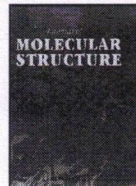




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Synthesis, crystal structure, Hirshfeld surface, DFT calculations, Z-scan and nonlinear optical studies of novel fluorinated hexahydropyrimidine

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ABSTRACT

A new fluorinated hexahydropyrimidine was synthesized and its crystal structure was elucidated using single crystal X-ray diffraction technique. This compound, C₁₅H₁₇F₃N₂O₆ crystallizes in monoclinic space group P2₁/c with cell parameters $a = 10.6345(3)$ Å, $b = 14.7074(4)$ Å, $c = 10.6677(4)$ Å, $\beta = 101.453(2)^\circ$ and $V = 1635.27(9)$ Å³. In this compound the hexahydropyrimidine ring (C7/C8/C12/N1/C14/N2) adopts sofa conformation. The puckering parameters are $Q = 0.5117$ Å, $\theta = 129.59^\circ$ and $\varphi = 304.0802^\circ$. The analysis of Hirshfeld surface indicates the presence of hydrogen bonds C–H...F, C–H...O, O–H...O, N–H...O and $\pi \cdots \pi$ stacking stabilizes the system. The energy optimized structure was calculated using Density Functional Theory (DFT) and were employed by hybrid functional theory (B3LYP) at 6-311++G(d,p) basis set in the Gaussian09_revision C0.1 program package. The natural bond orbital analysis results state that the highest energy transfer of 604.21 kJ/mol occur between the donor $\sigma(O_4-H_{43})$ to acceptor $\sigma^*(C_{34}-H_{36})$ through carboxylate chain. Moreover, the vibrational assignments, global reactivity descriptors, energy gap and molecular electrostatic potential (MEP) also gives clear insight about chemical and biological activity of the molecule. The first hyperpolarizability value 7.2987×10^{-30} esu of the synthesized compound is twenty times greater than that of urea (0.3728×10^{-30} esu). The one electron excitation of the synthesized crystal calculated by the time dependent-density functional theory (TD-DFT) calculation and comparatively studied using recorded UV spectrum. The single beam Z-scan unit equipped with 532 nm continuous Nd:YAG wave laser with 5ns pulse width was used to measure third order nonlinear optical property reveal that the investigated molecule possess effective two photon absorption with higher effective absorption coefficient. The imaginary and real parts of the third-order susceptibility values determined as $Im \chi^3 = 2.31 \times 10^{-6}$ cm W⁻¹ and $Re \chi^3 = 8.74 \times 10^{-8}$ cm² W⁻¹ respectively.

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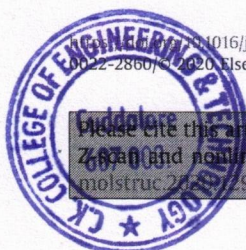
1. Introduction

Over the last two decades, organic nonlinear optical (NLO) materials have attracted a great deal of research owing to their electrochemical, electrical and optical properties. Nowadays with the advent of better design and synthesis of organic materials with strong nonlinear optical coefficients has received considerable attention [1]. The extended de-localized aromatic conjugation is a structural prerequisite for the observation of strong third-order NLO phenomena in organic materials. Moreover, the modern theoretical tools and experimental techniques suggests that

π -conjugated heteroatomic systems with intramolecular charge transfer properties are found to be suitable candidates for modern organic electronics and photonics [2–4]. Indeed, the structure-property relationships exert acute influence on optical properties of Donor(D)- π -Acceptor(A) organic based materials with some geometrical parameters like D-A strength, D-A relative position and extend conjugation. In this, the molecular asymmetry plays an important role for second and third-order nonlinearity [5,6]. Theoretical investigations have been playing a vital role in analyzing experimental studies to understand the microscopic origin of the molecular NLO responses. This helps tuning the molecular parameters that gives the desired optical property.

Among organic materials, pyrimidine derivatives have proven to be potential candidates for NLO applications [7–9]. The pyrim-

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