

Bis (3-methoxy-4-hydroxybenzaldehyde-2,4,6-trinitrophenol) organic cocrystal: Synthesis and physico-chemical properties*

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Abstract. A 3-methoxy-4-hydroxybenzaldehyde-2,4,6-trinitrophenol (mhba-tnp) cocrystal was grown by the slow evaporation solution growth technique using ethanol as a solvent. As-grown crystals were characterized by single crystal X-ray diffraction (XRD) study and crystallized with a centrosymmetric space group. Optical properties of the grown crystal have been studied by Ultraviolet-Visible (UV-Vis) absorption spectra in the range from 200 to 800 nm and the band gap energy of the crystal was obtained as 2.8 eV. Fourier transform infrared (FTIR) and micro Raman spectral analyses have been carried out to confirm the functional groups present in the title compound. Differential scanning calorimetry (DSC) and polarized light thermomicroscopy (PLTM) analyses were carried out to find the melting point. In addition, the optimized geometric parameters and the molecular orbitals were calculated using density functional theory (DFT) with the help of the Gaussian 03W software.

1 Introduction

Cocrystallization of organic molecules is a favourable crystal engineering technique for modifying the physical properties of materials compared to single-component crystals [1]. In many cocrystals, physical properties can be partially controlled by changing the constituting molecules as well as modifying the crystal structures. A cocrystal has different properties, such as solubility, melting point, crystallinity, hygroscopicity, physical and chemical stability with respect to the reagents or their mixtures, and this approach can be used to tailor the properties of an active pharmaceutical according to the bioavailability needs [2]. 3-methoxy-4-hydroxybenzaldehyde (mhba), also known as vanillin, is a trisubstituted benzene with $-\text{CHO}$, $-\text{OCH}_3$ and $-\text{OH}$ groups substituted at 1, 3, 4 positions of the ring. Vanillin crystallizes in the monoclinic non-centrosymmetric class with space group $P2_1$. Vanillin is an important compound used in the food industry, perfumery and cosmetics, animal feeds, manufacture of pharmaceutical and agrochemical products as a synthesis intermediate, etc. [3]. Vanillin displays antioxidant and antimicrobial properties. Vanillin is a donor-acceptor substituted benzene derivative in which a charge transfer exists between the para donor hydroxyl ($-\text{OH}$) and the carbonyl ($-\text{CHO}$) acceptors. The methoxy ($-\text{OCH}_3$) provides a minor contribution to the nonlinearity and plays an important role in promoting the formation of the non-centrosymmetric crystal structure. The SHG efficiency of mhba is 30 times higher than urea and the electro-optic coefficient is 22.99 pm/V [4]. Picric acid, which is known as 2,4,6-trinitrophenol (tnp), is an organic acid and it is used in the dyeing industry and as an explosive. The presence of three electron-withdrawing nitro groups makes it a good π -acceptor for neutral carrier donor molecules [5–7]. Moreover, it is an organic nonlinear optical (NLO) material by its shorter cut-off wavelength, optical quality, sufficiently large nonlinear coefficient, transparency in the UV region and high damage threshold [8–10]. Picric acid has a tendency to form charge transfer molecular complexes with many organic compounds mostly with aromatic amines, aliphatic amines, aromatic hydrocarbons, etc. [11–13]. An alternative approach to obtain a large NLO response is to devise molecular systems in which a charge transfer occurs between non-covalently bound chromophores, *i.e.*, by intermolecular or “through-space” charge transfer [14]. Picric acid has an activating $-\text{OH}$ group and deactivating

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