

Effects of Side-Chain and Electron Exchange Correlation on the Band Structure of Perylene Diimide Liquid Crystals: A Density Functional Study

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The structural and electronic properties of perylene diimide liquid crystal PPEEB are studied using *ab initio* methods based on the density functional theory (DFT). Using available experimental crystallographic data as a guide, we propose a detailed structural model for the packing of solid PPEEB. We find that due to the localized nature of the band edge wave function, theoretical approaches beyond the standard method, such as hybrid functional (PBE0), are required to correctly characterize the band structure of this material. Moreover, unlike previous assumptions, we observe the formation of hydrogen bonds between the side chains of different molecules, which leads to a dispersion of the energy levels. This result indicates that the side chains of the molecular crystal not only are responsible for its structural conformation but also can be used for tuning the electronic and optical properties of these materials.

Introduction

Organic semiconductors (OSs) are playing more important roles in the field of electronic materials.^{1–4} OSs are attractive mainly due to their low manufacturing costs, the relative facility of manufacturing them in the desired way, and the ability to deposit organic films in a variety of substrates.⁵ This class of material has been applied to a wide variety of devices, including displays based on organic light emitting diodes (OLEDs), organic field effect transistors, thin film organic transistors, and photovoltaic cells.^{6–15}

Liquid crystals based on perylene diimide derivatives consists of a class of organic semiconductors that have great potential for optoelectronic devices.^{16–19} They can be grown in a reasonably controlled way,²⁰ and their electronic properties have been studied both experimentally and theoretically.^{21–26} It is known, for example, that the choice of the side chain of perylene diimide can directly influence the packing conformation of these molecules and, consequently, the electronic properties of the material. Balakrishnan²³ has shown that, depending on the side-chain substituents, the materials grown have different morphologies and also different electronic structures. From a theoretical point of view, most previous works^{21,22,27,28} focus mainly on the central part of the perylene diimide (perylene core), that should be responsible for the π – π stacking and for the electronic structure of the material. It is usually assumed that both HOMO and LUMO levels are located in this part of the molecule. However, this type of study cannot describe the band structure of the material as a solid, with the corresponding dispersions, effective masses, and periodicity.

Perylene diimide is believed to be an n-type material, because its conductivity is due to electrons.^{11,29–33} For perylene diimide, the n-type doping can be achieved by substituting one C atom from the *side-chain* radical by an N atom.³⁴ However, as in

most organic semiconductors, its conductivity is low when compared to that of conventional semiconductors. Moreover, as in most organic semiconductors, perylene diimide has the doping asymmetry problem; that is, it cannot be doped p-type. Therefore, a good understanding about the basic physical and chemical properties of perylene diimide is very important in order to overcome these difficulties and make perylene diimide an excellent electronic material.

In this paper we have performed a theoretical study of perylene diimide in its solid state form. As far as we know, this is the first time that its crystal structure, as well as its electronic band structure has been calculated in its bulk form instead of as an isolated molecule. There are several different materials that can be constructed based on perylene diimides, where the basic difference is related to the radical, or side chain, that is attached to each of its N atoms.^{35,36} In this work, we will focus on perylene diimide PPEEB, that is shown in Figure 1. This material is a highly ordered organic semiconductor, and its structural properties have been investigated previously by X-ray diffraction,²⁰ which can provide comparison to our calculated structural properties.

Methodology

Most of the previous calculations for isolated molecules used quantum chemistry methods with localized basis sets. There are also calculations that use parametrized potentials in order to get the structural properties of these molecules.³⁷ This kind of calculation is usually done when one wants to understand the structural conformation between molecules, such as in solvents or solutions. However, it is already well established for liquids that, in order to get a good understanding of its collective properties, one should simulate a real liquid and not try to extrapolate the properties of an isolated molecule to a liquid.³⁸ Our objective in this work is to study a real molecular solid and obtain information about its structural and electronic (band structure) properties. Therefore, we use *ab initio*, parameter free, band structure methods that include periodic boundary conditions in all directions. This will provide a good description of

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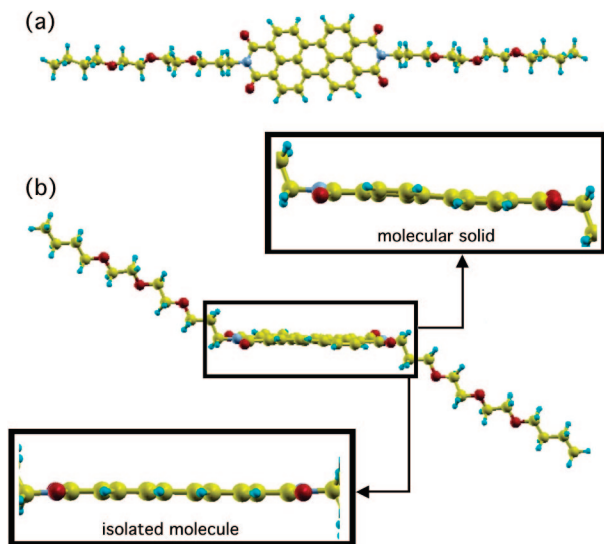


Figure 1. Ball and stick model of perylene diimide. In parts a and b, we show, respectively, top and side views for the structure of the molecule. The insets show structural differences for the perylene core in the isolated molecule and in the molecular solid.

the interaction between neighboring molecules and give us information about the anisotropy of the properties of this molecular solid.

To test the accuracy at different levels of approximation, we have used several implementations of density functional theory (DFT).^{39,40} The local density approximation (LDA) calculations are carried out using the localized basis SIESTA code,⁴¹ which employs the norm-conserving Troullier–Martins pseudopotentials⁴² in a fully separable Kleinman–Bylander⁴³ form. We also used the generalized gradient approximation (GGA) of Perdew, Burke, and Erzenhof (PBE), as implemented in the plane-wave basis set code (VASP).⁴⁴

It is well-known that standard DFT-based methods have limitations to treat organic materials.²¹ As the wave functions of organic materials are usually very localized, the effect of electronic self-interaction becomes important, and a self-interaction correction (SIC) is sometimes necessary to correctly predict their properties.⁴⁵ In order to avoid the self-interaction errors, we used an implementation of the SIC in the SIESTA code,⁴⁶ combined with the LDA. Additionally, we also used a hybrid-functional approach in the VASP code, where part of the exchange-correlation energy is taken from PBE and part from a Hartree–Fock functional.⁴⁷

In all cases, the total energy calculations are made in the reciprocal space in order to take advantage of the periodicity of the system.⁴⁸ We have used eight special k -points for the integration of the charge density in the reciprocal space. This is sufficient for this system because we have a large unit cell and the interaction between neighboring molecules is expected to be weak. The Hellman–Feynman forces in each atom were relaxed until the force in each Cartesian direction was smaller than 0.005 eV/Å.

Structural Properties

Experimental evidence indicates that the Bravais lattice of solid PPEEB is triclinic, but the available data is not enough to precisely describe the position of each atom in the unit cell nor the exact direction of each lattice vector. To simulate this material, we have used the available experimental crystallographic data as a guide in constructing the crystal structures.²⁰

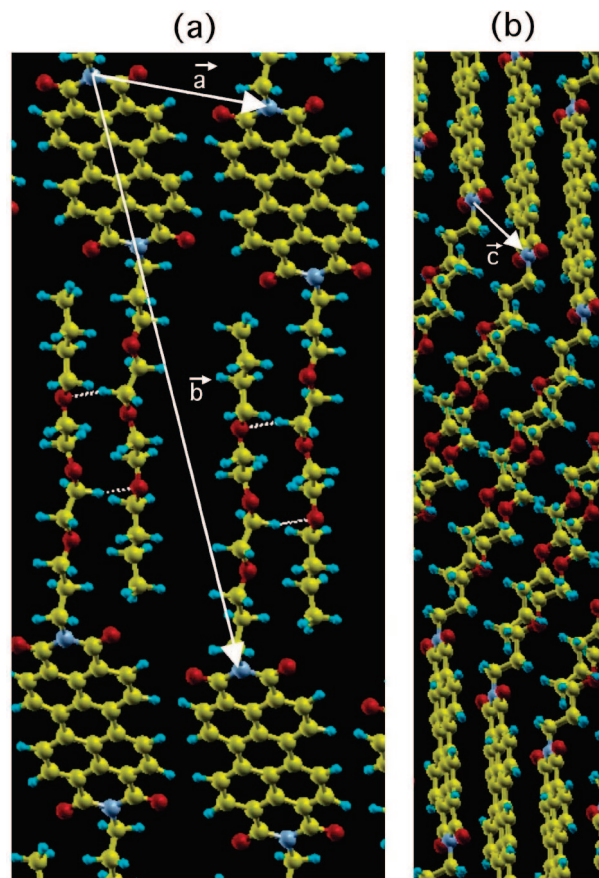


Figure 2. Lattice vector of the perylene diimide solid. Parts a and b show top (along the \vec{c} vector) and side (along the \vec{a} vector) views of the solid, respectively. Hydrogen bonds between side chains are identified by dashed lines.

This information is mainly related to the packing of the perylene cores, that are offset longitudinally by 3.1 Å and laterally by 0.8 Å. It also provided the π – π stacking distance, that is equal to 3.4 Å. Experimentally, it is also determined that the volume occupied by each molecule is about 1040 Å³.

For comparison and obtaining the relaxed coordinates of each atom in the molecular solid, we first calculated the isolated PPEEB and minimized the quantum mechanical forces in all atoms. To simulate the isolated PPEEB, we put it in a large periodic box, where each molecule is separated by a large vacuum region to avoid the interaction between the supercell images. This structure was then used as a motif to construct the molecular solid, imposing the appropriate periodic boundary conditions. Our proposed Bravais lattice is triclinic, as obtained experimentally, and the lattice vectors are

$$\begin{aligned}\vec{a} &= 8.78\hat{x} + 1.7\hat{z} \\ \vec{b} &= 4.39\hat{x} + 36.4\hat{y} \\ \vec{c} &= 0.8\hat{x} + 3.1\hat{y} + 3.4\hat{z}\end{aligned}\quad (1)$$

A ball and stick model of this structure, with the lattice vectors, is shown in Figure 2. The \vec{c} vector is entirely determined by the experiment. In our model, the perylene core is in the xy plane. The \hat{z} component of the \vec{a} vector is half the \hat{z} component of the \vec{c} vector. This means that the laterally neighboring molecules will not be in the same plane as the original one. We also propose that the \hat{x} component of the \vec{b} vector is half the value of the \hat{x} component of the \vec{a} vector. This is done in order for the neighboring molecules to be interdigitated. The

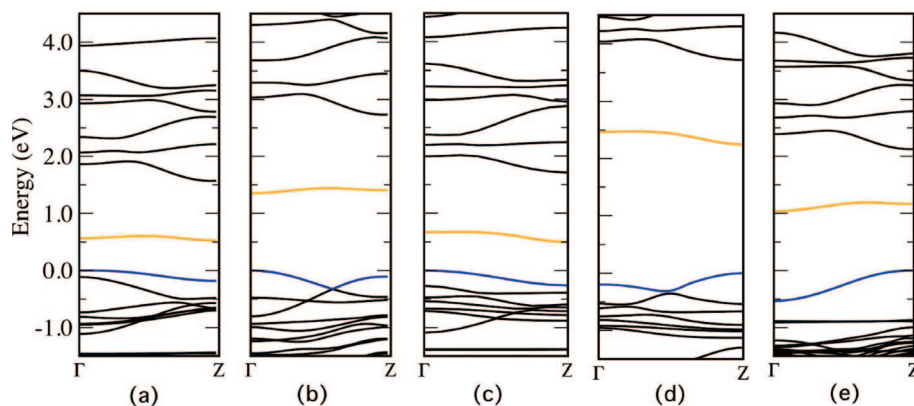


Figure 3. Band structure of solid perylene diimide in the direction of the reciprocal lattice vector Z , that is along the π - π stacking. The bands in blue (dark gray) are the highest energy occupied bands, and the bands in orange (light gray) are related to the lowest unoccupied band. The zero of the energy is at the valence band maximum. Part a is for the pure LDA calculation, part b is for LDA-SIC, part c is PBE, part d is for PBE0 (hybrid exchange), and part e is the LDA result when there are no oxygen atoms at the side chains.

missing components are then adjusted in order to get a volume near the experimental one. The lattice vectors shown in eq 1 lead to a volume of 1060 \AA^3 , that is near the experimental one (1040 \AA^3).

As can be seen in Figure 1, the atoms in the side chains are not as ordered as one could expect. This happens because of the presence of oxygen atoms in the side chains, which leads to the strong interactions between the O atoms and the neighboring H atoms, forming hydrogen bonds. The distortion of the molecule maximizes the strength of the hydrogen bonds between adjacent molecules. We have done some calculations for a similar molecule, but without oxygen atoms in the side chain. For these cases, as expected, the distortion does not appear, and the bond angles and distances are all uniform. We also observed that the perylene diimide core is slightly distorted, as shown in Figure 1b (the isolated molecule presents a planar core). The isolated molecule has a higher symmetry than the one in the molecular solid. This distortion is related to the atoms in the borderline of the core.

The hydrogen bonds are indicated by dotted lines in Figure 2a. The last oxygen atom in the chain makes a hydrogen bond with the other molecule with a distance of 2.16 \AA . Experimental evidence shows that hydrogen bonds induce changes in the molecule conformation.^{49,50} These results are clear evidence that, besides the interaction due to the π - π stacking of the perylene cores, the interaction between side chains is also important to understand the structure of the molecules. As will be shown later, these hydrogen bonds are also important to understand the electronic structure of this material.

At this point it is also important to present a discussion regarding the applicability of DFT to treat the weak interactions between PPEEB molecules. It is known that standard DFT functionals are not good to treat such systems.⁵¹ The bonding distance is usually very different than what is observed experimentally. In our case, this should not be a problem, since we are not minimizing the distance between the molecules. In all our calculations, we keep the lattice vectors fixed. As the change in the potential due to the inclusion of van der Waals interactions is usually very small, acting basically on the structural properties of the system, the inclusion of weak interactions in our functionals will not change the electronic properties of our system, since all the atoms are always kept in the same positions.

Electronic Properties

The electronic properties of the isolated perylene core have been reported by Kazmaier and Hoffmann.²² Based on the

isolated perylene core results and the transversal and longitudinal displacement in the staking of the perylene cores in the molecular crystal, the authors made some general arguments for several perylene derivatives. However, this simplistic model is based on the assumption that the side chains in the molecular crystal do not affect much of its band structure; for example, it assumes that both the HOMO and LUMO of this material are localized in the perylene core, while the side chains should be only important for the structural conformation of the material.²²

To obtain a deep understanding of the properties of PPEEB, we calculate the band structure of PPEEB for the crystal structure discussed above using different levels of optimization for DFT.²¹ In Figure 3 we show the band structure for PPEEB along the reciprocal lattice vectors Z , that goes along the direction of the π - π stacking. The bands along the other directions are basically dispersionless and are not shown here. This is typical of molecular semiconductors where the interaction between different molecules is small. On the other hand, in the Z direction we can observe some dispersion of the bands, showing a stronger interaction between neighboring molecules. In Figure 3a we used the standard LDA method. The valence band maximum (VBM), or HOMO,⁵² is at the Γ point, and the wave function related to this level is localized mainly in the side chains. The conduction band minimum (CBM), or LUMO, is at the Z point, and its wave function has mainly core character. The character of the VBM and CBM is shown in Figure 4. The shape of the CBM wave function (Figure 4b) is very similar to that reported for the perylene core.²² The VBM, on the other hand, is localized in the side chain, centered around the oxygen atoms. This contradicts previous expectations. Looking for lower energy bands, we observe a corelike level located at VBM-6 ($\sim -1.2 \text{ eV}$), at the Γ point. Therefore, a question arises from the LDA calculation: is the discrepancy of the order of bands caused by LDA error?

In order to analyze the origin of the localization issue, we repeated our band structure calculations by including the SIC. The molecular geometries in this case are kept similar to the LDA calculations.⁵³ The resulting band structure of our SIC calculations is shown in Figure 3b. We observe that the dispersion of the empty levels is very similar to the LDA results. This is because self-interaction error only occurs to filled levels, and so does the correction. The filled levels go down in energy, and this effect is larger for the more localized states, i.e., the states related to the side chains. With the SIC, the calculated band gap is closer to the experimental value of 2.3 eV .⁷ We also see a crossing between the original LDA VBM and the

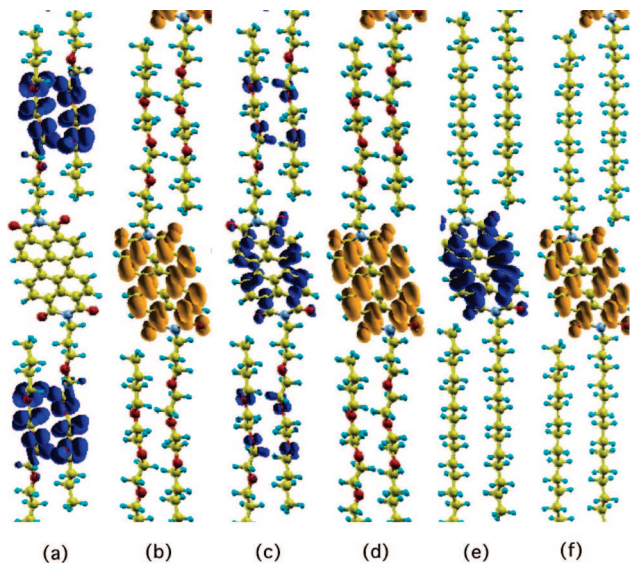


Figure 4. Localization of the VBM (blue) and CBM (orange) levels of PPEEB. Parts a and b are related to the LDA calculation. In parts c and d we use LDA-SIC. Parts e and f represent the VBM and CBM for the molecule without oxygen atoms in the side chains.

band that is localized in the core, i.e., the band whose energy increases as we go from the Γ point to the Z point. Although now there is a larger core character on the higher energy occupied levels, the VBM at Γ is still localized at the side chains, while the highest occupied orbital at Z has core character.

The charge densities for the VBM and CBM for the SIC calculations are shown in parts c and d, respectively, of Figure 4. Here, we plot the charge density at the top of the valence band and the bottom of the conduction band from Γ to Z. As can be seen, even with the SIC, we still have some side-chain character on the VBM. The dispersion observed in the VBM for the LDA and SIC-LDA calculations is mainly due to the hydrogen bonds formed by adjacent side chains. As the distance between side chains is smaller in the \vec{c} direction, this band only has dispersion along this lattice vector. This result shows that, besides having interesting transport and electronic properties on the core and along the stacking direction, the side chains also have important roles in determining these physical properties.

As discussed before, the bands at the valence band edge that are localized in the side chains are mainly derived from the oxygen atoms in the side chains. In Figure 3e we show the band structure for a perylene diimide to be very similar to PPEEB, but in which the oxygen atoms in the side chains are substituted by CH_2 . In this case, the side chain derived bands near the band gap disappear. It is now only possible to observe a band localized in the core region, which increases in energy when going from the Γ point to the Z point. Both VBM and CBM wave functions are now very similar to what is expected for the pure perylene core, as shown in Figure 4e and f.

Modern electronic structure calculations for solids are now using hybrid functionals to treat organic materials and localized systems. For perylene diimide PPEEB, we have also performed PBE0 hybrid functional calculations using the VASP code. The PBE0 is a mixture of the GGA-PBE and Hartree–Fock density functionals. For the pure GGA-PBE calculations, shown in Figure 3c, the band structure is very similar to the LDA calculations. The VBM is incorrectly localized at the side chains. The band gap is basically the same as the LDA, and we observe a band, at lower energies, that is related to the perylene core. Figure 3d shows the PBE0 results. The band gap within this

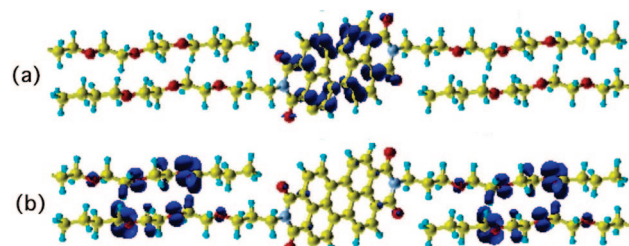


Figure 5. Partial charge density calculated with a hybrid functional (PBE0). Part a is the highest occupied orbital at the Z k-point, and part b is the highest occupied orbital at the Γ point.

correction is much larger than the standard PBE, with a new band gap of 2.3 eV, very close to experimental value. The dispersion of the bands is very similar to the PBE. However, contrary to the SIC calculation, the VBM is now located at the Z point. The highest occupied orbital at Γ is ~ 0.2 eV lower in energy.

In Figure 5 we plot the wave function of the highest occupied orbitals at both the Z and the Γ points. The VBM (at the Z point), shown in Figure 5a, is now localized at the perylene core, exactly as expected in previous studies about this kind of molecules. The highest occupied orbital at Γ , shown in Figure 5b has basically side-chain character, and is similar to the VBM obtained from LDA and PBE calculations.

The results presented here clearly show that, in order to correctly describe organic materials, one should use approaches that go beyond standard DFT. The PBE0 approach was shown to be better than a simple self-interaction corrected calculation. Moreover, in all our calculations, we find that there is a large dispersion of the levels around the VBM. These band dispersions are responsible for the good electronic and optical properties of this material. The dispersion also occurs to levels localized in the side chains, showing that they can also be important for designing functional materials.

Conclusions

In conclusion, we have carefully analyzed the structural and electronic properties of a perylene diimide liquid crystal, more explicitly PPEEB. Based on crystallographic data on this material, we built a structural model for it and completely described its lattice vectors and coordinates. According to our model, and also in agreement with experimental observations, the molecules are interdigitated, as shown in Figure 2. After optimizing the structure of the molecules, we observe the formation of hydrogen bonds between the side chains of different molecules. These hydrogen bonds lead to a distortion of the side chains, reducing the symmetry of the molecule. Owing to these hydrogen bonds, the binding between different molecules is expected to be stronger than the simple packing of the perylene cores.

Our calculated results for the electronic structure of the perylene diimide solid using the standard LDA and GGA show that the VBM of the material is localized in the perylene side chains, instead of the perylene core. This is not expected in previous theoretical calculations. We find that this occurs due to the strongly localized nature of the side-chain related levels. We have tested two different corrections to standard DFT, in order to obtain more accurate results. The use of the SIC lead to improved results; that is, the character of the VBM started to shift to the perylene core. We also tested a hybrid functional (PBE0). Using this functional, we observed a larger correction to the GGA calculations: the VBM became completely localized

in the perylene core, in agreement with previous calculations. This shows that hybrid functionals are indeed important in order to correctly describe localized states in organic materials.

The band structure of solid PPEEB has a large dispersion in the direction of the packing of the perylene cores. This is due to the van der Waals interaction between the cores and is what makes PPEEB an interesting electronic material. We also observed a dispersion in the levels related to the side chains. This dispersion occurs due to the formation of the hydrogen bonds between different side chains. The dispersion in these levels indicates that the side-chain radicals also could be used for tuning the electronic properties of this material and are not only important to set the structural conformation of the material.

It is also important to observe that, to have a correct theoretical description of organic solids, it is important to have a complete crystallographic characterization of the material. With this data, theorists can treat it as a real solid instead of making assumptions by treating it as isolated molecules or molecular clusters. To facilitate this, extended works on the crystallographic description of organic semiconductors are called for.

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