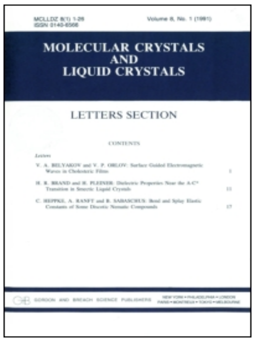

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Third-order NLO property of thienyl chalcone derivative: Physicochemical analysis and crystal structure determination

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ABSTRACT

Good-quality single crystals of an efficient nonlinear optical (NLO) chalcone derivative 1-(5-chlorothiophen-2-yl)-3-(2,3-dichlorophenyl)prop-2-en-1-one (CTDCP) which meets many of the physicochemical requirements like transparency in the entire visible region, thermal stability, mechanical hardness have been achieved. The crystal belongs to orthorhombic system with the centrosymmetric space group Pbca. The third-order NLO properties were investigated using a single beam Z-scan technique with nanosecond laser pulses at 532 nm. The nonlinear refractive index is found to be of the order of 10^{-11} cm^2/W. The magnitude of third-order susceptibility is of the order of 10^{-13} esu. The compound exhibits good optical limiting at 532 nm. The mechanical property of the crystals showed load dependent hardness. The static and frequency dependent molecular hyperpolarizabilities were computed using MOPAC 2012. Thermal study confirms that the crystal is dimensionally stable up to 179°C. The influence of direction of charge transfer on the nonlinearity of the molecule has been discussed in detail.

KEYWORDS

Chalcone derivative; crystal growth; X-ray diffraction; nonlinear optical material

Introduction

The molecular design of novel organic materials exhibiting third-order optical nonlinearity has attracted the attention of vast majority of researchers due to their potential applications in the field of information technology such as optical communication, optical computing, data storage, and optical limiting (OL) [1–2]. Among the organic compounds, chalcone and their derivatives have received significant interest due to the greater and faster response, synthetic flexibility, a strong acceptor-donor intermolecular interaction when properly substituted and a delocalized π electron system which enhances two photon absorption (TPA), facilitating nonlinear optical activity. In addition to this it has lower dielectric constant, high thermal stability, transparency, good crystallizability from cheaper organic solvents, excellent second harmonic generation (SHG) efficiency, promising third-order NLO susceptibility, and OL behavior with nanosecond laser pulse at 532-nm wavelength [3–5]. The microscopic hyperpolarizability (β) of NLO chromophores at molecular level can be improved by enhancing the charge transfer through the molecule by placing a strong electron donor and acceptor

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groups at the ends of the molecule. These structural features are also likely to give good OL behavior useful for application as optical sensors from high-intensity laser [6, 7]. The mechanisms such as excited-state absorption, TPA, free carrier absorption, and reverse saturable absorption (RSA) are responsible for originating OL process [8].

Recent studies on dibenzylidene acetone and its derivatives, substituted 4-methoxy chalcone derivatives, 1-(4-aminophenyl)-3-(3,4,5-trimethoxyphenyl)prop-2-en-1-one (APTP) and 1-(2-thiophene)-3-(2,3,5-trichlorophenyl)-2-propen-1-one (TPTP) show that chalcone derivatives are highly promising for photonic device applications [9, 10]. We have been working on the material synthesis, growth, crystal structure, and NLO response of thienyl derivatives over several years, in order to produce technologically useful nonlinear optical materials for device applications [11–13]. The second-order NLO properties of noncentrosymmetric chalcone derivatives have been investigated by many researchers [14, 15]. However, very few investigations on the third-order NLO properties have been carried out on centrosymmetric chalcones [16]. In the present study, the structural, optical, mechanical, nonlinear optical properties, and thermal stability of novel centrosymmetric crystal CTDCP has been carried out. The nonlinear absorption/refraction (NLA/NLR) and OL properties of CTDCP molecule was studied using the Z-scan technique [17] and the details are presented in this paper.

Materials and methods

All the chemicals with 99.99% purity were procured from Sigma Aldrich Inc. USA. The FT-IR spectrum was recorded using SHIMADZU- 8400S FT-IR spectrometer in the wave number range 400–4000cm^{-1}. ^{1}H NMR spectra was recorded using Bruker Ascend 400 MHz NMR spectrometer using $CDCl_3$ as solvent. The single crystal XRD data collection was made using an Oxford X calibur, Eos (Nova) CCD diffractometer [18]. The determination of space group, an empirical absorption correction, and data reduction were carried out using CrysAlisPro RED. The crystal structure is resolved by direct methods and refined by full-matrix least-square method using SHELXL97, in the WinGx package suite. Geometrical analysis and intermolecular interactions were carried out using PARST95 and PLATON. The surface morphology and growth pattern of single crystals are visualized by using the instrument JEOLJSM-6380LA. To determine the optical range of the title compound, UV-visible absorption spectrum has been recorded in the wavelength range from 200 to 800 nm using UV-1601PC, UV-Visible spectrophotometer. Vickers microhardness tester (CLEMEX digital micro hardness tester "MATSUZAWA", Japan) was used to study the mechanical properties of the crystals. Third-order NLO properties such as nonlinear refractive index and NLA coefficient of the compound was recorded using Z-scan technique [17]. In this technique, Q-switched, Nd: YAG laser (Spectra Physic GCR170) with pulse width of 7 ns at 532 nm, with a pulse repetition rate of 10 Hz and input peak-intensity of 2.39 GW/cm^2 was used. The nonlinear transmission data was recorded in the far-field using Laser probe Rj-7620 energy meter.

Synthesis and crystal growth

The compound CTDCP was synthesized using Claisen–Schmidt condensation reaction [19]. The chemical structure of the compound is given in Fig. 1. Solvents offering moderate solubility for a material and yielding pyramidal or prismatic growth habits are considered to be best solvents for growing single crystals of that material. To grow large single crystals of CTDCP, moderately soluble acetone has been used as solvent. Crystals of CTDCP were

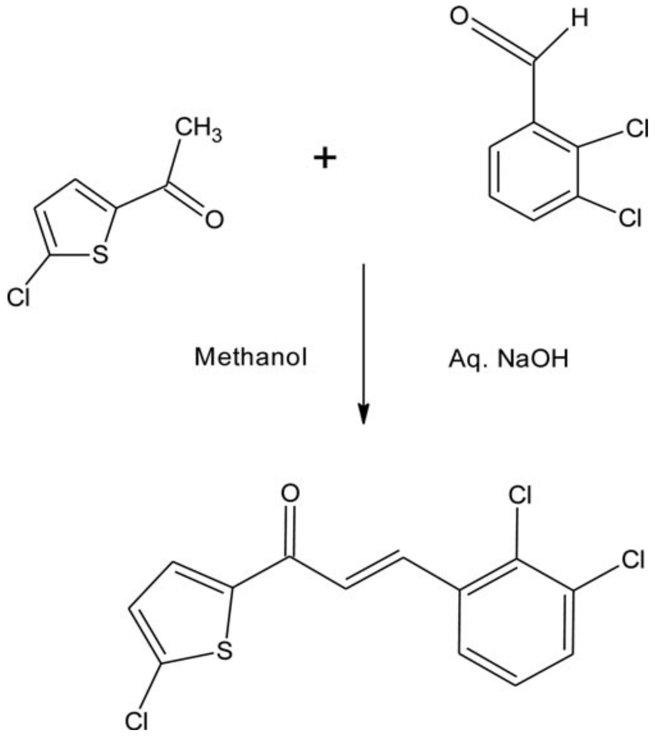


Figure 1. Scheme for the synthesis of CTDCP.

grown by the slow evaporation solution growth technique at room temperature [20]. A saturated solution of compound was prepared, filtered into a beaker to remove any suspended particles and kept covered till tiny crystals are formed which were allowed to grow further. Good quality single crystals of maximum size 3 × 2 × 2 mm^3 were obtained after two weeks which is shown in Fig. 2a. The morphology of the crystals were simulated using the WinXMorph software [21] where the data obtained from the single crystal XRD study were used as input to index the well-developed faces in the crystal and is shown in Fig. 2b. The CTDCP crystals are prismatic, with large habit face (1 0 0) and distinct cleavage plane (0 1 0). The crystal planes corresponding to larger surface area were identified as (1 0 0) and (1 0 0) planes.

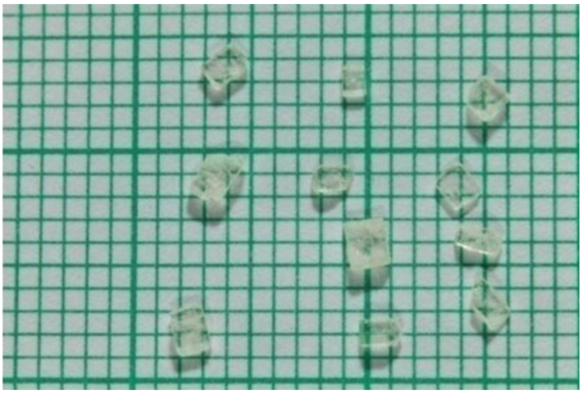


Figure 2a. Single crystals of CTDCP.

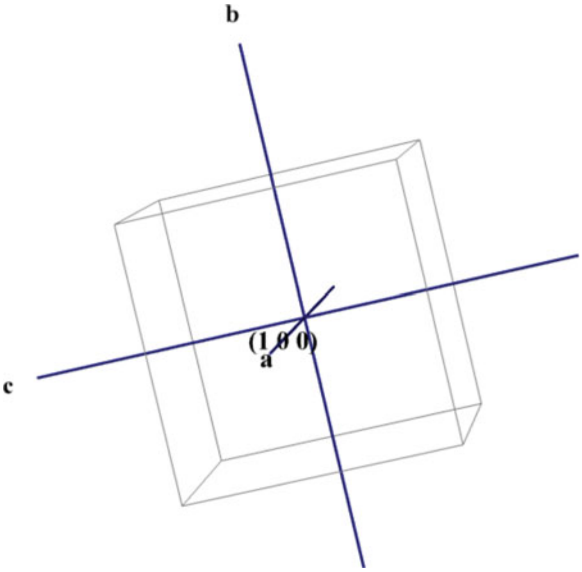
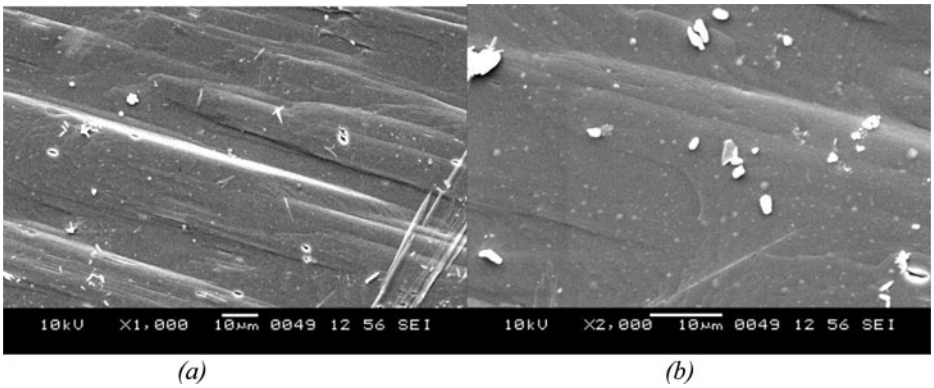


Figure 2b. Indexed morphology of CTDCP.

Results and discussion

The IR spectrum of the compound CTDCP shows weak absorption peak at 3086 cm^{-1} is due to aromatic C-H stretch. The strong absorption peak at 1645 cm^{-1} corresponds to the C = O stretching vibration. The peak at 1587 cm^{-1} implies the chalcone C = C stretching vibration, An absorption band at 1417 cm^{-1} is due to the alkyl C–H bending vibration of CH_3–O group. The signals obtained in ^{1}H NMR spectra are in agreement with the structure of the title molecule. The doublets observed at δ 8.1975 and 7.266 with a coupling constant of 15.9 corresponds to protons of –CH = CH– group. The other characteristic peaks observed in the spectrum are assigned as follows δ: 7.6115 (d, 1H, H of thiophene ring), 7.007 (d, 1H, H of thiophene ring), 7.627 (t, 1H, H of aromatic ring), 7.223 (d, 2H, H of aromatic ring), and 7.265 (d, 2H, H of aromatic ring). The SEM images of 1000× and 2000× magnification are shown in Fig. 3a and Fig. 3b, respectively. The Fig. 3a shows step-like structure on the surface, indication of two-dimensional growth mechanisms [22], which confirms the layered growth



(a) (b)

Figure 3. SEM images of CTDCP single crystal.

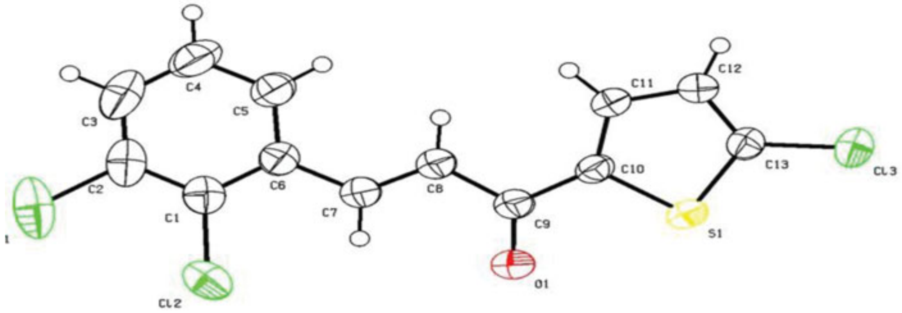


Figure 4a. The molecular structure of CTDCP, showing 50% probability ellipsoids.

Table 1. Geometries of intermolecular interactions obtained from structural analysis of CTDCP.

Interactions	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)	Symmetry
C11–H11···S1	0.929(2)	2.9635(6)	3.539(2)	121.6(2)	1.5−x,−1/2 + y,z
C11–H11···O1	0.929(2)	2.531(2)	3.439(3)	165.8(2)	1.5−x,1/2 + y,z
C10–S1···H11	1.722(2)	2.9635(6)	3.732(2)	102.35(8)	1.5−x,−1/2 + y,z
C9–O1···H11	1.225(3)	2.531(2)	3.472(2)	131.9(2)	1.5−x,1/2 + y,z
C2–Cl1···C2	1.727(3)	3.348(3)	4.546(3)	124.0(1)	−1/2 + x,y,1/2−z
C1–C2···Cl1	1.390(4)	3.348(3)	3.463(3)	82.9(2)	1/2 + x,y,1/2−z

pattern of the crystal. The Fig. 3b shows an uneven brighter regions due to the inclusion of solvent, which is common in solution grown crystals.

The single-crystal XRD analysis revealed that the title compound crystallizes in the orthorhombic crystal system with a centrosymmetric space group Pbca suggesting lack of second order nonlinear property for the crystal [23]. The final R values of the refinement are $R_1 = 0.0469$, w$R^2 = 0.1168$ for theta range of 1.33–28.29. The low value of R indicates the purity of the grown single crystal [24]. In the molecule CTDCP (Fig. 4a), the C = C exhibits an E conformation which is common in majority of chalcone derivatives. The molecule is nonplanar, with a dihedral angle of 11.78° between the chlorothiophene and dichlorophenyl rings. The chloro group at position 2 and 3 is coplanar with the benzene ring to which it is attached, making an angle of 7.94° with C–C = O plane. In the crystal, C–H···O intermolecular interactions (Table 1) generates chains of molecules extending along the b axis (Fig. 4b). The details of the crystal data and refinement are given in Table 2. CCDC deposition number 887291 contains the supplementary crystallographic data for this research article.

The purity of the crystal was ensured by measuring the density of the compound using specific gravity bottle at ambient temperature. The measured density value is 1.581 g/cm^3 and it is nearly equal to 1.575 g/cm^3 calculated value from single crystal XRD data. The UV-visible

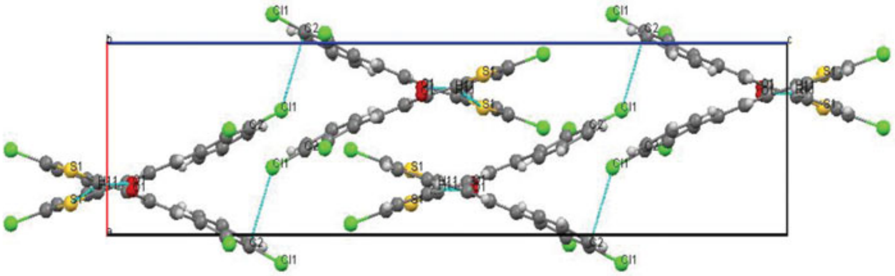


Figure 4b. Unit cell packing of the CTDCP showing intermolecular interactions with dotted lines.

Table 2. Crystal data and structure refinement of CTDCP crystal [CCDC number 887291].

Molecular formula	$C_{13}H_7Cl_3OS$
Crystal size (mm^3)	0.35 × 0.30 × 0.25
Formula weight ($gmol^{-1}$)	317.6
Crystal habit and color	Prismatic, colorless
Crystal system	Orthorhombic
Space group	Pbca
Unit cell parameters	$a = 7.6136(3)$ Å
Cell angles (deg)	$b = 11.4972(4)$ Å
Volume	$c = 30.6073(9)$Å
Radiation	$\alpha = 90.00, \beta = 90, \gamma = 90.00, Z = 8$
Radiation wavelength	2679.21(16)$Å^3$
Temperature	$M_{\circ}K_{\alpha}$ radiation
Density (Mg m^{-3})	0.71073 Å
Absorption coefficient μ (mm^{-1})	$T = 296(2)$K
F (000)	1.575
θ range for data collection (deg)	0.822
Refinement method	1280
No. of measured reflections	1.33–28.29
Measured number of unique reflections	Full-matrix least-squares on F^2
Final R indices with $I > 2\sigma$ (I)	23658
Goodness-of-fit on F^2	3320
R_{int}	$R_1 = 0.0469$
R indices (all data)	$wR^2 = 0.1168$
	1.087
	0.0279
	$R_1 = 0.0570$
	$wR^2 = 0.1244$

absorption spectrum of the crystal was shown in Fig. 5. The crystal has good transparency window in the entire visible region and the UV cut off wavelength is observed at 415 nm. The optical energy band gap of the crystal CTDCP is 2.99 eV. Due to this wide band gap, the crystal under study is expected to possess high laser threshold and a large transmittance in the visible region [25]. The very low absorption in the entire visible region and the wide band gap confirms its suitability for the fabrication of nonlinear optical devices.

Surface mechanical properties of the crystals were carried out for the applied loads (5–50 g) and were calculated using the formula [26].

VHN is the Vicker's micro hardness, P is the applied load (kg), d is the diagonal length (mm) of the indentation. The plot shown in Fig. 6, indicates hardness number initially decreases with load and saturates above 25 g of the applied load. The cracks initiated around

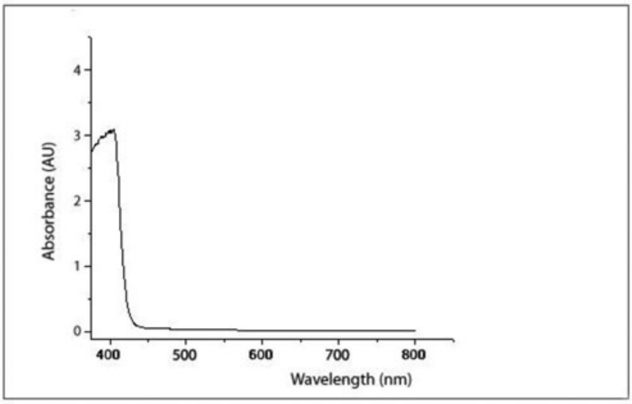


Figure 5. UV-Visible spectra of CTDCP.

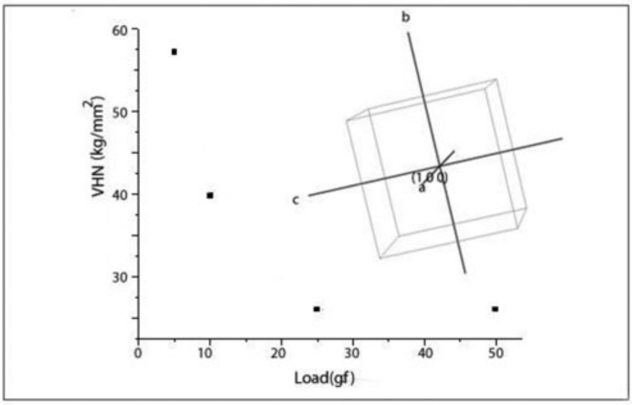


Figure 6. Load dependence of Vickers hardness of CTDCP crystal.

the indenter impression at the load of 25 g and severe cracks were observed at 50 g of the applied load, due to the liberation of the internal stress locally initiated by indentation. The refractive index of the crystal was measured using long arm spectrophotometer (homemade) working on the principle of Brewster's law. The refractive index of CTDCP was found to be 1.555 and 1.570 at 632.8 and 543.5 nm, respectively. The high refractive index values of CTDCP make it to be a promising material to modulate light intensity in optical limiters.

To examine the thermal stability of the crystal differential scanning calorimetry (DSC) analysis was carried out. The melting point of grown sample was found to be 179°C. As there is no decomposition of the material at the melting temperature, the crystal is thermally stable beyond the melting temperature. The significantly high melting point of the crystal having an advantage in the fabrication of devices. In case of chlorine-substituted chalcone derivatives substitution of chlorine group on phenyl ring (CTDCP) is more efficient than substitution of methyl group (CTTMP, CTDMP) [11, 13]. The melting points of some organic nonlinear optical materials by DSC plot are listed in Table 3.

Third-order optical nonlinearities of the samples were investigated using single beam Z-scan method [17]. The open aperture curve, closed aperture curve, and pure NLA curve of the samples are shown in Figs. 7a–c, respectively. It is observed that the curve is nearly symmetric with respect to the focal point ($z = 0$). At the focus sample shows minimum transmission, indicating intensity dependent absorption effect. The nature of the open aperture curve shows that the sample exhibits TPA [29]. From the open aperture Z-scan data, the measured values of NLA coefficient, β, and the imaginary part of third-order nonlinear optical susceptibility $\chi^{(3)}$ of the sample are given in Table 4. The valley and peak configuration observed in

Table 3. DSC data of some organic NLO compounds.

Crystal	Melting point by DSC plot (°C)
CTDMP [11]	111
CTTMP [12]	112
CPP [27]	133
4NP3AP [28]	178
CTDCP*	179

CTDMP-1-(5-chlorothiophen-2-yl)-3-(2,3-dimethoxyphenyl)prop-2-en-1-one
CTTMP-1-(5-chlorothiophen-2-yl)-3-(2,4,5-trimethoxyphenyl)prop-2-en-1-one
CPP-3-(4-chlorophenyl)-1-(pyridin-3-yl) prop-2-en-1-one
4NP3AP- 3-(4-nitrophenyl)-1-(pyridine-3-yl) prop-2-en-1-one
CTDCP*
present material.

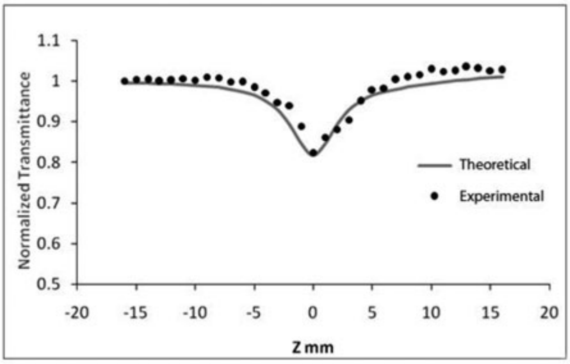


Figure 7a. Open aperture Z-scan curve of CTDCP crystal.

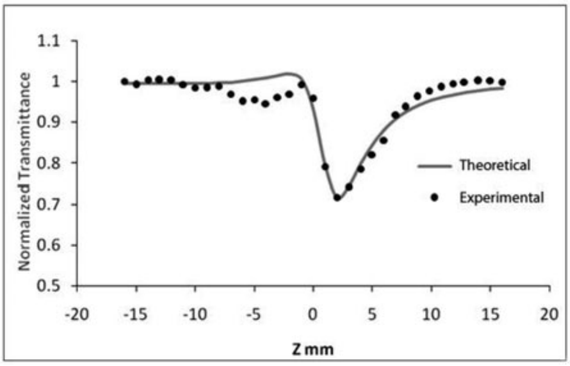


Figure 7b. Closed aperture Z-scan curve of CTDCP crystal.

Fig. 7c shows that the material has a negative nonlinear refractive index. This implies response is electronic in origin and the thermal effect is not the dominant effect for the third-order nonlinear response of the solution. From the pure NLA Z-scan data, the real part of third-order nonlinear optical susceptibility $\chi^{(3)}$ and nonlinear refractive index n_2, for sample have been calculated to be given in Table 4. The values are comparable with that of dibenzylidene acetone and its derivatives [30] and 4-methoxy chalcone derivatives [31]. Our results are better than that for the derivatives of hydrazones [32] and 4-aminophenyl derivatives [10].

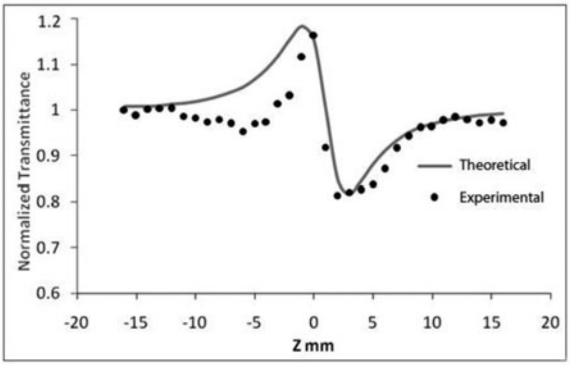


Figure 7C. Pure nonlinear refraction Z-scan curve of CTDCP crystal.

Table 4. Experimentally determined values of some organic nonlinear compounds.

Compound	β(cm/GW)	n_2 (x10^{-11} esu)	Im χ^3 (x10^{-13}esu)	Re χ^3 (x10^{-13}esu)
CTDCP*	2.083	– 1.042	0.321	– 1.116
APTP [10]	1.43	– 0.54	0.22	– 0.583
2-(4-methylphenoxy)-N0-[(1E)-(4-nitrophenyl)methylene]acetohydrazide [32]	1.13	– 0.79	0.14	– 0.72
2-(4-methylphenoxy)-N0-[(1E)-(4-methylphenyl)methylene]acetohydrazide [32]	0.44	– 0.53	0.05	– 0.49
N^1-{(1E)-[4-(dimethylamino)phenyl]methylene}-2-(4-ethylphenoxy)acetohydrazide [32]	1.23	– 0.69	0.15	– 0.63

APTP - 1-(4-aminophenyl)-3-(3, 4, 5-trimethoxyphenyl)prop-2-en-1-one
CTDCP
*-present work

The chalcone derivative investigated here is designed based on the scheme D-π-A-π-D. It is clear that the effect of electron donating group is considerable in the study of optical properties of the chalcones. In CTDCP, the chlorine substituted at both the ends of the molecule acts as an electron donor. The electron donating strength of chlorine is greater than that of bromine but less than that of methoxy (OCH_3) and the electron accepting strength of chlorine is larger than that of $C = O$, but smaller than NO_2 [13]. Here, the molecule have thiophene ring connected to phenyl ring via, carbonyl group through conjugated π-bond system. The donor groups substituted on the thiophene and phenyl ring greatly alters the molecular hyperpolarizability of the molecule. Two more chlorine atoms at the other end of the molecule also act as an electron donor. The molecule also contains an electron acceptor $C = O$ at the middle forms a D-π-A-π-D system. Thus CTDCP molecule possesses a push-pull structure where effective charge transfer takes place from ends to the center of the molecule. Hence, there is an increase in the conjugation; as a result the density of π-electrons is also increased, so one expects enhancements in the NLO response of this molecule, but it is less compared to CTTMP and CTDMP [13]. However, the compound exhibited good thermal stability (see Table 3).

Optical power limiting is an area of potential interest due to applications such as sensor and eye protection against high-intense light. Fig. 7d represents the variation of normalized transmittance with laser power density of CTDCP molecule. OL behavior of the molecule is

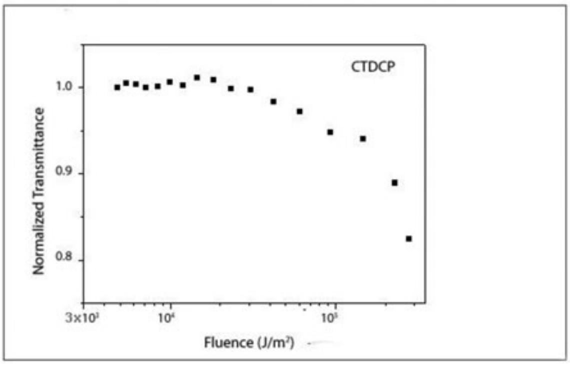


Figure 7d. Optical limiting behavior in CTDCP.

extracted from the open aperture Z-Scan data [33]. Below critical irradiance 3×10^4 J/m^2 the normalized transmittance is almost constant and at higher irradiance (beyond 3×10^4 J/m^2), the normalized transmittance starts to decrease and the sample becomes less transparent to the incident light beam. Beyond the critical irradiance the molecule exhibit OL characteristics [34]. Similar OL behavior has been observed in thiophene oligomers by Hein et al. [35], where it was attributed to saturation of instantaneous two-photon absorption. Thus, the title compound seems to be promising candidate for making optical power limiting devices.

Conclusions

A novel thienylchalcone was synthesized and crystallized by the slow evaporation solution technique. Crystal structure was determined using single crystal X-ray diffraction technique. Optical cut off wavelength of UV absorption is found to be 415 nm and the corresponding optical energy band gap is found to be 2.99 eV, which is higher than the values reported for other chalcone derivatives. The observed NLA is caused by TPA process due to which the material exhibits OL. It is to be noted that the value of $\chi^{(3)}$ for the centrosymmetric material under investigation is comparable to those of some representative third-order nonlinear optical materials. The nonlinear optical property along with good transparency in the visible region, high band gap and absence of phase transition before melting point (179°C), can make CTDCP crystal to be useful for nonlinear optical devices.

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