

Theoretical investigation of some specific features of the electronic structure and optical properties of Benzoic Acid 2-Amino-4,6-Dimethylpyrimidine (1:1) co-crystals



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ABSTRACT

Benzoic Acid 2-Amino-4,6-Dimethylpyrimidine (1:1) co-crystal have been comprehensively investigated by means of density functional theory. The electronic band structure show that the conduction band minimum (CBM) and the valence band maximum (VBM) are situated at the center of the Brillouin zone resulting in a direct band gap. Calculation were performed using the full potential linear augmented plane wave plus local orbitals (FP-LAPW + *lo*) method in a scalar relativistic version as embodied in the WIEN2k code within the local density approximation (LDA), gradient approximation (PBE-GGA), Engel-Vosko generalized gradient approximation (EV-GGA) and the recently modified Becke-Johnson potential (*mBJ*). The calculated density of states explore that the VBM is mainly formed by N-p state while the CBM is formed by the strongly hybridized N-p and C-p states. There exists a strong hybridizations between C-s/p, H-s, N-s/p and O-s/p states above and below the Fermi level (E_F). Which may led to covalent bonding between the states. To visualizes the charge transfer and the chemical bonding characters, the valence band's electronic charge density distribution were extensively investigated. The optical properties helps to get deep insight into the electronic structure therefore, details analysis to the calculated optical properties were performed. The optical properties confirm the existence of the band gap and the lossless regions.

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1. Introduction

Several experimental and theoretical research work on co-crystals is achieved due to their specific structure. It is found that the co-crystals are promising candidates for many applications due to their novel chemical and physical properties [1]. Benzoic Acid 2-Amino-4,6-Dimethylpyrimidine (1:1) is one of the co-crystals, in which the hydrogen bond interactions play an important role in composing the structure, etc. [2,3]. Therefore, it is necessary to investigate the hydrogen-bonded networks which are linked with mobile protons. From the hydrogen-bonded networks of the Benzoic Acid 2-Amino-4,6-Dimethylpyrimidine one can deduce very important information since the hydrogen-bonded networks are essential elements for the supermolecules in the biology systems and chemistry. Latajka et al. [4] theoretically investigated the hydrogen-bonded molecular complexes, they investigated the polarizability and first hyperpolarizability values

of the hydrogen-bonded complexes formed by nitrosubstituted phenols with pyridine and 4-aminopyridine have been calculated using PM3 and *ab initio* (STO-3G) methods. Li et al. [1] have prepared the Benzoic Acid 2-Amino-4,6-Dimethylpyrimidine and analysis the single crystal X-ray diffraction data and the experimental optical properties. In addition they perform a density functional calculations using CASTEP code within generalized gradient approximation (PBE-GGA).

Due to a lack of electronic structural information of Benzoic Acid 2-Amino-4,6-Dimethylpyrimidine (1:1) co-crystal, further insight into the electronic structure can be obtained from the optical properties. We would like to mention that we are not aware of calculations or experimental data for the electronic structure and linear optical susceptibilities of Benzoic Acid 2-Amino-4,6-Dimethylpyrimidine (1:1) co-crystal. Therefore we thought it worthwhile to calculate some specific features of the electronic structure and the optical properties. Calculations are performed using full potential method within four types of exchange correlation potentials in order to ascertain the effect of exchange correlation on the electronic structure and the optical

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properties. First-principles calculation is one strong and useful tool to predict the crystal structure and its properties related to the electron configuration of a material before its synthesis [5–8].

2. Details of calculations

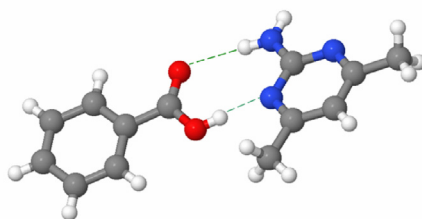
Benzoic Acid 2-Amino-4,6-Dimethylpyrimidine (1:1) co-crystal ($C_{13}H_{15}N_3O_2$) have been synthesized by Li et al. [1] from benzoic acid and 4,6-Dimethylpyrimidine in 1:1 molar ratio (see Fig. 1a). $C_{13}H_{15}N_3O_2$ crystallizes in a monoclinic structure, space group, $P2_1/c$ with lattice constants $a = 6.7019(9) \text{ \AA}$, $b = 7.647(1) \text{ \AA}$ and $c = 25.285(3) \text{ \AA}$, $\beta = 91.36(2)^\circ$, $V = 1295.4(3) \text{ \AA}^3$, $Z = 4$ [1]. The 2-Amino-4,6-Dimethylpyrimidine molecule linked to benzoic acid molecule by two hydrogen bonds [$O1 - H1 \cdots N1$, $H \cdots N = 1.819 \text{ \AA}$; $N3 - H3A \cdots O2$, $H \cdots O = 2.157 \text{ \AA}$] to form the asymmetric unit as shown in Fig. 1(a). Fig. 1(b) shows the discreet dimers are connected together in 1D-zigzag pattern. The calculation were performed using the density functional theory (DFT) within the full potential linear augmented plane wave plus local orbitals (FP-LAPW + lo) method in a scalar relativistic version as embodied in the WIEN2k code [9]. The exchange-correlation (XC) potential was solved using four different possible approximations. The XC were described by the local density approximation (LDA) [10] and gradient approximation (PBE-GGA) [11], which is based on exchange-correlation energy optimization to calculate the total energy. In addition, we have used Engel–Vosko generalized gradient approximation (EV-GGA) [12] and the recently modified Becke–Johnson potential (mBJ) [13] which optimizes the corresponding potential for electronic band structure calculations. The atomic positions were optimized by minimization of the forces acting on each atom. The optimization were achieved within PBE-GGA. The structure is fully relaxed until the forces on the atoms reach values less than (1 mRy/a.u.). The optimized atomic positions along with those obtained from XRD are listed in Table S1 (supplementary materials), good agreement was found. Once the

forces are minimized in this construction one can then find the self-consistent density at these positions by turning off the relaxations and driving the system to self-consistency. From the obtained relaxed geometry the electronic structure and the chemical bonding have been determined and various spectroscopic features can be simulated and compared with experimental data. The Kohn–Sham equations are solved using a basis of linear APW's. The potential and charge density in the muffin-tin (MT) spheres are expanded in spherical harmonics with $l_{\max} = 8$ and nonspherical components up to $l_{\max} = 6$. In the interstitial region the potential and the charge density are represented by Fourier series. Self-consistency is obtained using 300 \bar{k} points in the irreducible Brillouin zone (IBZ). We have calculated the electronic band structure, density of states, electronic charge density distribution and linear optical properties using 500 \bar{k} points in the IBZ. The self-consistent calculations are converged since the total energy of the system is stable within 0.00001 Ry.

3. Results and discussion

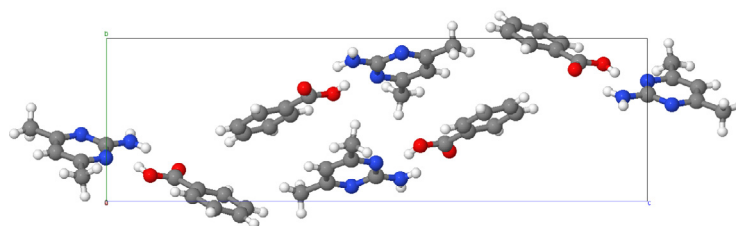
3.1. Electronic band structure and density of states

The electronic band structure of Benzoic Acid 2-Amino-4,6-Dimethylpyrimidine is plotted along the high symmetry points $\Gamma, Y, H, X, A, Z, \Gamma, X$ in the first Brillouin zone (Fig. 2). To investigate the influence of the exchange-correlation potential on the electronic band desparation, four types of exchange-correlation potentials are used to calculate the electronic band structure. In all cases the Fermi level is sited to be at 0.0 eV. It is clear that moving from LDA to PBE-GGA to EV-GGA cause to shift the conduction band minimum (CBM) toward the higher energies by around 0.1 eV. Whereas using mBJ cause to shift the CBM toward higher energies by around 1.0 eV with respect to the location of CBM obtained by LDA. Calculation show that the valence band maximum (VBM) and CBM are situated at center of the BZ. Therefore, the Benzoic



The 2-Amino-4,6-Dimethylpyrimidine molecule linked to benzoic acid molecule by two hydrogen bonds [$O1 - H1 \cdots N1$, $H \cdots N = 1.815 \text{ \AA}$; $N3 - H3A \cdots O2$, $H \cdots O = 2.149 \text{ \AA}$] to form the asymmetric unit.

(a) Asymmetric unit



(b)

Fig. 1. (a) the asymmetric unit, it shows the 2-Amino-4,6-Dimethylpyrimidine molecule linked to benzoic acid molecule by two hydrogen bonds [$O1 - H1 \cdots N1$, $H \cdots N = 1.815 \text{ \AA}$; $N3 - H3A \cdots O2$, $H \cdots O = 2.149 \text{ \AA}$] to form the asymmetric unit. (b) Fragment of the crystal structure of Benzoic Acid 2-Amino-4,6-Dimethylpyrimidine.

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