Molecular tectonics VIII: formation of 1D and 3D networks based on the simultaneous use of hydrogen bonding and ionic interactions†‡

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Using a combination of directional hydrogen bonding and ionic interactions, 1- and 3D molecular networks were obtained in the crystalline phase. It has been shown that a bisamidinium dication and dicarboxylate mono or dianions form one and two dimensional networks in the solid state. The formation of networks was based on a dihapto mode of hydrogen bonding between the complementary dication and dianion.

Tectonique moleculaire VIII: utilisation simultanée de liaisons hydrogène et interactions ioniques conduisant à la formation de réseaux moléculaires mono- et tridimensionnels à l'état cristallin. L'utilisation simultanée de liaisons hydrogène et d'interactions électrostatiques charge–charge a été mise à profit pour former des réseaux moléculaires uni- et bidimensionnels à l'état cristallin. Un dérivé dicationique de type bisamidinium capable de donner quatre liaisons hydrogène s'associe avec des mono- et dicarboxylates pour former des réseaux moléculaires à l'état solide. Les réseaux 1- et 3D ainsi obtenus peuvent être décrits comme la translation selon une ou trois directions de noeuds d'assemblage formé par un processus de reconnaissance moléculaire entre les donneurs et accepteurs de liaisons hydrogène.

In the solid state, molecular crystals are defined by the chemical nature of their molecular components and by their interactions with respect to each other. Whereas molecular chemistry deals with the design and the synthesis of the individual units, their assembly is governed by the concepts of supramolecular chemistry.[1]

In marked contrast with discrete molecules, molecular networks in the solid state are defined as chemical entities for which specific interaction patterns or assembling cores are repeated with a translational symmetry. The dimensionality of a molecular network depends on the number of translations operating at the level of the assembling cores. Thus, 1D or α-networks are formed when a single translation takes place. Similarly, β- (2D) and γ-networks (3D) are defined when two or three translations, respectively, of the same or different assembling cores are present (Fig. 1).[2]

In the past decade the design and formation of molecular networks in the solid state has been a subject of current interest and challenge.[3] Inherent to our limited knowledge of all subtle intermolecular interactions governing the crystalline phases, the complete understanding of crystal formation appears to be currently unreachable.[4] However, with our present ability to master some of the intermolecular interactions, one may design, using proper molecular construction units or tectons,[5] molecular networks with predicted structures.[6]

A possible strategy for the construction of molecular networks in the crystalline phase may be the self-assembly[7] of either a self-complementary or several complementary tectons (Fig. 2). Although a mono-component system composed of a self-complementary tecton (a tecton bearing properly localized and oriented complementary interaction sites) would be con-

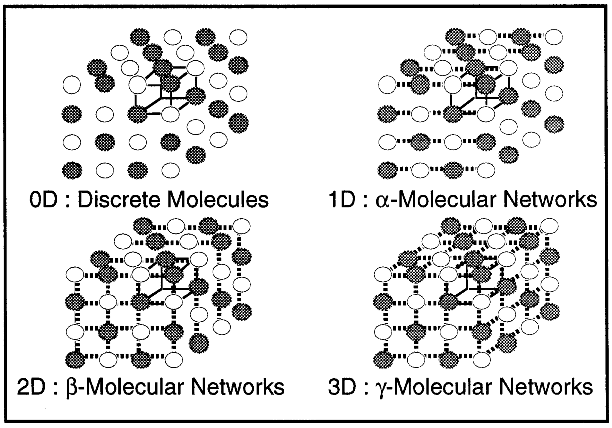

Fig. 1 Schematic representation of discrete molecules and molecular networks in the crystalline phase. The dimensionality of the network depends upon the number of translations of assembling cores, which may be defined as specific interaction motifs between modules defining the solid

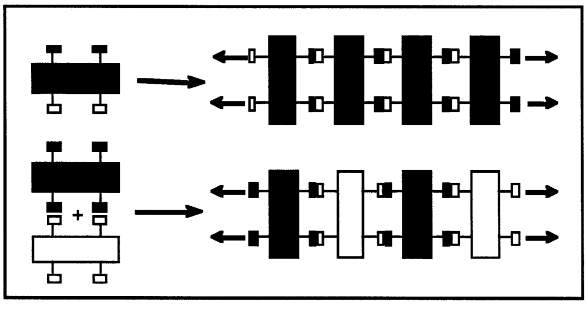

Fig. 2 Schematic representation of a 1D network formed by a single translation of an assembling core based on a dihapto mode of recognition. The 1D network may be formed by a self-complementary tecton (top) or by two complementary tectons (bottom)

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† This contribution is dedicated to the memory of Jean Rouxel.
‡ Part VII is reference 26.

sidered as the simplest situation, in practice such a system often produces insoluble powders difficult to study. A more viable strategy would be to use a two-component system composed of two complementary building blocks. In such a system, one may control a larger number of parameters such as concentration, the speed of mixing, *etc.*

The formation of molecular networks may be directed by the control and iteration of molecular recognition processes. When designing molecular networks one must take into account two types of geometrical features at the level of the tectons. One deals with the localization, within each of the two tectons, of compatible interaction sites leading to the assembling core and the other deals with the repetition of the assembling core.

All of the knowledge dealing with the understanding and control of weak intermolecular forces accumulated in the area of molecular recognition over the past thirty years may be used in the design of molecular networks. Since by definition molecular networks are based on the translation of the molecular recognition pattern, instead of using *endo*-receptors leading to discrete *endo*-molecular complexes, one should use *exo*-receptors in which the interaction sites are oriented in a divergent fashion. We have reported *exo*-receptors based on amidines,[8] macrocyclic bipyridines,[9] calixarenes[10,11] and porphyrins.[12]

The vast majority of molecular networks reported so far are based either on hydrogen bonding[13] or on coordination bonds.[14] Recently, we have demonstrated that inclusion processes based on van der Waals interactions may also be used as construction principles in the solid state for the construction of molecular networks.[15]

When dealing with hydrogen bonding using a monohapto (DH···A) mode of bonding, that is, a single hydrogen bond between a donor (D) and an acceptor (A), the overall topology of the molecular networks seems to be difficult to predict, due to the large angular (DHA) distribution.[16] However, by severely restricting the possibility space through use of a di- or trihapto mode of H-bonding, one may control and thus predict the connectivity pattern between components in molecular networks. This principle is widely used in nature. Indeed, the dihapto mode of interactions between amino acids such as arginine and aspartate residues in proteins or the di- and trihapto modes of H-bonding between nucleic acids in DNA and RNA are common features.

The majority of reported molecular networks are based on hydrogen bonding using nonionic components.[13] Only a few hydrogen-bonded molecular networks based on ionic interactions have been reported.[17] We have previously reported the formation of hydrogen-bonded 1- and 2D networks using strong charge–charge electrostatic interactions combined with the directional dihapto mode of H-bonding between dicationic units and dianionic units.[18–22]

Bis cyclic amidine **1**[23] is an interesting tecton for the crystal engineering of molecular networks in the solid state. Indeed, due to the conjugated nature of the amidine group, its diprotonated (**1**-2H$^+$) form possesses four acidic N—H protons pointing outward and thus capable of donating four hydrogen bonds. In the crystalline phase 1D and 2D molecular networks using the dicationic form of **1**-2H$^+$ and various mono- and dianionic carboxylate derivatives acting as hydrogen bond acceptors have been previously reported by us.[18–22] In particular, using a 1:1 ratio of **1**-2H$^+$ and isophthalate **2**$^{2-}$, a 1D network formed by interconnection through H bonds of the dianionic and dicationic tectons was obtained.[18] While keeping the isophthalic framework, in order to study the role of substituents on the aromatic ring, the formation of molecular networks in the presence of **1**-2H$^+$ was investigated by X-ray crystallography on mono crystals. The two analogues of isophthalic acids used were nitroisophthalic acid **3** and dinicotinic acid **4**. Furthermore, the effect of the ratio of the cation and the anion on the nature of the network was studied using the monocarboxylate derivative **3**$^-$.

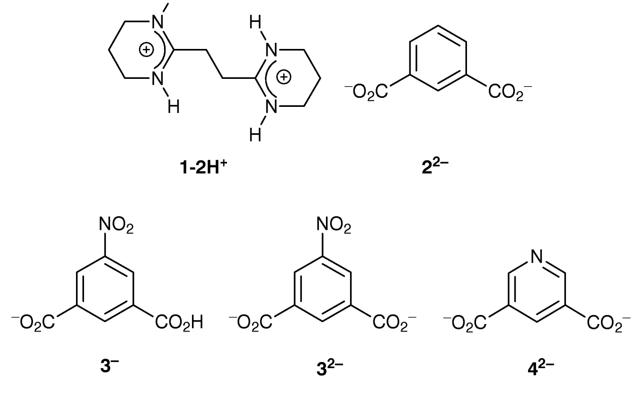
In the present contribution we describe the formation of 1- and 3D molecular networks formed between the complementary anionic units **3**$^{2-}$ and **4**$^{2-}$ and the dicationic module **1**-2H$^+$.

Results

Due to the large difference in the pK_b values between the free bisamidine **1** and the dicarboxylates **3**$^{2-}$ and **4**$^{2-}$, the mixing of the free base **1** with the diacids **3**-2H$^+$ or **4**-2H$^+$ in an EtOH–H$_2$O mixture leads exclusively, by an acid-base reaction, to the formation of (**1**-2H$^+$, **3**$^{2-}$) and (**1**-2H$^+$, **4**$^{2-}$) salts. The formation of hydrogen-bonded molecular networks engaging the dication **1**-2H$^+$ and the dicarboxylate **3**$^{2-}$ or **4**$^{2-}$ was investigated by X-ray diffraction methods on single crystals.

In the case of **1**-2H$^+$ (as the tetra H bond donor) and **3**$^{2-}$ (as the tetra H bond acceptor), as predicted and observed for the (**1**-2H$^+$, **2**$^{2-}$) salt,[18] the study revealed the formation of a 1D network in the solid state indicating that the nitro group does not prevent its formation. The (**1**-2H$^+$, **3**$^{2-}$) salt forms infinite linear chains exclusively composed of **1**-2H$^+$ dications and **3**$^{2-}$ dianions interconnected through hydrogen bonds and arranged in an alternating manner (Fig. 3). The (**1**-2H$^+$, **3**$^{2-}$) salt crystallizes also in the monoclinic crystal system with $C2/c$ as the space group. The unit cell is composed of **1**-2H$^+$ and **3**$^{2-}$. The X-ray analysis showed the following features: (1) all four acidic protons are localized on **1**-2H$^+$; (2) in each NCN fragment, the average C—N distance is 1.31 Å and the average N—C—N angle is 121.8°; (3) the ethylene chain connecting the two cyclic amidinium moieties is in a *trans* extended conformation; (4) both six-membered cycles adopt a half-chair conformation; (5) the two NCN planes of the two amidinium moieties are almost parallel but not coplanar; (6) for the dianionic fragment, the two carboxylate moieties are almost coplanar with slight tilt angles of $-1.4°$ and $-2.7°$ with respect to their connecting phenyl ring; (7) the nitro group is tilted by 4.7° with respect to the aromatic ring; (8) the shortest distance between the oxygen atom of the nitro group and one of the carbon atoms of the amidinium unit belonging to the next 1D network is 3.20 Å; (9) a dihapto mode of interaction between the dication and the dicarboxylate anion with strong H bonds is observed. The average N···O distance of 2.71 Å and the average NHO angle of *ca.* 169.8° clearly demonstrate the strong nature of the hydrogen bonding pattern.

It is worth noting that the diacid **3** forms also a 1D network (Fig. 4) in the crystalline phase through a dihapto mode of hydrogen bonding.[24] The formation of the 1D network between **1**-2H$^+$ and **3**$^{2-}$ may regarded as the substitution of two protons by the dicationic unit **1**-2H$^+$. Consequently, whereas in the case of the diacid **3**, the network is formed



Scheme 1

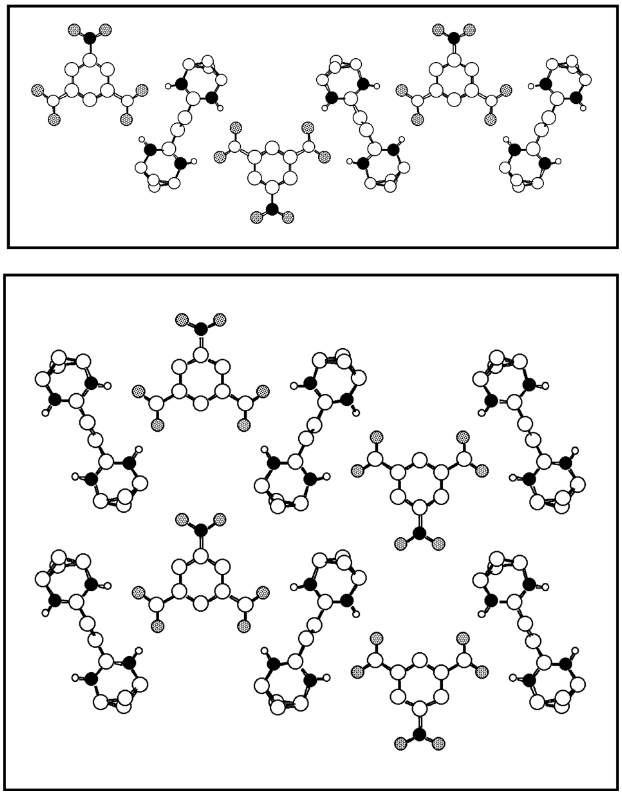


Fig. 3 A portion of the X-ray crystal structure of the ($\mathbf{1}$-2H$^+$, $\mathbf{3}^{2-}$) salt. The 1D network (top) is formed by a dihapto mode of H-bonding between dications and dianions. No specific interactions between 1D networks leading to a 2D network are observed in the crystalline phase (bottom). For the sake of clarity H atoms, except those involved in H-bonding, are not presented

between uncharged species, for the network obtained with **1**-2H$^+$, in addition to hydrogen bonds, strong charge–charge electrostatic interactions are also involved.

In dealing with the ($\mathbf{1}$-2H$^+$, $\mathbf{4}^{2-}$) salt, the X-ray study revealed the formation of a 3D network. As expected, a 1D network composed of **1**-2H$^+$ and $\mathbf{4}^{2-}$ interconnected, as in the previous case, through hydrogen bonds was obtained. However, the presence of water molecules and their role in forming a 3D network were not anticipated but rather revealed by the structural study (Fig. 5). Indeed, the 1D networks composed of **1**-2H$^+$ and $\mathbf{4}^{2-}$ were interconnected by water molecules into 2D networks [Fig. 6(*a*)] and the latter were again interconnected by a cluster of four water molecules into a 3D network [Fig. 6(*b*)].

The following features could be extracted from the X-ray study: (1) the ($\mathbf{1}$-2H$^+$, $\mathbf{4}^{2-}$) salt crystallizes also in the monoclinic crystal system with *C*2/*m* as the space group; the unit cell is composed of **1**-2H$^+$, $\mathbf{4}^{2-}$ and three water molecules; (2) again all four acidic protons are localized on **1**-2H$^+$; (3) in each NCN fragment, the average C—N distance (1.30 Å) and N—C—N angle (122.4°) are similar to those observed for the ($\mathbf{1}$-2H$^+$, $\mathbf{3}^{2-}$) salt; (4) the ethylene chain connecting the two cyclic amidinium moieties is again in a *trans* extended conformation with the same dihedral angle as in the previous case; (5) both six-membered cycles adopt a half-chair conformation; (6) the two NCN planes of the two amidinium moieties are almost parallel but not coplanar; (7) in the dianionic fragment, the two carboxylate moieties are almost coplanar with slight tilt angles of −3.7° and 3.7° with respect to their connecting pyridine ring; (8) a dihapto mode of interaction between the dication and the dicarboxylate anion with strong H bonds is observed. The average N···O distance of 2.78 Å and the average NHO angle of *ca.* 174.0° clearly demonstrate the strong nature of the hydrogen-bonding pattern; (9) the 1D networks formed between the dicationic **1**-2H$^+$ and the dianionic $\mathbf{4}^{2-}$ units are interconnected by water molecules; (10) the H bonds (O···O distance of *ca.* 2.83 Å) leading to the formation of the 2D network are between water molecules and carboxylate moieties of $\mathbf{4}^{2-}$ [Fig. 6(*a*)]; (11) no participation of the pyridine nitrogen in the formation of the 2D networks is observed; (12) the 2D networks mentioned above

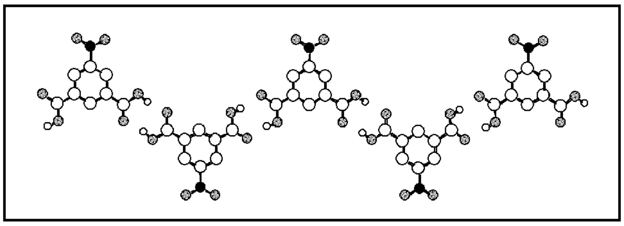


Fig. 4 A portion of the X-ray crystal structure of the diacid **3**.[24] The 1D network is formed by a dihapto mode of H-bonding between diacid units acting as both hydrogen donor and acceptor. For the sake of clarity H atoms, except those involved in H-bonding, are not presented

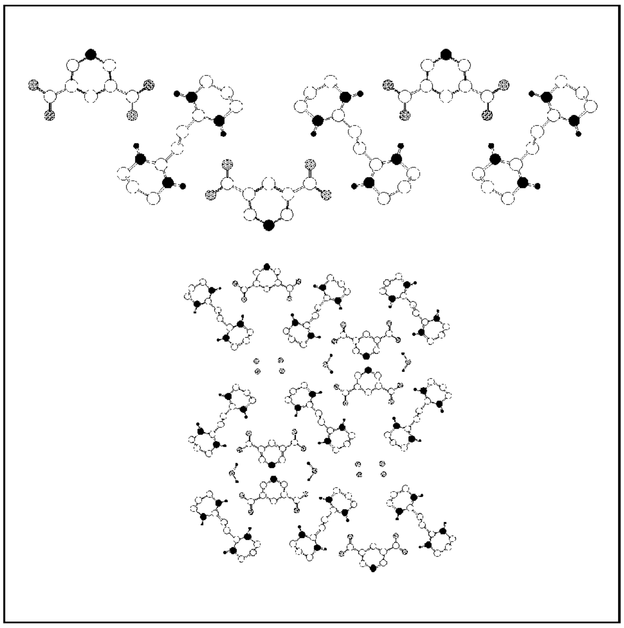


Fig. 5 A portion of the X-ray crystal structure of the ($\mathbf{1}$-2H$^+$, $\mathbf{4}^{2-}$, 3H_2O) salt. The 1D network (top) is formed by a dihapto mode of H-bonding between dications and dianions. The interconnection of the 1D networks by two water molecules leads to a 2D network (bottom). For the sake of clarity H atoms, except those involved in H-bonding, are not presented

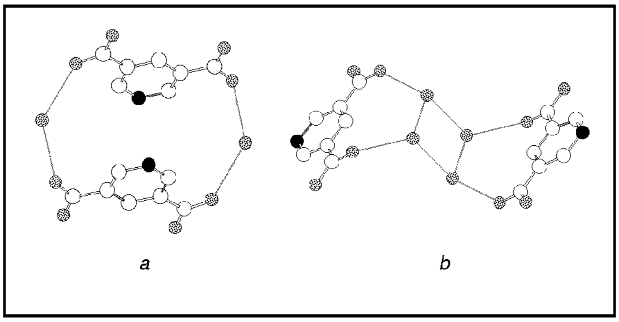


Fig. 6 A portion of the X-ray crystal structure of the dinicotinic acid showing the connectivity modes between water molecules and carboxylate moieties leading to the (*a*) 2D and (*b*) 3D networks. The average O···O distance for the isolated water molecules (*a*) and carboxylate anions was *ca.* 2.83 Å, whereas the average O···O distance for the water clusters (*b*) and carboxylate anions was *ca.* 2.70 Å. The average O···O distance between water molecules within each cluster (*b*) was *ca.* 2.72 Å. For the sake of clarity H atoms are not presented

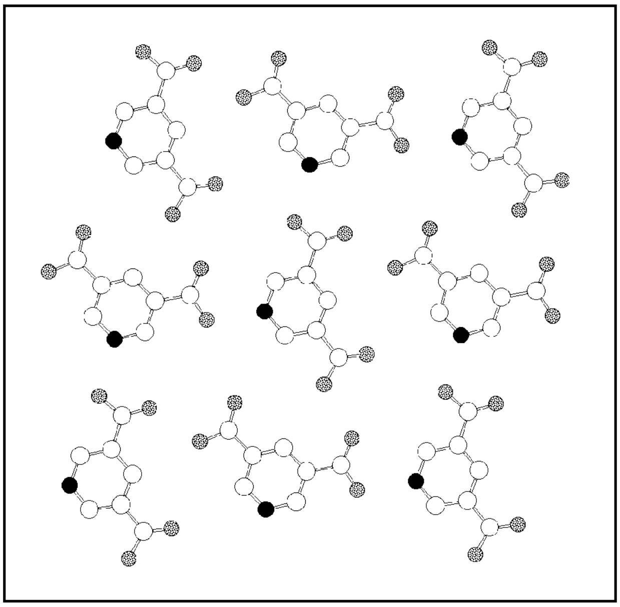


Fig. 7 A portion of the X-ray crystal structure of the dinicotinic acid **4**.[25] By adopting an intermediate structure between the neutral molecule and the zwitterion, it forms a 2D network based on strong OH···O and O···H···N hydrogen bonds. For the sake of clarity H atoms are not presented

are interconnected into a 3D network by water clusters composed of four water molecules with an average adjacent O···O distance of *ca.* 2.72 Å (Fig. 5), the hydrogen bonds were between the water clusters and carboxylate moieties [Fig. 6(*b*)].

The crystal structure of dinicotinic acid **4** has been reported[25] (Fig. 7). Two types of twinning crystals could be obtained by changing the pH of the recrystallization solution. Dinicotinic acid **4** adopts an intermediate structure between the neutral molecule and the zwitterion. Consequently, it forms a 2D network based on strong OH···O and O···H···N hydrogen bonds with distances of 2.59 Å and 2.51 Å, respectively, and angles of 174°. In marked contrast, in the presence of compound **1**, due to its strong basicity, both protons were centred on the amidinum dication, leading to **1**-$2H^+$ and thus preventing the formation of H bonds between the pyridinium and carboxylate units in $\mathbf{4}^{2-}$.

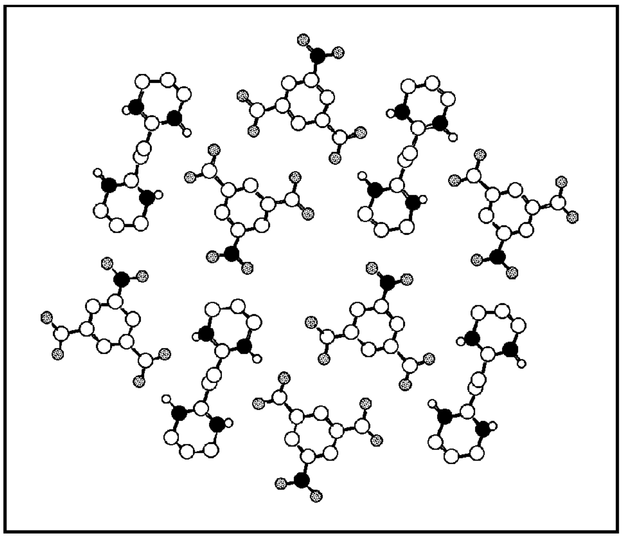


Fig. 8 A portion of the X-ray crystal structure of the (**1**-$2H^+$, **2**$\mathbf{3}^-$) salt. The 1D network is formed by a dihapto mode of H-bonding between dications and monoanions (see text). No specific interactions between 1D networks leading to a 2D network are observed in the crystalline phase. For the sake of clarity H atoms, except those involved in H-bonding, are not presented

Finally, the effect of the ratio of **1** and **3** was investigated by studying the crystal structure of the (**1**-$2H^+$, 2**3**$^-$) salt. The study revealed the formation of another type of 1D network in the crystalline phase. The (**1**-$2H^+$, 2**3**$^-$) salt forms infinite linear chains exclusively composed of the **1**-$2H^+$ dication and two $\mathbf{3}^-$ monoanions interconnected through two types of hydrogen bonds. (Fig. 8). The (**1**-$2H^+$, 2**3**$^-$) salt crystallizes also in the triclinic crystal system with $P\bar{1}$ as the space group. The unit cell is exclusively composed of **1**-$2H^+$ and two $\mathbf{3}^-$ units. The X-ray analysis revealed the following features: (1) in the **1**-$2H^+$ moieties the conformation, distances and angles are almost identical to those observed in the above mentioned (**1**-$2H^+$, $\mathbf{3}^{2-}$) salt; (2) the anionic unit $\mathbf{3}^-$ is the monocarboxylate derivative of **3** with an average CO bond length of 1.24 Å for

Table 1 Data collection and refinement for (**1**-$2H^+$, $\mathbf{3}^{2-}$) (**1**-$2H^+$, 2**3**$^-$) and (**1**-$2H^+$, $\mathbf{4}^{2-}$)

Crystal data	(**1**-$2H^+$, $\mathbf{3}^{2-}$)	(1-$2H^+$, 2**3**$^-$)	(**1**-$2H^+$, $\mathbf{4}^{2-}$)
Empirical formula	$C_{18}H_{23}N_5O_6$	$C_{26}H_{28}N_6O_{12}$	$C_{17}H_{23}N_5O_4 \cdot 3H_2O$
FW	405.41	614.53	415.5
Crystal size/mm	0.30 × 0.30 × 0.25	0.34 × 0.30 × 0.15	0.22 × 0.20 × 0.18
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	*C*2/*c*	$P\bar{1}$	*C*2/*m*
a/Å	18.688(1)	6.2393(9)	12.206(3)
b/Å	11.4664(8)	10.175(1)	21.832(6)
c/Å	10.0393(5)	11.149(1)	8.177(2)
α/deg		98.88(1)	
β/deg	117.072(4)	98.80(1)	112.21(2)
γ/deg		94.85(1)	
Volume/Å^3	1915.6(4)	686.9(3)	2017.3
Z	4	1	4
D_{calc}/g cm^{-1}	1.41	1.49	1.368
Wavelength/Å	0.71073	0.71073	1.5418
Radiation; μ/mm^{-1}	Mo-Kα; 0.100	Mo-Kα; 0.112	Cu-Kα; 8.588
T/K	294	294	173
θ−2θ scans; θ range/deg	2.5; 26.29	2.5; 26.28	3; 52
Reflect. collected	2169	2942	1241
Observed reflect. ($I > 3\sigma I$)	1182	1101	971
R	0.072	0.047	0.060
Rw	0.085	0.064	0.085
GOF	0.998	1.208	1.327

the carboxylate and bond lengths of 1.21 and 1.31 Å for the carboxylic acid moieties; (3) the carboxyl units are slightly tilted with respect to the aromatic ring, with the dihedral angle varying from −1.7 to 0.6°; (4) the nitro group is almost coplanar to the aromatic ring (dihedral angle varying from −0.3 to −0.6°); (5) the dication is hydrogen-bonded through a dihapto mode to two monocarboxylates with an average N···O distance of *ca.* 2.83 Å and angles of 151.7 and 131.5°; (6) the discrete motifs composed of one **1**-2H$^+$ and two **3**$^-$ are interconnected, forming thus a 1D network, by strong OH···O hydrogen bonds (average O···O distance of *ca.* 2.56 Å) between the carboxylic acid and carboxylate moieties of **3**$^-$.

Conclusions

In conclusion, using a combination of directional hydrogen bonds and charge–charge electrostatic interactions, 1D molecular networks based on a dihapto mode of H-bonding between hydrogen atom donors and acceptors were obtained in the crystalline phase. The strategy used was based on the use of a dicationic bisamidinium motif capable of acting as a tetra hydrogen bond donor and mono- or dicarboxylates as acceptors. Interestingly, in the case of dinicotinic acid a 3D network based on the interconnection of 1D networks by water molecules was observed.

Although at the present level of understanding, our approach is restricted to the structural aspects of crystal engineering, the extension to functional materials using functional tectons is under current investigation.

Experimental

The synthesis of compound **1** was achieved using published procedures.[23] Large, colourless, air-stable monocrystals composed of **1**-2H$^+$ and **3**$^-$, **3**$^{2-}$ or **4**$^{2-}$ anions were obtained upon cooling an EtOH–H$_2$O mixture containing the free amidine **1** and the diacids in a 1 : 1 or 1 : 2 ratio.

X-Ray crystallography

Crystal data for the (**1**-2H$^+$, **3**$^{2-}$) salt were collected using an Enraf-Nonius MACH3 diffractometer with graphite-monochromated Mo-Kα radiation. Crystal data for the (**1**-2H$^+$, **23**$^-$) salt were collected using an Enraf-Nonius CAD4-F diffractometer with graphite-monochromated Mo-Kα radiation. Crystal data for the (**1**-2H$^+$, **4**$^{2-}$) salt were collected using a Philips PW1100/16 diffractometer with graphite-monochromated Cu-Kα radiation. Hydrogen atom positions were located from difference Fourier maps. All three structures were solved using OpenMoleN 2.2. Table 1 provides crystallographic details for (**1**-2H$^+$, **3**$^{2-}$), (**1**-2H$^+$, **23**$^-$) and (**1**-2H$^+$, **4**$^{2-}$).

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