p hydrogen orbital with the HOMO and HOMO−1. Because the 2s and 2p orbitals have a much larger spatial extension than the 1s orbital, the presence of two wave function extrema with opposite phase is felt. The maxima are, therefore, especially in the case of 2s, less pronounced than those for 1s. For the 2p orbital, a maximum overlap with the HOMO and HOMO−1 is reached for the same shifts as for 1s: zero and slightly more than 1 d₀. For the 2s orbital, maxima in overlap are only reached for large shifts of 2−4 d₀.

We now relate the calculated overlap to the proposed crystal structures of the thin film polymorphs (see Figure 4). In the case of the single crystal, the 14.1 Å structure, $\lambda_{d0-b/2} = (\lambda_d - \lambda_{d0})$.
\( \lambda_b/2 = 0.05 \, \text{d}0 \) and \( \lambda_{a+b}/2 = 0.89 \, \text{d}0 \). These shifts are close to 0 \( \text{d}0 \) and 1 \( \text{d}0 \) and, therefore, very near maximum overlap.

For the 14.4 Å structure, \( \lambda_{a-b}/2 = 0.21 \, \text{d}0 \) and \( \lambda_{a+b}/2 = 0.73 \, \text{d}0 \) were proposed. For the 15.4 Å structure, \( \lambda_{a-b}/2 = \lambda_{a+b}/2 = 0.22 \, \text{d}0 \). The shifts for both structures are between maximum and minimum overlap.

For the 15.0 Å structure, \( \lambda_{a-b}/2 = 0.25 \, \text{d}0 \) and \( \lambda_{a+b}/2 = 0.59 \, \text{d}0 \). This last shift is near minimum overlap, indicating that this position is unfavorable. However, a positive or negative shift of one of the molecules by \( \sim 0.5 \, \text{d}0 \) would place the molecules in an almost optimum configuration. It would also break the inversion symmetry of the lattice.

In the above discussion, we’ve only considered overlap. It’s difficult to make an exact connection with binding energies. However, a rough estimate of the typical energy variations can be made using the Wolfsberg–Helmholz model. Taking an estimate of the typical variation in the overlap of 0.002, we found that the typical variation of the energy is 0.002 \times 2 \times 6.6 \, \text{eV} = 0.6 \, \text{kcal/mol/cell} \). Here 6.6 \, \text{eV} is the ionization potential,\(^\text{(42)}\) and 2 is the number of pentacene–pentacene contacts per cell.

### 3.2. Model Potential Approach

In this section, we use a simple force field to model the van der Waals interactions and electrostatic interactions between the molecules. Here it is straightforward to include also the interaction between the equivalent molecules (notably the interaction between periodic images along the \( a \) axis). Interaction between the layers is again neglected. With the force field potential, the energies of the different pentacene polymorphs are calculated as a function of the position of the \((1/2,1/2,0)\) molecule. So far, we assumed that inversion symmetry is preserved in all thin film polymorphs. However, when the inequivalent molecule is shifted along its length axis, the crystal structure symmetry is lowered.

#### 3.2.1. Force Field

DREIDING uses general constants for the different elements, which are not dependent on the particular combinations of atoms in the structure. These constants are accurate for a large number of organic compounds.

The crystal energy is obtained as a summation over interatomic, pairwise additive interactions. The pentacene molecules themselves are kept rigid. For the van der Waals energy, a Lennard-Jones type expression is used:

\[
E_{\text{LJ}} = D_0 [\rho^{-12} - 2 \rho^{-6}] \tag{1}
\]

where \( \rho = R/R_0 \), \( R \) (in Å) is the interatomic distance, \( R_0 \) is the van der Waals bond length, and \( D_0 \) is the van der Waals well depth. \( R_0 \) and \( D_0 \) are taken from ref 14. Electrostatic energies \( E_Q \) (in kcal/mol) are calculated using:

\[
E_Q = 322.0637 \times Q_i Q_j / R \tag{2}
\]

where \( Q_i \) and \( Q_j \) are the charges of atoms \( i \) and \( j \) in electron units. The distribution of the charges is not known. It is used as a parameter and varied over a physically plausible range.\(^\text{(43,44)}\) Calculations were carried out with \( |0.1 \, \text{e}| \) on the hydrogen atoms (and a compensating charge on the carbon atoms) and repeated with \( |0.2 \, \text{e}| \) (a recent Hartree–Fock calculation gives hydrogen charges in the range \( |0.9-1.8 \, \text{e}|\)). The leading order electrostatic interactions are between the quadrupoles of the molecules. Only interactions of molecules within a cutoff radius were included. The nearest neighbors along \( a, b, a+b, \) and \( a-b \) were taken into account, but interlayer interactions were omitted.

The energy is calculated using the specific shifts, \( \lambda_a \) and \( \lambda_b \), as determined for the thin film polymorphs; that is, the cell is fixed. Only the inequivalent molecule [chosen at \((1/2,1/2,0)\)] is allowed to shift, independently from the equivalent molecules [at \((0,0,0)\)]. Thus, the parameter \( \lambda_{IE} \) is varied. The energy is plotted as a function of \( \lambda_{IE} = \lambda_{IE} - (\lambda_a + \lambda_b)/2 \), so that \( \lambda_{IE} = 0 \) corresponds to inversion symmetry of the lattice. When an energy minimum is observed, \( \lambda_{IE} \) is fixed, and \( \lambda_a \) and \( \lambda_b \) are varied to check whether the minimum is stable.

#### 3.2.2. Results

Calculations were performed for the 14.1, 14.4, 15.0, and 15.4 Å structures, and for an imaginary structure in which the molecules are not shifted. The results of the calculations with only van der Waals interactions are depicted in Figure 7a. The absolute energy minimum is attained for the structure without shifts. Minima can also be observed for the
The minima around 1 and minimum. Also, drops below the 15.0 Å structure and becomes the absolute strength of the electrostatic contribution, the 14.1 Å structure than the 14.4 and 15.4 Å structures can attain. With increasing

Another trend (with increasing electrostatic strength) is that the internal structure of the cell is stable; that is, inversion is neither very stable nor very unstable. The force field approach shows that the interactions within a layer are expected to be much stronger than the interactions between layers, the structure of the layers is kept fixed to the ones described in section 2.46 The minima in energy were determined as a function of the position of one layer with respect to the adjacent layer. For all four polymorphs, an absolute and a local minimum were obtained. The results for the 14.1, 14.4, 15.0, and 15.4 Å structures are given in Table 3. A good agreement is obtained for the 14.1 Å structure: both d(001) and details of the single-crystal packing are reproduced; for example, interlayer contacts are predominantly mediated by hydrogen of crystallographically equivalent molecules. This is remarkable, in view of the crudeness of the model and the smallness of the interlayer interaction. The 14.4, 15.0, and 15.4 Å structures show a good agreement with the observed d(001) values.

4. Conclusions

On the basis of the herringbone motif, a structural model describing various pentacene thin film polymorphs and the single-crystal structure was constructed. It associates the d(001) values with the relative shifts of pentacene molecules within a molecular layer. The shifts could be determined for all known polymorphs (Figure 4), and the resulting values for d(001) were in reasonable agreement with experiments.

Two simple models were employed to rationalize the relation between the intermolecular, intralayer interactions and the polymorph’s structure. The models are complementary and span the whole range of possible types of intermolecular interactions: covalent, van der Waals, and electrostatic. Both models consistently explain the 14.1 and 15.0 Å structures, provided the symmetry for the 15.0 Å polymorph is lowered to P1. It is well known that the electrostatic interactions play a role in stabilizing the herringbone structure for acenes.47 We find evidence that also the rotation of the LMA away from c* is stabilized by electrostatic interactions.

The 14.4 and 15.4 Å structures cannot be well explained with either model. The overlap model predicts them to be neither very stable nor very unstable. The force field approach shows that the internal structure of the cell is stable; that is, inversion symmetry is preserved. However, the cell itself is at a saddle point and cannot be stable.

How can we understand these discrepancies? If the 14.4 and 15.4 Å polymorphs would adopt another structure, a double

<table>
<thead>
<tr>
<th>structure</th>
<th>calculated d(001) (Å)</th>
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</thead>
<tbody>
<tr>
<td>14.1 Å</td>
<td>14.1, 14.2</td>
</tr>
<tr>
<td>14.4 Å</td>
<td>14.3, 14.5</td>
</tr>
<tr>
<td>15.0 Å</td>
<td>15.2, 15.1</td>
</tr>
<tr>
<td>15.4 Å</td>
<td>15.4, 15.5</td>
</tr>
</tbody>
</table>

* Various numbers pertain to various (local) minima. Absolute minima have been labeled with an “*”.

(46) To be consistent with the discussion in section 3, for the 15.0 Å structure $\lambda_{ee} = 0.5d_0$ was imposed.

herringbone structure would be most likely. However, that does not fit any of the known experimental data, notably the powder diffraction on the 14.4 Å polymorph, which is perfectly consistent with a herringbone arrangement.

The most striking observation is that the 14.1 and 15.0 Å structures are grown on another substrate than are the 14.4 and 15.4 Å polymorphs (polyimide and a-SiO₂, respectively). We therefore speculate that the specific substrate induces the growth of the 14.4 and 15.4 Å polymorphs. This points to the possible relevance of interlayer effects (note that in a study of the initial stages of pentacene growth on a-Si, the first molecules were lying flat on the substrate). Moreover, we have argued that details in the intralayer herringbone stacking are not likely to change much. So intralayer effects seem to be ruled out.

In view of these considerations, we have to (re)consider the interlayer effects. We have assumed they are negligibly small, but we cannot rule out steric effects completely: repulsion between the H’s of two layers may frustrate a shear of one layer over the other. These effects cannot be very large. The strength of this interaction is sizable though, as the 14.4 Å polymorph is even stable without the support of the substrate. This suggestion is supported by Raman experiments.

The reconsideration of interlayer effects also motivated the calculation of the interlayer distance with the DREIDING force field. There is a qualitative similarity between the calculated layer stackings (local minima) found for the 14.1 and 14.4 Å polymorphs (a similarity is also observed for the other pair of polymorphs). The 14.1 Å structure is known from X-ray diffraction: interlayer interactions are predominantly mediated by hydrogens on crystallographically equivalent molecules. A similar layer stacking is observed for one of the model layer

structures. It is this stacking that we assign to the 14.1 Å polymorph. Raman experiments suggest that for the 14.4 Å (and 15.4 Å) polymorph, also interactions between crystallographically different molecules occur. Consistently, the model calculations predict also another layer stacking (local minimum), which we assign to the 14.4 Å polymorph.

Recently, Brillante et al., using Raman spectroscopy, have provided evidence that, apart from the well-known single-crystal structure, another single-crystalline polymer exists. Following Venuti et al., it was proposed to correspond to the structure originally reported by Campbell et al. As the Campbell structure has d(001) ≈ 14.5 Å, this structure is another candidate for the thin film 14.5 Å polymorph. However, the powder X-ray diffraction results for the thin film 14.4 Å polymorph are inconsistent with Campbell’s structure. Presently, insufficient data are available for this new single-crystalline polymorph to attempt a description with our model.

In conclusion, a comprehensive model description of pentacene polymorphs was presented. Intralayer relative shifts of the molecules are sufficient to give a reasonable picture of the structure, including its d(001). The structures can only be partially rationalized on the basis of intralayer interactions, and an extension to interlayer interactions seems desirable.

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