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A Persistent Preference for Layer Motifs in Self-Assemblies of Squarates and Hydrogen Squarates by Hydrogen Bonding [X−H···O; X = N, O, or C]: A Crystallographic Study of Five Organic Salts

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Abstract: The synthesis and single-crystal X-ray structures of hydrogen squarates of imidazole (**1**), histidine (**2**), and 2-aminopyridine (**4**) and squarates of histidine (**3**) and 4-aminopyridine (**5**) are reported. Both hydrogen squarate [HSQ]$^{1-}$ and squarate [SQ]$^{2-}$ ions participate in complementary hydrogen bonding [X−H···O; X = N, O, or C] networks. While the [HSQ]$^{1-}$ ion acts both as a donor and as an acceptor of hydrogen bonds in salts **1**, **2**, and **4** and creates head-to-tail infinite chains of anions in **1** and head-to-head ten-membered cyclic dimers in **4**, the [SQ]$^{2-}$ ion participates as a powerful acceptor of as many as six hydrogen bonds in **3** and **5**. In all cases, extensive hydrogen bonding and ionic interactions between the components lead to layered assemblies. In **1**, the cross-linking of the [HSQ]$^{1-}$ chains by protonated imidazolium ions through N−H···O bonds creates a two-dimensional ionic sheet which is further stabilized by the presence of C−H···O bonds resulting from the participation of the imidazolium C-H groups. In **2** and **3**, the layered structures are formed by cross-linking of the cationic self-assemblies (His-His infinite helices in **2** and His-His zigzag ribbons in **3**) by [HSQ]$^{1-}$ and [SQ]$^{2-}$, respectively. A novel feature in **3** is the presence of two C−H···O bonds between the more acidic CH group and the O1 in [SQ]$^{2-}$. In **4**, the cyclic dimers of [HSQ]$^{1-}$ are interwoven into a two-dimensional sheet with a checker-board motif by the participation of 2-aminopyridinium cation in horizontal and vertical N−H···O bonds. The two-dimensional layered assembly in **5** arises by extensive participation of water molecules in cross-linking of the alternating anion−cation conjugates both in horizontal and vertical directions. Irrespective of the presence of different types of hydrogen-bonding patterns in the structures of **1**−**5**, the persistent formation of a two-dimensional layered assembly is significant and may be a characteristic of squaric acid salts.

Introduction

Creation of specific structural assemblies in the solid state continues to be a theme of current interest[1] in the context of developing materials with enhanced optical, electrical or catalytic properties. Considerable progress has been made in recent years[2] in controlling the assembly and orientation of individual molecules to create specific two-dimensional or three-dimensional aggregates. Hydrogen bonding,[3−9] recognized as the most powerful force to organize molecules in the solid state is now emerging as an important strategy in crystal engineering.[10]

An attractive concept would be to use a combination of hydrogen bonding and ionic interactions in mutually compatible partners to engineer crystals, wherein, within a compact framework, maximum stabilization can be achieved. The strength of a hydrogen bond[11] between two neutral molecules normally lies in the range of 10−65 kJ mol^{-1}, but when one of the components is ionic, the range of hydrogen bond strength rises to 40−190 kJ mol^{-1}.

Squaric acid (SQ),[12] a very strong dibasic acid (pK_1 = 1.2−1.7; pK_2 = 3.2−3.5) with a four-atom-ring framework endowed with hydrogen bonding (donor as well as acceptor) and ionic organizational features, appeared particularly attractive as a template for generating tightly bound self-assemblies from polarizable cations in general and basic amino acids in particular. We envisaged that squaric acid which, by transfer of two protons can generate a squarate dianion [SQ]$^{2-}$, a rigid and truly

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(1) Hanessian, S.; Simard, M.; Roelens, S. *J. Am. Chem. Soc.* **1995**, *117*, 7630. Aakeroy, C. B.; Nieuwenhuyzen, M. J. *J. Am. Chem. Soc.* **1994**, *116*, 10983. Russel, V. A.; Etter, M. C.; Ward, M. D. *J. Am. Chem. Soc.* **1994**, *116*, 1941. Aakeroy, C. B.; Seddon, K. R. *Chem. Soc. Rev.* **1993**, *22*, 397. Mathias, J. P. Stoddart, J. F. *Chem. Soc. Rev.* **1992**, *21*, 215. Lehn, J.-M. *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1304. Desiraju, G. R. *Crystal Engineering: The Design of Organic Solids*; Elsevier: Amsterdam, 1989.

(2) For review see: MacDonald, J. C.; Whitesides, G. M. *Chem. Rev.* **1994**, *94*, 2383.

(3) Jeffrey, G. A.; Saenger, W. *Hydrogen Bonding in Biological Structures*, Springer-Verlag: Berlin, 1991.

(4) Chang, Y.-L.; West, M.-A.; Fowler, F. W.; Lauher, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 5991.

(5) Etter, M. C.; Reutzel, S. M. *J. Am. Chem. Soc.* **1991**, *113*, 2586.

(6) Simard, M.; Su, D.; Wuest, J. D. *J. Am. Chem. Soc.* **1991**, *113*, 1991.

(7) Etter, M. C. *Acc. Chem. Res.* **1990**, *23*, 120.

(8) Rebek, J., Jr. *Acc. Chem. Res.* **1990**, *23*, 399.

(9) Vaida, M.; Shimon, L. J. W.; VanMil, J.; Ernst-Labrera, K.; Addadi, L.; Leiserowitz, L.; Lahav, M. *J. Am. Chem. Soc.* **1989**, *111*, 1029.

(10) Reference 1 and: Di Salvo, F. J. *Science* **1990**, *247*, 649.

(11) Zeegers-Huyskens, Th.; Huyskens, P. In *Intramolecular Forces—An Introduction to Modern Methods and Results*; Huyskens, P. L., Luck, W. A. P., Zeegers-Huyskens, Th., Eds.; Springer-Verlag: Berlin, 1991; p. 1. Yamadagni, R.; Kebarle, P. *J. Am. Chem. Soc.* **1971**, *93*, 7139.

(12) For recent review see: Seitz, G.; Imming, P. *Chem. Rev.* **1992**, *92*, 1227. Squaric acid and structurally related or synthetically derived products from it have been investigated for the design of advanced materials, e.g., as xerogaphic photoreceptors, organic solar cells, and optical recording (Liebeskind, L. S.; Yu, M. S.; Yu, R. H.; Wang, J.; Hager, K. S. *J. Am. Chem. Soc.* **1993**, *115*, 9048 and references cited therein).

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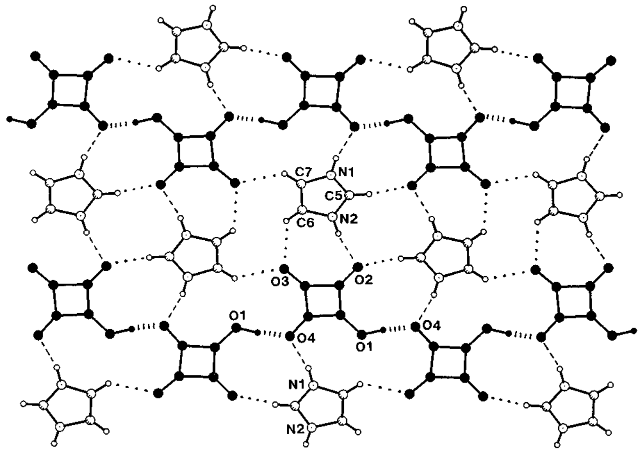

Figure 1. The two-dimensional hydrogen-bonded ionic sheet formed in salt **1**. Infinite parallel chains (horizontal) of $[HSQ]^{1-}$ anions (darkened) in Im:SQ, connected by OH···O hydrogen bonds (indicated by hash marks), are cross-linked by imidazolium cations with NH···O hydrogen bonds (indicated by dashes) and C−H···O hydrogen bonds (indicated by dots). All the available H-bond donors and acceptors have been utilized in the network.

delocalized planar aromatic dianion capable of acting as a powerful acceptor of hydrogen bonds, and by transfer of one proton a monohydrogen squarate $[HSQ]^{1-}$ which can act both as a donor as well as acceptor, would be an ideal scaffold for controlling the orientation and architecture of polarizable cations in self-assemblies by fine tuning its proton transfer[13] capabilities. The squarate dianion with a four-fold molecular topology was considered particularly suited for designing ordered two-dimensional hydrogen-bonded networks.

Discussion and Results

Initially, among the basic amino acids which can form polarizable cations, histidine (His) appeared particularly appealing as a squaric acid partner because of the presence of an imidazole ring in its side chain which can act both as a donor and as an acceptor of hydrogen bonds and has a crucial role as part of a charged relay network in the catalytic activity of numerous enzymes. Additionally, the positioning of proton donor and proton acceptor sites at almost opposite ends makes the imidazole unit ideally suited to act as a cross-linker.

In order to fully understand the role of the histidine side chain in the His:SQ assembly, the crystal structure of imidazolium hydrogen squarate (**1**) was examined first. The salt (**1**) was prepared by mixing equimolar amounts of imidazole and squaric acid in water. Slow evaporation gave **1** as colorless needles [mp 270 °C dec]. The crystal structure of **1**, as presented in Figure 1, showed that the hydrogen squarate anion in **1** creates parallel, infinite chains[14] formed by intermolecular OH···O hydrogen bonds. The protonated imidazolium cation possessing a rigid frame with hydrogen bond donors positioned at almost opposite ends of the frame provides cross-links for the adjacent horizontal chains of $[HSQ]^{1-}$ through two NH···O bonds forming the expected two-dimensional hydrogen-bonded sheet.

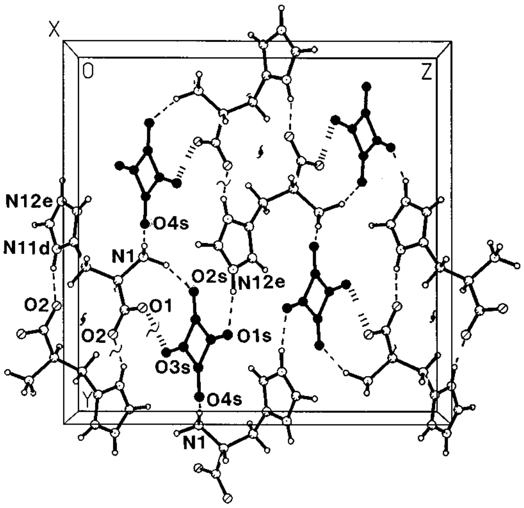

Figure 2. The hydrogen-bonded ionic assembly in 1:1 salt (**2**). The histidine cations are connected into continuous two-fold helices (perpendicular to the sheet) by N(11d)H···O2 hydrogen bonds (indicated by dashes). The $[HSQ]^{1-}$ ions lie between the His^{+} helices. Each $[HSQ]^{1-}$ forms four NH···O and one OH···O hydrogen bonds to five neighboring His^{+} cations.

A noteworthy feature of this assembly is the presence of a collection of C−H···O hydrogen bonds between Im^{+} and $[HSQ]^{1-}$ ions which are very well accommodated within the framework of stronger O−H···O and N−H···O interactions and further stabilize the sheet motif.[15] Each Im^{+} ion participates in three C−H···O bonds with three different $[HSQ]^{1-}$ ions. The more acidic C5H (Figure 1) interacts with O2 (C···O, 3.14 Å) of one $[HSQ]^{1-}$ ion while the less acidic aromatic protons, C6H and C7H (Figure 1), are each hydrogen bonded to O3 (C···O, 3.23 Å each) of different $[HSQ]^{1-}$ ions. The resulting compact and tightly interwoven ionic sheet in **1** involves the participation of all the available donors and acceptors in the O−H···O, N−H···O and C−H···O hydrogen-bonded network.

Squaric acid when mixed with histidine in a molar ratio of 1 and 0.5, respectively, afforded two salts, histidinium hydrogen squarate (**2**) and dihistidinium squarate (**3**), whose mp, IR, and UV behavior were very different from each other and from that of the individual components. While the 1:1 salt crystallized in small needles, the 2:1 salt was obtained as beautiful large plates (1.5−2 cm in length).

Crystal structures of **2** [mp 225−230 °C dec; λ_{max} (solid) 280, 320 nm] and **3** [mp 250−255 °C dec; λ_{max} (solid) 289, 339 nm] as presented in Figures 2 and 3, respectively, clearly bring out the role of histidine side chains in controlling the self-assembly. In contrast to **1** (Figure 1) in which the imidazolium cations provided cross-links between the adjacent $[HSQ]^{1-}$ chains, in **2** and **3**, the squarate anion (monovalent in **2** and divalent in **3)** acts as a cross-linker for the histidine assemblies (His-His infinite helices with a two-fold screw axis in **2** (Figure 2) and His-His infinite zigzag ribbons in **3** (Figure 3).

As can be seen in Figures 2 and 3, the self-assembly patterns of histidine molecules (present as zwitterionic species with a net charge of +1 on the imidazole ring) in the two salts are very different. While the amino acid molecules in 1:1 salt **2** arrange themselves in infinite helices around a two-fold screw axis, by connecting through N−H···O hydrogen bonds involving $N^{\delta}H$ and carboxylate O2 (Figure 2), the histidine molecules are

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(13) Proton-transfer triggered self-assembly of 4,4′-bipyridine with squaric acid has recently been reported (Reetz, M. T.; Hoger, S.; Harris, K. *Angew Chem., Int. Ed. Engl.* **1994**, *33*, 181).

(14) Monovalent anions of dicarboxylates have a pronounced tendency to form infinite chains via O−H···O bonds. Such anionic chains have recently been used to create 2-D ionic layers in the case of hydrogen malate anions (Aakeroy, C. B.; Nieuwenhuyzen, M. J. *J. Am. Chem. Soc.* **1994**, *116*, 10983).

(15) A similar structure for methylimidazolium hydrogen tartrate has recently been reported (Fuller, J. *Acta Crystallogr.* **1995**, *C51*, 1680) wherein methyl imidazolium cation provides cross-links for hydrogen-bonded infinite chains of hydrogen tartrate anions. See also: Aakeroy, C. B.; Hitchcock, P. B. *J. Mater. Chem.* **1993**, *3*, 1129.

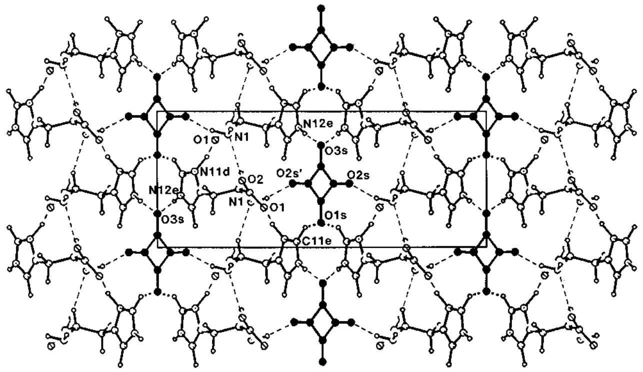

Figure 3. The hydrogen-bonded ionic assembly in 2:1 salt **3**. The histidine cations form vertical parallel zigzag ribbons by hydrogen bonds N(1)H(1)···O(2) and N(11d)H···O(1). Histidine cations in a ribbon are related by a two-fold screw axis. The $[SQ]^{2-}$ ions are placed in voids between the ribbons. Each $[SQ]^{2-}$ ion is bonded to six histidine molecules through four NH···O hydrogen bonds and two CH···O bonds (indicated by dots). The C11e···O1s and H···O1s distances are 2.97(1) and 2.06(1) Å, respectively.

Table 1. Geometrical Parameters for N−H···O, O−H···O, and Possible C−H···O Hydrogen Bonds Observed in the Crystal Lattices of Salts **1**, **2**, **3**, **4**, and **5**

salt	H-bond[a]	D···A (Å)	H···A (Å)	angle DH···A (deg)
1	N1···O4s	2.789(3)	1.91(3)	167
	N2···O2s	2.774(3)	1.88(3)	168
	O1s···O4s	2.551(3)	1.52(3)	174
	C5···O2s	3.146(3)	2.40(2)	144
	C6···O3s	3.230(3)	2.56(2)	131
	C7···O3s	3.239(3)	2.49(2)	140
2	N1···O4s	2.812(7)	1.78(7)	170
	N1···O4s	2.941(7)	2.07(7)	167
	N1···O2s	2.757(7)	1.84(5)	146
	N11d···O2 (ring)	2.644(7)	1.78(6)	165
	N12e···O1s (ring)	2.768(7)	1.87(6)	157
	O3s···O1	2.510(7)	*b*	
3	N1···O2	2.891(7)	2.01(5)	169
	N1···O2s	2.700(7)	1.75(5)	165
	N1···O2	2.884(7)	2.05*	154*
	N11d···O1 (ring)	2.716(10)	1.79(13)	134
	N12e···O3s (ring)	2.711(11)	1.83(5)	171
	C11e···O1s	2.973(11)	2.06(11)	136
4	N1..O2s	2.741(3)	1.72(3)	164
	N2..O1s	2.886(3)	1.95(3)	173
	N2..O2s	2.938(3)	2.03(3)	170
	O4s..O3s	2.514(3)	1.53(3)	162
5	N1..O1s	3.023(11)	2.00(7)	154
	N2..W1	2.935(12)	1.95(7)	170
	N2..W2	2.978(12)	2.22(7)	150
	W1..O1s	2.710(12)	*b*	
	W2..O2s	2.756(12)	1.82(8)	177

[a] s refers to squaric acid atoms; D and A refer to donor and acceptor atoms, respectively. [b] Hydrogen atoms not found experimentally.

organized into hydrogen-bonded, infinite zigzag ribbons centered around a 2_1 screw axis parallel to b in 2:1 salt **3** as shown in Figure 3. Each ribbon is stabilized by a pair of hydrogen bonds, one involving the amino nitrogen to carboxylate, N(1)···O(2), and the other between N^{δ} and carboxylate (O1), and their symmetry equivalents. Table 1 presents the hydrogen bond parameters in **1**−**5**.

From Figures 2 and 3 it appears that the two different histidine assemblies create voids in which squarate ions are contained. The squarate ions interact with the surrounding histidine ions by multiple hydrogen bonds, five hydrogen bonds with histidines which form part of three different helices in the 1:1 salt (Figure 2) and six hydrogen bonds with six histidines in adjacent zigzag ribbons in the 2:1 salt (Figure 3). A novel feature in the dihistidinium squarate assembly is the presence of two C−H···O bonds (C···O, 2.97 Å each) formed between the bifurcated O1s of the $[SQ]^{2-}$ ion and C11e atoms (Im^+ ring). Although realized as early as 1962[16a] that an activated C−H group as present in some heterocyclic bases, for example, caffeine, theophylline, uric acid and related compounds, tends to interact with oxygen atoms in the same way as an O−H or N−H group and the short (<3.4 Å) C···O contacts observed in the crystals of these molecules were interpreted as C-H···O hydrogen bonds, it was not until 1982[16b] that the existence of C−H···O hydrogen bonds in organic molecules was convincingly demonstrated and C−H···O bonds started gaining acceptance as a stabilizing force when adjusted within the framework of stronger forces such as N−H···O, O−H···O hydrogen bonds and donor-acceptance interactions.[16c] In ionic compounds reported here, the more acidic C−H group directly attached to two nitrogen atoms in the imidazolium ring is the most likely candidate for C−H···O bonding as demonstrated in the structure of **1** and **3**. In **1**, the less acidic aromatic C−H groups also appear to participate in C−H···O bonding. We believe that squaric acid anions because of the presence of a high ratio of hydrogen bond acceptors to hydrogen bond donors would, in general, show a strong tendency to form C−H···O bonds with acidic C−H groups wherever the situation permits.

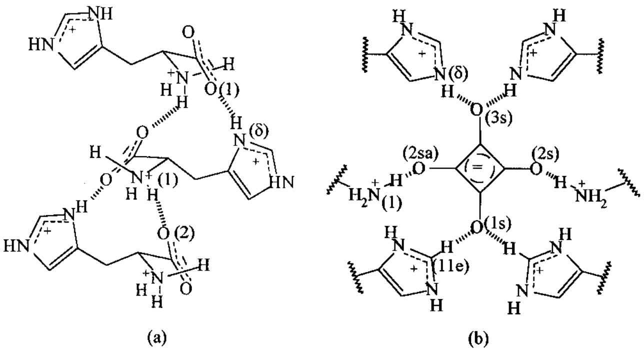

Figure 4. Schematic representation of (a) His-His hydrogen bonding in the ribbon assembly of **3**. Each molecule is bonded to two neighbors making two hydrogen bonds to each through N^{δ} and O1 atoms to one histidine and N1 and O2 atoms to the other molecule. (b) SQ^{2-}-His hydrogen bonding in **3**. Each $[SQ]^{2-}$ ion is bonded to six histidine molecules accepting a total of six hydrogen bonds. While O2s and its symmetry equivalent O2sa are each bonded to N1 of opposite His molecules, the O3s and O1s atoms each accept two hydrogen bonds from two N^{δ} atoms and two C11e atoms, respectively, of opposite His molecules.

A schematic representation of His-His and His-SQ hydrogen bonding in **3** is shown in Figure 4.

It is interesting to note that the central feature of the head-to-tail sequence of Z2 type observed in the aggregation of amino acid molecules in L-histidine[17] crystals is preserved in the ribbon assembly of dihistidinium squarate. A similar type of head-to-tail sequence is observed in the aggregation of histidine molecules in L-histidine semisuccinate trihydrate[18a] and L-histidine acetate.[18b] However, there is no similarity of any kind between the arrangement of histidine molecules in a free amino

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(16) (a) Sutor, D. J. *Nature* **1962**, *68*, 195. Sutor, D. J. *J. Chem. Soc.* **1963**, 1105. (b) Taylor, R.; Kennard, O. *J. Am. Chem. Soc.* **1982**, *33*, 5063. (c) For a review on C−H···O bonds see: Desiraju, G. *Acc. Chem. Res.* **1991**, *24*, 290.

(17) Madden, J. J.; McGandy, E. L.; Seeman, N. C.; Harding, M. M.; Hoy, A. *Acta Crystallogr.* **1972**, *28*, 2382. Madden, J. J.; McGandy, E. L.; Seeman, N. C. *Acta Crystallogr.* **1972**, *28*, 2377. Suresh, C. G.; Vijayan, M. *Int. J. Peptide Protein Res.* **1983**, *22*, 129.

(18) (a) Prasad, C. G.; Vijayan, M. *Biopolymers* **1993**, *33*, 383. (b) Suresh, S.; Prasad, G. S.; Vijayan, M. *Int. J. Peptide Protein Res.* **1994**, *43*, 139.

Table 2. Comparison of Torsional Angles (deg) in L-Histidine Residue in Squaric Acid Salts **2** and **3**[a] with Uncomplexed L-Histidine Amino Acid

	uncomplexed L-histidine[17]	2	3
O1C1′C1AN1	−28	−26	−11
O2C1′C1AN1	154	154	173
O1C1′C1AC1B	94	96	112
O2C1′C1AC1B	−84	−84	−64
N1C1AC1BC1G	-57	−70	−58
C1′C1AC1BC1G	181	168	179
C1AC1BC1GC12D	−128	91	110
C1AC1BC1GN11D	53	−88	−73

[a] Esd's for torsional angle values for **2** and **3** are all less than 1°. The angle values have been rounded off to the nearest whole number.

acid crystal and the histidinium hydrogen squarate which shows His molecules assembled in infinite helices with two-fold screw repetition.

A comparison of torsional angles of the histidine residue in squaric acid salts **2** and **3** with the uncomplexed histidine amino acid is presented in Table 2. The torsional angles of the L-histidine residue in **2** and **3** are quite similar to each other and for the first six values listed for the free base. The difference occurs in the orientation of the imidazolium ring with respect to the linear portion of the molecule. In the free base there is a rotation of approximately −130° about the C1B−C1G bond so that the ring is nearly flipped over as compared to **2** and **3**. This rotation brings N^{δ} in the ring to the same side as the amino N1 and makes possible an intramolecular hydrogen bond between N1 and N12D. In the salts, the N^{δ} and N^{ϵ} moieties in the imidazolium ring are engaged in strong external hydrogen bonds. Histidine salts **2** and **3** show SHG (second harmonic generation) activity in ∼18% efficiency, relative to urea as the standard.[19]

In an attempt to extend the scope of such phenomenon and to further demonstrate the persistent formation of layer motifs in proton transfer triggered assemblies of squaric acid, we examined the pyridinium salts of squaric acid. The 2-aminopyridine (2-AP) and 4-aminopyridine (4-AP) were chosen particularly because of the anticipation that the ionic conjugate initially formed by a proton transfer from SQ to the basic nitrogen of aminopyridine unit would be further stabilized by participation of the $-NH_2$ group in N−H···O hydrogen bonding that may lead to tightly bound layer assemblies as observed in histidine salts. This expectation was fully realized in the crystal structures of 2-aminopyridinium hydrogen squarate (**4**) and bis(4-aminopyridinium) squarate (**5**).

Equimolar amounts of SQ and 2-AP afforded a crystalline salt **4** from water as golden yellow needles which, during melting, changed to a brilliant red color at 215 °C and melted with decomposition at 320 °C. 2-Aminopyridinium (**4**) forms a well-defined and extremely ordered supramolecular self-assembly through a network of hydrogen bonds into a two-dimensional sheet as shown in the crystal structure (Figure 5).

A novel feature of the assembly in the crystal of **4** is the organization of four-molecule modules formed by flanking of a $[HSQ]^{1-}$ dimer by two 2-aminopyridinium ions into an infinite hydrogen-bonded layer with a checkerboard motif through a network of N−H···O bonds. Another interesting feature of the assembly is the presence of a ten-membered $[HSQ]^{1-}-[HSQ]^{1-}$ head-to-head hydrogen-bonded dimer formed through a pair of O−H···O bonds (O···O, 2.514(3) Å, Table 1) as part of the four-molecule module, which is reminiscent of a typical head-to-head cyclic dimeric motif of a monocarboxylic acid assembly. This feature of an $[HSQ]^{1-}$ assembly supports the notion that squaric acid can be regarded to harbor an expanded carboxylate moiety. It is interesting to note that all the available hydrogen bond donors and acceptors in **4** are engaged in a fully hydrogen-bonded supramolecular structure. The hydrogen bond parameters in **4** are presented in Table 1.

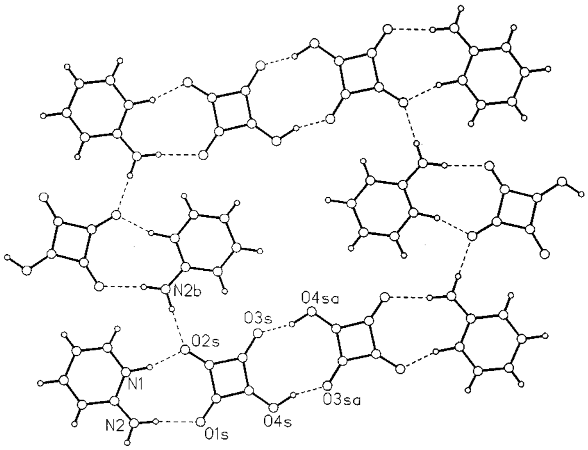

Figure 5. Two-dimensional sheet with a checkerboard motif formed in the crystal structure of **4** by the organization of four-molecule modules. The module can be considered as a head-to-head dimer of a 2-aminopyridinium hydrogen squarate unit connected through two O−H···O bonds. The ten-membered hydrogen bonded ring resulting from $[HSQ]^{1-}$-$[HSQ]^{1-}$ linking is reminiscent of a typical head-to-head cyclic motif of a monocarboxylic acid. The 2-aminopyridinium hydrogen squarate forms a nine-membered ring through a pair of NH···O bonds. The horizontal rows of four-molecule modules are interlinked by vertical N−H···O hydrogen bonds, resulting in an infinite sheet. All the available hydrogen bond donors and acceptors in **4** are engaged in the sheet assembly.

The next choice was to examine the SQ salt of 4-aminopyridine which would clearly bring out the consequences of the distal placement of the amino group on the AP:SQ assembly. Bis(4-aminopyridinium) squarate (**5**) prepared by mixing 4-AP and SQ in 2:1 molar proportion in water and obtained as pale yellow needles showed during heating a color change to bright yellow at 205 °C, finally melting at 207−210 °C.

The crystal structure of **5** as presented in Figure 6 clearly brings out the control of the amino group on the self-assembly arising from the different placement of this unit in the pyridine framework. The supramolecular structure is formed by assembling a three-molecule module formed by flanking of a squarate dianion by two 4-aminopyridinium ions, in horizontal chains with the help of water molecules which further cross-link the horizontal chains to make two-dimensional sheets. Each squarate ion in the chain participates in six hydrogen bonds. Four of the hydrogen bonds are acceptors from four water molecules, the other two hydrogen bonds are acceptors from the pairs of 4-AP molecules on either side of the squarate ion. A novel feature of the layer assembly is the presence of eight-membered hydrogen-bonded rings arising from the intermolecular cross-linking of two head-to-head oriented 4-AP units with water molecules through four N−H···O bonds.

A consequence of water mediated cross-linking of horizontal chains in the layer motif of **5** is the emergence of a three-dimensional structure. Each water molecule participates in four hydrogen bonds in an approximately tetrahedral array connecting

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(19) The SHG intensity was measured (powder method) by detection with a photomultiplier of 532 nm light generated from powder materials. Samples were held between two glass plates and set in an optical sphere. They were irradiated with a pulsed Nd:YAG laser at 1064 nm (11 ns, 400 mJ/pulse).

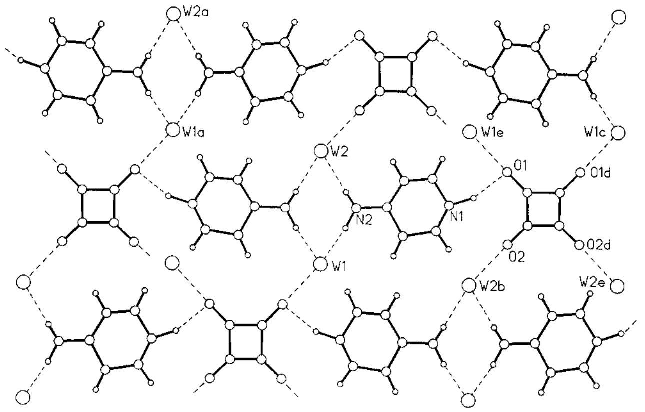
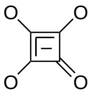
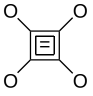


Figure 6. The two-dimensional sheet assembly in the crystal structure of **5** formed by cross-linking of horizontal chains of bis(4-aminopyridinium) squarate modules by intervening water (W) molecules through vertical O−H···O hydrogen bonds. Each $[SQ]^{2-}$ dianion in the assembly makes six hydrogen bonds. Four of these are acceptors from H_2O molecules and the remaining two are acceptors from the pair of 4-AP molecules on either side of the squarate. Within the horizontal chain, the bis(4-aminopyridinium) squarate modules are linked through two H_2O molecules making eight-membered N−H···O hydrogen-bonded rings. Each water molecule makes four bonds in a tetrahedral array. The fourth hydrogen bond (not shown here) connects the planar layers (3.4 Å apart) in a third dimension. All the available hydrogen bond donors and acceptors are fully utilized in the hydrogen-bonded network.

the 2-D layers into a 3-D layered structure wherein the interlayer separation is 3.4 Å. The hydrogen-bonding parameters are presented in Table 1. Based on hydrogen-bonding parameters (Table 1) and atomic distances and bond angles observed within the $[HSQ]^{1-}$ and $[SQ]^{2-}$ anions (Figure 7) in salts **1**−**5**, the $[HSQ]^{1-}$ in **1**, **2**, and **4** and $[SQ]^{2-}$ in **3** and **5** may be represented as in **i** and **ii** respectively as shown below.


i


ii

Conclusion

The present study has identified squaric acid as a promising scaffold for the design of tightly interwoven and highly compact self-assemblies formed by a combination of complementary hydrogen bonding (N−H···O, O−H···O and C−H···O) and ionic interactions with suitable polarizable cations as compatible partners. Both $[HSQ]^{1-}$ and $[SQ]^{2-}$ ions have been demonstrated to participate in the extensive hydrogen-bonding network. While $[HSQ]^{1-}$ acts both as a donor as well as an acceptor, the $[SQ]^{2-}$ participates only as an acceptor and is bonded to as many as six hydrogen donors in salts **3** and **5**. Both $[HSQ]^{1-}$ and $[SQ]^{2-}$ ions, because of the presence of a high ratio of hydrogen bond acceptors to hydrogen bond donors in their molecular framework, participate in C−H···O hydrogen bonding as shown in the crystal structures of **1** and **3**. The persistent formation of a two-dimensional layer motif in the squarate self-assemblies shown here may have significance in the design of molecular materials. A detailed study of squaric acid salts of basic amino acids is in progress in our laboratories.

Experimental Section

All starting materials were purchased from the Aldrich Chemical Co. and used as such. Infrared spectra were recorded on a Perkin-Elmer, Model 882, spectrometer as KBr pellets. Photoacoustic spectra were recorded in an EG&G Princeton Applied Research Model 6001 instrument at CCMB Hyderabad. All PA measurements were done using a modulation frequency of 40 Hz. Melting points are uncorrected.

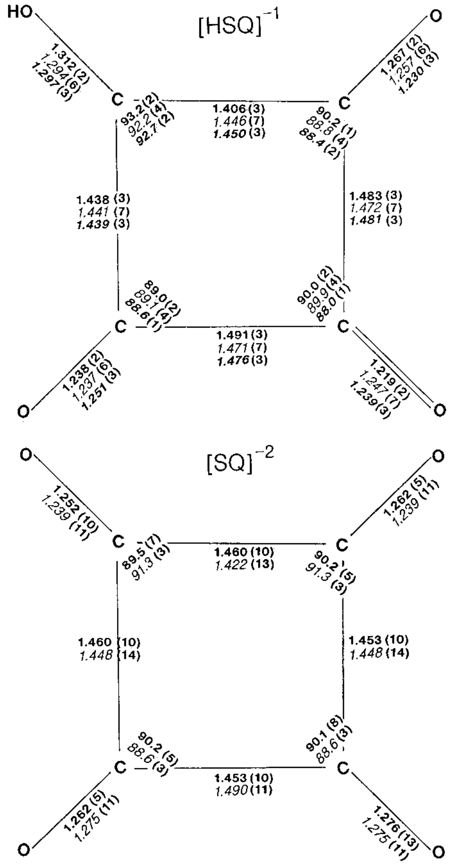


Figure 7. Bond lengths and angles in the $[HSQ]^{1-}$ and $[SQ]^{2-}$ ions. The crystal data has been grouped to correspond to the same bond in **1**, **2**, and **4** in $[HSQ]^{1-}$ and **3** and **5** in $[SQ]^{2-}$. The $[SQ]^{2-}$ ions have been observed to lie on a 2-fold rotation axis that passes between C−C atoms in **5** and through diagonally placed C atoms in **3**.

Preparation of Squaric Salts. In a typical procedure, squaric acid and the complement (imidazole, L-histidine, 2-aminopyridine, or 4-aminopyridine) were separately dissolved in hot water and mixed in a molar proportion of 1:1, 1:2, and 2:1, respectively. The mixture was allowed to crystallize slowly at room temperature and crystals were removed from solution as soon as they were formed and before complete evaporation of the solvent.

Selected Spectral Data. 1: IR (KBr) 3158, 3002, 2854, 2811, 1664, 1604, 1562, 1443, 1381, 1053, cm^{-1}. **2**: IR (KBr) 3176, 3099, 2932, 2881, 1802, 1645, 1632, 1597, 1529, 1494, 1470, 1399, 1326, 1245, 1152, 1095 cm^{-1}. **3**: IR (KBr) 3125, 3008, 2933, 2864, 2654, 1642, 1594, 1547, 1491, 1449, 1400, 1355, 1254, 1085 cm^{-1}. **4**: IR (KBr) 3314, 3093, 2711, 2360, 1814, 1690, 1646, 1586, 1522, 1489, 1439, 1390, 1334, 1247, 1165, 1089, 989, 924, 763, 724, 621 cm^{-1}; ^{1}H NMR (90 MHz, DMSO-d_6) δ 6.83 (1H, m), 7.83 (1H, m), 8.67 (2H brs); ^{13}C NMR (DMSO-d_6) δ 195.7, 154.1, 143.5, 136.1, 113.3, 119.1. **5**: IR (KBr) 3212, 2646, 2351, 2197, 1655, 1542, 1522, 1473, 1419, 1249, 1192, 1086, 1021, 827 cm^{-1}.

X-ray Structure Analysis. 1: $C_3H_4N_2{\cdot}C_4H_2O_4$, $P2_1/c$, $a = 9.3977(4)$ Å, $b = 11.0061(5)$ Å, $c = 7.5737(4)$ Å, $\beta = 100.20(1)°$, $V = 770.97(7)$ Å^3, $d = 1.569$ g/cm^3, $R = 0.044$. **2**: $C_6H_9N_3O_2{\cdot}C_4H_2O_4$, $P2_12_12_1$, $a = 4.936(1)$ Å, $b = 14.923(4)$ Å, $c = 15.068(3)$ Å, $V = 1109.9(5)$ Å^3, $d = 1.611$ g/cm^3, $R = 0.053$. **3**: $2C_6H_9N_3O_2{\cdot}C_4H_2O_4$, $C2$, $a = 19.282(3)$ Å, $b = 8.105(2)$ Å, $c = 5.888(1)$ Å, $\beta = 91.13(2)°$, $V = 920.9(3)$ Å^3, $d = 1.532$ g/cm^3, $R = 0.038$. **4**: $C_5H_6N_2{\cdot}C_4H_2O_4$, $P2_1/c$, $a = 3.722(1)$ Å, $b = 11.640(5)$ Å, $c = 20.973(7)$ Å, $\beta = 93.89(3)°$, $V = 906.5(5)$ Å^3, $d = 1.525$ g/cm^3, $R = 0.050$. **5**: $2C_5H_6N_2{\cdot}C_4H_2O_4{\cdot}2H_2O$, $C2$, $a = 10.557(2)$ Å, $b = 11.542(2)$ Å, $c = 6.545(1)$ Å, $\beta = 103.78(1)°$, $V = 774.5(2)$ Å, $d = 1.442$ g/cm^3, $R = 0.039$.

Parameters for all hydrogen atoms were refined isotropically except for one on the NH_3^+ group in **2**, one on the $[HSQ]^{1-}$ ion in **3**, and one on W1 in **5**.

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Supporting Information Available: Structural details, including coordinates, bond lengths, bond angles, anisotropic thermal parameters, and coordinates of hydrogen atoms for crystals **1** to **5** (32 pages). See any current masthead page for ordering and Internet access instructions.

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