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Crystal growth and characterization of second- and third-order nonlinear optical chalcone derivative: (2*E*)-3-(5-bromo-2-thienyl)-1-(4-nitrophenyl)prop-2-en-1-one

Parutagouda Shankaragouda Patil,^a Shivaraj R. Maidur,^a Mohd Shkir,^b* S. AlFaify,^b V. Ganesh,^b Katturi Naga Krishnakanth^c and S. Venugopal Rao^c

^aDepartment of Physics, KLE Institute of Technology, Opposite Airport, Gokul, Hubballi 580030, India, ^bAdvanced Functional Materials and Optoelectronic Laboratory (AFMOL), Department of Physics, Faculty of Science, King Khalid University, PO Box 9004, Abha 61413, Saudi Arabia, and ^cAdvanced Centre of Research in High Energy Materials (ACRHEM), University of Hyderabad, Hyderabad 500046, India. *Correspondence e-mail: shkirphysics@gmail.com

Experimental and computational studies of linear and nonlinear optical (NLO) properties of (2E)-3-(5-bromo-2-thienyl)-1-(4-nitrophenyl)prop-2-en-1-one (5B2SNC) single crystals are reported. Good-quality and large-sized single crystals of 5B2SNC were successfully grown and characterized by powder X-ray diffraction and high-resolution X-ray diffractometry techniques. 5B2SNC was found to crystallize in the monoclinic noncentrosymmetric space group Cc and possesses moderately good crystalline perfection. The linear optical properties were investigated using the absorption spectrum, which reveals a direct optical band gap of 3.1 eV. The thermal stability was studied with thermogravimetric analysis/differential thermal analysis. The powder second harmonic generation efficiency was evaluated by the Kurtz and Perry method, and 5B2SNC was found to be 26 times more efficient than urea standard. Third-order NLO properties were studied by the z-scan technique with a femtosecond laser. The second hyperpolarizability was obtained to be $\sim 1.45 \times 10^{-31}$ e.s.u. The molecule reveals a strong reverse saturation absorption and negative nonlinear refraction. The molecule exhibited good optical limiting properties, and its limiting threshold was measured to be \sim 3.2 mJ cm⁻². In addition, static electric dipole moments, linear polarizabilities, and first- and second-order hyperpolarizabilities were calculated by density functional theory (DFT). Highest occupied molecular orbital/lowest unoccupied molecular orbital band gaps were also evaluated by DFT calculations. The experimental and theoretical results showed that 5B2SNC exhibits excellent second- and third-order nonlinear optical properties.

1. Introduction

Second- and third-order nonlinear optical (NLO) materials have a wide range of practical applications (Suresh & Arivuoli, 2012), such as optical limiting (Patil *et al.*, 2015; Singh *et al.*, 2014), optical data storage (Åstrand *et al.*, 2000), terahertz wave generation (Krishnakumar & Nagalakshmi, 2008) and two-photon excited fluorescence microscopy (Ftouni *et al.*, 2013). In such applications, organic NLO materials are more promising than inorganic materials (Boyd, 2003; Bosshard *et al.*, 2001). Among the studied organic NLO materials, chalcone derivatives are attractive for their future use in NLO device functions like frequency conversion and optical limiting (Sunil Kumar Reddy *et al.*, 2014; Gu, Ji, Patil & Dharmaprakash, 2008; Ramkumar *et al.*, 2013; D'silva *et al.*, 2012*a*; Kiran *et al.*, 2010). The presence of a carbonyl group, a



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long conjugated chain and various donor/acceptor substituents to two aromatic rings makes chalcone derivatives potential materials for NLO applications. Several studies have been published on chalcones, with the aim of optimizing the nonlinear optical properties (Goto et al., 1990; Zhao et al., 2000; Ramkumar et al., 2015; Shkir et al., 2015; Gu et al., 2009, Gu, Ji, Patil, Dharmaprakash & Wang, 2008; D'silva et al., 2012b). The main idea behind these studies was to introduce various substituents [OCH₃, N(CH3)₂, NH₂, F, Cl, Br, I, CH₃, NO_2 , $COCH_3$] on either side of the benzene rings. The C=O group was always the acceptor. In this way, a number of acentric chalcone crystals exhibiting high nonlinear optical susceptibilities and transparent in the blue spectral region have been synthesized (Sunil Kumar Reddy et al., 2014; Gu, Ji, Patil & Dharmaprakash, 2008; Ramkumar et al., 2013, 2015; D'silva et al., 2012a,b; Kiran et al., 2010; Goto et al., 1990; Zhao et al., 2000; Shkir et al., 2015; Gu et al., 2009; Gu, Ji, Patil, Dharmaprakash & Wang, 2008).

It appeared to us of great interest to modify the chromosphere chalcone group by substituting a thiophene cycle with a bromo group as a substituent for the benzene ring in the styryl part of the molecule and to study the resulting NLO properties (Patil, Rosli et al., 2007; Patil, Ng et al., 2007). Recently, the single-crystal structure of one such synthesized chalcone derivative, (2E)-3-(5-bromo-2-thienvl)-1-(4-nitrophenvl)prop-2-en-1-one (5B2SNC), has been reported (Patil, Rosli et al., 2007). It crystallizes in the monoclinic noncentrosymmetric space group Cc with lattice constants a = 6.3062 (2), b =30.3062 (8), c = 13.1854 (4) Å, $\beta = 94.549$ (1)°, and there are eight molecules per unit cell (Patil, Rosli et al., 2007; Patil, Ng et al., 2007). It possess a $D-\pi - A - \pi - A$ type structure. The 5-bromo-2-thienyl group acts as donor on one end, with C=O as electron-withdrawing assembly in the center and NO₂ as acceptor at other end of molecule (see scheme below). As a part of extensive research on this molecule, herein we present a study of the bulk crystal growth, powder X-ray diffraction (PXRD), high-resolution X-ray diffraction (HRXRD), thermal expansion, transmittance, and second- and third-order NLO properties. The aim of this study is also to determine the linear and nonlinear properties of 5B2SNC through density functional theory (DFT) and Hartree-Fock (HF) methods. To this end, we present a DFT study using the procedure of supermolecular polarization to calculate the linear polarizability (α), first hyperpolarizability (β) and second hyperpolarizability (γ) . The computed values are in agreement with experimental findings. The study provides useful information for the design of new and efficient chalcone derivatives.

2. Experimental procedures

2.1. Synthesis and crystal growth

All reagents and solvents employed were commercially available and used without further purification. 5B2SNC was prepared by the Claisen–Schmidt condensation reaction between equimolar quantities (0.01 mol each) of 5-bromo-2thiophenecarbaldehyde and 4-nitroacetophenone in 60 ml of methanol as illustrated below (Patil, Rosli, *et al.*, 2007):



The final product was obtained as a red-brown microcrystalline solid.

A solubility study revealed that a mixture of acetone–N,Ndimethylformamide (DMF) (1:1) was a suitable solvent proportion for 5B2SNC crystal growth. Crystals were grown by a slow evaporation solution growth technique at room temperature. Solvent evaporation was controlled by a tight covering at the top of beaker, provided by a pored polythene sheet. Transparent red–brown bulk crystals of size $10 \times 4 \times$ 3 mm with definite morphology were obtained within 2 weeks (Fig. 1). The crystals are non-hygroscopic and stable at room temperature.

2.2. Characterization

The crystalline perfection was studied through HRXRD curves using a multicrystal X-ray diffractometer (Lal & Bhagavannarayana, 1989). The powder second harmonic generation (SHG) efficiency of 5B2SNC in comparison with urea standard was measured by a generic method devised by Kurtz and Perry using a Q-switching pulsed Nd:YAG laser



Figure 1 Photograph of grown single crystals of 5B2SNC.

(YAG is yttrium aluminum garnet; duration of pulses 8 ns, repetition rate 10 Hz) operating at 1064 nm (Kurtz & Perry, 1968; Patil & Dharmaprakash, 2007). A finely powdered crystal of 5B2SNC was densely packed in a microcapillary and exposed to a laser beam. The generated second harmonic wave of 532 nm was detected by a photomultiplier tube (Hamamatsu R5109, visible PMT) and converted into electrical signals. For the analysis of third-order NLO properties the *z*-scan technique was used, and its experimental details are given in the supporting material.

2.3. Computational details

Geometry optimization and calculation of molecular properties were achieved with the Gaussian 09 program (Frisch et al., 2009). The obtained results were visualized with the GaussView 5 program (Dennington et al., 2009). To obtain a stable molecular geometry and photophysical and NLO properties, the B3LYP/6-31G*, HF/6-31G*, CAM-B3LYP/6-31G* and wb97XD/6-31G* levels were applied. It is widely recognized that these methods are advantageous for determining sensible and precise geometries, vibrational frequencies, and photophysical and NLO properties, and the obtained results are found to be well correlated with those obtained by conventional experimental methods (Johnson et al., 1993; Reshak & Khan, 2014; Wong et al., 2009; Jia et al., 2014; Karakas et al., 2016; Shkir, Patil et al., 2017). Detailed information on the calculations of various nonlinear parameters is available in the literature (Abbas et al., 2015; Shkir, AlFaify et al., 2017).

3. Results and discussion

3.1. Structural analysis

For structural confirmation and lattice parameter determination, the PXRD pattern of a homogeneously powdered 5B2SNC specimen was recorded; this is shown in Fig. 1S (see supplementary information) with hkl indexing. The sharp peaks of the diffraction pattern confirm the high crystallinity of the grown crystals. The crystal system of the grown crystals

2.43 Å

is found to be monoclinic with space group *Cc*, which confirms the noncentrosymmetric structure. This is a necessary condition for the material to possess second-order NLO properties. The XRD data were used as input in the *POWDERX* software (Dong, 1999) to obtain lattice parameters a = 6.30642, b = 30.29775, c = 13.18594 Å, $\alpha = 90.014$, $\beta = 94.521$, $\gamma = 120.000^\circ$, V = 2172.81482 Å³, which are in good accord with the reported single-crystal data (Patil, Rosli *et al.*, 2007).

3.2. Molecular geometry study

The obtained geometry of 5B2SNC at the B3LYP/6-31G* level of theory is shown in Fig. 2. The initial geometry of 5B2SNC as an asymmetric unit (single molecule) was taken from the previous report (CCDC 636774; Patil, Rosli et al., 2007). The respective bond lengths of 3O-21H and 2S-19Hare found to be 2.89 and 2.44 Å at HF/6-31G*, 2.90 and 2.43 Å at B3LYP/6-31G*, 2.88 and 2.40 Å at CAM-B3LYP/6-31G*, and 2.88 and 2.43 Å at wb97XD/6-31G* levels of theory. These bond lengths are in agreement with the reported experimental values (2.88 and 2.44 Å; Patil, Rosli et al., 2007). The other key bond lengths and angles computed at B3LYP are found to be 1Br-27C = 1.87 Å, 2S-27C = 1.73 Å, 2S-22C = 1.76 Å,3O-17C = 1.22 Å, 4O-6N = 1.23 Å, 5O-6N = 1.23 Å, 6N-6N = 1 $11C = 1.47 \text{ Å}, 27C - 2S - 22C = 90.89^{\circ}, 4O - 6N - 5O =$ $124.78^{\circ}, 4O - 6N - 11C = 117.62^{\circ}, 5O - 6N - 11C = 117.59^{\circ},$ $3O-17C-18C = 121.53^{\circ}$ and $3O-17C-16C = 119.22^{\circ}$, which are also close to experimental values (Patil, Rosli et al., 2007). The results suggest that the parameters of the optimized molecular geometries at different levels of theory are in close accord with experimental values.

3.3. Multicrystal X-ray diffractometry

The recorded HRXRD curve of the 5B2SNC crystal is shown in Fig. 3. The solid line of the convoluted curve fits well with the experimental points, displayed as filled circles. The diffraction curve comprises two other peaks, which are 81 and 76" from the main peak. These extra peaks are due to internal structural low-angle (tilt angle ≥ 1 ' but less than a degree)





120 76' 5B2SNC Diffracted X-ray intensity [c/s] (040) Planes 100 ΜοΚα, (+, -, -, +)80 60 66' 73 40 20 0 0 100 200 300 400



boundaries (Sheik-Bahae *et al.*, 1990; Patil *et al.*, 2016). The full widths at half-maximum (FWHMs) of the main peak and low-angle boundaries are 66, 73 and 64^{''}, respectively, with an angular spread of $\sim 6'$. These characteristics demonstrate the high crystalline perfection of the grown 5B2SNC crystal.

3.4. Optoelectronic studies

3.4.1. Optical and TD-DFT analyses. The measured UVvis-NIR spectrum of 5B2SNC is shown in Fig. 4(*a*). The grown crystals are transparent in the 440–1500 nm wavelength region. The spectrum consists of three absorption bands, at ~366, 274 and 215 nm. The direct and indirect band gap values were calculated to be 3.1 and 2.95 eV, respectively [see inset of Fig. 4(*a*)].

For UV–vis analysis of the 5B2SNC molecule, the TD-DFT methods such as TD-B3LYP, TD-HF, TD-CAM-B3LYP and TD-wb97XD were used at the 6-31G* basis. Fig. 4(b) shows the UV–vis absorption spectra of 5B2SNC computed using the above-mentioned TD-DFT methods. Note that all of the TD-



Figure 4

(a) Experimental UV-vis-NIR absorption and (b) computed spectra of 5B2SNC, obtained with different TD-DFT methods using the $6-31G^*$ basis set.

Table 1

The values	of λ_{abs}	(nm),	E (eV)	and f_0	and	the	major	contribution	s for
transitions	obtained	d at di	fferent	levels	of the	eory			

λ_{abs}	Ε	f_0	Major contributions
405		,0	3
366	3.10	-	_
274	2.95	-	_
319.54	3.88	0.55	$H \rightarrow L + 1 (67\%)$
278.40	4.45	0.19	$H - 4 \rightarrow L(60\%)$
269.73	4.60	0.71	$H \rightarrow L (48\%)$
169.11	7.33	0.94	$H - 1 \rightarrow L + 2 (58\%)$
319.31	3.88	0.83	$H \rightarrow L (63\%)$
247.49	5.01	0.18	$H \rightarrow L + 1 (41\%)$
314.78	3.94	0.86	$H \rightarrow L (60\%)$
245.22	5.06	0.33	$H - 4 \rightarrow L (56\%)$
	$\begin{array}{c} \lambda_{abs} \\ \hline \\ 366 \\ 274 \\ 319.54 \\ 278.40 \\ 269.73 \\ 169.11 \\ 319.31 \\ 247.49 \\ 314.78 \\ 245.22 \end{array}$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c ccccc} \lambda_{\rm abs} & E & f_0 \\ \hline & & & \\ 366 & 3.10 & - \\ 274 & 2.95 & - \\ 319.54 & 3.88 & 0.55 \\ 278.40 & 4.45 & 0.19 \\ 269.73 & 4.60 & 0.71 \\ 169.11 & 7.33 & 0.94 \\ 319.31 & 3.88 & 0.83 \\ 247.49 & 5.01 & 0.18 \\ 314.78 & 3.94 & 0.86 \\ 245.22 & 5.06 & 0.33 \\ \hline \end{array}$

DFT methods reproduced the absorption bands reasonably as detected in the experimental spectrum. The excitation energies determined at the TD-B3LYP/6-31G* level of theory are found to be very close to experimental values for all the applied methods. The calculated absorption wavelengths (λ_{abs}) are 278 and 319 nm with oscillatory strength (f_0) of 0.55 and 0.19 at the TD-B3LYP/6-31G* level of theory, which are in close conformity with the experimentally observed values of 274 and 366 nm [see inset of Fig. 4(a)]. The oscillatory strength indicates the strength of optical/molecular interaction between molecules and in the current work its value is observed to be 0.18-0.94 for different methods (Shkir, 2017). The values of λ_{abs} , energy (E) and f_0 and the major contributions obtained with all applied methods are given in Table 1. The absorption bands at 278 and 319 nm are mainly due to $H - 4 \rightarrow L$ (60%) and $H \rightarrow L + 1$ (67%) transitions (one-toone).

3.4.2. HOMO-LUMO (highest occupied molecular orbital/ lowest unoccupied molecular orbital) analysis. Fig. 5 shows the three-dimensional images of HOMO, HOMO-1, LUMO and LUMO+1 determined at the B3LYP/6-31G* level of theory, and their values are given in Table 1S (see supplementary information). The calculated energy gap (3.401 eV)



Figure 5 Plots of HOMO–LUMO orbitals of the 5B2SNC molecule.

and chemical hardness (1.701 eV) values confirm the 5B2SNC molecule's good kinetic solidity. By using B3LYP/TD-DFT. the electronic transition of the 5B2SNC molecule has been found to be 3.41 eV. The observed value of 3.41 eV is related to charge transfer of electrons from the highest occupied states to the lowest occupied states and transfer of charges between ground and excited states of 5B2SNC molecules. The present theoretical values, 3.401 eV (HOMO-LUMO gap) and 3.88 eV (TD-DFT), are very close to the experimentally calculated value of 3.10 eV. The studied molecule comprises an NO₂ group at one terminal as a result of the strongly electron-withdrawing nature of the inductive and resonance effects. This effect also disables the benzene ring and brings the LUMO onto the NO₂ group adjacent to the ring. The HOMO is situated at the opposite end of the molecule, and the locations of the HOMO-1 and LUMO+1 orbitals explain the supremacy of the NO_2 group by transferring the charges from one part of the molecule to another.

3.5. Thermal analysis

The thermogravimetric analysis/differential thermal analysis (TGA/DTA) curves of 5B2SNC are depicted in Fig. 2S (see supplementary information). In the DTA curve, there is an irreversible endothermic peak at a temperature of 439.40 K, corresponding to the 5B2SNC melting point. The sharpness of the peak demonstrates the good crystallinity and purity of the chalcone. The exothermic peaks of the DTA at 560.76 and 678.10 K correspond to a loss of weight in the TGA plot due to degradation and evaporation of the sample. The open-capillary technique is also used to confirm that the melting point of 5B2SNC is \sim 439 K, which is similar to the result obtained by thermal analysis.

3.6. Nonlinear optical studies

3.6.1. Second harmonic generation. The SHG efficiency of 5B2SNC is observed to be 26 times higher than that of urea crystals of similar particle size. The 5B2SNC crystal is a $D-\pi$ - $A-\pi-A$ type of system, in which the charge transfer takes place from donor to acceptor of the molecule. The high value of SHG is due to the presence of strong electron donor and acceptor groups, in a head-to-tail configuration, and inter- and intramolecular hydrogen bonding (Patil, Rosli *et al.*, 2007).

3.6.2. Third-order nonlinear optical properties. Openaperture and closed-aperture z-scan transmittance curves of 5B2SNC are shown in Fig. 6. In the open-aperture z-scan (S =1) (Fig. 6a), the valley of transmittance is representative of reverse saturable absorption (RSA). The closed-aperture z-scan trace exhibits a peak-valley configuration, signifying a negative refractive nonlinearity (self-defocusing behavior) (Fig. 6b).

To evaluate the nonlinear parameters, the experimental transmittance was fitted by the expression (Ftouni *et al.*, 2013)

$$T(z) = 1 - \frac{\alpha_2 I_0 L_{\text{eff}}}{2(2^{1/2})(1+x^2)}.$$
 (1)

In equation (1), $x = z/z_0$, z_0 is the Rayleigh range, L_{eff} is the effective length of the sample, $L_{eff} = [1 - \exp(-\alpha_0 L)]/\alpha_0$, *L* is the thickness of the sample, and α_0 and α_2 are the linear and two-photon absorption coefficients (Hernández *et al.*, 2008, Maidur *et al.*, 2017).

The phase change $\Delta \Phi_0$ is related to the nonlinear refractive index n_2 as

$$n_2 = \Delta \Phi_0 / k I_0 L_{\rm eff}, \tag{2}$$

where I_0 is the input intensity of the laser beam at the focus (z = 0), and $k = 2\pi/\lambda$ is the wavevector.

The respective n_2 and α_2 values are obtained to be $\sim -3.93 \times 10^{-14} \text{ cm}^2 \text{ W}^{-1}$ and $\sim 1.85 \times 10^{-9} \text{ cm} \text{ W}^{-1}$. The obtained nonlinear coefficients are two orders of magnitude higher than those of 3,4,5-trimethoxy chalcones (Gu, Ji, Patil & Dharmaprakash, 2008) and approximately of the same order as those of 3,4-dimethoxy-4'-methoxychalcone under femtosecond excitation (Patil *et al.*, 2016). The results for n_2 and α_2 allow us to compute the real and imaginary parts of the third-order optical susceptibility, $\chi^{(3)}$, respectively, by the following equations (Kumar *et al.*, 2010):

$$\operatorname{Re}\chi^{(3)}(\text{e.s.u.}) = \frac{10^{-4} \left(\varepsilon_0 C^2 n_0^2 n_2\right)}{\pi}, \qquad (3)$$



Figure 6

(a) Open-aperture and (b) closed-aperture z-scan curves of 5B2SNC for 800 nm, 80 MHz laser pulse excitation.

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Table 2

The third-order NLO parameters of 5B2SNC in DMF solution (0.01 M) at 800 nm wavelength and 80 MHz laser repetition rate.

$lpha_0$ (cm ⁻¹)	$\alpha_2 \ (10^{-9} \text{ cm W}^{-1})$	$n_2 (10^{-14} \mathrm{cm}^2 \mathrm{W}^{-1})$	Re $\chi^{(3)}$ (10 ⁻¹² e.s.u.)	Im $\chi^{(3)}$ (10 ⁻¹² e.s.u.)	$\chi^{(3)}$ (10 ⁻¹² e.s.u.)	$\sigma_{\rm g} \ (10^{-17} {\rm cm}^2)$	$\sigma_{\rm ex} \ (10^{-15} {\rm cm}^2)$	$\gamma_{\rm h} \ (10^{-31} {\rm e.s.u.})$	Limiting threshold $(mJ \ cm^{-2})$
0.36	1.85	-3.93	-3.36	1.01	3.52	5.96	11.4	1.45	3.2

Im
$$\chi^{(3)}(e.s.u.) = \frac{10^{-2} (\varepsilon_0 C^2 n_0 \alpha_2 \lambda)}{4\pi^2},$$
 (4)

$$|\chi^{(3)}| = \left[\left(\operatorname{Re}\chi^{(3)} \right)^2 + \left(\operatorname{Im}\chi^{(3)} \right)^2 \right]^{1/2},$$
 (5)

where n_0 is the linear refractive index, ε_0 is the permittivity of free space and α_2 is the two-photon absorption coefficient. Additionally, $\chi^{(3)}$ is interrelated to the second-order hyperpolarizability (γ) as

$$\gamma_{\rm h} = \frac{\chi^{(3)}}{\left[(1/3)(n_0^2 + 2)\right]^4 N},\tag{6}$$

where $N (= N_A C \times 10^{-3} \text{ cm}^{-3})$ is the molecular density at a given concentration C and N_A is Avogadro's number. All calculated NLO parameters are given in Table 2.

Excited-state absorption data provide vital information to judge the lasing capability of a medium. The excited-state absorption cross section (σ_{ex}) of 5B2SNC can be obtained by fitting the open-aperture curve with the equation

$$T = \frac{\ln[1 + q_0/(1 + x^2)]}{[q_0/(1 + x^2)]},$$
(7)

where *T* is the normalized transmittance, $x = z/z_0$ and $q_0 = \alpha_0 \sigma_{\rm ex} F_0 L_{\rm eff}/2hv$. $F_0 = 2E/\pi\omega_0^2$, F_0 and ω_0 being the laser fluence and beam radius at the focus, hv is the incident photon energy, *E* is the average energy of the laser pulses and α_0 is the linear absorption coefficient. We also define $\sigma_g = \alpha_0/N_AC$ (Patil *et al.*, 2017). The value of $\sigma_{\rm ex} > \sigma_g$ (Table 2), which signifies the RSA condition.

3.6.3. Optical limiting. In the past two decades, much importance has been given to materials with strong optical limiting characteristics to guard optical instruments, particularly the human eye, from powerful laser beams (Suresh & Arivuoli, 2012; Patil *et al.*, 2015; Singh *et al.*, 2014; Åstrand *et al.*, 2000). Optical limiting refers to a high transmittance for low level inputs and decay of transmittance at intermediate levels of input as the intensity of the incident light rises (Krishnakumar & Nagalakshmi, 2008). Here, we establish the optical limiting performance of 5B2SNC in DMF solvent. The position-dependent fluence was evaluated from the equation

$$F(z) = 4(\ln 2)^{1/2} (E_{\rm in}/\pi^{3/2}) \omega(z)^2, \qquad (8)$$

where F(z) is the input fluence, E_{in} is the laser energy and $\omega(z)$ is the beam radius at a given position z along the beam. 5B2SNC displays a steady reduction in transmittance with increasing incident energy of the femtosecond pulses at 800 nm (Fig. 7), indicating a broadband response. When the normalized transmittance was reduced to 50% the equivalent incident power was 3.2 mJ cm⁻². 5B2SNC exhibits relatively good optical limiting properties (Zhou & Wong, 2011; Sauteret *et al.*, 1976; Samuel *et al.*, 1994; Zhou *et al.*, 2009; Dini *et al.*, 2016; Zhou *et al.*, 2007).

3.6.4. First hyperpolarizability study. The first hyperpolarizability value was calculated using methods including B3LYP/ 6-31G*, HF/6-31G*, CAM-B3LYP/6-31G* and wb97XD/6-31G*. The parameters obtained from the B3LYP/6-31G* level of theory, such as electronic total dipole moment (μ_{tot}), molecular total and anisotropy of polarizability (α_0 and $\Delta \alpha$), and static and total first hyperpolarizability (β_0 and β_{tot}), are given in Table 2S (see supplementary information). To elucidate the nature of the above-mentioned parameters using HF, the results for CAM-B3LYP and wb97XD are also provided in Tables 1R-3R. From these calculations, it is clear that the polarizability and hyperpolarizability values are provided by the diagonal components (i.e. components along the dipole moment axis) of α_{xx} and β_{xxx} . However, the present calculations also indicate that the hyperpolarizability values in B3LYP theory are higher than those in the other applied techniques as given in Fig. 3S. μ_{tot} is observed to be 5.944 D and the largest of its components is μ_x (= -5.756 D), which is a major contributor to the hyperpolarizability. The value of total first hyperpolarizability (β_{tot}) is found to be 53 \times 10^{-30} e.s.u., which is 241 times superior to that of urea (0.22 × 10^{-30} e.s.u.) computed with the same theory, and the SHG efficiency measured by the Kurtz powder technique was found to be 26 times higher than that of urea in our experimental studies. The observed values are found to be many times higher than those for many organic and other molecules obtained at same level of theory in the literature (Shkir et al., 2015; Shkir, Patil *et al.*, 2017). Hence, the higher values of β_{tot} and SHG make the studied molecule a unique candidate for optical device applications.



Broadband optical limiting property of 5B2SNC in DMF.

Table 3 The static second hyperpolarizability $\gamma(0; 0, 0, 0)$ components and their isotropic average values for 5B2SNC at the B3LYP/6-31G* level of theory.

Components	γ_{xxxx}	γ_{yyyy}	γ_{zzzz}	γ_{xxyy}	γ_{xxzz}	γ_{yyzz}	γ (iso)
In a.u.	136.335	12655.6	1230770	748.052	5059.61	80244.4	283137
In e.s.u. (10 ⁻³⁶)	0.0687	6.374	619.901	0.377	2.548	40.417	142.608

3.6.5. Second hyperpolarizability. The static second hyperpolarizability values were computed using the B3LYP/6-31G* level of theory. The obtained tensor components and their isotropic average values of static second hyperpolarizabilities are given in Table 3. The values suggest that the charge transfer occurs along the z axis, since the longitudinal component of second hyperpolarizability γ_{zzzz} is the dominant component with respect to the average isotropic value (Hatua & Nandi, 2013). The computed average static second hyperpolarizability $\langle \gamma \rangle = 0.143 \times 10^{-33}$ e.s.u. is in accordance with the experimentally obtained molecular second hyperpolarizability $\gamma_h = 1.45 \times 10^{-31}$ e.s.u. at 800 nm wavelength. The obtained value of second hyperpolarizability for 5B2SNC is found to be higher than or comparable to the values for many earlier reported materials (Patil et al., 2017; Maidur et al., 2017; Almeida et al., 2017). The deviation in the results occurs because the experiment was done in the liquid phase, while theoretical studies were performed in the gaseous phase.

4. Conclusions

In this study, the linear and nonlinear optical susceptibility and hyperpolarizability of 5B2SNC were investigated both experimentally and theoretically (DFT). Optical quality crystals of 5B2SNC were grown, which are transparent between 435 and 1400 nm. The chalcone 5B2SNC is 26 times more SHG efficient than urea standard. *z*-scan measurements on 5B2SNC yield a two-photon absorption coefficient $\alpha_2 =$ 1.85×10^{-9} cm W⁻¹ and a nonlinear refraction index $n_2 =$ -3.93×10^{-14} cm² W⁻¹. Furthermore, the optical limiting threshold of 5B2SNC is as low as ~3.2 mJ cm⁻², better than most of the similar organic materials reported so far, and hence it may be used as an effective optical limiter. The current investigations open up paths in the search for new chalcones for technological applications.

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