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Structure and electronic properties of perylene and coronene under pressure: First-principles calculations

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ABSTRACT

The structural and electronic properties of crystalline perylene and coronene have been investigated within the framework of density functional theory including van der Waals interactions. The investigation of β, γ and dimeric form of polycyclic aromatic hydrocarbons allowed for study of relationship between molecular arrangement and band structure. The computed lattice parameters have good agreement with experimental data. I study on the structural and electronic properties of the crystals under the hydrostatic pressure of 0–20 GPa. The predicted results are compared with each other. It has been established that pressure has different effect on γ- and β-form of the coronene. The values of the bulk moduli of crystals are in the range 9–11 GPa. The all crystals have indirect band gap.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAH) have a wide field of application [1–9]. These compounds are very interesting in terms of their potential to create optoelectronic devices such as, e.g., organic light emitting diodes or organic photo-voltaic cells [1–4]. They are also an excellent model systems to study the fundamental properties of organic semiconductors. These reasons maintain stable interest to these systems.

Desiraju and Gavezzotti suggested classifying hydrocarbons using the four types of molecular packing [10]. In this work we use the designation offered by them. Naphthalene is a typical example of the α-form. The structural data of the γ-coronene [11] and dimeric (or sandwich herringbone, SHB) form of perylene [12] have been known far. The β-polymorph of coronene is stable, its structure is preserved under certain conditions (ambient conditions and zero magnetic field) [13]. The fact that molecular crystal has several forms allow for investigation of molecular packing influence on the properties of the crystal. The objective of this work is to study different forms of PAH in order to learn both how hydrostatic pressure influence the molecules arrangement in a crystal and how it affects structural and electronic properties of the crystal.

As is known, van der Waals interaction plays the key role in forming molecular crystals. Dispersion interaction is caused by electronic *correlation*, which is not taken into account in standard approximations of density functional theory (DFT). The schemes have been developed where intermolecular interaction is included in DFT [14–16]. There are detailed reviews describing this problem [17–20]. It has earlier been shown that taking into account of a dispersion term allows for correct description of crystal behavior both in ambient conditions and under pressure [21–23].

Fedorov et al. studied electronic structure of γ-coronene [24] and dimeric form of perylene [25] at the normal conditions. Potticary et al., having grown β-coronene, have made calculations of its band spectrum [13]. Chanyshev et al. have conducted experimental research of hydrostatic pressure (7–15 GPa) on PAH [8]. Thereby, the pressure effect on perylene and coronene electronic properties has not been studied.

At the normal conditions the coronene unit cell has the space group $P2_1/a$ (γ-form) [11], perylene (dimeric form) $-P2_1/c$ [12]. The β-coronene has the space group $P2_1/n$ [13]. Botoshansky et al. have determined the structure of γ-form perylene, which has the space group $P2_1/c$ [26]. The unit cells are shown in Fig. 1. The unit cells of β-coronene and γ-coronene are presented in Fig. 2. The perylene and coronene molecule in the crystal is presented in Fig. 3.

2. Computational details

A plane-wave pseudopotential approach within DFT was used to calculate total energy. The PWscf program [27], which is incorporated into Quantum ESPRESSO (QE) [28] suite of electronic structure programs with the functional of Perdew, Burke, and Ernzerhof (PBE) [29], was used to carry out the computations. The ultrasoft pseudopotentials of the Rabe-Rape-Kaxiras-Joannopoulos type

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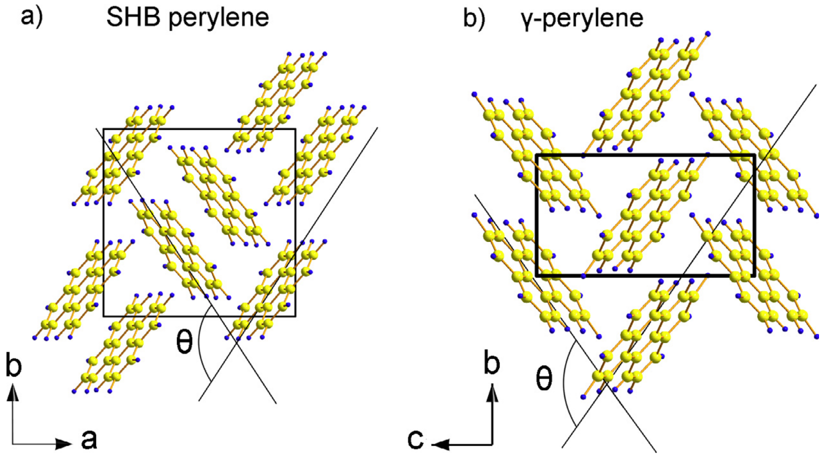

Fig. 1. The unit cell of SHB perylene (a) and γ-perylene (b).

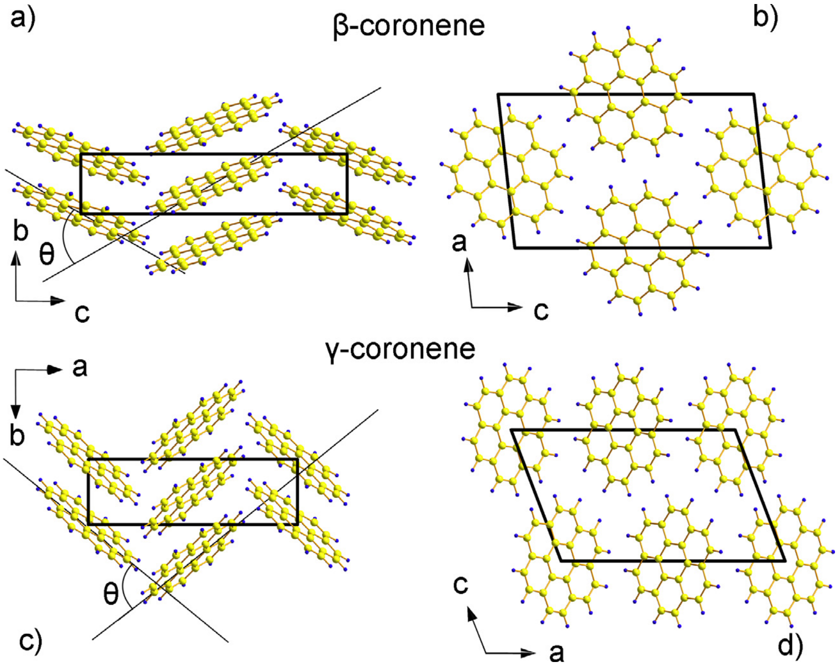

Fig. 2. The unit cell of β-coronene (a, b) and γ-coronene (c, d).

were used for calculations [28,30]. The crystal structures were optimized with the Broyden-Fletcher-Goldfarb-Shanno (BFGS) method [31]. Monkhorst–Pack scheme [32] was used for the Brillouin zone sampling. The kinetic energy cutoff and the **k**-points ensured the convergence of total energies. The energy cutoff equals 55 Ry. The k-point grid are $2 \times 2 \times 2$ (dimeric perylene), $2 \times 4 \times 2$ (γ-form perylene), $3 \times 6 \times 2$ (β-coronene), and $2 \times 4 \times 3$ (γ-coronene).

Geometry relaxation was completed when all components of all forces are smaller than 0.1 mRy (a.u.)$^{-1}$. As the starting point structural data [11–13,26] were used. Besides, the computations were carried out with the CRYSTAL14 [33], using the PBE0 hybrid functional [34]. All calculations were performed by using standard 6-31G* basis set [35]. Structural data, computed by QE, were used as the entry data. Other options for the computations were not changed.

DFT-D3(BJ) was used to take into account intermolecular interaction. The details of our calculations are in our earlier work [24,25]. This approach was applied by Potticary et al. both to study ubiquitous γ-herringbone structure and to study a new form of β-coronene [13]. The same scheme was used for study of hydrostatic pressure effect on structural and electronic properties of crystalline naphthalene (α-form) [22]. In this scheme the empirical potential was added to the exchange–correlation potential and the total energy is given by

$$E_{\text{DFT-D}} = E_{\text{KS-DFT}} + E_{\text{disp}} \qquad (1)$$

where $E_{\text{KS-DFT}}$ is the Kohn–Sham energy and E_{disp} is a dispersion correction [16].

The QE and CRYSTAL14 include the DFT-D2 scheme [36–38]. We performed computations within the DFT-D3(BJ) [39–43]. The dispersion energy is

$$E_{\text{disp}} = -\frac{1}{2}\sum_{A \neq B} s_6 \frac{C_6^{AB}}{R_{AB}^6 + [f(R_{AB}^0)]^6} + s_8 \frac{C_8^{AB}}{R_{AB}^8 + [f(R_{AB}^0)]^8}, \qquad (2)$$

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