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COMMUNICATIONS

Probing Pentacene Polymorphs by Lattice Dynamics Calculations

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Received July 24, 2001

Worldwide studies are currently devoted to the characterization of molecular organic semiconductors, particularly after the discovery of extremely high current mobilities,[1] opening the way to their application as organic field effect transistors, charge-injected superconductors, or solid-state injected lasers.[2] High-purity single crystals or thin films of these materials are necessary for observing these outstanding physical properties, but also crucial is the control of the conditions under which the molecules assemble to form the solid.[3,4]

The solid phases of pentacene have been the object of several investigations.[3−10] It has been recently shown by Siegrist et al.[8] that a new pentacene polymorph with enhanced physical properties (hereafter referred to as structure **S**) can be obtained by vapor-phase growth. Previously, pentacene single crystals had been grown from solutions of trichlorobenzene, as reported by Campbell et al.[9] (structure **C**) and by Holmes et al.[7] (structure **H**). Furthermore, thin films grown on SiO_2 substrates[3,5,6] exhibit two different phases, one of which is thought to be induced by the substrate itself, whereas the other is attributed to the bulk phase **C**. Overall, the phase diagram is far from being understood, and it is not clear yet how many different phases of pentacene have been identified.

Complete X-ray data, which are available for the three structures **H**, **S**, and **C**,[7−9] have not been sufficient to clarify the issue. Structural differences between the **C** and **S** structures have been detected [8] by counting at various cutoff distances the average number of carbon atom contacts and measuring the *d* spacings along the (001) reflections. Despite being quite subtle, the differences are found to be critical in determining different carrier mobilities in the two phases.[8] It has been noted[7] that the crystallographic parameters of the two solution-grown structures **C** and **H** are in disagreement. Instead, the unit cells of **H** and **S** seem to match[8] and therefore are expected to be coincident, although there is no evidence of this as yet.

In this communication we aim to discern among the various phases by computing their equilibrium structures. As discussed below, we identify unambiguously phase **S** as coincident with phase **H**, and confirm that instead phase **C** is significantly different. These conclusions are drawn by comparing the "inherent structures" of the various phases. We use the concept of inherent structure[11] as a device to eliminate the "noise" due to the thermal expansion. The inherent structure of a system in a given configuration is the structure of *mechanical* equilibrium at the local minimum of the many particle potential energy hypersurface which is reached by steepest descent minimization starting from that configuration. Different X-ray structures of the same thermodynamic phase, measured in different conditions of temperature and pressure, should all be situated in the attraction basin of a *single* local minimum of the potential energy and should therefore converge toward identical inherent structures. Since identical minima involve identity of energy, lattice data, and phonon frequencies, the comparison of these parameters can be used to diagnose the identity, or lack of identity, of two phases.

Indeed, such a comparison can be hindered by another source of noise, that is different molecular geometries in the various crystal structures. Usually, choosing the X-ray experimental geometry of each structure is a good computational strategy. Nonetheless, in such a tricky case like pentacene, where the polymorphs seem to differ so little, all with triclinic unit cells belonging to the same space group $P\bar{1}$, $Z = 2$, and close volumes, it is wise to employ a common geometry for all structures. The calculations reported in this paper have been performed with the geometry determined by ab initio methods for the isolated molecule using a 6-31G(d) basis set in combination with an exchange-correlation functional B3LYP. We have also probed several planar geometries with D_{2h} symmetry obtained by averaging the X-ray geometries and obtained exactly the same relationships among the various structures. Therefore, once the strategy of a shared geometry has been established, the choice of which one is to be preferred is largely irrelevant to our purposes.

We have determined the inherent structure separately for each of the three phases **H**, **S**, and **C**, starting from their X-ray structures,[7−9] first by replacing the experimental molecular geometries with the ab initio one and then by minimizing the total potential energy of the crystal Φ_0 with respect to the lattice parameters, molecular positions, and orientations. For the intermolecular potential we have adopted an atom−atom Buckingham model $\Phi(r) = A_{ij} \exp(-B_{ij}r) - C_{ij}/r^6$. Various sets of parameters A_{ij}, B_{ij}, and C_{ij} for the C and H atoms have been tested, with results which despite being numerically different gave identical phase relationships. In other words, exactly as it happens for the molecular geometry mentioned above, also the choice of a specific potential model is essentially irrelevant. The present results are for the parameter set IV by Williams.[12]

The minimum potential energy Φ_0 and cell volumes V_0 calculated for the inherent structures **H**, **S**, and **C** are reported in Table 1, while the lattice phonon wavenumbers, also computed at the minima, are reported in Table 2. For none of these quantities is there a corresponding observable value. Tables 1 and 2 show that the inherent structures of phases **S** and **H** have identical energy Φ_0, volume V_0, and phonon frequencies, within numerical round-off. The values for the **C** phase, instead, are different. This result confirms the findings of ref 8, where the vapor-phase-grown phase **S** and the solution-grown phase **C** were recognized as being distinct. It also shows, however, that the vapor-phase-grown phase **S** is coincident with phase **H**, which is grown from solution.[7]

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10.1021/ja0166949 CCC: $22.00

Table 1. Minimum Potential Energy Φ_0 and Cell Volumes V_0 for the Inherent Structures of the Phases **H**, **S**, and **C** of Pentacene[a]

structure		Φ_0 (kJ/mol)	V_0 (Å^3)	T (K)	V (Å^3)	a (Å)	b (Å)	c (Å)	α (deg)	β (deg)	γ (deg)
H	calcd	−171.19	656.85	180	642.51	5.976	7.432	14.884	77.591	85.369	85.930
	exptl	- -	- -	180	677.32	6.275	7.714	14.442	76.752	88.011	84.524
S	calcd	−171.19	656.84	293	658.65	6.047	7.490	14.986	77.295	85.296	85.598
	exptl	- -	- -	293	685.50	6.265	7.786	14.511	76.65	87.50	84.61
C	calcd	−171.85	654.70	295	672.81	7.617	5.953	16.103	100.335	110.490	86.846
	exptl	- -	- -	295	692.40	7.90	6.06	16.01	101.9	112.6	85.8

[a] The X-ray data[7−9] are compared to the structural parameters calculated at the minimum free energy at the temperatures T of the experiments with the experimental molecular geometries.

Table 2. Lattice Phonon Wavenumbers Calculated at the Inherent Structures for Phases **H**, **S**, and **C** of Pentacene[7−9]

structure	A_g modes (cm^{-1})						A_u modes (cm^{-1})		
H	164.1	157.9	110.2	76.9	64.1	33.5	130.5	61.2	21.0
S	164.2	157.9	110.2	76.9	64.1	33.5	130.5	61.2	21.0
C	164.8	155.8	115.0	72.5	57.2	46.7	129.3	63.5	28.1

Once the relationships among the structures **H**, **S**, and **C** are clarified, we are left with the problem of reproducing lattice parameters as determined by the experiments at different temperatures. To achieve this, we account for the effects of temperature with a quasi-harmonic lattice dynamics (QHLD) approach,[13−16] which has proved to be a powerful and computationally inexpensive method to determine structural and vibrational properties of molecular crystals as a function of temperature T and pressure p, and to clarify the phase diagram when polymorphs are present. The main feature of QHLD is that the vibrational contribution to the free energy $G(p,T)$ of the crystal at given p,T is approximated by the free energy of the phonons calculated in the harmonic approximation at the average lattice structure. The structural parameters at thermodynamic equilibrium for the phases **H**, **S**, and **C**, determined by minimizing the free energy $G(p,T)$ at the temperatures of the experiments,[7−9] are reported in Table 1. The computed values account for the small differences between the two inequivalent molecules in the unit cell by employing the X-ray molecular geometries and therefore can be compared with the experimental data.[10]

The overall agreement between experiments and calculations is good, with differences ∼3% for the unit cell axes, and ∼2% for the angles. The systematically smaller cell volumes obtained with the X-ray geometries are partly a consequence of the unphysically short C−H bond lengths estimated by the experiments, which result in smaller molecular volumes. The shortest C−H lengths, 0.91 Å, appear in structure **S**. This is a problem often encountered and can be easily overcome by normalizing the C−H distances to a suitable value for hydrocarbons (e.g. 1.08−1.09 Å). Once this effect has been taken into account, all observed trends are readily justified. Thus, at room T the calculated density of structure **S** is ∼2% larger than structure **C**, with the experimental difference of ∼1%. The calculated volume expansion in going from the **H** structure at 180 K to the **S** structure at 293 K is also overestimated due to excessive differences in the molecular geometries. In fact, by compensating for the differences in the X-ray C−H lengths, we find a thermal expansion of ∼1%, in good agreement with the experiments.

Interesting hints are given by a closer inspection of the lattice phonon wavenumbers reported in Table 2. It can be noticed that the three lowest lattice modes display, in percentages, the largest differences between polymorphs **S** and **C**. From the analysis of the corresponding eigenvectors these modes are found to be an A_u mode involving a translation parallel to the long molecular axis L, and two A_g modes representing librations around the M and N axes, perpendicular to L, which in pentacene have the largest inertia moments, $I_M \approx I_N$.

A close relationship between crystal structures and vibrational properties can then be found. The two inequivalent molecules in both **S** and **C** polymorphs are arranged in a herringbone-type packing, but they are shifted differently against each other in a direction parallel to axis L.[8] It is therefore plausible for the translation parallel to the direction of the shift and the librations about axes perpendicular to it to be the modes mostly affected by the phase change. Thus, by recording and comparing the experimental phonon spectra of the various structures, beside verifying the phase identity, one could probe the “shear” due to the mutual shift of nearby molecules along the L-axis.

In conclusion, we have shown that two distinct bulk crystalline phases of pentacene exist, with very subtle differences. The method of crystal growth (from solution or vapor) is not the determining factor for obtaining either structure. We suggest that sample purity or growth temperature are more critical. The calculated potential energy difference between the two phases is very small, and a more detailed QHLD study is under way to clarify the pentacene p,T phase diagram. We also plan calculations in which the potential energy hypersurface is extensively searched for other possible stable polymorphs. The studies will pave the way to understand how the different packings affect the physical properties, and possibly also the origin of the T-induced crossover from hopping to band conduction.[10,17]

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JA0166949