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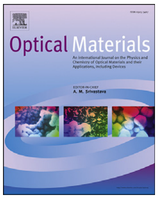

Key functions analysis of a novel nonlinear optical D-π-A bridge type (2*E*)-3-(4-Methylphenyl)-1-(3-nitrophenyl) prop-2-en-1-one chalcone: An experimental and theoretical approach

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ABSTRACT

In the current work a new third-order nonlinear optical organic single crystal of (2*E*)-3-(4-Methylphenyl)-1-(3-nitrophenyl) prop-2-en-1-one (**ML3NC**) has been grown with well-defined morphology using the slow evaporation solution growth technique. X-ray diffraction technique was used to confirm the crystal system. The presence of functional groups in the molecular structure was identified by robust FT-IR and FT-Raman spectra by experimental and theoretical analysis. The ultraviolet-visible-near infrared and photoluminescence studies shows that the grown crystals possess excellent transparency window and green emission band (~560 nm) confirms their use in green OLEDs. The third-order nonlinear and optical limiting studies have been performed using femtosecond (fs) Z-scan technique. The third-order nonlinear optical susceptibility ($\chi^{(3)}$), second-order hyperpolarizability (γ), nonlinear refractive index (n_2) and limiting threshold values are found to be 4.03×10^{-12} esu, 14.2×10^{-32} esu, -4.33×10^{-14} cm^2/W and 2.41 mJ/cm^2, respectively. Furthermore, the quantum chemical studies were carried out to achieve the ground state molecular geometry and correlate with experimental results. The experimental value of absorption wavelength ($\lambda_{abs} = 328$ nm) is found to be in excellent accord with the theoretical value ($\lambda_{abs} = 328$ nm) at TD-DFT/B3LYP/6-31G* level of theory. To understand the static and dynamic NLO behavior, the polarizability (α) and second hyperpolarizability (γ) values were determined using TD-HF method. The computed second hyperpolarizability $\gamma(-3\omega;\omega,\omega,\omega)$ at 800 nm wavelength was found to be 0.499×10^{-32} esu which is in good agreement with experimental value at the same wavelength. These results confirms the applied nature of title molecule in optoelectronic and nonlinear optical devices.

1. Introduction

The use of continuous wave (CW) and pulsed lasers at power levels ranging from mW to kW in various applications, the need for protections of the human eye and solid state optical sensors from powerful lasers has become increasingly important [1,2]. In this context, a lot of attention is being headed for seeking the new and low cost optical power limiters. The organic NLO molecules are very attractive due to their high nonlinearities and transparency in the visible region of electromagnetic spectrum [3–5]. Among the organic NLO materials the chalcone derivatives have attracted significant attention mainly because of their availability in natural products, structural flexibility, and high optical nonlinearities that they can exhibit due to the significant delocalization of the electronic clouds [6–8]. In the current work, a relatively new chalcone derivative, (2*E*)-3-(4-methylphenyl)-1-(3-nitrophenyl) prop-2-en-1-one has been selected on which only crystal structure report is available so far [9].

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Due to such excellent applications of organic chalcones it seems to be necessary to perform the synthesis, crystal growth, and linear and nonlinear optical studies. Hence, herein we account the synthesis, single crystal growth, experimental and computational spectral, linear and third order NLO chattels of **ML3NC**. The grown crystals were subjected to X-ray diffraction (XRD), FT-IR and FT-Raman, UV–Vis–NIR, Photoluminescence (PL) spectroscopic studies. The third-order NLO properties were investigated by adopting femtosecond Z-scan technique. The experimental studies are supported with the computational density functional theory (DFT). The DFT/TD-DFT studies are observed to be quite pertinent to experimental results for determining the stable geometry, vibrational and photophysical and NLO characteristics [10–19]. The obtained experimental and computational results are compared and discussed.

2. Experimental

2.1. Synthesis and crystal growth

To synthesize (2*E*)-3-(4-Methylphenyl)-1-(3-nitrophenyl) prop-2-en-1-one (**ML3NC**), all chemicals of analytical grade were used. The synthesis of **ML3NC** was achieved by Claisen–Schmidt condensation reaction of 4-methylbenzaldehyde and 3′-nitroacetophenone. A solution of 4-methylbenzaldehyde (0.01mol) and 3′-nitroacetophenone (0.01mol) in methanol (60 ml) was stirred well and 10% NaOH solution (5 ml) was added. The reaction mixture was stirred for about 2 h. Resulting crude solid was congregate by filtration and dried which was further cleansed by repeated crystallization from acetone. The synthesis process and molecular structure of **ML3NC** is shown in Fig. 1 (a). A filtered acetone solution of **ML3NC** was transferred into a beaker and allowed to evaporate slowly under room temperature. Transparent single crystals of considerable size were obtained in a period of about ten days [Fig. 1b].

2.2. Characterization techniques

XRD measurement was carried out using a Shimadzu X-600 Japan X-ray diffractometer at the scan rate 2°/m over angular range of $5^\circ \geq 2\theta \geq 70^\circ$ at 300 K for structural confirmation of the titled crystals. The FT-IR and FT-Raman spectroscopy measurements were carried out in the wavenumber range of 4000–400 cm^{-1} and 3500 - 20 cm^{-1} respectively using THERMO SCIENTIFIC, DXR FT-IR and FT-RAMAN spectrometer. JASCO V-570 UV-VIS-NIR spectrophotometer was used to record the optical absorbance spectrum in the wavelength range of 190–1300 nm at 300 K. The photoluminescence (PL) spectrum was measured using a Lumina fluorescence spectrophotometer (Thermo Fisher Scientific) having PMT of voltage 700 V, in the wavelength range of 200–900 nm at room temperature. The third-order NLO properties were estimated using the standard well known Z-scan technique which was developed by Sheik-Bahae et al. in 1990 [20]. More detail on the experimental part on Z-scan measurement is provided in Supporting information.

2.3. Computational details

For molecular geometry optimization and photophysical properties calculations the GAUSSIAN 09 [21] and Gauss view 5 visualization programs [22] were used. The stable molecular geometry of **ML3NC** molecule has been obtained using B3LYP [23,24] with 6-31G* basis set. Further the stability of optimized molecular geometry was confirmed by evaluating their analytical frequencies at the same level of theory. These methods are having the advantage to ascertain the reasonable and exact molecular geometries and vibrational frequencies. For calculating the photophysical properties the five diverse methods like: hybrid functionals B3LYP, PBE0 [25] and MO6 [26], long range corrected functionals CAM-B3LYP [27] and wb97xd [28] have been applied. It is well known that these methods are capable of calculating such properties and provides good correlation with conventional methods [13–15,29–36]. The static and dynamic NLO properties of **ML3NC** were computed using the time-dependent Hartree-Fock (TDHF) method which is developed in the GAMESS program [37]. The calculations were performed with the 6-31G(d) basis set. The frequency-dependent polarizability $\alpha(-\omega;\ \omega)$and second hyperpolarizabilities $\gamma\ (-3\omega;\ \omega,\omega,\omega)$ were calculated at the input frequency (ω = 0.05695 a.u) same as that of laser wavelength (800 nm) used in experimental Z-scan technique. The isotropic average of polarizability $\langle\alpha\rangle$ and second hyperpolarizability $\langle\gamma\rangle$ values are obtained by using the equations [18,38]:

$$\langle\alpha\rangle = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \tag{1}$$

$$\langle\gamma\rangle = \frac{1}{5}\left[\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2\left(\gamma_{xxyy} + \gamma_{xxzz} + \gamma_{yyzz}\right)\right] \tag{2}$$

3. Results and discussions

3.1. X-ray diffraction and molecular geometry analyses

The powder X-ray diffraction curve was recorded as shown in Fig. 1S (see supplementary data) for the powdered specimen of the grown crystals. The triclinic crystal system was confirmed with space group P21. The lattice parameters were calculated using POWDERX software and found to be a = 8.09417 Å, b = 11.50771 Å, c = 14.69892 Å, α = 80.325°, β = 74.778°, γ = 84.372° with unit cell volume 1300.21683 $Å^3$. These calculated lattice parameters are found to be in first-class harmony with the earlier reported values [9]. It is clear from the diffraction pattern that the grown crystals are highly crystalline in nature. The optimized geometry of **ML3NC** molecule calculated at B3LYP/6-31G* level of theory along with experimentally obtained geometry is shown in Fig. 2S (a & b) (see supplementary data). The molecular geometry was also optimized using CAM-B3LYP/6-31G*, and wb97XD/6-31G* levels of theory. The calculated molecular geometry as well as geometrical parameters are in good agreement with experimental values [9]. The bond lengths of O1-C15, O2-N4 and O3-N4 are found to be 1.227 Å, 1.228 Å and 1.231 Å respectively which are close to the experimental values [9], similarly the other bond length values are also found to be close to experimental values.

3.2. Vibrational study

The experimental (Exp.) and theoretically (Theo.) derived IR transmittance and Raman spectra of **ML3NC** ($C_{16}H_{13}NO_3$) chalcone crystal are presented in Fig. 2 (a1, b1) and 4 (a2, b2) respectively to tentatively assign the vibrational peaks of phenyl rings and functional groups [39–42] in 4000–400 cm^{-1}. The broad IR transmittance band of water (H-O-H) stretching vibrations at 3433 cm^{-1} with weak superimposed components at 3312 and 3236 cm^{-1} are observed in Fig. 2 (a1) IR (Exp.) spectrum. Phenyl ring, olefin and methyl C-H stretching modes were observed in 3150–3050 cm^{-1}, 3035-2980 cm^{-1} and 2925-2830 cm^{-1}. In **ML3NC** crystal, ketone C=O functional group is bonded in conjugation to nitrophenyl at C3