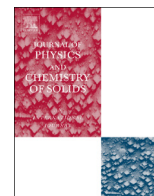




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Structure of clusters of pentacene molecules and their polarizabilities

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ABSTRACT

We calculate and compare the ground state structures of one, two and three pentacene molecule clusters, using B3LYP and B97-D density functionals, and polarizabilities in the ground state structure to examine the extent of anisotropy for applications in electronic device fabrication. B3LYP and B97-D functionals perform sufficiently well for a single pentacene molecule, but for two and three molecule clusters, the inclusion of dispersive interactions through B97-D becomes necessary. For two and three molecule clusters the energy landscape near ground state is flat in molecular coordinates, implying multiple related structures may be accessible at room temperature. Further, for the ground state structures, the polarizability along the long axis of the molecule is larger than the other two directions. This may make it possible to explain the beneficial effect of applying an electric field during processing of pentacene films in electronic devices, as observed experimentally; specifically, in this context, the structural and polarizability data presented could allow for development of models for nucleation and growth of pentacene films.

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1. Introduction

Pentacene has emerged as an important organic semiconductor due to high charge mobility. As a consequence, it has become the most prevalent material for use in thin film transistor (TFT). A common method for obtaining pentacene films is to thermally evaporate it. The process entails evaporation of molecules, as single molecule or in small clusters, from a heated powder in vacuum. The evaporation flux then arrives at a substrate, where the molecules are assembled in form of a thin film.

One of the goals of the evaporation process is to seek alignment of the molecules on the substrate, in which case the mobility is highest. Since, the pentacene molecule has a long axis, it is likely to exhibit anisotropy in electric polarization. One of the aims is to examine whether or not it will be possible to apply an electric field during deposition to align the molecules, so as to enhance the charge mobility further. That is, if the polarizability in the long direction of the molecule is sufficiently larger than in the other directions, then it may be possible to align the pentacene molecules by application of an electric field during evaporation. Therefore, in this paper, we have calculated equilibrium structure of

small clusters and their polarizability and examined the potential for alignment of molecules during evaporation. Based on this work and using calculated polarizability for single pentacene molecules, we have recently demonstrated the applicability of the idea experimentally [1]. The TFTs that were prepared by depositing pentacene films under influence of an electric field were shown to perform much better. An analysis demonstrated that even though pentacene molecules exhibit anisotropic polarizability, small values of molecular polarizabilities do not allow massive alignment of molecules in presence of kT energies. However, it was also shown that, first, large alignment is not needed for reported increase in carrier mobilities. Also, even without an electric field, pentacene films form local crystallites. Therefore, when an electric field is applied during evaporation process, it is the nucleation and growth process that takes advantage of even a small preferential alignment of molecules and magnifies the overall effect. For example, in presence of electric field, nuclei form in preferred orientations. Then the evaporated molecules or cluster that arrive with preferred orientation would exhibit higher sticking coefficient during the growth process, overall magnifying the effect of electric field in film formation.

Therefore, in order to describe the nucleation and growth process under electric field, it is required to determine the structure of small clusters of pentacene, for example dimers and trimers, and their polarizabilities. First we examine the available literature on the subject. In a system composed of large organic

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molecules, such as pentacene, dispersive interactions play a significant role [2,3]. These interactions arise from the fluctuations in the square of the dipole moment which do not cancel under time averaging [4–6]. Therefore, the usual density functional Theory (DFT) functionals used to determine the ground state are not well equipped to deal with van der Waals interaction (vdW), as demonstrated by calculations of binding energies for dimers of various molecules [7,8]. The DFT functionals predicted the benzene dimer to be underbound and completely failed to describe the interactions in the long range regime. It is expected that this mismatch will be enhanced for larger acene systems.

In approaches other than DFT, Møller–Plesset second order perturbation theory (MP2) [9] and coupled cluster calculations (CCSD(T)) [10] can also be used for including the vdW forces. Further, MP2 overestimates the non-dynamical long range interactions [7,11], which can be improved by spin component scaling [11]. However, though the second order MP2 and CCSD(T) describe electron correlation more accurately, they are very expensive and it is preferable, for large-sized systems, to modify the DFT functional instead. A widely used approach is to add an empirically determined dispersion term to a DFT functional, such as the Grimme's functional (DFT-D2) which adds a dispersion correction term for longer distances using damped coefficients [12]. The DFT-D level of theory, for example, has been shown to be consistent with experimental results related to atomic force microscope imaging of a pentacene molecule [13]. In a recent study on various dimers with strong π - π interactions in benzene, naphthalene and anthracene dimers [14], the authors compared the results of DFT-D, Zhao and Truhlar's functionals (M05-2X [15] and M06-2X [16]) and CCSD (T) calculations and found that dispersion corrected Becke B97 functional (B97-D) [12,17] had the best overall performance.

In the following, we calculate the ground state structures of one, two and three molecule pentacene clusters, along with their polarizabilities. The calculations for the structure optimizations are done with B97-D and the polarizabilities are calculated with parameter free density functional model (PBE0) [18–20] and Aug-cc-pVDZ [21]. These results are then compared with a previous calculation where the polarizability values are obtained for a single pentacene molecule using CCSD, PBE0 and Becke–Lee–Yang–Parr hybrid exchange–correlation three-parameter functional [22,23] (B3LYP) [24]; the structure and polarizability of clusters, however, is not available in literature.

2. Computational details

Calculations are done using GAUSSIAN 09 [25] mainly with the basis set 6–31 G (d,p), suitable for large systems with dispersive interaction [26]. Furthermore, wherever necessary, the counterpoise (CP) correction is included, taking into account the basis set superposition error (BSSE) [27,28]. For comparison we have also done a calculation with the triple zeta valence plus polarization (TZVP) [29] basis set. We have used B3LYP or B97-D. While B3LYP does not include vdW interactions, B97-D (Grimme's correction) takes into account the dispersion interactions, especially important for pentacene clusters. For self-consistent-field (SCF) calculations default, tight convergence is used and the threshold value for root mean squared (RMS) force is 0.0003 Hartree/Bohr for geometric optimizations.

While it is the intention of this work to look for stable molecular clusters of pentacene, a systematic and exhaustive search of the energy landscape is not at all feasible. Hence, a possible arrangement of a cluster is guessed and used as the initial input for geometric optimization. Thereafter, calculations are carried out to determine if the eigenvalues of the Hessian matrices are real and the cluster structure is a local minima.

Finally, the polarizability tensor was calculated by using the Gaussian code via analytical method for the final structure obtained from the geometric optimizations for the single pentacene molecule as well as the clusters using the functional PBE0 and the basis set Aug-cc-pVDZ.

3. Results and discussions

A commonly used DFT functional for organic molecules is B3LYP; however, when dealing with clusters, it would be necessary to include the dispersive interactions between molecules. Hence, we have first compared the structures and energies obtained by three methods (B3LYP and B97-D) for single and two-molecule pentacene cluster.

3.1. Structure of a single pentacene molecule

Structures of a single pentacene molecule optimized with B97-D (Fig. 1a) and B3LYP (Fig. 1b) and LDA (Local Density Approximation) [30] are very similar; the C–C bond lengths for all three differ by less than 0.03 Å. Further, the bond lengths in Fig. 1a are similar to that obtained experimentally [31]. When looking at the Mulliken atomic charges (Fig. 1c), it is seen the carbon atoms have acquired a slight negative charge and the hydrogen atoms a slight positive charge.

Though, it is observed that B97-D, LDA and B3LYP did not yield significantly different results for a single pentacene molecule, for the pentacene dimer we expect that the vdW interactions would play a more important role and there will be substantial differences when different functionals are used. These differences are investigated and thereafter various equilibrium pentacene structures obtained with B97-D are described.

3.2. Equilibrium pentacene clusters

We first compare equilibrium structures for a pentacene dimer system obtained using different density functionals. Results for LDA calculations are compiled from a study by Lee and Yu [30] where they had compared the binding energies for two pentacene molecules in various configurations. They reported that the shifted side to side configuration was the most stable with the binding energy of -1.85 eV; the binding energy of the shifted face to face configuration was -0.65 eV. Our calculations for B97-D predict nearly zero binding in shifted side to side configuration and a significantly different equilibrium structure. It is well known that LDA does not incorporate vdW interactions adequately; thus, the dimer structures optimized in [30] cannot be considered reliable.

A free optimization of structure with B97-D (Figs. 2a and b) predicted the shifted face to face configuration to be the most stable. Whereas, in the B3LYP optimized structure, as shown in Fig. 2d, the pentacene molecules do not overlap on top of each other, although the two molecules are separated in z-direction. This means in B3LYP the molecules repulse each other and the two separate apart, much like non-interacting molecules (binding energy being only -0.8 meV). Physically, face to face will yield greater interaction due to dispersion forces and hence be more stable. Therefore, the structure determined by B97-D calculations appears more realistic compared to B3LYP, which does not account for dispersion. In the following sections, therefore, all the calculations are done with B97-D and the dimer structure in Figs. 2a and b is described in greater detail.

In Fig. 2a it can be observed that there is an overlap between the two molecules in the x–y plane and they are separated in the z-direction by an average distance of 3.31 Å (Fig. 2b). The molecules do not lie completely flat in the x–y plane but are slightly

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