Geometric and Electronic Structures of Acene Crystals: 
A van der Waals Density Functional Theory Study

Ryota MIYAZAKI And Ikutaro HAMADA*

Department of Precision Science and Technology, Graduate School of Engineering, Osaka University, 2-1 Yamada-Oka, Suita, Osaka 565-0871
*e-mail: ihamada@prec.eng.osaka-u.ac.jp

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We demonstrate that accurate prediction of the crystal structures of anthracene and its derivatives is possible with the van der Waals density functional. Based on the calculated crystal structures, we investigate their electronic structures and discuss the correlation between crystal structure/molecular configuration and the electronic structure, in particular, the dispersion of the bands composed of the highest occupied molecular orbitals, which are important to discuss the charge carrier transport property.

Keywords: Organic semiconductor, Molecular crystal, Acene, Density functional theory, Van der Waals density functional

1 Introduction

Organic semiconductors have attracted considerable attention as an alternative to the conventional silicon based electronic materials, owing to their chemical diversity, flexibility, and the low cost for processing, and electronic devices such as organic light emitting diodes and organic photovoltaic cells have been developed. One of the prerequisites to commercialize these organic devices is to develop materials with high mobility, and it is desirable to have a strategy to design and engineer the organic semiconductors tailored for specific purposes. In this regard, density functional theory (DFT) has become a powerful tool to understand and predict the materials properties. However, it is well known that conventional semilocal approximation such as local density and generalized gradient approximations are less accurate for weak interaction, such as van der Waals (vdW) interaction, and the precise description of organic semiconductors, in which organic molecules are bonded via the vdW interaction, is challenging for semilocal DFT. Recent development of the van der Waals density functional (vdW-DF) [1] and its offsprings enables one to study the structural and electronic properties of organic semiconductors very accurately [2]. Here, we focus on anthracene and its derivatives, and investigated the crystal and electronic structures by using vdW-DF.

2 Method

The calculations were based on the projector augmented wave (PAW) method [3] as implemented in the Quantum-ESPRESSO package [4]. We used the PAW potentials adopted from the pslibrary-1.0.0 [5]. We used rev-vdW-DF2 [6], one of the vdW-DF functionals, for the exchange-correlation functional. Wave functions and augmentation charge were expanded in terms of the plane-wave basis set with the kinetic energy cutoffs of 80 Ry and 800 Ry, respectively. Brillouin zone sampling was performed by using a Monkhorst-Pack $4 \times 4 \times 4$ k-point set. All the degrees of freedom were relaxed until the forces acting on atoms became less than $2 \times 10^{-4}$ Ry/Bohr. We consider the crystals of anthracene and its derivatives as shown in Figure 1, namely, 9-methylanthracene, 9-n-propylanthracene, 9-i-propylanthracene, 9-pentylanthracene, and 9,10-dimethylanthracene.
3 Results and Discussion

To assess the accuracy of rev-vdW-dF2 to describe the geometry and energetics of the organic semiconductor crystal, we first optimized the structure of anthracene in the \( P2_1/a \) symmetry by using different vdW-DF functionals as shown in Table 1. Overall, the errors for the lattice parameters obtained by using the vdW-DFs are small, in particular, those by rev-vdW-dF2 are exceedingly small, suggesting that it gives an accurate description of the crystal structures of anthracene and its derivatives.

We then performed the crystal structural optimization of anthracene derivatives using rev-vdW-DF2. As shown in Figure 2, we found that the mean error for the lattice parameter ranges from 0.1 to 2.8%, and mean absolute error is less than 1.1% (the mean error for the volume is 1.9%), demonstrating that the functional is indeed accurate for the description of the crystals of anthracene derivatives.

Figure 3 displays calculated band structures of anthracene and 9-methylanthracene. The estimated band widths are 0.38 eV and 0.40 eV for the former and the latter, respectively. The origin of the larger band width is the larger overlap of the molecular orbitals due to its \( \pi \)-stacking structure. For other crystals, we found the much smaller band widths (0.12 eV for 9-i-propylanthracene, for instance), because of the larger molecular spacing and small orbital overlap. The results suggest that the crystal structure has a significant impact on the band structure, in particular, molecular arrangement and spacing.

4 Summary

We have shown that the rev-vdW-DF2 functional is able to describe the crystal structures of anthracene and its derivatives, and that there is a clear correlation between molecular configuration and electronic structure. Further systematic study on the organic semiconductor will provide more insight into the structure-electronic property relation, thereby leading to a rational design principle of organic semiconductor materials with desired properties.
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