J Chem Crystallogr (2011) 41:1085–1092
DOI 10.1007/s10870-011-0050-6

ORIGINAL PAPER

Hydrogen Bonded 3D Supramolecular Architectures of Three Saccharinate Salts

Shouwen Jin · Daqi Wang

Received: 27 June 2010 / Accepted: 7 March 2011 / Published online: 18 March 2011

Abstract Three saccharinate salts (2-aminopyrimidine): (saccharin) (**1**), (4-phenylthiazol-2-amine): (saccharin) (**2**), and (2-methylquinoline): (saccharin) (**3**) were prepared and structurally characterized by X-ray crystallography. Salt **1** crystallizes in the monoclinic, space group P2(1)/c, with $a = 7.1782(9)$ Å, $b = 13.5105(16)$ Å, $c = 12.2251(12)$ Å, $\beta = 93.3410(10)°$, $V = 1183.6(2)$ Å^3, $Z = 4$. Compound **2** crystallizes in the triclinic, space group P-1, with $a = 7.4584(7)$ Å, $b = 8.6930(9)$ Å, $c = 12.9179(14)$ Å, $\alpha = 108.952(2)°$, $\beta = 91.7510(10)°$, $\gamma = 97.2280(10)°$, $V = 783.57(14)$ Å^3, $Z = 2$. Compound **3** crystallizes in the monoclinic, space group P2(1)/c, with $a = 7.781(8)$ Å, $b = 19.4209(19)$ Å, $c = 10.9719(12)$ Å, $\beta = 107.7390(10)°$, $V = 1579.2(16)$ Å^3, $Z = 4$. The different hydrogen bonding interaction modes of the saccharinate anions and the cations lead to 3D network structure, 3D staircase structure, and 3D ABAB layer structure for **1**, **2**, and **3** respectively. Despite variations in the cation shape on the aromatic N–heterocyclic compounds, there all existed strong intermolecular N–H···O(carbonyl) hydrogen bonds. In compounds **1**, and **3** the N^+–H···O interaction between the N^+–H group of the cation and the C=O group of the saccharinate anion is the most important interaction in this family of salts. However, in **2**, there was a N–H···O interaction between the amino proton and the C=O group of the saccharinate anion. At the next level, the aromatic C–H proton interacts with the sulfonyl O atom. There are also π–π interactions in compounds **1**–**2**, there is CH_3–π interaction in **3**. Under these interactions the three compounds exhibit synthons I–III respectively. These interactions are responsible for the high-yielding supramolecular assembly of N-containing aromatic bases and the saccharinate into salts.

Keywords Synthesis · Structure characterization · Hydrogen bonding · Saccharinate salt · N-heterocyclic base

S. Jin (✉)
Faculty of Science ZheJiang A & F University,
Lin'An 311300, People's Republic of China
e-mail: jinsw@zafu.edu.cn

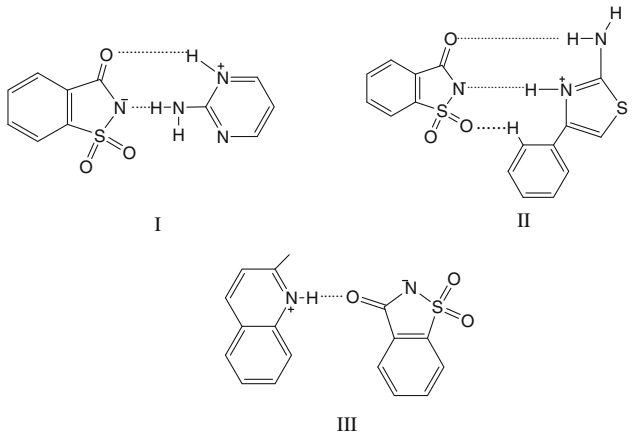
D. Wang
Department of Chemistry, Liaocheng University,
Liaocheng 252059, People's Republic of China

Introduction

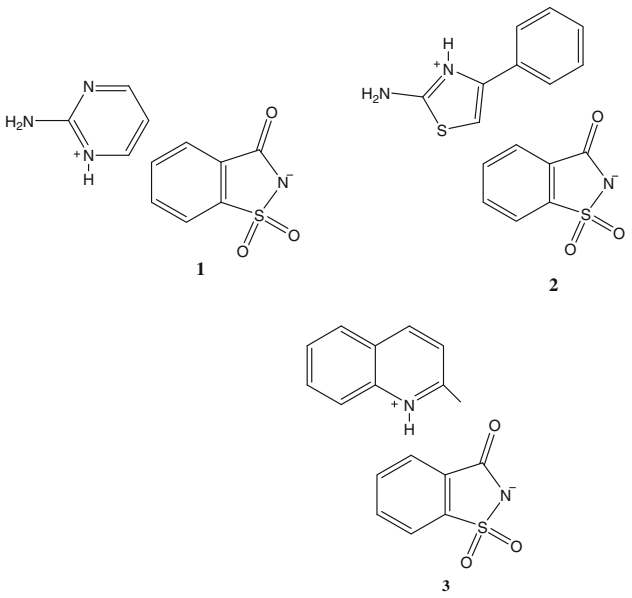
The self-assembly of molecular species in the solid-state via weak non-covalent interactions is a fundamental aspect of supramolecular chemistry [1–3] and an important component in the synthesis and manipulation of functional materials [4]. Supramolecular assemblies are often stabilized by hydrogen bonding, π–π stacking, as well as electrostatic interactions between ionic groups [1–5]. Nowadays, hydrogen bonding has been widely investigated in the area of crystal engineering, supramolecular chemistry, material science, and biological recognition [6–12]. The application of intermolecular hydrogen bonds is a well known and efficient tool to regulate the molecular arrangement in a crystal structure [11, 12]. Through hydrogen bonds we can form cocrystals and organic salts. In pharmaceuticals, salt formation is often used in order to modify the properties of the compounds [13]. Salt formation can be used to increase or decrease solubility, to improve stability and to reduce hygroscopicity of a drug product. There are many interesting hydrogen bonded topological structures from infinite 1-D chain to 3-D supramolecular framework [14, 15].

Saccharin (Hsac = $C_7H_5SO_3N$, *o*-sulfobenzoimide or 1,2-benzisothioazole-3(2H)-one-1,1-dioxide) was discovered more than 100 years ago and is one of the best known and most widely used artificial sweetener. The imino hydrogen of saccharin is acidic with p*K*a of 2.2. Saccharin has been used as an acid in the pharmaceutical industry [16, 17] and the crystal structures, physical properties such as solubility and solution pH characteristics of several API (active pharmaceutical ingredient) saccharinates have been reported by Desiraju recently [18–20]. The saccharin is a polyfunctional ligand with three hydrogen bond acceptor (one carbonyl and two sulfonyl O atoms) and one hydrogen bond donor (imino group NH). Metal complexes of sac(saccharin) have received much attention due to their physical and chemical properties [21].

Recently N-heterocyclic compounds have been widely studied as building block to form supramolecular compounds under the multiple hydrogen bonding action [22]. As the N-containing heterocyclic aromatic compounds 2-aminopyrimidine, 4-phenylthiazol-2-amine, and 2-methylquinoline may act as potentially tridentate or monodentate ligands (NNN, NSN, and N). The binary organic salts of the saccharin and N-containing heterocyclic aromatic compounds may display the different hydrogen-bonding patterns from the these acceptor atoms. As an extension of our study of weak interactions (hydrogen bonding, π–π interaction, and halogen bonding) concerning N-heterocyclic derivatives [23–25], herein we report the preparation and structures of three organic salts assembled from 2-aminopyrimidine (L1), 4-phenylthiazol-2-amine (L2), 2-methylquinoline (L3) and saccharin (Scheme 1), respectively. In the present work, three adducts (**1**–**3**) of the singly protonated ligand L1, L2 or L3 with saccharin have been obtained. The three organic salts are (2-aminopyrimidine): (saccharin) [$(HL1)^+\cdot(sac)^-$] (**1**) (sac = saccharin), (4-phenylthiazol-2-amine): (saccharin) [$(HL2)^+\cdot(sac)^-$] (**2**), and (2-methylquinoline): (saccharin) [$(HL3)^+\cdot(sac)^-$] (**3**) (Scheme 2).



Scheme 1 Hydrogen bond synthons discussed in this paper



Scheme 2 The three organic salts described in this paper, **1**–**3**

Experimental Section

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. 4-Phenylthiazol-2-amine was prepared by the method described in the literature [26]. The FT-IR spectra were recorded from KBr pellets in range 4,000–400 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.

Preparation of the Compounds **1**–**3**

*(2-Aminopyrimidine): (saccharin) [$(HL1)^+\cdot(sac)^-$] (**1**)*

To an ethanol solution (5 mL) of 2-aminopyrimidine (19 mg, 0.2 mmol) was added saccharin (36.6 mg, 0.2 mmol) in 10 mL ethanol. The solution was stirred for a few minutes, then the solution was filtered. The solution was left standing at room temperature for several days, colorless crystals were isolated after slow evaporation of the solution in air. The crystals were collected and dried in air to give the title compound [$HL1^+\cdot(sac)^-$] (**1**). Yield: 45 mg, 80.85%. m.p. 185–186 °C. Anal. Calcd for $C_{11}H_{10}N_4O_3S$ (278.29): C, 47.43; H, 3.59; N, 20.12; S, 11.49. Found: C, 47.41; H, 3.47; N, 20.02; S, 11.37. Infrared spectrum (KBr disc, cm^{-1}): 3382s(ν_{as}(NH)), 3136s(ν_s(NH)), 3113m, 3064m, 2390w, 2196w, 1988w, 1692s(C=O), 1601m,

1557m, 1490m, 1361m, 1279s(μ-asym.(SO_2)), 1157vs (μ-sym.(SO_2)), 781m, 740m, 682m, 636m, 608m, 540m, 480m, 440m.

*(4-Phenylthiazol-2-amine): (saccharin) $[(HL2)^+\cdot(sac)^-]$ (**2**)*

To a methanol solution (5 mL) of 4-phenylthiazol-2-amine (35.2 mg, 0.2 mmol) was added saccharin (36.6 mg, 0.2 mmol) in 10 mL ethanol. The solution was stirred for 10 min, then the solution was filtered. The solution was left standing at room temperature for several days, colorless crystals were isolated after slow evaporation of the methanol–ethanol solution in air. The crystals were dried in air to give the title compound $[HL2^+\cdot(sac)^-]$ (**2**). Yield: 61 mg, 84.86%. m.p. 206–208 °C. Anal. Calcd for $C_{16}H_{13}N_3O_3S_2$ (359.41): C, 53.42; H, 3.61; N, 11.68; S, 17.81; Found: C, 53.31; H, 3.49; N, 11.61; S, 17.74. Infrared spectrum (KBr disc, cm^{-1}): 3438s(ν_{as}(NH)), 3115s(ν_s(NH)), 3072m, 3012m, 2442w, 2288w, 1962w, 1684s(C=O), 1596m, 1536m, 1480m, 1333m, 1275s(μ-asym.(SO_2)), 1152vs(μ-sym.(SO_2)), 732m, 682m, 630m, 567m, 452m.

*(2-Methylquinoline): (saccharin) $[(HL3)^+\cdot(sac)^-]$ (**3**)*

To a methanol solution (2 mL) of 2-methylquinoline (28.6 mg, 0.2 mmol) was added saccharin (36.6 mg, 0.2 mmol) in 10 mL ethanol. The solution was stirred for 10 min, then the solution was filtered. The solution was left standing at room temperature for several days, colorless crystals were isolated after slow evaporation of the solution in air. The crystals were dried in air to give the title compound $[(HL3)^+\cdot(sac)^-]$ (**3**), yield 58 mg, 88.86%. m.p. 186–188 °C (decomp.). Elemental analysis performed on crystals exposed to the atmosphere: Calc. for $C_{17}H_{14}N_2O_3S$ (326.36): C, 62.50; H, 4.29; N, 8.58; S, 9.80. Found: C, 62.45; H, 4.21; N, 8.54; S, 9.70. Infrared spectrum (KBr disc, cm^{-1}): 3452s(ν_{as}(NH)), 3231s(ν_s(NH)), 3086m, 3024m, 2442w, 2296m, 1978w, 1687s(C=O), 1616m, 1596m, 1565m, 1474m, 1336m, 1277s(μ-asym.(SO_2)), 1237m, 1154vs(μ-sym.(SO_2)), 1052s, 802m, 712m, 618m, 558m, 470m.

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 [27]. 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 [28].

All hydrogen atoms were placed in calculated positions and their coordinates were refined using a riding model. Further details of the structural analysis are summarized in Table 1. Selected bond lengths and angles for the salts **1**, **2**, and **3** are listed in Table 2, the relevant hydrogen bond parameters are provided in Table 3.

Results and Discussion

Preparation and General Characterization

2-Aminopyrimidine, 4-phenylthiazol-2-amine, and 2-methylquinoline all have good solubility in common organic solvents, such as acetone, methyl alcohol, ethyl alcohol, methylene chloride, methyl trichloride, and acetonitrile. The crystals were grown by slow evaporation of the corresponding polar solution at room temperature.

The preparation of the compounds **1**–**3** were carried out with saccharin and the corresponding organic base in 1:1 ratio. The three compounds are not hygroscopic, and they all crystallized without solvent molecules accompanied. The molecular structures and their atom labelling schemes for the three structures are illustrated in Figs. 1, 2, and 3, respectively.

In the preparation of the organic salts **1**, **2**, and **3** the organic acids were mixed directly with the base in the corresponding solution, which was allowed to evaporate at ambient conditions to give the final crystalline products. The elemental analysis data for the three compounds are in good agreement with their compositions. The infrared spectra of the three compounds are consistent with their chemical formulas determined by elemental analysis and further confirmed by X-ray diffraction analysis. In **1**, and **2** it is the most basic ring N atoms that have been protonated which fits well with published results [29], and the saccharin moiety exists as the anion.

The very strong and broad features at approximately 3,500–3,100 cm^{-1} in the IR spectra of the compounds **1**, **2**, and **3** arise from N–H stretching frequencies. Aromatic and pyrimidic and thiazolic ring stretching and bending are attributed to the medium intensity bands in the regions of 1,500–1,630 and 600–750 cm^{-1}, respectively. The stretching vibrations of μ-asym.(SO_2) and μ-sym.(SO_2) occur characteristically at ca. 1,280 and 1,150 cm^{-1}, respectively. For **1**, **2**, and **3** the absorption bands of the carbonyl group of sac appear at ca. 1,690 cm^{-1} as a very strong single band, which indicated that the saccharinate salts formation have occurred (ca. 1,720 cm^{-1} in saccharin).

Table 1 Summary of X-ray crystallographic data for complexes **1**, **2**, and **3**

	1	**2**	**3**
Formula	$C_{11}H_{10}N_4O_3S$	$C_{16}H_{13}N_3O_3S_2$	$C_{17}H_{14}N_2O_3S$
Fw	278.29	359.41	326.36
T (K)	298(2)	298(2)	298(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	P2(1)/c	P-1	P2(1)/c
a (Å)	7.1782(9)	7.4584(7)	7.7811(7)
b (Å)	13.5105(16)	8.6930(9)	19.4209(19)
c (Å)	12.2251(12)	12.9179(14)	10.9719(12)
α (°)	90	108.952(2)	90
β (°)	93.3410(10)	91.7510(10)	107.7390(10)
γ (°)	90	97.2280(10)	90
V (Å^3)	1183.6(2)	783.57(14)	1579.2(3)
Z	4	2	4
D_{calcd} (mg/m^3)	1.562	1.523	1.373
Absorption coefficient (mm^{-1})	0.284	0.361	0.221
F(000)	576	372	680
Crystal size (mm^3)	0.42 × 0.39 × 0.35	0.44 × 0.38 × 0.35	0.47 × 0.46 × 0.34
θ range (°)	2.25–25.01	1.67–25.02	2.10–25.01
Limiting indices	$-8 \le h \le 7$	$-8 \le h \le 8$	$-9 \le h \le 9$
	$-16 \le k \le 16$	$-10 \le k \le 10$	$-14 \le k \le 23$
	$-14 \le l \le 11$	$-15 \le l \le 14$	$-12 \le l \le 12$
Reflections collected	5823	4106	7852
Reflections independent (R_{int})	2091(0.0270)	2722(0.0213)	2780(0.0584)
Goodness-of-fit on F^2	1.050	1.028	1.027
R indices [$I > 2\sigma I$]	0.0369, 0.0882	0.0446, 0.0937	0.0522, 0.1290
R indices (all data)	0.0569, 0.1039	0.0767, 0.1126	0.1078, 0.1664
Largest diff. peak and hole (e Å^{-3})	0.231, −0.305	0.229, −0.302	0.262, −0.361

Structural Descriptions

*X-ray Structure of (2-Aminopyrimidine): (Saccharin) [(HL1)$^+$·(sac)$^-$] (**1**)*

The compound **1** of the composition [(HL1)$^+$·(sac)$^-$] (**1**) was prepared by reaction equal mol of 2-aminopyrimidine and saccharin, in which the acidic NH of saccharin was ionized. Compound **1** crystallizes in the monoclinic space group P2(1)/c. Its single crystal structure shows the expected proton transfer from the acid to the pyrimidyl nitrogen atom, i. e. the acid protonates the adjacent hetero nitrogen of the pyrimidine ring. Protonation of the pyrimidine base on N2 site is reflected in a change in bond angle. The angle C(9)–N(4)–C(8) at unprotonated atom N4 is 117.0(2)°, while for protonated N2 the C(11)–N(2)–C(8) angle is 120.4(2)°. This also occurs with the salt bis(2-aminopyrimidin-1-ium) dichromate(VI) [30].

The asymmetric unit of **1** contains a mono-protonated ligand (HL1$^+$ cation), and one (sac)$^-$ anion, as shown in Fig. 1. As expected, the protonated ligand in this compound adopts an almost planar conformation with rms deviation of 0.0040 Å. The sac ligand present in the complex is roughly planar with a rms deviation of the non-hydrogen atoms (excluding the sulfonyl O atoms) from the best least square plane of approximately 0.0257(2) Å, the dihedral angle between the cation and the anion is 11.4(1)°. The rms deviation of the phenyl ring and the five membered ring of the anion are 0.0072(3) Å, and 0.0180(1) Å respectively, and the interplanar angle between the two rings is 2.9(2)°.

One anion is bonded to one cation through one N–H···N$^-$ and one N$^+$–H···O hydrogen bonds to form a heteroadduct with a $R_2^2(8)$ loop motif (Scheme 1). The N–H···N$^-$ hydrogen bond is formed between the amino proton of the cation and the sac N$^-$ group with N–N distance of 2.997(3) Å, which is shorter than the van der waals contact (3.1Å) [31]. The N$^+$–H···O interaction exists between NH$^+$ and the carbonyl group of the sac with N–O distance of 2.631(3) Å. There are π–π interactions between

Table 2 Selected bond lengths [Å] and angles [°] for compounds **1**, **2**, and **3**

1			
N(1)–C(1)	1.346(3)	N(1)–S(1)	1.616(2)
N(2)–C(11)	1.346(3)	N(2)–C(8)	1.352(3)
N(3)–C(8)	1.320(3)	O(1)–S(1)	1.4406(19)
O(2)–S(1)	1.4322(19)	O(3)–C(1)	1.242(3)
S(1)–C(3)	1.764(2)	C(1)–N(1)–S(1)	110.74(16)
C(11)–N(2)–C(8)	120.4(2)	O(2)–S(1)–O(1)	114.86(12)
O(2)–S(1)–N(1)	112.20(12)	O(1)–S(1)–N(1)	110.57(11)
O(2)–S(1)–C(3)	109.97(12)	O(1)–S(1)–C(3)	110.72(11)
N(1)–S(1)–C(3)	97.16(11)	O(3)–C(1)–N(1)	124.9(2)
C(11)–N(2)–C(8)	120.4(2)	C(9)–N(4)–C(8)	117.0(2)
O(3)–C(1)–C(2)	121.2(2)	C(9)–N(4)–C(8)	117.0(2)
2			
S(1)–O(1)	1.434(2)	S(1)–O(2)	1.434(2)
S(1)–N(1)	1.626(2)	S(1)–C(3)	1.755(3)
S(2)–C(8)	1.707(3)	S(2)–C(10)	1.725(3)
N(1)–C(1)	1.340(4)	N(2)–C(8)	1.340(3)
N(2)–C(9)	1.396(3)	N(3)–C(8)	1.305(4)
O(3)–C(1)	1.247(3)	O(1)–S(1)–O(2)	115.49(14)
O(1)–S(1)–N(1)	111.40(13)	O(2)–S(1)–N(1)	111.07(14)
O(1)–S(1)–C(3)	110.44(15)	O(2)–S(1)–C(3)	110.01(14)
N(1)–S(1)–C(3)	96.87(13)	C(8)–S(2)–C(10)	90.57(15)
C(1)–N(1)–S(1)	110.8(2)	C(8)–N(2)–C(9)	114.7(2)
3			
N(1)–C(1)	1.332(5)	N(1)–S(1)	1.606(3)
N(2)–C(9)	1.319(4)	N(2)–C(13)	1.359(4)
O(1)–S(1)	1.427(2)	O(2)–S(1)	1.422(3)
O(3)–C(1)	1.245(4)	S(1)–C(3)	1.756(3)
C(1)–N(1)–S(1)	110.9(2)	C(9)–N(2)–C(13)	123.7(3)
O(2)–S(1)–O(1)	115.65(19)	O(2)–S(1)–N(1)	111.35(17)
O(1)–S(1)–N(1)	110.44(16)	O(2)–S(1)–C(3)	111.05(17)
O(1)–S(1)–C(3)	109.79(15)	N(1)–S(1)–C(3)	97.02(16)
O(3)–C(1)–N(1)	124.1(3)	O(3)–C(1)–C(2)	121.3(3)

the neighboring heteroadducts with the closest centroid centroid separation of 3.309(2) Å to form a heteroadduct dimer. In the dimers the corresponding anion and cation of the two heteroadducts were antiparallely arranged. The dimers were connected by S=O···π interaction to form a 1D chain along the *a* axis direction in which the O atom is at ca. 2.995 Å from the gravity center of the pyrimidine ring. This distance is similar to the distances reported for O···π interaction concerning SO_4^{2-} [32]. Such chains were connected in the *c* axis direction by C–H···O interaction between 3-CH of the cation and S=O of the anion with C–O distance of 3.337(2) Å. Such chains were also connected in the *b* axis direction through one N–H···O hydrogen bond (between the amino group and the sulfonyl group with N–O distance of 2.996(3) Å), and one CH–O interaction (between the phenyl CH and the sulfonyl group with C–O distance of 3.432(3) Å). With the assistance of these interactions the compound displays a 3D network structure, which is shown in Fig. 4. In this case the N^+–H···O interaction between the cation NH^+ and the C=O group is stronger than the N–H···O hydrogen bond between the amino proton and the sulfonyl group.

*X-ray Structure of (4-Phenylthiazol-2-amine): (saccharin) [$(HL2)^+\cdot(sac)^-$] (**2**)*

The structure of the anhydrous salt **2** with the composition of [$(HL2)^+\cdot(sac)^-$] was evidenced by X-ray single crystal diffraction. The asymmetric unit of **2** consists of one crystallographically independent 4-phenylthiazolium-2-amine cation, one crystallographically independent saccharinate anion in its asymmetric unit (Fig. 2). Compound **2** crystallizes in the triclinic space group P-1. Its single crystal structure shows the expected proton transfer from the acidic NH to the more basic hetero nitrogen atom of L2. The bond length N(3)–C(8) (1.305(4) Å) is shorter than

Table 3 Hydrogen bond distances and angles in studied structures of **1**, **2**, and **3**

D–H···A	*d*(D–H) (Å)	*d*(H···A) (Å)	*d*(D···A) (Å)	∠(DHA) (°)
1				
N(3)–H(3B)···N(1)#1	0.86	2.14	2.997(3)	174
N(3)–H(3A)···O(1)	0.86	2.16	2.996(3)	164
N(2)–H(2)···O(3)#1	0.86	1.77	2.631(3)	176
2				
N(3)–H(3B)···O(3)#1	0.86	2.05	2.833(3)	151
N(3)–H(3A)···O(3)#2	0.86	1.90	2.763(3)	176
N(2)–H(2)···N(1)#2	0.86	2.13	2.970(3)	165
3				
N(2)–H(2)···O(3)	0.86	1.78	2.636(4)	178

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

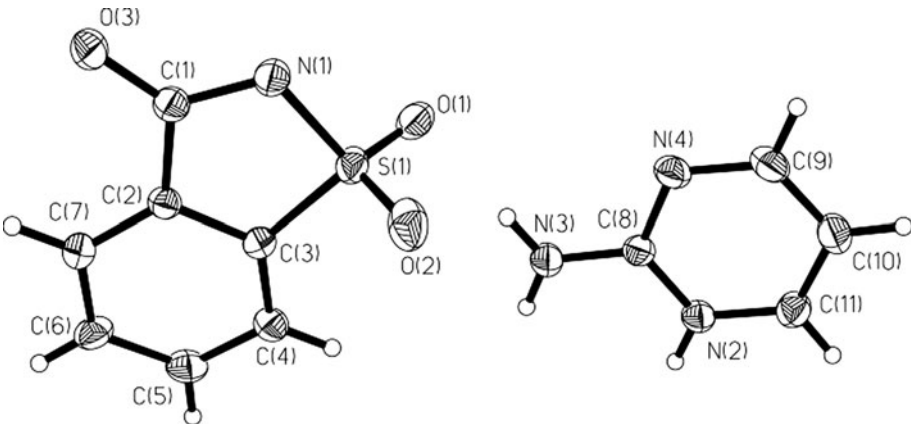


Fig. 1 Molecular structure of **1** showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level

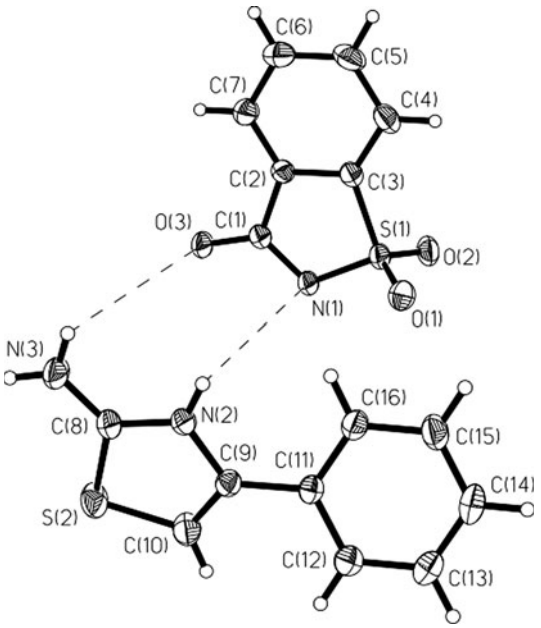


Fig. 2 The structure of **2**, showing the atom-numbering scheme. Displacement ellipsoids were drawn at the 30% probability level

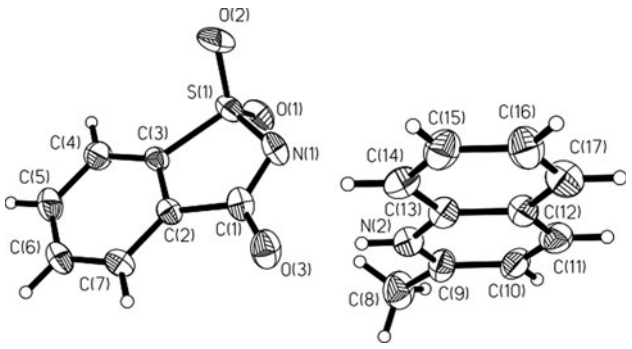


Fig. 3 The structure of **3**, showing the atom-numbering scheme. Displacement ellipsoids were drawn at the 30% probability level

N(2)–C(8) (1.340(3) Å). This suggests that the extent of orbital overlap is more between the N(3) and C(8) atoms than between N(2) and C(8) atoms. For similar 2-amino heterocyclic compounds, shorting of the C–NH_2 bonds has been explained by the attraction of a more electron-accepting heterocyclic ring [22].

The angle C8–S2–C10 (90.57(15)°) is larger than the corresponding angle in the neutral molecule (88.7(2)°) [33] and in the salt 2-amino-4-phenylthiazole hydrobromide monohydrate (90.17°) [34]. This may be due to the difference of the hydrogen bonding strength in the corresponding compound. The dihedral angle between the planes of the phenyl and thiazole rings in the same cation of **2** is 22.5(3)°, which is larger than the value (19.23(6)°) in 2-amino-4-phenylthiazole hydrobromine monohydrate. But compound **2** is less planar than the neutral L2 in which the dihedral angle between the phenyl ring and the thiazole ring is (6.2(3) °). The planarity of **2** is further verified by the shorter C(9)–C(11) bond distance [1.463(4) Å] in **2** compared with the value of 1.506(3) Å found in 2-amino-4-phenylthiazole hydrobromine monohydrate [33].

The sac ligand is also planar with a rms. deviation of 0.055(2) Å, and the interplane angle between the 5-membered ring and benzene ring in the same sac ion is 0.6(1)°. The rms deviation of the cation is 0.1784(6) Å. The dihedral angle between the cation and the anion is 5.3(2)°.

One cation and one anion form a heteroadduct by one N^+–H···N^- and one N–H···O hydrogen bonds to generate a $R_2^2(8)$ motif which is shown in Scheme 1. Although **2** has the same hydrogen-bonded $R_2^2(8)$ loop motif as compound **1** and the reported pyrimidyl saccharinate [29], the pair of donors and acceptors are significantly different. Here N–H···N interaction is formed between the NH^+ cation and the anion N^- with N–N separation of 2.970(3) Å which is similar to the N–N separation in compound **1**. The N–H···O hydrogen bond existed between the amino proton and the carbonyl group with N–O distance of 2.763(3) Å. There also exists one C–H···$O_{sulfonyl}$ interaction with C–O distance of 3.255(4) Å, for this contact the anion and the cation also formed a $R_2^2(9)$ hydrogen bonding graph set. These two kinds of hydrogen bonding geometry were fused together through the shared N^+–H···N^- hydrogen bond. Two

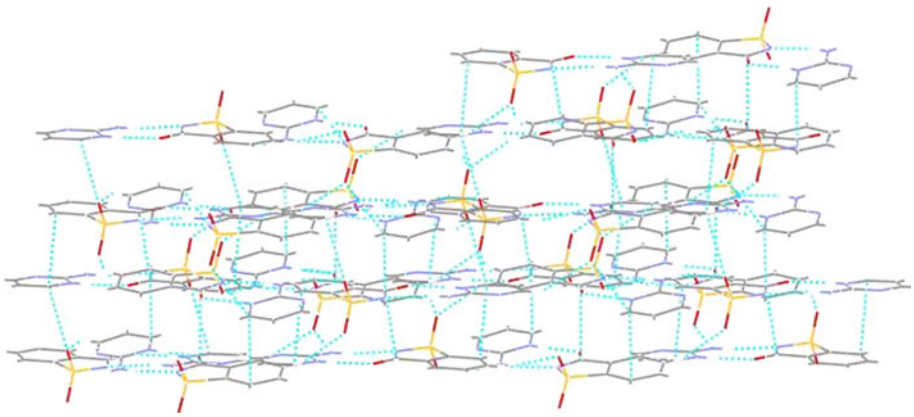


Fig. 4 3D network structure of **1**

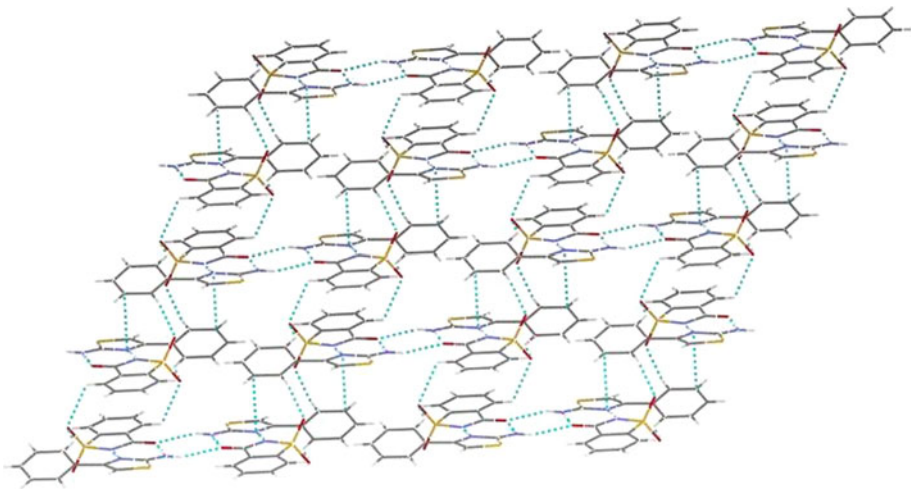


Fig. 5 3D staircase structure of **2** viewed along the *b* axis direction

heteroadducts were joined together through π–π interaction between the cationic phenyl ring of one heteroadduct and the cationic thiazole ring of its adjacent heteroadduct with centroid centroid separation of 3.202(8) Å to form dimers. In the dimers the corresponding two pairs of ions were anti-parallelly arranged. The dimers were further connected by a pair of C–H···O interaction between the two anions with C–O distance of 3.258(6) Å to form a 1D staircase structure running along the *a* axis direction. Such staircases were also connected by two N–H···O hydrogen bonds between the amino proton of the cation and the carbonyl group of the anion with N–O distance of 2.832(3) Å to form a 3D staircase structure, as shown in Fig. 5.

*X-ray Structure of (2-Methylquinoline): (Saccharin) [$(HL3)^{+}\cdot(sac)^{-}$] (**3**)*

Compound **3** was also prepared by reaction equal mol of 2-methylquinoline and saccharin, it is also a 1:1 adduct. The complex **3** crystallizes in the monoclinic space group P2(1)/c. The crystals of a new 2-methylquinoline salt, $C_{10}H_{10}N^{+}\cdot C_7H_4SO_3N^{-}$, are built up from one protonated 2-methylquinoline (+1) residue, and one saccharinate (−1) anion. The cations and the anions are roughly planar with rms deviations of 0.0124(2) Å, and 0.0103(2) Å respectively. The dihedral angle between the cation and the anion is 81.3(3)°, indicating an almost perpendicular arrangement of both ions.

The cation and the anion were bonded together perpendicularly through the only N^{+}–H···O hydrogen bond, which is different from the pyridyl saccharinates in which there are N^{+}–H···O hydrogen bonding accompanied with C–H···O, and C–H···N interactions [29]. The N–H···O hydrogen bond is formed between the NH^{+} cation and the carbonyl O with N–O distance of 2.636(4) Å. The distance between the N1 and N2 is too great to imply N–H···N hydrogen bond (ca. 3.325(3) Å which is larger than the van der waals radii of two N atom (3.10) Å). The N^{-} group in the saccharinate is not involved in any close contact which is different from the sildenafil saccharinate [20].

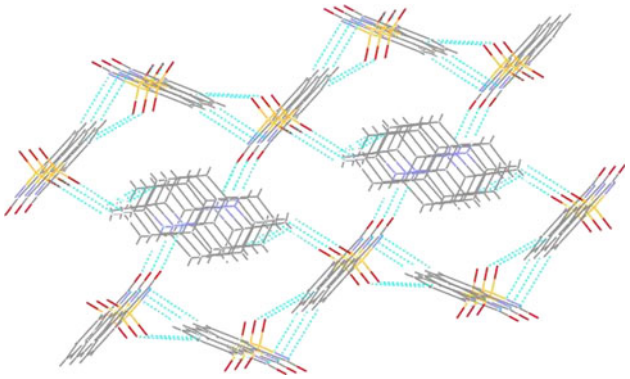


Fig. 6 3D ABAB layer structure of **3** viewed along the *a* axis direction

The anions form a 1D corrugated sheet by two C–H···O (between two sulfonyl O and two phenyl CH of two different anions with C–O distances ranged from 3.265(3) to 3.293(3) Å) and one CH–π interaction (between one anion phenyl CH and the five-membered ring of another anion with C-Cg distance of 3.538(4) Å), running along the ac plane. The cations were connected to the corrugated sheet perpendicularly through N^+–H···O hydrogen bonds between the NH^+ and the C=O group with N–O distance of 2.636(3) Å. And there are two CH_3–π interactions (with C-Cg distance of 3.669(8) Å) between adjacent cations that were bonded to two neighboring sheets respectively through N^+–H···O hydrogen bonds. With the assistance of this interaction, the cations formed dimers. In the dimer the two cations were antiparallely arranged. The cationic dimers were sandwiched between two anionic corrugated sheets to form a 3D ABAB layer network structure, which is shown in Fig. 6.

Supporting Information Available

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic data center, CCDC Nos. 766263 for **1**, 765443 for **2**, and 765439 for **3**. 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.

Acknowledgment The authors are grateful for the financial support of the Education Office Foundation of Zhejiang Province (project No. Y201017321) and the Zhejiang A and F University Science Foundation (project No. 2009FK63).

References

1. Lehn JM (1995) Supramolecular chemistry: concepts and prospectives, Chap. 9. VCH, Weinheim
2. Desiraju GR, Sharma CVK (1995) Perspectives in supramolecular chemistry. Wiley, Chichester
3. MacGillivray LR, Atwood JL (1999) Angew Chem Int Ed 38:1018
4. Boncheva M, Bruzewicz DA, Whitesides GM (2003) Langmuir 19:6066
5. Lehn JM (1990) Angew Chem Int Ed 29:1304
6. Jeffrey GA, Saenger W (1991) Hydrogen bonding in biological structures. Springer-Verlag, Berlin
7. Aakeröy CB, Beatty AM (2001) Aust J Chem 54:409
8. Steed JW, Atwood JL (2000) Supramolecular chemistry. Wiley, Chichester
9. Burrows AD (2004) Struct Bond 108:55
10. Braga D, Maini L, Polito M, Grepioni F (2004) Struct Bond 111:1
11. Etter MC (1990) Acc Chem Res 23:120
12. Holman KT, Pivovar AM, Swift JA, Ward MD (2001) Acc Chem Res 34:107
13. Gould PJ (1986) Int J Pharm 33:201
14. Shan N, Bond AD, Jones W (2002) Cryst Eng 5:9
15. Bhogala BR, Basavoju S, Nangia A (2005) CrystEngComm 7:551
16. Räder K, Stoss P US. Publication number, US4362730, 7 Dec 1982
17. Rayburn JW, Int. Publication number, WO 00/12067, 9 Mar 2000
18. Bhatt PM, Ravindra NV, Banerjee R, Desiraju GR (2005) Chem Commun 1073
19. Banerjee R, Bhatt PM, Ravindra NV, Desiraju GR (2005) Cryst Growth Des 5:2299
20. Banerjee R, Bhatt PM, Desiraju GR (2006) Cryst Growth Des 6:1468
21. Baran EJ, Yilmaz VT (2006) Coord Chem Rev 250:1980
22. Lynch DE, Jones GD (2004) Acta Crystallogr B60:748
23. Jin SW, Liu B, Chen WZ (2007) Chin J Struct Chem 26:287
24. Jin SW, Chen WZ (2007) Chin J Inorg Chem 23:270
25. Jin SW, Wang DQ, Wang XL, Guo M, Zhao QJ (2008) J Inorg Organomet Polym 18:300
26. Potewar TM, Ingale SA, Srinivasan KV (2008) Tetrahedron 64:5019
27. Bruker (2004) SMART and SAINT. Bruker AXS, Madison
28. Sheldrick GM (2000) SHELXTL, Structure Determination Software Suite, version 6.14. Bruker AXS, Madison
29. Banerjee R, Saha BK, Desiraju GR (2006) CrystEngComm 8:680
30. Sieroń L (2007) Acta Crystallogr E63:m2336
31. Bondi A (1964) J Phys Chem 68:441
32. Galstyan A, Sanz Miguel PJ, Lippert B (2010) Chem Eur J 16:5577
33. Au-Alvarez O, Peterson RC, Crespo AA, Esteva YR, Alvarez HM, Stiven AMP, Hernández RP (1999) Acta Crystallogr C55:821
34. Form GR, Raper ES (1974) Acta Crystallogr B30:342