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Structural, thermal, linear and nonlinear optical studies of an organic optical limiter based on reverse saturable absorption



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ABSTRACT

A new derivative of chalcone, 3-(4-bromophenyl)-1-(pyridin-4-yl) prop-2-en-1-one (4BP4AP), crystallizing in centrosymmetric structure has been synthesized using the Claisen–Schmidt condensation reaction method. The FTIR and FT-Raman spectral studies were carried out on 4BP4AP for structural conformation. The single crystals were grown using slow evaporation solution growth technique. The single crystal XRD of the crystal shows that the crystal system of 4BP4AP is triclinic with space group P-1. Scanning electron microscope images enunciate the surface smoothness and the two dimensional growth mechanisms in the crystal. The crystal is transparent in the entire visible region as indicated by the UV-VIS-NIR spectrum. The thermal stability and phase transition of the compound was studied by thermogravimetric and differential scanning calorimetric analysis and found to be stable up to 200 °C. By performing the open aperture z-scan experiment, nonlinear absorption and optical limiting behavior of the crystal were studied. The crystal can be used for optoelectronic application due to its excellent photophysical properties.

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1. Introduction

Currently nonlinear optical (NLO) materials exhibiting strong two photon absorption (TPA) are of great interest due to their wide range of applications. Among the variety of molecular and bulk materials studied for NLO properties, organic materials are of particular importance due to their optical and electronic properties, which are tunable through structural modifications [1]. Organic materials with large third order NLO coefficients are attractive for various photonic applications such as optical communication, signal processing, optical modulation, optical disc data storage, electro-optic modulation, optical switching and optical limiting [2,3]. Chalcone and its derivatives are one of the important classes of optically nonlinear organic materials. These are open chain flavonoids with two aromatic rings joined by a carbonyl group and two α , β -unsaturated carbon atoms [4]. The presence of extensive conjugation in these molecules provides a charge transfer axis. Also

* Corresponding author. E-mail address: mapraveen.80@gmail.com (A.P. Menezes). one can tune one of the aromatic rings of chalcones as donor and the other as acceptor by incorporating suitable functionalities on the aromatic rings so that the charge transfer takes place from the donor to the acceptor through the charge transfer axis [5,6]. Due to the overlapping of π orbital in these molecules, delocalization of electronic charge distribution increases the mobility of the electron density which in turn enhances the optical nonlinearity [7].

Heterorings such as furan, pyridine and thiophene, due to their lower aromatic stabilization energy than benzene have been reported to provide more effective π -conjugation between donors and acceptors, resulting in larger nonlinearities [8]. Recently our research group has reported a number of pyridine based chalcone molecules with efficient NLO response [9–14]. Among them BPP [14] showed a SHG efficiency of 1.4 times that of urea. In this compound a bromo group is substituted at the para position of phenylene moiety seeing that para substitution is more effective in forming noncentrosymmetric crystal structures [13]. Moreover, BPP is designed by just replacing the benzene ring of 4-bromochalcone (4BC) by the pyridine ring in which a nitrogen atom is placed at the meta position to the carbonyl group and this results in the improved SHG efficiency [15]. In continuation of our study on pyridine based substituted chalcones, we synthesized a new molecule called 3-(4-bromophenyl)-1-(pyridin-4-yl) prop-2-en-1one (4BP4AP), in which a nitrogen atom is placed at the para position of the carbonyl group (Fig. 1). Both 4BC and BPP crystallized in noncentrosymmetric crystal form with good SHG efficiency but interestingly, the molecule 4BP4AP crystallizes in centrosymmetric structure and thus the possibility of SHG is ruled out. The linear optical and thermal studies revealed that this crystal is transparent down to the blue region with very good thermal stability. Therefore, in order to explore the usability of the crystal for device applications, its third order NLO studies were also carried out.

In recent times, a number of chalcone derivatives have been investigated for their third order NLO properties such as nonlinear absorption (NLA), nonlinear refraction (NLR) etc [16–21]. Materials with large reverse saturable absorption are found to exhibit good optical limiting behavior and such materials find applications in protective devices for human eyes and also for various optical sensors [22]. The third order NLO properties of chalcones can be explored by single beam z-scan technique using which the third order NLO behavior of 4BP4AP is explored [23]. In this article, we report the growth of a chalcone derivative 4BP4AP by employing slow evaporation solution growth technique and the experimental results on its structural, thermal, linear and nonlinear optical properties.

2. Experimental procedure: synthesis, solubility and crystal growth

Chalcone derivatives are synthesized by the Claisen–Schmidt condensation reaction [9]. It is the reaction of a substituted acetyl pyridine with substituted benzaldehyde in the presence of an alkali. The compound 4BP4AP was synthesized by stirring a mixture of Analytical Reagent (AR) grade chemicals 4-acetyl pyridine (0.01 mol) and 4-bromobenzaldehyde (0.01 mol) in methanol (50 ml) without further purification. Sodium hydroxide (5 ml, 20%) was then added drop wise to the solution, and the mixture was stirred for 2 h. The mixture is stirred by maintaining the solution within the temperature range of 27-30 °C. The contents of the flask were poured into a beaker containing ice-cold water. The crude product was collected by filtration, washed with excess water and dried. The synthetic scheme for the title compound is shown in

Fig. 2.

The solubility studies of the compound in various solvents were carried out to select a suitable solvent for the growth of the single crystals. To grow large single crystals of 4BP4AP, we used N, Ndimethyl formamide (DMF) due to the suitable solubility in this solvent and crystals were grown by the slow evaporation of the solvent at room temperature [13]. A saturated solution of 3-(4bromophenyl)-1-(pyridin-4-yl) prop-2-en-1-one was prepared in DMF in a 100 ml beaker at 30 °C and the solution was filtered to remove suspended particles. The beaker was covered with a polythene sheet and kept in a dust free atmosphere. Transparent single crystals of 4BP4AP were harvested from the growth solution after allowing them to grow to the maximum possible dimensions $(4 \times 2.5 \times 1 \text{ mm}^3)$. High quality single crystals were selected for further study. A photograph of the grown crystals is presented in Fig. 3a. The morphology of crystal simulated by WinXMorph [24] computer program is shown in Fig. 3b. The point group, lattice parameters and (h k l) values obtained from single crystal x - ray diffraction study were used as data input. By looking at the actual morphology of the crystal, the well developed faces were indexed by editing the distance from the centre of the model to its face. The crystal is elongated slightly along the b – direction due to a higher growth rate along this axis compared to the other two directions.

3. Results and discussion

3.1. CHN and EDAX analysis

The percentage composition of the elements present in 4BP4AP was confirmed by performing carbon, hydrogen, nitrogen (CHN) analysis. The Elementar Vario EL III CHN analyzer was used for the purpose. The result of the analysis is presented in Table 1. Theoretical values of CHN were calculated from the molecular formula $C_{14}H_{10}BrNO$. The micro analysis of the sample showed a good agreement with the calculated values, confirming the formation of the compound. Energy dispersive Analysis of X rays (EDAX) of the crystal was carried out using JEOL JSM-6380LA analytical scanning electron microscope (SEM) system. The resulted spectrum over a certain area is given in Fig. 4. The characteristic peaks in the spectrum reveal the presence of various elements in the grown crystal.



Fig. 1. Scheme for the structure of some chalcone derivatives.



Fig. 2. Synthetic scheme of 4BP4AP.



Fig. 3. [a] Photograph of 4BP4AP single crystals. [b] Simulated Crystal Morphology.

Table 1 CHN Analysis data o	f 4BP4AP.	
Element	Experimental (%)	Computed

Element	Experimental (%)	Computed (%)		
Carbon	58.61	58.36		
Hydrogen	3.38	3.50		
Nitrogen	4.72	4.86		

3.2. Fourier transform infrared (FT-IR) and FT-Raman spectral studies

To investigate the presence of functional groups in 4BP4AP and their vibrational modes, FT-IR and FT-Raman spectral analysis was carried out. The FTIR spectrum was recorded between 500 and



Fig. 4. EDAX spectrum of 4BP4AP.

 $3500\ {\rm cm^{-1}}$ by KBr pellet technique using the Thermo Nicolet,

4.00

5.00

Avatar 370 FT-IR spectrometer equipped with KBr beam splitter and a DTGS detector, with a spectral resolution of 4 cm⁻¹ and the spectrum is shown in Fig. 5. The FT-Raman spectrum was recorded using the BRUKER RFS 27, Stand alone FT-Raman Spectrometer, having a spectral resolution of 2 cm⁻¹ with an exciting wavelength of 1064 nm from an Nd: YAG laser source. Fig. 6 displays the FT-Raman spectrum. The characteristic IR absorption and Raman bands observed are consistent with the functional groups present in the compound and the corresponding assignments are recorded in Table 2.

3.3. Surface morphology

The surface morphology of the 4BP4AP single crystal was studied by using a JOEL JSM-6380LA analytical scanning electron microscope (SEM). SEM was operated at an accelerating voltage of 20 kV and probe current of 1 nA by keeping the sample in high vacuum. Due to the non-conducting behavior of the organic materials, gold coating is done by the sputtering technique using JOEL JFC-1600 auto fine coater before subjecting the surface of 4BP4AP crystal to electron beam. The SEM images of $100 \times$ and $5000 \times$ magnification are shown in Fig. 7. It can be observed from the figure that the surface appears smooth with some micro crystallites grown on the surface. These inclusions are formed during the growth of the crystal and influenced by the growth conditions. Fig. 6a indicates a layered growth pattern which confirms the two dimensional growth mechanisms [14].

3.4. Single crystal X - ray diffraction study

The grown crystal was subjected to single-crystal X-ray diffraction (XRD). A Supernova Dual diffractometer with Atlas detector [Agilent (2012)] using the mirror monochromated Cu Ka radiation of wavelength 1.54184 Å was used for data collection. The cell refinement and data reduction was done using CrysAlis PRO [Agilent, 2012]. The crystal structure was solved by the direct method and refined by the full matrix least squares method using SHELXL-97 [25] in the WinGx package suite [26]. The X-seed [27] and the Mercury [28] softwares were used for molecular graphics. The details of the crystal data and refinement are given in Table 3.



Fig. 5. FTIR spectrum of 4BP4AP.



Fig. 6. FT-Raman spectrum of 4BP4AP.

Single-crystal XRD data shows that the crystal is triclinic in structure with centrosymmetric space group P-1. The asymmetric unit of the title chalcone derivative contains two independent molecules A and B of similar geometry adopting an E configuration about the C7A=C8A [1.326 Å] and C7B=C8B [1.342 Å] double bonds. The dihedral angle between the benzene and the pyridine rings is 9.41° in the molecule A and it is 41.49° in the molecule B. Thus, the molecule A has an almost planar structure where as the structure of molecule B is twisted. The mean plane of phenyl ring (C9-C14) in molecule A and molecule B is deviated by an angle of 8.17⁰ and 18.78° respectively from a plane C6–C9. Similarly the plane through pyridine rings of A and B molecules are deviated from the plane C6–C9 by 10.09° and 25.11° respectively. The thermal ellipsoid plot of the molecule at 60% probability is shown in Fig. 8. In the crystal structure, it is observed that the molecules are packed in anti parallel layers where the molecules are interconnected in a head to tail fashion (Fig. 9) and the structure is stabilized by the hydrogen bonds (Fig. 10).

3.5. Thermal studies

The Differential Scanning Calorimetric (DSC) data was recorded using Mettler Toledo DSC 822e thermal analyzer on a sample weight of 0.9460 mg in the temperature range 25 °C-300 °C, at a heating rate of 10 °C per minute in the nitrogen atmosphere. The thermogravimetric analysis (TGA) and differential thermal analysis (DTA) was done using a Perkin Elmer TG/DTA analyzer to study the rate of change of weight of the sample with respect to temperature. About 1.62 mg of powdered compound was used for this analysis. The sample was analyzed under the nitrogen atmosphere at a heating rate of 10 °C per minute in the temperature range of 25 °C-630 °C. The results of the analysis are presented in Fig. 11. The sharp peak at 200 °C in the DSC curve corresponds to the melting point of the crystal. The sharpness of the peak indicates the good crystallinity of 4BP4AP [29]. It is evident from the TG plot that the mass of the sample remains unchanged till 160 °C after which there is about 4.8% weight loss due to dehydration. The decomposition of the material starts at around 215 °C and continues up to 305 °C. A major weight loss of 92.8% was observed in the temperature range. The steep weight loss around 265 °C is because of the boiling of the melt. After heating the sample beyond 305 °C, the residual weight is approximately 1.5% of the initial weight. The

Table 2	
Assignment of vibrational	frequencies.

Wave number (cm ⁻¹)		Assignments
Infrared lines	Raman lines	
3039.79	3064.1	aromatic C–H stretching vibration
2972.76, 2922.65	_	C-H stretching vibration
1675.28	_	C=O stretching vibration
1597	1583.9	aromatic ring vibration
1552.08	1559.9	C=C stretching vibrations (chalcone)
1485.22	1492.7	aromatic C=C stretching vibrations
1409.6	1402.1	C–H bending vibration
1350.57	1346.1	C–N stretching vibration
1218.7, 1068.83	1176.9, 1076.7	aromatic C–H in-plane bending vibrations
810.98	894	C–Br stretching vibration
677.8	664.9	Out of plane C–H aromatic bending or wagging vibrations



Fig. 7. SEM images of 4BP4AP crystal.

differential thermal gravimetric (DTG) curve coincides well with the TGA curve. Furthermore, the high melting point of the crystal is due to the presence of Br group in the crystal structure as Br group improves the melting points of the compounds [30]. The high thermal stability of the crystal and its ability of not getting decomposed till the melting temperature may be advantageous in device fabrication.

The molar enthalpy of fusion $\Delta_{fus}H_m$ of the single crystal 4BP4AP was obtained from the DSC curve using the area integration method and is found to be 159.03 J/g. The molar entropy of fusion $\Delta_{fus}S_m$ is calculated using the thermodynamic equation [9] $\Delta_{fus}S_m = \Delta_{fus}H_m/T_m$, where T_m is the melting point of the crystal. The calculated molar entropy of fusion is 0.336 J/Kg.

3.6. Linear optical studies

Organic NLO materials having optical absorption edge in the 400 nm region are used for blue—violet frequency conversion. It is necessary that there is no absorption in the visible region for 4BP4AP crystal since it has to be exploited for NLO applications at room temperature. UV—VIS—NIR absorption spectrum of the 4BP4AP crystal was recorded using a Varian, Cary 5000 UV—VIS spectrophotometer in the wavelength range of 200–1000 nm. A solution of 4BP4AP in acetone was placed in a 1 cm thick cuvette for measurement. The recorded spectrum is shown in Fig. 12. It is evident from the spectrum that the crystal has a wider

transparency range extending into the entire visible and the IR region (cut off 417 nm). By converting the observed UV-VIS spectrum in to Tauc's plot (as shown in the Fig. 13a), the optical energy gap of the crystal is estimated [31]. The linear behavior exhibited by the Tauc's graph can be considered as an evidence of direct transition [32]. The intercept of linear fitting line of $(\alpha h\nu)^2$ and the zero absorption coefficient line gives the direct optical band gap and the value thus obtained is 3.09 eV (Fig. 13 (b). This value is very close to the value obtained from the cutoff wavelength (λ_C) of the crystal using the relation $E_g = hc/\lambda_C$ which is equal to 2.98 eV.

From the UV-VIS transmittance data, the extinction coefficient (K) can be calculated using the equation,

$$K = \frac{\lambda \alpha}{4\pi} \tag{1}$$

The transmittance (T) is related to the reflectance (R) through the equation [32],

$$T = \frac{(1-R)^2 e^{-\alpha t}}{1-R^2 e^{-2\alpha t}}$$
(2)

where $\alpha = ln(T^{-1})/t$, the optical absorption coefficient and t is the thickness of the sample. When the absorption is high, the refractive index (n) of the sample can be calculated from the reflectance data using equation [33,34],

Table 3
Crystal data of 4BP4AP Crystal.

Molecular formula	C ₁₄ H ₁₀ Br N O
Formula weight/g mol ⁻¹	288.14
Crystal shape and colour	plate, yellow
Crystal System	triclinic
Space group	P-1
Unit cell parameters	a = 5.9544(4) Å
	b = 7.8143(6) Å
	c = 24.7471(13) Å
Cell Angles (deg)	$\alpha = 83.329(5), \beta = 84.815(5), \gamma = 82.092(6).$
	Z = 4
Volume	1129.55(13)Å ³
Radiation	Cu Ka radiation
Radiation Wavelength	1.54184 Å
Temperature	T = 100.0(2) K
Density	1.694 Mg/m ³
Absorption Coefficient (μ /mm ⁻¹)	4.796
F (000)	576
θ range for data collection (deg)	3.61-75.30
h _{min,max} , k _{min,max} ,l _{min,max}	(-7 6), (-9 9), (-31 26)
Max. and min. Transmission	0.8313 and 0.4472
Refinement method	Full-matrix least-squares on F ²
No. of measured reflections	11,951
No. of independent reflections	4672
No of reflections with $I > 2\sigma(I)$	4138
No. of parameters	307
No. of restraints	1
Goodness-of-fit on F ²	1.12
Final R indices $[I > 2\sigma (I)]$	R1 = 0.0986, $wR2 = 0.2655$
R indices all data	R1 = 0.1087, $wR2 = 0.2725$
$\Delta \rho_{min, max}/e \text{ Å}^{-3}$	-1.595, 2.917



Fig. 8. ORTEP of 4BP4AP. Thermal ellipsoids were drawn at 60% probability level.

$$R = \frac{(n-1)^2}{(n+1)^2} \Leftrightarrow n = \frac{1+R+\sqrt{R}}{1-R}$$
(3)

In the present case, the optical absorption is minimum and hence the refractive index can be calculated from the transmittance data using the equation [35],

$$T = \frac{2n}{n^2 + 1} \Leftrightarrow n = \frac{1 + \sqrt{1 - T^2}}{T}$$

$$\tag{4}$$

Refractive index of 4BP4AP is almost a constant in its transmission window as shown in the Fig. 14a. The value of n for the crystal is 1.8 in the range 460–1000 nm. From these values of n and K, the electric susceptibility (χ_c) can be calculated using the relation



Fig. 9. Packing of molecules in anti parallel layers where molecules in a layer are aligned in head to tail fashion in the crystal structure of 4BP4AP when viewed down a-axis. Hydrogen atoms are omitted for clarity.

[36].

$$\chi_c = \frac{n^2 - K^2 - \varepsilon_0}{4\pi} \tag{5}$$

where ε_0 is the dielectric constant when there is no contribution from the free carriers. The electric susceptibility of 4BP4AP crystal



Fig. 10. Packing of 4BP4AP viewed down the a-axis showing hydrogen bond interactions.

at 1000 nm is found to be 0.2615.

Further, real part (ε_r) and imaginary part (ε_i) of dielectric constant can be calculated from the relations [36],

$$\varepsilon_r = n^2 - K^2$$
 and $\varepsilon_i = 2nK$ (6)

The values of ε_r and ε_i at 1000 nm are 3.285 and 4.828 \times 10⁻⁶ respectively.

The optical conductivity (σ) of the crystal is related to the optical absorption coefficient (α) through the relation, $\sigma = nc\alpha/4\pi$, where c is the velocity of light [37]. A plot between the optical conductivity versus photon energy for 4BP4AP single crystal is shown in Fig. 14b. It is clear from the graph that the optical conductance remains constant up to the photon energy of 2.7 eV beyond which it increases with increase in the photon energy.

3.7. Nonlinear optical studies

The Kurtz and Perry powder SHG efficiency test was performed to check the second order NLO activity of the 4BP4APcrystal [38]. A



Fig. 11. Thermal plots of 4BP4AP single crystal.



Fig. 12. Optical absorption and transmittance spectrum of 4BP4AP.

Q-switched, 8 ns Nd: YAG laser beam of wavelength 1064 nm, with beam energy of 3.3 mJ/pulse was used. The powdered 4BP4AP crystal was packed in a micro-capillary of uniform bore and exposed to laser radiations. As expected, no green light was generated. This indicates that the crystal is SHG inactive due to its centrosymmetric crystal structure.

To explore the third order nonlinearity of the crystal, the open aperture z-scan experiment was performed. A 0.02 M solution of 4BP4AP in DMF was taken in a 1 mm quartz cuvette and exposed to a Q-switched Nd: YAG laser beam of wavelength 532 nm having a repetition rate of 10 Hz and pulse width of 5 ns. Cuvette containing the sample solution was moved along the z-axis with the help of a stepper motor, controlled by a computer. The laser beam was focused with the help of a 20.5 cm convex lens and the normalized transmittance data was collected using RJP 735 pyroelectric detector. The experimental open z-scan aperture trace of 4BP4AP for a laser input energy of 50 μ J is shown in the Fig. 15.

To calculate the nonlinear absorption (NLA) coefficient (β_{eff}) the experimental open aperture z-scan data was fitted with the theoretical open aperture z-scan equation [23]:



Fig. 13. Tauc's plots of 4BP4AP.



Fig. 14. Plots of (a) Refractive Index as a function of wavelength, (b) Optical Conductivity Versus photon energy.



Fig. 15. Open aperture Z –scan curve of 4BP4AP. The solid line is the theoretical fit of the experimental data in the nanosecond excitation regime.

$$T(z) = 1 - \frac{I_0 L_{eff} \beta_{eff}}{2\sqrt{2}} \left(\frac{1}{1 + z^2/z_0^2}\right)$$
(7)

In the above equation, I_0 is the on-axis peak irradiance at focus, z is the distance of the sample from the focus, $z_0 = \pi w_0^2 / \lambda$ is the Rayleigh length of the sample (λ is the wavelength and w_0 is the beam waist at the focus), L_{eff} is the effective thickness of the sample given by $L_{eff} = [1 - e^{-\alpha L}]/\alpha$, α being the linear absorption coefficient. It is clear from the z-scan trace (Fig. 14) that at focus the transmission is least and hence there is maximum absorption. This implies that 4BP4AP has positive NLA coefficient. The NLA in a medium may be due to excited state absorption, two photon absorption (TPA), free carrier absorption and reverse saturable absorption (RSA) [17]. The relation between the NLA coefficient (β) and the molecular TPA coefficient (σ_2) is $\beta = \sigma_2 N_A C \times 10^{-3}$, where C is the concentration (mole/litre), N_A is Avogadro number. The molecular TPA cross section (σ_2^1) can be calculated from the equation, $\sigma_2^1 = \sigma_2 h\nu$, where $h\nu$ is the photon energy. The excited state absorption (σ_{ex}) can be determined by fitting normalized open aperture z-scan data with the equation [17]:

$$T(z) = \frac{\ln(1 + q_0/1 + x^2)}{q_0/1 + x^2}$$
(8)

where $x = z/z_0$, z is the distance of the sample from the focus, z_0 is the Rayleigh length. q_0 can be calculated from the relation,

$$q_0 = \frac{\pi \sigma_{ex} F_0 L_{eff} \alpha}{h\omega} \tag{9}$$

Here F_0 is the on-axis fluence at focus, ω is the angular frequency, ' α ' is the linear absorption coefficient of the sample. The ground state absorption is given by $\sigma_g = \alpha/N_AC$. The calculated values of $\beta_{effi}\sigma_2, \sigma_2^1$, σ_{ex} , and σ_g are 3.2 cm/GW, 2.66 $^{-28}$ cm⁴/W, 9.92 $^{-47}$ cm⁴S, 4.05 × 10⁻¹⁸ cm² and 1.5 × 10⁻²⁰ cm² respectively. The value of σ_{ex} is 270 times greater than that of σ_g and hence the condition for RSA is satisfied [39], β_{eff} of 4BP4AP is compared with some of the reported NLO materials and found that the effective beta of 4BP4AP is greater than many of the chalcone derivatives (Table 4), it is greater than that of benzilidine derivatives [40] and hydrazone derivatives [8]. Further, β_{eff} of 4BP4AP is 2.1 times that of terphenyl chalcone, 3-(4-bromophenyl)-1-(4,4"-difluoro-5'-methoxy-1,1':3',1"-terphenyl-4'-yl)prop-2-en-1-one [41]. This shows that 4BP4AP is an efficient new entrant for NLO device applications.

The molecular static and frequency dependent first hyperpolarizabilities of the crystal 4BP4AP were calculated using the semiempirical computer program molecular orbital package, MOPAC 2012 [44]. For calculations PM7 Hamiltonian was used [45]. The geometry obtained from the single crystal XRD study of the molecule was used as an input to this program. To optimize the geometry the default geometry optimizer, Eigenvector Following (EF) geometry optimizer was used. The Time-Dependent Hartree-Fock (TDHF) theory was used to compute the molecular hyperpolarizabilities. The keyword "PRESICE" was used as the convergence criterion for PM7. The computed static (β_0) and frequency dependent (β_{1064nm}) first molecular hyperpolarizabilities of 4BP4AP are 3.5×10^{-30} esu and 7.02×10^{-30} esu respectively.

The compound under investigation 4BP4AP, possesses a donor $-\pi$ – acceptor (D– π –A) type push–pull structure. In this compound, both pyridine and carbonyl group act as electron acceptors, whereas the bromo phenyl group acts as an electron donor. The intramolecular charge transfer thus takes place from one end of the molecule to other through the conjugated -CH=CH-double bond.

Table 4	4					
Third	order	NLO	Coefficients	of	Some	Chalcone
deriva	tives.					

Crystal	β (cm/GW)
4MSTP [17]	1.1
CDAC [18]	1.3
TTCP [42]	2.463
CTDMP [21]	3.05
3bisMPC [43]	3.25
MPNP [43]	2.65
4BP4AP*	3.2

CDAC - 1-(4-chlorophenyl)-3-(4-dimethylaminophenyl) prop-2-en-1-one.

4MSTP 1-[4-(methylsulfanyl)phenyl]-3-(2,4,5trimethoxyphenyl)prop-2-en-1-One.

1-(2'-thiophen)-3-(2,3,5-trichlorophenyl)-2-TTCP propen-1-one.

3bisMPC - 1,3-bis(4-methoxyphenyl)prop-2-en-1-one. MPNP-1-(4-methoxyphenyl)-3-(3-nitro- phenyl)prop-2en-1-one.

CTDMP 1-(5-chlorothiophen-2-yl)-3-(2,3dimethoxyphenyl)prop-2-en-1-one.

*present work.

Br group being strong electron donor pushes the electron towards the acceptor groups and hence there is an effective charge transfer taking place across the molecule. The molecules are held together in the crystal structure by a network of C-H ... O and C-Br ... N hydrogen bonds (Fig. 10). These hydrogen bonds offer a charge asymmetry in the molecule which is a necessary condition for NLO property [46]. The asymmetric unit of the compound contains a planar molecule with dihedral angle between the benzene and pyridine of 9.41°. This kind of planar structure increases the degree of π -conjugation which in turn increases the extent of charge transfer across the molecule thus contributing to the nonlinearity. Further, as can be seen in the packing diagram of the crystal (Fig. 9), the molecules are arranged in anti parallel layers and in each layer there is a head to tail molecular arrangement. Thus, observed third order nonlinearity in 4BP4AP may be attributed to its molecular structure and packing of molecules in the crystal structure.

3.8. Optical power limiting studies

Optical limiters are the devices which have a high transmittance for low intensity signals but a low transmittance for high intensity signals such as for laser beams. Optical limiters (OL) are used to protect the optical sensors from high intensity laser beams. They are also used to protect the human eye. For nanosecond laser pulses, molecules with reverse saturable absorption (RSA) exhibit strong optical limiting behavior. RSA occurs in materials where the ground state absorption cross section is lesser than that of the excited state [47]. Since σ_{ex} is greater than σ_{g} for 4BP4AP, the optical limiting property is achievable in this molecule. Optical limiting property of the 4BP4AP molecule is extracted from the open aperture z-scan data [48]. Fig. 16 shows the variation of normalized transmittance of 4BP4AP molecule with laser power density. It is clear that the transmittance decreases with increase in the input laser intensity. At lower irradiance, 4BP4AP responds linearly to the input intensity and obeys Beer's law. But as the input intensity increases, the transmittance of the sample decreases and this variation of transmittance indicate the optical limiting behavior of 4BP4AP.

4. Conclusion

The NLO material, 4BP4AP was synthesized and single crystals of



Fig. 16. Optical limiting behavior of 4BP4AP crystal.



this compound were successfully grown by the solution growth technique at room temperature using DMF as the solvent. The molecular structure of the grown crystals was confirmed by EDAX, FTIR, FT-Raman and single crystal XRD analysis. 4BP4AP is highly transparent both in the visible and in the IR region with a cutoff wavelength of 417 nm. Using the approximate formulae the various optical parameters were evaluated from the spectrophotometric measurement. The optical energy band gap obtained from Tauc's plot is 3.09 eV. The SEM studies showed a two dimensional growth pattern with smooth surface morphology. The crystal is thermally stable up to its melting point. From the open aperture z-scan experimental studies, it was found that the crystal has a positive nonlinear absorption coefficient. The decrease in nonlinear transmission with the increase in the input laser intensity indicates that 4BP4APsingle crystal can be used as an optical limiter.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.molstruc.2016.04.052.

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