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Structure-property correlation of halogen substituted benzothiazole crystals



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ABSTRACT

We have synthesized 3 benzothiazole crystals (1–3) based on existing knowledge of combining flexibility and optical properties towards achieving applications for flexible optoelectronics. However, one crystal was found to be elastically bendable and was found to comply necessary packing features for elasticity. Other two crystals do not obey packing features for elasticity hence they are brittle in nature. Further, Hirshfeld analysis illustrates that elastic crystal 1 possess more number of weak and dispersive interactions compared to other crystals. These interactions were instrumental in invoking elasticity. Moreover, crystals 1–3 were found to be fluorescent as well at specific excitation wavelengths. Therefore, among these crystals, particularly crystal 1 is considered as more promising candidate for flexible optoelectronics.

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1. Introduction

Nowadays, Flexible crystals have been a frequently researched topic among the scientific communities owing to its promising applications in flexible optoelectronics [1,2], optical waveguides [3-5], sensors, flexible OLEDs etc. By systematic incorporation of optical properties with flexibility make some of the crystalline materials suitable candidates for flexible optoelectronics. There are several reports of flexible crystals such as elastically bendable [6–8], plastically bendable [9–11] and helically twisted [12] and so on. Each type of flexibility is associated with certain set of crystal packing features along with presence of weak interactions such as halogen bonding, hydrogen bonding etc. [13-16]. In general, elastic bending of crystals are associated with criss-cross packing in isotropic structure and presence of weak and dispersive interactions so called strain buffer or interaction buffer interactions [17,18]. In order to combine flexibility with optical properties suitable π conjugated molecules having reasonably good light absorbing or bright fluorescence can be chosen. Substituents of the molecule can be fine-tuned in order to meet requisite criteria for elasticity. Further, π conjugated molecules have tendency to form slip stacked assembly in dense state due to $\pi \cdots \pi$ interactions. While stacked assembly of the molecules can give rise to enhanced fluorescence in solid state due to J-aggregates the substituents in the periphery develop noncovalent interactions necessary for flexible behavior. Hence, crystal engineering can be gainfully employed to design property based molecular crystals. Very recently, several reports of fluorescent elastic organic crystals as optical waveguides are known. For instance, Naumov et al. have shown in their recent reports the dual-mode light transduction in optical waveguides by using elastic flexible organic crystals [4]. Hayashi et al. exhibited the role of elastic organic crystals comprising of fluorescent π -conjugated molecules in mechanofluorochromism and optical waveguides [5]. Zhang et al. showed optical waveguiding organic single crystals exhibiting physical and chemical bending features. However, some appropriate substituents may be introduced at particular positions in order to fine tune the molecules and should be apparently impervious to packing modes of crystals. Therefore, perfect compatibility should be carefully taken into consideration for designing of multiple stimuli responsive organic bending crystals [19]. Recently, we have showed how micromanipulation of organic crystals can led to microwaveguides [20]. Micromanipulation of flexible molecular crystals necessitates usage in miniature devices. Therefore, the single organic crystal that can withstand high mechanical flexibility similar to soft materials such as elastomers, thin films, and polymers can be of prime importance

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Fig. 1. Synthesized Crystals 1, 2 and 3.

for the design of future smart materials [21]. So far, the reports on plasticity and elasticity of molecular crystals have been revolving around the supramolecular synthons like: (1) polyhalogenated N-benzylideneanilines [22], (2) ester spacer based molecules, (3) organic co-crystals [12], (4) naphthalene diimides derivatives, (5) thiophenyl, (6) tetrafluoropyridyl based π -conjugated derivatives (7) vanillin derivatives [23], (8) pyrimidine [24], (9) terephthalamide (10) trisubstituted haloimidazoles, (11), fluorobenzoic acid derivative etc. and formation of these derivatives involved substitution of halogens or tedious synthetic routes. Benzothiazole is well known compound for its optical properties as it is used as a flurophore extensively and also as ligands for co-ordinating towards metals like Iridium, Platinum etc. and studied for the interactions in biological systems [17,25-28]. Herein, we have synthesized three halogen substituted benzothiazole crystals based on existing knowledge of combining flexibility with optical properties. However, we obtained one elastically bendable crystal 1 while other two were brittle in nature. Structure-property correlation study was done extensively. Crystal 1 was found to comply with necessary packing features for elasticity whereas 2 and 3 do not obey and hence are brittle in nature (Fig. 1).

2. Experimental section

2.1. Materials

2-Amino-4-Chloro benzenethiol, 4-Chloro benzaldehyde, 4-Pyridine carboxaladehyde, 4-methoxy salicylaldehyde were purchased from TCI, Alfa Aesar and used for synthesizing the required molecules and recrystallized in different solvents. Commercially available solvents were used as received without further purification.

2.2. Synthesis of benzothiazole derivatives

A series of crystals were synthesized by charging a variety of halogen substituted aldehyde (1.5 mmol), 2- amino-4chlorobenzenethiol (1.25 mmol), and DMSO (5 ml) in a round bottom flask and stirred for minimum of 6 h at 60 °C. Reaction was monitored by TLC. After the reaction water (50 ml) was charged and extracted with ethyl acetate for three times. The combined organic layer was distilled under vacuum to get crude product. It was purified by crystallization with acetone, methanol, ethanol and a variety of solvents.

2.3. Single crystal preparation

Some amount of synthesized substituted benzothiazole compounds are dissolved in minimum amount of solvents (different solvents such as ethanol, methanol, acetone, chloroform etc.) and kept for crystallization in slow evaporation method in small conical flask. Long, good diffraction quality crystals were obtained after 4–5 days.

2.4. Powder X-ray diffraction

The PXRD patterns were collected on a Bruker (D8 Advance) diffractometer with a Cu K α radiation (1.540 Å). The tube voltage and amperage were set at 40 kV and 50 mA respectively. Each powder sample was scanned between 5 and 50° 2θ with a step size of 0.02° (Figure S1-S3). The instrument was previously calibrated using a silicon standard.

2.5. Single crystal X-ray crystallography

Single crystal X-ray diffraction data were collected using a Rigaku XtaLABmini X-ray diffractometer equipped with Mercury CCD detector with graphite monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) using ω scans. The crystal structures were solved by using ShelXT [29] and were refined using ShelXL97 [30] through Olex2 suite [31]. All the hydrogen atoms were geometrically fixed and refined using the riding model. Multi-scan method was employed for absorption correction.

2.6. Melting point

Melting points of the synthesized crystals were measured using a Digital Melting point apparatus VEEGO (Model: VMP-PM).

2.7. Differential scanning calorimetry (DSC)

DSC experiments were conducted on a Netzsch Polyma 214 instrument by taking accurately weighed samples (2–3 mg) in a sealed aluminum crucibles having a pin hole on lid and scanned from 30 °C to 300 °C at a heating rate of 10 °C/min under a dry nitrogen atmosphere (flow rate 100 mL/min).

2.8. TGA/DTA studies

TGA/DTA studies were done on a Netzsch STA Regulus2500 by loading a small amount of sample in an alumina crucible and



Fig. 2. Snapshot of the bendable cycles of Crystal 1.

scanned from 30 °C to 600 °C at a heating rate of 20 °C/min under a dry nitrogen atmosphere (flow rate 100 mL/min) (Figure S10).

2.9. UV- Visible Spectrometry (UV-Vis)

Solution state UV–Vis absorption spectra of the crystals were done by dissolving it in dimethyl sulfoxide (DMSO). These were recorded by Agilent Cary 5000 spectrophotometer. The absorption maxima (λ_{max}) for Crystal **1**, **2** and **3** were found out to be 307 nm, 351 nm and 297 nm respectively.

2.10. IR spectroscopy

Transmission infrared spectra of the solids were obtained using a Fourier-transform infrared spectrometer (Schimadzu IR Tracer-100 in KBr method. An averaging of 2000 scans was collected at 4 cm⁻¹ resolution for each sample and the spectra were measured over the range of 4000–500 cm⁻¹.

2.11. Fluorescence microscopy study

Some crystals were checked under LEICA DM6B fluorescence microscope to capture optical images. This was checked with different ranges of excitation wavelengths and these were found to be fluorescent (Figures S7-S9, ESI).

3. Results and discussion

Crystals of **1** were grown from methanol solvent as long acicular crystals (Dimension approx. 10 mm \times 0.09 mm \times 0.074 mm) having triclinic space group $P\bar{1}$. The crystals were found to be elastically bendable when pressure is applied from any of the side faces. When the long needle crystal of **1** was held with forceps and pressure was applied from opposite sides with needle the crystal can be quickly bent and regains original shape upon pressure retraction. With increasing applied pressure it shows propensity to bend further and eventually half loop can be constructed as shown in Fig. 2. This bending is under the elastic limit and when the pressure exceeds limit it ultimately breaks down. The process can be repeated several times reflecting reversible and non-fatigue elastic bendability as it is evident from snapshots in Fig. 2. (Supporting video)

In order to establish structure-property correlation face indexing was performed for the crystal. It has been noted bendable side faces are assigned as $(011/0\overline{1}\overline{1})$ and $(0\overline{1}1/01\overline{1})$ (Fig. S6, ESI). Crystal packing analysis shows two molecules form dimeric motif via C-H•••O (2.992 Å) interactions. Further dimeric motifs are connected by C-H•••Cl (3.087 Å) and Cl•••S (3.598 Å) to form zigzag tapes. Within the tape there is presence of type II Cl•••Cl (3.996 Å) which plays sustainability within the tape. Neighbouring tapes are connected by mainly two interactions Cl•••S (3.766 Å) and C-H•••Cl (3.233 Å, 3.22 Å) to form corrugated network. Criss-cross packing view is clearly evident from (011) and $(0\overline{1}1)$ side faces (Fig. 3). From packing analysis it is quite clear that the crystal possess requisite criteria for elastic bending, i) absence of slip planes with isotropic criss-cross packing and ii) presence of multiple weak and dispersive interactions such as Cl+++Cl, Cl+++S, C-H+++Cl and C-H•••O etc. These restorative interactions play significant role in imparting elasticity. The bonds can be broken or reformed easily thereby invoking spring-like motion of the molecules with respect to their thermodynamic positions. When the pressure gets released the molecules come back to their original thermodynamic position rendering elasticity [13,14,16]. In bent state in outer arc molecules gets stretched out while in inner arc molecules gets compressed leaving interfacial angle same during bending. As a result outer arc increases and inner arc compresses to same extent [17,18,21,22]. Molecules located in middle arc do not change their mean position invariably. When the applied stress exceeds the threshold limit the crystal breaks. However, broken parts retain elasticity owing to intrinsic crystal packing. Elastic strain was estimated from the bent crystal and was found to be approximately ~ 3% (Fig. 3a and Fig. S5, ESI).

Crystals of **2** were grown from methanol solvents as plate shaped crystals (Dimension approx. 0.5 mm × 0.05 mm × 0.5 mm) in monoclinic space group $P_{2_1/c}$. 4-Methoxy salicylaldehyde and 4chloro-2-amino thiols were used as precursor materials for synthesizing benzothiazole compounds of **2**. In crystals of **2**, in individual molecule both benzothiazole ring and aromatic rings are coplanar with respect to C–C (C7–C8) bond. Total six molecules are interconnected *via* Cl•••Cl (3.467 Å) and C–H•••O (2.706 Å) interactions to form ring motif R_4^4 (54) (Fig. 4). Also two molecules are separately connected *via* C–H•••O (2.588 Å) interaction to form dimeric motif R_2^2 (16). Further dimeric motifs are connected to another R_4^4 (54) ring motif. Hence, this leads to interconnected network packing with absence of slip planes [17,18].

As the crystal do not comply necessary packing features such as criss-cross packing and presence of weak and dispersive interactions they are brittle in nature. Moreover, the interactions are less variant in nature (C-H•••O and Cl•••Cl) compared to interactions in crystal **1**. Packing clearly shows absence of slip plane or criss-cross arrangement of molecules in lattice considered as prerequisite criteria for slippage or elastic flexibility (Fig. 5). The relatively robust interactions in the lattice do not facilitate easy breaking or reformation of weak interactions under applied stress. Hence, overall crystal packing and noncovalent interactions are not enough to endow elasticity in crystals of **2**. Therefore, the crystals are not compliant in nature similar in line of **1** [13–18].

Crystals of **3** were grown as long needles (Dimension approx. 5 mm \times 0.08 mm \times 0.12 mm) from methanol, ethanol etc. The crystals were grown in monoclinic $P2_1/c$ space group. Molecules are connected mainly by C-H•••S (3.032 Å), C-H•••N (2.962 Å) and C-H••• π (2.895 Å) to form zigzag tape along *b* axis. Further, neighboring tapes are connected *via* type I Cl•••Cl (3.434 Å) and C-H•••N (2.797 Å) to form corrugated sheet in *bc* plane. Overall structure is isotropic and corrugated pattern is clearly visible from side faces along *b* and *c* axes (Fig. 6). Crystals do not comply packing feature similar to **1** and hence are brittle in nature (Fig. S4, ESI). Lesser number of weak and dispersive interactions such as Cl•••Cl interactions and presence of relatively stronger interactions such as C-H•••S hinders spring like motion of the molecules under applied stress [17,18].

Hirshfeld analysis can be used to define space of the molecule and gives some insights of the type and number of noncovalent interactions present in them. The marked white area indicates the area of separation between neighbouring atoms equivalent to sum



Fig. 3. (a) Crystal of 1 can be bent into half loop. (b) Crystal packing view perpendicular to (011), (0-11) and (100) faces. Criss-cross packing view is clearly evident from bendable side faces.



Fig. 4. Crystal packing of 2 shows ring motifs $R_4^4(54)$ and $R_2^2(16)$.

of van der Waal's radii and can be estimated by H•••H interactions. Blue regions indicate no interaction between neighbouring atoms because of their wide separation from each other. Red and blue region in the shape index represent the surface area surrounding acceptor and donor atoms in the molecule. C•••C contacts denote $\pi \bullet \bullet \pi$ distance between consecutive molecules. From Hirshfeld surface analysis it is quite evident that crystal 2 and 3 lacks several weak and dispersive interactions compared to 1. From relative percentage composition of weak interactions it is clear that crystal 1 possess more number of interactions resulting an important role in rendering elasticity (Fig. 7). As weak and dispersive interactions act as "strain buffer" interactions, numbers as well as strength of these interactions play as decisive factor in invoking elasticity. More number of relatively weaker interactions in 1 can be broken or reformed easily allowing easy movement of molecules under applied stress. Hence, number and type of weak interactions play significant role in deciding elastic bending behavior (Table 1 and Fig. 8).

3.2. Thermal analysis

3.2.1. Diffrential scanning calorimetry

A detailed DSC experiments were carried out of all the above crystals to study their thermal behavior. Crystals (1–3) are showing characteristic melting endotherms and their melting points are tabulated below (Table 2). The melting transition temperatures of

Table 1		
Crystallographic	Information	Table.

Compounds	1	2	3
Formula	C ₁₃ H ₇ Cl ₂ NS	C14H10ClNO2S	C ₁₂ H ₇ ClN ₂ S
Formula weight	280.17	291.74	246.7
T/K	298.0	298.0	298.0
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	P 1	P 2 ₁ /c	$P 2_1/c$
a/Å	3.8994(9)	14.1643(10)	3.9298(3)
b/Å	15.242(3)	5.8445(3)	11.6031(8)
c/Å	23.426(8)	15.3897(11)	23.5663(18)
$\alpha / ^{o}$	86.67(3)	90	90
β/°	89.72(2)	94.022(6)	90.921(15)
γ/°	84.376(19)	90	90
Volume/Å ³	1383.3(6)	1270.87(14)	1074.43(14)
Ζ	2	4	4
ρ , Mg.cm ⁻³	1.345	1.525	1.525
μ /mm $^{-1}$	0.596	0.460	0.518
Reflections collected	10,152	7182	12,412
Independent Reflections	4837	4203	3518
R _{int}	0.0454	0.0216	0.0332
GOF	0.985	1.032	0.924
Final $R[I > 2\sigma]$	0.0596	0.0453	0.0457
R_1 / wR_2	0.1272	0.1089	0.1045
CCDC Number.	2,033,995	1,987,126	1,987,127

all the crystals were different from either of the individual components confirming the formation of new phase. Further, the absence



(c)

Fig. 5. Crystal packing view of 2 along a axis (a), b axis (b) and c axis (c).





Fig. 6. Crystal packing view of 3 along a axis (a), b axis (b) and c axis (c).



Fig. 7. (a) and (b) Hirshfeld surface analysis and percentage contributions of interactions in crystal 1. (c) and (d) Hirshfeld surface analysis and percentage contributions of interactions in crystal 2. (e) and (f) Hirshfeld surface analysis and percentage contributions of interactions in crystal 3.

of any other endotherm excludes the formation of solvate or hydrate. Also there is no phase transition during course of heating. The thermogram shows the stability of the crystal and points out there is no weight loss upto melting of each form (Fig. 9).

3.3. FTIR analysis

Powdered samples were examined for FTIR spectrum using KBr pellet where the sample is mixed thoroughly with KBr powder and made as a pellet and analysis were done. Fig. 10a shows FTIR spec-



Fig. 8. Number of inter molecular interactions (close contacts) are more in 1 (a) compare to 2 (b) and 3 (c).

Table 2Melting points of the resultantcrystals.

Crystal	Melting Point ($^{\circ}C$)
1	155.9
2	228.8
3	182.8

trum for crystals from 4000 to 2000 cm⁻¹. In Crystal 2, a broad peak around region of 3200 cm⁻¹ confirms the presence of -OH bond. Fig. 10b for crystal 1 shows aromatic C-H stretching peak appears at 2980 cm⁻¹ as a sharp peak with high intensity, C = C vibrational mode appears at 1434 cm⁻¹ as sharp peak and C-C stretching frequency comes at around 1092 cm⁻¹. There is a presence of C-S stretching vibrational mode at 623 cm^{-1} and C = N mode at 1646 cm⁻¹. Halogen substitution gives the C-Cl stretching peak at 831 cm⁻¹. This shows sharp characteristic peak of O- CH_3 stretching mode at 1203 cm⁻¹ for crystal **2**. Aromatic C-H bond stretching vibrational mode is showing a high intense peak in 1881 cm⁻¹. C = C stretching vibrational mode appears at 1433 cm⁻¹ and C–C stretching mode comes around 1200 cm⁻¹. There is a presence of C–S stretching vibrational mode at 643 cm^{-1} and a weak intense peak corresponding to C = N at 1646 cm⁻¹. Halogen substitution gives the C-Cl stretching peak at 808 cm⁻¹. Similarly this is also evident for crystal 3. Aromatic C-H stretching vibrational mode appears as high intense peak in 2900 cm^{-1} and C = Cstretching vibrational mode appears at 1436 cm⁻¹. Here also there is a presence of C–S stretching vibrational mode at 633 cm⁻¹ and C = N weak intense peak at 1652 cm⁻¹. Halogen substitution gives the C–Cl stretching peak at 820 cm⁻¹ [32,33,34] (Table 3).



Fig. 9. The endotherm of the DSC corresponds to the melting of the respective crystals (1–3).

Table 3 FTIR frequency table.			
	1	2	3
C-H stretching	1872	1881	1732
C = N	1646	1646	1652
C-S	623	643	633
C-Cl	831	808	820
0-H	-	3425	-
O-CH ₃ strectching	-	1203	-



Fig. 10. The FT-IR spectrum of Crystal (a) 4000 to 2000cm⁻¹ and (b) 2000 to 400cm⁻¹.

4. Conclusion

We have synthesized three halogen substituted benzothiazole crystals based on existing knowledge of combining flexibility with optical properties. However, we got one elastically bendable crystal **1** while other two were brittle in nature. Structure-property correlation study shows crystal **1** was found to comply with necessary packing features for elasticity whereas **2** and **3** do not comply and hence are brittle in nature. Furthermore, Hirshfeld analysis reflects the fact that more number of weak and dispersive interactions in crystal **1** is instrumental in pertaining elasticity. Thermal and FTIR analysis were done extensively.

Credit author statement

Dr. Soumyajit Ghosh the corresponding author designed the work and analysed the results obtained from several experiments and wrote the manuscript.

Mr. Nipun P Thekkeppat has performed all the experiments including synthesis of benzothiazole compounds, characterization and analysis.

Dr. Priyadip Das helps to interpret few experimental observations including UV–VIS studies.

Dr. Angshuman Roy Choudhury, Ms. Labhini Singla and Dr. Srinu Tothadi have helped in getting crystal structure solutions and face indexing images.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2021.130765.

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