

Hydrogen-bonding behaviour of benzene-1,2,4,5-tetracarboxylic acid: supramolecular structures of different dimensionality in the 2:1 adducts formed with 4,4'-bipyridyl and hexamethylenetetramine

A. J. Lough,^a P. S. Wheatley,^b G. Ferguson^{b†} and C. Glidewell^{b*}

^aLash Miller Chemical Laboratories, University of Toronto, Toronto, Ontario, Canada M5S 3H6, and ^bSchool of Chemistry, University of St Andrews, St Andrews, Fife KY16 9ST, Scotland

† On leave from: Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1.

Correspondence e-mail: cg@st-andrews.ac.uk

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Co-crystallization of benzene-1,2,4,5-tetracarboxylic acid, C₁₀H₆O₈, with 4,4'-bipyridyl, C₁₀H₈N₂, or with hexamethylenetetramine, C₆H₁₂N₄, from methanol solutions yields in each case a 2:1 salt, [(C₁₀H₉N₂)⁺]₂·[(C₁₀H₄O₈)²⁻] (1) and [(C₆H₁₃N₄)⁺]₂·[(C₁₀H₄O₈)²⁻] (2). In (1) the carboxylate anions lie across centres of inversion, but they contain no intramolecular O—H···O hydrogen bonds: the cations and anions are linked by strong O—H···N and N—H···O hydrogen bonds into a chain-of-rings, and these chains are further linked into a three-dimensional framework structure by means of C—H···O hydrogen bonds and aromatic π··π stacking interactions. Compound (2) contains two independent three-molecule aggregates, comprising a central anion and two cations, linked to the anion by means of short N—H···O hydrogen bonds. One of these aggregates is centrosymmetric, but the other is not, and the two types of anion both form two intramolecular O—H···O hydrogen bonds. The two types of three-molecule aggregate, in which all the anions are virtually parallel, are linked by short C—H···O hydrogen bonds into a molecular staircase.

1. Introduction

Benzene-1,3,5-tricarboxylic acid, C₆H₃(COOH)₃, trimesic acid, is trigonally symmetric and as such has been extensively employed as a building block in supramolecular chemistry (Herbstein & Kapon, 1979; Herbstein *et al.*, 1985; Sharma & Zaworotko, 1996; Melendez *et al.*, 1996; Meehan *et al.*, 1997; Sharma *et al.*, 1997; Ferguson *et al.*, 1998).

By contrast, the use in supramolecular chemistry of the rectangularly symmetric analogue benzene-1,2,4,5-tetracarboxylic acid, C₆H₂(COOH)₄, pyromellitic acid, has hardly been explored: only the adduct of this acid with 2,2'-bipyridyl has been reported (Mrvos-Sermek *et al.*, 1996) and this product is discussed below (§3.4). Here we report the synthesis and structural characterization of hydrogen-bonded adducts of benzene-1,2,4,5-tetracarboxylic acid with two organic bases, 4,4'-bipyridyl, NC₅H₄—C₅H₄N, and hexamethylenetetramine, C₆H₁₂N₄ (HMTA). These two products have similar stoichiometry, 2[amine]·C₁₀H₆O₈, and both are salts: [(C₁₀H₉N₂)⁺]₂·[(C₁₀H₄O₈)²⁻] (1) and [(C₆H₁₃N₄)⁺]₂·[(C₁₀H₄O₈)²⁻] (2), but they have wholly different supramolecular structures, dominated by the wholly different hydrogen-bonding behaviour of the (C₁₀H₄O₈)²⁻ anions in the two salts.

2. Experimental

2.1. Syntheses

Equimolar quantities of the acid and either of the amines, 4,4'-bipyridyl or hexamethylenetetramine, were separately

Table 1
Experimental details.

	(1)	(2)
Crystal data		
Chemical formula	C ₁₀ H ₄ O ₈ ·2(C ₁₀ H ₉ N ₂)	C ₁₀ H ₄ O ₈ ·2(C ₆ H ₁₃ N ₄)
Chemical formula weight	566.52	534.54
Cell setting	Triclinic	Triclinic
Space group	<i>P</i> 1	<i>P</i> 1
<i>a</i> (Å)	7.3974 (3)	9.7029 (6)
<i>b</i> (Å)	9.6352 (4)	10.9369 (7)
<i>c</i> (Å)	10.1688 (3)	16.7647 (11)
α (°)	64.872 (2)	84.271 (3)
β (°)	72.375 (2)	79.399 (3)
γ (°)	76.612 (2)	75.264 (3)
<i>V</i> (Å ³)	620.92 (4)	1688.55 (19)
<i>Z</i>	1	3
<i>D_x</i> (Mg m ⁻³)	1.515	1.577
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α
Wavelength (Å)	0.71073	0.71073
No. of reflections for cell parameters	2832	6124
θ range (°)	2.91–27.47	4.09–25.34
μ (mm ⁻¹)	0.112	0.122
Temperature (K)	100 (1)	100 (1)
Crystal form	Block	Block
Crystal size (mm)	0.35 × 0.27 × 0.25	0.25 × 0.25 × 0.20
Crystal colour	Colourless	Colourless
Data collection		
Diffractometer	KappaCCD	KappaCCD
Data collection method	φ scans and ω scans with κ offsets	φ scans and ω scans with κ offsets
Absorption correction	Multi-scan	Multi-scan
<i>T</i> _{min}	0.9618	0.9701
<i>T</i> _{max}	0.9725	0.9759
No. of measured reflections	9749	14 292
No. of independent reflections	2832	6124
No. of observed reflections	2272	2853
Criterion for observed reflections	<i>I</i> > 2 σ (<i>I</i>)	<i>I</i> > 2 σ (<i>I</i>)
<i>R</i> _{int}	0.031	0.078
θ _{max} (°)	27.47	25.34
Range of <i>h</i> , <i>k</i> , <i>l</i>	0 → <i>h</i> → 9 –11 → <i>k</i> → 12 –12 → <i>l</i> → 13	0 → <i>h</i> → 11 –12 → <i>k</i> → 13 –19 → <i>l</i> → 20
Refinement		
Refinement on	<i>F</i> ²	<i>F</i> ²
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)]	0.0378	0.0482
<i>wR</i> (<i>F</i> ²)	0.1076	0.1142
<i>S</i>	1.082	0.839
No. of reflections used in refinement	2832	6124
No. of parameters used	195	518
H-atom treatment	H atom parameters constrained	H atom parameters constrained
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0668P)^2 + 0.0415P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0392P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$
(Δ/σ) _{max}	0.000	0.000
$\Delta\rho$ _{max} (e Å ⁻³)	0.259	0.275
$\Delta\rho$ _{min} (e Å ⁻³)	–0.328	–0.269
Extinction method	None	SHELXL97 (Sheldrick, 1997a)
Extinction coefficient	–	0.0016 (5)
Source of atomic scattering factors	<i>International Tables for Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	<i>International Tables for Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Computer programs		
Data collection	KappaCCD server software (Nonius, 1997)	KappaCCD server software (Nonius, 1997)
Cell refinement	DENZO-SMN (Otwinowski & Minor, 1997)	DENZO-SMN (Otwinowski & Minor, 1997)
Data reduction	DENZO-SMN (Otwinowski & Minor, 1997)	DENZO-SMN (Otwinowski & Minor, 1997)
Structure solution	SHELXS97 (Sheldrick, 1997a)	SHELXS97 (Sheldrick, 1997a)
Structure refinement	NRCVAX96 and SHELXL97 (Sheldrick, 1997b)	NRCVAX96 and SHELXL97 (Sheldrick, 1997b)
Preparation of material for publication	NRCVAX96, SHELXL97 and WordPerfect macro PRPKAPPA (Ferguson, 1999)	NRCVAX96, SHELXL97 and WordPerfect macro PRPKAPPA (Ferguson, 1999)

dissolved in methanol. The solutions were mixed and set aside to crystallize. In the case of 4,4'-bipyridyl, (1) was readily obtained in analytically pure form; analysis: found C 63.6, H 3.9, N 9.8%; C₃₀H₂₂N₄O₈ requires C 63.6, H 3.9, N 9.9%. With hexamethylenetetramine, crystallization within 24 h yielded (2); analysis: found C 49.8, H 5.6, N 20.8%; C₂₂H₃₀N₈O₈ requires C 49.4, H 5.7, N 21.0%. Entirely analogous results were obtained, for both (1) and (2), using molar ratios of acid-to-amine in the range 1:2–2:1. However, when attempts were made, by the use of slower crystallization regimes, to improve the crystal quality of (2), the sole product obtained was the ammonium salt [(NH₄)⁺]₂·[(C₁₀H₄O₈)²⁻] (3); analysis: found 41.7, H 4.1, N 9.7%; C₁₀H₁₂N₂O₈ requires C 41.7, H 4.2, N 9.7%. Crystals of (1) and (2) suitable for single-crystal X-ray diffraction were selected directly from the analytical samples.

2.2. Data collection, structure solution and refinement

Diffraction data for (1) and (2) were collected at 100 (1) K using a Nonius Kappa-CCD diffractometer, with graphite-monochromated Mo *K* α radiation ($\lambda = 0.71073$ Å). Other details of cell data, data collection and refinement are summarized in Table 1, together with details of the software employed (Ferguson, 1999; Gabe *et al.*, 1989; Johnson, 1976; Nonius, 1997; Otwinowski & Minor, 1997; Sheldrick, 1997a,b; Spek, 1999). The structures were solved by direct methods and refined with all data on *F*². A weighting scheme based upon

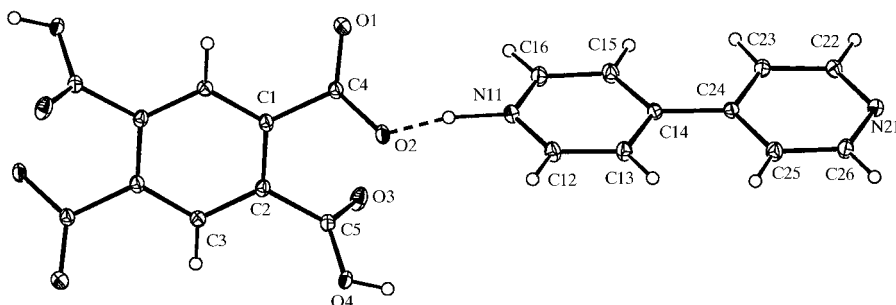


Figure 1
The molecular components of (1), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

$P = [F_o^2 + 2F_c^2]/3$ was employed in order to reduce statistical bias (Wilson, 1976).

For (1) the space group $P\bar{1}$ was chosen and confirmed by the successful structure solution and refinement. All H atoms in (1) were located from difference maps: H atoms bonded to C and O were included in the refinement as riding atoms. Atom H11, bonded to N11, was fully ordered, but its position was almost midway between N11 and O2 (Table 2); consequently, its coordinates and its U_{iso} were refined.

Compound (2) is also triclinic and the structure was apparently solved readily in space group $P\bar{1}$ to reveal three HMTA molecules and one acid molecule in general positions, together with another acid lying across a centre of inversion: the molar ratio of HMTA to acid is thus 2:1, consistent with the elemental analysis. The resulting value of $Z' = 1.5$ is extremely rare in space group $P\bar{1}$ (Wilson, 1993; Brock & Dunitz, 1994). In this structure solution (denoted A) the molecular units are arranged into two very similar three-component aggregates, in each of which a dianion ($C_{10}H_4O_8$)²⁻ is flanked by two ($C_6H_{13}N_4$)⁺ cations: one of

these aggregates is centrosymmetric and the other is not. It was clear before refinement commenced that in this solution the centrosymmetric aggregate appeared to be ordered, but the other aggregate showed clear signs of disorder: when this disorder was modelled with two independent orientations for each cation, the s.o.f.s refined to 0.68 (1) and 0.32 (1) for both of the independent cations. However, in all such refinements the R factor consistently remained above 0.10.

Despite the E statistics for (2), which pointed strongly to a centrosymmetric space group, structure solution in space group $P1$ was therefore also investigated. The structure solved smoothly in $P1$ (structure solution B) to give, as expected, six independent cations and three independent anions, arranged in three similar but independent three-component aggregates, as found in solution A. All H atoms in (2) were located from difference maps and those bonded to C and N were included in this refinement as riding atoms: the H atoms in the O—H...O units were all ordered at sites close to the mid-points of the O...O vectors: the coordinates of these H atoms were obtained from difference maps, and were thereafter fixed. With N and O anisotropic and C and H isotropic, solution B converged to R of 0.0495 for 697 variables and 6124 data, while with C, N and O all anisotropic, R converged to 0.0463 for 1027 variables, albeit with a data/parameter ratio of only 5.96. At this point a search for missing symmetry was made using the January 1999 version of *PLATON* (Spek, 1999): a possible inversion centre was identified, but this related only *ca* 80% of the independent non-H atoms and a significant number of atoms showed displacements of up to 0.29 Å from the posi-

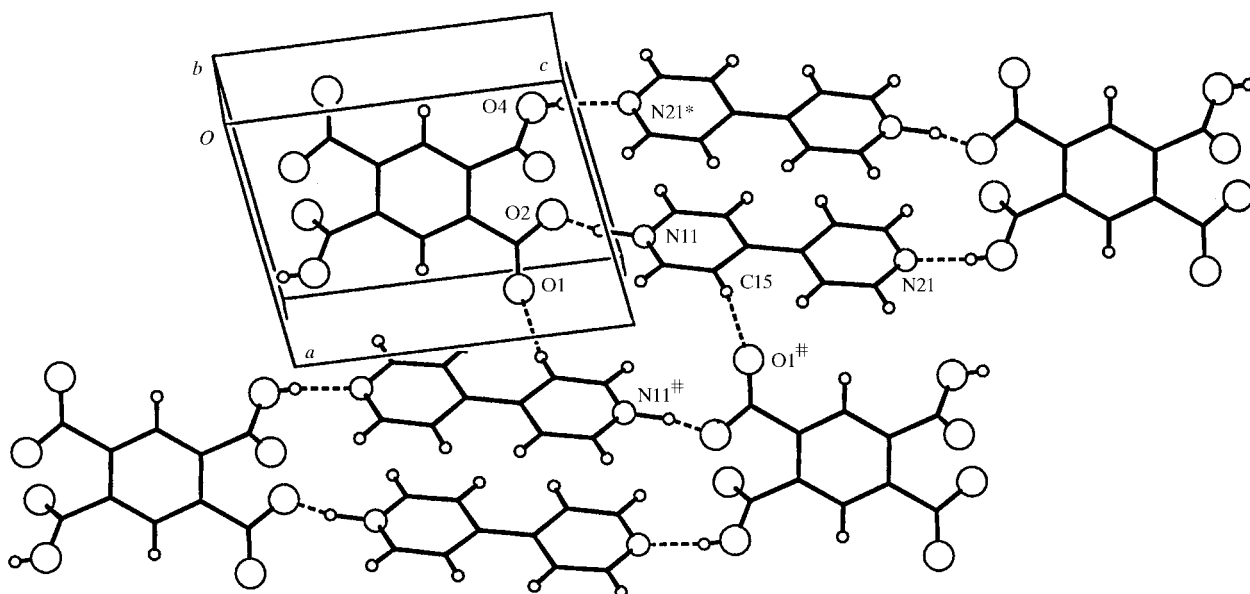


Figure 2
Part of the crystal structure of (1), showing two $C_2^2(17)$ [$R_4^4(32)$] chains-of-rings running parallel to $[01\bar{2}]$ and linked by C—H...O hydrogen bonds. Atoms marked with a star (*) or hash (#) are at the symmetry positions $(1 - x, -y, 3 - z)$ and $(2 - x, -y, 2 - z)$, respectively.

Table 2
Hydrogen bond parameters (Å, °).

Compound (1)					
N11...O2	2.521 (2)	H11...O2	1.32 (2)	N11—H11...O2	168 (2) [†]
O4...N21 ⁱ	2.613 (2)	H4...N21 ⁱ	1.78	O4—H4...N21 ⁱ	173
C3...O1 ⁱⁱ	3.312 (2)	H3...O1 ⁱⁱ	2.41	C3—H3...O1 ⁱⁱ	158
C12...O2 ⁱⁱⁱ	3.259 (2)	H12...O2 ⁱⁱⁱ	2.33	C12—H12...O2 ⁱⁱⁱ	167
C15...O1 ^{iv}	3.243 (2)	H15...O1 ^{iv}	2.32	C15—H15...O1 ^{iv}	165
Compound (2)					
O13...O12	2.409 (3)	H13...O12	1.57	O13—H13...O12	178
O23...O22	2.404 (3)	H23...O22	1.57	O23—H23...O22	175
O27...O26	2.402 (3)	H27...O26	1.56	O27—H27...O26	178
N31...O11	2.727 (3)	H31...O11	1.85	N31—H31...O11	157
N41...O21	2.750 (3)	H41...O21	1.82	N41—H41...O21	174
N51...O25	2.709 (3)	H51...O25	1.79	N51—H51...O25	168
C46...O14 ^v	3.218 (4)	H46A...O14 ^v	2.28	C46—H46A...O14 ^v	157
C56...O28 ^{vi}	3.273 (4)	H56B...O28 ^{vi}	2.30	C56—H56B...O28 ^{vi}	168

Symmetry codes: (i) $1-x, -y, 3-z$; (ii) $-1+x, y, z$; (iii) $1-x, 1-y, 2-y$; (iv) $2-x, -y, 2-z$; (v) $1-x, 1-y, 1-z$; (vi) $2-x, -y, -z$. [†] Refined bond length N11—H11 is 1.22 (2) Å

tions required for centrosymmetry. When the atom coordinates from the $P1$ refinement were used as the starting point for a $P\bar{1}$ refinement based upon 1.5 acid units and six independent cations, each with 0.5 occupancy, the R factor remained above 0.20, and the behaviour of the displacement parameters was far from satisfactory. The original $P\bar{1}$ structure (solution A), with an effective 2:1 ratio between the major and minor orientations of the disordered cations, cannot readily be

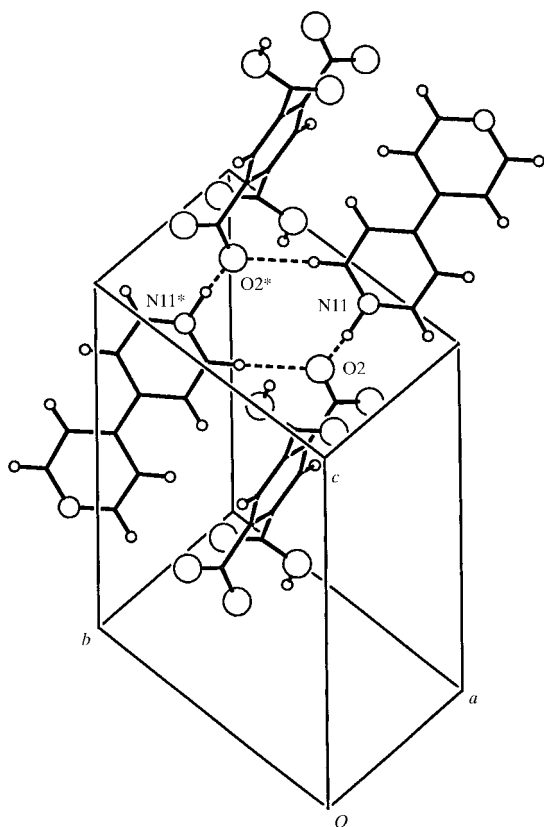


Figure 3
Part of the crystal structure of (1), showing formation of one of the centrosymmetric $R_4^2(10)$ rings: for the sake of clarity, only a small number of molecular components are drawn. Atoms marked with a star (*) are at the symmetry position $(1-x, 1-y, 2-z)$.

reconciled with a pseudo-centrosymmetric superimposition of two independent sets of sites, as this would require s.o.f.s of 0.5, rather than the 0.68 (1) and 0.32 (1) found. Careful inspection of packing diagrams derived from the refined solution B suggested the presence of centres of inversion. When the centroid of one of the acid units was arbitrarily placed at (0.5, 0.5, 0.5), the centroids of the other two acid units were close to (0.17, 0.83, 0.83) and (0.83, 0.17, 0.17), respectively, and there appeared to be a centre of inversion at (0.333, 0.667, 0.667). After a suitable origin shift and coordinates transformation, this structure solution in space group $P\bar{1}$ refined smoothly and rapidly, with all non-H atoms anisotropic, to $R = 0.0483$ for 518 variables. In the refinement of solution C all H atoms, having been located in ordered sites from difference maps, were included as riding atoms.

The current, July 1999, version of *PLATON* successfully detected these inversion centres. The two $P\bar{1}$ structure solutions (denoted A and C) thus differ only in the identity of the centrosymmetric aggregate. In the $P1$ solution B , from which solution C was directly derived, there are four types of short $C-H \cdots O$ hydrogen bonds, reduced to only two independent $C-H \cdots O$ hydrogen bonds in solution C . It was, in fact, the pattern generated by these hydrogen bonds (for the $P\bar{1}$ structure) which materially assisted in the identification of the inversion centre actually present in the $P1$ structure. Thus, after the *SHELXS97* direct methods solution had generated a structure, A , different from the correct one by an origin shift of $(-0.333, 0.333, 0.333)$, and the symmetry-detecting routines in the January 1999 version of *PLATON* had failed to locate the inversion centre in solution B , the clear pattern of the soft intermolecular interactions provided the key clue to the correct structure. It is interesting to note that attempted solution of the structure (2) in $P\bar{1}$ led to a false solution; the structure could be solved readily in space group $P1$ and then transformed back to the centrosymmetric $P\bar{1}$ system by appropriate origin choice. Quite the opposite situation was found for the tetragonal compound 2,2'-biphenol-1,4-diazabicyclo[2.2.2]octane (2/1), where the E statistics pointed strongly to space group $P4/m$; no centrosymmetric solution was possible, however, and the structure could only be solved and successfully refined in the non-centrosymmetric space group $P\bar{4}$ (Glidewell *et al.*, 1999). It has recently been noted that the use of tests based on E statistics alone to distinguish between space groups $P1$ and $P\bar{1}$ can sometimes be misleading and indeed can lead to conclusions which are chemically seriously in error (Walker *et al.*, 1999).

The diagrams were prepared with the aid of *PLATON* (Spek, 1999). Hydrogen-bond dimensions are presented in Table 2 and other selected dimensions in Table 3.¹ Fig. 1 shows the molecular components of (1) and Figs. 2–5 illustrate

¹ Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR0006). Services for accessing these data are described at the back of the journal.

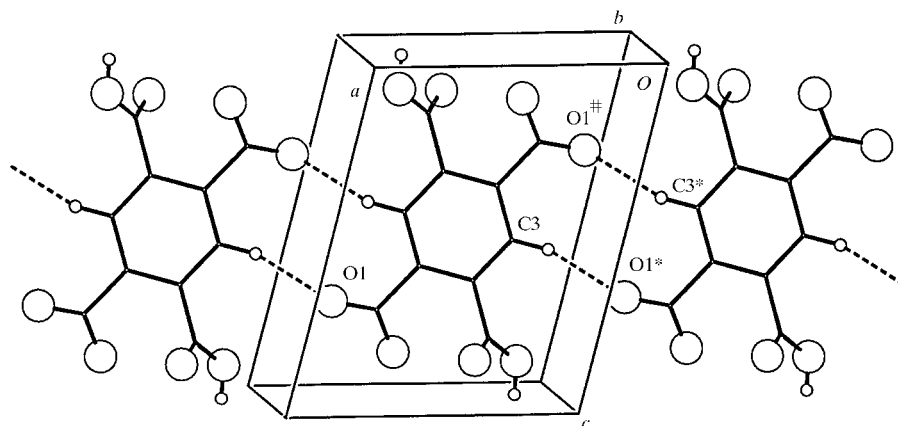


Figure 4
Part of the crystal structure of (1) showing a $C(6)R_2^2(10)$ chain-of-rings running parallel to $[100]$. Atoms marked with a star (*) or hash (#) are at the symmetry positions $(-1+x, y, z)$ and $(1-x, 1-y, 1-z)$, respectively.

aspects of the supramolecular structure of (1); similarly, for (2), Fig. 6 shows the molecular components, and Figs. 7 and 8 illustrate aspects of the supramolecular structures. Figs. 9–13 illustrate aspects of related structures retrieved from the Cambridge Structural Database (Allen & Kennard, 1993).

3. Results and discussion

3.1. Co-crystallization behaviour

Co-crystallization, from solutions in methanol, of mixtures of benzene-1,2,4,5-tetracarboxylic acid and 4,4'-bipyridyl

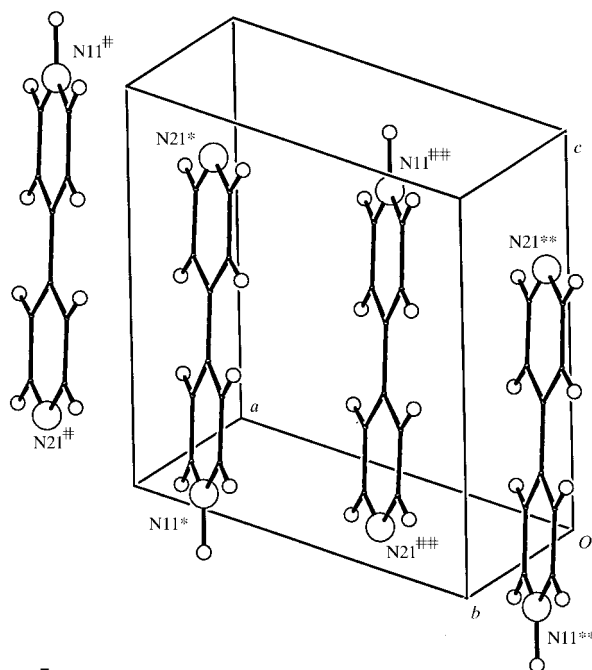
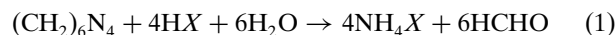


Figure 5
Part of the crystal structure of (1) showing a sequence of parallel $\pi \cdots \pi$ stacked 4,4'-bipyridyl units: cations marked with a single or double star (*) are at the symmetry positions $(x, 1+y, -1+z)$ and $(-1+x, 1+y, -1+z)$, and those marked with a single or double hash (#) are at the symmetry positions $(2-x, -y, 2-z)$ and $(1-x, 1-y, 2-z)$, respectively.

having a wide range of initial compositions always yielded (1) in analytically pure form: no evidence was obtained for any crystalline products containing methanol of solvation. It may therefore be concluded that (1) represents a particularly deep minimum on the potential energy surface of this three-component system, whose phase behaviour is correspondingly simple.

The behaviour of mixtures of benzene-1,2,4,5-tetracarboxylic acid and hexamethylenetetramine, on the other hand, is complicated by chemical reaction. Most crystallization attempts yielded the ammonium salt $[(\text{NH}_4)^+]_2 \cdot [(\text{C}_{10}\text{H}_4\text{O}_8)^{2-}]$ (3) as the sole

crystalline product, obtained in analytically pure form direct from the initial crystallization process. The formation of (3) is an example of the well known acid-promoted decomposition of HMTA to yield ammonium salts and methanal [equation (1)].



With a molar ratio of benzene-1,2,4,5-tetracarboxylic acid to HMTA of 2:1, this process can be effectively quantitative.

However, when reasonably fast crystallization was employed (2) was obtained: since the formation of (2) from the starting components requires only proton transfer from the acid to the HMTA, it seems plausible that (2) is the primary intermediate in the multi-step process summarized in equation (1). While several salts, $(\text{C}_6\text{H}_{13}\text{N}_4)^+ \cdot \text{X}^-$, derived from simple inorganic acids have been reported (Mak *et al.*, 1983; Chou *et al.*, 1987; Tebbe & Nagel, 1995), the Cambridge Structural Database (Allen & Kennard, 1993) contains only one example of such a salt formed by an organic acid. The 1:1 compound formed with suberic acid, $\text{HOCO}(\text{CH}_2)_6\text{COOH}$, has an incommensurate structure in which the H atoms could not be unambiguously located (Gaillard *et al.*, 1996), but the C–O bond lengths were consistent with a single proton transfer to form the salt $[(\text{C}_6\text{H}_{13}\text{N}_4)^+][\{\text{HOCO}(\text{CH}_2)_6\text{COO}\}^-]$.

3.2. Supramolecular structures of (1) and (2)

3.2.1. Compound (1). Compound (1) is a salt, $[(\text{C}_{10}\text{H}_9\text{N}_2)^+]_2 \cdot [(\text{C}_{10}\text{H}_4\text{O}_8)^{2-}]$, in which each molecule of the tetracarboxylic acid has transferred two protons, one to each of two 4,4'-bipyridyl molecules: all the H atoms are fully ordered. The anion $(\text{C}_{10}\text{H}_4\text{O}_8)^{2-}$ lies across a centre of inversion and the $(\text{C}_{10}\text{H}_9\text{N}_2)^+$ cation lies in a general position. Each cation acts as both donor and acceptor of hard (Braga *et al.*, 1995) hydrogen bonds, and the centrosymmetric anion acts as a double donor and a double acceptor. The molecular components (Fig. 1) are linked by hard hydrogen bonds of O–H \cdots N and N–H \cdots O types into a chain-of-rings (Bernstein *et al.*, 1995; Fig. 2) and these chains are further linked by

Table 3
Selected geometric parameters (Å, °).

Compound (1)			
C4—O1	1.228 (2)	C4—O2	1.285 (2)
C5—O3	1.214 (2)	C5—O4	1.314 (2)
N11—C12	1.340 (2)	N11—C16	1.331 (2)
N21—C22	1.340 (2)	N21—C26	1.338 (2)
C2—C1—C3 ⁱ	119.8 (1)	C1—C2—C3	120.0 (1)
C2—C1—C4	120.7 (1)	C1—C2—C5	119.8 (1)
C3 ⁱ —C1—C4	119.5 (1)	C3—C2—C5	120.0 (1)
C1 ⁱ —C3—C2	120.2 (2)		
O1—C4—O2	126.4 (1)	O3—C5—O4	125.3 (1)
C12—N11—C16	120.0 (1)	C22—N21—C26	117.8 (1)
O1—C4—C1—C2	145.8 (2)	O2—C4—C1—C2	-35.2 (2)
O3—C5—C2—C1	-67.6 (2)	O4—C5—C2—C1	113.1 (2)
Interplanar angle: (N11—C16)^(N21—C26)			3.2 (1)
Compound (2)			
C14—O11	1.243 (3)	C14—O12	1.280 (3)
C15—O13	1.305 (3)	C15—O14	1.212 (3)
C27—O21	1.246 (3)	C27—O22	1.283 (3)
C28—O23	1.295 (3)	C28—O24	1.231 (3)
C29—O25	1.245 (3)	C29—O26	1.280 (3)
C210—O27	1.311 (3)	C210—O28	1.220 (3)
N31—C32	1.523 (3)	N33—C32	1.441 (3)
N31—C36	1.512 (3)	N35—C36	1.454 (3)
N31—C37	1.512 (3)	N310—C37	1.441 (3)
N41—C42	1.517 (3)	N43—C42	1.454 (3)
N41—C46	1.524 (3)	N45—C46	1.438 (3)
N41—C47	1.515 (3)	N410—C47	1.447 (3)
N51—C52	1.508 (3)	N53—C52	1.441 (3)
N51—C56	1.521 (3)	N55—C56	1.441 (3)
N51—C57	1.521 (3)	N510—C57	1.448 (3)
N33—C34	1.466 (4)	N33—C38	1.481 (3)
N35—C34	1.476 (4)	N35—C39	1.471 (3)
N310—C38	1.469 (4)	N310—C39	1.461 (4)
N43—C44	1.480 (3)	N43—C48	1.470 (3)
N45—C44	1.464 (3)	N45—C49	1.461 (3)
N410—C48	1.470 (4)	N410—C49	1.475 (3)
N53—C54	1.476 (3)	N53—C58	1.472 (3)
N55—C54	1.470 (4)	N55—C59	1.467 (3)
N510—C58	1.473 (4)	N510—C59	1.486 (3)
C12—C11—C14	128.6 (3)	C12—C11—C13 ⁱ	118.0 (2)
C13 ⁱ —C11—C14	113.5 (3)	C11—C12—C13	117.4 (3)
C11—C12—C15	129.7 (3)	C11 ⁱ —C13—C12	124.6 (3)
C13—C12—C15	112.8 (3)		
C22—C21—C27	127.7 (3)	C26—C21—C22	117.8 (3)
C26—C21—C27	114.4 (3)	C21—C22—C23	117.0 (3)
C21—C22—C28	129.7 (3)	C22—C23—C24	125.5 (3)
C23—C22—C28	113.2 (3)	C23—C24—C25	117.6 (3)
C25—C24—C29	128.8 (3)	C24—C25—C26	117.2 (3)
C23—C24—C29	113.5 (3)	C25—C26—C21	124.8 (3)
C24—C25—C210	129.3 (3)		
C26—C25—C210	113.5 (3)		
O11—C14—O12	121.2 (3)	O13—C15—O14	120.6 (3)
O21—C27—O22	121.9 (3)	O23—C28—O24	120.5 (3)
O25—C29—O26	122.2 (3)	O27—C210—O28	120.9 (3)
O11—C14—C11—C12	177.6 (3)	O12—C14—C11—C12	-3.3 (4)
O14—C15—C12—C11	-173.2 (2)	O13—C15—C12—C11	6.7 (4)
O21—C27—C21—C22	-166.9 (2)	O22—C27—C21—C22	11.9 (4)
O24—C28—C22—C21	-177.0 (2)	O23—C28—C22—C21	3.3 (4)
O25—C29—C24—C25	170.3 (2)	O26—C29—C24—C25	-7.3 (4)
O28—C210—C25—C24	177.1 (3)	O27—C210—C25—C24	-4.2 (4)

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

soft (Braga *et al.*, 1995) C—H···O hydrogen bonds into a continuous three-dimensional framework (Figs. 2–4), but there are no O—H···O hydrogen bonds within the structure of (1).

Within the asymmetric unit, the protonated N11 acts as a donor to one of the carboxylate O atoms, O2; the hydroxyl O atom, O4, in the anion at (x, y, z) acts as a hydrogen-bond donor to the neutral N21 in the cation at $(1 - x, -y, 3 - z)$. These two hydrogen bonds, one O—H···N and one N—H···O, thus produce a centrosymmetric $R_4^4(32)$ ring (Fig. 2); between the anions centred at $(0.5, 0.5, 0.5)$ and $(0.5, -0.5, 2.5)$ lies the $R_4^4(32)$ ring centred at $(0.5, 0, 1.5)$. These hydrogen bonds and the centrosymmetric nature of the anions combine to generate a $C_2^2(17) [R_4^4(32)]$ chain-of-rings (Fig. 2) running parallel to the $[01\bar{2}]$ direction.

There are three types of C—H···O hydrogen bonds which link the $[01\bar{1}]$ chains, forming further chains running in the $[01\bar{1}]$, $[10\bar{1}]$ and $[100]$ directions (Figs. 2–4), thus forming a three-dimensional continuum. Atom C15 in the cation at (x, y, z) acts as a hydrogen-bond donor to O1 at $(2 - x, -y, 2 - z)$, while C15 at $(2 - x, -y, 2 - z)$ in turns acts as a donor to O1 at (x, y, z) . The effect of these C—H···O hydrogen bonds is to link the $R_4^4(32)$ rings centred at $(0.5, 0, 1.5)$ and $(1.5, 0, 0.5)$, see Fig. 2, and propagation of these interactions generates a $C_2^2(14) [R_4^4(16)]$ chain-of-rings running parallel to the $[10\bar{1}]$ direction (Fig. 2). Atom C12 in the cation at (x, y, z) acts as a donor to O2 at $(1 - x, 1 - y, 2 - z)$, thus forming a centrosymmetric $R_4^2(10)$ ring (Fig. 3), where the excess of donors over acceptors is accounted for by both O2 atoms acting as double acceptors. These interactions link the $R_4^4(32)$ rings centred at $(0.5, 0, 1.5)$ and $(0.5, 1, 0.5)$, thus generating a $C_2^2(15) [R_4^2(10)]$ chain-of-rings running parallel to the $[01\bar{1}]$ direction (Fig. 3). The third type of C—H···O hydrogen bond generates a chain-of-rings motif involving only the anions (Fig. 4). Atom C3 at (x, y, z) acts as a donor to O1 at $(-1 + x, y, z)$, while C3 at $(-1 + x, y, z)$ in turn acts as a donor to O1 at $(1 - x, 1 - y, 1 - z)$; C3 at (x, y, z) and O1 at $(1 - x, 1 - y, 1 - z)$ form part of the same anion centred at $(0.5, 0.5, 0.5)$. Hence, a $C(6)[R_2^2(10)]$ chain-of-rings is generated running parallel to the $[100]$ direction.

In addition to the hydrogen bonds, the supramolecular structure is stabilized by aromatic $\pi \cdots \pi$ stacking interactions (Fig. 5). Within each of the centrosymmetric $R_4^4(32)$ rings in the $[01\bar{2}]$ chains (Fig. 2), the cationic pyridyl ring at (x, y, z) is almost parallel to the neutral ring at $(2 - x, -y, 3 - z)$ [dihedral angle between the ring planes, $3.2(1)^\circ$] and the perpendicular distance between these planes is $3.34(1)$ Å; similarly, between neighbouring chains the perpendicular separation of the corresponding aryl rings is $3.45(1)$ Å. Hence, there is a series of essentially parallel bipyridyl units whose relative disposition is ideal for aromatic $\pi \cdots \pi$ stacking interactions (Fig. 5).

3.2.2. Compound (2). Compound (2) is also a salt, $[(C_6H_{13}N_4)^+]_2[(C_{10}H_4O_8)^{2-}]$, in which each molecule of the tetracarboxylic acid has transferred two protons, one to each of two hexamethylenetetramine molecules: all the H atoms are

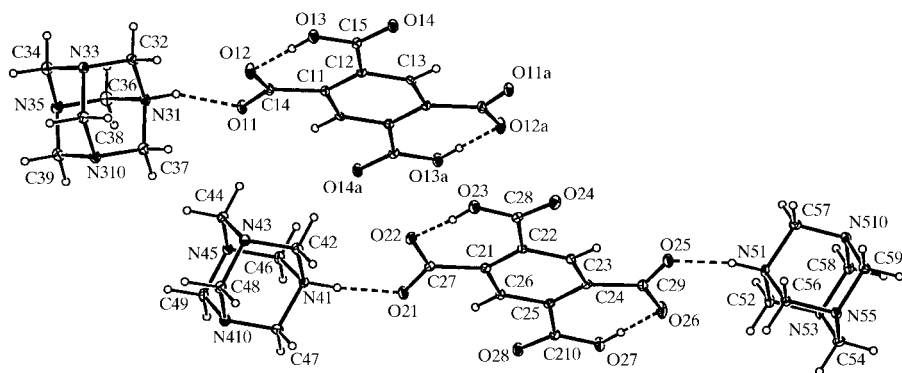


Figure 6
The molecular components of (2), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

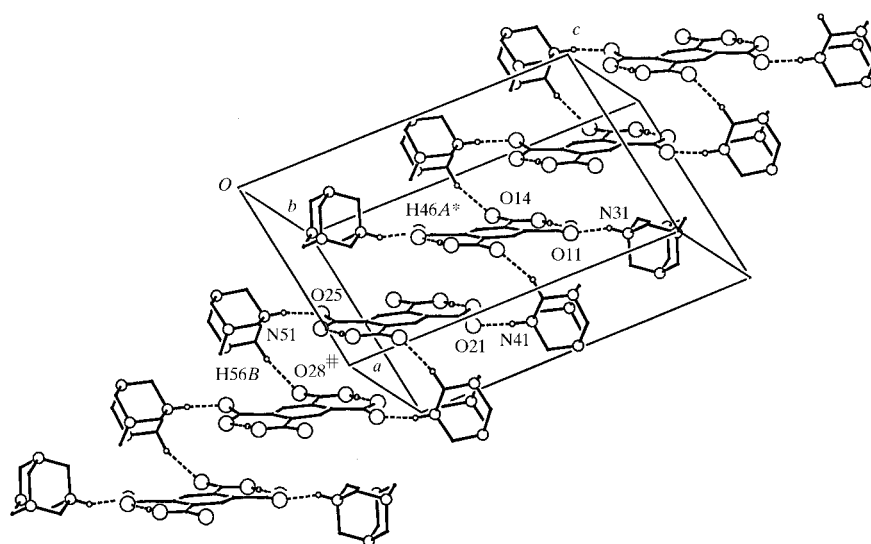


Figure 7
Part of the crystal structure of (2), showing a $C_6^6(35)$ [$R_4^4(20)$] chain-of-rings running parallel to $[\bar{1}11]$. For the sake of clarity, H atoms bonded to C but not participating in hydrogen-bond formation are omitted. Atoms marked with a star (*) or hash (#) are at the symmetry positions $(1-x, 1-y, 1-z)$ and $(2-x, -y, -z)$, respectively.

fully ordered. Each cation acts just as a donor of hard hydrogen bonds, of N—H...O type, and each anion as a double acceptor of such bonds: the O—H...O hydrogen bonds are all intramolecular and there are no O—H...N hydrogen bonds (Table 2). The nature and the distribution of the hard hydrogen bonds in (1) and (2) are thus entirely different.

The asymmetric unit consists of three cations and one anion lying in general positions and one half of an anion lying across a centre of inversion (Fig. 6). In each of the independent anions, there are short intramolecular O—H...O hydrogen bonds and each anion acts as an acceptor of two N—H...O hydrogen bonds from a pair of cations (Fig. 6). The unit cell thus contains three of these three-component aggregates, one of which is centrosymmetric, while the other two are non-centrosymmetric. The anions are all essentially parallel to one another and both types of anion are acceptors of C—H...O

hydrogen bonds in which the cation are the donors. These C—H...O hydrogen bonds serve to link the three-component aggregates into a continuous chain-of-rings, which takes the form of a molecular staircase (Figs. 7 and 8). The anion of type 1 containing atoms C1 n and O1 m ($n = 1-5$, $m = 1-4$), which is centrosymmetric, is an acceptor of two C—H...O hydrogen bonds from two different cations. The anion of type 2, containing atoms C2 n and O2 m ($n = 1-10$, $m = 1-8$), accepts just one C—H...O hydrogen bond (Figs. 7 and 8). The cations containing N41 and N51 (cations of types 4 and 5, respectively) each act as a donor of one C—H...O hydrogen bond, but that containing N31 (cation 3) forms no such bonds (Fig. 7 and Table 2).

Atom C56 in the type 5 cation at (x, y, z) acts as hydrogen-bond donor, via H56B, to O28 in the type 2 anion at $(2-x, -y, -z)$, while N51 in this cation is donor to O25 in the type 2 anion, also at (x, y, z) ; this same anion also accepts an N—H...O hydrogen bond from the type 5 cation at $(2-x, -y, -z)$ and this same cation at $(2-x, -y, -z)$ is a donor, in a C—H...O hydrogen bond, to O28 at (x, y, z) . These two types of hydrogen bond thus generate a centrosymmetric $R_4^4(20)$ ring centred at $(1, 0, 0)$, and this ring is linked to a similar ring centred at $(0, 1, 1)$ via the type 1 anion centred at $(0.5, 0.5, 0.5)$, see Fig. 7 and Table 2. The type 4 cation at (x, y, x) forms an N—H...O hydrogen bond to

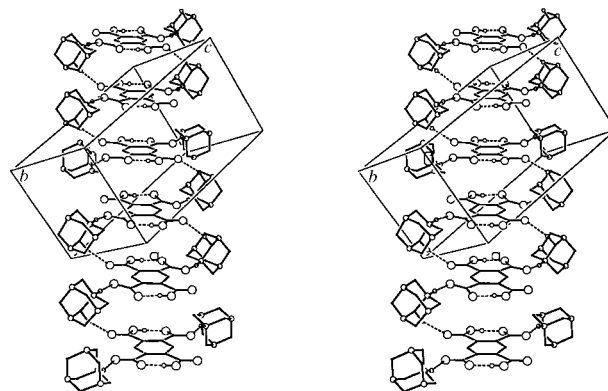


Figure 8
Stereoview of part of the crystal structure of (2), showing the molecular staircase rising along the $[\bar{1}11]$ diagonal of the unit cell. For the sake of clarity, H atoms bonded to C but not participating in hydrogen-bond formation are omitted.

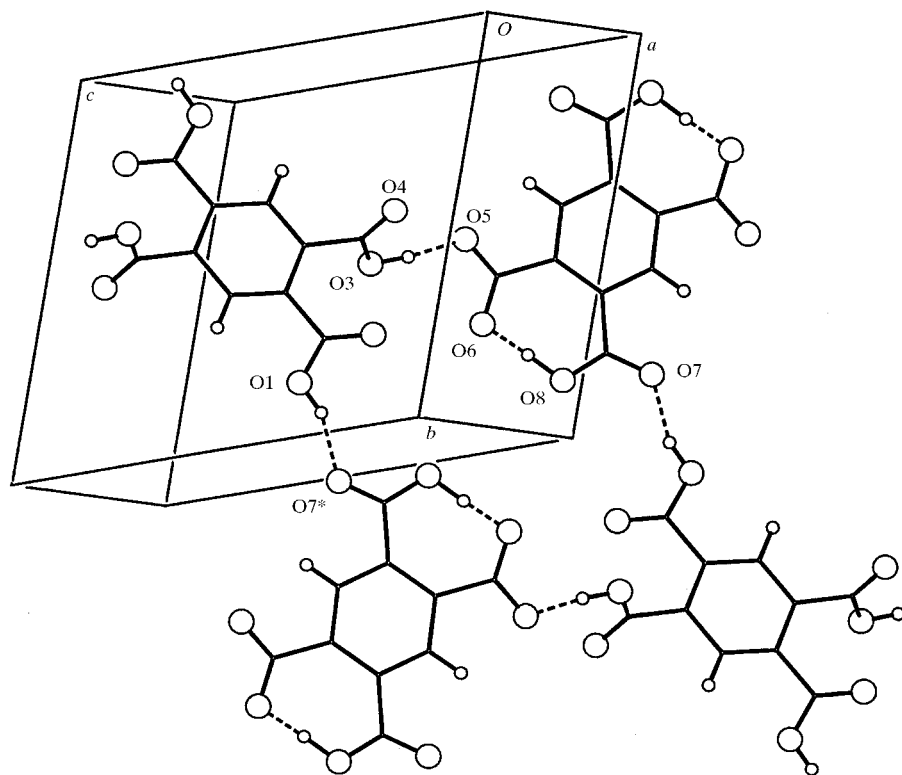


Figure 9
Part of the crystal structure of $[[2,2'\text{-bipyridyl}]\text{H}]^+_2 \cdot [(\text{C}_{10}\text{H}_4\text{O}_8)^{2-}] \cdot (\text{C}_{10}\text{H}_6\text{O}_8)$ (Mrvos-Sermek *et al.*, 1996), showing a two-dimensional $R_4^4(28)$ net built from acid species only. The atom marked with a star (*) is at the symmetry position $(1-x, 2-y, -z)$.

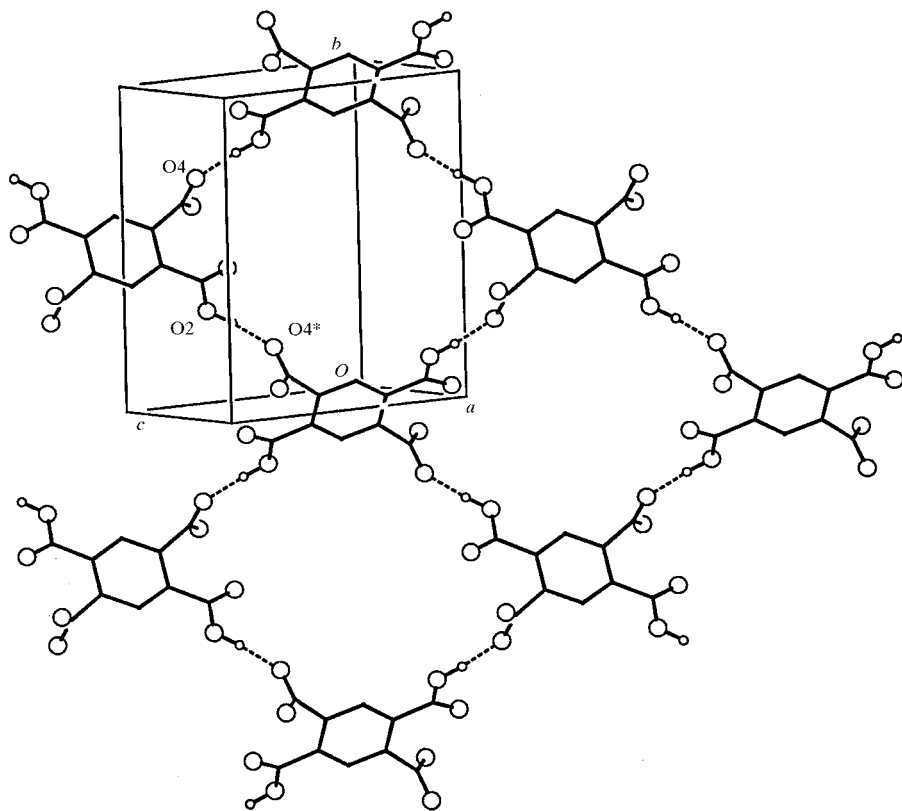


Figure 10
Part of the crystal structure of $[(\text{NH}_4)^+]_2 \cdot [(\text{C}_{10}\text{H}_4\text{O}_8)^{2-}]$ (Jessen *et al.*, 1992) showing a two-dimensional $R_4^4(28)$ net built from anions only. H atoms bonded to C are omitted for the sake of clarity; the atom marked with a star (*) is at the symmetry position $(1-x, -\frac{1}{2}+y, \frac{3}{2}-z)$.

O21 at (x, y, z) and a $\text{C}-\text{H} \cdots \text{O}$ hydrogen bond to O14 at $(1-x, 1-y, 1-z)$. The symmetry-related O14 at (x, y, z) , in the same anion, is an acceptor from C46 in the type 4 cation at $(1-x, 1-y, 1-y)$ and this cation is also a donor to O21 at $(1-x, 1-y, 1-z)$. Hence, the type 2 anions at $(2-x, -y, -z)$ and $(1-x, 1-y, 1-z)$ are linked in a $C_6^6(35)[R_4^4(20)]$ chain-of-rings running parallel to the $[\bar{1}11]$ direction (Fig. 7). The almost parallel anions flanked by two rows of cations produce a supramolecular motif in the form of a molecular staircase rising across one of the body-diagonals of the unit cell (Figs. 7 and 8).

3.2.3. General comments on the structures of (1) and (2). Although the compositions of (1) and (2), $[[(\text{amine})\text{H}]^+]_2 \cdot [(\text{C}_{10}\text{H}_4\text{O}_8)^{2-}]$, are similar, their supramolecular structures are very different, as are the conformational and hydrogen-bonding behaviour of their common anion. However, the structures do have a number of features in common.

Firstly, both structures contain short, ionic $\text{N}^+-\text{H} \cdots \text{O}^-$ hydrogen bonds, with in each case a cation acting as a donor to one of the anionic carboxylate substituents, rather than to one of the neutral $-\text{COOH}$ groups: the consequences of this for the geometry of the anion are discussed below (§3.4.2). Secondly, all the hydrogen bonds in (1) and (2) are short; in particular, the $\text{O}-\text{H} \cdots \text{N}$ and $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds in (1) and the intramolecular $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds in (2) are all very short for their types. Similarly, the $\text{C}-\text{H} \cdots \text{O}$ hydrogen bonds in both (1) and (2), where the maximum $\text{C} \cdots \text{O}$ distance is only just over 3.3 Å (Table 2), are all short for their type (Desiraju, 1991, 1996). The $D-\text{H} \cdots A$ angles in the intermolecular hydrogen bonds range from 157 to 174°.

It is noteworthy that in (1) it is two of the $\text{C}-\text{H}$ bonds in the protonated pyridyl ring which participate in $\text{C}-\text{H} \cdots \text{O}$ hydrogen bonds, while in (2) interactions of this type are formed only by $\text{C}-\text{H}$ bonds adjacent to the protonated N atoms N41 and N51. In both structures, therefore, the ionic nature of

the building blocks and in particular the charged donor and acceptor sites all serve to enhance the strength not only of the hard hydrogen bonds, but of the soft C—H...O hydrogen bonds also (Gilli *et al.*, 1994).

3.3. Comparison with other structures containing the $(C_{10}H_4O_8)^{2-}$ anion

The structures of (1) and (2) contain no intermolecular O—H...O hydrogen bonds. By contrast, the formation of $R_2^2(8)$ rings containing paired intermolecular O—H...O bonds is one of the dominant structural motifs in aromatic carboxylic acids containing unionized —COOH groups, as in both (1) and (2). Such ring motifs occur in, for example, benzoic acid to give dimers (Sim *et al.*, 1955; Wilson *et al.*, 1996); all three isomers of benzenedicarboxylic acid (Bailey & Brown, 1967; Alcalá & Martínez-Carrera, 1972; Ermer, 1981), all of which form chains; and in trimesic acid (Duchamp & Marsh, 1969), where interwoven nets occur. It is thus of interest to compare the behaviour of the anion $(C_{10}H_4O_8)^{2-}$ in (1) and (2) with that in other structures retrieved from the CSD (Allen & Kennard, 1993).

The compound formed by benzene-1,2,4,5-tetracarboxylic acid with 2,2'-bipyridyl (TEKLOK; Mrvos-Sermek *et al.*, 1996) has a 1:1 stoichiometry, in contrast to the 2:1 compound (1) containing the isomeric 4,4'-bipyridyl. In the 2,2'-bipyridyl compound, there are equal numbers of $(C_{10}H_4O_8)^{2-}$ anions and neutral $C_{10}H_6O_8$ molecules. The centrosymmetric anions contain two short, but asymmetric, intramolecular O—H...O hydrogen bonds and they act as fourfold acceptors of intermolecular hydrogen bonds, while the neutral $C_{10}H_6O_8$ molecules, also centrosymmetric, form no intramolecular hydrogen bonds, but instead act as fourfold donors in intermolecular hydrogen bonds. The combination of equal numbers of fourfold donors and fourfold acceptors generates a two-dimensional net built from a single type of centrosymmetric $R_4^4(28)$ ring (Fig. 9). An anion $(C_{10}H_4O_8)^{2-}$ of similar type to those found in (2) and in TEKLOK has also been observed in the $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ salt (PAHXIF; Jessen *et al.*, 1992). This salt crystallizes in the rare (Brock & Dunitz, 1994) space group $P2/m$ and the anions are located at sites of $2/m$ (C_{2h}) symmetry. The intramolecular O—H...O hydrogen bonds lie across the mirror planes and the H atoms were reported to be ordered and lying on the mirror planes.

In contrast to these analogues of the $(C_{10}H_4O_8)^{2-}$ anions in (2), the conformation of the anion in (1) is closely mimicked by that in the ammonium salt $[(\text{NH}_4)^+]_2 \cdot [(C_{10}H_4O_8)^{2-}]$ (3) (PAHXOL; Jessen *et al.*, 1992), where, as in (1), no intramolecular O—H...O hydrogen bonds are found. The overall supramolecular structure is three-dimensional, with the ammonium ions forming one N—H...O hydrogen bond to each of four different anions disposed approximately tetrahedrally about the cation. The centrosymmetric anions are themselves linked by O—H...O hydrogen bonds into a two-dimensional network in which each anion acts as a double donor and a double acceptor. Hence, an approximately square net results, but from a single type of centrosymmetric $R_4^4(30)$

ring (Fig. 10). As with several previous examples of three-dimensional supramolecular architectures (Gregson *et al.*, 2000), it is possible to identify here a substructure having lower dimensionality and built from just a subset of the molecular components.

Closely related to the anion $(C_{10}H_4O_8)^{2-}$ is the uninegative anion $(C_{10}H_5O_8)^-$, observed in the salt $[(\text{Bu}_4\text{N})^+][(\text{C}_{10}H_5O_8)^-]$ (PAHXUR; Jessen *et al.*, 1992), but surprisingly not found in TEKLOK (Mrvos-Sermek *et al.*, 1996) where equal numbers of $(C_{10}H_4O_8)^{2-}$ and $C_{10}H_6O_8$ occur instead. In PAHXUR the anion $(C_{10}H_5O_8)^-$ contains an intramolecular O—H...O hydrogen bond and it acts as both a double donor and a double acceptor of hydrogen bonds, again forming an approximately square net (Fig. 11) built from non-centrosymmetric $R_4^4(30)$ rings.

While all three of TEKLOK, PAHXOL and PAHXUR contain two-dimensional cation-free nets of acid units linked by intramolecular O—H...O hydrogen bonds, all three of these nets are different (Figs. 9–11). That in TEKLOK (Fig. 9) contains two different molecular building blocks, while the $R_4^4(30)$ nets in PAHXOL and PAHXUR (Figs. 10 and 11) differ in their symmetry.

In benzene-1,2,4,5-tetracarboxylic acid itself, which crystallizes as a dihydrate (PYMELL10; Takusagawa *et al.*, 1971), there are no intermolecular O—H...O hydrogen bonds, nor do the carboxyl groups form the usual $R_2^2(8)$ motif so characteristic of aromatic carboxylic acids. Instead, there is a three-dimensional hydrogen-bonded framework within which two dominant motifs can be identified: the acid molecules and the water molecules combine to generate two-dimensional nets parallel to (001) built from three different types of centrosymmetric ring, of $R_4^4(8)$, $R_4^4(18)$ and $R_4^4(20)$ types (Fig. 12), and these nets are linked by chains along the $[1\bar{1}1]$ direction built from a most unusual $R_2^2(14)$ carboxylic dimer motif (Fig. 13).

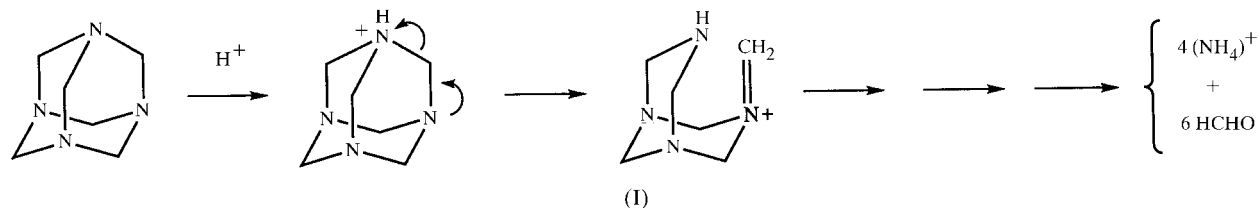
3.4. Molecular dimensions and conformations in (1) and (2)

3.4.1. Cation dimensions. In (1) the two hetero-aromatic rings in the protonated 4,4'-bipyridyl are nearly parallel (Table 3) and the C—N—C angle at the protonated N11 is significantly larger than that at the unprotonated N21.

In (2) the three independent cations all have very similar geometries, all have approximate C_{3v} molecular symmetry and their C—N bond lengths fall into three distinct categories (Table 3). The C—N bonds involving protonated N atoms (N31, N41 and N51) have lengths in the range 1.508 (3)–1.524 (3) Å [mean 1.517 (5) Å]; the bonds β to protonated N atoms ($Nn3$ — $Cn2$, $Nn5$ — $Cn6$ and $Nn10$ — $Cn7$, for $n = 3, 4$ or 5) have lengths in the range 1.438 (3)–1.454 (3) Å [mean 1.445 (6) Å]; the remainder, the six C—N bonds in each cation most remote from the protonated N sites, have lengths ranging from 1.461 (3) to 1.486 (3) Å [mean 1.472 (7) Å]. It is notable that these three ranges show no overlaps.

While the mean length of the C—N bonds of sixfold multiplicity is entirely as expected for a tertiary aliphatic amine [mean of 1042 values, 1.469 Å (Allen *et al.*, 1987)], the

bonds to $Nn1$ are very much longer and the bonds β to $Nn1$ are much shorter. It is of interest to consider the pattern of the C–N bond lengths in terms of the likely mechanism for the early steps in the acid-promoted decomposition of HMTA [Scheme (I)], where a C–N bond adjacent to the protonated N is cleaved, while the corresponding β bond is converted to the C=N double bond of an iminium cation. The observed cation structure in (2) suggests that this cation is well advanced along the reaction coordinate from the T_d structure of neutral, tricyclic HMTA to the bicyclic iminium intermediate [Scheme (I)].



3.4.2. Anion dimensions. In (2) the two independent anions ($C_{10}H_4O_8$)²⁻ are both virtually planar, consequent upon the strong, short intramolecular O–H...O hydrogen bonds. Although the O...O distances in these hydrogen bonds are all very short (Table 2), the H atoms are clearly localized and ordered, bonded to O13, O23 and O27. This is somewhat unexpected as the O...O distances are typical of those for

late groups, with one bond typically shorter than the other by *ca* 0.045 Å. In every case, the longer of the two bonds [C4–O2 in (1); C14–O12, C27–O22 and C29–O26 in (2)] involves the O atom, which acts as an acceptor of an N–H...O hydrogen bond from the cation. The presence of the short, strong N–H...O hydrogen bond clearly provides a significant perturbation to the electron density within the carboxylate group, so that the resulting geometry (2) is intermediate between the fully delocalized form (1), where the C–O bond lengths are equal with an average length in aromatic carboxylates of 1.255 Å (Allen *et al.*, 1987), and the fully localized neutral –COOH form (3).

There are also consistent differences between the two independent C–O distances in each of the anionic carboxy-

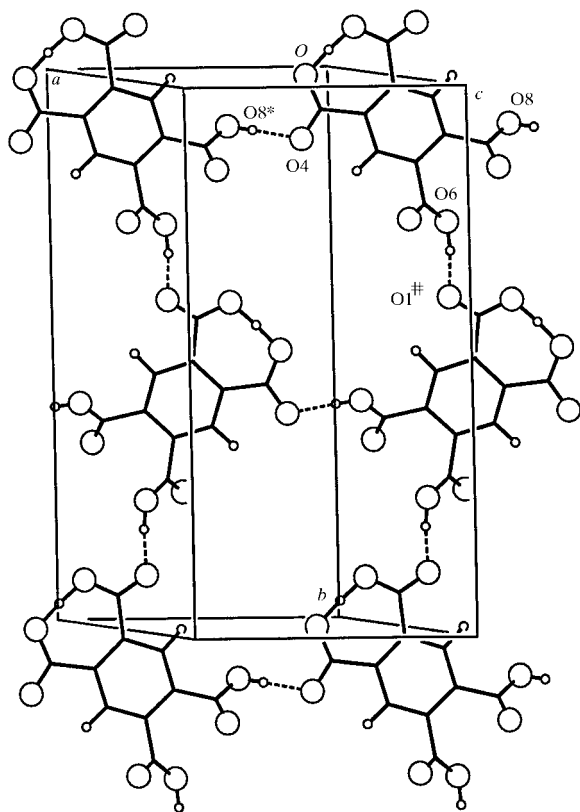
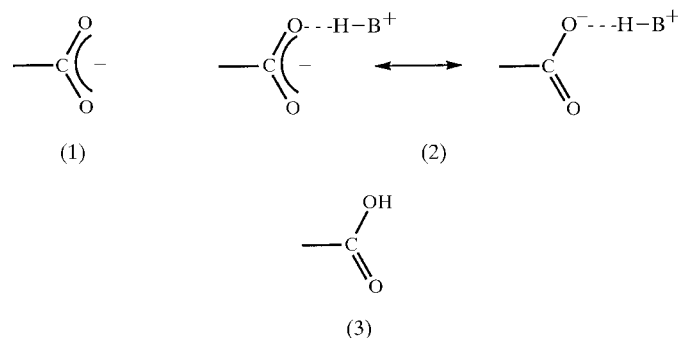


Figure 11

Part of the crystal structure of $[(Bu_4N)^+][C_{10}H_5O_8]^-$ (Jessen *et al.*, 1992), showing a two-dimensional $R_4^4(28)$ net built from anions only. Atoms marked with a star (*) or a hash (#) are at the symmetry positions $(\frac{1}{2} + x, y, z)$ and $(-x, \frac{1}{2} + y, \frac{3}{2} - z)$, respectively.

late groups, with one bond typically shorter than the other by *ca* 0.045 Å. In every case, the longer of the two bonds [C4–O2 in (1); C14–O12, C27–O22 and C29–O26 in (2)] involves the O atom, which acts as an acceptor of an N–H...O hydrogen bond from the cation. The presence of the short, strong N–H...O hydrogen bond clearly provides a significant perturbation to the electron density within the carboxylate group, so that the resulting geometry (2) is intermediate between the fully delocalized form (1), where the C–O bond lengths are equal with an average length in aromatic carboxylates of 1.255 Å (Allen *et al.*, 1987), and the fully localized neutral –COOH form (3).



The bond angles involving the exocyclic substituents in the anions show a strong dependence on the overall conformation. It may be assumed that the conformation of the anion in (1) is essentially strain-free, as the bond angles at C1, C2, C4 and C5 (Table 3 and Fig. 1) are all typical of their types: in particular, the bond angles at C1 and C2, both within and external to the aromatic ring, are all close to 120°. In (2), however, where both anions are almost planar, the exocyclic angles at C11, C12, C21, C22, C24 and C25 (Table 3 and Fig. 6) all show large deviations from 120°. Within the three hydrogen-bonded S(7) rings, the C–C–C bond angles range from 127.7 (3) to 129.7 (3)°. At the same time, the O–C–O angles are all close to 120°, possibly reflecting some steric compression between

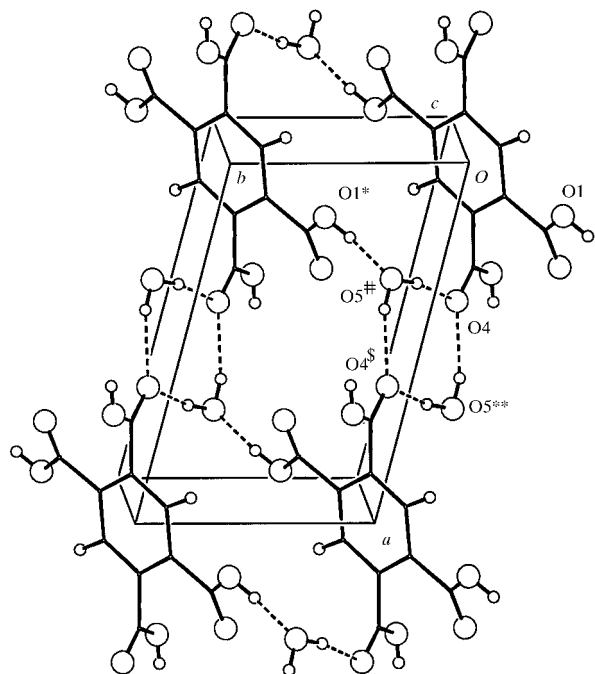


Figure 12

Part of the crystal structure of benzene-1,2,4,5-tetracarboxylic acid dihydrate (Takusagawa *et al.*, 1971), showing a two-dimensional (001) net built from $R_4^2(8)$, $R_4^4(18)$ and $R_4^4(20)$ rings. Atoms marked with a single or double star (*) are at symmetry positions $(x, 1 + y, z)$ and $(1 + x, y, z)$, respectively; those marked with a hash (#) or a dollar sign (\$) are at symmetry positions $(-x, -y, -z)$ and $(1 - x, -y, -z)$, respectively.

the $-\text{COO}(\text{H})$ groups and the neighbouring aromatic $\text{C}-\text{H}$ bonds.

4. Conclusions

The hydrogen-bonding behaviour of the anion $(\text{C}_{10}\text{H}_4\text{O}_8)^{2-}$, as manifested both in the structures of (1) and (2), and in the structures of other salts recorded in the literature, exhibits a surprising diversity, such that none of the observed supra-molecular structures could readily have been predicted even at the gross connectivity level. Despite this diversity of behaviour, the numbers of structures so far reported is too small for any pattern of behaviour to be discernible. A noteworthy feature in the structure of (2) is the formation of $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds, which are short and strong for their type, in which aliphatic $\text{C}-\text{H}$ bonds, α to the protonated N sites, act as donors. It is likely, however, that stable organic salts containing the protonated HMTA cation $(\text{C}_6\text{H}_{13}\text{N}_4)^+$ will remain rather few in number, because of the very great ease with which this cation undergoes hydrolytic decomposition in solution.

X-ray data were collected at the University of Toronto using a Nonius Kappa-CCD diffractometer purchased with funds from NSERC (Canada). We thank Dr A. L. Spek for making available to us the July 12 1999 version of *PLATON*.

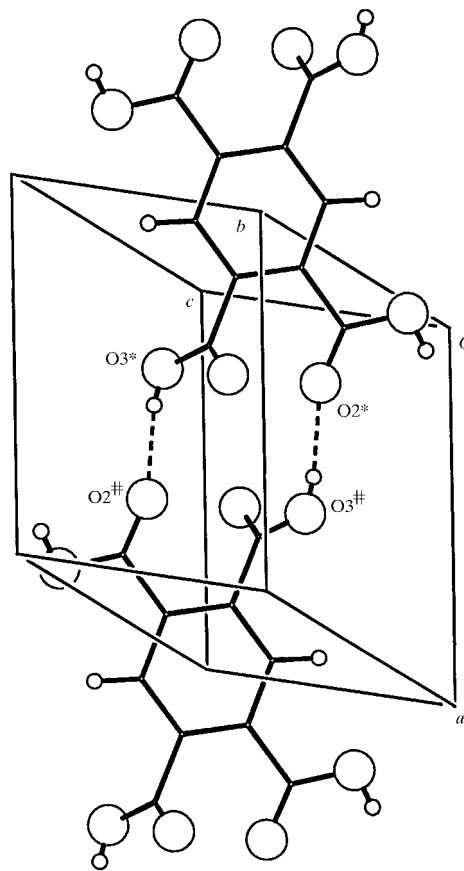


Figure 13

Part of the crystal structure of benzene-1,2,4,5-tetracarboxylic acid dihydrate (Takusagawa *et al.*, 1971) showing the centrosymmetric $R_2^2(14)$ motif generating a $[1\bar{1}1]$ chain. Atoms marked with a star (*) or a hash (#) are at the symmetry positions $(x, 1 + y, z)$ and $(1 - x, -y, 1 - z)$, respectively.

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