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Crucial role of molecular planarity on the second order nonlinear optical property of pyridine based chalcone single crystals

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An efficient nonlinear optical material 2E-3-(4-bromophenyl)-1-(pyridin-3-yl) prop-2-en-1-one (BPP) was synthesized and single crystals were grown using slow evaporation solution growth technique at room temperature. Grown crystal had prismatic morphology and its structure was confirmed by various spectroscopic studies, elemental analysis, and single crystal X- ray diffraction (XRD) technique. The single crystal XRD of the crystal showed that BPP crystallizes in monoclinic system with noncentrosymmetric space group P2₁ and the cell parameters are a =

5.6428(7) Å, b = 3.8637(6) Å, c = 26.411(2) Å, β = 97.568(11) deg and v = 575.82(12) Å³. The UV-Visible spectrum reveals that the crystal is optically transparent and has high optical energy band gap of 3.1 eV. The powder second harmonic generation efficiency (SHG) of BPP is 6.8 times that of KDP. From thermal analysis it is found that the crystal melts at 139° C and decomposes at 264° C. High optical transparency down to blue region, higher powder SHG efficiency and better thermal stability than that of urea makes this chalcone derivative a promising candidate for SHG applications. Furthermore, effect of molecular planarity on SHG efficiency and role of pyridine ring adjacent to carbonyl group in forming noncentrosymmetric crystal systems of chalcone family is also discussed.

Keywords

Nonlinear optical Crystal growth X-ray diffraction Second harmonic generation Thermal analysis

1. Introduction

The demonstration of second harmonics in quartz single crystal by Franken et al led to the development of an exhilarating field of modern times known as nonlinear optics (NLO) which has plethora of applications in the field of opto-electronics [1-3]. The most desirable properties for a material to be the best NLO material are high power conversion efficiency, large transparency extending down to UV region, high melting point, high mechanical stability, high chemical inertness, high laser damage threshold, phase matching etc [4,5]. Among the various classes of materials investigated for NLO properties, organic materials received unique consideration. The optical nonlinear behavior in this class of materials is electronic in origin and can be tuned through structural modifications [6]. These are characterized by an extremely extended π -conjugated chain with strong electron acceptor-donor pairs at the ends (D– π –A) [4, 7]. Organic NLO materials are very often formed by hydrogen bonds and Van der Waals forces and hence posses high degree of delocalization. Due to the overlap of π orbits, delocalized electronic charge distribution leads to high mobility of the electron density. The optical nonlinearity can be increased by functionalizing the ends of the π bond system with apt electron donor and acceptor groups [8]. Hence, the search for new NLO materials had never ceased.

Chalcone derivatives are an interesting type of organic NLO materials which can be tuned to match the requirements. In these systems, two aromatic rings have to be substituted with suitable electron donor or acceptor groups like -OCH3, -SCH3, -Cl, -Br etc to increase the asymmetric charge distribution in either or both ground state and excited states, giving rise to an enhanced optical nonlinearity [9,10]. The substitution of electron acceptors/donors on either of the benzene rings of chalcones significantly influences the noncentrosymmetric crystal packing structures requisite for second harmonic generation (SHG) [11]. Thus, chalcones can be considered as cross-conjugated molecules that possess two independent hyperpolarizable parts to have a two-dimensional β character [12]. Recently several chalcone derivatives have been reported where the phenyl moiety adjacent to carbonyl group was replaced with pyridine moiety [13-19]. The results show that these derivatives exhibit good second order NLO response. Among these, the chloro substituted chalcone [17] showed a SHG efficiency of 3.68 times that of urea and methoxy group substituted chalcone MPP [13] showed a SHG efficiency of 4.7 times that of urea. This high SHG response is attributed to the donor group substituted at *para* position of the phenylene moiety and the zigzag head-to-tail alignment of molecular dipoles in the crystal structure. This shows that a para substituent on the phenyl ring and the zigzag head-to-tail alignment of molecular dipoles connected through strong intermolecular hydrogen bonds in the crystal structure is necessary for enhancing the SHG activity of organic materials [12, 20]. It is well known that for a material to have highly efficient NLO properties, the constituting molecules must exhibit large molecular hyperpolarizabilities (β). Further, β increases with the increase in the electron donating strength of the substituent [21]. The electronagativity of Br group is 2.8 (Pauling value) [22] and hence its electron donating ability is greater than that of chloro and methoxy groups. Also it is reported that the Br substitution in chalcones results in non-centrosymmetric crystal structure, required for a crystal to exhibit second order optical nonlinearity [23]. With the anticipation of an efficient NLO material, a pyridine based bromo substituted donor- π -acceptor (D- π -A) type chalcone derivative was designed. The present article describes the synthesis, crystal growth and characterization of a nonlinear optical material, 2E-3-(4-bromophenyl)-1-(pyridin-3-yl) prop-2-en-1-one (BPP).

2. Experimental procedure

2.1. Material synthesis and single crystal growth

BPP was synthesized by the Claisen–Schmidt condensation reaction [24]. A mixture of Analytical Reagent grade chemicals, 3-acetyl pyridine (0.01mol) and 4-bromobenzaldehyde (0.01mol) in methanol (50 ml) was prepared without further purification. Aqueous solution of

sodium hydroxide (5 ml, 20%) was then added drop wise, and the mixture is stirred for 2 hours. The temperature of the solution was maintained within the range of $26-30^{\circ}$ C throughout the stirring process. The contents of the flask were poured into a beaker containing ice-cold water and kept aside for 24hrs. The crude product was then collected by filtration, washed with excess of water and dried. The crude product was used for the single crystal growth without further purification. The synthetic scheme of the product is shown in Fig. 1.

Single crystals of BPP were grown by slow evaporation solution growth technique using N,N-dimethyl formamide (DMF) as the solvent at room temperature. A saturated growth solution was prepared by dissolving the synthesized compound in DMF in a 100 ml beaker at room temperature; the solution was filtered to remove suspended particles. The solvent was allowed to evaporate slowly by covering the beaker with a polythene sheet with few pin holes in it. Single crystals of BPP were harvested from the growth solution after 45-50 days. Good quality single crystals were selected for further study. A photograph of the grown crystals is shown in Fig. 2a. The morphology of the single crystal of BPP was simulated using the software WinXMorph [25, 26]. Data obtained from the single crystal XRD study were used as the input to index the faces in the crystal and is shown in Fig. 2b. The crystal has a higher growth rate along crystallographic baxis compared to other two axes which results in the elongation of the crystal along this direction. Morphology of BPP may change if it is crystallized by changing the solvent.



Fig. 1. Scheme for synthesis of BPP.





2.2. Characterization methods

In order to establish that the material (BPP) obtained is certainly that of the desired compound, energy dispersive X-ray analysis (EDAX) was carried out on the sample. The grown crystal was subjected to EDAX analysis using JEOL JSM-6380LA analytical scanning electron microscope (SEM) system. The recorded spectrum of BPP is shown in Fig. 3. The peaks in the EDAX spectrum confirm the presence of C, N, O and Br in the compound. The EDAX elemental analysis confirms the formation of the compound.



Fig. 3. EDAX spectrum of BPP

The surface morphology of the BPP single crystal was studied by scanning electron microscopy (SEM). A JOEL JSM-6380LA analytical scanning electron microscope was used for the analysis. SEM was operated at 20 kV and probe current was 1 nA and the sample was kept in high vacuum. Due to the non-conducting behavior of the organic materials, gold coating is done by sputtering technique before subjecting the surface of BPP crystal to electron beam.

The FT-Raman and FT-IR spectral analysis of BPP was carried out to identify the presence of functional groups and their vibrational modes. A BRUKER RFS 27, Stand alone FT-Raman Spectrometer, having spectral resolution of 2 cm⁻¹ with an exciting wavelength of 1064 nm from an Nd: YAG laser source was used to record the FT-Raman spectrum. The FT-IR spectrum was obtained by mixing the compound with KBr pellets. The spectrum was recorded between 500 cm⁻¹ and 3500 cm⁻¹ by a Thermo Nicolet, Avatar 370 FTIR spectrometer outfitted with KBr beam splitter and a DTGS detector, with a spectral resolution of 4 cm⁻¹.

A Bruker Avance III FT-NMR spectrometer was used to record the ¹H NMR spectrum of BPP with CDCl3 as the solvent and tetramethylsilane (TMS) as the internal standard. The grown crystal was subjected to single-crystal X-ray diffraction (XRD) studies. A Bruker SMART APEX diffractometer with CCD area detector using graphite monochromated MoKα radiation of wavelength 0.71073 Å was used to solve the three dimensional structure. Crystal data were collected with a scan width of 1°. The crystal structures were solved by direct method and refined by full matrix least squares method using SHELXL-97 [27] in the WinGx package suite [28] with isotropic temperature factors for all the atoms. For molecular graphics X-seed [29] and Mercury [30] software was used. A transmission spectrum is very important for any NLO materials as a non linear material can be used for practical applications such as frequency doubling if it has wider transparency window [31]. In this view UV–VIS–NIR absorption spectrum of the BPP crystal was recorded using a Varian, Cary 5000 UV–VIS spectrophotometer in the wavelength range of 200–1100 nm.

To study the thermal stability of the crystal BPP, thermo gravimetric (TG)/differential thermal (DT) analysis and differential scanning calorimetric (DSC) analysis was carried out. TG/DT analysis was done using a Perkin Elmer simultaneous TG/DTA analyzer. Powder sample of the crystal was taken for this purpose and the analysis was carried out under the nitrogen atmosphere at a heating rate of 10° C per minute in the temperature range from 30° C to 350° C. The DSC plot for the crystal BPP was obtained using Mettler Toledo DSC 822e thermal analyzer on a sample weight of 1.188 mg in the temperature range 50° C to 190° C, at a rate of 10° C /min,

in nitrogen atmosphere. Kurtz and Perry Technique [32] of powder SHG efficiency measurement enables one to measure SHG efficiency of a new material relative to standard KDP or urea. A Q-switched 8 ns Nd: YAG laser beam delivering energy of 4.4 mJ/pulse at a wavelength of 1064 nm with 10 Hz repetition rate is used as light source in the experiment. A fine powder of BPP crystal was tightly packed in a micro-capillary of uniform bore and exposed to laser radiations. The output from the sample was monochromated and the intensity of 532 nm component was collected. The emission of green light confirms the generation of second harmonics. The electrical signal corresponding to the SHG output was displayed on a storage oscilloscope for measurement. Urea and KDP, powdered to the same particle size as that of the experimental sample, were used as indication materials for the present measurement.

3. Results and Discussion

The SEM images of 70x and 5000x magnification are shown in Fig. 4a and 4b respectively. From the Fig. 4a, it is clear that the surface of the crystal appears smooth with some micro-crystals on the surface. These inclusions are formed during the crystal growth and are influenced by the growth conditions. Fig. 4b shows a layered growth pattern which is an indication of two dimensional growth mechanisms [33]. The uneven darker and brighter regions seen on the surface are might be due to the inclusion of solvent, a common event in solution grown crystals.



Fig. 4. SEM images of BPP

FTIR and FT-Raman spectra are shown in Fig. 5 and Fig. 6 respectively. The characteristic frequencies and corresponding assignments confirming the presence of various functional groups in the material are tabulated in the Table 1. The FT-IR and FT-Raman spectral study ascertains the various functional groups present in the compound.

Table 1

Wave number (cm ⁻¹)		Assignment
FT-IR lines	FT Raman lines	
3081.9	3064	aromatic C-H stretching
1658.1	1658.8	C=O stretching vibration
1588.9	1583.9	aromatic ring vibrations
1481.9	1484.4	chalcone C=C stretching vibrations
1396.6	1401.4	aromatic C=C stretching vibrations
-	1351.3	C-N stretching vibration
1317.7	-	C-H bending vibration
1233.18, 1186.49	1242.8, 1176.2	aromatic C-H in-plane bending
1039.59	1027.2	vibrations
970.25	976.4	CH=CH stretching vibration
799.62	-	C-Br stretching vibration
691.5, 614.64	702.5, 627.7	Out of plane C – H aromatic bending
		vibrations
C		

Assignments of vibrational frequencies:



Fig.6. FT-Raman spectrum of BPP crystal.

The ¹H NMR spectrum displayed in Fig.7 shows two doublets centered at δ =7.761 ppm and 7.496 ppm with a coupling constant of 15.6Hz each corresponds to –C8-H8 and –C7-H7 protons of -CH=CH- moiety. The estimated strong coupling constant J = 15.6 Hz represents the *trans* coupling of the adjacent protons, and this confirms the trans geometry of the double bond of chalcone. A multiplet signal resonated at 7.564-7.590 ppm integrates for three protons (2H, -C2-H2 & -C6-H6 of 4-bromophenyl ring and 1H, -C13-H13 of pyridine ring). The peak at 7.26 ppm is due to the solvent CDCl3. The other characteristic peaks observed in the spectrum are assigned as given below. Thus the ¹H NMR spectral study confirm the functional groups present in the title compound BPP and hence the molecular structure.

δ (ppm): 9.223-9.228(dd, 1H, -C10-H10 of pyridine ring), 8.805-8.821(td, 1H, -C12-H12 of pyridine ring), 8.273-8.302(td, 1H, -C14-H14 of pyridine ring), 7.513-7.503(d, 2H, -C3-H3 & -C5-H5 of 4-bromophenyl ring).



From single-crystal XRD studies, it has been found that the compound crystallizes in the monoclinic crystal system with a space group $P2_1$, which suggests that the crystal is noncentrosymmetric in nature, thus satisfying one of the essential requirements for the SHG activity of the crystal. An ORTEP plot of the molecule at 50 % probability is shown in Fig. 8. The details of the crystal data and refinement are given in Table 2.

The molecule of the title chalcone derivative exists in *E* configuration with respect to the -C7=C8- double bond [1.336 Å]; the torsion angle C6-C7-C8-C9 is 176.28°. The dihedral angle between the pyridine and 4-bromophenyl rings is 19.96° and therefore the molecule is almost planar. The carbonyl group is also planar with respect to the adjacent pyridine unit showing a torsional angle O1-C6-C1-C5 of 5.65°. The degree of planarity of molecule correlates with the degree of π -conjugation throughout the molecule. This increases the donor-acceptor interactions across the molecule which in turn enhances the degree of molecular charge transfer and degree of nonlinearity [32]. The bromine atom is displaced from C9 - C14 mean plane by 0.006 Å. Atoms of the propenone bridge (C7, C8, C9 and O1) lie almost on the same plane and the torsion angle O1-C6-C7-C8 is -10.11°. The mean plane through this bridge makes dihedral angles of 7.32° and 19.37° with the planes of pyridine and benzene rings respectively. The packing diagram displayed in Fig. 9 shows that the molecular dipoles are aligned in zigzag head to tail fashion stacked along b axis. The crystal structure is stabilized by weak intermolecular C-H^{...}O and C-H."N hydrogen bonds (Fig. 10) which forms an infinite molecular chain along a axis. It is interesting to note that the arrangement of molecules in the crystal structure of BPP is very similar to that in CPP [17].



Fig.8. ORTEP diagram of BPP. Thermal ellipsoids were drawn at 50 % probability level.



Fig. 9. Packing diagram viewed down the a-axis. Red arrow indicates the molecular dipole calculated from MOPAC 2012 semi empirical package and green arrows indicate the alignment of the dipoles in the crystal structure.

TABLE 2

Crystal data of BPP Crystal

	Empirical formula	C ₁₄ H ₁₀ Br NO
	Formula weight	288.14 g mol ⁻¹
	Crystal Size	0.3 x 0.10 x 0.03 mm ³
	Crystal System	monoclinic
	Space group	P 2 ₁
	Unit cell parameters	a = 6.0063(7) Å
		b = 5.0134(6) Å
	0	c = 20.246(2) Å
	Cell Angles	$\alpha = 90, \beta = 97.568(11), \gamma = 90 \text{ (deg)}$
		Z = 2
	Volume	604.35(12) Å ³
v	Radiation	Mo Kα radiation
	Radiation Wavelength	0.71073 Å
	Temperature	T = 295(2) K
	Density	1.606 kg/m^3
	Absorption Coefficient	3.383 µ/mm ⁻¹
	F(000)	296

θ range for data collection	3.04 - 27.55 (deg)
Limiting indices	-7<=h<=7, -6<=k<=6, -26<=l<=26
Max. And min. Transmission	0.9053 and 0.4302
Refinement method	Full-matrix least-squares on F ²
No. of measured reflections	3030
Measured No. of unique reflections	2166
No. of independent reflections	1443
No. of parameters	154
Goodness-of-fit on F^2	0.984
No. of restraints	1
R_all, R_obs.	0.0938, 0.0604
wR_2 _all, wR_2 _obs.	0.1483, 0.1237
$\Phi_{min, max}/e Å^{-3}$	-0.638, 0.528



Fig. 10. Partial packing diagram of BPP viewed down the b-axis. The only hydrogen atoms involved in bonding are shown for clarity.

The recorded UV–VIS-NIR spectrum is shown in Fig. 11. The spectrum shows that the crystal possesses a wide transparency from 419 nm to 1100 nm, 419 nm being the lower cut-off wavelength. The absence of absorbance and overtones due to electronic transitions above this wavelength is an essential parameter for frequency doubling process using solid- state and diode lasers [34]. The inset of Fig.8 shows a reflectance of more than 85% in the entire visible region. Thus the crystal can be used to obtain SHG in the visible region.

The optical band gap, which is responsible for the sharpness of the absorption edge of the single crystals, can be found out by the mechanism of band to band transitions. The optical absorption coefficient (α) has been evaluated from the recorded absorbance (A)-wavelength data of the crystal using the relation, $\alpha = (2.303/d) \times A$ where 'd' is the thickness of the crystal. This value is used to determine optical band gap of the grown crystal following the Tauc's relation, $\alpha = (h\nu - Eg)^n$. Here h is Planck's constant; ν is the frequency of the incident radiation and E_g is the optical energy band gap [35]. A plot of $(\alpha h\nu)^2$ versus h ν (Fig. 12), gives the direct band gap of the crystal. The band gap value (3.1 eV) is obtained as the intercept of the linear fit of $(\alpha h\nu)^2$ with the abscissa (Fig. 12(b)).



Fig. 11. Optical absorption spectrum of BPP. Inset figure shows the reflectance spectrum of the crystal



Fig. 12. Tauc plot of the crystal BPP

The results of the thermal analysis are shown in the Fig. 13. The DTA curve shows that the compound undergoes an irreversible endothermic transition at 122.4° C where melting begins. The peak of the endothermic, which represents the temperature 139.78° C at which melting terminates corresponds to the melting point of the crystal and the same was also observed in the DSC plot. The sharp endotherm in the DSC response curve represents solid state transition of relatively pure material [36]. In the TG curve, no weight loss was observed at the melting point. Below the melting temperature, no endothermic or exothermic peaks were observed which indicates the absence of any phase transitions and its thermal stability in this region. The resistivity of the crystal against thermal crack is clearly evident as the DSC curve is smooth up to the melting point. In the TG curve, weight loss begins to occur at about 175° C which is due to the volatilization of the compound without decomposition. A weight percentage of 96.83% at this temperature may be attributed to the loss of water. A major weight loss of 87% was observed in the TG curve between 198° C and 279° C and is due to the decomposition of BPP. The peak at 264.5° C in the DTA plot shows the complete dissociation of the compound into gaseous products. Thermal stability of BPP is better than that of standard urea (130° C) and do not get decomposed till the melting temperature. This ensures the firmness of the crystal for NLO applications involving laser where the crystal has endure very high temperatures.

From the DSC curve, the molar enthalpy of fusion $\Delta_{fus}H_m$ of the crystal BPP was estimated adopting the area integration method and is found to be 81.47 Jg⁻¹. The molar entropy of fusion $\Delta_{fus}S_m$ was calculated using the thermodynamic equation [18] $\Delta_{fus}S_m = \Delta_{fus}H_m/T_m$, where T_m is the melting point of the crystal. The calculated molar entropy of fusion is 0.197 JK⁻¹g⁻¹.



Fig.13. TG/DTA/DSC response curves of BPP

Nonlinear Optical Property: Structure-Property Relationship.

The SHG conversion efficiency of BPP crystal measured by the classical powder SHG efficiency test was found to be 6.8 times that of KDP and 1.4 times that of urea. SHG efficiency of BPP is nearly 7 times greater than that of 3-(2,3-dimethoxyphenyl)-1-pyridin-2-yl)prop-2-en-1-one [15], twice that of 1-(4-chlorophenyl)-3-(4-chloroyphenyl)-2-propen-1-one [8], 1.5 times greater than that of 1,3-bis-(4-methoxyphenyl)prop-2-en-1-one [37], 3-(2,3-dichorophenyl)-1-pyridin-2-yl)prop-2-en-1-one [16] and 1-(4-methylphenyl)-3-(4-N,N-dimethylaminophenyl)-2-propen-1-one[38] and comparable to that of 2,4-dichloro-4 -bromochalcone[39].

Using semiempherical computer program molecular orbital package, MOPAC 2012 [40] the molecular static and frequency dependent first and second hyperpolarizabilities of BPP

crystal were calculated using PM7 Hamiltonian [41]. The geometry obtained from the single crystal XRD study of the BPP molecule was used as an input to the MOPAC 2012 program. The geometry was optimized using the default geometry optimizer, Eigenvector Following (EF) geometry optimizer. Using Time-Dependent Hartree–Fock (TDHF) theory, the molecular hyperpolarizabilities were calculated. As a convergence criterion for PM7 calculation of geometries and the NLO properties, the keyword "PRESICE" was used. The computed static and frequency dependent first (β_0 , β_{1064nm}) and second (γ_{1064nm}) molecular hyperpolarizabilities of BPP are 5.54x10⁻³⁰ esu, 11.88x10⁻³⁰ esu and 25.36x10⁻³² esu respectively. The molecular first hyperpolarizabilities at 1064 nm of some of the reported chalcones along with other properties are presented in Table 3.

Table 3.

Properties of some chalcone derivatives.



Compound	R	R ₁	β_{1064nm}	SHG	Melting	Dipole	λ_{cutoff}
			$(10^{-30} esu)$	(XJrea) po	$\operatorname{point}(^{0}\mathrm{C})$ n	noment (D) (nm)
1[23]	С	OCH3	46.70	8.5	73	2.45	440
2[13]	o-N	OCH3	35.62	4.7	81	1.53	410
3[17]	m- N	Cl	11.57	3.7	133	1.23	417
4[23]	С	Br	86.40	7	125	2.12	435
5*	m-N	Br	11.88	1.4	139	1.16	419

*Present work

The title molecule BPP has a D- π -A push pull structure formed by the electron donating Br group at one end and the carbonyl group along with pyridine ring acting as electron accepting moiety being at the other end of the molecule. This means that the direction of the contributing charge transfer or the dipole moment is form carbonyl to bromo group (Fig. 9). As result there is delocalization of the electronic charge within the molecule. The donor-acceptor groups are interconnected by conjugated -C=C- double bond which forms the pathway for the effective charge transfer across the molecule.

Chalcone derivatives, such as CPP[17], 4NP3AP[18], MPP[13] and PDBA[42] reported earlier by our group, showed very good SHG efficiency and is ascribed to the arrangement of

molecular dipoles in the crystal structure. The zigzag head-to-tail alignment of dipoles stacked in to parallel columns and the fashion in which they are interconnected through the hydrogen bond interactions in these crystals resulted in a net polarization due to the reckoning of individual dipole contributions. This kind of head-to-tail configuration was also observed for *p*-methoxy chalcone [43] and MMONS [44] crystals possessing a very high SHG of 8.5 and 1259 times that of urea respectively. In the present case, the molecular dipoles are stacked in parallel columns along the crystallographic b - axis in a zigzag fashion as shown in Fig. 9. The C-H⁻⁻⁻O and C-H⁻⁻⁻N hydrogen bond interactions shown in the partial packing diagram (Fig. 10) consolidate the structure in enantiomorphic form and controls the orientation of molecules. This establishes the observed high SHG efficiency of BPP.

Table 4.

Sl. No.

6 [45]

7 [46]

8 [47]

9 [48]

R

С

Ν

С

N

H

OCH3

OCH3

OCH₃

Η

Η

OCH₃

OCH3

OCH3

Hyperpolarizabilities, space group and dipole moments of trimethoxy substituted chalcone derivatives.

			25	Ry Ry	
R_1	R ₂	R ₃ R ₄	R_5	Space	β_{1064nm}
				Group	$(10^{-30} esu)$
Н	OCH ₃	OCH ₃ OCH ₃	Н	P2 ₁ /c	12.9

OCH₃

Η

Η

Η

OCH3

OCH3

Pna₂

 $P2_1/c$

Fdd2

Dipole

moment (D)

2.50

2.76

5.54

5.01

21.7

13.7

23.3

For a material to exhibit strong macroscopic second order nonlinearity, the constituting molecules must exhibit large molecular hyperpolarizabilities (β), which is evident from Table 3. Further, the macroscopic SHG depends on the orientation of molecules in the crystal structure. Since acentric crystal structure is necessary for strong SHG, the molecules should possess small ground state dipole moments which lead to a favorable molecular orientation in the crystal by minimizing the dipole-dipole interaction. Zhao *et al* [23] and Fichou *et al* [49] suggested the bulky bromo group as an effective substituent at the *para* position of the phenylene moiety of the chalcones for obtaining noncentrosymmetrics crystal structures. As can be seen from table 3, the

replacement of benzene ring near to the carbonyl group by pyridine ring brings down the dipole moment and results in the crystallization of the compounds in acentric style. The table 4 provides further evidence for this argument. The expected SHG efficiency in compounds 6 and 8 is zero, since these compounds crystallize in centrosymmetric space group $P2_1/c$ [20]. But compounds 7 and 9 where in a pyridine ring is substituted adjacent to carbonyl group, crystallizes in noncentrosymmetric crystal system which is a prerequisite condition for SHG activity. Thus, in addition to the bromo group, the pyridine moiety at the benzoyl arm instead of phenyl moiety is also an effective replacement. But this resulted in decreased β value and hence the SHG of compounds 2 and 5 in comparison with that of compounds 1 and 4. This decrease in SHG can be attributed to the variation in the extent of charge transfer across the molecule due to the difference in the planarity of the molecules and electron donating abilities of methoxy and bromo groups. The degree of π -conjugation depends on the degree planarity of molecule. The planar structure increases the extent of intramolecular charge transfer across the molecule and hence the degree of nonlinearity and any deviation from planarity results in its reduction [17]. The degree of planarity in compound 2 is high as indicated by the dihedral angle between phenyl and pyridine rings of 2.04° . The molecule of compound **3** is almost planar as indicated by the dihedral angle of 19.53° . In the present case (compound 5) the dihedral angle is 19.96° due to which the crystal BPP shows a lower SHG efficiency. Thus, though Br group is a better electron donor compared to Cl group, the lower SHG of BPP when compared to compound 3 may be due an extra twist of small angle between phenyl and pyridine rings in BPP. Moreover, pyridine ring improves the thermal stability and optical transparency of the material.

4. Conclusion

An efficient NLO material 3-(4-bromophenyl)-1-(pyridin-3-yl) prop-2-en-1-one was synthesized and single crystals were grown at room temperature from DMF by the solution growth technique. The functional groups in the compound and hence its structure was established by FTIR and FT-Raman spectral analysis. EDAX elemental analysis and ¹H NMR spectral study confirms the purity of the sample. The crystals are optically transparent in the region above 419 nm and optical energy gap of the material is found to be 3.1 eV. Material is nonlinear optically active with a powder SHG efficiency of 6.8 times that of KDP. Thermal study by TG/DTA and DSC analysis showed that the compound does not get decomposed till its melting temperature of 139^oC. Surface features of the crystals were studies by SEM analysis. The study showed that BPP crystal may be a promising candidate for frequency doubling and other technological applications involving second order NLO property. The investigation of structure – property

relationship of BPP in comparison with other reported compounds reveals pyridine ring as an effective replacement for benzene ring in forming the enantiomorphic crystal structures needed for second order nonlinearity. Further, small deviation from molecular planarity results in a drastic change in the SHG response of the chalcones.

Appendix A. Supplementary information

The crystallographic information file for this paper containing full details of the X-ray data collection and final refinement parameters including anisotropic thermal parameters and full list of the bond lengths and angles has been deposited by us in the Cambridge structure database (CCDC 1026995). These data can be obtained free of charge from The Cambridge Crystallographic Data Center via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK).

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Crucial role of molecular planarity on the second order nonlinear optical property of pyridine based chalcone single crystals



HIGHLIGHTS

- Efficient NLO single crystals are grown by slow evaporation solution growth technique.
- Scanning Electron Microscope image reveals that the crystal has smooth surface morphology.
- Crystal melts at 139°C and decomposes at 264°C.
- Molecular dipoles are stacked in zigzag head-tail fashion in the crystal structure consolidated by hydrogen bonds.
- The pyridine ring plays a significant role in forming enantiomorphic crystal system.