



Crystal Structure and Third Order Nonlinear Optical Studies on 2-phenylbenzimidazolium-*p*-toulenesulphonate

C.SUDHAKAR^{1,2}, M.SARAVANABHAVAN³, M.SEKAR^{2*}, B.BABU⁴ and J.CHANDRASEKARAN⁴

¹Research and Development Centre, Bharathiar University, Coimbatore – 641 046, Tamil Nadu, India.

²Chikkaiah Naicker College, Erode-638004, Tamilnadu, India

³Department of Chemistry, Dr. N.G.P. Institute of Technology, Coimbatore -641048, Tamil Nadu, India.

⁴Post-Graduate and Research Department of Chemistry, Sri Ramakrishna Mission Vidyalaya College of Arts and Science, Coimbatore – 641 020, Tamil Nadu, India.

⁵Post-Graduate and Research Department of Physics, Sri Ramakrishna Mission Vidyalaya College of Arts and Science, Coimbatore – 641 020, Tamil Nadu, India.

Corresponding author E-mail: drmsbavan@gmail.com

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ABSTRACT

A new third order nonlinear optical single crystal of 2-phenylbenzimidazolium-*p*-toulenesulphonate (PBITS) was grown by the solvent evaporation technique using methanol as a solvent. The single crystal XRD analysis reveals that crystals belong to the triclinic system. An NMR and FTIR study confirms the formation and vibrational analysis present in the compound. UV-Vis absorption studies were also carried out for the crystal. Nonlinear refractive index (n_2), absorption coefficient (β) and third order nonlinear optical susceptibility ($\chi^{(3)}$) of the crystals were evaluated by Z-Scan studies.

Keyword: Crystal, 2-phenylbenzimidazolium-*p*-toulenesulphonate (PBITS), Crystal XRD, NMR and FTIR study.

INTRODUCTION

A fascinating new field of research termed “nonlinear” optics was introduced to the scientific and engineering community after the invention of laser. Nonlinear optics has arisen as one of the most attractive fields of current research in view of

its vital applications in areas of optical switching, optical data storage for the developing technologies in telecommunications, frequency mixing, optical parametric oscillation, optical bi-stability, optical logic gates, laser radiation protection, optical image processing, under water communication, biomedical and signal processing analysis etc¹⁻⁵.

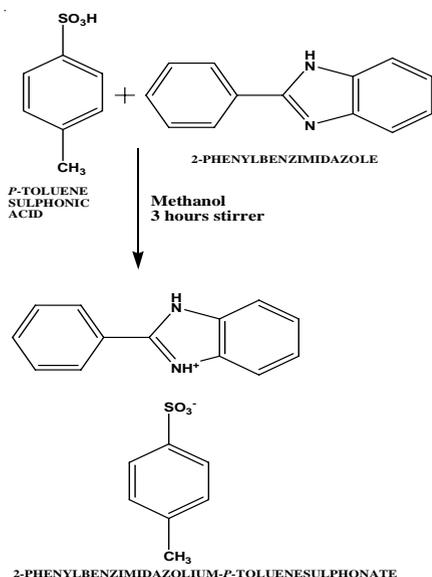


Organic NLO single crystals are very efficient for THz generation and high signal to noise ratios detection due to their large nonlinear optical susceptibilities and ultrafast response times^{6,7}. It has been understood that the second-order and third-order molecular nonlinearity can be enhanced by large delocalized π -electron systems with strong donor and acceptor groups⁸⁻¹⁰. Based on these specifies in the present investigation donor-acceptor based crystals of 2-phenylbenzimidazolium-*p*-toulenesulphonate has been grown by the slow evaporation technique and its structural, optical, and third order nonlinear optical properties were discussed in detail.

EXPERIMENTAL

Material synthesis and growth of pbittsingle crystal

Equimolar ratio of *p*-toluenesulphonic acid in methanol and 2-phenylbenzimidazole in methanol were prepared at room temperature, mixed and stirred well for about 3 h to get clear solution. This solution was filtered using Whatmann 41 filter paper and kept aside unperturbed in a dust-free room for the growth of single crystals. Well defined, transparent crystals were collected at the end of 6th day. The collected crystals were recrystallized using dry methanol to get good quality crystals. The reaction scheme and the chemical structure were illustrated.



Scheme 1. Synthesis of 2-phenylbenzimidazolium-*p*-toulenesulphonate

Materials and instrumentation

All the chemicals were purchased from Sigma-Aldrich in the highest purity available. Solvents were purified and dried according to the standard procedure. Single crystal X-ray diffraction data of PBITS compound was collected at room temperature on a Bruker Diffractometer equipped with a fine focused sealed tube. The unit cell parameters were determined and the data collections of PBITS was performed using a graphite-mono chromate Mo K α ($\lambda = 0.71073 \text{ \AA}$) radiation by φ and ω scans. The structure of the compound was solved by direct method using SHELXS-97, which revealed the position of all non-hydrogen atoms, and was refined by full-matrix least squares on F^2 (SHELXL-97)¹¹. All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were placed in calculated positions and refined as riding atoms. The electronic absorption spectrum was measured in methanol using SHIMADZU 1601 UV-Vis spectrophotometer in the range of 200-600 nm. In order to confirm the functional groups of the crystal was subjected to FT-IR spectral analysis by Perkin Elmer FT-IR 8000 spectrophotometer in the range of 4000-400 cm^{-1} using the KBr pellets method. To confirm the molecular structure of the compound the ^1H and ^{13}C NMR spectra were recorded employing a Bruker AV III 400 MHz spectrometer in deuterated dimethyl sulfoxide as solvent using TMS as an internal standard. The nonlinear optical measurements were carried out by using single beam Z-scan technique with a He-Ne laser operated at a repetition rate of 1 kHz and at the wavelength of 632 nm.

RESULTS AND DISCUSSIONS

Single crystal XRD analysis

From X-ray diffraction studies, it is known that the crystal belongs to the triclinic system with the space group of P-1 and the lattice parameters are $a = 8.2912(5) \text{ \AA}$, $b = 9.7197(6) \text{ \AA}$, $c = 11.4293(9) \text{ \AA}$, $\alpha = 82.311(4)^\circ$, $\beta = 89.626(3)^\circ$, $\gamma = 77.915(3)^\circ$. The crystal data and details of the data collection and the structure refinement are given in Table. 1. The bond length and bond angles of PBITS crystal are given in Table 2 and 3 respectively. Fig. 1 shows the ORTEP view of the molecule drawn at 50% probability thermal displacement ellipsoids with the atom numbering scheme. The packing arrangement

of the molecule viewed down a, b and c axis are shown in Fig. 1. a, b, and c respectively. From molecular structure of PBITS, we could see that there is an intermolecular hydrogen bonding between N-H group of 2-phenylbenzimidazolium cation and *p*-toluenesulphonate anion. The N-atom of the 2-phenyl benzimidazole cation forms N-H.....O hydrogen bonds with the O atom of the 2-phenyl sulphonate anion. In the title compound the C=NH group of the 2-phenylbenzimidazole residue is

engaged in the strong hydrogen bonding with the *p*-toluenesulphonatesulphonate anion. The selected bond distance and angles are shown in Table 4 respectively. The molecule is stabilized by C-H.....O bifurcated hydrogen bonds. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were placed in geometric positions and refined as riding atoms except for those bound to oxygen and nitrogen, which were freely refined.

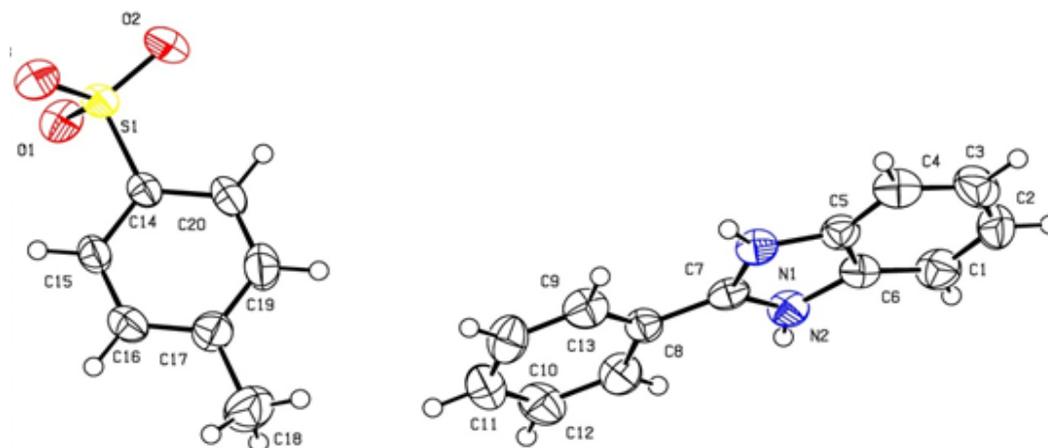


Fig. 1. ORTEP diagram of PBITS

NMR spectral analysis

The ^1H NMR spectrum of the PBITS single crystal was recorded employing a Bruker 400 MHz spectrometer using TMS as the internal reference standard. The ^1H NMR spectrum of the PBITS is depicted in Fig. 2. The singlet peak observed at δ 2.298 has been assigned to three protons of the methyl group in the 2-phenylbenzimidazolium *p*-toluenesulphonate. The doublet peak centred at δ 7.146 ($J = 8$ Hz) is due to the C_{19} and C_{16} protons of the same kind in aromatic ring of 2-phenylbenzimidazolium-*p*-toluenesulphonate. Another doublet peak centred at δ 8.226 ($J = 6.8$ Hz) is due to the C_{15} and C_{20} protons of the same kind in aromatic ring of 2-phenylbenzimidazolium-*p*-toluenesulphonate. The multiplet peak centred at δ 7.901-7.572 is due to the C_1 , C_2 , C_3 , C_4 , C_9 , C_{10} , C_{11} , C_{12} and C_{13} protons of the same kind of the aromatic ring of 2-phenylbenzimidazolium-*p*-toluenesulphonate. The NH proton appeared as singlet at δ 5.4.

The ^{13}C NMR spectrum of the PBITS single crystal was recorded employing a Bruker 400 MHz spectrometer using TMS as the internal reference standard. The ^{13}C NMR spectrum of the PBITS is depicted in Fig. 3. In the downfield carbon signal at δ 154.25 is correspond to the C_7 carbon of 2-phenylbenzimidazole moiety. The carbon signal at δ 150.22 is belongs to the C_{14} carbon of *p*-toluenesulphonicacid moiety. The carbon signal at δ 143.41 is correspond to the C_5 carbon of *p*-toluenesulphonicacid moiety. The carbon signal at δ 138.63 is belongs to the C_4 carbon of 2-phenylbenzimidazole moiety. The sharp and intense signal at δ 137.06 is due to the C_{15} and C_{20} carbons of the same kind in the *p*-toluenesulphonicacid moiety. The carbon signal at δ 134.94 is correspond to the C_8 and C_{11} carbons of 2-phenylbenzimidazole moiety. The sharp and intense signal at δ 133.20 is due to the C_9 and C_{13} carbons of the same kind in the 2-phenylbenzimidazole moiety. The carbon signal at δ 131.28 is belongs to the C_{10} and C_{12}

carbon of 2-phenylbenzimidazole moiety. The carbon signal at δ 130.74 is correspond to the C₁₆ and C₁₉ carbon of 2-phenylbenzimidazole moiety. The sharp and intense signal at δ 128.31 is due to the C₂ and C₃ carbons of the same kind in the p-

toluenesulphonicacid moiety. The sharp and intense signal at δ 119.36 is due to the C₁₇ carbon of the same kind in the 2-phenylbenzimidazole moiety. The carbon signal at δ 26.02 is correspond to the methyl carbon of 2-phenylbenzimidazole moiety.

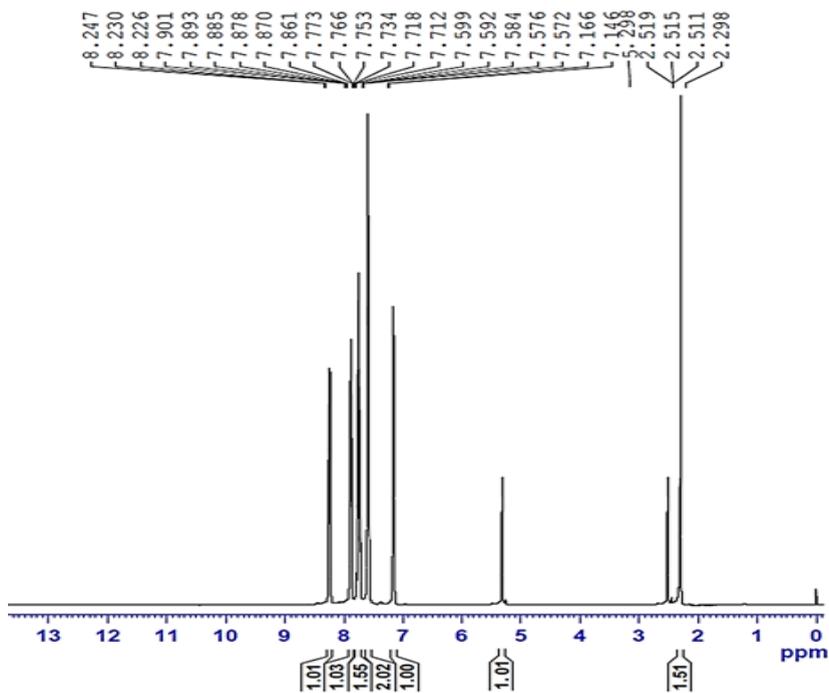


Fig. 2. ¹H NMR spectrum of PBITS

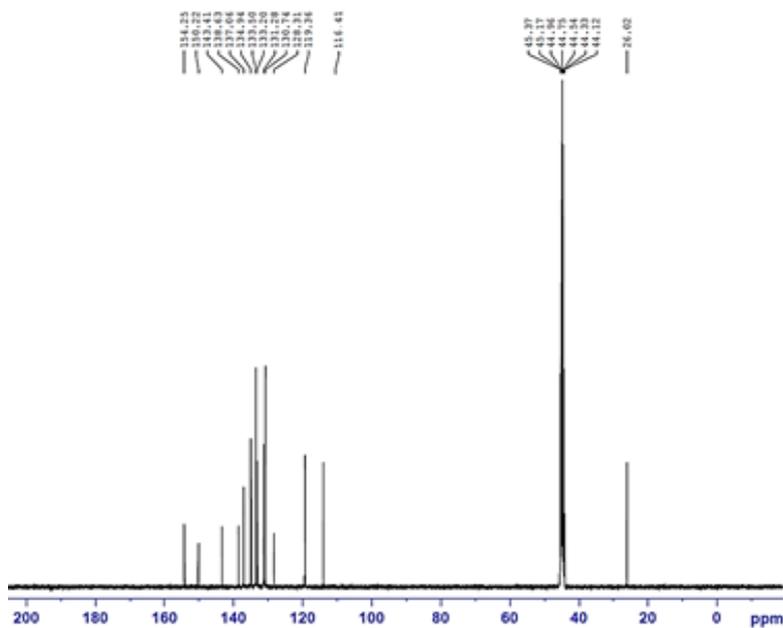


Fig. 3. ¹³C NMR spectrum of PBITS

FT-IR SPECTRAL STUDIES

The FT-IR spectrum of PBITS crystal was recorded employing a Perkin Elmer FT-IR spectrometer using KBr pellet technique in the range 4000-400 cm^{-1} and the FT-IR spectrum of PBITS crystal is depicted in Fig. 4. The recorded FT-IR spectrum was analyzed to ascertain the functional groups presented in the compound. The formation of the PBITS during the reaction between *p*-toluenesulphonic acid and 2-phenylbenzimidazole strongly evident by the presence of the main characteristic infrared band present in the crystal. The formation of PBITS is evident by the presence of most prominent group in PBITS crystal such as N-H, C-H, C=N, C-N and SO_2 groups. The band observed at 3336 cm^{-1} is due to the N-H symmetric stretching vibration. The aromatic C-H stretching vibration is observed at 3062 cm^{-1} , 2930 cm^{-1} and 2853 cm^{-1} . The band observed at 1634 cm^{-1} indicates the presence of C=N group in the PBITS molecule. The aromatic C-H bending vibration is observed at 1457 cm^{-1} . The band 1396 cm^{-1} indicates the presence of C-N stretching vibration in the molecule. The sharp band observed at 1166 cm^{-1} indicates the presence of aromatic SO_2 symmetric stretching vibration.

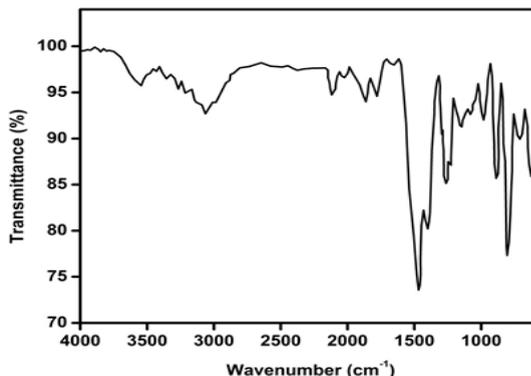


Fig. 4. FT-IR spectrum of PBITS

Electronic absorption spectroscopic studies

The UV-Visible absorption spectrum of PBITS crystal was recorded employing a systronics make double beam spectrophotometer 2202 in a range from 200 to 600 nm using DMSO as solvent and the spectrum shown in Fig. 5. From the spectrum, it is observed that the compound exhibits two characteristic absorption bands. The bands at about 296.0 and 329.6 nm are assigned to $\pi \rightarrow \pi^*$ transition of the title compound. Also the absence of absorption in the region between 330 nm to 600 nm makes the crystal suitable for optical applications^{7,12}.

Table. 1: Crystal data and structure refinement for PBITS

Empirical formula	$\text{C}_{20}\text{H}_{18}\text{N}_2\text{O}_3\text{S}$
Formula weight	366.42
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 8.2912(5) Å, alpha = 82.311(4) deg b = 9.7197(6) Å, beta = 89.626(3) deg c = 11.4293(9) Å, gamma = 77.915(3) deg
Volume	892.33(10) Å ³
Z, Calculated density	2, 1.364 Mg/m ³
Absorption coefficient	0.204 mm ⁻¹
F(000)	384
Crystal size	0.35 x 0.30 x 0.25 mm
Theta range for data collection	1.80 to 28.36 deg.
Limiting indices	-11 ≤ h ≤ 8, -12 ≤ k ≤ 11, -15 ≤ l ≤ 15
Reflections collected / unique	6971 / 4272 [R(int) = 0.0167]
Completeness to theta = 28.36	95.90%
Absorption correction	Semi-empirical from equivalents
Max. and min. Transmission	0.9508 and 0.9320
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4272 / 0 / 236
Goodness-of-fit on F ²	1.071
Final R indices [I > 2σ(I)]	R1 = 0.0543, wR2 = 0.1481
R indices (all data)	R1 = 0.0670, wR2 = 0.1642
Largest diff. peak and hole	0.643 and -0.471 e.Å ⁻³

Table. 2: Bond lengths [Å] for PBITS

S(1)-O(2)	1.4383(17)
S(1)-O(3)	1.4562(15)
S(1)-O(1)	1.4584(16)
S(1)-C(14)	1.772(2)
N(1)-C(7)	1.325(3)
N(1)-C(5)	1.397(3)
N(1)-H(1N1)	0.86
N(2)-C(7)	1.328(3)
N(2)-C(6)	1.389(3)
N(2)-H(2N2)	0.86
C(3)-C(4)	1.383(4)
C(3)-C(2)	1.410(4)
C(3)-H(3)	0.93
C(4)-C(5)	1.380(3)
C(4)-H(4)	0.93
C(5)-C(6)	1.378(3)
C(7)-C(8)	1.475(3)
C(8)-C(9)	1.398(3)
C(8)-C(13)	1.399(3)
C(9)-C(10)	1.368(4)
C(9)-H(6)	0.93
C(10)-C(11)	1.364(4)
C(10)-H(10)	0.93
C(11)-C(12)	1.363(4)
C(11)-H(11)	0.93
C(2)-C(1)	1.364(4)
C(2)-H(2)	0.93
C(1)-C(6)	1.379(3)
C(1)-H(1)	0.93
C(13)-C(12)	1.369(4)
C(13)-H(13)	0.93
C(12)-H(12)	0.93
C(14)-C(20)	1.381(3)
C(14)-C(15)	1.384(3)
C(15)-C(16)	1.379(3)
C(15)-H(15)	0.93
C(16)-C(17)	1.383(3)
C(16)-H(16)	0.93
C(17)-C(19)	1.384(4)
C(17)-C(18)	1.510(4)
C(18)-H(18A)	0.96
C(18)-H(18B)	0.96
C(18)-H(18C)	0.96
C(20)-C(19)	1.385(4)
C(20)-H(20)	0.93
C(19)-H(19)	0.93

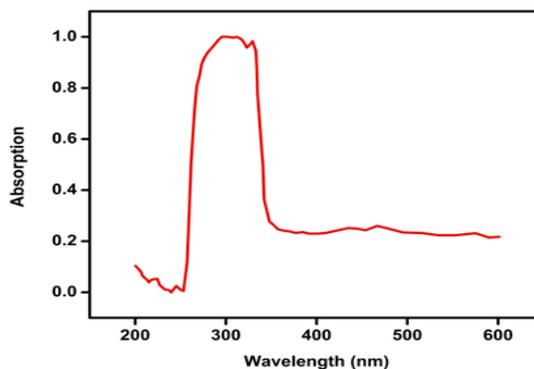
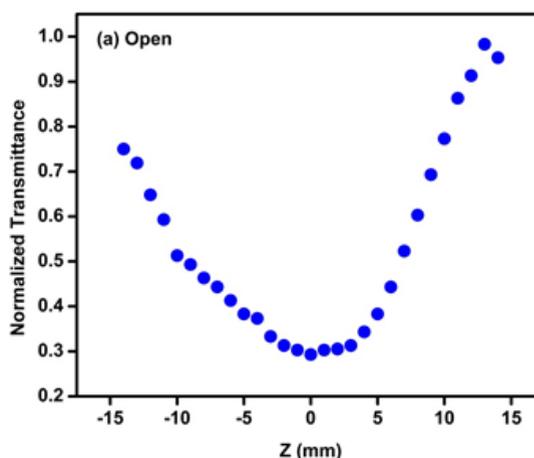
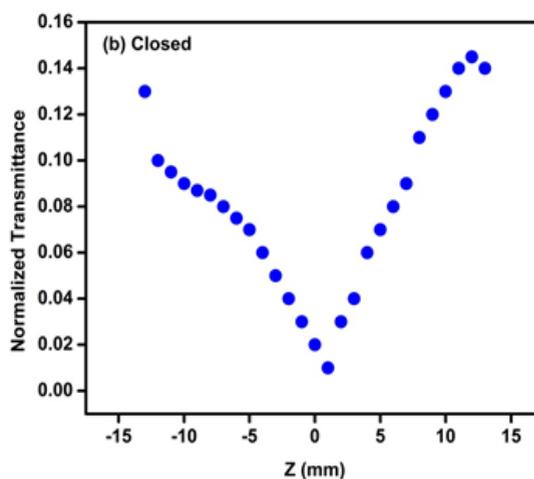
**Fig. 5. Electronic absorption spectrum of PBITS****Fig. 6(a). Normalized transmittance with open aperture****6(b) Normalized transmittance with closed aperture**

Table 3: Bond angles [Å] forPBITS

O(2)-S(1)-O(3)	114.48(11)	C(12)-C(13)-C(8)	119.5(2)
O(2)-S(1)-O(1)	114.15(12)	C(12)-C(13)-H(13)	120.3
O(3)-S(1)-O(1)	110.06(10)	C(8)-C(13)-H(13)	120.3
O(2)-S(1)-C(14)	106.17(11)	C(11)-C(12)-C(13)	111.1(2)
O(3)-S(1)-C(14)	105.48(10)	C(11)-C(12)-H(12)	119.4
O(1)-S(1)-C(14)	105.63(9)	C(13)-C(12)-H(12)	119.4
C(7)-N(1)-C(5)	108.24(18)	C(20)-C(14)-C(15)	119.2(2)
C(7)-N(1)-H(1N1)	125.9	C(20)-C(14)-S(1)	120.99(17)
C(5)-N(1)-H(1N1)	125.9	C(15)-C(14)-S(1)	119.78(16)
C(7)-N(2)-C(6)	108.24(18)	C(16)-C(15)-C(14)	120.4(2)
C(7)-N(2)-H(2N2)	125.9	C(16)-C(15)-H(15)	119.8
C(6)-N(2)-H(2N2)	125.9	C(14)-C(15)-H(15)	119.8
C(4)-C(3)-C(2)	121.1(2)	C(15)-C(16)-C(17)	121.0(2)
C(4)-C(3)-H(3)	119.4	C(15)-C(16)-H(16)	119.5
C(2)-C(3)-H(3)	119.4	C(17)-C(16)-H(16)	119.5
C(5)-C(4)-C(3)	115.9(2)	C(16)-C(17)-C(19)	118.2(2)
C(5)-C(4)-H(4)	122.1	C(16)-C(17)-C(18)	120.5(2)
C(3)-C(4)-H(4)	122.1	C(19)-C(17)-C(18)	121.3(2)
C(6)-C(5)-C(4)	122.6(2)	C(17)-C(18)-H(18A)	109.5
C(6)-C(5)-N(1)	106.4(2)	C(17)-C(18)-H(18B)	109.5
C(4)-C(5)-N(1)	131.0(2)	H(18A)-C(18)-H(18B)	109.5
N(1)-C(7)-N(2)	110.2(2)	C(17)-C(18)-H(18C)	109.5
N(1)-C(7)-C(8)	124.95(19)	H(18A)-C(18)-H(18C)	109.5
N(2)-C(7)-C(8)	124.81(19)	H(18B)-C(18)-H(18C)	109.5
C(9)-C(8)-C(13)	118.8(2)	C(14)-C(20)-C(19)	119.9(2)
C(9)-C(8)-C(7)	120.9(2)	C(14)-C(20)-H(20)	120.1
C(13)-C(8)-C(7)	120.3(2)	C(19)-C(20)-H(20)	120.1
C(10)-C(9)-C(8)	119.9(2)	C(17)-C(19)-C(20)	121.3(2)
C(10)-C(9)-H(6)	120.0	C(17)-C(19)-H(19)	119.3
C(8)-C(9)-H(6)	120.0	C(20)-C(19)-H(19)	119.3
C(11)-C(10)-C(9)	120.7(2)		
C(11)-C(10)-H(10)	119.6		
C(9)-C(10)-H(10)	119.6		
C(12)-C(11)-C(10)	120.0(2)		
C(12)-C(11)-H(11)	120.0		
C(10)-C(11)-H(11)	120.0		
C(1)-C(2)-C(3)	122.1(3)		
C(1)-C(2)-H(2)	119.0		
C(3)-C(2)-H(2)	119.0		
C(2)-C(1)-C(6)	116.4(2)		
C(2)-C(1)-H(1)	121.8		
C(6)-C(1)-H(1)	121.8		
C(5)-C(6)-C(1)	121.9(2)		
C(5)-C(6)-N(2)	106.9(2)		
C(1)-C(6)-N(2)	131.2(2)		

Z-scan studies

The Z-scan is a well-known experimental technique to measure the intensity dependent third order nonlinear susceptibility of the materials^{13,14}. The open and closed aperture Z-scan configurations are used to investigate the nonlinear absorption coefficient β and nonlinear refractive index n_2 . Fig 6a shows the normalized transmittance (T) with a closed aperture as a function of the distance z along the lens axis in the far field. The Fig. 6(b) shows the normalized transmittance with open aperture as a function of the distance z along the lens axis in the far field. The nonlinear refractive index (n_2) of the crystal was calculated using the standard relations given below:

$$\Delta\phi_0 = \frac{\Delta T_{p-v}}{0.406 (1-s)^{0.25}} \quad (1)$$

where ΔT_{p-v} is the difference between the normalized peak and valley transmittance and S is the linear transmittance of the aperture. The nonlinear refractive index (n_2) and nonlinear absorption coefficient (β) are given by,

$$n_2 = \frac{\Delta\phi}{kI_0L_{eff}} \quad (2)$$

$$\beta = \frac{2\sqrt{2}\Delta T}{I_0L_{eff}} \quad (3)$$

where k is the wave number $k = 2\pi/\lambda$ and

$$L_{eff} = \frac{1 - e^{-\alpha L}}{\alpha} \quad (4)$$

with $I_0 = \frac{P}{\pi\omega_0^2}$ defined as the peak intensity within the sample, where L_{eff} is the thickness of the sample and α is the linear absorption coefficient. The real and imaginary parts of the third order nonlinear susceptibility $\chi(3)$ are defined as

$$Re\chi^{(3)} = 10^{-4} \frac{(\epsilon_0 C^2 n_0^2 n^2)}{\pi} (esu) \quad (5)$$

$$Im\chi^{(3)} = 10^{-2} \frac{(\epsilon_0 C^2 n_0^2 \lambda \beta)}{4\pi^2} (esu) \quad (6)$$

where ϵ_0 is the vacuum permittivity, n_0 is the linear refractive index of the sample and c is the velocity of light in vacuum. Thus, we can easily obtain the absolute value of $\chi(3)$ using the following formula

$$|\chi^{(3)}| = [(Re\chi^{(3)})^2 + (Im\chi^{(3)})^2]^{\frac{1}{2}} \quad (7)$$

As seen from the closed aperture Z scan curve, the prefocal transmittance valley is followed by the post focal peak, which is the positive nonlinearity¹⁵. The calculated value of the nonlinear refractive index (n_2) is $6.40149 \times 10^{-8} \text{ cm}^2/\text{W}$. The value of the nonlinear absorption coefficient (β) estimated from the open aperture Z-scan curve is $2.4603 \times 10^{-4} \text{ cm/W}$. The third order susceptibility of PBITS is $1.3061 \times 10^{-7} \text{ esu}$. As the material has a positive refractive index, it results in self-focusing nature of the material, which is an essential property for all optical switching devices¹⁶.

Table. 4: Hydrogen bonds for PBITS

D-H...A	d(D-H)	d(H..A)	<DHA	d(D..A)	Symmetry
N1—H1N1...O1	0.860	1.82	170	2.674	x, y, z+1
N2—H2N2...O3	0.860	1.87	160	2.691	x,-1+y,1+z
C9—H6...O1	0.930	2.56	160	3.450	x,y,1+z
C16—H16...O2	0.930	2.54	156	3.410	-1+x,y,z
C20—H20...O2	0.930	2.51	105	2.892	

CONCLUSIONS

New bright, transparent organic compound, PBITS was synthesized and crystal grown by slow evaporation solution growth method at room temperature. The material synthesized characterized by various analytical, spectroscopic and single crystal XRD studies. From X-ray diffraction studies, PBITS single crystal is observed

that the crystal belongs to the triclinic system with the space group of P-1. UV-Visible absorption spectrum confirms the suitability of the title crystal for various optical applications. The molecular structure of the compound was confirmed by the FT-IR, ¹H and ¹³C NMR spectral studies. Z-scan studies reveal the self-focusing nature of the material, which is a vital property for all optical switching and optical limiting applications.

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