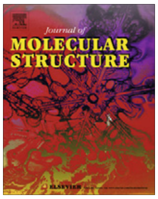
Journal of Molecular Structure 1016 (2012) 55–63

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Structure

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



Salt and co-crystal formation from 6-bromobenzo[d]thiazol-2-amine and different carboxylic acid derivatives

Shouwen Jin [a,*], Pinhui Yan [b], Daqi Wang [c], Yijie Xu [b], Yingyan Jiang [b], Liangliang Hu [b]

[a] Tianmu College of ZheJiang A & F University, Lin'An 311300, PR China
[b] School of Engineering, ZheJiang A & F University, Lin'An 311300, PR China
[c] Department of Chemistry, LiaochengUniversity, Liaocheng 252059, PR China

ARTICLE INFO

Article history:
Received 22 September 2011
Received in revised form 8 February 2012
Accepted 16 February 2012
Available online 24 February 2012

Keywords:
Crystal structure
Noncovalent interactions
6-Bromobenzo[d]thiazol-2-amine
Carboxylic acids

ABSTRACT

Studies concentrating on non-covalent interactions between the organic base of 6-bromobenzo[d]thiazol-2-amine, and carboxylic acid derivatives have led to an increased understanding of the role 6-bromobenzo[d]thiazol-2-amine has in binding with carboxylic acid derivatives. Here anhydrous and hydrated multicomponent organic acid–base adducts of 6-bromobenzo[d]thiazol-2-amine have been prepared with the carboxylic acids as p-nitrobenzoic acid, fumaric acid, L-tartaric acid, and terephthalic acid. The four crystalline compounds were characterized by X-ray diffraction analysis, infrared (IR), melting point (mp), and elemental analysis. All structures adopted hetero $R_2^2(8)$ supramolecular synthons except the salt **3**. Analysis of crystal packing of the compounds under study suggests that there are N—H···O, O—H···N, and O—H···O hydrogen bonds (charge assisted or neutral) between acid and base components in the supramolecular assemblies.

1. Introduction

Intermolecular interactions are responsible for crystal packing and gaining an understanding of them allows us to comprehend collective properties and permits the design of new crystals with specific physical and chemical properties [1]. Intermolecular interactions, such as hydrogen bonding, π···π stacking, C—H···π/CH$_2$···π/CH$_3$···π interactions, C—H···O/CH$_2$···O/CH$_3$···O interactions, ion pairing, and donor–acceptor interactions are famous for making aggregates of molecules [2]. Hydrogen bonding is one of the several types of non-covalent interactions in many organic and inorganic species, which results in aggregation and controls self-assembly, in some cases [3–6].

The design and construction of multicomponent supermolecules or supramolecular arrays utilizing non-covalent bonding is a rapidly developing area in supramolecular synthesis. Thus, the supramolecular synthesis successfully exploits hydrogen-bonding and other types of non-covalent interactions, in building supramolecular systems [7]. There are many interesting topological structures such as one-dimensional (1-D) chains, two-dimensional (2-D) sheets, and three-dimensional (3-D) networks which have been constructed through hydrogen bonding interactions [8–10]. The carboxylic acid bears the important hydrogen bonding functional group COOH for crystal engineering [11]. Carboxylic acids aggregate in the solid state as dimer, catemer, and bridged motifs [12]. Besides the COOH group, the functional groups such as NO$_2$ and OH groups are both good groups in forming organic solid through non-covalent interactions [13], thus we select some carboxylic acids bearing additional groups such as NO$_2$ and OH. It is interesting to exploit the robust and directional recognition of carboxylic acids with nitrogen containing heterocyclic compounds [14].

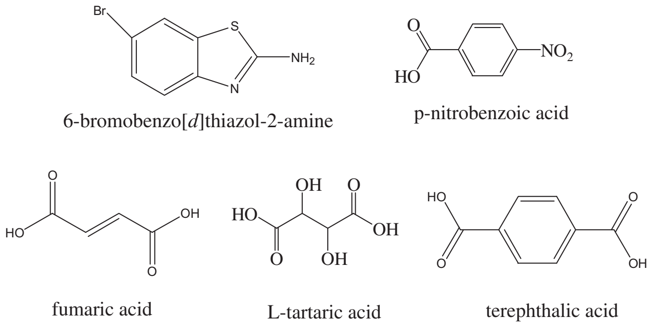
Recently 2-aminoheterocyclic compounds have been reported to form supramolecular compounds with the carboxylic acid derivatives under the multiple hydrogen bonding action [15,16]. As a 2-aminoheterocyclic compound, 6-bromobenzo[d]thiazol-2-amine exhibited moderate Anthelmintic activity [17]. Like other 2-aminoheterocyclic compounds 6-bromobenzo[d]thiazol-2-amine is a potentially tridentate ligand (NSN). Furthermore the halogen (Br) atoms can generate halogen–halogen bond which has been widely utilized in crystal engineering [18].

The binary adducts of the carboxylic acids and 6-bromobenzo[d]thiazol-2-amine may show the different hydrogen-bonding patterns from the three different acceptor atoms. In recent years, our research group has been involved in the study of organic acid–base adducts based on carboxylic acids and organic bases. As an extension of our study of supramolecular assemblies concerning aromatic N-containing derivatives [19], herein we report the preparation and structures of four supramolecular compounds assembled from 6-bromobenzo[d]thiazol-2-amine (L), and the corresponding carboxylic compounds (Scheme 1), respectively. The four compounds are (6-bromobenzo[d]thiazol-2-amine): (p-nitrobenzoic acid) (**1**) [(L) (Hnba), Hnba = p-nitrobenzoic acid],

---

* Corresponding author. Tel./fax: +86 571 6374 6755.
E-mail address: jinsw@zafu.edu.cn (S. Jin).

0022-2860/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.molstruc.2012.02.036



Scheme 1. Hydrogen bond building blocks discussed in this paper.

(6-bromobenzo[d]thiazol-2-amine): (fumaric acid)$_{0.5}$ (**2**) [(L).(H$_2$fum)$_{0.5}$, H$_2$fum = fumaric acid], (6-bromobenzo[d]thiazol-2-amine): (L-tartaric acid): 2H$_2$O (**3**) [(HL1$^+$). (Htart$^-$)···2H$_2$O, Htart$^-$ = hydrogen tartarate], and (6-bromobenzo[d]thiazol-2-amine)$_2$: (terephthalic acid) (**4**) [(L)$_2$ (H$_2$tpa), H$_2$tpa = terephthalic acid], respectively (Scheme 2).

2. Experimental section

2.1. Materials and physical measurements

The chemicals and solvents used in this work are of analytical grade and available commercially and were used without further purification. The FT-IR spectra were recorded from KBr pellets in range 4000–400 cm^{-1} on a Mattson Alpha-Centauri spectrometer. Microanalytical (C, H, N, S) data were obtained with a Perkin–Elmer Model 2400II elemental analyzer. Melting points of new compounds were recorded on an XT-4 thermal apparatus without correction.

2.2. Preparation of the supramolecular compounds *1–4*

2.2.1. (6-Bromobenzo[d]thiazol-2-amine): (p-nitrobenzoic acid) [(L) (Hnba)] (*1*)

To an ethanol solution (8 mL) of 6-bromobenzo[d]thiazol-2-amine (22.9 mg, 0.1 mmol) was added p-nitrobenzoic acid (16.6 mg, 0.1 mmol). The solution was stirred for a few minutes, then the solution was filtered into a test tube. The solution was left standing at room temperature for 16 days, light yellow crystals were isolated after slow evaporation of the ethanol solution to ca. 1 mL in air. The crystals were collected and dried in air to give the title compound [(L). (Hnba)] (**1**). Yield: 29 mg, 73.19% (based on L). m. p. 221–222 °C. Anal. Calcd for $C_{14}H_{10}BrN_3O_4S$ (396.22): C, 42.40; H, 2.52; N, 10.60; S, 8.07. Found: C, 42.35; H, 2.47; N, 10.54; S, 8.03. Infrared spectrum (KBr disc, cm^{-1}): 3616s(ν(OH)), 3385s(ν$_{as}$(NH)), 3215s(ν$_s$(NH)), 3087 m, 2984s, 2508 m, 1896 m, 1668s(ν(C=O)), 1620 m, 1536s(ν$_{as}$(NO$_2$)), 1486 m, 1442 m, 1400 m, 1320s(ν$_{as}$(-NO$_2$)), 1292s(ν(C—O)), 1246 m, 1202 m, 1162 m, 1094 m, 1006 m, 952w, 861w, 811 m, 767w, 714 m, 656w, 618w.

2.2.2. (6-Bromobenzo[d]thiazol-2-amine): (fumaric acid)$_{0.5}$ [(L).(H$_2$fum)$_{0.5}$] (*2*)

To an ethanol solution (8 mL) of 6-bromobenzo[d]thiazol-2-amine (22.9 mg, 0.1 mmol) was added fumaric acid (12 mg, 0.1 mmol) in 5 mL methanol. The solution was stirred for a few minutes, then the solution was filtered into a test tube. The solution was left standing at room temperature for 25 days, light yellow crystals were isolated after slow evaporation of the solution to ca. 3 mL in air. The crystals were dried in air to give the title compound [(L). (Hfum)$_{0.5}$] (**2**). Yield: 24 mg, 83.58% (Based on L). m. p. 232–233 °C. Elemental analysis performed on crystals exposed to the atmosphere: Calcd for $C_9H_7BrN_2O_2S$ (287.14): C, 37.61; H, 2.44; N, 9.75; S, 11.14. Found: C, 37.56; H, 2.39; N, 9.72; S, 11.08. Infrared spectrum (KBr disc, cm^{-1}): 3560s(ν(OH)), 3412s(ν$_{as}$(NH)), 3213s(ν$_s$(NH)), 3092 m, 2996 m, 2498 m, 1904 m, 1701s(ν(C=O)), 1622 m, 1542 m, 1488s, 1436s, 1296s(ν(C—O)), 1186 m, 1132 m, 1105 m, 1054 m, 1012 m, 936 m, 859 m, 808 m, 738 m, 680 m, 620 m.

2.2.3. (6-Bromobenzo[d]thiazol-2-amine): (L-tartaric acid): 2H$_2$O [(HL$^+$). (Htart$^-$) 2H$_2$O] (*3*)

To an ethanol solution (8 mL) of 6-bromobenzo[d]thiazol-2-amine (22.9 mg, 0.1 mmol) was added L-tartaric acid (15 mg, 0.1 mmol). The solution was stirred for 3 min, then the solution was filtered into a test tube. The solution was left standing at room temperature for 2 h, light yellow crystals were isolated. The crystals were dried in air to give the title compound [(HL1$^+$). (Htart$^-$)···2H$_2$O] (**3**). Yield: 32 mg, 77.07% (Based on L). m. p. 188–189 °C. Elemental analysis performed on crystals exposed to the atmosphere: Calcd for $C_{11}H_{15}BrN_2O_8S$ (415.22): C, 31.79; H, 3.61; N, 6.74; S, 7.70. Found: C, 31.72; H, 3.58; N, 6.69; S, 7.66. Infrared spectrum (KBr disc, cm^{-1}): 3645s(ν(OH)), 3462s(ν$_{as}$(NH)), 3332s(ν$_s$(NH)), 3078 m, 1730s(ν(C=O)), 1631 m, 1598s(ν$_{as}$(COO$^-$)), 1550 m, 1484 m, 1426 m, 1382s(ν$_s$(COO$^-$)), 1358 m, 1302s(ν(C—O)), 1196 m, 1122 m, 1054 m, 940 m, 853 m, 803 m, 732 m, 676 m, 616 m.

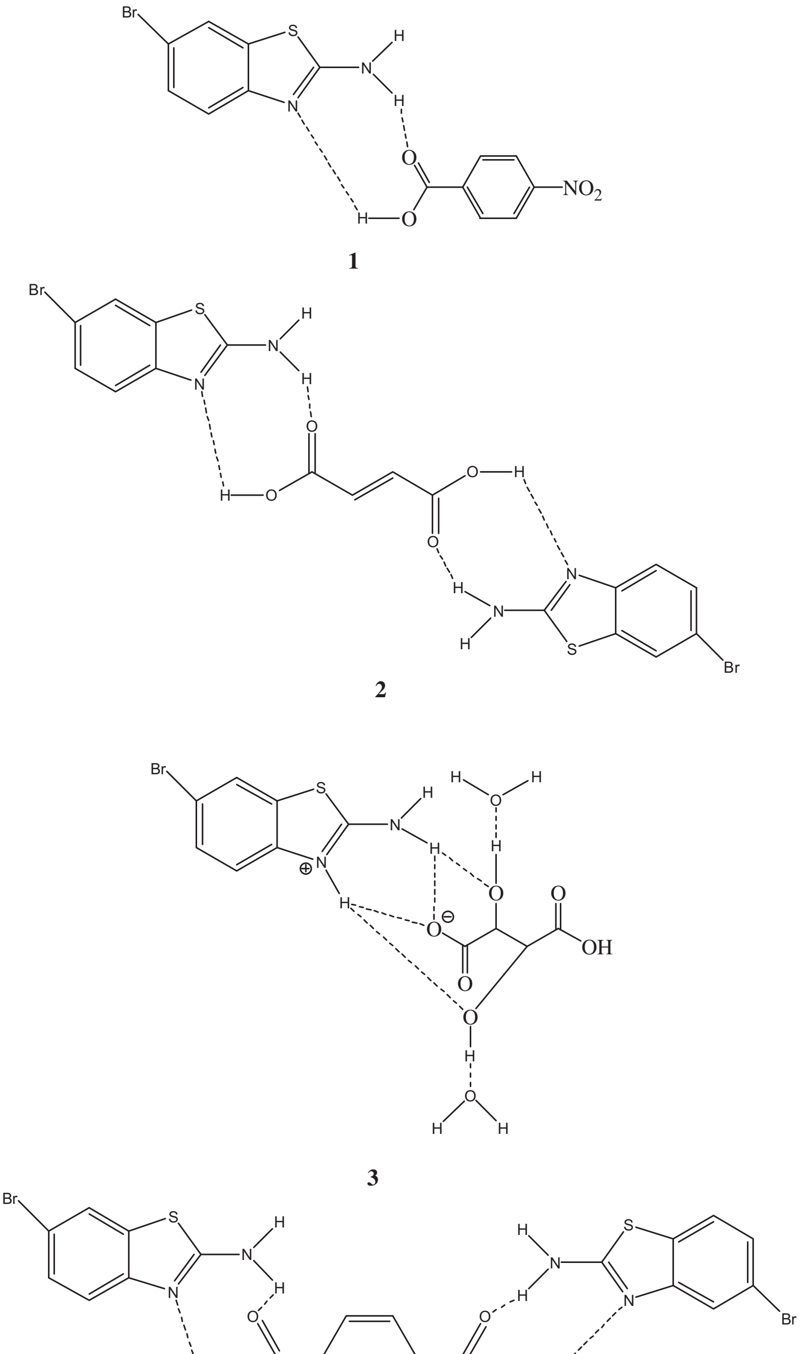
2.2.4. (6-Bromobenzo[d]thiazol-2-amine)$_2$: (terephthalic acid) [(L)$_2$ (H$_2$tpa)] (*4*)

To a methanol solution (8 mL) of 6-bromobenzo[d]thiazol-2-amine (22.9 mg, 0.1 mmol) was added terephthalic acid (17 mg, 0.1 mmol) in 10 mL methanol. The solution was stirred for half an hour, then the solution was filtered into a test tube. The solution was left standing at room temperature for 27 days, light yellow block crystals were isolated after slow evaporation of the methanol solution to ca. 5 mL in air. The crystals were dried in air to give the title compound [(L)$_2$ (H$_2$tpa)] (**4**). Yield: 27 mg, 86.49% (Based on L). m. p. 265–266 °C. Elemental analysis performed on crystals exposed to the atmosphere: Calcd for $C_{22}H_{16}Br_2N_4O_4S_2$ (624.33): C, 42.28; H, 2.56; N, 8.97; S, 10.25; Found: C, 42.24; H, 2.52; N, 8.89; S, 10.19. Infrared spectrum (KBr disc, cm^{-1}): 3584s(ν(OH)), 3348s(ν$_{as}$(NH)), 3242s(ν$_s$(NH)), 3085 m, 2496 m, 1906 m, 1712s (C=O), 1629 m, 1542 m, 1492 m, 1416 m, 1342 m, 1286s(C—O), 1240 m, 1192 m, 1108 m, 1056 m, 1002 m, 944 m, 878 m, 813 m, 786 m, 722 m, 668 m, 629 m.

2.3. X-ray crystallography and data collection

Suitable crystals were mounted on a glass fiber on a Bruker SMART 1000 CCD diffractometer operating at 50 kV and 40 mA using Mo Kα radiation (0.71073 Å). Data collection and reduction were performed using the SMART and SAINT software [20]. The structures were solved by direct methods, and the non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least squares on F^2 using SHELXTL package [21].

Hydrogen atom positions for all of the structures were located in a difference map and refined independently. Further details of the structural analysis are summarized in Table 1. Selected bond lengths and angles for the compounds **1–4** are listed in Table 2, the relevant hydrogen bond parameters are provided in Table 3.



Scheme 2. The four supramolecular compounds described in this paper, **1**–**4**.

3. Results and discussion

3.1. Preparation and general characterization

6-Bromobenzo[d]thiazol-2-amine has good solubility in common organic solvents, such as methanol, ethanol, dichloromethane, chloroform, and acetonitrile. The preparation of compounds **1**–**4** were carried out with 6-bromobenzo[d]thiazol-2-amine and the corresponding carboxylic acid derivatives in 1:1 ratio in the corresponding polar hydroalcoholic solution, which was allowed to evaporate at ambient conditions to give the final crystalline products. In all of the structures except **3**, the heteroaromatic Lewis base molecules are not protonated therefore **1**, **2**, and **4** can be classified as cocrystals, while **3** is an organic salt. The four compounds are not hygroscopic, and they all crystallized with no solvent molecules accompanied except salt **3**. The molecular structures and their atom labelling schemes for the four structures are illustrated in Figs. 1, 3, 5 and 7, respectively. The elemental analysis data for the four compounds are in good agreement with their compositions. The infrared spectra of the four compounds are consistent

Table 1
Summary of X-ray crystallographic data for compounds **1**, **2**, **3**, and **4**.

	1	**2**	**3**	**4**
Formula	$C_{14}H_{10}BrN_3O_4S$	$C_9H_7BrN_2O_2S$	$C_{11}H_{15}BrN_2O_8S$	$C_{22}H_{16}Br_2N_4O_4S_2$
Fw	396.22	287.14	415.22	624.33
T (K)	298(2)	298(2)	298(2)	298(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
space group	P2(1)	P2(1)/c	C2	P2(1)/c
a (Å)	8.5977(8)	17.8409(15)	22.777(2)	13.9610(13)
b (Å)	4.9726(3)	5.1980(4)	9.6721(8)	3.9045(3)
c (Å)	17.3935(15)	11.7711(11)	7.1880(6)	22.9854(16)
α (°)	90	90	90	90
β (°)	90.1620(10)	106.9590(10)	97.7670(10)	109.717(4)
γ (°)	90	90	90	90
V (Å^3)	743.62(10)	1044.15(15)	1569.0(2)	1179.49(16)
Z	2	4	4	2
D_{calcd} (Mg/m^3)	1.770	1.827	1.758	1.758
Absorption coefficient (mm^{-1})	2.928	4.116	2.796	3.652
F(000)	396	568	840	620
Crystal size (mm^3)	0.45 × 0.21 × 0.12	0.44 × 0.17 × 0.10	0.35 × 0.11 × 0.08	0.41 × 0.36 × 0.13
θ range (°)	2.64–25.04	3.46–25.02	2.29–25.02	2.81–25.01
Limiting indices	$-9 \le h \le 10$ $-5 \le k \le 5$ $-20 \le l \le 16$	$-14 \le h \le 21$ $-5 \le k \le 6$ $-14 \le l \le 13$	$-27 \le h \le 22$ $-11 \le k \le 11$ $-8 \le l \le 8$	$-16 \le h \le 15$ $-4 \le k \le 4$ $-19 \le l \le 27$
Reflections collected	3734	4899	4027	5416
Reflections independent (R_{int})	2421 (0.0710)	1837 (0.0887)	2720 (0.0429)	2078 (0.0822)
Goodness-of-fit on F^2	0.998	1.016	0.907	1.087
R indices [$I > 2\sigma I$]	0.0554, 0.1358	0.0454, 0.1103	0.0456, 0.0947	0.0705, 0.1935
R indices (all data)	0.0682, 0.1428	0.0721, 0.1250	0.0639, 0.1007	0.1072, 0.2150
Largest diff. peak and hole (e.Å^{-3})	0.451, −0.557	0.621, −0.423	0.440, −0.429	1.023, −0.941

Table 2
Selected bond lengths (Å) and angles (°) for compounds **1–4**.

1			
Br(1)—C(5)	1.893(6)	S(1)—C(1)	1.741(6)
S(1)—C(3)	1.764(6)	N(1)—C(1)	1.313(8)
N(1)—C(2)	1.390(8)	N(2)—C(1)	1.342(8)
O(1)—C(8)	1.311(7)	O(2)—C(8)	1.215(7)
C(1)—S(1)—C(3)	88.7(3)	C(1)—N(1)—C(2)	110.3(5)
N(1)—C(1)—N(2)	123.2(6)	N(1)—C(1)—S(1)	115.9(4)
N(2)—C(1)—S(1)	120.9(5)	O(2)—C(8)—O(1)	123.9(6)
2			
Br(1)—C(5)	1.904(4)	S(1)—C(3)	1.745(4)
S(1)—C(1)	1.767(4)	N(1)—C(1)	1.308(5)
N(1)—C(2)	1.393(5)	N(2)—C(1)	1.321(5)
O(1)—C(8)	1.223(5)	O(2)—C(8)	1.305(5)
C(3)—S(1)—C(1)	89.1(2)	C(1)—N(1)—C(2)	112.2(3)
N(1)—C(1)—N(2)	124.5(4)	N(1)—C(1)—S(1)	114.4(3)
N(2)—C(1)—S(1)	121.1(3)	O(1)—C(8)—O(2)	124.8(4)
3			
Br(1)—C(5)	1.898(6)	N(1)—C(1)	1.319(8)
N(1)—C(2)	1.395(8)	N(2)—C(1)	1.299(7)
O(1)—C(8)	1.260(6)	O(2)—C(8)	1.230(7)
O(3)—C(11)	1.294(6)	O(4)—C(11)	1.221(7)
O(5)—C(9)	1.416(7)	O(6)—C(10)	1.427(6)
S(1)—C(1)	1.740(6)	S(1)—C(3)	1.754(6)
C(1)—N(1)—C(2)	115.6(5)	C(1)—S(1)—C(3)	90.3(3)
N(2)—C(1)—N(1)	124.9(6)	N(2)—C(1)—S(1)	123.2(5)
N(1)—C(1)—S(1)	111.9(4)	O(2)—C(8)—O(1)	125.6(5)
O(4)—C(11)—O(3)	124.5(6)		
4			
Br(1)—C(5)	1.892(8)	N(1)—C(1)	1.320(10)
N(1)—C(2)	1.381(9)	N(2)—C(1)	1.324(10)
O(1)—C(8)	1.300(8)	O(2)—C(8)	1.236(9)
S(1)—C(3)	1.731(7)	S(1)—C(1)	1.750(8)
C(1)—N(1)—C(2)	110.2(6)	C(3)—S(1)—C(1)	89.7(3)
N(1)—C(1)—N(2)	123.7(7)	N(1)—C(1)—S(1)	115.2(6)
N(2)—C(1)—S(1)	121.1(6)	O(2)—C(8)—O(1)	123.6(7)

Table 3
Hydrogen bond distances and angles in studied structures of **1–4**.

D—H···A	d(D—H) (Å)	d(H···A) (Å)	d(D···A) (Å)	<(DHA) (°)
1				
O(1)—H(1)···N(1)#1	0.82	1.81	2.627(7)	173.9
N(2)—H(2B)···O(3)#2	0.86	2.58	3.106(7)	120.7
N(2)—H(2B)···O(4)#3	0.86	2.35	3.154(8)	154.7
N(2)—H(2A)···O(2)#4	0.86	2.12	2.946(7)	159.7
2				
O(2)—H(2)···N(1)#2	0.82	1.82	2.637(4)	170.7
N(2)—H(2B)···O(1)#3	0.86	2.52	2.991(5)	115.0
N(2)—H(2B)···O(2)#4	0.86	2.34	3.155(5)	159.2
N(2)—H(2A)···O(1)#5	0.86	2.15	2.981(5)	161.2
3				
O(8)—H(8D)···O(4)#1	0.85	1.96	2.801(6)	170.3
O(8)—H(8C)···O(4)#2	0.85	2.01	2.847(6)	170.3
O(7)—H(7D)···O(2)#3	0.85	1.94	2.784(6)	174.9
O(7)—H(7C)···O(1)#4	0.85	1.90	2.745(5)	174.9
O(6)—H(6)···O(8)	0.82	1.84	2.657(5)	171.6
O(5)—H(5)···O(7)	0.82	1.92	2.734(6)	174.7
O(3)—H(3)···O(2)#3	0.82	2.64	3.252(6)	133.0
O(3)—H(3)···O(1)#3	0.82	1.72	2.521(5)	167.1
N(2)—H(2B)···O(7)#4	0.86	2.01	2.857(6)	170.0
N(2)—H(2A)···O(5)	0.86	2.37	3.049(6)	135.7
N(2)—H(2A)···O(2)	0.86	2.25	2.919(7)	134.3
N(1)—H(1)···O(2)	0.86	2.27	2.915(7)	131.9
4				
O(1)—H(1)···N(1)	0.82	1.84	2.653(8)	169.9
N(2)—H(2B)···O(2)#2	0.86	2.07	2.918(9)	169.5
N(2)—H(2A)···O(2)	0.86	2.06	2.895(9)	162.3

Symmetry transformations used to generate equivalent atoms for **1**: #1 x, $y+1$, z; #2 $-x+1$, $y+1/2$, $-z$; #3 $x+1$, $y+1$, z; #4 x, $y-1$, z. Symmetry transformations used to generate equivalent atoms for **2**: #2 x, $y+1$, z; #3 $-x+1$, $y-1/2$, $-z+1/2$; #4 x, $-y+3/2$, $z-1/2$; #5 x, $y-1$, z. Symmetry transformations used to generate equivalent atoms for **3**: #1 $-x+1$, y, $-z+1$; #2 x, y, $z+1$; #3 x, y, $z-1$; #4 $-x+3/2$, $y+1/2$, $-z+1$. Symmetry transformations used to generate equivalent atoms **4**: #2 $-x$, $y-1/2$, $-z+1/2$.

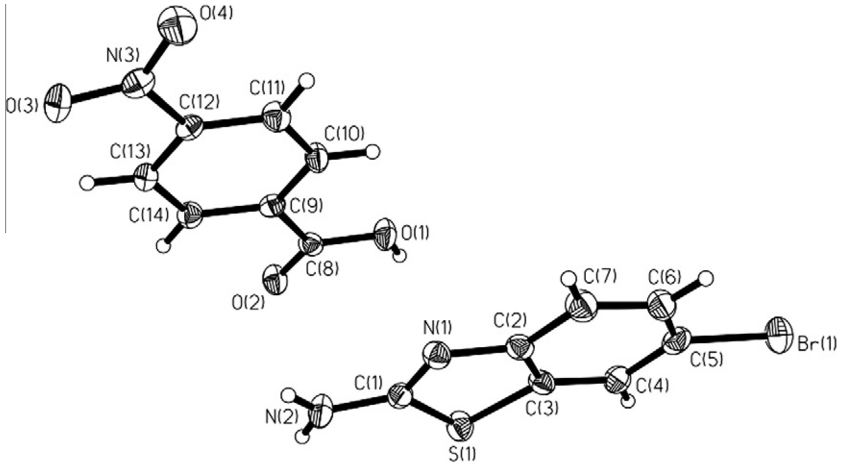


Fig. 1. Molecular structure of **1** showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

with their chemical formulas determined by elemental analysis and further confirmed by X-ray diffraction analysis. H atoms connected to O or N atoms were well found from the difference electron density map.

The very strong and broad features at approximately 3700–3200 cm^{-1} in the IR spectra of the four compounds arise from O—H or N—H stretching frequencies. Aromatic, and benzo[d]thiazolic ring stretching and bending are attributed to the medium intensity bands in the regions of 1500–1630 cm^{-1} and 600–750 cm^{-1}, respectively. All of the four compounds show the characteristic bands for COOH, while compound **3** displays additional strong IR peaks for COO^{-} groups. The presence of two broad bands at ca. 2500 cm^{-1} and 1900 cm^{-1} in compounds **1**, **2**, and **4**, characteristic of a neutral O—H···N hydrogen-bond interaction, was viewed as evidence for co-crystal formation [22].

3.2. Structural descriptions

3.2.1. X-ray structure of (6-bromobenzo[d]thiazol-2-amine): (p-nitrobenzoic acid) [(L) (Hnba)] (1)

The compound **1** of the composition [(L) (Hnba)] was prepared by reaction equal mol of 6-bromobenzo[d]thiazol-2-amine and p-nitrobenzoic acid, in which the proton of the p-nitrobenzoic acid was not transferred to the N atoms at the L molecule. This structure is not a solvate. In the asymmetric unit of **1** there existed one molecule of 6-bromobenzo[d]thiazol-2-amine, and one molecule of p-nitrobenzoic acid, as shown in Fig. 1.

The C—O distances of COOH of the p-nitrobenzoic acid are ranging from 1.215(7) to 1.311(7) Å. The difference (Δ is 0.096 Å) in bond distances between O(1)—C(8) (1.311(7) Å) and O(2)—C(8) (1.215(7) Å) in the carboxyl group in compound **1** is in accordance with the values in the protonated carboxyl groups. As expected, the benzo[d]thiazol moiety is planar (the mean deviation from plane is 0.0104 Å). The r.m.s deviation of the benzene ring of the p-nitrobenzoic acid from the mean plane of the ring is 0.0021 Å, which forms dihedral angle of 1.7° with the benzo[d]thiazol unit. The carboxyl and the nitro groups deviate by 2.2°, and 9.2°, respectively from the benzene ring of the p-nitrobenzoic acid molecule.

The p-nitrobenzoic acid was bonded to the 6-bromobenzo[d]thiazol-2-amine molecule through one N—H···O, and one O—H···N hydrogen bonds to form a bicomponent adduct with graph set $R_2^2(8)$. The N—H···O hydrogen bond is between the amine group and the carbonyl group with N—O distance of 2.946(7) Å, the O—H···N hydrogen bond is between the OH of the carboxyl unit and the ring N atom with N—O distance of 2.627(7) Å. This kind of neighboring adducts were connected together via the N—H···O contact between the nitro group and the NH$_2$ with N—O distance of 3.154(8) Å, and O—S association between the same O atom of the nitro group and the ring S atom with O—S separation of 3.311 Å to form a 1D chain running parallel to the *a* axis direction. Such kind of parallel chains were joined together by the O···π interactions between the nitro group and the benzene ring of the p-nitrobenzoic acid with O—Cg distance of 3.20 Å, and C(carbonyl)···π interaction between the carboxyl group and the benzene ring of the p-nitrobenzoic acid with C—Cg distance of 3.343 Å to form 2D sheet extending on the *ab* plane (Fig. 2). It is worthy to note that the p-nitrobenzoic acid molecules at adjacent chains of the same 2D sheet were not in face to face position, they slipped some distance along the chain extending direction. Two such sheets were combined together along the c axis direction via the intersheet CH—O associations between the benzene CH and the carbonyl group with C—O distance of 3.224 Å, N—H···O hydrogen bond between the amine group and the nitro group with N—O distance of 3.106(7) Å, and O—N contact between the nitro group with O—N distance of 3.027 Å to form double sheet structure. Herein the chains at the two different sheets were almost perpendicular to each other.

3.2.2. X-ray structure of (6-bromobenzo[d]thiazol-2-amine): (fumaric acid)$_{0.5}$ [(L) (H$_2$fum)$_{0.5}$] (2)

The compound **2** was also prepared by reaction of 6-bromobenzo[d]thiazol-2-amine with fumaric acid in 1:1 ratio, which crystallizes as monoclinic block crystals in the space group P2(1)/c. The asymmetric unit of **2** consists of one molecule of 6-bromobenzo[d]thiazol-2-amine, and half a molecule of fumaric acid, as shown in Fig. 3. Compound **2** is also a cocrystal. The carboxylic acid groups have C═O and C—O bond distances, indicative of a protonized character, in which no Hs transfer to the 6-bromobenzo[d]thiazol-2-amine molecules has occurred. The ratio of C—O(long) to C═O (short) bond distances is 1.067, for the carboxyl group on C(8). These values are characteristic for unionized COOH (ionized COOH groups have a lower ratio of about 1.030) [23]. One fumaric acid and two 6-bromobenzo[d]thiazol-2-amine molecules produced a heteroadduct via the neutral N—H···O and O—H···N hydrogen bonds. For the presence of the hydrogen bonds every carboxyl moiety of the fumaric acid and the 6-bromobenzo[d]thiazol-2-amine molecule formed a $R_2^2(8)$ motif. The adjacent heteroadducts were connected together via the Br···Br bonds to form a

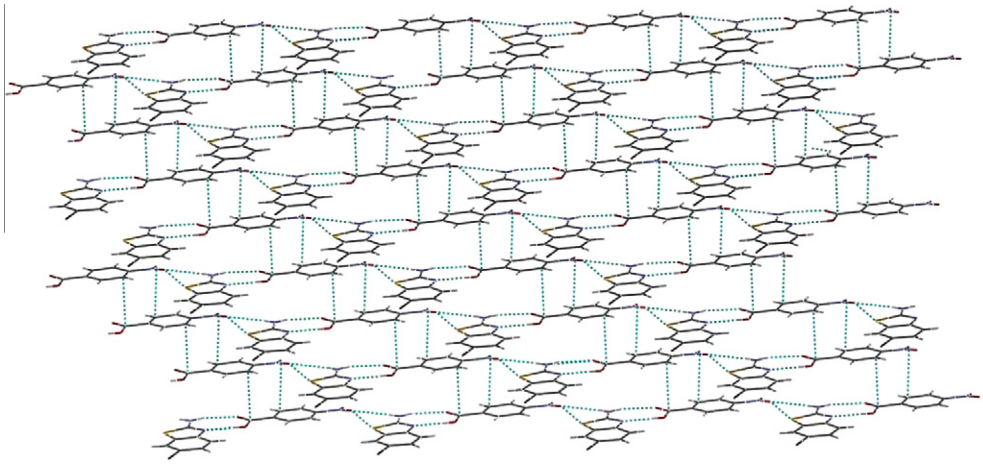


Fig. 2. 2D sheet structure of **1** extending on the *ab* plane.

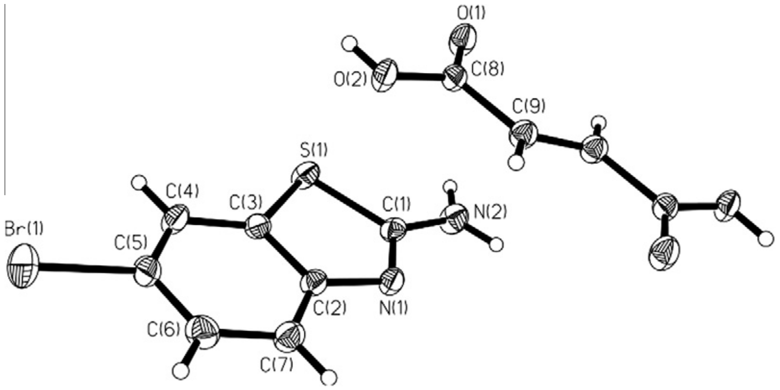


Fig. 3. Molecular structure of **2** showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

1D chain running along the *a* axis direction. In this regard the Br···Br distance (3.520 Å) is significantly shorter than the documented data (4.0–4.2 Å) [18].

The 1D chains were combined together by the interchain C(carbonyl)···π interaction with C—Cg distance of 3.276 Å, and O(carbonyl)···C(carbonyl) interaction between the carbonyl group and the C atom of the carboxyl group with O—C distance of 3.130 Å to form a 2D corrugated sheet running along the *ab* plane (Fig. 4). Such kind of 2D corrugated sheets stacked along the *c* axis direction and joined together by the N—H···O (one NH of the amine group formed a bifurcated N—H···O association with the carbonyl unit of one carboxyl group, and the OH unit of another COOH with N—O distances of 2.991(5) Å, and 3.155(5) Å, respectively), and CH—S (between 8-CH of the 6-bromobenzo[d]thiazol-2-amine and the S atom of 6-bromobenzo[d]thiazol-2-amine belonging to adjacent sheets with C—S separation of 3.734 Å) interactions to form 3D ABAB layer network structure. In this regard the adjacent sheets made an angle of ca 60° with each other. In addition the third sheet was parallel to the first sheet, but the third sheet was slipped some distance from the first sheet along the a, and b axis directions respectively, so did the second sheet and the fourth sheet.

*3.2.3. X-ray structure of (6-bromobenzo[d]thiazol-2-amine): (L-tartaric acid): $2H_2O$ [(HL$^+$) (Htart$^-$) $2H_2O$] (**3**)*

The compound **3** crystallizes as monoclinic block crystals in the space group C2. X-ray analysis reveals that the compound consists of one 6-bromobenzo[d]thiazolium-2-amine cation, one hydrogen tartrate anion, and two water molecules (Fig. 5). The present investigation clearly shows that the positive charge (coming from the

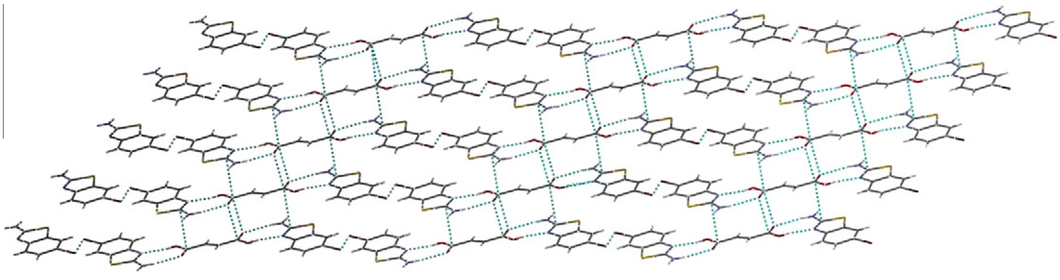


Fig. 4. 2D corrugated sheet running along the *ab* plane.

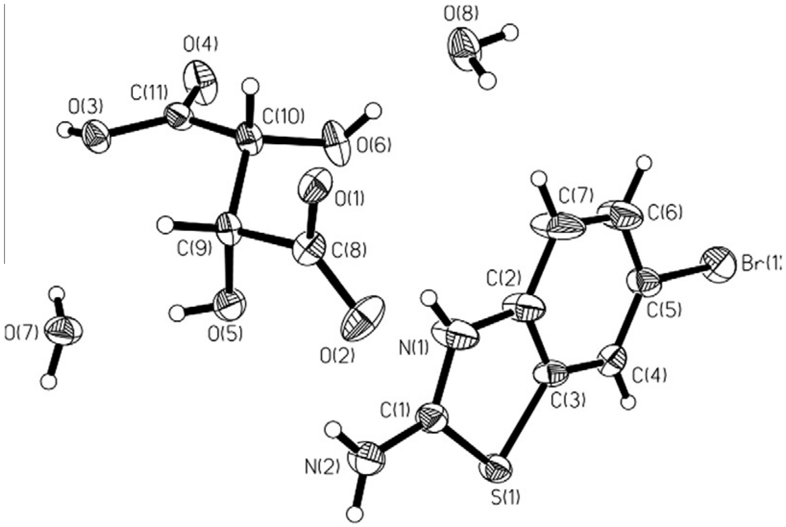


Fig. 5. Molecular structure of 3 showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

carboxylic H of L-tartaric acid) in the title compound is on the ring nitrogen atom not at the extra-ring amine group, forming an ion pair, which is different from compounds **1**, and **2**. Here only one proton of the acid was ionized to exhibit a valence number of −1. As shown in Table 2, all the bond angles and bond distances are in the normal range.

In the COOH (C(11)—O3—O4) group, two C—O bond lengths are obviously different between O(3)—C(11) (1.294(6) Å) and O(4)—C(11) (1.221(7) Å) with the Δ value of 0.073 Å, indicating protonized COOH group character. The relatively larger Δ value which is expected for neutral C—O and C=O bond distances [24] is also confirming the reliability of adding H atoms experimentally by different electron density onto O atoms. But for the COO^- group, two C—O bond lengths (The C—O distances of COO^- of the hydrogen tartrate are ranging from 1.230(7) to 1.260(6) Å, Δ = 0.030 Å) are basically not equal with an average value of 1.245(6) Å, which is shorter than that of the single bond of O(3)—C(11) (1.294(6) Å), but longer than that of the double bond of O(4)—C(11) (1.221(7) Å) in the carboxyl group of the hydrogen tartrate. It is clear that the difference in bond lengths of C—O within the carboxyl group (0.073 Å) is greatly larger than the one found in the carboxylate group (0.030 Å), which also confirms the deprotonation of only one carboxylic H.

There is also not significant conformational difference in the hydrogen tartrate anion, the characteristic O5—C9—C10—O6 torsion angle being −60.76(2)°, which compares with the values [−63.5 (3), −65.11(17), and −70.5(2)°] in the three hydrogen tartrate anions reported by Graham Smith [25].

In the compound, there are consistently ionic hydrogen bonds formed between the NH^+ cation and the CO_2^- anions, which is to be expected [26]. The anions were arranged in head to tail fashion along the *c* axis direction via the O—H···O associations between the OH of the carboxyl group and the carboxylate to form a 1D chain. In the chain there are also stitched water molecules through O—H···O hydrogen bonds in which the water molecule acts both as the hydrogen bond donor forming hydrogen bond with one O atom of the carboxylate and acceptor forming hydrogen bond with the alcohol group of the anion. Such chains were arranged parallelly at the *bc* plane and were held together by the cations to form 2D grid structure (Fig. 6). In the grid there existed the hydrogen-bonded $R_1^2(5)$, $R_1^2(6)$, and $R_3^3(12)$ motifs, respectively. Two adjacent grids were combined together by the CH—O interactions to form 2D sheet structure. In this case the anions at the two adjacent grids in the 2D sheet were antiparallel to each other, so did the cations. The cations of the second grid layer were located at the centre of the first grid layer. The 2D sheets were further stacked along the *a* axis direction via the O—H···O, and N—H···O interactions to form 3D layer network structure. In this case the third 2D sheet has the same projection on the *bc* plane as the first 2D sheet, so does the second 2D sheet and the fourth 2D sheet.

*3.2.4. X-ray structure of (6-bromobenzo[d]thiazol-2-amine)$_2$: (terephthalic acid) [(L)$_2$ (H$_2$tpa)] (**4**)*

Similar to **2**, the asymmetric unit of **4** consists of one molecule of 6-bromobenzo[d]thiazol-2-amine and half a molecule of terephthalic acid, as shown in Fig. 7. The C—O distances of the COOH of the terephthalic acid are ranging from 1.236(9) to 1.300(8) Å, which suggest that the carboxyl group is not ionized.

Two L molecules are bound to one terephthalic acid molecule through one N—H···O hydrogen bond (N(2)—H(2A)···O(2)) generated by the NH_2 of L and the carbonyl group with N—O distance of 2.895(9) Å, and one O—H···N hydrogen bond (O(1)—H(1)···N(1)) between the carboxyl OH and the ring N atom of L with N—O distance of 2.653(8) Å to generate a heteroadduct with the $R_2^2(8)$ graph set. In the heteroadduct the two L and one terephthalic acid molecules are almost in the same plane. Such kind of heteroadducts were joined together via the N—H···O hydrogen bond between the amino group of L and the carbonyl group belonging to terephthalic acid with N—O distance of 2.918(9) Å to form a 1D zigzag chain running along the *c* axis direction (Fig. 8). In the chain the adjacent tricomponent heteroadducts made an angle of ca.130° with each other, while the third tricomponent heteroadduct was parallel to the first tricomponent heteroadduct, so did the second tricomponent heteroadduct and the fourth tricomponent heteroadduct. The 1D chains were further stacked along the *b* axis direction via the interchain N—H···O hydrogen bond between the amino group and the carbonyl group with N—O distance of 2.918(9) Å to form 2D corrugated sheet extending parallel to the bc plane.

4. Conclusions

Four supramolecular compounds with different topologies have been prepared and structurally characterized. The different hydrogen bond interaction modes of the carboxylic acids and the 6-bromobenzo[d]thiazol-2-amine led to a wide range of different

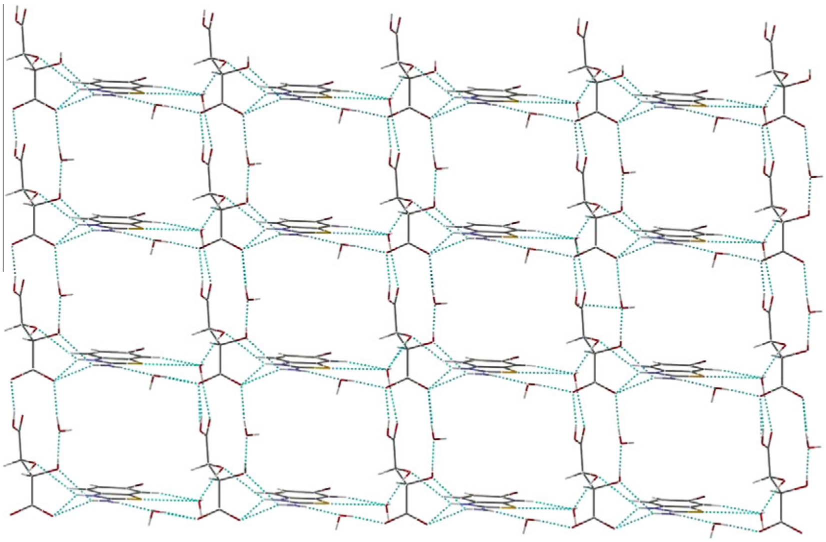


Fig. 6. 2D grid structure of **3** extending at the *bc* plane.

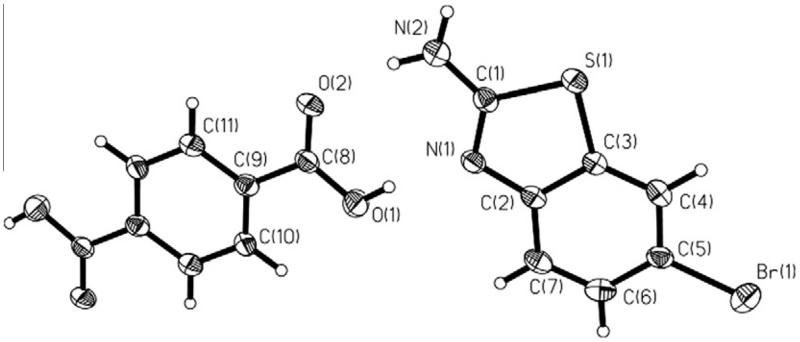


Fig. 7. Molecular structure of **4** showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

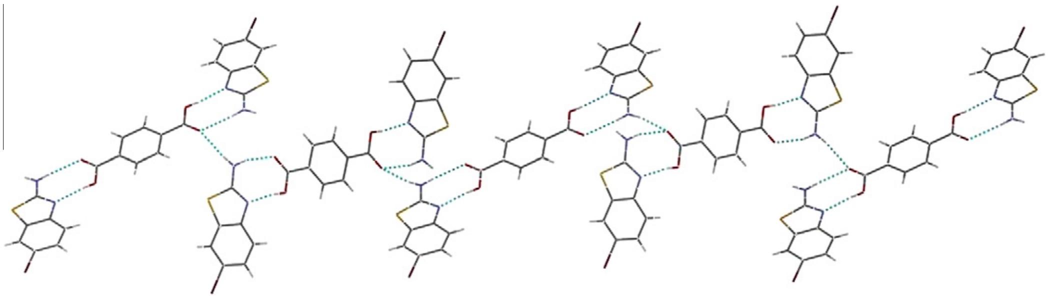


Fig. 8. 1D chain structure of **4** running along the *c* axis direction.

structures such as 2D double sheet structure, 3D ABAB layer network structure, 3D layer network structure, and 2D corrugated sheet structure.

Despite variations in molecular shape on the carboxylic acid derivatives, there all featured strong intermolecular hydrogen bonds between the carboxylic acid and the 6-bromobenzo[d]thiazol-2-amine. In the compounds **1**, **2**, and **4**, the COOH remained protonated, while in **3**, one COOH group of the L-tartaric acid was deprotonated. This phenomenon may be explained by the fact: for the carboxylic acids present in **1**–**4**, the L-tartaric acid has the smallest Pka (Pka_1) among all of the acids discussed in this manuscript which may led the ΔPka (between the L and the carboxylic acid) to be in the range for salt formation (pKa(base) – pKa(acid) $\geqslant$ 3). While the ΔPka for **1**, **2**, and **4** may be out of the range of salt formation.

This study has demonstrated that the O—H···N/N–H···O hydrogen bond is the primary intermolecular force in a family of structures containing the OH···6-bromobenzo[d]thiazol-2-amine synthons. In addition the nonclassical weak interactions were also played important role in structure extension. In all of the compounds except **3**, the most common hydrogen-bonded hetero $R_2^2(8)$ graph sets for 2-aminoheterocyclic derivatives have been observed. Salt **3** has the hydrogen-bonded $R_1^2(5)$, $R_1^2(6)$, and $R_3^3(12)$ motifs.

In conclusion, we have shown that 2D/3D structures can be constructed by the collective weak interactions such as strong directional hydrogen bond, mixture of strong and weak hydrogen bond and some other non-covalent interactions.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic data center, CCDC Nos. 841391 for **1**, 845147 for **2**, 841388 for **3**, and 841396 for **4**. Copies of this information may be obtained free of charge from the +44 (1223)336-033 or Email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk.

Acknowledgments

We gratefully acknowledge the financial support of the Education Office Foundation of Zhejiang Province (Project No. Y201017321) and the financial support of the Zhejiang A & F University Science Foundation (Project No. 2009FK63).

References

[1] C.K. Lam, T.C.W. Mak, Tetrahedron 56 (2000) 6657.
[2] (a) S. Tanase, E. Bouwman, G.J. Long, A.M. Shahin, A.M. Mills, A.L.S. Jan Reedijk, Eur. J. Inorg. Chem. (2004) 4572;
(b) C. Janiak, J. Chem. Soc., Dalton Trans. (2000) 3885;
(c) O. Takahashi, Y. Kohno, M. Nishio, Chem. Rev. 110 (2010) 6049;
(d) Z. Berkovitch-Yellin, L. Leiserowitz, Acta Cryst. B40 (1984) 159;
(e) K.H. Cho, K.T. No, H.A. Scheraga, J. Phys. Chem. A 104 (2000) 6505;
(f) W. Koch, G. Frenking, J. Gauss, D. Cremer, J. Am. Chem. Soc. 108 (1986) 5808.
[3] G.R. Desiraju, Acc. Chem. Res. 35 (2002) 565.
[4] D. Braga, L. Maini, F. Paganelli, E. Tagliavini, S. Casolari, F. Grepioni, J. Organomet. Chem. 637–639 (2001) 609.
[5] J.Q. Liu, Y.Y. Wang, L.F. Ma, W.H. Zhang, X.R. Zeng, F. Zhong, Q.Z. Shi, S.M. Peng, Inorg. Chim. Acta 361 (2008) 173.
[6] C. Biswas, M.G.B. Drew, D. Escudero, A. Frontera, A. Ghosh, Eur. J. Inorg. Chem. (2009) 2238.
[7] M. Maamen, D.M. Gordon, Acc. Chem. Res. 28 (1995) 37 (and references therein).
[8] N. Shan, A.D. Bond, W. Jones, Cryst. Eng. 5 (2002) 9.
[9] D.R. Weyna, T. Shattock, P. Vishweshwar, M.J. Zaworotko, Cryst. Growth Des. 9 (2009) 1106.
[10] M. Du, Z.H. Zhang, X.J. Zhao, Cryst. Growth Des. 5 (2005) 1247.
[11] G.R. Desiraju, Crystal engineering, The Design of Organic Solids, Elsevier, Amsterdam, 1989.
[12] (a) L. Leiserowitz, Acta Crystallogr. B32 (1976) 775;
(b) S.V. Kolotuchin, E.E. Fenlon, S.R. Wilson, C.J. Loweth, S.C. Zimmerman, Angew. Chem. Int. Ed. Engl. 34 (1995) 2654;
(c) S.S. Kuduva, D.C. Craig, A. Nangia, G.R. Desiraju, J. Am. Chem. Soc. 121 (1999) 1936;
(d) J. Bernstein, M.C. Etter, L. Leiserowitz, Struct. Correl. 2 (1994) 431;
(e) B. Moulton, M.J. Zaworotko, Chem. Rev. 101 (2001) 1629;
(f) L.S. Reddy, S.J. Bethune, J.W. Kampf, N. Rodríguez-Hornedo, Cryst. Growth Des. 9 (2009) 378;
(g) I.S. Lee, D.M. Shin, Y.K. Chung, Cryst. Growth Des. 3 (2003) 521;
(h) B.R. Bhogala, A. Nangia, Cryst. Growth Des. 3 (2003) 547.
[13] (a) V.R. Pedireddi, J. Prakashareddy, Tetrahedron Lett. 43 (2002) 4927;
(b) M.S. Refat, A. Elfalaky, E. Elesh, J. Mol. Struct. 990 (1–3) (2011) 217;
(c) P. Metrangolo, H. Neukirch, T. Pilati, G. Resnati, Acc. Chem. Res. 47 (2005) 386;
(d) T.R. Shattock, K.K. Arora, P. Vishweshwar, M.J. Zaworotko, Cryst. Growth Des. 8 (2008) 4533;
(e) K. Biradha, G. Mahata, Cryst. Growth Des. 5 (2005) 61.
[14] (a) J.C. MacDonald, P.C. Dorrestein, M.M. Pilley, Cryst. Growth Des. 1 (2001) 29;
(b) M.L. Highfill, A. Chandrasekaran, D.E. Lynch, D.G. Hamilton, Cryst. Growth Des. 2 (2002) 15;
(c) P. Vishweshwar, A. Nangia, V.M. Lynch, J. Org. Chem. 67 (2002) 556;
(d) G.S. Nichol, W. Clegg, Cryst. Growth Des. 9 (2009) 1844;
(e) Y.B. Men, J.L. Sun, Z.T. Huang, Q.Y. Zheng, CrystEngComm. 11 (2009) 978.
[15] D.E. Lynch, G.D. Jones, Acta Cryst. B60 (2004) 748 (and the references cited therein).
[16] S. Skovsgaard, A.D. Bond, CrystEngComm. 11 (2009) 444.
[17] D. Munirajasekhar, M. Himaja, S.V. Mali, IRJP 2 (2011) 114.
[18] (a) R. Al-Far, B.F. Ali, K. Al-Sou'oud, J. Chem. Cryst. 36 (2006) 523;
(b) H.F. Liberman, R.J. Davey, D.M.T. Newsham, Chem. Matter. 12 (2000) 490;
(c) I.G. Dance, New J. Chem. 27 (2003) 22;
(d) R.D. Willett, F. Awwadi, R. Butcher, S.F. Haddad, B. Twamley, Cryst. Growth Des. 3 (2003) 301.
[19] (a) S.W. Jin, W.B. Zhang, L. Liu, H.F. Gao, D.Q. Wang, R.P. Chen, X.L. Xu, J. Mol. Struct. 975 (2010) 128;
(b) S.W. Jin, D.Q. Wang, Z.J. Jin, L.Q. Wang, Polish J. Chem. 83 (2009) 1937;
(c) S.W. Jin, D.Q. Wang, J. Chem. Crystallogr. 40 (2010) 914.
[20] Bruker, SMART and SAINT, Bruker AXS, Madison, 2004.
[21] G.M. Sheldrick, Acta Cryst. A64 (2008) 112.
[22] C.B. Aakeröy, J. Desper, M.E. Fasulo, CrystEngComm. 8 (2006) 586.
[23] C.B. Aakeröy, M.E. Fasulo, J. Desper, Mol. Pharmaceutics 4 (2007) 317.
[24] (a) S.L. Childs, G.P. Stahly, A. Park, Mol. Pharmacol. 4 (2007) 323;
(b) C.B. Aakeröy, I. Hussain, J. Desper, Cryst. Growth Des. 6 (2006) 474;
(c) I. Majerz, Z. Malarski, L. Sobczyk, Chem. Phys. Lett. 274 (1997) 361.
[25] G. Smith, U.D. Wermuth, Acta Cryst. C66 (2010) o5.
[26] M. Felloni, A.J. Blake, P. Hubberstey, C. Wilson, M. Schröder, CrystEngComm. 4 (2002) 483.