Research Article

Crystal structures of salts and cocrystal of 1,3,5-triazine derivatives with thiophene carboxylic acid derivatives: an investigation on supramolecular interactions

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Abstract

Present work gives an account of different types of non covalent interactions encountered in the supramolecular architectures of new salts and cocrystal formed between derivatives of 1,3,5-triazine and thiophene carboxylic acid. The novel salts formed between derivatives of thiophene carboxylic acid and 1,3,5-triazine are 2, 4-diamino-6-methyl-1,3,5-triazin-1-ium 5-carboxythiophene-2-carboxylate monohydrate, $C_4H_8N_5^+ \cdot C_6H_3O_4S_1^- \cdot H_2O$ (**I**) and 2,4-diamino-6-methyl-1,3,5-triazin-1-ium 3-bromothiophene-2-carboxylate monohydrate, $C_4H_8N_5^+ \cdot C_5H_2O_2S_1Br_1^- \cdot H_2O$ (**II**). The new cocrystal is a 1:1 cocrystal formed between 2,4-diamine-6-phenyl-1,3,5-triazine and 2,5-dichlorothiophene-3-carboxylic acid, $C_9H_9N_5 \cdot C_5H_2O_2S_1Cl_2$ (**III**). The newly synthesized salts (**I** and **II**) and cocrystal (**III**) have been characterized by single-crystal X-ray diffraction. Supramolecular heterosynthons, homosynthons observed via N–H···O, N–H···N and O–H···N hydrogen bonds are also discussed. Anion···π interaction between carboxylate oxygen and aromatic rings of thiophene and triazine are observed in salt (**I**). π···π interaction is present between thiophene and triazine rings in salt (**II**). $R_2^2(8)$ ring motif is formed in cocrystal (**III**) via N–H···O and O–H···N hydrogen bonds. Further stabilisation of cocrystal (**III**) via Cl···O, Cl···Cl interactions as well as π···π interactions (triazine···triazine rings and triazine···phenyl rings) are also investigated.

Keywords Supramolecular interactions · Ring motif · Heterosynthon · Homosynthon

1 Introduction

Supramolecular chemistry deals with studies on non-covalent interactions and molecular assemblies. This knowledge acts as a basic tool for design of new multi-component crystalline materials or supramolecular materials. These supramolecular materials show various applications in catalysis [1, 2], magnetism [3, 4], photo-luminescence [5, 6], drug delivery and design [7, 8], gas storage [9, 10]. Among the various non-covalent interactions, hydrogen bonding interactions like O–H···O, N–H···O, N–H···N and C–H···O have received considerable attention as they play important role in molecular recognition [11]. Anion···π interactions, cation···π interactions and π···π interactions are the commonly occurring non-covalent interactions leading to generate unique supramolecular network from simple building blocks [12]. In addition to these interactions, halogen substituted carboxylic acid derivatives perform a significant role in altering the supramolecular architectures via various halogen (X) involving interactions like X···X, X···O, X···π interactions etc. [13]. Halogen bonding is a strong tool for constructing supramolecular networks due to its strength and directionality. Halogen bonds have recently been widely applied in supramolecular chemistry as an alternative to hydrogen bonds to control solid-state structures. There are studies which have investigated the competition between hydrogen bond and halogen bond in cocrystals [14]. Here we selected halogen substituted thiophene carboxylic acids to investigate halogen

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involving interactions due to the halogen substitution. Impact of halogen bonds in crystal engineering has been widely studied in halogenated aromatic compounds [14].

Aminotriazines are selected for the study as they have proven their great potential in crystal engineering as they contain large number of coordination/hydrogen bonding sites, for their π-interaction abilities [12]. Investigation on various supramolecular motifs and molecular self assemblies among aminotriazine derivatives were always interest of research. A series of 1, 3, 5-triazine based compounds are found to have activity against protozoan parasites which causes a number of diseases to human [15]. Studies are going on to investigate the structure–activity relationship by altering the substituents of 1, 3, 5-triazine derivatives [15]. Antimicrobial activities were evaluated for 1,3,5-triazine derivatives against various bacteria [16]. Studies of 1,3,5-triazine derivatives showed that length of alkyl substitution and presence of nitrogen atom in triazine has significant effects on anticancer activity [17]. Apart from biological activities, triazine derivatives have eminent capacity as light stabilizers for polymers [18].

2 Experimental

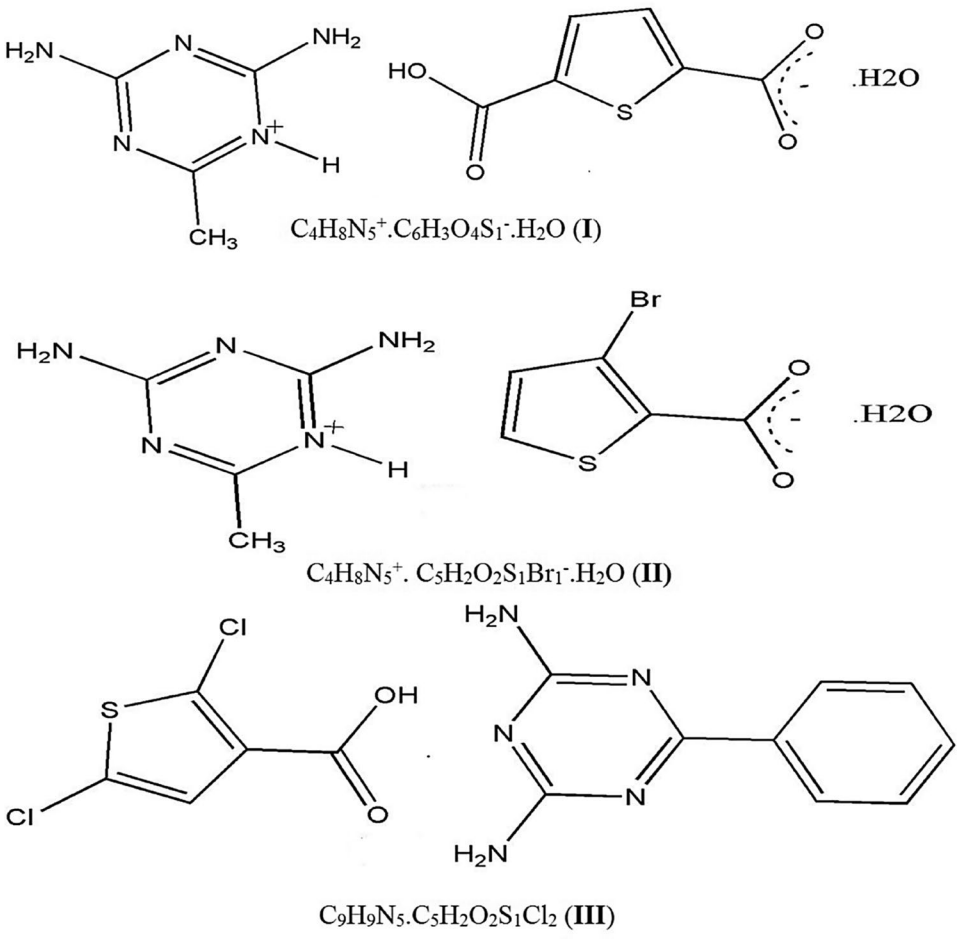
2.1 Synthesis and crystallization

Compounds (**I**)–(**III**) were prepared by mixing hot methanol–water (1:1 v/v) solutions (total volume 0.03 L) of 2,4-diamino-6-methyl-1,3,5-triazine with thiophene dicarboxylic acid [for **I**], 2,4-diamino-6-methyl-1,3,5-triazine with 3-bromothiophene-2-carboxylate [for **II**] and 2,4-diamine-6-phenyl-1,3,5-triazine with 2,5-dichlorothiophene-3-carboxylic acid [for **III**]. The solutions were warmed to 343 K over a water bath for 30 minutes and then cooled slowly to 298 K after filtration. Colourless crystals were collected from the respective mother liquor solutions after 7 days. Chemical Structures of novel salts and cocrystal are presented in Scheme 1.

2.2 Measurements (single crystal x-ray diffraction)

Intensity data sets were collected at 293 K for on a SuperNova dual with an Atlas diffractometer. Data reduction was done by CrysAlis PRO [19]. The structures were solved

Scheme 1 Chemical structures of **I-III**



SUPERFLIP [20] and subsequent Fourier analyses, refined anisotropically by full-matrix least-squares method using SHELXL2014 [21] within the WINGX suite of software, based on F^2 with all reflections. The molecular structures were drawn using the PLATON [22] and Mercury [23]. The crystals remained stable throughout the data collection.

Crystal data and structure refinement details are summarized in Table 1. All the hydrogen atoms were initially located in difference Fourier maps and were subsequently treated as riding atoms in geometrically idealized positions, with C–H = 0.93 (aromatic) or 0.96 Å (methyl), N–H = 0.86 Å and O–H = 0.82 Å (hydroxyl), whereas hydrogen atom coordinates in water molecules were refined by constraining the O–H bond length (**I**, **II**). All H atoms were refined with $U_{iso}(H) = kU_{eq}(C,N,O)$, where $k = 1.5$ for hydroxy, water and methyl H atoms and 1.2 for all other H atoms.

3 Results and discussions

3.1 Structural commentary

The salt (**I**) crystallizes in triclinic system with space group *P*-1. The asymmetric unit of salt (**I**) consists of one 2, 4-diamino-6-methyl-1,3,5-triazin-1-ium (DAMT) cation, one 5-carboxythiophene-2-carboxylate (CTC) anion and a water molecule (Fig. 1). The triazinium cation is protonated at the N1 position. It is confirmed by increase in internal bond angle. Internal angle at unprotonated N3 (C2–N3–C4) is 115.7 (2)° and at N5 (C4–N5–C6) is 115.4 (7)°, while internal angle at protonated N1 (C6–N1–C2) is 119.2 (2)°. There is not much discrepancy between the external bond angles at the carbon (C8) of carboxylate ion (C9–C8–O2 = 120.77 (17)° and C9–C8–O1 = 113.87(15)°).

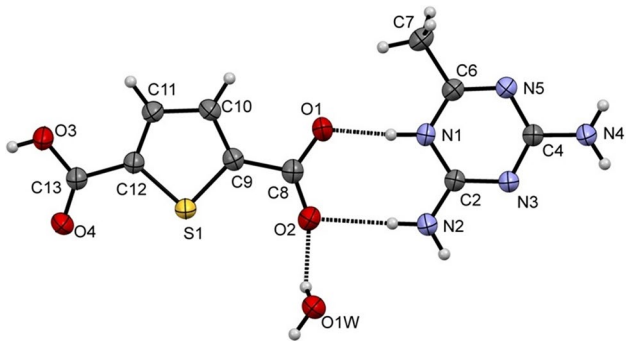


Fig. 1 ORTEP view of (**I**) with the atom-numbering scheme. Displacement ellipsoids are drawn at 50% probability level. Dashed lines represent hydrogen bonds

Table 1 Experimental details

Crystal data	(I)	(II)	(III)
Empirical formula	C10 H13 N5 O5 S	C9 H12 Br N5 O3 S	C14 H11 Cl2 N5 O2 S
Formula weight	315.31	690.46(12)	384.24
Temperature (K)	293	293	293
λ (Å)	0.71073	1.54184	1.54184
Crystal system	*P*-1	*P*-1	*P*-1
Space group	Triclinic	Triclinic	Triclinic
a (Å)	8.3921(6)	8.0095(8)	7.1038(12)
b (Å)	9.6250(8)	9.2549(9)	7.9449(11)
c (Å)	10.2803(9)	9.9864(10)	15.4870(14)
α (°)	62.339(9)	78.831(8)	86.934(9)
β (°)	74.447(7)	75.860(8)	81.930(11)
γ (°)	66.819(8)	76.434(8)	65.759(15)
V ($Å^3$)	672.37(11)	690.46(12)	789.1(2)
Z	2	2	2
ρ calcd (g/cm^3)	1.558	1.684	1.617
μ (mm^{-1})	0.272	5.609	5.117
F (000)	328.0	352.0	392.0
Crystal size (mm)	0.05 × 0.20 × 0.40	0.10 × 0.25 × 0.30	0.30 × 0.30 × 0.10
No of reflections collected	3084	2624	2991
Goodness-of-fit on F^2	1.036	1.035	1.000
Final R1 index [I > 2σ(I)]	0.0469	0.0509	0.0361
wR_2 (all data)	0.1334	0.1580	0.1037
Largest difference in peak and hole (e $Å^{-3}$)	0.442, −0.286	0.998, −0.654	0.293, −0.349

C8–O1 and C8–O2 distances are similar [1.272(3) Å and 1.238(2) Å, respectively]. The two external bond angles at the carbon C13 of the carboxyl group are 124.0 (2)° and 112.5 (2)°. The high discrepancy between these two angles is typical of a unionized carboxyl group, and the C=O distance is 1.216 (3) Å and C–OH distance of 1.314 (3) Å [14]. These parameters indicate that carboxylic group of one arm (with C8) of thiophene is in deprotonated form and the other arm (with C13) is in neutral form.

Salt (**II**) crystallizes in the triclinic system with space group *P*-1. The asymmetric unit of salt (**II**) consists of a 2, 4-diamino-6-methyl-1,3,5-triazin-1-ium cation, 3-bromothiophene-2-carboxylate anion and a water molecule (Fig. 2). Internal angle at unprotonated N3 (C2–N3–C4) is 115.7 (2)° and at N5 (C4–N5–C6) is 115.8 (2)°, while internal angle at protonated N1 (C6–N1–C2) is 119.2 (2)°. There is not much discrepancy between the external bond angles at the carbon of carboxylate ion (C9–C8–O2 = 119.4 (4)° and C9–C8–O1 = 115.5 (3)°). C8–O1 and C8–O2 distances are similar [1.266 (5) Å and 1.240 (5) Å, respectively].

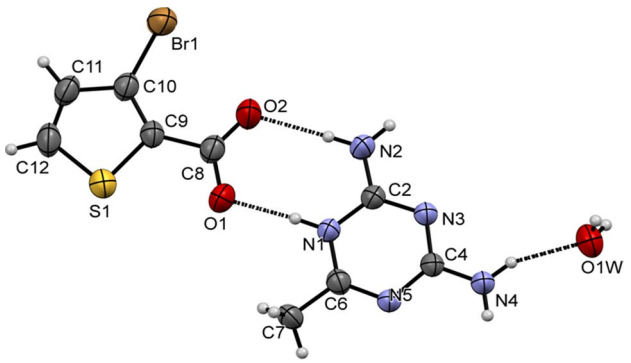


Fig. 2 ORTEP view of (**II**) with the atom-numbering scheme. Displacement ellipsoids are drawn at 50% probability level. Dashed lines represent hydrogen bonds

Cocrystal (**III**) crystallizes in the triclinic system with space group *P*-1. The asymmetric unit of the cocrystal (**III**) consists of one molecule of 2,4-diamine-6-phenyl-1,3,5-triazine (DAPT) and 2,5-dichlorothiophene-3-carboxylic acid (DCTPC) (Fig. 3). Internal angle at unprotonated N3 (C2–N3–C4) is 115.54 (15)°, at N5 (C4–N5–C6) is 114.80 (15)°, and at N1 (C6–N1–C2) is 114.50 (16)°. The two external bond angles at the carbon of the carboxyl group are 121.3 (2)° and 114.5 (1)°. The high discrepancy between these two angles is typical for unionized carboxyl group, and the C=O distance is 1.213 (3) Å and C–OH distance of 1.299 (3) Å. The bond parameters of the thiophene rings (**I**–**III**) agree with those in structures reported earlier [24].

3.2 Supramolecular features of (I), (II) and (III)

Among the three crystals, two are salts (**I** and **II**) and one is cocrystal (**III**) of thiophene carboxylic acid derivatives and substituted 1,3,5-triazine.

In salt (**I**), a robust $R_2^2(8)$ ring motif (supramolecular heterosynthon) is formed via N–H···O hydrogen bond interactions between DAMT ions (atoms N1 and N2) and CTC ions (atoms O1 and O2) [25]. Oxygen atom (O2) acts as bifurcated acceptor via N2–H2A···O2 and O1W–H2W···O2 hydrogen bonding. The symmetry related molecules of DAMT interact through a pair of N–H···N hydrogen bonds to form a discrete bimolecular homosynthon. Oxygen (O4) atom is involved in N4–H4B···O4^{iv} and N2–H2B···O4^{ii} hydrogen bonding [symmetry code (iv) x − 1, y + 1, z + 1, (ii) − x + 2, − y, − z + 1]. N–H···O and N–H···N hydrogen bonds between two DAMT and CTC ions leads to a ring motif with $R_3^2(8)$ graph-set. Hydrogen bond parameters of (**I**) are listed in Table 2. Similarly, O–H···O, O–H···N and N–H···O hydrogen bonds between DAMT, water and CTC lead to a ring motif with $R_3^3(10)$ graph-set. In this salt, supramolecular ribbon containing $R_3^2(8)$, $R_2^2(8)$ and $R_3^3(10)$ ring motifs generating a quadruple DADA (D = hydrogen-bond donor

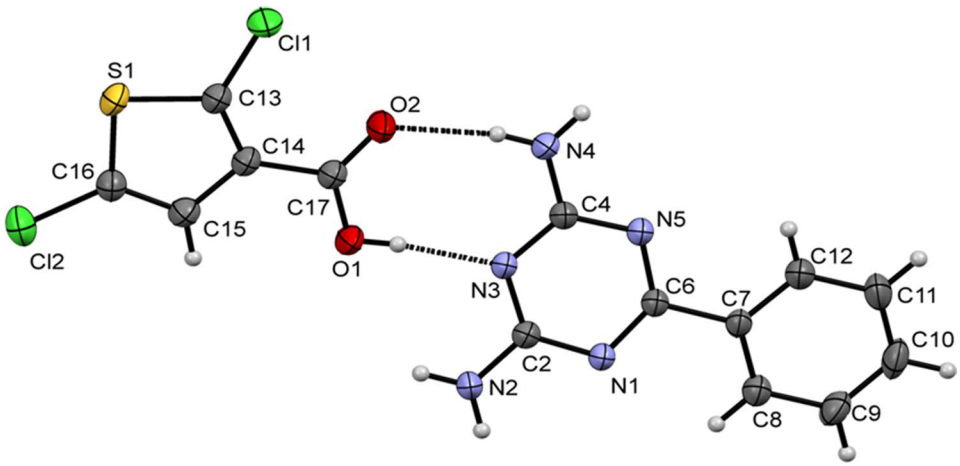


Fig. 3 ORTEP view of (**III**) with the atom-numbering scheme. Displacement ellipsoids are drawn at 50% probability level. Dashed lines represent hydrogen bonds

Table 2 Hydrogen-bond geometry (Å, °) for (**I**)

D–H···*A*	*D*–H	H···*A*	*D*···*A*	*D*–H···*A*
O3–H3···O1W^{i}	0.82	1.77	2.551(2)	159.1
N1–H1···O1	0.86	1.70	2.556(2)	173.7
N2–H2B···O4^{ii}	0.86	2.24	3.092(2)	170.7
N2–H2A···O2	0.86	2.05	2.907(2)	171.4
N4–H4A···N3^{iii}	0.86	2.12	2.959(2)	166.7
N4–H4B···O4^{iv}	0.86	2.19	2.8894(19)	138.9
O1W–H1W···N5^{v}	0.820(10)	1.988(11)	2.802(2)	172(3)
O1W–H2W···O2	0.815(10)	2.096(16)	2.868(2)	158(3)

Symmetry codes: (i) *x*, *y*, *z* − 1; (ii) −*x* + 2, −*y*, −*z* + 1; (iii) −*x* + 1, −*y* + 1, −*z* + 2; (iv) *x* − 1, *y* + 1, *z* + 1; (v) *x* + 1, *y* − 1, *z*

and A = hydrogen bond acceptor) array of hydrogen bonds is observed. This supramolecular ribbon is connected by water molecule via O1W-H1W···O2 hydrogen bonding to form large ring motif, $R_6^7(33)$, which leads to the formation of supramolecular sheet (Fig. 4). The commonly occurring carboxyl···carboxylate and carboxyl···carboxyl interactions are not present in the crystal structure [26]. This may be due to the hydrogen bonds involving water and the presence of $R_2^2(8)$ heterosynthon and $R_2^2(8)$ homosynthon (base pair).

Anion···π interaction occurs whenever an anion is perpendicular to the aromatic ring at a distance less than 4.5 Å, in this structure carboxylate oxygen (O1) interacts with nearly perpendicular aromatic ring of thiophene and that of triazine at distances of 3.180 (2) Å and 3.483 (2) Å, respectively with ˂C8–O1···cg1 = 91.1(1)° and ˂C8–O1···cg2 = 86.3(1)° (Fig. 5) [27].

In salt (**II**), a primary $R_2^2(8)$ ring motif is formed via N1–H1···O1^{i} and N2–H2···O2^{i} [symmetry code (i); 1 − x, 1 − y, 2 − z] hydrogen bonding interactions between the DAMT and BTPC ions (Fig. 5). DAMT ions self assemble via N–H···N hydrogen bonding with $R_2^2(8)$ ring motif generating a quadruple DADA hydrogen bonding array. This forms a supramolecular chain. This supramolecular chain interacts with water and BTPC via O–H···O, N–H···O and C–H···O hydrogen bonds with $R_3^2(8)$ and $R_4^3(10)$ ring motifs forming a supramolecular ribbon (Fig. 6). Hydrogen bond parameters of (**II**) are listed in Table 3. DAMT ions form N–H···N intermolecular hydrogen bonds forming $R_2^2(8)$ ring motif has been reported [28].

π···π (Cg1···Cg2^{v} and Cg2···Cg1^{vi}) interactions with interplanar distance of 3.843 (2) Å and slip angle 23.2° [symmetry code; vi = 1 + x, y, z, v = − 1 + x, y, z] between the triazine ring and thiophene ring are present (Fig. 7).

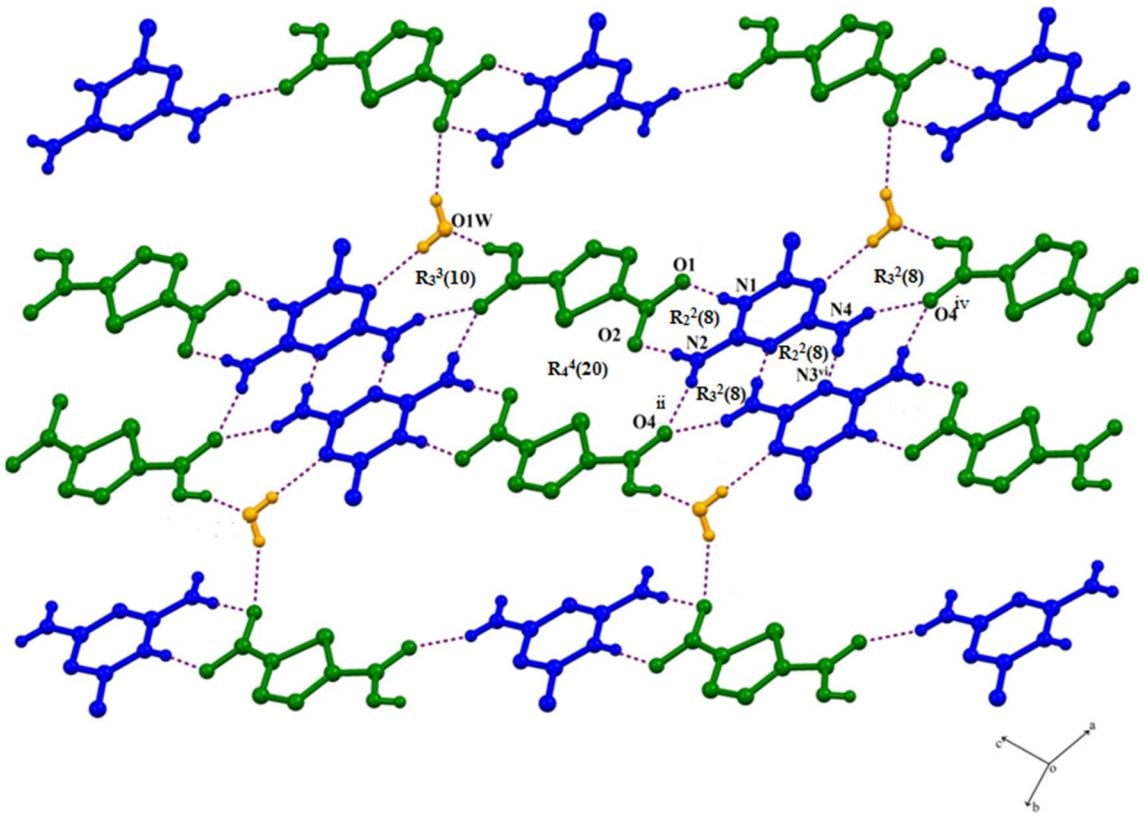


Fig. 4 Supramolecular architecture developed via N–H···O and O–H···O hydrogen bonds in (**I**)

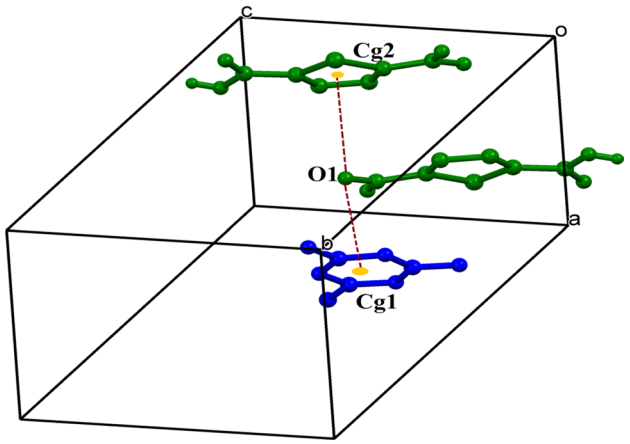


Fig. 5 Anion···π interactions present in (**I**)

Table 3 Hydrogen-bond geometry (Å, °) for (**II**)

D–H···*A*	*D*–H	H···*A*	*D*···*A*	*D*–H···*A*
N1–H1···O1^{i}	0.86	1.83	2.689(4)	175.1
N2–H2B···N3^{ii}	0.86	2.24	3.084(4)	166.8
N2–H2A···O2^{i}	0.86	1.99	2.842(4)	171.3
N4–H4A···O1W	0.86	2.01	2.794(4)	151.0
N4–H4B···N5^{iii}	0.86	2.15	3.004(4)	175.5
O1W–H1W···O1^{ii}	0.821(10)	2.02(2)	2.823(5)	167(7)
O1W–H2W···O2^{iv}	0.818(10)	1.988(15)	2.800(5)	172(7)

Symmetry codes: (i) $-x+1, -y+1, -z+2$; (ii) $-x+1, -y+1, -z+1$; (iii) $-x, -y+2, -z+1$; (iv) $x, y, z-1$

In cocrystal (**III**), one molecule of 2,4-diamine-6-phenyl-1,3,5-triazine (DAPT) and one molecule of 2,5-dichlorothiophene-3-carboxylic acid interact via N4–H4A···O2 and O1–H1···N3 hydrogen bonds to form the robust $R_2^2(8)$ ring motif (supramolecular heterosynthon) (Fig. 8). Hydrogen bond parameters of (**III**) are listed in Table 4. Two types of base pairing are present among DAPT molecules via N2–H2A···N1^{i} and N4–H4B···N5^{ii} hydrogen bonds [symmetry code: (i) $-x+1, -y, -z+1$; (ii) $-x+2, -y+1, -z+1$], forming $R_2^2(8)$ ring motifs, leading to a supramolecular chain. Similar type of base pairing via N–H···N hydrogen bonds leading to $R_2^2(8)$ ring motifs are observed among

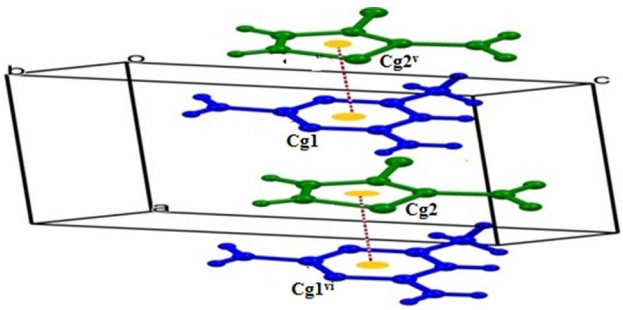


Fig. 7 π···π interactions present in (**II**)

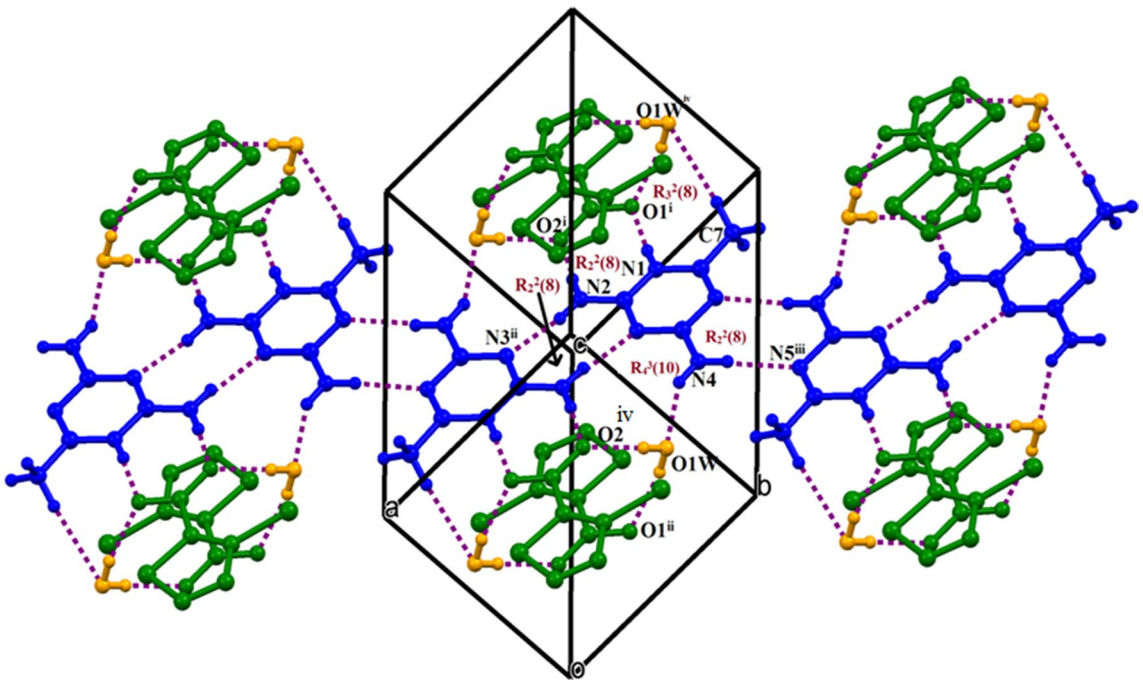


Fig. 6 Supramolecular architecture developed via N–H···O, O–H···O and C–H···O hydrogen bonds in (**II**)

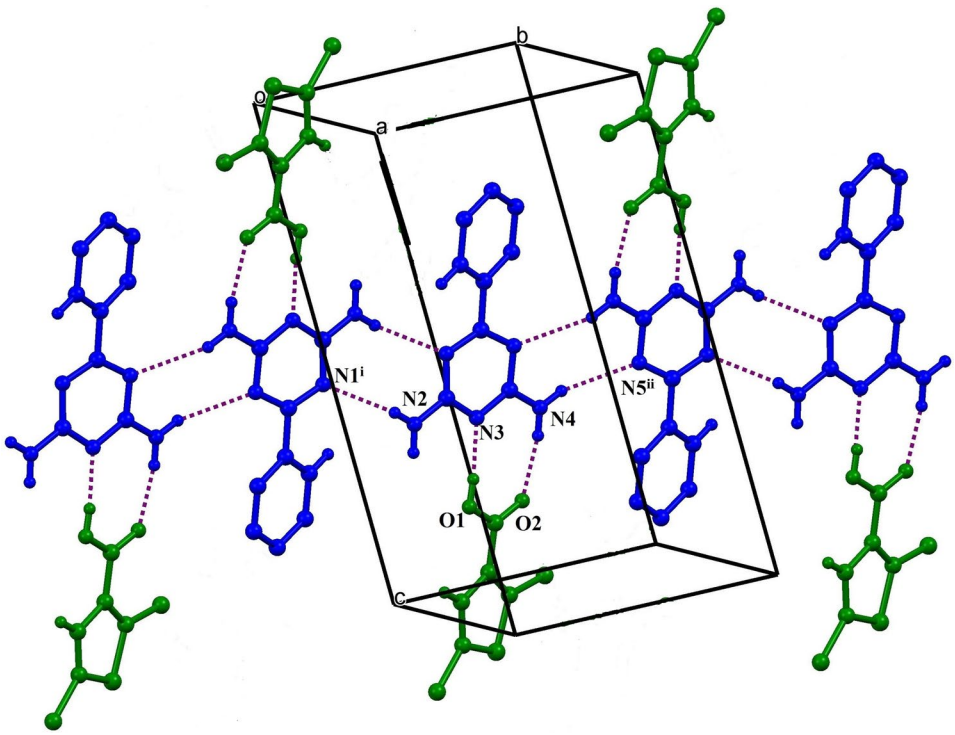


Fig. 8 Supramolecular architecture developed via N–H···O and N–H···N hydrogen bonds in (**III**)

Table 4 Hydrogen-bond geometry (Å, °) for (**III**)

D–H···*A*	*D*–H	H···*A*	*D*···*A*	*D*–H···*A*
O1–H1···N3	0.82	1.84	2.6585(19)	173.3
N2–H2A···N1^{i}	0.86	2.37	3.185(2)	157.3
N4–H4B···N5^{ii}	0.86	2.45	3.242(2)	154.0
N4–H4A···O2	0.86	2.01	2.858(2)	169.2
C15–H15···Cl1^{iii}	0.93	2.77	3.647(2)	158.5

Symmetry codes: (i) $-x+1, -y, -z+1$; (ii) $-x+2, -y+1, -z+1$; (iii) $x-1, y, z$

DAPT molecules [29]. Carboxyl interaction leads to the formation of $R_2^2(8)$ motif in which DCTPC molecules are appended to the ribbon of DAPT molecules (Fig. 8).

Halogen bonds have several applications in design strategies like an element for structural insulation. Recently halogen interactions are receiving wide attention and they are used in crystal engineering. Cocrystal (**III**) contains Cl···O interaction (halogen bond) and Cl···Cl interactions. Cl1···O1 interaction at a distance of 3.1528 (18) Å with C13–Cl1···O1 angle of 167.96 (8)° (Fig. 9), shorter than the sum of the van der Waals radii 3.27 Å [11, 26]. The Type I halogen···halogen (Cl2···Cl2 interaction at a distance of 3.4949 (11) Å) interaction [30] has also been observed (Fig. 9). Further π···π interactions between triazine···triazine (Cg1···Cg1 = 3.6542 (11) Å, symmetry code; 2 − x, − y, 1 − z) and triazine···phenyl rings (Cg1···Cg2 = 3.7455 (12) Å, symmetry code; 1 − x, 1 − y, 1 − z) (Fig. 10) are also observed. Stabilization of supramolecular network by π···π interactions between triazine···phenyl rings among DAPT molecules with centroid to centroid distance of 3.8396(16) Å is already reported [29].

Among the various non-covalent interactions present, in all the three cases we observe base pairs formed via N–H···N hydrogen bonds among symmetry related molecules/ions. Literature also shows N–H···N base pairs were present predominantly among self assemblies of aminotriazine derivatives [29].

4 Conclusions

Single crystals of two salts, 2,4-diamino-6-methyl-1,3,5-triazin-1-ium 5-carboxythiophene-2-carboxylate monohydrate (**I**), 2,4-diamino-6-methyl-1,3,5-triazin-1-ium 3-bromothiophene-2-carboxylate monohydrate (**II**) and a 1:1 cocrystal, 2,4-diamine-6-phenyl-1,3,5-triazine and 2,5-dichlorothiophene-3-carboxylic acid (**III**) have been synthesised and characterised by single-crystal X-ray diffraction. O–H···O, N–H···O and N–H···N hydrogen bonding interactions are dominant in salt (**I**). Anion···π interactions stabilises (**I**) further. O–H···O, N–H···O, N–H···N and C–H···O hydrogen bonding interactions are dominant in salt (**II**). Salt (**II**) is further stabilised by π···π interactions. O–H···N, N–H···O and N–H···N hydrogen bonding interactions are dominant in cocrystal (**III**). Cocrystal (**III**) is further stabilised by Cl···O, Cl···Cl as well as π···π interactions.

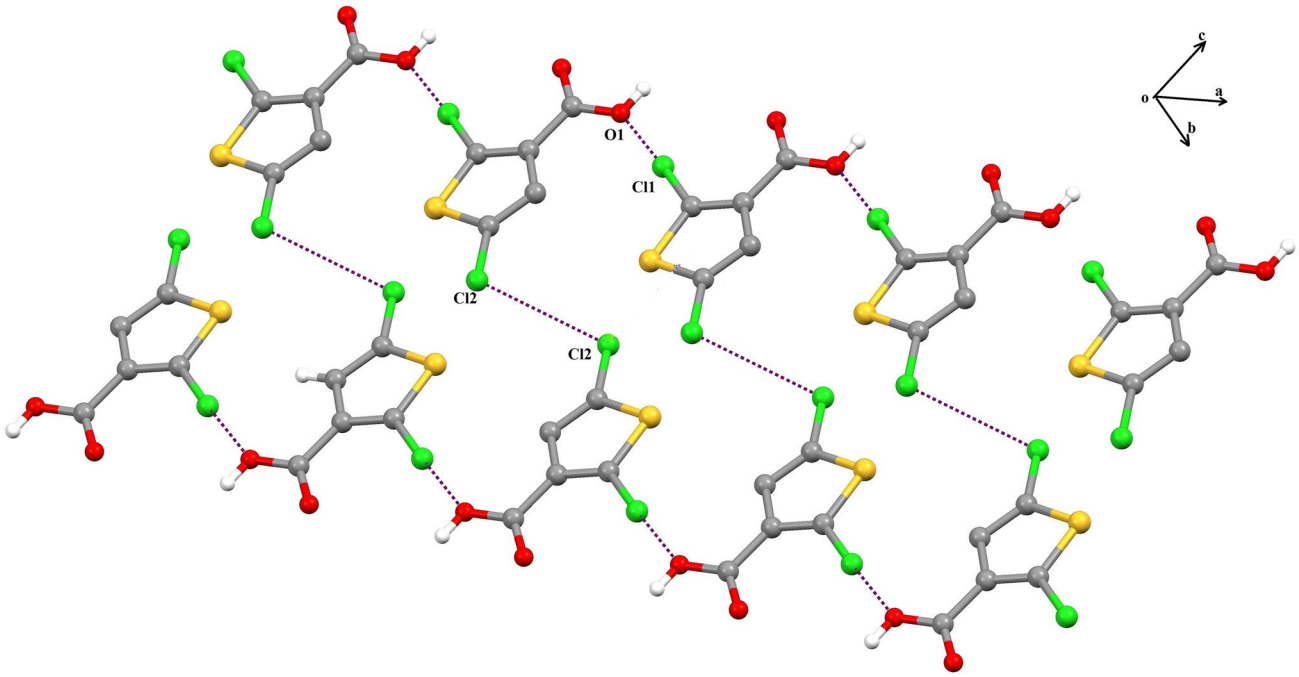


Fig. 9 Supramolecular architecture developed via Cl···O and Cl···Cl interactions in (**III**)

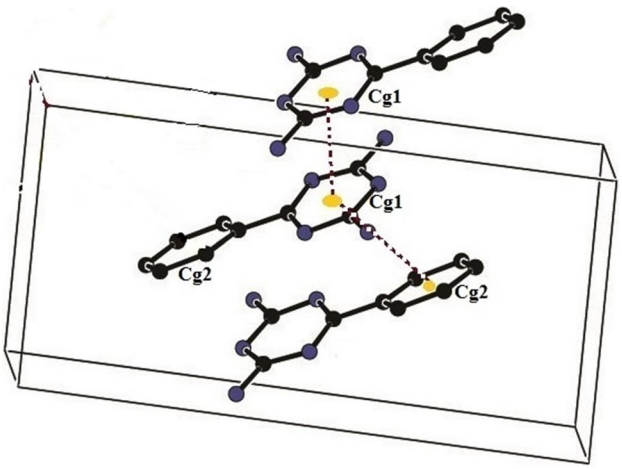


Fig. 10 π···π interactions present in (**III**)

The non-covalent interactions exhibited by (**I**), (**II**) and (**III**) generate a variety of recurring supramolecular architectures in three-dimensional space.

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Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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