

Hydrostatic pressure effects on structural and electronic properties of pentacene from first principles calculations

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Abstract. The structural and electronic properties of crystalline pentacene has been investigated within the framework of density functional theory including van der Waals interactions. The computed lattice parameters have good agreement with experimental data. We studied on the structural and electronic properties of the pentacene under the hydrostatic pressure of 0–10 GPa. The isothermal equations of state calculated from the results show good agreement with experiment in the pressure intervals studied. Using the Murnaghan equation of state it has been established that compression bulk modulus is $B_0=11.42$ GPa and it has good agreement with the experimental value. We have also calculated the quasiparticle band structure of pentacene with the G_0W_0 approximation.

Keywords: pentacene, density functional calculations, dispersion interaction, equation of state, quasiparticle band structure.

1. Introduction

Currently, oligoacenes are widely used for practical applications and due to their optical properties still have prospects for other practical applications. Pentacene is a typical representative of these compounds, besides, the first pentacene-based organic processor has recently been made. One of the most perspective trends of organic crystal applicability is the possibility to create new and simple semiconductor devices. Notable achievements have been made in this field and there are sufficient conditions for creating stable organic semiconductor transistor. The main advantage of organic semiconductors is that they are flexible and easy-to-manufacture, therefore, that makes it possible to create new pentacene –based electronic devices. Flexibility is one of the main advantages of organic semiconductors. For this reason it is interesting to investigate the effects of mechanical deformations on electronic properties. The perylene unit cell has the symmetry group $P\bar{1}$ under normal conditions [1]. The projection of the unit cell on the cb plane is shown in Fig. 1. The unit cell contains two molecules involved in van der Waals interactions. The pentacene molecule in the crystal is presented in figure 1.

2. Computational details

First-principles total energy calculations were carried out within density-functional theory with a plane-wave pseudopotential approach. The computations were performed with the Quantum ESPRESSO (QE) [2, 3] suite of electronic structure, using the Perdew–Burke–Ernzerhof (PBE) parametrization [4]. The cutoff energy of plane waves was set to 55 Ry. Brillouin zone sampling was



performed by using the Monkhorst–Pack scheme [5] with a k -point grid of $3 \times 2 \times 2$. The values of the kinetic energy cutoff and the k -point grid were determined to ensure the convergence of total energies. We used in our study the fully non-local exchange–correlation rev-vdW-DF2 [6, 7, 8]. Also, we used a London-type empirical correction for dispersion interactions DFT-D3(BJ) [9]. Structural data [1] were used as the initial geometry. Also, the calculations were performed with the CRYSTAL09 [10], using hybrid functional PBE0. In this case structural parameters, calculated using QE, were used as the input data. We have used the implementation of the G_0W_0 approximation [11, 12] provided by the code YAMBO [13]. The cutoff energy of plane waves was set to 65 Ry. The dielectric function is calculated using the plasmon-pole approximation. The GW dielectric matrix cutoff is 8 Ry. To obtain convergence, we used 400 unoccupied states.

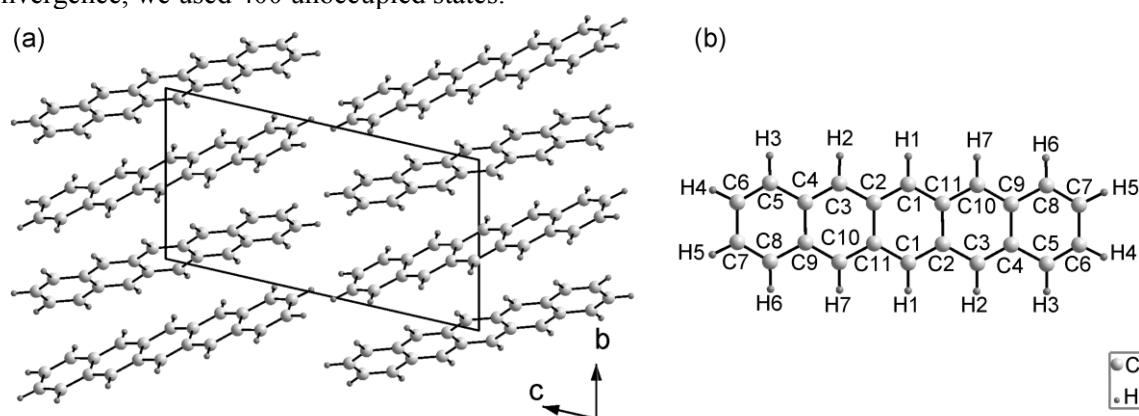


Figure 1. Crystal structure of pentacene viewed along a axis (a). The pentacene molecule in the crystal (b).

The main idea of the DFT-D algorithm consists in adding the empirical potential to the exchange–correlation potential. The total energy is given by

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

where $E_{\text{KS-DFT}}$ is the usual self-consistent Kohn–Sham energy as obtained from the chosen DF and E_{disp} is an empirical dispersion correction. The DFT-D2 scheme is included in the QE [2]. We carried out computations within the DFT-D3(BJ) [9].

3. Results and discussion

3.1. Equation of state

Our computed lattice parameters for the pentacene are given in table 1. Experimental values are also listed. The modern versions of the DFT-D and vdW-DF predict the lattice parameters that have good agreement with the experimental data.

Figure 2 shows the variation of the lattice parameters and unit cell volume for pentacene with pressure as predicted using DFT-D3(BJ). The obtained results were comparable to the experimental values [14]. There is good agreement between the computed and experimental values. As the computation was performed at $T = 0$ K, the $V(P)$ dependence should be below experimental data ($T=100$ K). Generally, DFT-D3(BJ) leads to good agreement with the experimental data. There is the difference between the experimental and theoretical data at high pressure. Similar results were observed for the values calculated using rev-vdW-DF2 and other schemes [15].

Pressure dependence on volume is usually written in the form of isothermal equation of state for solids. The parameters of this equation are V_0 - equilibrium volume, B_0 - isothermal bulk modulus and B'_0 - its pressure-derivative, defined at zero pressure. Two semi-empirical isothermal equation of state

(EOS) – Vinet, and Murnaghan – were used to analyze the compression curves for pentacene. These equations are as follows:

$$P(V) = \left(\frac{B_0}{B'_0}\right) \left(\left(\frac{V}{V_0}\right)^{-B'_0} - 1\right), \quad (2)$$

$$P(V) = 3B_0 \left(\frac{V}{V_0}\right)^{-\frac{2}{3}} \left(1 - \left(\frac{V}{V_0}\right)^{\frac{1}{3}}\right) \exp\left[\frac{3}{2}(B'_0 - 1)\left(1 - \left(\frac{V}{V_0}\right)^{\frac{1}{3}}\right)\right]. \quad (3)$$

Table 1. Computed and experimental lattice parameters for pentacene at ambient pressure.

	DFT-D3(BJ)	Rev-vdW-DF2	Exp. [1]
a , Å	6.243	6.228	6.266
b , Å	7.769	7.572	7.775
c , Å	14.432	14.331	14.53
α , °	76.269	77.384	76.475
β , °	88.414	88.285	87.682
γ , °	84.573	84.446	84.684
V_0 , Å ³	676.955	656.491	685.155

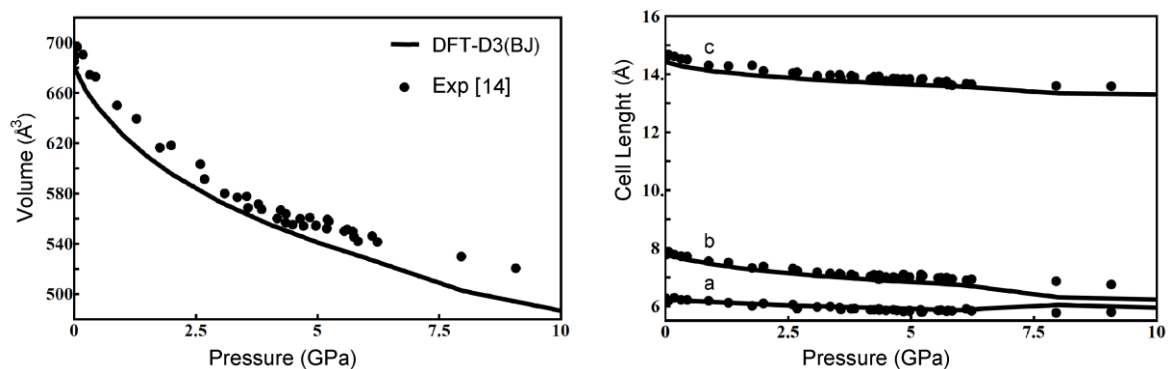


Figure 2. Unit cell dimensions as a function of pressure from DFT-D3(BJ) and experiment [14].

Table 2 shows parameter values which were fitted for the both isothermal equations of state. The computed bulk modulus and its pressure derivative have good agreement with the experimental values and computations of other authors. The values calculated using DFT-D3(BJ) have better agreement with the experimental data. Depending on the conditions of crystal growth, pentacene under normal conditions may be in two stable forms. There is only one phase at pressure 0.2 GPa and higher, which has been studied in present work. Thus, there are some problems in experimental definition of crystal volume under normal conditions, and this leads to scattering of parameter values of equations of state.

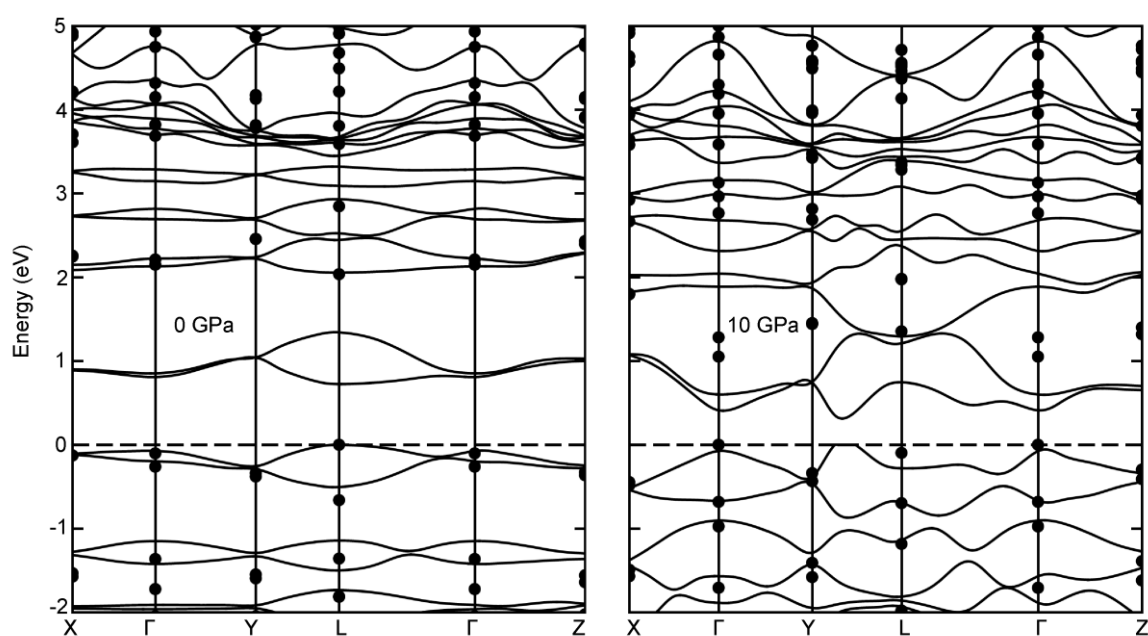
3.2. Band structures

The calculated band structure for crystalline pentacene is presented in figure 3. The reference point is the top of the valence band. The designation of points and choice of lines are in accordance with [16]. The values of band gaps (E_{gap}) are listed in table 3. At the ambient pressure the band gap $E_{\text{gap}} = 1.72$ eV (PBE0). We have also calculated the band structure of pentacene with the G_0W_0 approximation ($E_{\text{gap}} = 2.03$ eV). The top of the valence band and the minimum value of the conduction band is realized at the L point. Thus, the fundamental band gap is a direct gap.

Table 2. Comparison of bulk modulus (B_0) and its pressure-derivative (B'_0) determined from the EOS analyses of pentacene.

Method	$V_0(\text{\AA}^3)$	Murnaghan		Vinet	
		$B_0(\text{GPa})$	B'_0	$B_0(\text{GPa})$	B'_0
DFT-D3(BJ)	676.955	11.42	5.21	10.54	6.70
Rev-vdW-DF2	655.679	14.11	5.20	13.22	6.54
Exp. [14]	696.0 \pm 3.7	9.6 \pm 1.0	6.4 \pm 0.5	-	-

The band structure presents weakly dispersive energy levels originated in molecular orbitals. Figure 3 shows the band structures under hydrostatic pressure of 10 GPa. The pressure increases band dispersion and decreases band gap. Lower unoccupied bands are particularly strongly split. The calculated quasiparticle band gap at 10 GPa equal 1.05 eV. This behaviour of the band gap is confirmed by both experimental [17] and theoretical data [15].

**Figure 3.** Band structure $E(\mathbf{k})$ of crystalline pentacene within GGA/PBE (solid lines) and G_0W_0 approximation (points) at ambient and hydrostatic pressure of 10 GPa. The top of the valence band indicated by the Fermi level (dashed line).**Table 3.** The band gaps (eV) of pentacene obtained using various of the exchange–correlation functionals.

G_0W_0	PBE	PBE0	PBE[15]	HSE03[15]	PBE0[15]
2.03	0.54	1.72	0.858	1.431	2.031

One of the important characteristics of chemical bond is the distance between the atoms. The effect of pressure is shown in reduction of the distance between the molecules, however, the changes in bond lengths within the molecule are much smaller. Mulliken population analysis has allowed us to determine the crystal atomic charges (table 4). Though in the presented schemes they do not have a clear physical sense, they allow establishing the atom charge change.

3.3. Electron densities

The electron densities were calculated with PBE0 hybrid density functional. The distribution of total and deformation electron densities (difference between total and superposition atomic electron densities) on the plane is presented in figure 4. Pentacene molecule in the crystal is not planar molecule. The positive values are marked by solid line, negative by dashed line, while the null contour is marked by a dotted line. The interval between the isolines equals $0.05 e \text{ \AA}^{-3}$. It has been established that when a chemical bond in the molecule is formed, the charge leakage occurs in the C–C bond line as well as in the C–H antibonding regions. The distribution of deformation density is typical for sp^2 hybridization. The peaks of electron density between carbon atoms are stretched perpendicular to the C–C bond lines. The nonhybridized p-orbitals are perpendicular to the molecule plane and responsible for the so-called p-stacking. The pressure of 10 GPa causes a slight change for the distribution of deformation density, atomic charges and interatomic distance. Thus, the pressure of 10 GPa has significant impact on the energy bands, which is caused by the convergence of molecules, but the molecules remain virtually undeformed.

Table 4. Atomic charges calculated according to Mulliken scheme for the pentacene ($|e|$).

Atom	Pressure, GPa		
	0	5	10
C(1)	-0.171	-0.175	-0.184
C(2)	-0.011	-0.021	-0.009
C(3)	-0.169	-0.175	-0.186
C(4)	-0.012	-0.025	-0.022
C(5)	-0.163	-0.164	-0.167
C(6)	-0.188	-0.204	-0.206
C(7)	-0.187	-0.197	-0.193
C(8)	-0.145	-0.139	-0.148
C(9)	-0.019	-0.028	-0.014
C(10)	-0.168	-0.171	-0.176
C(11)	-0.012	-0.019	-0.011
H(1)	0.179	0.191	0.192
H(2)	0.179	0.190	0.191
H(3)	0.177	0.182	0.181
H(4)	0.171	0.177	0.178
H(5)	0.171	0.179	0.179
H(6)	0.186	0.198	0.197
H(7)	0.179	0.190	0.192

4. Conclusions

According to the *ab initio* calculations, crystalline pentacene has been studied. The relaxed lattice parameters, band structure, distribution of electronic densities, bulk modulus and its pressure-derivative of the pentacene were computed in the framework of DFT. The determined dependencies of the values of lattice parameters on pressure are in good agreement with experimental data. It is established that within DFT-D3(BJ) bulk modulus is $B_0=11.42$ GPa, that has good agreement with experimental data. The quasiparticle band gap at ambient pressure and 10 GPa is computed with the G_0W_0 approximation and equals 2.03 and 1.05 eV, respectively. The pressure leads to the decrease in the distance between the crystal molecules and increases overlapping of their molecular orbitals.

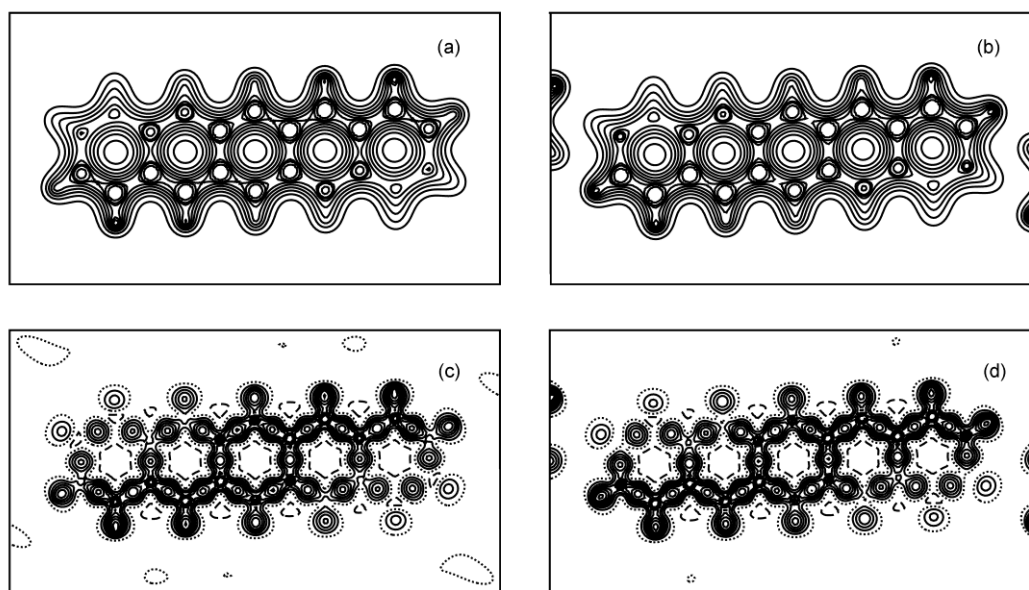


Figure 4. Total electron density map of crystalline pentacene at the ambient (a) and hydrostatic pressure of 10 GPa (b) (in logarithmic scale). Deformation electron density map at the ambient (c) and hydrostatic pressure of 10 GPa (d).

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