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Rosa E. Meléndez[a]; Michael J. Zaworotko[a]
[a] Department of Chemistry, Saint Mary's University, hali, Nova Scotia

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Toward Crystal Engineering of Organic Porous Solids: Diammine Salts of Trimesic Acid[1]

ROSA E. MELÉNDEZ and MICHAEL J. ZAWOROTKO*

Department of Chemistry, Saint Mary's University, Halifax, Nova Scotia, B3H 3C3, Canada

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We report the synthesis and X-ray crystallographic characterization of three new dibasic organic cation salts of 1,3,5-benzenetricarboxylic acid, trimesic acid. The focus of the study concerns crystal engineering of organic solids with predictable but fine-tuneable porosity. All three salts self-assemble into 2-D grids *via* interionic hydrogen bonding. Full details of single crystal X-ray diffraction studies of the salts are reported: (**1**) *N,N,N′,N′*-tetramethylethylenediammonium dihydrogentrimesate dihydrate, $[HMe_2NCH_2CH_2NMe_2H]2[1\text{-}CO_2\text{-}3,5(CO_2H)_2C_6H_3]\cdot 2H_2O$, a = 12.583(3), b = 15.1177(13), c = 15.407(3), β = 113.466(20), $P2_1/c$, $d_{calc}(Mg/m^3) = 1.42$, Z = 4, 3515 unique reflns., $R_f = 0.061$, $R_w = 0.055$; (**2**) *N,N,N′,N′*-tetraethylethylenediammonium dihydrogentrimesate, $[HEt_2NCH_2CH_2NEt_2H]2[1\text{-}CO_2\text{-}3,5(CO_2H)_2C_6H_3]$, a = 6.6196(18), b = 9.243(2), c = 12.360(4), α = 75.16(4), β = 75.88(5), γ = 84.297(22), $P\bar{1}$, $d_{calc}(Mg/m^3) = 1.39$, Z = 1, 1844 unique reflns., $R_f = 0.056$, $R_w = 0.050$; (**3**) *N,N,N′,N′*-tetramethylethylenediammonium hydrogentrimesate, $[HMe_2NCH_2CH_2NMe_2H][1,3\text{-}(CO_2)_2\text{-}5\text{-}(CO_2H)C_6H_3]$, a = 8.636(4), b = 21.6877(17), c = 9.436(5), β = 114.49(6), $P2_1/c$, $d_{calc}(Mg/m^3) = 1.35$, Z = 4, 2820 unique reflns., $R_f = 0.050$, $R_w = 0.054$.

INTRODUCTION

That bulk physical properties are critically dependent upon solid state architecture has spawned the relatively recent emergence of the field of crystal engineering[2]. The fundamental precept of crystal engineering is that crystals are *de facto* manifestations of self-assembly and that control over the directionality of noncovalent interactions therefore imparts control over crystalline architecture. Taken to its ultimate extreme, control over the symmetry and directionality of the self-assembly process in three dimensions can even afford very specific control over space group selection[3]. Hence, understanding noncovalent[4] forces such as electrostatic, hydrogen bonding and π-π interactions is a critical prerequisite for controlling the architecture of organic solids. Hydrogen bonding is particularly well understood and can be regarded as being both directional and strong[5]. Indeed, hydrogen bond motifs have been extensively studied and analyzed[6] and have already been successfully exploited for the design of polar organic solids[7].

This study concerns the rational design of porosity in organic solids. Several criteria must be considered before a system is selected for study, the most important being that one must inherently be able to control intermolecular interactions in at least two dimensions. Carboxylic acid

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*Corresponding author. Fax: (902) 4968106. E-mail: mzaworot@science.stmarys.ca.

hydrogen bonding motifs have been of interest in the study of 1-D[6b,8], 2-D[9] and 3-D[10] organic solids. Trimesic acid (H_3-TMA), 1 (Fig 1a), represents a prototypical building block or tecton[11] for 2-D networks and presence of porosity since it is a flat trigonal molecule which self-assembles through self-complementary carboxylic acid dimer motifs, thereby forming 2-D infinite honeycomb grids. These grids are predictably 14 Å in diameter (Fig 1b), however, the pores generated are typically filled by interpenetration or catenation of three other H_3-TMA grids[12]. Our general strategy for crystal engineering invokes a second criterion: generation of 2-D structures from a multicomponent or modular system such as a salt or cocrystal. In such systems there are at least two complementary components, a *director*, which acts as a template to control the symmetry of the network, and a *propagator*, typically a linear difunctional spacer (Fig 2). In principle, the modular approach[3] offers both fine-tunability and, in the case of salts, high lattice energies[5]. A conceptually similar approach has recently been used to generate porous coordination polymers in which trigonal or tetrahedral transition metal moieties are the directors and difunctional ligands such as 4,4'-dipyridyl and pyrazines are the propagators[3,13]. H_3-TMA is only likely to act as a director in a modular system if it is deprotonated by a strong linear difunctional base. The resulting salts would consist of complementary counterions: one with excess hydrogen bond acceptors (TMA) and one with excess hydrogen bond donors (dication) and should therefore generate the motif illustrated in Fig 3. Whereas H_3-TMA itself has been extensively studied because it forms a variety of inclusion compounds, to our knowledge we are the first to attempt crystal engineering of modular grids using trimesate anions.

RESULTS AND DISCUSSION

The following difunctional bases were investigated: *N,N,N',N'*-tetramethylethylenediamine (TMEDA) and *N,N,N',N'*-tetraethylethylenediamine (TEEDA). These bases are not only linear, difunctional and relatively strong, but when protonated they have only two strong hydrogen bond donor sites, thereby limiting the number of possible hydrogen bond motifs. Three compounds, *N,N,N',N'*-tetramethylethylenediammonium dihydrogentrimesate dihydrate, $[HMe_2NCH_2CH_2NMe_2H]2[1\text{-}CO_2\text{-}3,5(CO_2H)_2C_6H_3]\cdot 2H_2O$, 1; *N,N,N',N'*-tetraethylethylenediammonium dihydrogentrimesate,

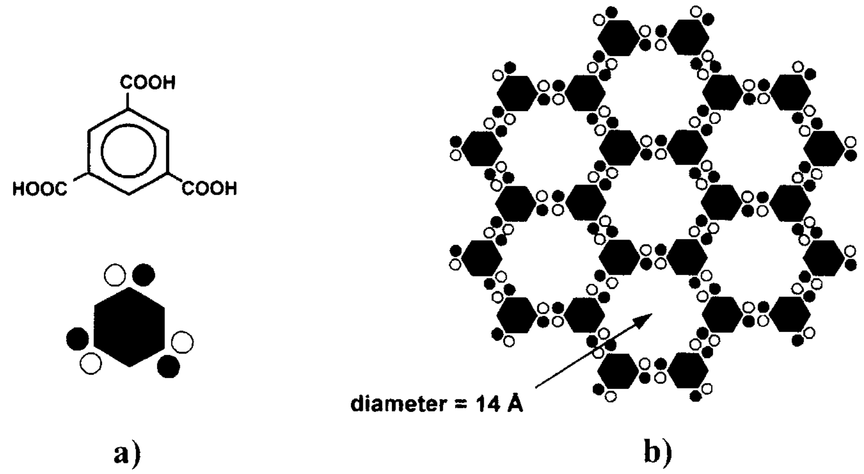

FIGURE 1 a) Trimesic acid (H_3-TMA) is a prototypical building block for crystal engineering due to its trigonal symmetry. b) Schematic representation of 2-D hexagonal grids formed by self-assembly of H_3-TMA through the carboxylic acid dimer.

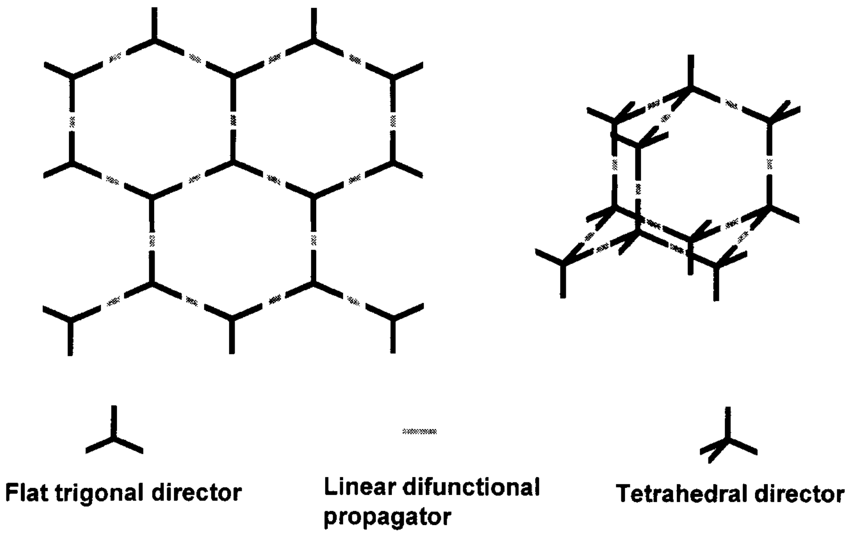

FIGURE 2 The modular approach to crystal engineering involves a multicomponent system of complementary molecules. The "director" controls the architecture of the solid and the "propagator" manifests the geometry of the director. This schematic illustrates the formation of 2-D hexagonal and 3-D diamondoid networks using the modular approach.

$[HEt_2NCH_2CH_2NEt_2H]2[1\text{-}CO_2\text{-}3,5(CO_2H)_2C_6H_3]$, **2**; *N,N,N′,N′*-tetramethylethylenediammonium hydrogentrimesate, $[HMe_2NCH_2CH_2NMe_2H][1,3\text{-}(CO_2)_2\text{-}5\text{-}(CO_2H)C_6H_3]$, **3**, were isolated and classified by the observed cation : anion stoichiometries as 1 : 2 and 1 : 1 salts. Crystallographic parameters for **1–3** are presented in Table I. A summary of hydrogen bond distances is presented in Table II.

1:2 Salts

Compounds **1** and **2** are 1 : 2 salts. Water of solvation is present in **1** (Fig. 4a) and plays an integral role in the resulting hydrogen bond network. The structure of **1** is best described as two parallel hydrated H_2-TMA grids which are cross-linked by H_2-TMEDA cations. The resulting network is a "double-decker" sheet that is

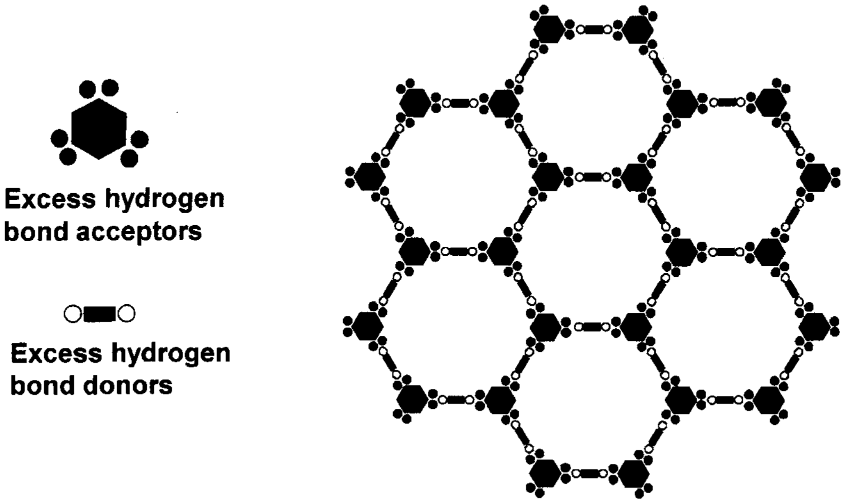

FIGURE 3 A schematic illustration of how hexagonal grids of H_3-TMA can in principle can increased in size using the modular approach.

TABLE I Crystallographic data for 1–3.

compound	1	2	3
formula	$O_{14}N_2C_{24}H_{32}$	$O_{12}N_2C_{28}H_{36}$	$O_6N_2C_{15}H_{22}$
f.w. (g/mol)	572.52	592.59	326.35
space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a (Å)	12.583(3)	6.6196(18)	8.636(4)
b (Å)	15.1177(13)	9.243(2)	21.6877(17)
c (Å)	15.407(3)	12.360(4)	9.436(5)
α (°)		75.16(4)	
β (°)	113.466(20)	75.88(5)	114.49(6)
γ (°)		84.297(22)	
V ($Å^3$)	2688.4(9)	708.4(4)	1608.3(12)
Z	4	1	4
d_{calc} (Mg/m^3)	1.42	1.39	1.35
crystal size (mm)	0.3 × 0.4 × 0.5	0.2 × 0.4 × 0.5	0.3 × 0.6 × 0.8
radiation	MoKα^a	MoKα^a	MoKα^a
μ (mm^{-1})	0.11	0.10	0.10
trans. range	0.822–0.996	0.873–0.999	0.383–0.997
T (°C)	17	17	17
# unique reflns	3515	1844	2820
# reflns used	1993^b	1157^b	2168^c
# variables	361	190	208
R_f	0.061	0.056	0.050
R_w	0.055	0.050	0.054
$2\theta_{max}$(°)	44.8	44.9	50.0
G.O.F.	2.74	3.15	5.26
$(\text{shift/error})_{max}$	0.000	0.000	0.000

[a] (λ = 0.70930Å)
[b] I > 2.5σ(I)
[c] I > 3σ(I)

sustained by ionic hydrogen bonds. The hydrogen bonding scheme can be rationalized based upon the expected hierarchy of hydrogen bond strengths. Cations *selectively* hydrogen bond to

TABLE II Interionic hydrogen bond distances (Å) and angles (°).

compound	O^-....O	N^+....O^-	O....O
1	O1-O13 2.545(6)	N21-O2 2.744(6)	O3-O41c 2.952(6)
	O3-O11 2.599(5)	N21-O1 3.052(6)	O5-O41 2.659(6)
	O2-O42a 2.635(6)	N22-O12 2.741(6)	O13-O42d 3.071(7)
	O12-O41b 2.748(6)	N22-O11 3.077(6)	O15-O42 2.655(6)
2	O1-O6 2.549(5)	N1-O2 2.712(5)	O3-O4e 2.639(5)
		N1-O1 3.193(5)	
3	O3-O5f 2.566(3)	N21-O1 2.628(3)	
		N21-O2 3.101(3)	
		N22g-O4 2.609(3)	

a = x, 1.000 + y, z
b = 1.000 + x, −1.000 + y, z
c = −x, −0.500 + y, 0.500 − z
d = 1.000 − x, 0.500 + y, 0.500 − z
e = −x, 1.000 − y, 1.000 − z
f = 1.000 + x, y, z
g = 2.000 − x, −0.500 + y, 0.500 − z

both oxygen atoms of the lone carboxylate group of the anion *via* N^+-H....O^- bifurcated hydrogen bonds. Studies by R. Taylor *et al.* demonstrated that 78% of positively charged N^+-H species form unsymmetrical bifurcated hydrogen bonds[14]. In **1**, the N....O distances are 2.741(6), 3.077(6) and 2.744(6), 3.052(6) Å. Formation of these bifurcated hydrogen bonds can be regarded as predictable because they involve the strongest hydrogen bond donor and a complementary strong hydrogen bond acceptor, thus obeying Etter's hydrogen bonding rules for organic solids[6a]. H_2-TMA anions self-assemble *via* carboxylic acid and carboxylate moieties, forming a strong hydrogen(bis)carboxylate hydrogen bond with O-H....O^- distances of 2.545(6) and 2.599(5) Å. Homonuclear O-H....O^- hydrogen bonding has been a topic of recent interest due to its strength and directionality. Such bonds are usually classified as very strong (<2.50 Å), strong (2.50–2.65 Å), medium (2.65–2.80 Å), or weak (>2.80 Å)[15]. The carboxylate groups also form hydrogen bonds with the water molecules, d(O....O) = 2.635(6) and 2.748(6). These distances are within the expected range for hydrogen bonds to ternary carboxylates, d(O....D) D = O or N[16]. The remaining carboxylic acid groups hydrogen bond to water molecules, d(O....O) ranging from 2.655(6) to 3.071(7) Å (Table II). These distances are longer than those observed in H_3-TMA hydrated inclusion compounds[17] (average d(O....O) = 2.63). The angular nature of the water molecules mitigates against porosity as revealed by Fig 4b, which presents a perspective view of the "double-decker" framework of **1**. A search of the Cambridge Structural Database[18] revealed no other examples of H_2-TMA structures.

The complicated hydrogen bonding pattern seen in **1** results from the presence of three chemically different residues. Preparation and determination of the crystal structure of an anhydrous analogue of **1**, **2**, was the next step in our study. The hydrogen bond pattern of **2** (Fig. 5a) can be rationalized based upon the stoichiometry and hydrogen bond strength hierarchy. There are two crystallographically independent H_2-TMA ions which self-assemble via hydrogen-(bis)carboxylate hydrogen bonds, d(O....O) = 2.549(5) Å. The H_2-TEEDA cation forms a bifurcated hydrogen bond to the carboxylate group, d(N....O) = 2.712(5) and 3.193(5) Å, and the remaining carboxylic acid group of one of the H_2-TMA anions self-assembles *via* the dimer motif to an adjacent H_2-TMA (O....O distances are 2.639(5) Å). This hydrogen bonding pattern generates an infinite 2-D flat porous sheet with, after taking van der Waals radii into account,[19] square holes of effective dimensions 6.7 × 4.8 $Å^2$ (Fig. 5b). Unfortunately, although cavities are achieved in the sheets of **2**, the ethyl groups of the cations of adjacent sheets orient themselves into the cavities and therefore fill the voids (Fig. 6).

1:1 Salt

To promote further deprotonation of the acid, more severe reaction conditions were used to generate **3** (Fig. 7a). The structure of **3** can best be described as a 2-D infinite flat non-porous sheet (Fig. 7b). The hydrogen bonding pattern in **3** can be rationalized in a manner similar to that detailed for **1** and **2**. N^+-H....O^- hydrogen bonds occur between the H_2-TMEDA cations and the carboxylate moieties, one being bifurcated (N....O = 2.628(3) and 3.101(3) Å) and one discrete (N....O = 2.609(3) Å). The carboxylic acid moiety does not form a dimer with adjacent H-TMA anions, which would have generated a porous 2-D grid, rather, it forms a hydrogen(bis)carboxylate hydrogen bond with an adjacent anion (O....O = 2.566(3) Å).

It is interesting to note that, according to solution pK_a values, complete deprotonation of H_3-TMA (pK_{a1} = 2.12, pK_{a2} = 3.89, pK_{a3} = 4.70[20])1 should have occurred in all three reactions. We attribute incomplete deprotonation of H_3-TMA in **1–3** to solubility factors in our solvent.

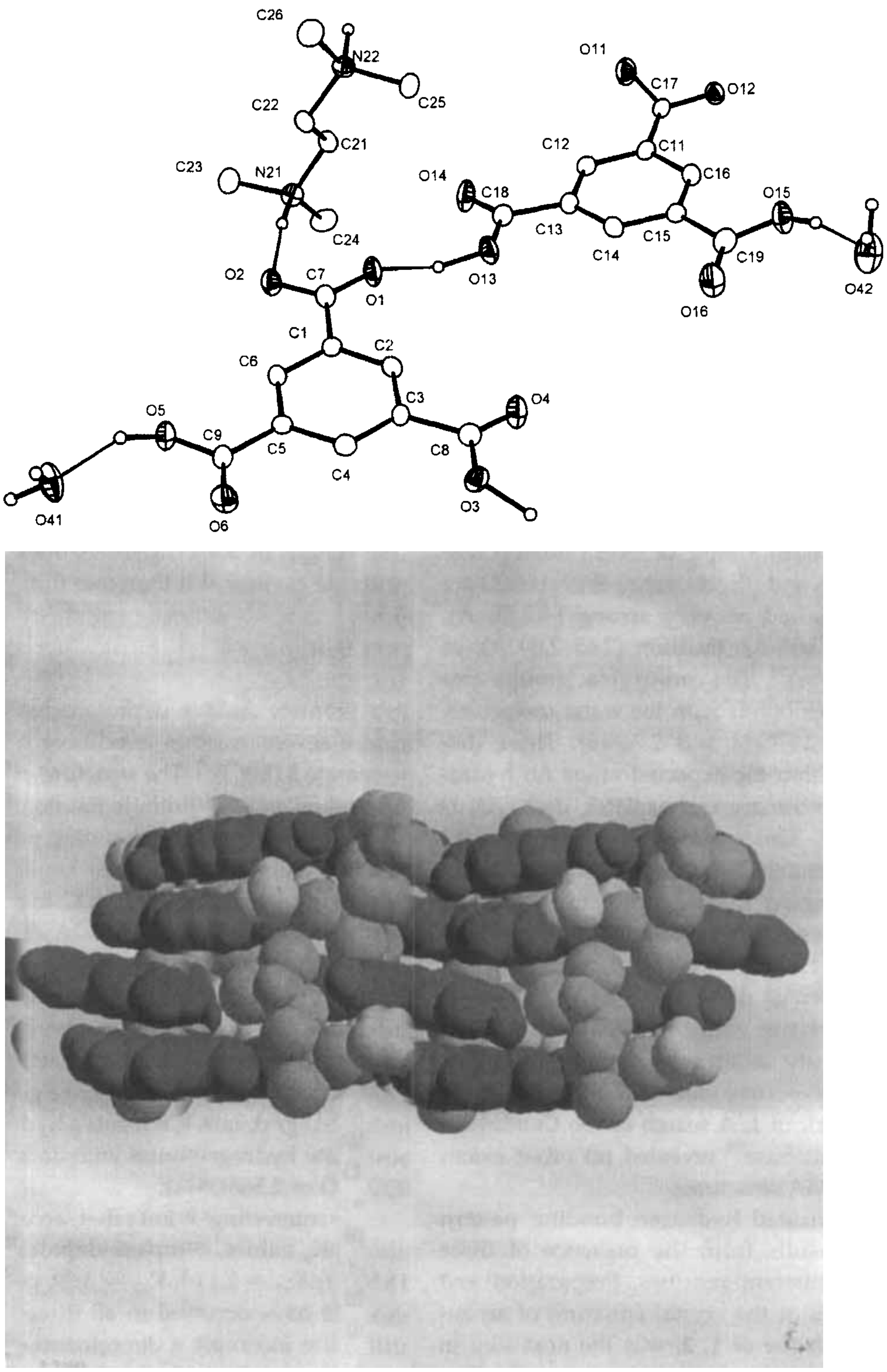

FIGURE 4 (a) ORTEP plot of **1** with atom labelling scheme and (b) perspective view of the double decker sheets formed by **1**. Porosity is precluded by the angular nature of the water molecules (in white).

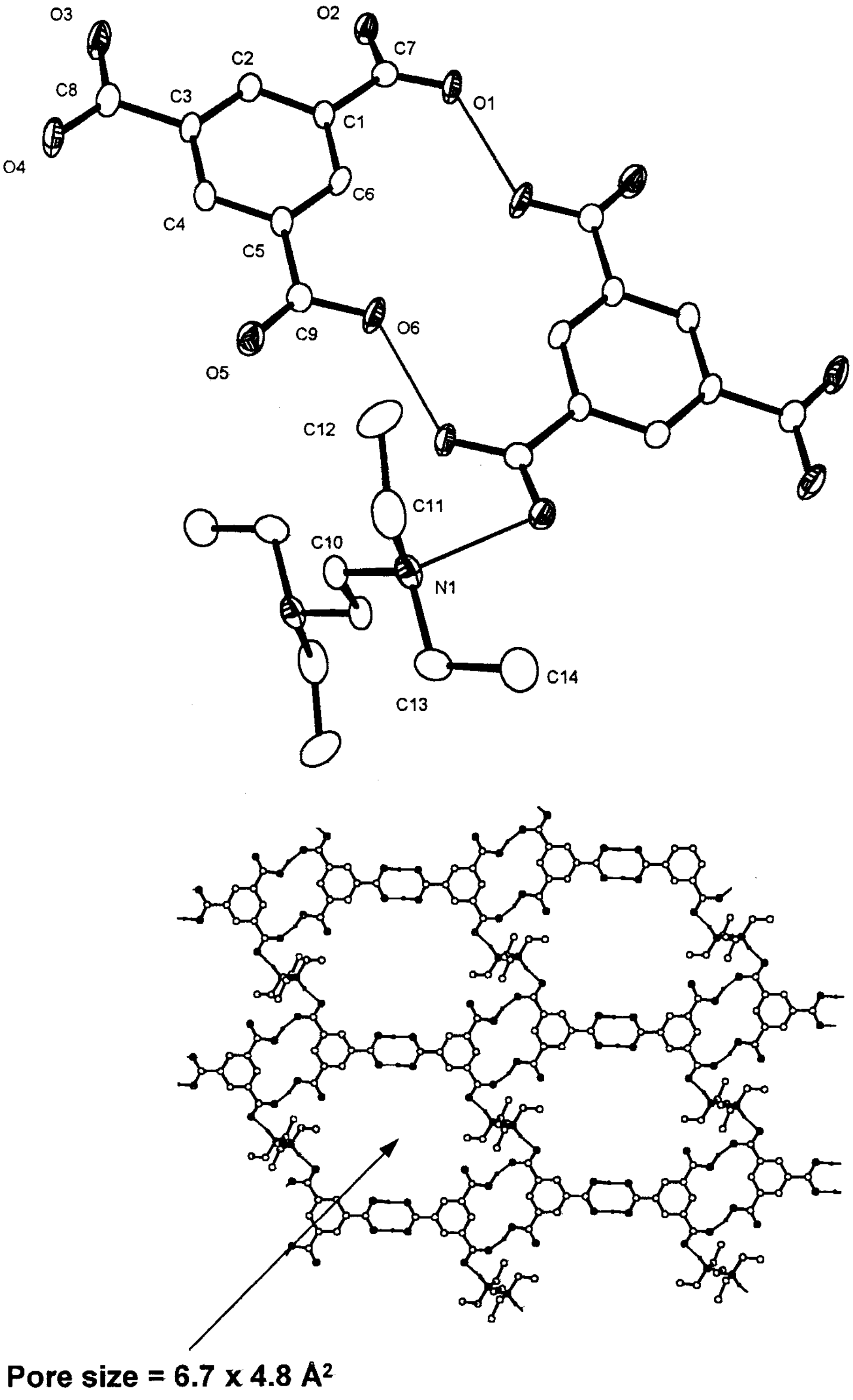

FIGURE 5 (a) ORTEP plot of **2** with atom labelling scheme. (b) Infinite 2-D sheets with cavities of 6.7 × 4.8 Å^2 (after taking van der Waals radii into account) are generated.

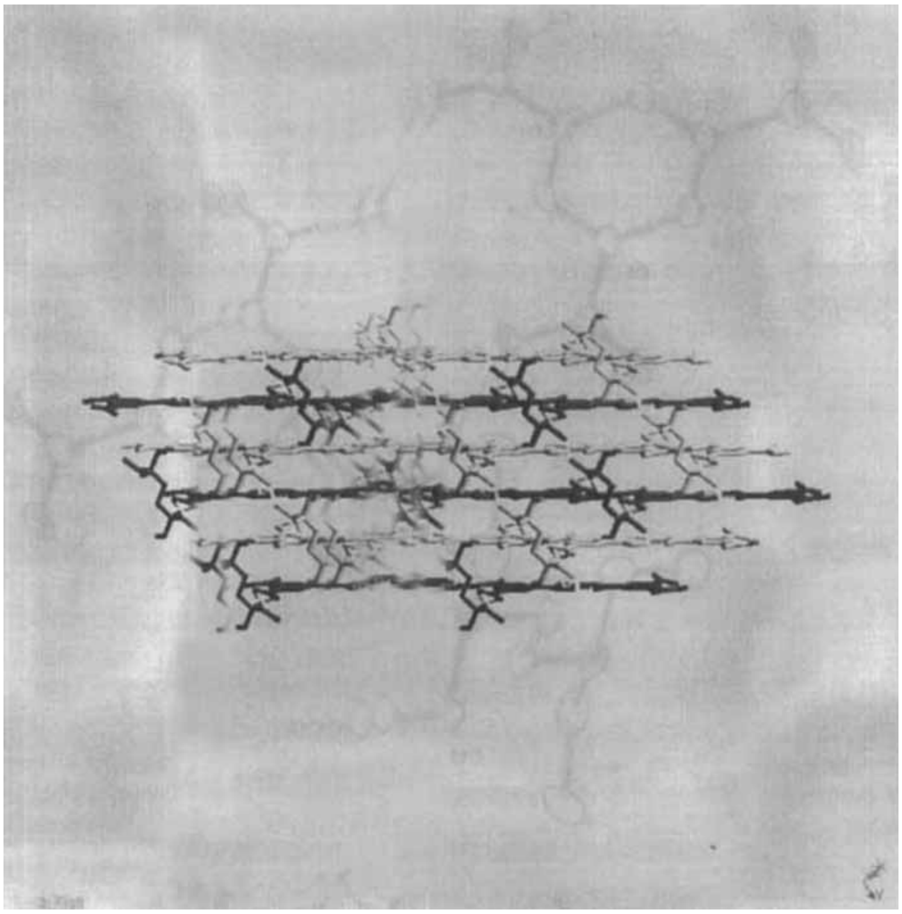

FIGURE 6 An illustration of how porosity in **2** is eliminated by ethyl groups on adjacent sheets.

Evidence of Proton Transfer in 1–3

Since hydrogen atom coordinates are difficult to determine accurately via x-ray crystallography we sought other evidence to support the formulations assigned to **1–3**. X-ray crystallography can provide evidence supporting acid deprotonation if one considers C-O distances. Average bond lengths of C=O and C-O(H) are typically 1.22 and 1.30 Å, respectively, in crystal structures that involve H_3-TMA[9]. These distances are consistent with data reported in simpler carboxylic acids[8]. However, in carboxylate anions the two C-O distances are expected to be about the same, 1.25 Å[21]. Infrared spectroscopy can also be used to determine whether or not deprotonation has occured. The carboxylate anion has two strongly coupled C-O bonds with strengths intermediate between C=O and C-O giving rise to two bands: a strong asymmetrical stretching band at 1650–1550 cm^{-1} and a weaker symmetrical stretching band near 1400 cm^{-1} [21]. Table III summarizes the appropriate data for **1–3** and supports the formulations assigned earlier.

CONCLUSIONS

Analysis of the hydrogen bonding patterns in **1–3** reveals that hydrogen bonding *predictably* acts as a strong directing force or synthetic vec-

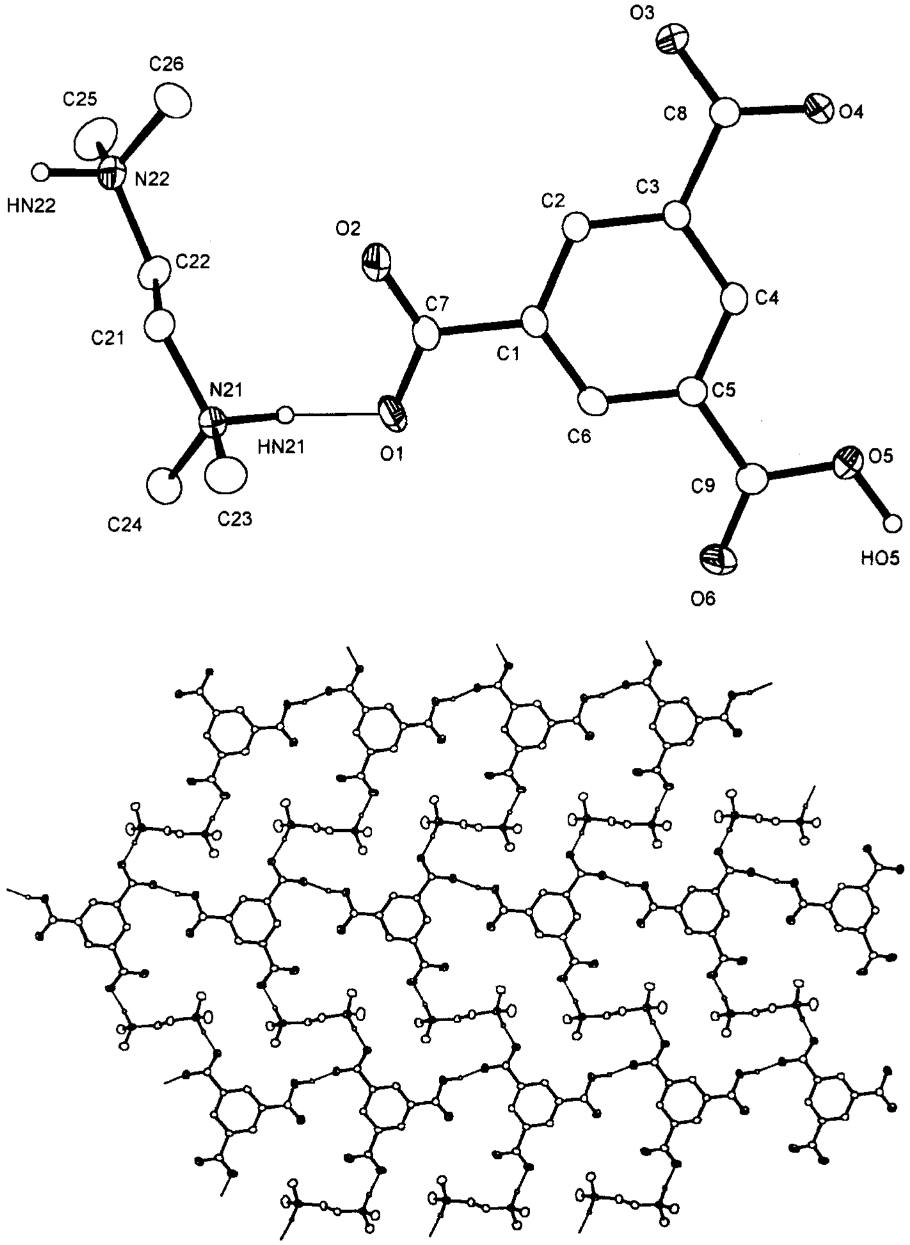

FIGURE 7 (a) ORTEP plot of 3 with atom labelling scheme and (b) overhead illustration of the 2-D infinite flat grids formed *via* strong ionic hydrogen bonding in 3.

tor[4]. We consider the following observations to be particularly salient in the context of future studies:

(i) Formation of ammonium-carboxylate anion-cation hydrogen bonding is favoured over competing molecule-molecule interactions.

TABLE III Summary of evidence for proton transfer in 1–3

compound	C-O distances (Å)	IR stretch (cm^{-1})
1	C7-O1 1.238(8) C7-O2 1.261(8)	1630 and 1416 (CO_2^-) 3340 (N^+-H)
2	C7-O1 1.260(7) C7-O2 1.261(7)	1561 and 1396 (CO_2^-) 3134 (N^+-H)
3	C7-O1 1.268(4) C7-O2 1.233(4) C8-O3 1.237(4) C8-O4 1.253(3)	1629 and 1579 (CO_2^-) 3342 (N^+-H)

(ii) The hydrogen(bis)carboxylate hydrogen bond is formed in **1–3** wherever feasible.

(iii) Anions of trimesic acid are predisposed to sustain infinite 2-D sheets because of their trigonal flat geometry.

(iv) The relatively high thermal stability and melting point of these salts is expected when one considers their polymeric nature and the thermodynamic strength of ionic hydrogen bonds.

(v) There is absence of catenation or interpenetration of the 2-D sheets in these new salts.

Further studies concerning the ability of anions derived from H_3-TMA to direct 2-D grid architecture are currently in progress, in particular $H_{1.5}$-$TMA^{1.5-}$ and TMA^{3-}.[23]

EXPERIMENTAL

General Methods

All chemicals were purchased from Aldrich Chemical Company Inc. and used as supplied. Methanol, 99.8%, was purchased from Caledon Laboratories Ltd. and was distilled over calcium hydride under dinitrogen. Deionized water was obtained from a Barnstead-Thermolyne D3700 NANOpure system. Melting points were determined on a Fisher-Johns melting point apparatus. ^1H NMR spectra were recorded at the Atlantic Regional Magnetic Resonance Center on a Bruker AC 250F Spectrometer. Infrared spectra were recorded on a Perkin-Elmer 1600 Fourier Transform Spectrophotometer by diffuse reflectance in potassium bromide.

Preparation of Salts

1 $[HMe_2NCH_2CH_2NMe_2H]2[1\text{-}CO_2\text{-}3,5(CO_2H)_2\text{-}C_6H_3]\cdot 2H_2O$ 2.00 g (9.52 mmol) of trimesic acid were dissolved in 35.0 mL of freshly distilled methanol. 1.66 g (2.15 ml, 14.3 mmol) of *N,N,N′,N′*-tetramethylethylenediamine were then added dropwise to this solution. The white precipitate which immediately formed was collected by suction filtration. X-ray quality crystals were obtained by dissolving 0.10 g of the white solid in 100 mL of hot deionized water and cooling to room temperature. Yield of crude product = 3.01 g, (6.11 mmol, 64.2%); m.p. = sublimed at 280°C. IR (KBr) cm^{-1}: N-H, s, 3578.3; O-H, b s, 3340.2; C-H, w, 2913; Ar-H, w, 3029.8; C=O, s, 1709.0; CO^{-2}, s, 1610.5 and 1438.9; C-H (oop), s, 772 and 747. ^1H NMR (DMSO): δ 2.49 (s, 12H, N-CH_3); δ 2.88 (s, 4H, -CH_2-N); δ 4.59 (s b, 4H, H_2O); δ 8.64 (s, 6H, Ar-**H**); δ 4.59 (s b, 2H, N^+-**H**)

2 $[HEt_2NCH_2CH_2NEt_2H]2[1\text{-}CO_2\text{-}3,5(CO_2H)_2\text{-}C_6H_3]$ 1.00 g (4.76 mmol) of trimesic acid was dissolved in 50.0 ml of deionized water. 1.21 g (1.52 ml, 7.03 mmol) of *N,N,N′,N′*-tetraethylethylenediamine were added dropwise. The reaction was to stirred at 100°C for 1 hour and solvent was removed via rotary evaporation at 70°C, affording a pale yellow solid. X-ray quality crystals were obtained by dissolving a small amount of the solid in hot methanol and cooling to room temperature. Yield of crude product = 2.12 g, (3.56 mmol, 74.8%); m.p. = partially melted at 189–93°C, turned brown at 270°C and melted at 289–91°C. IR (KBr) cm^{-1}: N-H, O-H, s b, 3629–3374; C-H, m, 2980; CO^{-2}, s, 1700 and 1562; C=C, m, 1612; C-N, w, 1354; C-H (oop), s, 771 and 745. ^1H NMR (DMSO): δ 1.06 (t, 12H, N-CH_2-CH_3); δ 2.50 (q, 8H, N-CH_2-CH_3); δ 2.80 (s, 4H, CH_2-N); δ 8.61 (s, 6H, Ar-**H**); δ 3.48 (s, 2H, N^+-**H**)

3 $[HMe_2NCH_2CH_2NMe_2H][1,3\text{-}(CO_2)_2\text{-}5\text{-}(CO_2H)C_6H_3]$ 1.00 g (4.76 mmol) of trimesic acid was dissolved in 50.0 ml of deionized water. 1.66 g (2.15 ml, 14.3 mmol) of *N,N,N′,N′*-tetramethylethylenediamine were added dropwise to the acidic solution. The reaction was refluxed at 100°C for 5 hours and allowed to cool to room temperature. Solvent was removed at 70°C via rotary evaporation, affording a slightly yellow viscous liquid. X-ray quality crystals were obtained by allowing the product to stand for 45 days at room temperature. Yield of crude product = 1.23 g, (2.73 mmol, 57.3%); m.p. = the crystals became opaque at 163–70°C, but did not melt below 300°C. IR (KBr) cm^{-1}: N-H, O-H, s b, 3288–2900; Ar-H, w, 3018; C-H, m, 2902; CO^{-2}, s, 1708 and 1578; C═C, m, 1629; C-N, w, 1357; C-H (oop), s, 781 and 757. ^1H NMR (DMSO): δ 2.61 (s, 12H, $N\text{-}CH_3$); δ 3.49 (s, 4H, $CH_2\text{-}N$); δ 8.58 (s, 3H, Ar-**H**)

X-Ray Crystallography

Single crystals suitable for x-ray crystallography were mounted and sealed in thin-walled glass capillaries and optically centered in the x-ray beam of an Enraf-Nonius CAD-4 diffractometer. Unit cell dimensions were determined *via* least squares refinement of the setting angles of 24 high angle reflections and intensity data were collected using the ω-2θ scan mode. Data were corrected for Lorentz, polarization and absorption effects but not for extinction. Pertinent data collection and structure refinement parameters are presented in Table I. The structures were solved using direct methods, all non-hydrogen atoms being refined with anisotropic thermal parameters. O-H, N-H and methyl hydrogen atoms were located *via* Fourier map inspection. Methylene and sp^2 hydrogen atoms were calculated with $D_{C\text{-}H}$ = 1.08 Å and $D_{C\text{-}H}$ = 1.00 Å, respectively. Thermal parameters and fractional coordinates were assigned based upon the atom to which they are bonded, and fixed during least squares refinement. Weights based upon counting statistics were used with the weight modifier, k in kF_o^2, being determined *via* evaluation of variation in the standard reflections that were obtained during the course of data collection. Values of R and R_w were given by $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ and $R_w = [\Sigma(w|F_o| - |F_c|)^2/\Sigma(wF_o^2)]^{1/2}$. All crystallographic calculations were conducted using the PC version of the NRCVAX[22] system implemented on 80486 based IBM compatible computers. Crystallographic figures were generated using ORTEP[22c]. Atomic coordi nates and anisotropic thermal parameters are available from the Cambridge Crystallographic Database.

Acknowledgments

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