

Contents lists available at SciVerse ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy



journal homepage: www.elsevier.com/locate/saa

Synthesis, growth and spectral studies of S-benzyl isothiouronium nitrate by density functional methods

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HIGHLIGHTS

- S-benzyl isothiouronium nitrate, a new NLO crystal was grown by slow evaporation method.
- ► STBN crystallized in monoclinic system with space group *P2*₁/*C*.
- SBTN exhibits second order NLO susceptibility, due to intermolecular charge transfer.
- UV-Vis spectral study reveals that SBTN crystals are transparent in the wavelength region 200–1000 nm.
- The TGA study supports the crystal is thermally stable up to 196 °C. SHG efficiency of SBTN is 0.45 times of urea.

ARTICLE INFO

Article history: Received 3 November 2012 Received in revised form 30 January 2013 Accepted 31 January 2013 Available online 20 February 2013

Keywords: S-benzyl isothiouronium nitrate Non-linear optical material Single X-ray diffraction FTIR UV NMR DFT calculation

G R A P H I C A L A B S T R A C T



ABSTRACT

S-benzyl isothiouronium nitrate (SBTN), was synthesized and characterized by X-ray diffraction, FTIR, UV–Vis and NMR spectra. The Centro-symmetric single crystal of S-benzyl isothiouronium nitrate (SBTN), which crystallizes in monoclinic crystal system with space group P_{2I}/C , exhibits second order non-linear optical (NLO) susceptibility, due to intermolecular charge transfer. S-benzyl isothiouronium ion forms well defined charge transfer (CT) salt with anion nitrate through N–H···O and C–H···O hydrogen bonds. It is to identify the direction of specific N–H···O hydrogen bond between the $-NH_2$ group and O⁻ in the anion and also sacking in the solid state responsible for NLO activity in this crystal. The SHG technique confirms the non-linear optical property of the grown crystals. Density functional theory (DFT) calculation has been carried out to study the nature of hydrogen involved in the SBTN crystal. The bond lengths and bond angles of the structure of SBTN crystal calculated using B3LYP method with 6–311+(2d,2p) basis set. These calculations are compared with experimental values to provide deep insight into its electronic structure and property of grown crystal.

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Introduction

New non-linear optical (NLO) frequency conversion materials can have a significant impact on laser technology [1], optical

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communication [2], and optical data storage technology [3]. These applications have unique and often competing material requirements and illustrate that no single nonlinear material will be suitable for all uses. Organic compounds are often formed by weak van der Waals bonds and hydrogen bonds and hence possess high degree of delocalization. Thus they are expected to be optically more nonlinear than inorganic compounds. Some of the

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advantages of organic materials include ease of varied synthesis, scope for altering the properties by functional group substitutions, inherently high nonlinearity, high damage resistance, etc. The prototype organic nonlinear optical (NLO) material contains one or more delocalized bonds, typically a ring structure like benzene. Owing to the high polar nature of the molecules, organic NLO materials often tend to crystallize as long needles or thin platelets. The high optical thresholds and much versatility in the molecular design of organic materials provide many more opportunities for improving the second harmonic generation (SHG) response [4]. SHG is one of the most important aspects to NLO research since it leads itself to a myriad of applications: from telecommunications to visible light lasers, through to surface-enhanced Raman spectroscopy [5–7]. The level of SHG response of a given material is inherently dependent upon its structural attributes. On a molecular scale, the extent of charge transfer (CT) across the NLO chromophore determines the level of SHG output [8–12]: the greater the CT, the larger the SHG output. The presence of strong intermolecular interactions, such as hydrogen bonds can extend this level of CT into the supramolecular realm, owing to their electrostatic and directed nature, thereby enhancing the SHG response. The structural characteristic of S-benzyl isothiouronium nitrate (SBTN), on the molecular scale, reveals that they are: extremely p-conjugated, good planarity and strong electron donor and acceptor groups at opposite ends of the molecule. Density functional theory (DFT) is a cost-effective ab initio quantum chemistry procedure for studying physical, chemical and electronic properties of the molecules. DFT calculations have shown promising conformity with experimental results [13-15]. Therefore, in this present investigation DFT is used to study the geometry, complete spectral studies, vibrational assignment, electronic transitions and nature of hydrogen bonding in the SBTN crystal have been studied and reported for the first time.

Experimental

Material synthesis

S-benzylisothiouronium chloride (SBTC) was synthesized by mixing 5 g of thiourea (99% AR, Merck) and 5 ml of benzyl chloride (99%, AR, Merck) in ethanol. The contents were refluxed for half an hour and on cooling a white crystalline precipitate of S-benzylisothiouronium chloride salt was obtained. The synthesized material was washed several times with doubly distilled water to remove the impurities. The sample was repeatedly recrystallized from 0.2 M HCl to enhance the degree of purity. Equimolar solutions of Sbenzyl isothiouranium chloride (SBTC) and potassium nitrate were prepared separately in minimum amount of water and mixed together. The mixture was refluxed for half an hour and cooled to room temperature. The precipitate was filtered and washed thor-



Fig. 1. Photograph of as grown SBTN single crystals.

oughly with triple distilled water. The salt was repeatedly recrystallised from 0.2 M HNO₃ to get the material of very high purity. The melting point of the SBTN was determined to be 190 °C. The formation of SBTN has been represented by the following scheme:



Crystal growth

A clear saturated solution of SBTN was prepared using 0.2 N HNO₃ and the solution was filtered through a quantitative whatmann filter paper to eliminate the suspended impurities. The filtered solution was kept at a room temperature and optimally closed with a perforated mica paper for controlled evaporation. Care was taken to minimize mechanical shock and temperature fluctuations. A well grown transparent and high quality optical single crystal of SBTN was harvested in a span of 15 days. The as grown crystal of title material is shown in Fig. 1.

Computational details

Density functional theory has been used to investigate the electronic structure of the SBTN crystal. The geometry optimization of the SBTN crystal was carried out using density functional method with B3LYP exchange–correlation functional [16–18] at 6-311G+(2d,2p) basis set. The vibrational frequencies computed using the analytical second derivatives at B3LYP/6-311G+(2d,2p) [Becke 3-parameters (Exchange), Lee, Yang and Parr (Correlation) level of theory for SBTN. There is no imaginary frequency, which implies that the optimization is at global minima. The geometry, electronic charge densities have been calculated using atoms-in

Table 1

Crystal data and structure refinement for SBTN.

Empirical formula	$C_8H_{11}N_2S\cdot NO_3$
Formula weight	229.26 gm
Temperature	293 (2) K
Wavelength	0.71073 A
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 5.8569 (4) Å, b = 7.5931 (5) Å
	$c = 23.9488 (16) \text{ Å } \alpha = \gamma = 90;$
	$\beta = 93.3^{\circ}$
Volume	1063.28 (12) Å ³
Ζ	4
Density	1.376 kg/m ³
Absorption coefficient	0.30 mm^{-1}
F(0 0 0)	480
Theta range for data collection	1.99–28.01°
Index ranges	$-6 = h \leqslant 6$; $-9 = k \leqslant 9$; $-28 = l \leqslant 28$
Reflections collected	11,620
Independent reflections	2492 [<i>R</i> (int) = 0.021]
Completeness to theta = 25.00°	99.9%
Refinement method	Full-matrix least square on F ²
Data/restraints/parameters	2337/0/110
Goodness-of-fit on F^2	1.0332
Final R indices [I > 2sigma(I)]	<i>R</i> 1 = 0.02884, <i>wR</i> 2 = 0.0838
R indices (all data)	<i>R</i> 1 = 0.0309, <i>wR</i> 2 = 0.0862
Extinction coefficient	0.0200(16)
Largest diff. peak and hole	1.08 e $Å^{-3}$ and -0.79 e $Å^{-3}$



Fig. 2. ORTEP diagram of structure of SBTN.

Table 2Hydrogen bonding geometry (Å).

D–H···A	$d(D{\cdot}{\cdot}{\cdot}H)$	$d(H{\cdot}{\cdot}{\cdot}A)$	$d(D{\cdot}{\cdot}{\cdot}A)$	<(DHA)
N1-H1A \cdots O2 ⁱ	0.86	2.211	3.046	163.84
N1−H1A· · ·O1 ⁱ	0.86	2.558	3.236	136.36
N1−H1B· · ·O2 ⁱⁱ	0.86	2.125	2.915	152.52
N2-H2C···01 ⁱ	0.86	1.980	2.804	160.03
N2−H2D···O3 ⁱⁱⁱ	0.86	2.237	3.015	150.49

Symmetry transformations used to generate equivalent atoms.

 $x^{i} x - 1, y - 1, z.$

 $x^{ii} -x + 1, -y, -z + 1.$

ⁱⁱⁱ -x, -y + 1, -z + 1.



Fig. 3. Optimized structure of SBTN at B3LYP/6-311+G(d,p).

Table 3

The optimized bond length, bond angle and electron density (ρ) (at bond critical point) in (a.u) of the SBTN Complex calculated using B3LYP methods with 6-311+G(2d,2p) basis set.

Nature	Bond length	Bond angle	Electron density
$\begin{array}{c} N_{11} {-} H_{21} {\cdots} O_{25} \\ N_{10} {-} H_{22} {\cdots} O_{25} \end{array}$	1.816	142.074	0.035154
	1.641	150.310	0.056793

molecule (AIM) analysis. All the calculations have been performed using the Gaussian 03 W program [19].

Results and discussion

Single crystal X-ray diffraction analysis

Single crystal X-ray analysis shows that SBTN crystal belongs to monoclinic system with space group $P2_1/c$ symmetry and the unit cell dimensions of the crystal is a = 5.8569 Å, b = 7.5931 Å, c = 23.9488 Å; $\alpha = \gamma = 90^\circ$; $\beta = 93.3^\circ$, are shown in Table 1. The analysis was carried out using Nonius CAD-4/MACII 3 diffractometer with Mo K α (0.71073 Å) radiation. An ORTEP (Oak Ridge Thermal Ellipsoid Plot) of SBTN crystal structure is shown in Fig. 2. S-benzyl

Table 4

Molecular geometry of SBTN crystal selected bond lengths (Å), bond angles determined by X-ray diffraction* and DFT calculations.

Bond lengths (Å)	X-ray data (*)	B3LYP/6-311G+(2d,2p)
C(1)-N(2)	1.3038	1.375
C(1)-N(1)	1.3073	1.331
C(2)-H2A	0.9700	1.102
C(2)-H2B	0.9700	1.008
C(4)-H(4)	0.9300	1.008
C(8)-H(8)	0.9300	1.107
C(1)-S(1)	1.654	1.783
S(2)-C(3)	1.665	1.783
N(1)-H1A	0.8600	0.996
N(1)-H1B	0.8600	0.994
N(1)-H1C	0.8600	1.000
N(1)-H1D	0.8600	1.009
N(3)-O(2)	1.2088	1.204
N(3)-O(3)	1.2345	1.224
N(3)-O(1)	1.2702	1.264
Bond angles (°)		
C(1)-N(1)-N(2)	120.76	119.94
C(1)-N(2)-S(1)	122.60	122.91
C(1)-N(1)-S(1)	116.63	116.85
C(2)-C(3)-S(1)	107.84	115.25
C(2)-C(3)-H2A	110.14	111.32
C(2)-H2A-H2B	108.45	110.45
C(4)-C(5)-H(4)	119.64	121.60
C(5)-C(4)-H(5)	120.03	121.05
N(1)-C(1)-H1A	120.00	120.56
N(2)-C(1)-H2C	120.00	119.25
N(3)-O(2)-O(3)	128.89	122.14
N(3)-O(2)-O(1)	116.44	116.70
N(3)-O(3)-O(1)	114.65	116.25

Ref. [20].

isothiouronium ion forms well defined crystalline charge transfer (CT) salt with anion nitrate through well-defined N–H···O and C– H···O hydrogen bonds. The present study aims at identifying the direction of specific N–H···O hydrogen bond between the-NH₂ group and O⁻ in the anion and also sacking in the solid state responsible for NLO activity in these crystals. The molecular structure of SBTN was solved by direct method as implemented in SHEL-XS-97 (Shledrick 1997) and refined by full matrix-least-squares refinement using SHELXL-97 (Shledrick 1997) program. The intensity data were collected for $-6 \le h \le 6$; $-9 \le k \le 9$; $-28 \le l \le 28$. The final refinement converged to an *R*-value of 0.0309. The final difference Fourier map had the maximum and minimum values of the residual electron density 1.08 and $-0.79 e^{A^{-3}}$, respectively.

Hydrogen bonding

The bond angles for O1-N3-O3 or O25-N12-O24 is 128.7 (4); 01-N3-O2 or 025-N12-O26 is 116.7 (4); 03-N3-O2 or 024-N12-O25 is 114.6 (3), which indicates slight deviation in the bond angle of O1-N3-O3 or O25-N12-O24. The molecule is stabilized N-H...N, and N-H...O intramolecular interactions between the S-benzylisothiouronium moiety and the nitrate moiety. The bond length of both C8-N1 and C8-N2 is 1.3073 Å and 1.3038 Å respectively. The values are intermediate between carbon-nitrogen double and single bond lengths. This partial double nature of C-N bond in S-benzyl isothiouronium ion has been attributed to the resonance effect. The distance N-O bonds in the anion vary from 1.2088 Å to 1.2702 Å. The C8–S1 or bond length is 1.7331 Å whereas C7-S1 bond length is slightly longer than the previous one, which has been determined to 1.8186 Å. The crystal packing is stabilized by N-H-...O and C-H-...O intermolecular interactions [20]. In SBTN, the orientation of the S-benzylisothiouronium and nitrate ions facilitates the formation of expected weak hydrogen bonds between the hydrogen at N1 of S-benzylisothiouronium

Table 5						
Observed and	l calculated	FTIR	wavenumbers	for	SBTN cry	stal.

Observed wavenumber (cm ⁻¹) FTIR	Wavenumber (cm ⁻¹)	Ir (Rel. Intensity)	Assignments
425(m)	425	0.64	Lattice vibrations
	449	25.08	τ (Ring deformation)
474(m)	473	86.46	τ (Ring deformation)
	492	8.17	τ (Ring deformation)
515(s)	521	1.37	v(CS) + ring deformation
568(s)	543	12.15	(CNH) deformation
	654	0.02	$\gamma(NCS)_1 + \gamma(CCS)_2 + \delta(NOO)_1$
708(s)	712	12.33	$\gamma(CCS)_2 + \delta(CNH)_2$
	748	26.92	$\gamma(NCS)_1 + \gamma(CCS)_{21}$
767(s)	768	37.69	$\gamma(CCS)_2$
	817	86.07	$\gamma(NCS)_2 + \gamma(CCS)_2 + \delta(NOH)_2$
825(s)	826	9.46	$\gamma(NCS)_2$
(-)	848	129.81	$\beta(NCS)_1 + \beta(CCS)_2 + \delta(CNH)_1$
870(ms)	870	134.06	$\delta(CNH)_1$
0,0(110)	875	17.69	$\gamma(NCS)_1 + \gamma(CCS)_2 + \delta(CNH)_2$
909(w)	909	0.45	$\gamma(CCH)_{2} + ring(CCH)_{1}$
000(11)	939	79.95	$\gamma(CCH)_2 + ring(CCC)_2$
	964	127.14	$\gamma(CCH)_2 + ring(CCC)_2$
	982	6.60	$\gamma(CCH)_2 + \delta(NO_2)_2$
1042(w)	1040	0.16	v(CCH) _n
10-12(W)	1058	0.10	B(SCH)
1065(w)	1050	1.43	B(SCH)
1100(m)	1102	0.05	$\beta(CNH)_{1} + \gamma(CCH)_{2}$
1140(m)	1135	81.60	$\beta(CNH)_1 + \gamma(CCH)_2$
1160(m)	1155	0.22	$\rho(CNH)$
1100(W)	1102	7.42	$\rho(CNH) \pm \rho(NOH)$
1220(m)	1241	1.45	$p(CCH) = p(NOH)_2$
1230(11) 1248(m)	1241	61 70	$\gamma(CCH)_2$
1248(11)	1247	01.79	$\gamma(CCH)_2$
	1202	0.10	v(CCII) ₂
1200(m)	1203	0.49	v(CCII) ₂
1500(11)	1252	0.14	v(CCII)
	1220	0.49	
	1402	5.40	$\beta(CCH)_2$
	1402	43.42	$\beta(CCH)_1$
1480()	1455	2.11	$p(CCH)_2 + p(CCH)_1$
1549(c)	1487	12.40	$\rho(CCII)$
1546(5)	1577	19.40	$p(CCH)_1$
1039(vs)	1625	10.02	$v_{s}(CNH_{2})_{2}$
	1623	7.79	$v_{s}(CNH_2)_1 \neq p(CCC)_2$
	1720	1.12	$V_{\rm s}(\rm CC)_1$
	1745	2.46	$V_{\rm s}(\rm CC)_1$
	1743	5.40 2.79	$V_{s}(CC)_{1} + \rho(CCH)_{2}$
1820()	1/05	2.78	$\partial(\ln n_2)_2$
1820(IIIS) 2072(ms)	1838	0.68	$\partial(\mathbf{NH}_2)_1$
3072(1115)	3027	1.14	$V_{\rm s}(\rm CH)_1$
	3030	2.82	$V_{\rm s}(\rm CH)_1$
	3140	0.60	V _s (CH) ₅
	5144	0.46	$V_{as}(NH_2)_1$
	3231	0.53	$v_{s}(NH_{2})_{1}$
	3259	3.28	$v_{\rm s}({\rm INH}_2)_2$
	3260	3./1	v _s (CH) ₅
22224	3266	8.68	v _s (CH) ₃
3280(w)	3277	4.49	v _s (CH) ₁
	3343	32.45	$v_{as}(NH_2)_1$
	3355	14.57	$v_{as}(NH_2)_2$

s, strong; m, medium; vs, very strong; w, weak; vw, very weak; v, stretching; v_s , symmetric stretching; v_{as} , asymmetric stretching; β , in-plane-bending; γ , out-of-plane bending; δ , scissoring; ω , wagging; ρ , rocking; t, twisting; τ , torsion.

moiety and O1 of nitrate ion whereas the one formed between the hydrogen at N2 of the same moiety and O1 of the nitrate ion is comparatively stronger as has been evidenced by the data given in Table 2. The molecular association through intermolecular hydrogen bonding is presumably the root cause for the SHG property in this crystal.

DFT calculations

The optimized structure of SBTN crystal at DFT level is shown in Fig. 3. Table 3 lists the bond lengths and bond angles of the structure of SBTN crystal calculated using B3LYP method at 6-311+(2d,2p) basis set. In this case oxygen acts as the proton accep-

tor and S-benzylisothiouronium as proton donor. The bond angles for N11–H21···O25 and N10–H22···O25 bonds in SBTN complex are 142.074° and 150.310° respectively. An understanding of the nature of a hydrogen bond can be analyzed through the study of electron density at the bond critical point (BCP) of the various hydrogen bonds involved. The values of electron density (ρ) (in atomic units) at BCP of N–H···O bond calculated using AIM approach are presented in Table 4. The electron densities at the values indicate the presence of hydrogen bond in the complex in accordance with Popelier's criteria [21]. It is expected that the strong bonds are usually associated with higher electron density values, indicating higher structural stability, as is observed for the N10–H12···O25 bond in the SBTN complex, which has higher



Fig. 5. UV-Vis spectrum of SBTN crystal.

electron density (0.056793 a.u) and strong hydrogen bond (1.641 Å). The correlation between the hydrogen bond length and electron density is inverse, that is, an increase in bond length corresponds to a decrease in the electron density, which is expected, since increase in distance results in reduced orbital overlap and hence low electron density along the bond. DFT calculations predict N10–H22 \cdots O25 to be the strong hydrogen bond present in SBTN, which is in accordance with experimental results given in Table 4. The AIM analysis augments the former result indicating a large electron density value for the hydrogen bond.

Natural bond orbital analysis

It is known that, the hydrogen bonds (H-bonds) are formed between proton donor and proton acceptor, and the amount of charge transfer is significant for the elongation and contraction of hydrogen bonds. In order to study the charge transfer between the donor and acceptor natural bonding analysis (NBO) [22] was carried out. The value of NBO occupation numbers for the proton donor antibonds (H–Y) and proton acceptor lone pairs n(X) for N11–H21…O25 and N10–H22…O25 bonds in SBTN shows the bonding nature. The occupation numbers for N11–H21and N10– H22 proton donor are found to be 0.04574 e and 0.09429 e respectively. The corresponding value for N–H in monomer is found to be 0.00614 e. This increase in occupation number from monomer to complex is due to charge transfer from the proton donor O25 of nitrate ion. The amount of charge transfer is large (0.09429e) in N10–

Table 6	
Electronic transistion state of SBTN at TD-DFT/6-31G(d,p) leve	el

H22...025 hydrogen bond when compared with N11–H21...025 hydrogen bond, due to which the former hydrogen bond length is shorter than the latter. Further the charge transfer energy $E^{(2)}$ is found to be 28.34 kcal/mol in the case of N10–H22...025, which is large when compared with N11–H21...025 hydrogen bond with 8.35 kcal/mol. Both the large charge transfer and charge transfer energy in N10–H22...025 could be attributed to the bond angle of the H-bond which is 150.31° while for N11–H21...025 H-bond it is142.07°. A remarkable deviation of calculated hydrogen bonding distance and angle with experimental value is noticed. It is due to the fact that anharmonicity with the real system, which includes neighborhood interactions also.

FTIR spectral analysis

The FTIR spectrum of SBTN was recorded using SHIMADZU FTIR spectrometer in the region 4000–400 cm⁻¹ and is shown in Fig. 4 (Provided in Supplementary part) The -NH₂ symmetric and asymmetric stretches in the range 3545–3433 cm⁻¹ are in agreement with experimental value of 3280 cm⁻¹ is assigned to NH₂ stretching vibrations. The aromatic CC stretch known as semicircle stretching predicted at 1630 at DFT levels of calculation is in agreement with observed value at 1639 cm⁻¹. This very sharp band with intensity of 7.2 is assigned to CC stretching vibrations [23]. The CN stretching wavenumbers in the side chains is a difficult task, because there are problems in identifying these wavenumbers from other vibrations. The band observed at 1480 cm⁻¹ is assigned to CN stretch. The peaks lying in between 3300 and 3000 cm⁻¹ are due to hydrogen bonded NH and aromatic CH stretching vibrations. The aromatic ring skeletal vibration is observed at 1454 cm⁻¹. The peak at 703 cm⁻¹ is due to aromatic C–H out of plane bending. The peak at 1639 cm^{-1} represents the NH₂ bending. The NO stretch is seen as a well resolved peak at 1548 cm⁻¹. The CS stretching is different from other vibrations in both aliphatic and aromatic sulfides [23]. Normally, thiocarbonyl group exhibit weak to medium peaks. In the present study the band observed at 568 cm⁻¹ and a sharp band at 708 cm⁻¹ are assigned to thiocarbonyl stretch and bend vibrations. The absorption peaks at 1384 cm⁻¹ and 825 cm⁻¹ are due to NO symmetric stretching and NO bending vibrations, respectively. The fundamental modes of vibrations of assignment for SBTN crystal is shown in Table 5.

UV-Vis spectral analysis

Optical transparency of 1 mm thick plate SBTN crystal was recorded using a Shimadzu 3100 PC UV–Vis spectrophotometer. The recorded transmission spectrum is shown in Fig. 5. The transmission range extends from 200 nm in the UV to 1000 nm in the IR region. The crystal has a good transmission in the entire visible range. The extended transmission window will enable higher harmonic generation and wavelength extension by cascaded frequency conversion process. From the spectrum, it is evident that

No	State of excitation	Energy (cm ⁻¹)	Wavelength (nm)	Oscillator strength (f)	State dipole (Debye)	Wavelength (nm) observed
1	Singlet	21427.5	466.7	0.002522	4.999392	-
2	Singlet	26518.0	377.1	0.002375	5.241358	-
3	Singlet	32905.3	303.9	0.000151	8.484894	-
4	Singlet	36874.6	271.2	0.004776	3.582994	-
5	Singlet	41502.8	240.9	0.042371	6.188184	-
6	Singlet	42603.9	234.7	0.067188	14.529789	-
7	Singlet	43363.9	230.6	0.116801	16.313392	-
8	Singlet	46658.2	214.3	0.029070	23.210926	-
9	Singlet	46838.1	213.5	0.083272	7.453551	-
10	Singlet	48044.6	208.1	0.239041	1.957221	208

Table 7NMR assignments for SBTN crystal.

Chemical shift (σ) value	e in ppm	Assignments
4.2864		Methylene protons of S-benzyl isothiouronium nitrate moiety
4.6704		Amino protons of the same moiety
1.2/3/		Alomatic protons

SBTN crystal has UV cutoff around 208 nm, which is sufficiently low for SHG laser radiation at 1064 nm, and has transmission over 25% and above 382 nm the material observed to be highly transparent with transmission over 64%.

Further, the optical and electronic properties of SBTN were investigated by means of TD-DFT calculations at the molecular level. The main orbital compositions of the computed lower lying 10 singlet excited states and transition features of the molecule obtained at the B3LYP/6-311G+(2d,2p) level. It is observed from the Table 6, that the lowest energy absorption found at 208 nm belongs to the dipole allowed π – π * transitions from HOMO to LUMO, corresponding to 208.1 nm with the largest oscillator strength calculated at the B3LYP/6-311+G(d,p) levels. The charge transfer is not from HOMO to LUMO but from allowed π – π * transitions [24]. The calculated outcomes are in good agreement with experimental data and provide deep insight into their electronic and charge transfer characteristics of SBTN crystals.

NMR spectral analysis

Nuclear magnetic resonance is a very versatile technique in the identification of organic and semi-organic compounds. It is also an important tool for examination of electronic structure. The ¹H NMR spectrum of SBTN crystal is shown in Fig. 6 (provided in Supplementary part). The assignments of various absorptions of the compound are shown in Table 7. It is observed from the figure that a singlet at 4.2864 ppm is due to $-CH_2$ protons present in the compound. The intense singlet peak at 4.6704 ppm has been assigned

Fable	8				
Gross	atomic	charge	density	of SI	BTN.

to the protons of the amino groups. The four protons of two amino groups appear at the same frequency due to resonance. The multiplet at 7.72787 ppm is due to aromatic protons. The identification of functional groups and their assignments confirms the structure of SBTN crystal.

Electron charge density

The gross atomic charges of SBTN with chemical shifts are given in Table 8. This data would be used to explain the preferred position of nucleophilic attack of this molecule. In the present study, we employed DFT levels to calculate the atomic charges. The gross atomic charges at the carbon C9 attached to NH₂ and oxygen atoms in NO₃ are electron deficient compared to other carbon atoms. In general, electron deficient atoms have the higher δ value than an electron rich atom. The carbon attached to N and O has lesser electron densities than the other carbons and hence these are more unshielded as shown in Table 8. So the C9 position is the preferred nucleophilic center. The net electron densities on all hydrogen atoms attached to the carbon are electropositive. In general, electron deficient atoms are more unshielded and hence they absorb at downfield. The chemical shift at δ 128.8 was assigned to the C–NH₂.

Thermo gravimetric analysis

Thermal analysis is used to provide quantitative information on weight losses due to decomposition and/or evaporation of low molecular material as a function of time and temperature, thus greatly facilitating the interpretation of thermal degradation processes. Computational quantum chemistry provides additional data, which can be utilized successfully for the interpretation of experimental results which may be used in the description and prediction of primary fragmentation processes. The thermal stability of SBTN was identified by thermo gravimetric (TG) and differential thermal analysis (DTA). The thermal analyses were carried out simultaneously employing Perkin Elmer thermal analyzer between 28 and 800 °C at a heating rate of 10.0 °C/min in nitrogen atmo-

No.	Atom	Gross atomic charge	Calculated chemical shift (δ) ¹ H and ¹³ C NMR	Observed chemical shift (δ) ¹ H NMR
1	С	-0.22093	31.2	
2	S	0.215301		
3	С	0.168963	70.2	
4	Ν	-0.3948		
5	Ν	-0.3935		
6	С	-0.07799	128.7	
7	С	-0.07861	127.2	
8	С	-0.07998	128.7	
9	С	-0.08793	128.8	
10	С	-0.0133	137	
11	С	-0.08176	128.8	
12	Н	0.091891	3.70	1.572
13	Н	0.116474	4.80	
14	Н	0.261495	2.0	
15	Н	0.223167	2.0	
16	Н	0.250575	7.14	7.425
17	Н	0.228101	7.07	7.372
18	Н	0.082671	7.14	7.267
19	Н	0.08305	7.07	
20	Н	0.084544	7.06	
21	Н	0.094308	2.0	
22	Н	0.078738	2.0	
23	0	-0.23737		
24	Ν	0.20102		
25	0	-0.21885		
26	0	-0.29529		



Fig. 7. Thermogram (TGA/DTA) of SBTN crystal.

sphere. The SBTN sample weighing 6.698 mg was taken for the analysis and the thermogram is illustrated in Fig. 7. The material is moisture free and stable up to 190 °C with the elimination of NO₂ gaseous product. The DTA reveals exactly same changes shown by TGA. This represents the absence of water molecule and moisture in the sample. The melting point of the sample is found to be 190 °C. Thermo-gravimetric results confirm the melting point and also indicate the single stage of weight loss starts at 196 °C without any intermediate stages. The compound is expected to evaporate at the same temperature thereby the loss in its weight is justified.

Non-linear optical analysis

The NLO efficiency of grown SBTN crystal was measured using Kurtz powder technique [25]. It consists of an Nd: YAG passively Q-switched laser of wavelength 1064 nm whose beam is focused onto a thin section of the material powder contained in a 3 mm cuvette. The specifications of the laser source used are 9 J pulse energy, 100 mW peak power, 8.62 kHz repetition rate and pulse width 860 ps. Urea crystal was used as reference material in SHG measurement. The samples used for SHG were obtained from the powdered SBTN crystal with uniform particle size. The efficiency of this material is 0.45 times that of urea.

Conclusion

The single crystal of SBTN is monoclinic with space group $P_{1/C}$ and it exhibits second-order NLO susceptibility due to intermolecular hydrogen bonding. The geometry of the crystal was analyzed by X-ray diffraction studies and compared with DFT methods. The better linearity in the NH₂ with NO₃ bond may have aided for large charge transfer and charge transfer energy. The presence of functional groups and their characteristics of SBTN crystal have been identified by FTIR and NMR spectral studies. The optical transmittance was studied using UV–Vis spectrum and lower cut off at 200 nm makes the crystal for NLO applications. The thermal analysis shows the grown crystal is thermally stable up to 208 C. The hydrogen bonding present in SBTN helps to create the delicate

balance between competing molecular and supramolecular CT effects, thus to create SHG active material which is 45% efficiency of standard NLO material.

Acknowledgments

The authors thank Prof. E.M. Subramanian, Department of Chemistry, Pachaiyappas College for Men, Kanchipuram, Tamil Nadu, India, for valuable discussions. The authors are thankful to Sophisticated Analytical Instrumentation Facility (SAIF), IIT Madras, Chennai, and NIT, Trichy for recording spectral measurements.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2013.01.080.

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