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Crystal engineering studies on the salts of *trans*-4,4′-stilbenedicarboxylic acid in the context of solid state [2 + 2] cycloaddition reaction†‡

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A series of molecular salts of *trans*-4,4′-stilbenedicarboxylic acid (H_2SDC) with various amines (cyclohexylamine **1**, ethylenediamine **2**, 1,3-diaminopropane **3**, 1,4-diaminobutane **4**, cystamine **5**, guanidine **6**, 4-aminopyridine **7**, piperizine **8**) have been synthesized and their structures have been determined by X-ray crystallography to understand the influence of various dominant non-covalent interactions in their crystal packing to attain energy minima in the solid state architectures. The well-defined patterns of these interactions have been analysed to assign the corresponding graph set notations and the concept of 'supramolecular synthon' has been justified. The presence of olefinic double bond and its orientations in these molecular salts make it interesting to study their photoreactivity towards UV light for [2 + 2] cycloaddition reaction. In the salt of 1,3-diaminopropane, the dianion was found to align perfectly parallel, congenial for solid state [2 + 2] cycloaddition reaction, undergoing quantitative dimerization under a UV lamp. Although the dianion was found to align perfectly parallel in salt **1**, the photostability of this salt justifies Schmidt's distance criterion. The slip-stacked orientation of the dianion makes the molecular salt **4** photostable. A zigzag water cluster chain stabilised by various H-bonding interactions was identified in the molecular salt **6**. The photoreactivity of the salts with 3,3′-dipropylamino amine **9** and with ammonia **10** are also accounted to discuss the possible relation between the chain length of the dications.

Introduction

'Crystals engineering', an interdisciplinary field of research, deals with the understanding of non-covalent intermolecular interactions that holds molecules together in preferred orientations to form molecular architectures in the crystalline solid.[1] Understanding crystal engineering principles and utilizing them to generate functional molecular solids with desired properties has become the ultimate goal of researchers in this field. A multi-component crystal in which the components that are solid at ambient condition co-exist through hydrogen bonding interactions is known as a co-crystal.[2] When different molecules with complementary functional groups construct hydrogen bonding that are energetically more favourable than those between like molecules of each component, then the formation of a co-crystal is favoured thermodynamically.[3] The position of acidic proton between an acidic molecule and its base partner in such supramolecular networks or in active pharmaceutical ingredients (APIs) is of primary importance to confirm it to be a neutral (O–H···N) or ionic ($^+$N–H···O$^-$) or an in between situation (N···H···O).[4] The formation of a neutral co-crystal or an ionic one (molecular salt) from an acid–base pair can be predicted by the difference in pK_a values [$\Delta pK_a = pK_a(\text{base}) - pK_a(\text{acid})$] of the reactants.[5] Although there are many exceptions,[6] the formation of a salt is favoured when ΔpK_a value is sufficiently large *viz.* greater than 2 or 3.

On the other hand, Schmidt's topochemical postulates for the solid state [2 + 2] cycloaddition reaction require parallel orientation of photoreactive double bonds maintaining centre-to-centre distance in the range 3.5–4.2 Å.[7] The parallel orientations of photoreactive ethylene double bonds and their photodimerization in organic molecular salts have been reported in literature. The deprotonation of the acidic protons in the mono- or dicarboxylic acids by strong base leads to the molecular salts where photodimerization occurs between two anionic moieties.[8] Whereas the pyridyl derivatives containing C=C bonds can be protonated by adding strong acids to form salts where photodimerization occurs between two cationic moieties, often stacked by cation–π interactions.[9] The counteranions have significant roles in such [2 + 2] cycloaddition reactions controlling the orientations of the cationic monomers (*e.g.* head-to-head or head-to-tail) and hence dictate the product formation.[9c] Organic molecular salts are

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increasingly being popular for [2 + 2] cycloaddition reaction in the solid state because of several reasons: greater stability due to robust charge assisted hydrogen-bonded supramolecular ionic synthons over their neutral counterparts; better control of the stoichiometry; better solubility and easy of separation of the dimeric product. Electrostatic interaction, being less directional compared to other supramolecular interactions, makes it a challenge to rationalize the orientations of ionic counterparts in solid molecular salts compared to co-crystals where remarkable success has been achieved in synthesising functional molecular solids utilising the directionality of the H-bonding.[10]

In this contribution, we have chosen *trans*-4,4′-stilbenedicarboxylic acid (H_2SDC) to synthesize molecular salts with several amines for various reasons. The identification of the 'supramolecular synthons'[11] and the patterns of the charge assisted hydrogen bonded motifs[12] constructing the solid state architecture is very significant to characterize molecular salts of the dicarboxylate crystallographically. The ethylenic double bonds in the linear dicarboxylic acids render itself as functional group for the synthesis of cyclobutane derivatives *via* photochemical [2 + 2] cycloaddition reaction in the solid state. In this respect, we have recently reported the synthesis of 1,2,3,4-tetrakis-(4′-carboxyphenyl)-cyclobutane, the dimer of H_2SDC, *via* the salt formation with 1,3-diaminopropane.[13] Herein, we shall present the full details of the synthetic strategy identifying the 'supramolecular synthons' present in the series of molecular salts.

Result and discussion

Materials and synthesis

Trans-4,4′-stilbenedicarboxylic acid (H_2SDC) was synthesized *via* dehydrodimerization reaction as reported in literature.[14] All the amines used were purchased from common commercial sources and were used without further purification. The amines used in this study are all moderately strong to snatch acidic protons from H_2SDC to form molecular salts in aqueous medium[15] (pK_a values are listed in ESI‡). Single crystals of all the molecular salts were grown from water. Solid H_2SDC was dissolved in water by adding equivalent amount of amines with sonication. The resultant clear solutions were allowed to evaporate slowly to obtain suitable single crystals of **1**–**4** and **7**–**8**. For the molecular salts **5** and **6**, triethylammonium salts of H_2SDC were mixed with corresponding hydrochloride salts of the amines in aqueous media.

Crystal structure of cyclohexylammonium–stilbenedicarboxylate (SDC) salt

The structure of the salt of composition $C_{42}H_{57}N_3O_6$ (**1**) was refined in the triclinic space group $P\bar{1}$.§ The asymmetric unit contains one and a half anions $C_{16}H_{10}O_4$ and three cations $C_6H_{14}N$ where one of the cations is disordered. The crystal structure is stabilized by the charge assisted H-bonding interactions between NH_3^+ and CO_2^- units. Each carboxylate unit interacts with three different NH_3^+ units where one carboxylate oxygen interacts with two NH_3^+ proton donors (Fig. 1a). On the other hand, each NH_3^+ unit of the cation donates H-bond to three carboxylate groups of three different SDC^{2-} anions (Fig. 1b). The hydrogen bonding assembly propagates in all the directions which result a complicated three dimensional network. Among the H-bonding patterns that exist in the packing, the rings are identified with graph set notations $\mathbf{R}_4^4(12)$ and $\mathbf{R}_4^2(8)$ and are described in Fig. 1c. Another interesting feature of this salt is that the SDC^{2-} anions are in offset parallel

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§ Crystal data for **1** at 223 K: $C_{42}H_{57}N_3O_6$, $M = 699.91$, triclinic space group, $P\bar{1}$; $a = 12.1042(10)$ Å, $b = 12.6256(10)$ Å, $c = 15.2007(11)$ Å, $\alpha = 110.722(2)°$, $\beta = 111.880(2)°$, $\gamma = 95.796(2)°$; $V = 1942.3(3)$ Å^3, $Z = 2$, $D_{calcd} = 1.197$ g cm^{-3}, $\mu = 0.080$ mm^{-1}, GOF = 1.034, final $R_1 = 0.0793$, w$R_2 = 0.1976$ [for 5245 data $I > 2\sigma(I)$].
Analysis found: C 72.05, H 7.92, N 5.94. $C_{42}H_{57}N_3O_6$ requires: C 72.07, H 8.21, N 6.00%.
Crystal data for **2** at 100 K: $C_{18}H_{20}N_2O_4$, $M = 328.36$, monoclinic space group, $P2_1/c$; $a = 10.156(2)$ Å, $b = 9.334(2)$ Å, $c = 8.385(2)$ Å, $\beta = 94.400(5)°$; $V = 792.5(3)$ Å^3, $Z = 2$, $D_{calcd} = 1.376$ g cm^{-3}, $\mu = 0.098$ mm^{-1}, GOF = 1.100, final $R_1 = 0.0795$, w$R_2 = 0.1516$ [for 1265 data $I > 2\sigma(I)$].
Analysis found: C 65.52, H 6.22, N 8.66. $C_{18}H_{20}N_2O_4$ requires: C 65.84, H 6.14, N 8.53%.
Crystal data for **3** at 223 K: $C_{19}H_{24}N_2O_5$, $M = 360.40$, monoclinic space group $P2_1/c$; $a = 16.0565(8)$ Å, $b = 11.7861(6)$ Å, $c = 9.6935(5)$ Å, $\beta = 104.5700(10)°$; $V = 1775.44(16)$ Å^3, $Z = 4$, $D_{calcd} = 1.348$ g cm^{-3}, $\mu = 1.362$ mm^{-1}, GOF = 1.044, Final $R_1 = 0.0495$, w$R_2 = 0.1343$ [for 4329 data $I > 2\sigma(I)$].
Analysis found: C 63.24, H 6.60, N 7.81. $C_{19}H_{24}N_2O_5$ requires: C 63.32, H 6.71, N 7.77%.
Crystal data for **4** at 223 K: $C_{20}H_{28}N_2O_6$, $M = 392.44$, triclinic space group, $P\bar{1}$; $a = 7.4542(13)$ Å, $b = 9.7070(16)$ Å, $c = 13.610(2)$ Å, $\alpha = 100.688(2)°$, $\beta = 96.117(3)°$, $\gamma = 90.070(3)°$; $V = 962.0(3)$ Å^3, $Z = 2$, $D_{calcd} = 1.355$, $\mu = 0.100$ mm^{-1}, GOF = 1.097, final $R_1 = 0.0629$, w$R_2 = 0.1722$ [for 3637 data $I > 2\sigma(I)$].
Analysis found: C 61.27, H 7.40, N 7.24. $C_{20}H_{28}N_2O_6$ requires: C 61.21, H 7.19, N 7.14%.
Crystal data for **5** at 100 K: $C_{20}H_{24}N_2O_4S_2$, $M = 420.53$, triclinic space group, $P\bar{1}$; $a = 8.9392(4)$ Å, $b = 10.5683(5)$ Å, $c = 12.3610(6)$ Å, $\alpha = 71.1670(10)°$, $\beta = 75.9040(10)°$, $\gamma = 67.6480(10)°$ $V = 1012.43(8)$ Å^3, $Z = 2$, $D_{calcd} = 1.379$ g cm^{-3}, $\mu = 0.292$ mm^{-1}, GOF = 1.035, final $R_1 = 0.0320$, w$R_2 = 0.0866$ [for 4425 data $I > 2\sigma(I)$].
Analysis found: C 57.25, H 5.45, N 6.55. $C_{20}H_{24}N_2O_4S_2$ requires: C 57.12, H 5.75, N 6.66%.
Crystal data for **6** at 223 K: $C_9H_{15}N_3O_4$, $M = 229.24$, monoclinic space group, $P2_1/c$; $a = 11.6939(8)$ Å, $b = 10.6964(7)$ Å, $c = 8.8496(6)$ Å, $\beta = 93.170(2)°$; $V = 1105.24(13)$ Å^3, $Z = 4$, $D_{calcd} = 1.378$ g cm^{-3}, $\mu = 0.109$ mm^{-1}, GOF = 1.056, final $R_1 = 0.0482$, wR_2 0.1260 [for 2279 data $I > 2\sigma(I)$].
Analysis found: C 47.22, H 6.41, N 18.05. $C_9H_{15}N_3O_4$ requires: C 47.16, H 6.60, N 18.33%.
Crystal data for **7** at 223 K: $C_{26}H_{28}N_4O_6$, $M = 492.52$, monoclinic space group, $P2_1/n$; $a = 8.5009(6)$ Å, $b = 10.6106(7)$ Å, $c = 13.7800(9)$ Å, $\beta = 101.6510(10)°$; $V = 1217.34(14)$ Å^3, $Z = 2$, $D_{calcd} = 1.344$ g cm^{-3}, $\mu = 0.097$ mm^{-1}, GOF = 1.042, final $R_1 = 0.0460$, w$R_2 = 0.1292$ [for 2386 data $I > 2\sigma(I)$].
Analysis found: C 62.96, H 5.60, N 11.25. $C_{26}H_{28}N_4O_6$ requires: C 63.40, H 5.73, N 11.38%.
Crystal data for **8** at 100 K: $C_{20}H_{22}N_2O_4$, $M = 354.40$, monoclinic space group, $P2_1/c$; $a = 12.5672(16)$ Å, $b = 8.3029(10)$ Å, $c = 8.2837(11)$ Å, $\beta = 94.708(3)°$; $V = 861.44(19)$ Å^3, $Z = 2$, $D_{calcd} = 1.366$ g cm^{-3}, $\mu = 0.096$ mm^{-1}, GOF = 1.130, final $R_1 = 0.0491$, w$R_2 = 0.1222$ [for 1802 data $I > 2\sigma(I)$].
Analysis found: C 67.88, H 6.12, N 7.94. $C_{20}H_{22}N_2O_4$ requires: C 67.78, H 6.26, N 7.90%.
The composition for the salt **9** was determined from elemental analysis and was supported by TGA (in ESI‡). Analysis found: C 59.33, H 7.11, N 6.83. $C_{60}H_{86}N_6O_{20}$ requires: C 59.49, H 7.16, N 6.94.
The composition of the ammonium salt (**10**) was determined as $C_{16}H_{15}NO_4$ from elemental analysis data. Analysis found: C 67.04, H 5.17, N 4.67. $C_{16}H_{15}NO_4$ requires: C 67.36, H 5.30, N 4.91.

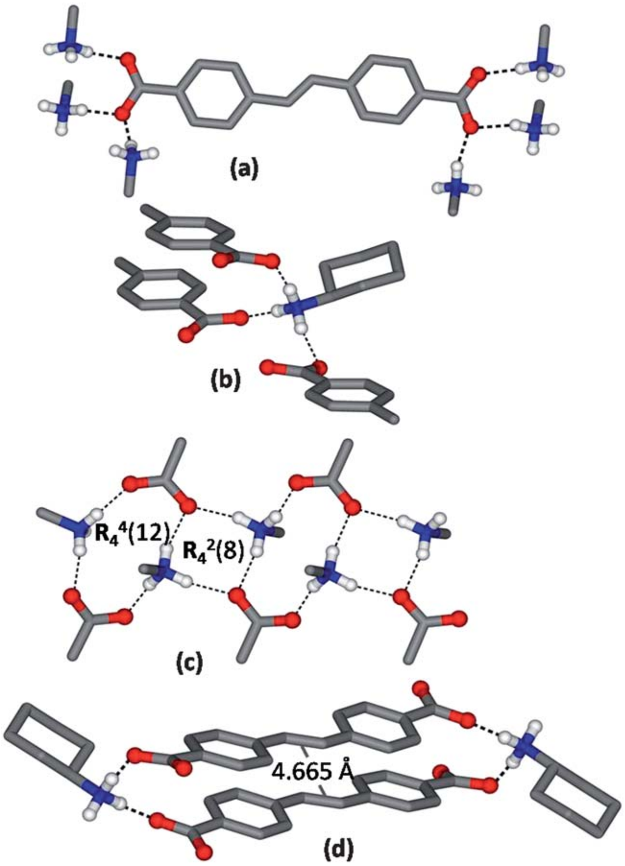

Fig. 1 Various hydrogen bonding interactions in the crystal structure of **1**.

alignment. NH_3^+ unit acts as clipping template towards SDC^{2-} anions and organises them with a separation of 4.665 Å between the centres of the olefinic double bonds (Fig. 1d). The distance is beyond the Schmidt's criteria for solid state [2 + 2] cycloaddition reaction, the salt was also found to be photo-stable.

Crystal structure of ethylenediammonium–SDC salt

Single-crystal X-Ray diffraction analysis§ reveals that the asymmetric unit of the salt of composition $C_{18}H_{20}N_2O_4$ (**2**), contains one anion $C_{16}H_{10}O_4$ and one cation $C_2H_{10}N_2$. The structure was refined in monoclinic P2$_1$/c space group. The anions and cations are held together by various charge assisted NH–O hydrogen bonds. Each NH_3^+ unit of the diammonium cation interacts with three carboxylate groups of three different SDC^{2-} anions (Fig. 2a). Both the carboxylate units of each SDC^{2-} anion interact with three NH_3^+ units while two oxygen atoms in a carboxylate unit interact dissimilarly (Fig. 2b). One carboxylate oxygen accepts one H-bond from NH_3^+ unit whereas other one accepts two H-bonds from two NH_3^+ units. Both the NH_3^+ end of one ethylene-diammonium cation act as H-bond donors toward three carboxylates units that result in an undefined three dimensional hydrogen bonded network. A view on the *ac* plane shows the organised arrangement of cations and anions where the dications are interspersed between the anionic layers. A closer look to the H-bonding pattern reveals that there is H-bonded ring with graph set $\mathbf{R}_4^4(12)$ formed by two NH_3^+ and two carboxylate units (See ESI‡).

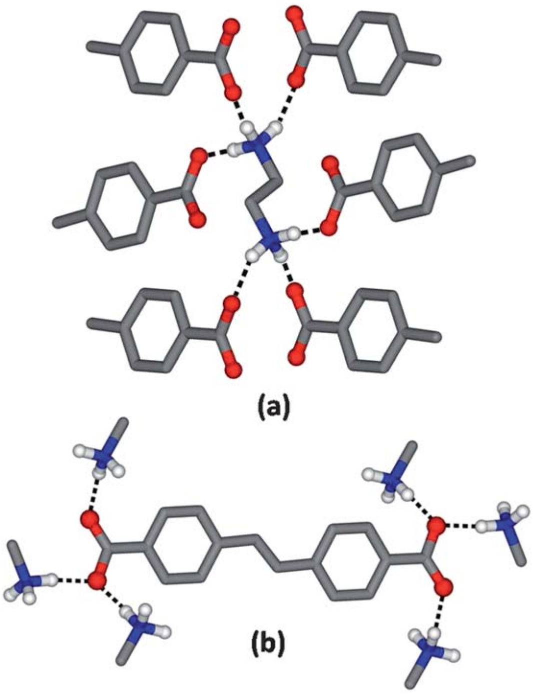

Fig. 2 Supramolecular synthons that play prominent roles in the construction of solid state architecture, as observed in **2**.

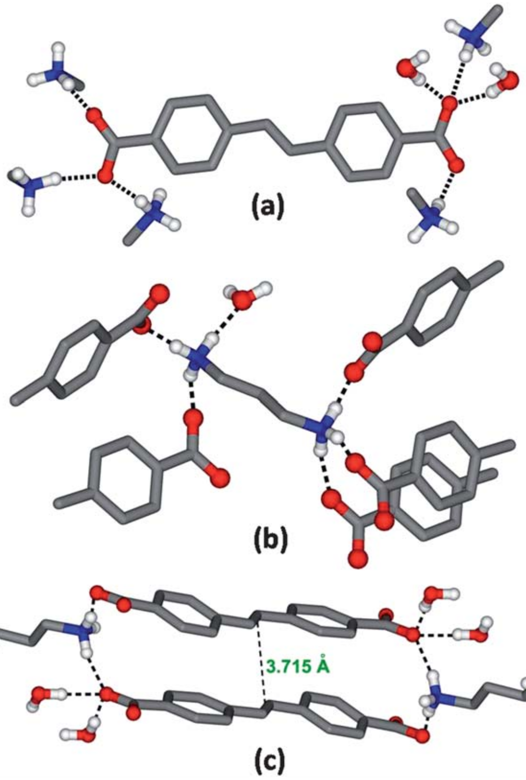

Fig. 3 Various hydrogen bonding interactions present in the crystal structure of **3** are highlighted.

Crystal structure of 1,3-diammonium propane (DAP)–SDC salt

A preliminary version of the structure of the hydrate salt has been described before.[13]§ The asymmetric unit of the salt contains one anion $C_{16}H_{10}O_4$ and one cation $C_3H_{12}N_2$ and one water molecule. Each CO_2^- unit of SDC^{2-} anion is involved in charge assisted H-bonding interactions with NH_3^+ units of different DAP cations and H-bonding interaction with water molecules present in the crystal (Fig. 3a). In terms of supramolecular interactions exhibited, two carboxylate ends of each SDC^{2-} anion, like two NH_3^+ units of each DAP cations, are uneven. One carboxylate unit involves in charge assisted H-bonding interaction with three different NH_3^+ units of three different DAP cations. The other carboxylate unit interacts with two water molecules and two NH_3^+ units of two different DAP cations. Similarly, one end of DAP interacts with three carboxylate units of three SDC^{2-} where as the other end interacts with two carboxylate units of two SDC^{2-} unit one water molecules (Fig. 3b). Each water molecule plays the role of H-bond donor to two carboxylates end as well as acceptor to one NH_3^+ unit. The hydrogen bonded assembly of cation, anion and water molecules propagates in all the directions to result in a three dimensional network with undefined topology. Thermogravimetric analysis (TGA) confirms the composition and supports for the strong H-bonding interactions of lattice water with DAP and SDC (5.2% wt. loss at ~100 °C).

A thorough examination of the H-bonding patterns in the packing structure (See ESI‡) reveals that there is a H-bonded ring with graph set $\mathbf{R}_4^2(8)$ as shown in (See ESI‡). The most interesting property of this salt is the parallel orientation of the SDC^{2-} anions where the centre-to-centre distance between two parallel aligned SDC^{2-} anions is 3.715 Å that satisfies the Schmidt's criteria for solid state photochemical reaction (Fig. 3c). Here, NH_3^+ units of the diamonium act as clipping templates for aligning dicarboxylate units with the help of water molecules present in the crystal. Upon irradiation under UV light for 30 h the salt was observed to undergo quantitative photodimerization to yield 1,2,3,4-tetrakis-(4′-carboxyphenyl)-cyclobutane salt. The mechanochemical synthesis and the characterizations of this compound from this salt has been described where we have shown it to be a potential candidate for co-crystal and metal organic framework synthesis.[13]

Crystal structure of 1,4-diammonium butane (DAB)–SDC salt

The structure of this salt of composition $C_{20}H_{28}N_2O_6$ (**4**) was refined in the triclinic space group $P\bar{1}$.§ The asymmetric unit contains two halves of the anion $C_{16}H_{10}O_4$, one cation $C_4H_{14}N_2$ and two water molecules. Each carboxylate oxygen atom of each SDC^{2-} is interacting with one water molecule and one NH_3^+ unit of a DAB (Fig. 4a). Each water molecule acts as H-bond donor to two carboxylate oxygen atoms and H-bond acceptor to one NH_3^+ unit. Each NH_3^+ unit of DAB is connected to two carboxylate units of two different SDC^{2-} anions through charge assisted H-bonding and one water molecule (Fig. 4b).

A detailed scrutiny to the packing (see ESI‡) of the crystal structure reveals the presence of two types of H-bonded rings with graph set $\mathbf{R}_3^3(8)$ and $\mathbf{R}_7^5(16)$ (see ESI‡). Another interesting feature of the salt is that the SDC^{2-} anions are involved in π–π stacking interactions. The distance between two planes of parallel aligned offset SDC^{2-} anions is 3.592 Å and between the centroids of two nearest aromatic rings is 3.867 Å (Fig. 4c). However, the crystal is found to be photostable as the olefinic double bonds of two parallel aligned SDC^{2-} anions are slipped away.

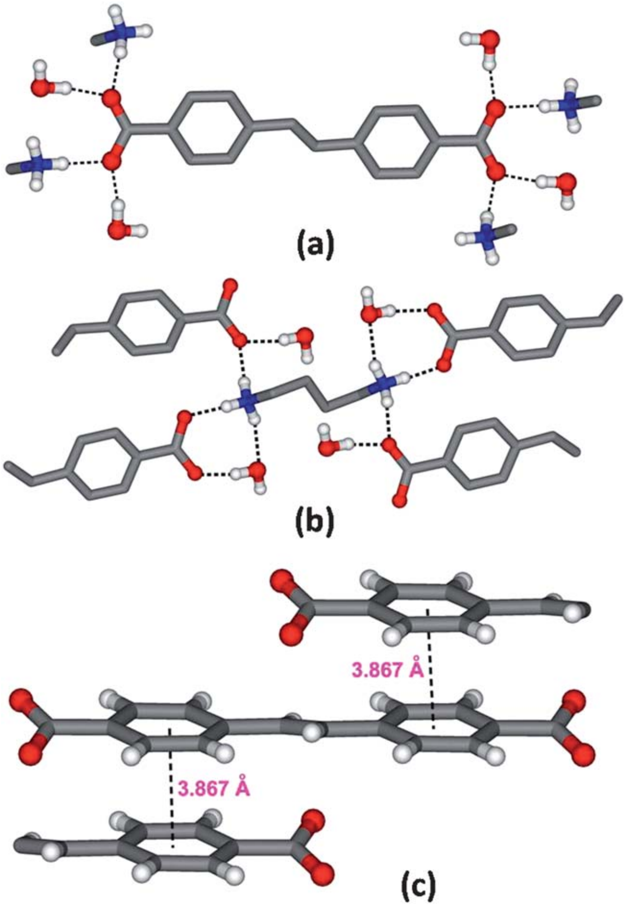

Fig. 4 Various aspects in the crystal structure of **4** are analyzed.

Crystal structure of 2,2′-dithiobis(ethanammonium)–SDC salt

Single crystal X-ray diffraction analysis shows§ that the asymmetric unit of the salt of composition $C_{20}H_{24}N_2O_4S_2$ (**5**), contains two halves of the anion $C_{16}H_{10}O_4$ and one cation $C_4H_{14}S_2N_2$. Both the carboxylate units of SDC^{2-} anions are interacting with three NH_3^+ units of three 2,2′-dithiobis (ethanammonium)cations. One carboxylate oxygen accepts H-bonding from two NH_3^+ units and while the other one from a single NH_3^+ unit only (Fig. 5a). On the other hand, each NH_3^+ unit of the cation is hydrogen bonded to three CO_2^- units (Fig. 5b). In the crystal structure of the salt, we find two dimensional sheets where SDC^{2-} ions orient in such a way that they undergo point-to-face π–π interactions with a distance of 3.908 Å (Fig. 6) between carbon to centroid of the phenyl ring (see ESI‡). Two dimensional sheets of such kind are stacked parallel also by point-to-face π–π interaction between phenyl rings of the SDC^{2-} anions having a distance of 3.673 Å (Fig. 5c). The H-bonded motifs present in the structure can be represented

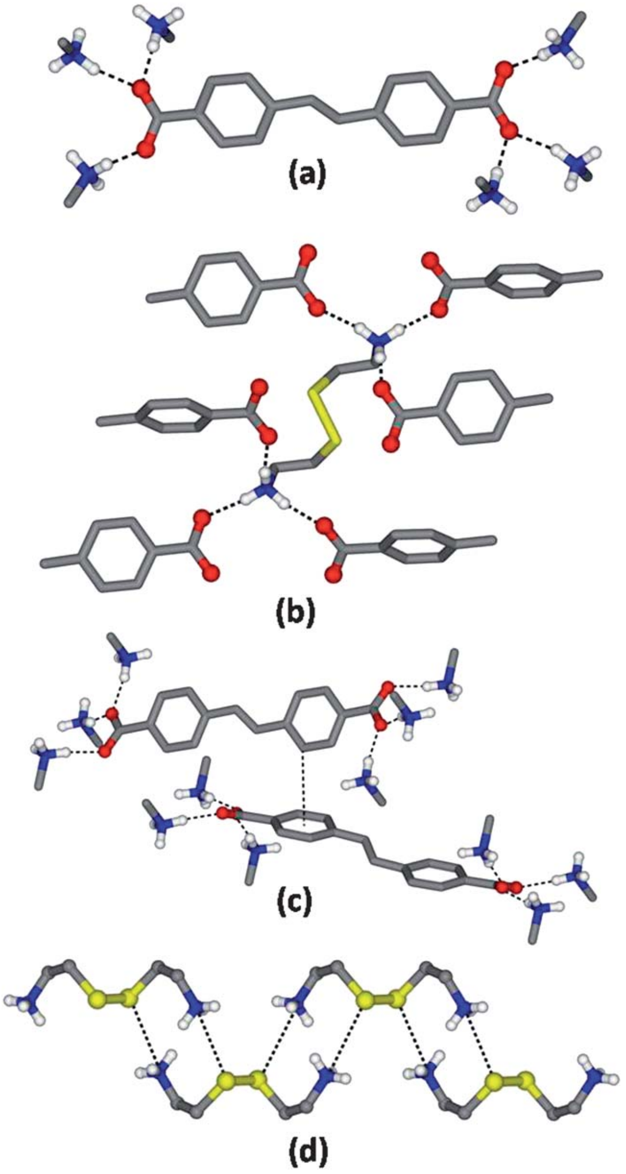

Fig. 5 The analysis of different features in the crystal structure of **5**.

by graph set notation as $\mathbf{R}_4^2(8)$ and $\mathbf{R}_4^4(12)$ as described in (also see ESI‡).

Another interesting feature of the packing is the conformation of the dication. Dithiobis-(ethanammonium) dications present in both the M- and P-type helical conformation and this particular conformation is stabilised by the weak interactions between sulfur and NH_3^+ units of the two types of conformers (Fig. 5d). The distances between sulfur and nitrogen of NH_3^+ are 3.283 Å and 3.487 Å that are in order of the sum of the van der Waal radii of nitrogen and sulfur. Hence, the existing weak interaction between sulfur and NH_3^+ is responsible for the helical conformation as shown in Fig. 6. The existence of helical conformation of this cation has been noted before in the literature.[16]

Crystal structure of guanidinium–SDC salt

The asymmetric unit of the title salt of composition $C_9H_{15}N_3O_4$ (**6**) crystallized in the monoclinic space group $P2_1/c$§ contains half an anion $C_{16}H_{10}O_4$ and one cation CN_3H_6 and two water molecules. Each carboxylate unit interacts with two guanidinium cations and two water molecules where one carboxylate oxygen is bonded to two N–H (guanidinium) and one O–H (water) and the other one with one N–H (guanidinium) and one O–H (water) (Fig. 7a). Generally, the guanidinium cation due to its inherent 3-fold axial symmetry, is able to form three pairs of strong hydrogen bonds to various oxyanions to construct (6,3) connected Rosette like networks with C_3-symmetric oxoanion building blocks.[17] Again, guanidine hydrochloride was utilised by Ito to make two different co-crystals of fumaric acid that undergo photodimerization partially under UV light.[8d]

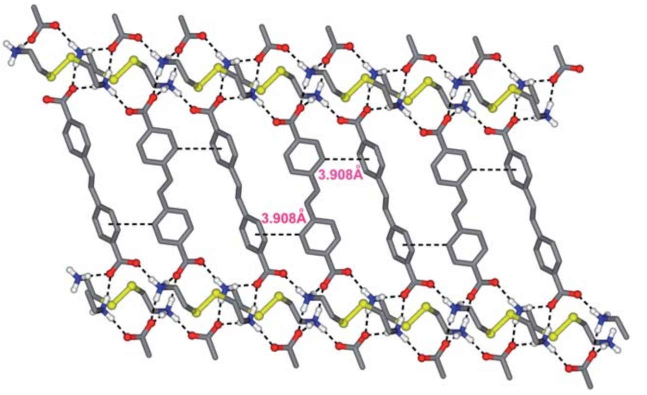

Fig. 6 Two dimensional sheet-like structure and point-to-face π–π interaction in **5**.

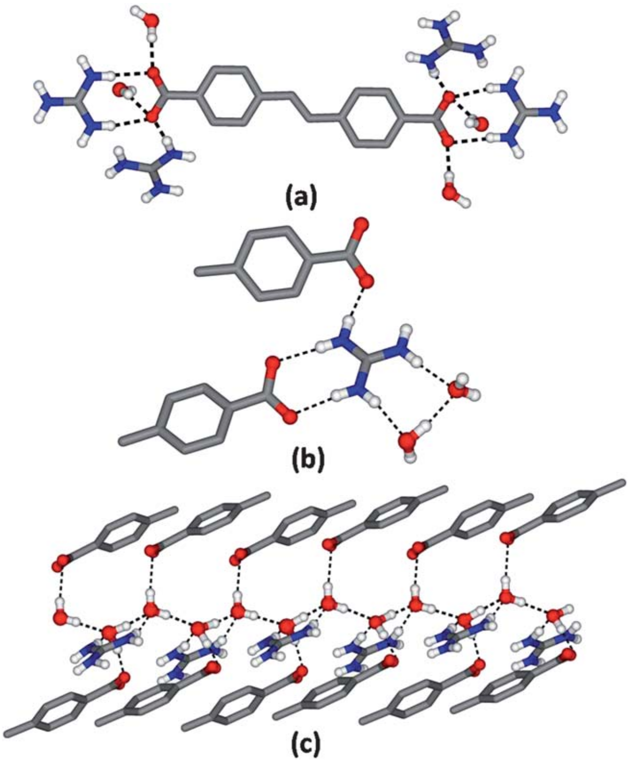

Fig. 7 Various hydrogen bonding interactions around various functional groups (a and b) and existence of 1D water chain in the crystal structure of **6**.

However, in the present study, guanidinium cation has been used for synthesising molecular salts with SDC^{2-} where each guanidinium cation is bonded to two SDC^{2-} anions and two water molecules. The structure resembles neither with the (6, 3) connected Rosette networks nor the SDC^{2-} anions are found parallel. The supramolecular interactions between neutral fumaric acids with guanidinium cations in the co-crystals (where Cl$^-$ ions balances the charge)[8d] are different from that of between SDC^{2-} anions and the same cations in **6**. H-bonding centred around each guanidinium cation can be represented by graph set notation as $\mathbf{R}_2^2(8)$ and $\mathbf{R}_3^2(8)$ (Fig. 7b). A through perusal of the H-bonding patterns in the packing of this salt reveals that there is 1D zigzag water chain passing along *c*-direction. Various H-bonds stabilise the water chain in the crystal. Each water molecule acts as H-bond donor to one carboxylate oxygen and one water molecule; whereas it accepts two H-bond from another water molecule and one N–H from guanidinium ion (Fig. 7c). A discrete $(H_2O)_{32}$ cluster, encapsulated in an organic salts of guanidinium cations, has been reported in literature.[18]

Crystal structure of 4-aminopyridinium–SDC salt

Single-crystal X-ray diffraction analysis reveals§ that the asymmetric unit of the title salt of composition $C_{26}H_{28}N_4O_6$ (**7**), contains half of the SDC^{2-} anion, one cation $C_5N_2H_7$ and a water molecule. Two-point ionic synthon $PyNH^+\cdots{}^-O_2C$ plays the key role in the building of hydrogen-bonded network in the solid state structure. The protonation to Py-N rather than NH_2 group can be rationalized from all possible pK_a values of 4-aminopyridine (see ESI‡). Both the carboxylate groups are bonded to pyridinium cation *via* charge assisted two-point (cyclic) $PyNH^+\cdots{}^-O_2C$ synthon and also bonded to two water molecules *via* H-bonding. The NH_2 groups of the cations are pointed towards each other and are bridged by two water molecules *via* H-bonding (Fig. 8). From the packing of the crystal structure (see ESI‡), it can be observed that the cations and anions involve π-stacking interaction and cations are interspersed between two SDC^{2-} anions. A closer look to the H-bonding pattern reveals that there are three types of H-bonded motifs and can be represented by graph set notation as $\mathbf{R}_2^2(7)$, $\mathbf{R}_4^2(8)$, $\mathbf{R}_4^4(12)$ (also see ESI‡).

Crystal structure of piperizine–SDC salt

The asymmetric unit of this salt of composition $C_{20}H_{22}N_2O_4$ (**8**)§ contains half an anion $C_{16}H_{10}O_4$ and half a cation $C_4H_{12}N_2$. The ionic synthon, $NH_2^+\cdots{}^-O_2C$ plays principal role in the formation of the solid state architecture. Each carboxylate unit is bonded to four NH_2^+ units of four cations and each piperizine cation is bonded to four carboxylate units of four SDC^{2-} anions in $\mathbf{C}(2)$ fashion (Fig. 9).

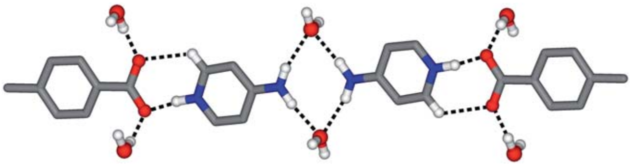

Fig. 8 A view of the hydrogen bonding interactions forming a chain in the solid state architecture in **7**.

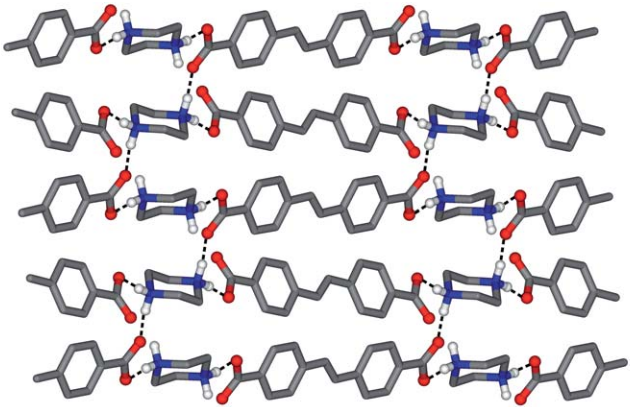

Fig. 9 A perspective view of packing diagram along *c*-direction shows the supramolecular synthons present in **8**.

Discussion

Having aimed in mind to synthesize 1,2,3,4-tetrakis(4′-carboxyphenyl) cyclobutane *via* [2 + 2] cycloaddition reaction of H_2SDC, we have studied this series of molecular salts. The photostable nature of H_2SDC in the solid state demands crystal engineering and the limited solubility of H_2SDC in common organic solvents prompted us to employ the salts formation route over co-crystals strategy. In the crystal structures of all these molecular salts, we have identified the supramolecular synthons that are exploited in the robust three dimensional ionic architectures in the solid state. The complex nature of these synthons are due to the less directional charge-assisted hydrogen bonding generated by the interactions between NH_3^+ and CO_2^- units of two ionic counterparts. The formation of molecular salts in aqueous media is in good agreement with the differences in the pK_a values (see ESI‡) of H_2SDC and the amines used for this study. The orientation of ionic counterparts in crystalline solids built on electrostatic interaction is less directional and hence imposes designing challenge as opposed to hydrogen bonds in co-crystals. In the salt with cyclohexylamine, SDC^{2-} anions are aligned parallel with a distance of 4.665 Å, which is over the Schmidt's distance limit and thus found to be photostable under UV light. Whereas in the case of DAP, the centre-to-centre distance of two SDC^{2-} anions aligned parallel is 3.715 Å and undergoes quantitative dimerization under UV light obeying Schmidt's topochemical postulates. Although, in the case DAB the SDC^{2-} anions are parallel, the crystal was found to be photostable as the olefinic double bonds of two parallel aligned SDC^{2-} anions are slip-stacked. In the series of linear primary diamines, only DAP was found to result the parallel alignment of SDC^{2-} anion that suggest the possibility of some correlation between the chain length of the diamine and the parallel orientation of the ionic counterparts in the solid state. One can rationalize our findings to the $n = 3$ rule for the intramolecular excimer formation in bichromophoric molecules linked by a short flexible chain.[19] Also, our result can be correlated with the enhancement of photocyclization of trimethylene dicinnamates.[20] In **5**, 2,2′-dithiobis (ethanammonium) cations are identified to adopt a rare finite helical shape (called 'helicate') which is stabilised by the weak interactions between sulfur and NH_3^+ units. The so called 'ladder-like' hydrogen-bonded motifs observed in **1**, **3** and **6** is prevalent in the literature.[21]

These results observed for **3** motivated us to find out another salt (**9**) of H_2SDC with 3,3′-dipropylamino amine [$H_2NCH_2CH_2CH_2N(H)CH_2CH_2CH_2NH_2$], where NH and NH_2 groups are separated by trimethylene chain. The salt of composition, $C_{60}H_{86}N_6O_{20}$§ undergoes 62% photodimarization upon irradiation under UV light for 40 h. Although we were unable to grow data collection quality single crystals, the result helps us to understand the relation between the chain length of the diamine and the parallel stacking of SDC^{2-} anion. An infinite arrangement of the SDC^{2-} anions is proposed to account for the partial solid-state photochemical activity. In the series of these salts we have studied the ammonium salt (**10**)§ (by reacting H_2SDC with NH_4OH) of the same carboxylate. To our disappointment we were unable to grow suitable single crystals of data collection quality. However, the salt was found to undergo 80% photodimerization after 50 h of irradiation under UV light. Although we do not have the solid state structure of this salt, the orientation of the SDC^{2-} anions can be predicted to be parallel.

For the purpose of aligning SDC^{2-} anions in parallel orientation we basically need two hydrogen atoms in the protonated amines. We see three hydrogen atoms available in the protonated form of the primary amines to form charge assisted hydrogen bonding. We therefore, have chosen piperizine as a secondary amine which can thus serve the purpose. Yet it is observed that C=C bonds in the SDC^{2-} anions are not in parallel alignment in the solid state structure of **8**. At this stage, it is thus a very formidable task to design or predict the solid state structure of organic salts where the robust and non-directional charge assisted hydrogen bonding predominant in the solid state architecture. More work should be carried out in order to understand whether these types of non-covalent interactions can be reliably employed to rationally design the molecular packing in the solid state.

Conclusions

In this contribution, we have analysed the crystals structure of a series of molecular salts of H_2SDC to exhibit interesting patterns and packing. The complex nature of the supramolecular synthons is due to the less directional nature of electrostatic interaction over predictable H-bonding interactions. SDC^{2-} can be aligned parallel with a distance suitable for [2 + 2] cycloaddition reaction in the molecular salt with 1,3-diaminopropane that leads to the synthesis of the dimer compound in quantitative yield. It appears that there must have some correlation between the orientation of SDC dianions and the chain length of the diamines in the series.

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