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Christer B. Aakeröy[a]; Deirdre P. Hughes[b]; James M. McCabe[b]; Mark Nieuwenhuyzen[b]
[a] Department of Chemistry, Kansas State University, Manhattan, KS, USA [b] School of Chemistry, The Queen's University of Belfast, Belfast, Northern Ireland

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Aromatic Dicarboxylic Acids as Building Blocks of Extended Hydrogen-bonded Architectures

CHRISTER B. AAKERÖY[a], DEIRDRE P. HUGHES[b], JAMES M. McCABE[b] and MARK NIEUWENHUYZEN[b]

[a] *Department of Chemistry, Kansas State University, Manhattan, KS, 66506, USA;*
[b] *School of Chemistry, The Queen's University of Belfast, Belfast BT5 9AG, Northern Ireland*

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An examination of the crystal structures of four compounds, 5-amino *iso*-phthalic acid hemihydrate (monoclinic, $P2_1/n$, $a = 8.142(2)$, $b = 17.444(3)$, $c = 11.140(2)$ Å, $\beta = 94.19(3)°$, $D_c = 1.601\,g\,cm^{-3}$, $Z = 8$, $R^2_w = 0.106$ for 1401 unique reflections), piperazinium(2+) 5-amino *iso*-phthalate (monoclinic, $P2_1/c$, $a = 11.820(2)$, $b = 9.516(2)$, $c = 12.618(3)$ Å, $\beta = 116.70(3)°$, $D_c = 1.400\,g\,cm^{-3}$, $Z = 4$, $R^2_w = 0.104$ for 2222 unique reflections), 2-chloro-benzylammonium 2-carboxylate-6-carboxylic pyridine (monoclinic, $P2_1/c$, $a = 22.391(2)$, $b = 9.322(3)$, $c = 13.274(2)$ Å, $\beta = 92.567(11)$, $D_c = 1.482\,g\,cm^{-3}$, $Z = 8$, $R^2_w = 0.113$ for 3610 unique reflections), and 3-fluoro-benzylammonium 2-carboxylate-6-carboxylic pyridine hydrate (monoclinic, $P2_1/c$, $a = 9.862(2)$, $b = 13.246(3)$, $c = 21.153(4)$ Å, $\beta = 98.00(3)$, $D_c = 1.463\,g\,cm^{-3}$, $Z = 8$, $R^2_w = 0.154$ for 2552 unique reflections), has identified a robust hydrogen-bonded, ribbon-like motif, generated by the geometric fit and hydrogen-bond complementarity of the $[-COO]^-$ and the $[-COOH]$ functionalities. This preferred interaction between neighbouring anions results in infinite 1-D anionic architectures that are held together by short and near-linear O—H···O hydrogen bonds. In 1 and 2, the amino functionality acts as a crosslink (through N—H···O interactions) between adjacent sheets, thereby generating extended 2-D architectures. 5-Amino *iso*-phthalic acid exists as a zwitterion in the solid state, an observation which was also indicated by vibrational spectroscopic data. The crystal packing in both 3 and 4 consists of 2-D domains of anions and cations, stacked in an ..AABBAABB.. manner where the anionic sheets are constructed around the carboxylic-carboxylate supramolecular connector.

Keywords: Crystal engineering, hydrogen bonding, carboxylic acids

INTRODUCTION

Crystal engineering is concerned with the structural manifestations of intermolecular forces and the way in which such forces can be utilized for controlling the assembly of molecular building blocks into predictable architectures. Despite the inherent difficulties with using weak forces as primary synthetic tools, considerable progress has been made during the last decade. Cocrystals of melamines and barbiturates have been used to create a variety of structural motifs [1], and aromatic spacers have provided reliable backbones for well-organized, extended structures [2,3]. The selectivity and directionality of the hydrogen bond has been instrumental in the preparation of distinctive and predictable structural aggregates [4], notably in molecular solids [5], and the use of hydrogen bonding as a steering force is now emerging as the most important strategy in crystal engineering [6–8]. Despite such progress, much more work is needed in order to identify robust supramolecular connectors that can be used in the programmed assembly of extended networks and new functional solids.

Although most efforts in crystal engineering have focused on molecular solids, an increasing number of strategies for the assembly of predictable ionic architectures have appeared recently [9]. We have previously demonstrated that substituted aliphatic dicarboxylic acids [9a, b] and monoamides [9c] of dicarboxylic acids can be used as versatile building blocks of low-dimensional architectures in organic salts. In this paper we report on the crystal structures of four compounds that are built around aromatic dicarboxylic acids, where the dominating hydrogen-bond interaction takes place between carboxylic and carboxylate moieties in a head-to-tail fashion; 5-amino *iso*-phthalic acid hemihydrate **1**, piperazinium (2+) 5-amino *iso*-phthalate **2**, 2-chloro-benzylammonium 2-carboxylate-6-carboxylic pyridine **3** and 3-fluoro-benzylammonium 2-carboxylate-6-carboxylic pyridine hydrate **4**. In the case of **1** and **2**, we wanted to combine the [COO$^-$···COOH] supramolecular interaction with the hydrogen-bond donating ability of an amino group positioned almost perpendicular to the expected chain. This creates as an opportunity for crosslinking of neighbouring chains which could result in a 2-D structure. We were also interested in comparing the structural influence of the amino moiety in *iso*-phthalic acid, with the influence of the —CH moiety in the corresponding position in 2,6-dicarboxylic acid pyridine. The only previously reported structure related to this work is that of 2,6-dicarboxylic acid pyridine hydrate [10].

EXPERIMENTAL SECTION

Preparation of 5-Amino *iso*-Phthalic Acid Hemihydrate

A commercial sample (Aldrich) of 5-amino *iso*-phthalic acid was showly recrystallized at ambient temperatures from an aqueous solution to produce irregular, colourless crystals: mp. > 300° (dec.) Calc. (found) for $C_8H_8NO_{4.5}$; C, 50.53 (50.3); H, 8.08 (8.2); N, 7.76 (7.6)%.

Preparation of Piperazinium (2+) 5-Amino *iso*-Phthalate

An aqueous solution of 5-amino *iso*-phthalic acid (0.20 g; 1.10 mmol) was prepared by dissolving the acid in water (75 cm^3) and bringing the mixture to boil. Piperazine (0.095 g; 1.10 mmol) was dissolved in distilled water (15 cm^3) and added to the warm acidic solution. The volume was reduced by boiling to approximately 20 cm^3 and the remaining solvent was allowed to evaporate at ambient temperatures. This produced large, colourless crystals which were collected by filtration, washed with a small amount of cold ethanol and allowed to dry in air: mp. 275–277°C. Calc. (found) for $C_{12}H_{17}N_3O_4$; C, 53.93 (53.5); H, 6.37 (6.3); N, 15.73 (15.6)%.

Preparation of 2-Chloro-Benzylammonium 2-Carboxylate-6-Carboxylic Acid Pyridine

2-Chlorobenzylamine (0.18 ml, 1.5 mmol) was added to an aqueous solution of 2,6-dicarboxylic acid pyridine (0.25 g, 1.5 mmol). The mixture was gently heated for a few minutes, and then left at ambient temperature. After a few days colourless needle-like crystals were produced; mp. 209–210°C. Calc. (found) for: $C_{14}H_{13}N_2O_4Cl$, C, 54.46 (54.2); H, 4.21 (4.4); N, 9.08 (9.4)%.

Preparation of 3-Fluoro-Benzylammonium 2-Carboxylate-6-Carboxylic Acid Pyridine Hydrate

2,6-Dicarboxylic acid pyridine (0.25 g, 1.5 mmol) was dissolved in methanol, and added to 3-fluorobenzylamine (0.19 ml, 1.5 mmol). The mixture was gently heated for a few minutes and then left at ambient temperature. After a few days, a pale yellow crystalline solid appeared. The product was filtered off and recrystallized twice from methanol to produce pale yellow rod-like crystals; mp. 206–207°C. Calc. (found) for $C_{14}H_{15}N_2O_5F$; C, 54.19 (54.5); H, 4.84 (4.8); N, 9.03 (9.5)%.

Crystallography and Vibrational Spectroscopy

Crystal data were collected using a Siemens P4 four-circle diffractometer with graphite monochromated Mo-K_α radiation at ca. 150 K in a dinitrogen stream. Crystal stabilities were monitored by measuring standard reflections every 100 reflections, and there were no significant variations ($< \pm 1\%$). Cell parameters were obtained from 35 accurately centred reflections in the 2-θ range 10°–25°. ω scans were employed for data collection and Lorentz and polarization corrections were applied.

The structures were solved by direct methods and for compounds **1–3** the non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen-atom positions were located from difference Fourier maps and a riding model with fixed thermal parameters ($U_{iso}=1.2U_{eq}$ for the atom to which they are bonded), was used for subsequent refinements. For compound **4** the carbon atoms were refined isotropically and all other non-hydrogen atoms were refine anisotropically. Hydrogen atoms were added at idealised positions for the carbon atoms and those attached to the nitrogen and oxygen atoms were located from difference a Fourier map. A riding model with fixed thermal parameters ($U_{iso}=1.2U_{eq}$ for the atom to which they are bonded), was used for subsequent refinements. For compound **1–4** the function minimised was $\Sigma[(\sigma^2|F_0|-|F_c|^2)]$ with reflection weights $\omega^{-1}=[\sigma^2|F_0|^2+(g_1P)^2+(g_2P)]$ where $P=[\max|F_0|^2+|F_c|^2]/3$. The SHELXTL PC and SHELXL-93 packages were used for data reduction and structure solution and refinement [11]. Additional material available from the Cambridge Crystallographic Data Centre comprises atomic coordinates, thermal parameters and relevant tables of observed and calculated structure factor amplitudes.

Data for structure determinations of **1–4** are listed in Table I. Geometry, labeling schemes (thermal ellipsoids (50%) for **1–3**) are shown in Figures 1a–d.

The infrared spectrum (KBr disk) of 1 was obtained on a Perkin 1430 spectrophotometer.

RESULTS AND DISCUSSION

The IR spectrum of **1** contains several bands that indicate that 5-amino *iso*-phthalic acid hemihydrate exists as a zwitterion, and not as a neutral molecule, in the solid state. Bands at 1402 cm^{-1} (s) and 1554 cm^{-1} (m), can be assigned to the symmetric and asymmetric Ar-COO^- stretches respectively. There are no distinctive bands in the 3400–3500 cm^{-1} region, where the symmetric and asymmetric R-NH_2 stretches would be expected to appear. Instead, there is a broad absorption at 2615 cm^{-1} and a well-defined band at 1591 cm^{-1} that can be assigned to $[-NH_3]^+$ stretching and bending modes, respectively.

The crystal structure determination of 5-amino *iso*-phthalic acid, **1**, conformed that the compound exists as a zwitterion, as indicated by the spectroscopic data. All protons were located, and the two C—O bond lengths, r[C(8)–C(81) 1.258(2) Å; C(8)–C(82) 1.261(2) Å] demonstrate that this is indeed a carboxylate moiety.

TABLE I Data Collection and Refinement for **1** and **2**

Crystal data	**1**	**2**
Empirical formula	$C_8H_8NO_{4.5}$	$C_{12}H_{17}N_3O_4$
MW	190.15	267.29
Crystal size (mm)	0.4 × 0.30 × 0.10	0.6 × 0.43 × 0.51
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$
a (Å)	8.142 (2)	11.820 (2)
b (Å)	17.444 (3)	9.516 (2)
c (Å)	11.140 (2)	12.618 (3)
α (deg)	90	90
β (deg)	94.19 (3)	116.70 (3)
γ (deg)	90	90
Volume (Å^3)	1578.0 (6)	1267.9 (5)
Z	8	4
D_{calc} (g cm^{-3})	1.601	1.400
$F(000)$	792	568
μ(Mo-K$_\alpha$) (mm^{-1})	0.133	0.106
Temp (K)	153	293
ω scans; θ range (deg)	2.34–25.00	2.80–24.98
Range h	−1 to 9	0 to 14
Range k	−18 to 20	0 to 11
Range l	−13 to 16	−15 to 13
Reflns collected	1558	2337
Unique reflns	1401	2222
Data : parameter ratio	11.39	12.92
Refinement	full-matrix least squares	full-matrix least-squares
R/R_w^2 (obs data)	0.038/0.099	0.038/0.096
R/R_w^2 (all data)	0.054/0.106	0.051/0.104
$\Delta\rho_{\text{max/min}}$ (e Å^{-3})	0.244/−0.222	0.205/−0.283
S	1.065	1.091

Data Collection and Refinement for **3** and **4**

Crystal data	**3**	**4**
Empirical formula	$C_{14}H_{13}N_2O_4Cl$	$C_{14}H_{14}N_2O_{4.5}F$
MW	308.71	301.27
Crystal size (mm)	0.30 × 0.20 × 0.10	0.42 × 0.22 × 0.30
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	22.391 (2)	9.862 (2)
b (Å)	9.322 (3)	13.246 (3)
c (Å)	13.274 (2)	21.153 (4)
α (deg)	90	90
β (deg)	92.567 (11)	98.00 (3)
γ (deg)	90	90
Volume (Å^3)	2767.9 (7)	2736.5 (9)
Z	8	8
D_{calc} (g cm^{-3})	1.482	1.463
$F(000)$	1280	1256
μ(Mo-K$_\alpha$) (mm^{-1})	0.294	0.119
Temp (K)	153	173
ω scans; θ range (deg)	1.82–22.50	2.09–20.00
Range h	−24 to 24	0 to 9
Range k	−1 to 10	−12 to 12
Range l	−1 to 14	−20 to 20
Reflns collected	4756	2744
Unique reflns	3610	2552
Data : parameter ratio	9.53	10.08
Refinement	full-matrix least squares	full-matrix least-squares
R/R_w^2 (obs data)	0.048/0.099	0.079/0.110
R/R_w^2 (all data)	0.080/0.113	0.207/0.154
$\Delta\rho_{\text{max/min}}$ (e Å^{-3})	0.244/−0.283	0.291/−0.297
S	1.037	1.01

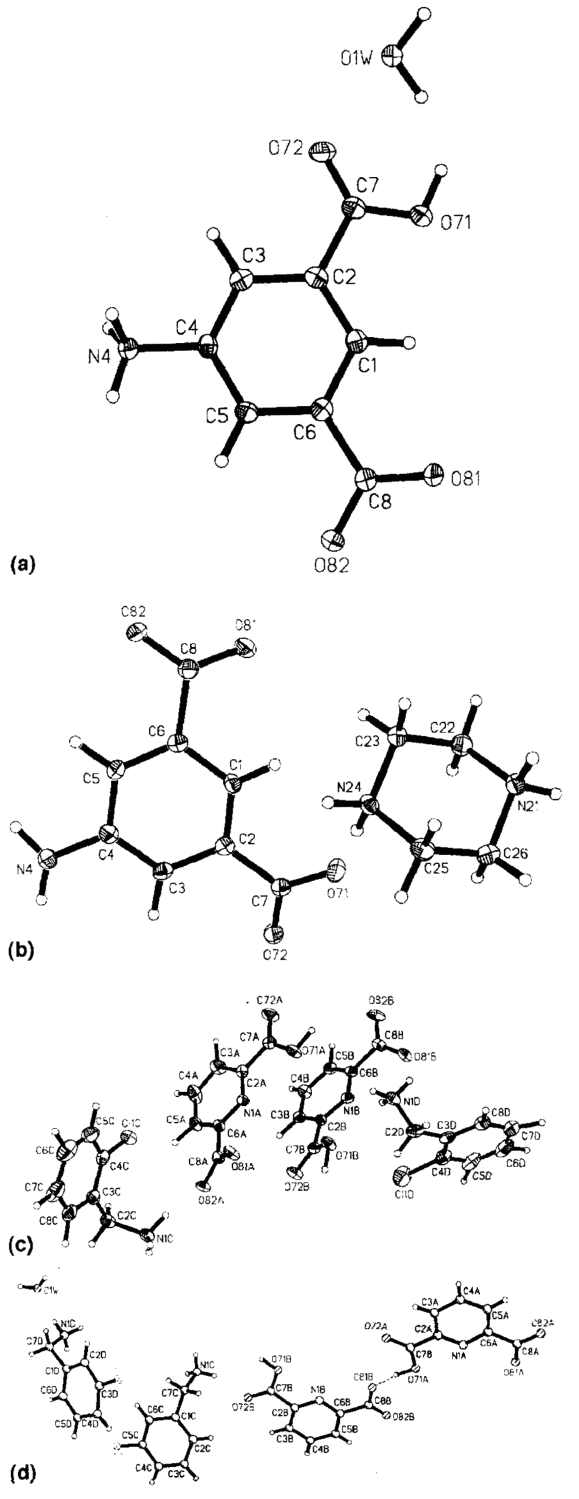

FIGURE 1 Geometry and labeling schemes for **1**–**4** (thermal ellipsoids at 50% for **1**–**3**).

Neighbouring zwitterions are linked by two symmetry related hydrogen bonds, *r*[N(4)-H(41)···O(82) 2.897(2) Å] to form dimeric units, Figure 2, Table II. At the same time, there is a short hydrogen-bond interaction *r*[O(71)-H(710)···O(81) 2.537(2) Å] between ions related by the screw axis parallel to *b*. This interaction, in combination with a C—H···O hydrogen bond (albeit long), gives rise to an infinite sheet of zwitterions, Figure 3. The water molecule is positioned between layers and is connected to neighbouring layers *via* two O—H···O hydrogen bonds, Figure 4. There is half a water molecule per zwitterion.

The structure determination of piperazinium(2+) 5-amino *iso*-phthalate (2−) shows that the amine has removed both acidic protons from the acid. Two symmetry related hydrogen bonds, *r*[N(4)-H(42)···O(72) 3.020(2) Å] link adjacent anions into a dimeric unit, Figure 5, Table III, which is identical to the one observed in the structure of **1**. This motif persists even in the presence of a divalent cation and even though the electronic structure of the acid has changed considerably. The geometric compatibility and the mutual complementarities of the $[-NH_3]^+$ group or $[-NH_2]$ group with the carboxylate functionality in **1** and **2** respectively, are adding considerable stability to the two structures. The robustness of this interaction means that we may consider this dimeric unit to be a new supramolecular synthon [12]. Through a combination of complimentary N—H···O and C—H···O interactions, the anions assemble in

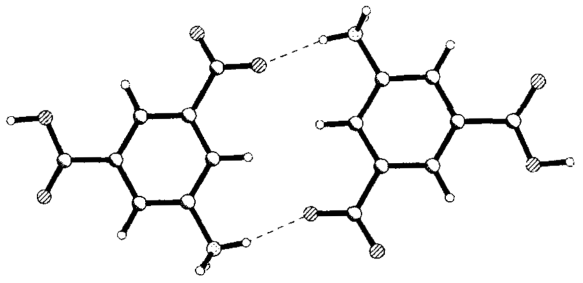

FIGURE 2 The dimeric motif of neighbouring zwitterions in **1**.

TABLE II Geometry of the hydrogen bonds in **1**

D—H···A	r(H···A)/Å	r(D···A)/Å	∠(D—H···A)/°
N(4)—H(41)···O(82)^{i}	2.046(2)	2.897(2)	155.42(6)
N(4)—H(42)···O(82)^{ii}	1.816(2)	2.757(2)	166.58(6)
N(4)—H(43)···O(1W)^{iii}	1.849(2)	2.783(2)	169.07(6)
O(71)—H(710)···O(81)^{iv}	1.546(2)	2.537(2)	177.21(7)
O(1W)—H(1W)···O(81)^{v}	1.773(2)	2.735(2)	174.04(5)
C(3)—H(3)···O(72)	2.933(2)	3.880(2)	157.36(5)

Symmetry code: ^{i} $-x, -y, 1-z$; ^{ii} $x, -y, -(1/2)+z$; ^{iii} $1-x, -y, -z$; ^{iv} $(1/2)+x, (1/2)-y, -(1/2)+z$; ^{v} $(1/2)-x, (1/2)-y, -z$.

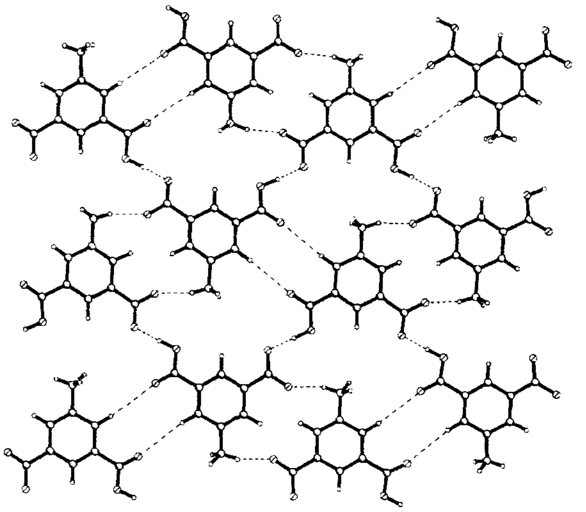

FIGURE 3 Infinite layer in **1**.

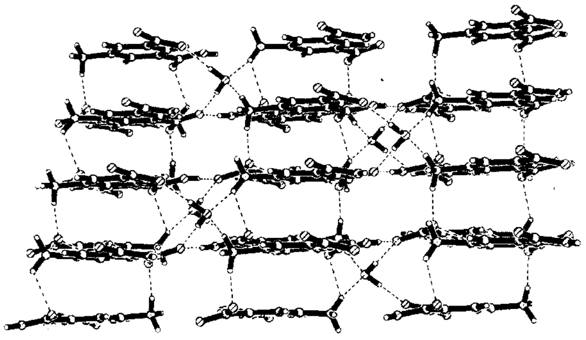

FIGURE 4 Edge-on view of layers of zwitterions bridged by water molecules in **1**.

layered manner, although this 2-D motif is very buckled, Figure 6. Each nitrogen atom on the cation is involved in two hydrogen bonds to carboxylate moieties on different anions, Table III, and the cation is providing a bridge between anionic motifs in the same way as the water molecule acts as a 'glue' between layers in **1**.

The structure of **3** has two ion-pairs in the asymmetric unit. The unique anions form infinite chains, parallel with *c*, through short head-to-tail interactions, r[O(71B)···O(81B) 2.494(5) and O(71A)···O(81A) 2.505(5) Å] Table IV. Adjacent chains are crosslinked *via* C—H···O interactions which results in infinite 2-D layers. Each layer only contains one type of anion leading to two unique anionic sheets, Figures 7a, b. The anionic layers are arranged in bilayers interconnected *via* three C—H···O interactions. The cations are attached to only one side of each anionic layer *via* three N—H···O hydrogen bonds. The overall packing can be described as alternating bilayers, ..AABBAABB..,

TABLE III Geometry of the hydrogen bonds in **2**

D—H···A	r(H···A)/Å	r(D···A)/Å	∠(D—H···A)/°
N(24)—H(242)···O(82)^{i}	1.824(2)	2.728(2)	164.50(6)
N(24)—H(241)···O(71)	1.832(2)	2.690(2)	171.25(6)
N(21)—H(212)···O(72)^{iii}	1.766(2)	2.726(2)	158.77(6)
N(21)—H(211)···O(82)^{iv}	1.858(2)	2.770(2)	126.36(8)
N(4)—H(42)···O(72)^{v}	2.159(2)	3.020(2)	101.79(6)
N(4)—H(41)···O(81)^{vi}	2.040(2)	2.990(2)	117.79(7)
C(5)—H(5)···O(81)^{ii}	2.574(2)	3.378(2)	138.22(5)

Symmetry code: ^{i} $2-x, -y, 1-z$; ^{ii} $x, (1/2)-y, -(1/2)+z$; ^{iii} $3-x, -y, 2-z$; ^{iv} $2-x, -(1/2)+y, 1(1/2)-z$; ^{v} $3-x, -y, 1-z$; ^{vi} $x, (1/2)-y, -(1/2)+z$.

TABLE IV Geometry of the hydrogen bonds in 3

D—H···A	r(H···A)/Å	r(D···A)/Å	∠(D—H···A)/°
N(1D)—H(11D)···O(72B)^{i}	2.019(5)	2.840(4)	152.20(11)
N(1D)—H(12D)···O(82A)^{i}	1.985(4)	2.860(4)	144.80(11)
N(1C)—H(11C)···O(82B)^{v}	2.028(4)	2.822(4)	169.91(11)
N(1C)—H(12C)···O(82A)	1.947(4)	2.853(4)	157.69(11)
O(71A)—H(71A)···O(81A)^{i}	1.522(3)	2.505(5)	159.84(13)
O(71B)—H(71B)···O(81B)^{iii}	1.305(3)	2.494(5)	170.33(16)
C(4A)—H(4A)···O(72A)^{ii}	2.700(5)	3.432(5)	127.13(11)
C(5A)—H(5A)···O(72A)^{ii}	2.756(5)	3.460(5)	122.50(9)
C(3B)—H(3B)···O(82B)^{ii}	2.705(5)	3.439(5)	125.36(10)
C(4B)—H(4B)···O(82A)^{iv}	2.433(5)	3.350(5)	149.29(10)
C(6A)—H(6C)···O(72A)^{vi}	2.494(5)	3.355(5)	139.86(14)
C(7D)—H(7D)···O(81B)^{vii}	2.582(5)	3.462(5)	132.00(12)
N(1D)—H(13D)···N(1B)^{v}	2.146(4)	2.961(4)	160.87(11)
N(1C)—H(13C)···N(1A)^{iii}	2.138(4)	2.990(4)	163.87(11)

Symmetry code: ^{i} x, $(1/2)-y$, $(1/2)-z$; ^{ii} x, $1(1/2)-y$, $z+(1/2)$; ^{iii} x, $(1/2)-y$, $z+(1/2)$; ^{iv} x, $1(1/2)-y$, $(1/2)-z$; ^{v} x, y, $1+z$; ^{vi} $1-x$, $(1/2)-y$, $(1/2)-z$; ^{vii} $-x$, $(1/2)-y$, $(1/2)-z$;

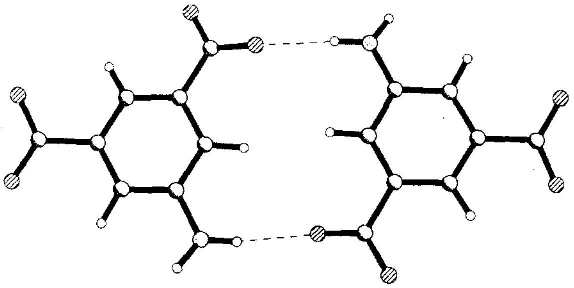

FIGURE 5 The dimeric motif of neighbouring anions in 2.

FIGURE 6 Edge-on view of buckled anionic sheets in 2.

Figure 8 and there are no significant Cl···Cl contacts in this structure.

The structure of 4 also contains two unique ion-pairs and the anionic 2-D sheets resulting from anion-anion contacts in 4 have the

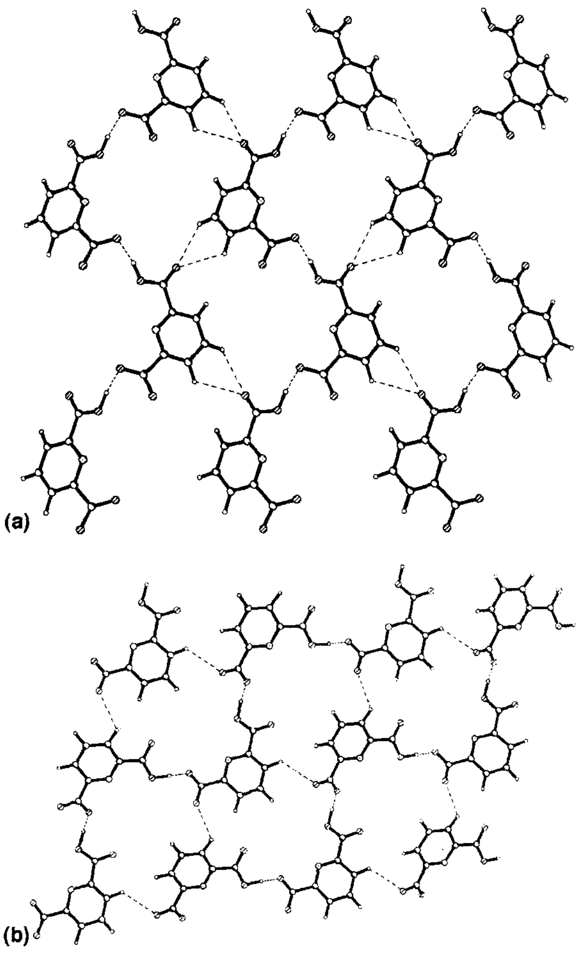

FIGURE 7 The two unique anionic sheets in 3.

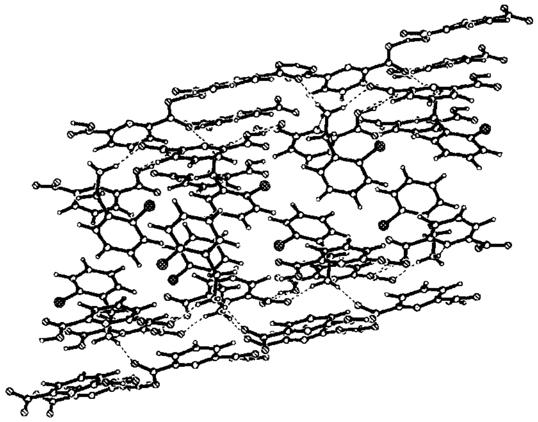

FIGURE 8 Side-ways view of the packing in **3** with alternating bilayers of cations and anions.

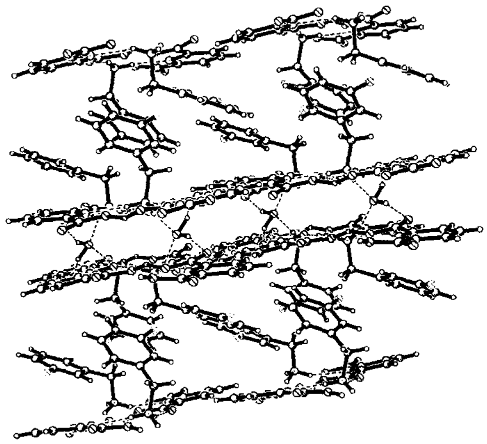

FIGURE 10 Edge-on view of the packing of alternating bilayers of cations and anions in the crystal structure of **4**.

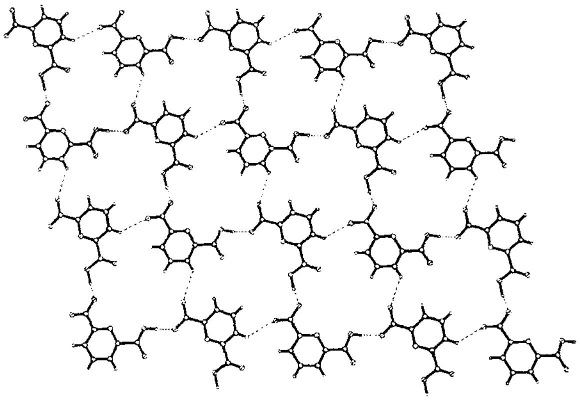

FIGURE 9 The two anions in **4** generate infinite sheets through O—H· · ·O and C—H· · ·O interactions.

same general apperance as the anionic networks in **3**, with O· · ·O hydrogen-bond distances of *r*[O(71B)· · ·O(81A) 2.512(9) and O(71A)· · ·O(81B) 2.526(10) Å], Table V. In addition, the two independent anions are present within the same 2-D network, Figure 9. Anionic sheets are arranged in bilayers which are interconnected by two O· · ·O hydrogen bonds involving the water molecule. Again, the overall packing is of the ..AABBAABB.. type, Figure 10, and there are no significant F· · ·F contacts between neighbouring cations.

Both 5-amino *iso*-phthalic acid and 2,6-dicarboxylic acid pyridine are able to act as building blocks (both in the form of zwitterion, monoanion and dianion) of reliable extended hydrogen-bonded anionic architectures even in the presence of different counterions and solvent molecules. Consequently, they represent additions to the collection of molecules that may be employed in the supramolecular synthesis of robust and transferable structural scaffolding for new materials. The strength of the carboxylic-carboxylate interaction is emphasised by the fact that replacing $[-NH_3]^+$ or $[-NH_2]$ (in **1** and **2**, respectively) with —CH (on the anion **3** and **4**) has little impact upon the assembly of the extended anionic motifs.

It is also worth pointing out that the overall shape (albeit with very different hydrogen-bonding possibilities) of 5-amino *iso*-phthalic acid is, in some ways, similar to that of trimesic acid which has been used extensively in the design and construction of predictable structures [13]. We intend to further examine how, and to what extent, competition and balance between functional groups on substituted aromatic dicarboxylic acids lead to predictable extended anionic assemblies.

TABLE V Geometry of the hydrogen bonds in **4**

D—H···A	r(H···A)/Å	r(D···A)/Å	∠(D—H···A)/°
N(1C)—H(1C3)···O(1W)^{ix}	1.968(14)	2.820(9)	160.10(27)
N(1C)—H(1C1)···O(72B)	1.958(12)	2.819(10)	163.25(28)
N(1C)—H(1C2)···O(81A)^{i}	2.336(10)	2.811(10)	114.62(25)
N(1C)—H(1C2)···O(71A)^{i}	2.584(10)	2.891(9)	100.17(21)
C(4A)—H(4A)···O(1W)^{vi}	2.711(11)	3.419(11)	133.46(23)
N(1D)—H(1D2)···O(1W)	1.915(13)	2.796(9)	167.89(28)
N(1D)—H(1D3)···O(81B)^{i}	2.282(10)	3.988(10)	118.47(26)
N(1D)—H(1D3)···O(71B)^{i}	2.636(9)	2.801(10)	96.28(21)
O(71B)—H(71B)···O(81A)^{i}	1.488(9)	2.512(9)	174.12(36)
O(71A)—H(71A)···O(81B)	1.439(10)	2.526(10)	158.58(35)
O(1W)—H(10W)···O(82B)^{iv}	2.034(9)	2.644(9)	149.13(26)
O(1W)—H(20W)···O(82A)^{v}	1.771(9)	2.711(9)	144.22(31)
C(3A)—H(3A)···O(82B)^{ii}	2.585(12)	3.263(12)	130.09(28)
C(3B)—H(3B)···O(82A)^{iii}	2.706(13)	3.311(13)	123.41(28)
C(3C)—H(3C)···F(1C)^{vii}	2.537(14)	3.275(14)	136.56(30)
C(6D)—H(6D)···F(1D)^{vii}	2.714(13)	3.357(13)	127.01(29)
C(7D)—H(7D)···F(1D)^{vii}	2.614(12)	3.506(12)	153.04(26)
N(1D)—H(1D3)···N(1B)^{i}	2.074(17)	2.946(11)	166.10(25)
N(1C)—H(1C2)···N(1A)^{i}	2.101(11)	2.933(11)	155.29(76)

Symmetry code: $^{i}x, 1-y, z$; $^{ii}\ x-1, y, z$; $^{iii}\ 1+x, y-1, z$; $^{iv}\ -x, -y, -z$; $^{v}\ x, y-2, z$; $^{vi}\ -1-x, -y, -z$; $^{vii}\ -1-x, (1/2)+y, (1/2)-z$; $^{viii}-x, -(1/2)+y, (1/2)-z$; $^{v}\ -x, -1-y, -z$.

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