Optical Materials 86 (2018) 138–147

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

Crystal structure, Hirshfeld and third-order nonlinear optical properties of 3-(4-dimethylamino)phenyl)-1-(4-methoxyphenyl)prop-2-en-1-one: A potential material for optical limiting applications

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ARTICLE INFO

Keywords:
Chalcones
Crystal structure
Hirshfeld surface analysis
Z-scan
Optical limiting

ABSTRACT

A potential organic nonlinear optical (NLO) material 3-(4-dimethylamino)phenyl)1-(4-methoxyphenyl)prop-2-en-1-one (DMLNH$_2$MC) with a molecular formula $C_{18}H_{19}NO_2$ has been synthesized and crystallized in ethanol solution. The crystals of DMLNH$_2$M were characterized using NMR and FTIR spectroscopy techniques and the functional groups present in the molecule are identified. Thermo gravimetric analysis (TGA) and differential scanning calorimetry (DSC) studies established the thermal stability of DMLNH$_2$MC crystal. The crystal is thermally stable up to 300 °C and melts at 129 °C. Single crystal X-ray diffraction data of DMLNH$_2$MC confirms the monoclinic crystal structure with, $P2_1$ space group. The phase purity of the crystal was determined using powder X-ray diffraction method. Hirshfeld surface analysis of the molecule was performed to visualize the presence of C—H···O and C—H···π interactions. UV Visible spectral studies show that the material is transparent in the entire visible region with a band gap energy of 3.32 eV. Z-scan technique is used to determine the third-order NLO parameters and optical limiting (OL) using a Diode-Pumped Solid StateLaser operating at 532 nm wavelength. The results of optical limiting studies show that the material exhibits two photo assisted excited state absorption, leading to reverse saturable absorption (RSA). High melting point, thermal stability, transparency in the visible region of the electromagnetic spectrum, negative value of nonlinear refractive index n_2 (-1.79×10^{-9} cm^{2}W^{-1}) leading to self defocusing effect and optical limiting threshold of 4.32 kJ/cm^2 of the material makes it a potential NLO material.

1. Introduction

Theoretical and experimental aspects of third-order nonlinear optical response of wide range of organic materials with their nonlinear optical (NLO) applications were discussed in detail by J. L. Bredas and others [1]. These studies revealed the potential applications of organic materials in nonlinear optics. The selection and optimization of organic materials for nonlinear device applications require profound understanding of nonlinear properties at the molecular level. The organic materials are of interest because of their low cost and the fact that they can be easily fabricated into devices. Their chemical structure can be fine tuned to obtain the required NLO properties. They also possess high laser damage thresholds, fast nonlinear optical response times, high nonlinear optical susceptibilities and low dielectric constants compared

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https://doi.org/10.1016/j.optmat.2018.10.007
Received 29 July 2018; Received in revised form 21 September 2018; Accepted 2 October 2018

to inorganic materials [2–4]. Organic molecules with delocalized π-electron system are attractive candidates for NLO materials. In these molecules, due to the overlapping of π orbitals, delocalization of electronic charge distribution leads to a high mobility of the electron density. The appropriate electron donor and acceptor groups at both ends of the molecule can enhance the asymmetric electronic distribution. This leads to increased optical non-linearity in the ground and the excited states. The structure property relationships of the molecules are used to investigate the linear polarizabilities and hyperpolarizabilities [5–12]. The molecules exhibiting two photon absorption (TPA) have applications in three dimensional fluorescence imaging, frequency up lasing, multi photon microscopy, eye and sensor protection and optical signal reshaping, etc. [13–16]. Among the several organic materials studied, chalcones are promising NLO materials because of their relatively lesser cost, and ease of synthesis and they can be grown into transparent good quality crystals. They show good optical limiting (OL) property and third-order nonlinearity [17,18]. Two aromatic rings are connected through a conjugated double bond in chalcone derivatives which provide the required structural configuration to give third-order nonlinear optical (TNLO) properties [19]. A large number of extended tetra-thiafulvalene (TTF) derivatives bearing one or two 1,4-dithiafulven-6-yl substituents have been studied by Najoua Terkia-Derdra et al. The effect of π conjugation and introduction of electron-withdrawing groups on these extended TTF derivatives has been explored [20]. Ethylenic tetrathiafulvalene derivatives are investigated by B. Sahraoui and others [21] for large third order optical nonlinearities with picoseconds laser showed that only one-photon processes contribute to the third-order nonlinear optical activity of the molecules. A study of bis-iminopyridine tetrathiafulvalene appended ligand and its corresponding zinc metal complex revealed that it is possible to control the nonlinear optical response of these systems by a metal cation complexation [22]. The nonlinear refraction (NLR), reverse saturation absorption (RSA) and OL are some of the other fascinating properties investigated by researchers [23–27].

In this paper, we report a new organic compound, 3-[4-dimethylamino)phenyl]-1-(4-methoxyphenyl)prop-2-en-1-one, which belongs to chalcone family. The OL studies and TNLO properties are investigated in this paper. Hirshfeld surface analysis of the molecule was also performed to visualize the presence of C—H···O and C—H···π interactions in the molecule.

2. Materials and methods

2.1. Synthesis and crystal growth

The reagents and solvents for the synthesis were obtained from Aldrich Chemical Co., and were used without additional purification. 4-(Dimethylamino)benzaldehyde (0.01 mol) and 4-methoxyacetophenone (0.01 mol) were dissolved in 20 mL methanol. Few drops of a solution of sodium hydroxide were added as catalyst to the above solution with vigorous stirring. The reaction mixture was stirred for 6 h at room temperature. The formation of product was evinced by TLC. The crude product thus formed was filtered, washed successively with distilled water and recrystallized from ethanol to obtain 3-(4-dimethylamino)phenyl)1-(4-methoxyphenyl)prop-2-en-1-one ($DMLNH_2MC$) (Scheme 1) as yellow crystalline solid. The formation of the desired product and its purity were confirmed by analytical and spectroscopic techniques. The single crystals of $DMLNH_2MC$ suitable for X-ray diffraction studies were obtained from its solution in a mixture of methanol-acetone (1:1 v/v) at room temperature. A saturated solution of $DMLNH_2MC$ in methanol-acetone was warmed slightly to obtain a homogeneous mixture. The mouth of the beaker was covered with filter paper to ensure slow evaporation. The defect free seed crystals obtained this way were used as seed crystals to grow bulk crystals. The representative crystals are shown in Fig. 1.

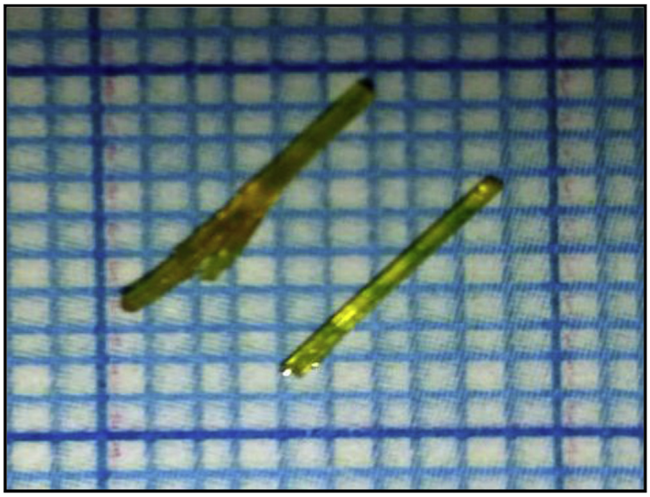


Fig. 1. Crystals grown by the slow evaporation technique.

3. Characterization

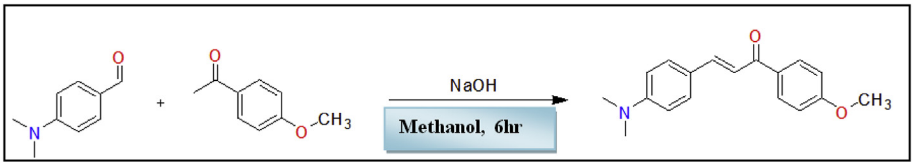
3.1. Fourier transform infrared (FTIR) spectroscopy

The FTIR spectrum of $DMLNH_2MC$ was recorded between 400 and 4000 cm^{-1} using Perkin Elmer 100300 and KBr pellet method [Fig. 2] [28]. The absorption band present at 1600 cm^{-1} is assigned to $C{=}O$ stretching vibrations. The characteristic IR absorptions observed are consistent with the functional groups present in $DMLNH_2MC$. The peak assignments are listed in Table 1 in detail.

3.2. ^1H and $^{13}C\{^1H\}$ NMR spectroscopy

^1H and $^{13}C\{^1H\}$ NMR spectra of $DMLNH_2MC$ crystals were recorded using Bruker AV-400 spectrometer in $CDCl_3$ solution using TMS as an internal standard. The ^1H NMR and $^{13}C\{^1H\}$ NMR spectra are presented in Figs. 3 and 4, respectively. The chemical shifts are represented in ppm (parts per million). The multiplicities are designated as singlet (s), doublet (d) and multiplet (m). The NMR signals are in accordance with the proposed structure.

^1H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, 2H, $J = 8.8$ Hz, H-Ar-OMe), 7.78 (d, 1H, $J = 15.6$ Hz, propenone-3-H), 7.54 (d, 2H, $J = 9.2$ Hz, H-Ar-NMe_2), 7.34 (d, 1H, $J = 15.6$ Hz, propenone-1-H), 6.96 (d, 2H, $J = 8.8$ Hz, H-Ar-OMe), 6.69 (d, 2H, $J = 8.8$ Hz, H-Ar-NMe_2), 3.88 (s, 3H, -OMe), 3.03 (s, 3H, -NMe_2). $^{13}C\{^1H\}$ NMR (400 MHz, $CDCl_3$): δ 189.0 (—C(O)—), 163.0, 152.0, 145.0, 131.9, 130.6, 130.3, 122.9, 116.8, 113.7, 111.9 (Aromatic and propenone C), 55.5 (—OCH_3), 40.2 (—OCH_3).



Scheme 1. Synthesis of $DMLNH_2MC$.