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Channel- and layer-type anionic host structures in inclusion compounds of urea, tetraalkylammonium terephthalate/trimesate and water

Feng Xue and Thomas C. W. Mak*

Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong SAR, Peoples' Republic of China

Correspondence e-mail: tcwmak@cuhk.edu.hk

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New crystalline adducts of tetraalkylammonium terephthalate/trimesate with urea and water molecules result from hydrogen-bond directed assembly of complementary acceptors and donors, and the anionic host lattices are described using the graph-set notation to identify distinct hydrogen-bonding motifs and patterns. Tetra-*n*-butylammonium terephthalate–urea–water (1/6/2), $C_{46}H_{104}N_{14}O_{12}$ (1), triclinic, space group $P\bar{1}$, $a = 8.390\,(2)$, $b = 9.894\,(2)$, $c = 18.908\,(3)$ Å, $\alpha = 105.06\,(2)$, $\beta = 94.91\,(1)$, $\gamma = 93.82\,(2)^\circ$, $Z = 1$, is composed of hydrogen-bonded terephthalate–urea layers, which are intersected by urea layers to generate a three-dimensional network containing large channels for accommodation of the cations. Tetraethylammonium terephthalate–urea–water (1/1/5), $C_{25}H_{58}N_4O_{10}$ (2), triclinic, $P\bar{1}$, $a = 9.432\,(1)$, $b = 12.601\,(1)$, $c = 14.804\,(1)$ Å, $\alpha = 79.98\,(1)$, $\beta = 79.20\,(1)$, $\gamma = 84.18\,(1)^\circ$, $Z = 2$, has cations sandwiched between hydrogen-bonded anionic layers. Tetraethylammonium trimesate–urea–water (1/2/7.5), $C_{35}H_{86}N_7O_{15.5}$ (3), triclinic, $P\bar{1}$, $a = 13.250\,(1)$, $b = 14.034\,(1)$, $c = 15.260\,(1)$ Å, $\alpha = 72.46\,(1)$, $\beta = 78.32\,(1)$, $\gamma = 66.95\,(1)^\circ$, $Z = 2$, manifests a layer-type structure analogous to that of (2). Tetra-*n*-propylammonium hydrogen trimesate–urea–water (1/2/5), $C_{35}H_{78}N_6O_{13}$ (4), orthorhombic, $Pna2_1$, $a = 16.467\,(3)$, $b = 33.109\,(6)$, $c = 8.344\,(1)$ Å, $Z = 4$, features hydrogen trimesate helices in a three-dimensional host architecture containing nanoscale channels each filled by a double column of cations.

1. Introduction

Much of the current research in crystal engineering, namely the attempt to create multi-component supramolecular architectures based on intermolecular interactions, involves the optimized formation of hydrogen bonds as the primary design strategy (Aakeröy & Seddon, 1993; Aakeröy, 1997; Desiraju, 1996; Fyfe & Stoddart, 1997). Carboxylic acids display a very high tendency toward molecular association by means of hydrogen bonding and often the cyclic dimeric motif is observed for those containing aromatic groups (Videnova-Adrabiñska, 1996). Thus, terephthalic acid (1,4-benzenedicarboxylic acid, TPA) and trimesic acid (1,3,5-benzenetricarboxylic acid, TMA) are judicious choices as supramolecular synthons for crystal engineering (I*a*). It has been shown that two-dimensional sheet-like structures exist in terephthalate clathrate adducts (Moritani & Kashino, 1991; Centore *et al.*, 1991; Furey *et al.*, 1996; Hosseini *et al.*, 1994) and quasi-hexagonal honeycomb grids in trimesate adducts (Herbstein, 1987, 1996; Kolotuchin *et al.*, 1995; Melendez *et al.*, 1996;

Sharma & Zaworotko, 1996). On the other hand, the inclusion compounds of urea are well known classical examples of channel-type host–guest systems (Fetterly, 1964; Takemota & Sonoda, 1984; Harris & Thomas, 1990; Harris *et al.*, 1991; Hollingsworth & Harris, 1996). By using terephthalic acid or trimesic acid and urea as supramolecular synthons to incorporate both the chemical and geometrical recognition features of the component molecules, one can expect to generate extended hydrogen-bonded motifs in view of the complementary interaction of the $-NH_2$ donor sites of urea with the $-COO^-$ acceptor sites of terephthalate or trimesate (I*b*). We report herein four new inclusion compounds which exhibit two molecular topologies: (1) and (4) manifest nanoporous channel structures, whereas (2) and (3) constitute sandwich-like networks:

$[(n\text{-Bu})_4N^+]_2[1,4\text{-}C_6H_4(COO^-)_2]\cdot 6(NH_2)_2CO\cdot 2H_2O$ (1)
$(Et_4N^+)_2[1,4\text{-}C_6H_4(COO^-)_2]\cdot (NH_2)_2CO\cdot 5H_2O$ (2)
$(Et_4N^+)_3[1,3,5\text{-}C_6H_3(COO^-)_3]\cdot 2(NH_2)_2CO\cdot 7.5H_2O$ (3)
$[(n\text{-Pr})_4N^+]_2[1,3,5\text{-}C_6H_3(COO^-)_2(COOH)]\cdot 2(NH_2)_2CO\cdot 5H_2O$ (4).

Graph-set analysis is one of the most promising systematic approaches to recognize, and then utilize, patterns of hydrogen bonding for the understanding and design of molecular crystals (Etter, 1990; Bernstein *et al.*, 1995). It allows rather complicated networks to be described in an efficient shorthand manner for the comparison and cataloguing of a large variety of related structures, as illustrated by the present series of inclusion compounds.

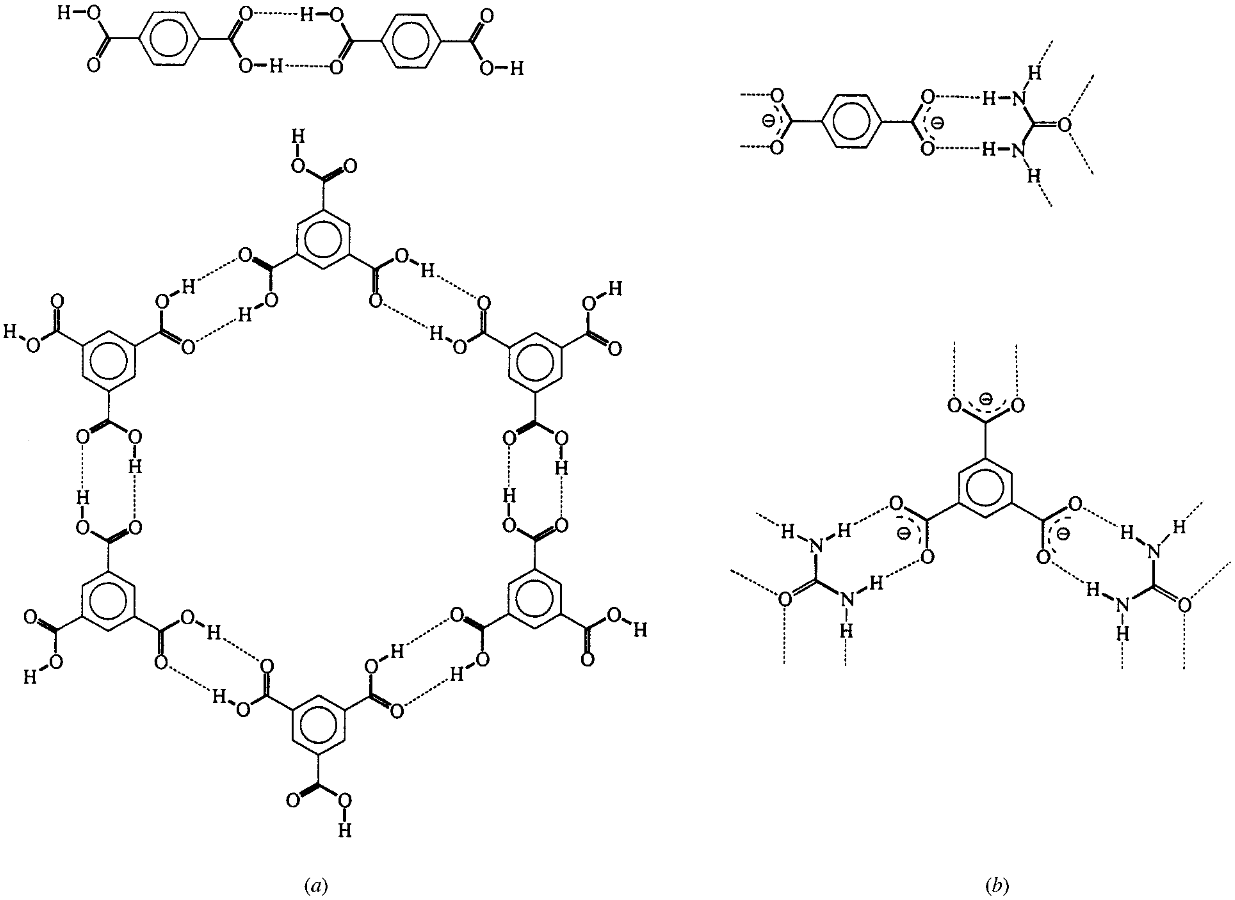
2. Experimental

2.1. Synthesis

Adducts (1) and (2) were prepared by refluxing terephthalic acid and urea in an aqueous solution of the corresponding tetraalkylammonium hydroxide R_4NOH (40 wt % for R = Bu, 35 wt % for R = Et), in a molar ratio of 1:2:2, for 1 h. Adducts (3) and (4) were prepared in the same manner using trimesic acid, urea and aqueous tetraalkylammonium hydroxide (40 wt % for R = Bu, 1 *M* for R = Pr). The solutions were subjected to slow evaporation of solvent at ambient temperature in a desiccator charged with drierite. Colorless crystals appeared in the form of prisms [(1)], small blocks [(2) and (3)] or thin plates [(4)].

2.2. Data collection, structure solution and refinement

Information concerning crystallographic data collection and structure refinement of all compounds is summarized in Table 1. Intensity data of (1) and (4) were collected at 294 K in the variable ω-scan mode on a Rigaku AFC-7*R* four-circle diffractometer using Mo $K\alpha$ radiation (λ = 0.71073 Å) from a



(*a*) (*b*)

(I)

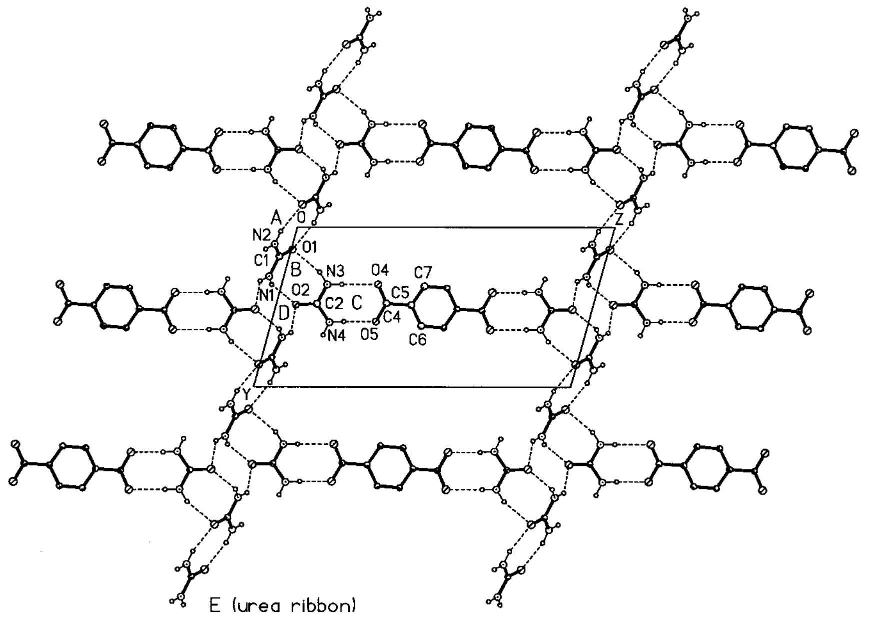


Figure 1
Projection on (100) showing a hydrogen-bonded layer constructed from urea dimers and terephthalate anions in (1). The axial labels *Y* and *Z* represent *b*sin γ and *c*sin β, respectively. Various hydrogen-bonding motifs as discussed in the text are labeled by letters A–E and similar labels are used in other figures.

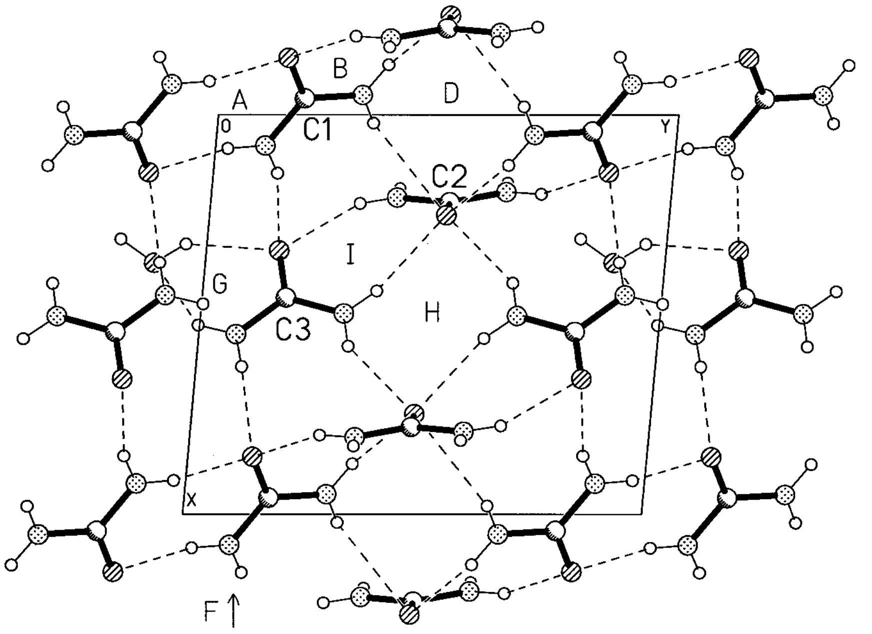


Figure 2
Projection on (001) showing hydrogen-bonding patterns between urea *C*(3) and adjacent *C*(1)···*C*(2) urea ribbons, which constitute the vertical portion of the hydrogen-bonded layer of (1). The terephthalate anions have been omitted for clarity. The axial labels *X* and *Y* represent *a*sin β and *b*sin α, respectively.

Rigaku RU-200 rotating-anode generator operating at 50 kV and 90 mA. Unit-cell parameters were calculated from least-squares fitting of 2θ angles for 25 selected reflections. Crystal stability was monitored by recording three check reflections at intervals of 197 data measurements and no significant variation was detected. Empirical absorption corrections were applied by fitting a pseudo-ellipsoid to the ψ-scan data of selected strong reflections over a range of 2θ angles (Kopfmann & Huber, 1968). Intensity data of (2) and (3) were collected at 294 K on a MSC/Rigaku RAXIS IIC imaging-plate detector system (Tanner & Krause, 1994; Krause & Phillips, 1992; Sato *et al.*, 1992) from the same Rigaku RU-200 generator. Data collection and reduction were performed using *bioteX* software (MSC, 1995). For (2), the data were collected to 0.82 Å resolution (80% complete) by taking oscillation frames in the range 0–180°, $\Delta\varphi$ = 6°, exposure 8 min per frame; for (3), the data were collected in a similar way with $\Delta\varphi$ = 5°, exposure 10 min per frame. A self-consistent semi-empirical absorption correction based on the Fourier coefficient fitting of symmetry-equivalent reflections was applied using the *ABSCOR* program (Higashi, 1995).

Determination of the crystal structures of (1)–(4) by direct methods yielded the positions of all non-H atoms, which were refined with anisotropic thermal parameters. H atoms attached to C atoms were generated assuming idealized geometry (C—H bond lengths fixed at 0.96 Å), assigned appropriate isotropic thermal parameters and allowed to ride on their parent C atoms. H atoms involved in the hydrogen-bonding scheme were unambiguously located from difference electron density maps, assigned isotropic thermal parameters 1.2–1.5 times those of their parent non-H atoms and refined using the riding model (N—H bond lengths refined to 0.86 Å, while O—H bond lengths refined to 0.82–0.85 Å). All computations were performed on an IBM compatible PC with *SHELXL*97 (Sheldrick, 1997) for full-matrix least-squares refinement against F^2 and the *SHELXTL/PC* program package (Siemens, 1990) for preparing the diagrams. Analytical expressions of neutral-atom scattering factors were employed and anomalous dispersion corrections were incorporated (Ibers & Hamilton, 1974*a*,*b*). Final fractional coordinates and equivalent isotropic thermal parameters, along with their e.s.d.s, are presented in Table 2 and selected dimensions in Table 3.[1]

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[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: HR0043). Services for accessing these data are described at the back of the journal.

Table 1
Experimental details.

	(1)	(2)	(3)	(4)
Crystal data				
Chemical formula	$2[N(C_4H_9)_4]^+ \cdot C_8H_4O_4^{2-} \cdot 6(CH_4N_2O) \cdot 2H_2O$	$2[N(C_2H_5)_4]^+ \cdot C_8H_4O_4^{2-} \cdot CH_4N_2O \cdot 5H_2O$	$3[N(C_2H_5)_4]^+ \cdot C_9H_3O_6^{3-} \cdot 2(CH_4N_2O) \cdot 7.5H_2O$	$2[N(C_3H_7)_4]^+ \cdot C_9H_4O_6^{2-} \cdot 2(CH_4N_2O) \cdot 5H_2O$
Chemical formula weight	1045.43	574.75	853.11	791.03
Cell setting	Triclinic	Triclinic	Triclinic	Orthorhombic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$Pna2_1$
a (Å)	8.390 (2)	9.432 (1)	13.250 (1)	16.467 (3)
b (Å)	9.894 (2)	12.601 (1)	14.034 (1)	33.109 (8)
c (Å)	18.908 (3)	14.804 (1)	15.260 (1)	8.344 (1)
α (°)	105.06 (2)	79.98 (1)	72.46 (1)	90
β (°)	94.91 (1)	79.20 (1)	78.32 (1)	90
γ (°)	93.82 (2)	84.18 (1)	66.95 (1)	90
V (Å^3)	1503.6 (2)	1697.7 (3)	2478.1 (3)	4549.2 (6)
Z	1	2	2	4
D_x (Mg m^{-3})	1.155	1.124	1.143	1.155
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
No. of reflections for cell parameters	25	95	118	25
θ range (°)	5–15	2–26	2–26	5–15
μ (mm^{-1})	0.084	0.086	0.089	0.087
Temperature (K)	293 (2)	293 (2)	293 (2)	293 (2)
Crystal form	Prism	Block	Block	Plate
Crystal size (mm)	0.40 × 0.38 × 0.22	0.40 × 0.32 × 0.30	0.60 × 0.50 × 0.40	0.60 × 0.36 × 0.20
Crystal color	Colorless	Colorless	Colorless	Colorless
Data collection				
Diffractometer	Rigaku AFC-7*R*	Rigaku RAXIS IIc	Rigaku RAXIS IIc	Rigaku AFC-7*R*
Data collection method	ω scans	Oscillation	Oscillation	ω scans
Absorption correction	Empirical ψ-scan	Empirical	Empirical	Empirical ψ-scan
T_{min}	0.951	0.907	0.863	0.768
T_{max}	1.000	1.060	1.138	1.000
No. of measured reflections	5604	4604	6973	4787
No. of independent reflections	5277	4604	6973	4787
No. of observed reflections	2982	3909	5849	2341
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.0185	–	–	–
θ_{max} (°)	25.14	25.53	25.54	25.99
Range of h, k, l	$-9 \rightarrow h \rightarrow 9$ $0 \rightarrow k \rightarrow 11$ $-22 \rightarrow l \rightarrow 21$	$-11 \rightarrow h \rightarrow 11$ $-15 \rightarrow k \rightarrow 0$ $-17 \rightarrow l \rightarrow 16$	$-16 \rightarrow h \rightarrow 14$ $-17 \rightarrow k \rightarrow 0$ $-18 \rightarrow l \rightarrow 17$	$0 \rightarrow h \rightarrow 20$ $0 \rightarrow k \rightarrow 40$ $0 \rightarrow l \rightarrow 10$
No. of standard reflections	3	0	0	3
Frequency of standard reflections	Every 197 reflections	–	–	Every 197 reflections
Intensity decay (%)	−0.36	0	0	−5.72
Refinement				
Refinement on	F^2	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$	0.0503	0.0690	0.0723	0.0577
$wR(F^2)$	0.1642	0.1925	0.2151	0.1732
S	1.029	1.112	1.083	0.953
No. of reflections used in refinement	5277	4604	6973	4787
No. of parameters used	325	431	646	493
H-atom treatment	Mixed	Mixed	Mixed	Mixed
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0779P)^2 + 0.1259P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0917P)^2 + 0.3593P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0987P)^2 + 0.6009P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0895P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.000	0.001	0.002	0.000
$\Delta\rho_{max}$ (e Å^{-3})	0.319	0.230	0.452	0.222
$\Delta\rho_{min}$ (e Å^{-3})	−0.313	−0.148	−0.402	−0.213
Extinction method	None	None	*SHELXL*97 (Sheldrick, 1997)	None
Extinction coefficient	–	–	0.037 (4)	–
Source of atomic scattering factors	*International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	*International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	*International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	*International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1 (continued)

	(1)	(2)	(3)	(4)
Computer programs				
Data collection	*MSC/AFC* (MSC, 1988)	*BioteX* (MSC, 1995)	*BioteX* (MSC, 1995)	*MSC/AFC* (MSC, 1988)
Cell refinement	*MSC/AFC* (MSC, 1988)	*BioteX* (MSC, 1995)	*BioteX* (MSC, 1995)	*MSC/AFC* (MSC, 1988)
Data reduction	*MSC/AFC* (MSC, 1988)	*BioteX* (MSC, 1995)	*BioteX* (MSC, 1995)	*MSC/AFC* (MSC, 1988)
Structure solution	*SHELXS*97 (Sheldrick, 1997)	*SHELXS*97 (Sheldrick, 1997)	*SHELXS*97 (Sheldrick, 1997)	*SHELXS*97 (Sheldrick, 1997)
Structure refinement	*SHELXL*97 (Sheldrick, 1997)	*SHELXL*97 (Sheldrick, 1997)	*SHELXL*97 (Sheldrick, 1997)	*SHELXL*97 (Sheldrick, 1997)

$R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR = \{[\Sigma w(F_o^2 - F_c^2)^2]/[\Sigma w(F_o^2)^2]\}^{1/2}$; $S = \{[\Sigma w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$.

3. Results and discussions

Description of the anionic host structures of (1)–(4) is facilitated by the use of graph-set analysis to identify hydrogen-bonding motifs and patterns; details of the definition, terminology and notation in the graph-set approach are given in the works of Etter and Bernstein (Etter, 1990; Etter *et al.*, 1990; Bernstein *et al.*, 1995).

3.1. Crystal structure of $[(n\text{-Bu})_4N^+]_2[1,4\text{-}C_6H_4(COO^-)_2]\cdot 6(NH_2)_2CO\cdot 2H_2O$ (1)

The asymmetric unit of (1) consists of one-half of a centrosymmetric terephthalate anion, a tetra-*n*-butylammonium cation, three independent urea molecules and one water molecule. As shown in Fig. 1, independent urea molecules *C*(1) (composed of C1, O1, N1 and N2) and *C*(2) (composed of C2, O2, N3 and N4) are connected by a pair of N—H$_{syn}\cdots$O hydrogen bonds to form a twisted cyclic dimer [*B*, $N_2 = R_2^2(8)$], the conformation of which can be described by the dihedral angle of 64.5° between the urea molecules, and the torsion angles C1—N1$\cdots$O2—C2 43.8° and C2—N3$\cdots$O1—C1 50.6°. Pairs of centrosymmetrically related N—H$_{syn}\cdots$O hydrogen bonds centered at (0, 0, 0) [*A*, $N_1 = R_2^2(8)$] and $(0, \frac{1}{2}, 0)$ [*D*, $N_2 = R_4^2(8)$] , respectively, link the urea dimers into a zigzag ribbon [*E*, $N_3 = C_3^2(10)$] running parallel to the *b* axis. Note that the urea molecules of type *C*(2) are arranged about the inversion center at $(0, \frac{1}{2}, 0)$ [*D*, $N_2 = R_4^2(8)$] in an unusual head-to-head fashion, which place each urea molecule in a favorable orientation to form a pair of donor N—H$_{anti}\cdots$O hydrogen bonds [*C*, $N_2 = R_2^2(8)$] to a neighboring carboxylate group. The terephthalate anions orientated nearly parallel to the *c* axial direction thus bridge the urea ribbons to generate a puckered layer normal to the *a* axis (Fig. 1).

The third independent urea molecule *C*(3) (composed of C3, O3, N5 and N6) in the asymmetric unit connects adjacent urea ribbons *E* to form a urea layer *via* three N—H$\cdots$O hydrogen-bond motifs, *F*, $N_2 = C_2^2(8)$, *H*, $N_2 = R_4^2(8)$ and *I*, $N_2 = R_2^2(8)$ (Fig. 2). The cross-linkage is further consolidated by a bridging water molecule which forms O—H$\cdots$O donor hydrogen bonds with O atoms of the terephthalate anion and a hydrogen motif *G*, $N_2 = R_2^2(6)$, with urea molecule *C*(3).

The terephthalate–urea and urea layers intersect to generate a channel-type host network (Fig. 3), the puckered terephthalate–urea layer forms a stair-like profile in a view along the *b* axis, in which the rigid terephthalate anions constitute the level portion with step width *ca* 16.7 Å and urea layers the vertical portion with step height *ca* 5.9 Å. A three-dimensional hydrogen-bonded network is thus formed with large, elongated hexagonal channels extending along the *b* axis, the dimension of the cross section of each channel being *ca* 7.9 × 16.7 Å. The tetra-*n*-butylammonium ions are arranged in two columns within each channel in a well ordered pattern.

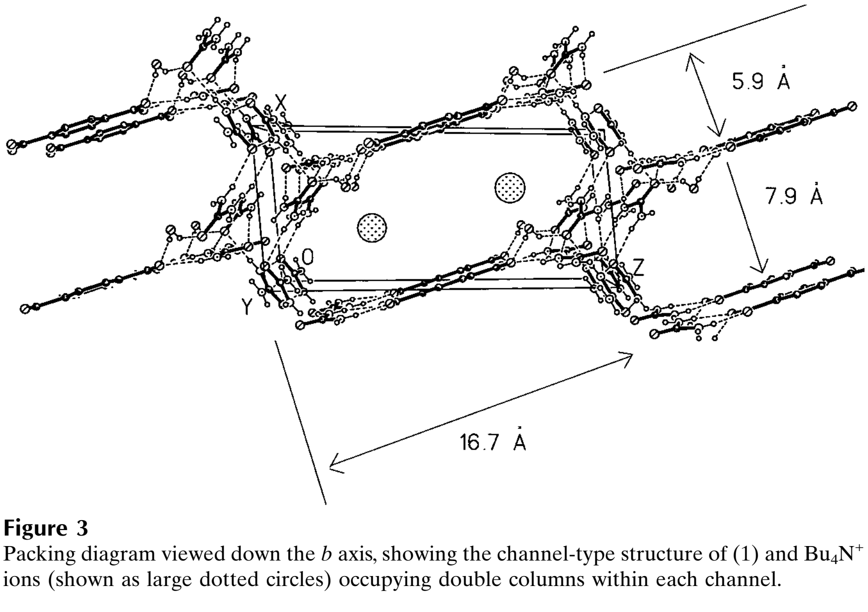

Figure 3
Packing diagram viewed down the *b* axis, showing the channel-type structure of (1) and Bu$_4$N$^+$ ions (shown as large dotted circles) occupying double columns within each channel.

3.2. Crystal structure of $[Et_4N^+]_2[1,4\text{-}C_6H_4(COO^-)_2]\cdot(NH_2)_2\text{-}CO\cdot 5H_2O$ (2)

The asymmetric unit of (2) consists of a terephthalate anion, two independent tetraethylammonium cations, one urea molecule and five water molecules. One tetraethylammonium cation is located at an inversion center and accordingly disordered. Urea molecule *C*(1) (composed of C1, O1, N1 and N2) forms a pair of N—H$_{anti}\cdots$O hydrogen bonds with one carboxylate group

Table 2

Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2).

$$U_{\rm eq} = (1/3)\Sigma_i \Sigma_j U^{ij} a^i a^j \mathbf{a}_i \mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
(1)				
C1	0.9589 (3)	0.1839 (2)	−0.0318 (1)	0.0526 (6)
O1	0.8567 (2)	0.1406 (2)	0.0038 (1)	0.0605 (4)
N1	0.9502 (3)	0.3089 (2)	−0.0468 (1)	0.0653 (6)
N2	1.0768 (2)	0.1074 (2)	−0.0569 (1)	0.0667 (6)
C2	0.7819 (3)	0.4801 (2)	0.1281 (1)	0.0482 (5)
O2	0.7496 (2)	0.4851 (2)	0.06272 (8)	0.0593 (4)
N3	0.8076 (2)	0.3595 (2)	0.1442 (1)	0.0610 (5)
N4	0.7935 (2)	0.5958 (2)	0.1834 (1)	0.0587 (5)
C3	0.5428 (3)	−0.1820 (2)	0.0994 (1)	0.0518 (6)
O3	0.6611 (2)	−0.1579 (2)	0.14637 (8)	0.0598 (4)
N5	0.5029 (3)	−0.3112 (2)	0.0554 (1)	0.0668 (6)
N6	0.4510 (3)	−0.0807 (2)	0.0919 (1)	0.0802 (7)
C4	0.8915 (3)	0.4774 (2)	0.3463 (1)	0.0483 (5)
O4	0.8560 (2)	0.3583 (2)	0.3035 (1)	0.0752 (6)
O5	0.8868 (2)	0.5911 (2)	0.32875 (8)	0.0661 (5)
C5	0.9462 (2)	0.4881 (2)	0.4263 (1)	0.0416 (5)
C6	0.9891 (3)	0.6183 (2)	0.4756 (1)	0.0508 (6)
C7	0.9575 (3)	0.3699 (2)	0.4516 (1)	0.0510 (6)
N7	0.3708 (2)	0.6717 (2)	0.2988 (1)	0.0488 (4)
C8	0.5364 (3)	0.7504 (2)	0.3172 (1)	0.0518 (6)
C9	0.5672 (3)	0.8544 (3)	0.3918 (1)	0.0627 (7)
C10	0.7370 (3)	0.9250 (3)	0.4021 (2)	0.0677 (7)
C11	0.7790 (4)	1.0211 (3)	0.4783 (2)	0.088 (1)
C12	0.3359 (3)	0.5858 (2)	0.3525 (1)	0.0527 (6)
C13	0.4496 (3)	0.4770 (3)	0.3593 (1)	0.0640 (7)
C14	0.3828 (3)	0.3866 (3)	0.4059 (2)	0.0697 (7)
C15	0.4895 (4)	0.2761 (3)	0.4160 (2)	0.090 (1)
C16	0.3691 (3)	0.5771 (3)	0.2213 (1)	0.0555 (6)
C17	0.2167 (3)	0.4846 (3)	0.1899 (1)	0.0742 (8)
C18	0.2381 (4)	0.3874 (3)	0.1157 (2)	0.0789 (8)
C19	0.3482 (4)	0.2767 (3)	0.1162 (2)	0.098 (1)
C20	0.2394 (3)	0.7721 (2)	0.3036 (1)	0.0562 (6)
C21	0.2467 (3)	0.8726 (3)	0.2561 (2)	0.0761 (8)
C22	0.1143 (4)	0.9754 (4)	0.2745 (2)	0.117 (1)
C23	0.1241 (6)	1.0900 (4)	0.2389 (3)	0.142 (2)
O1*w*	0.6301 (3)	0.1113 (3)	0.2461 (2)	0.121 (1)
(2)†				
C1	0.3299 (3)	0.6145 (2)	1.4769 (2)	0.0816 (8)
O1	0.3653 (3)	0.5898 (2)	1.5562 (1)	0.1159 (8)
N1	0.3833 (3)	0.5558 (2)	1.4091 (2)	0.0849 (7)
N2	0.2381 (3)	0.6987 (2)	1.4571 (2)	0.1020 (8)
C2	0.2816 (3)	0.7086 (2)	1.1962 (2)	0.0721 (7)
O2	0.3509 (2)	0.6187 (2)	1.2101 (1)	0.0886 (6)
O3	0.2293 (3)	0.7638 (2)	1.2592 (1)	0.0978 (6)
C3	0.2553 (3)	0.7520 (2)	1.0977 (2)	0.0639 (6)
C4	0.1961 (3)	0.8573 (2)	1.0753 (2)	0.0731 (7)
C5	0.1615 (3)	0.8933 (2)	0.9876 (2)	0.0711 (7)
C6	0.1821 (2)	0.8253 (2)	0.9205 (2)	0.0615 (6)
C7	0.2442 (3)	0.7214 (2)	0.9420 (2)	0.0657 (6)
C8	0.2816 (3)	0.6858 (2)	1.0299 (2)	0.0660 (6)
C9	0.1344 (3)	0.8643 (2)	0.8269 (2)	0.0678 (6)
O4	0.1681 (2)	0.8051 (2)	0.7651 (1)	0.0949 (6)
O5	0.0618 (3)	0.9516 (2)	0.8176 (1)	0.0981 (6)
O1*w*	0.3839 (2)	0.4550 (2)	0.8876 (2)	0.1071 (7)
O2*w*	0.1312 (3)	0.8682 (2)	0.5819 (1)	0.1141 (8)
O3*w*	0.2538 (3)	0.5925 (2)	0.7408 (1)	0.0985 (6)
O4*w*	−0.1285 (3)	1.0364 (2)	0.7016 (2)	0.139 (1)
O5*w*	0.1698 (3)	1.0568 (2)	0.4420 (2)	0.133 (1)
N3	0.7398 (2)	0.6989 (2)	1.7988 (2)	0.0855 (7)
C10	0.8649 (3)	0.6965 (3)	1.7187 (2)	0.101 (1)
C11	0.8906 (5)	0.5950 (4)	1.6748 (3)	0.138 (2)
C12	0.7559 (3)	0.6035 (2)	1.8752 (2)	0.091 (1)
C13	0.8946 (4)	0.5943 (3)	1.9142 (3)	0.120 (1)
C14	0.5972 (3)	0.6887 (3)	1.7682 (3)	0.109 (1)
C15	0.5568 (5)	0.7789 (5)	1.6925 (4)	0.188 (3)
C16	0.7410 (4)	0.8046 (3)	1.8347 (3)	0.126 (1)
C17	0.6252 (5)	0.8229 (4)	1.9190 (4)	0.156 (2)
N4	0.2766 (2)	0.2169 (2)	0.7016 (2)	0.0857 (7)
C18	0.1396 (4)	0.2144 (3)	0.7763 (3)	0.088 (1)
C19	0.1195 (7)	0.3024 (6)	0.8349 (5)	0.123 (2)
C20	0.2774 (5)	0.1225 (4)	0.6522 (3)	0.102 (1)
C21	0.412 (1)	0.1065 (8)	0.5774 (6)	0.162 (4)
C22	0.2752 (5)	0.3257 (4)	0.6374 (4)	0.111 (2)
C23	0.1460 (8)	0.3526 (7)	0.5875 (5)	0.151 (3)
C24	0.4084 (4)	0.2107 (3)	0.7479 (3)	0.092 (1)
C25	0.421 (1)	0.1050 (8)	0.8203 (7)	0.184 (5)
C18′	0.265 (2)	0.317 (1)	0.742 (1)	0.114 (5)
C19′	0.135 (3)	0.323 (3)	0.822 (2)	0.23 (2)
C20′	0.161 (2)	0.201 (1)	0.648 (1)	0.138 (6)
C21′	0.140 (3)	0.291 (2)	0.568 (2)	0.18 (1)
C22′	0.421 (1)	0.217 (1)	0.629 (1)	0.118 (5)
C23′	0.465 (3)	0.113 (2)	0.587 (2)	0.16 (1)
C24′	0.299 (2)	0.109 (1)	0.768 (1)	0.178 (9)
C25′	0.435 (1)	0.112 (1)	0.812 (1)	0.079 (5)
(3)‡				
C1	0.8271 (2)	0.2969 (2)	0.4902 (2)	0.0695 (7)
O1	0.8353 (2)	0.3139 (2)	0.5628 (1)	0.0899 (6)
N1	0.7696 (3)	0.2378 (3)	0.4882 (2)	0.104 (1)
N2	0.8763 (2)	0.3354 (2)	0.4101 (2)	0.0823 (7)
C2	0.9701 (5)	0.4703 (4)	−0.3393 (4)	0.147 (2)
O2	1.0148 (2)	0.5136 (2)	−0.4161 (2)	0.0959 (7)
N3	0.8719 (3)	0.4385 (2)	−0.3370 (2)	0.098 (1)
N4	1.0286 (5)	0.4406 (4)	−0.2462 (3)	0.232 (2)
C3	0.7876 (2)	0.2378 (2)	0.2483 (2)	0.0578 (6)
O3	0.7399 (2)	0.2004 (2)	0.3216 (1)	0.0784 (5)
O4	0.8536 (2)	0.2835 (2)	0.2438 (1)	0.0777 (5)
C4	0.7632 (2)	0.2291 (2)	0.1592 (2)	0.0553 (6)
C5	0.8084 (2)	0.2748 (2)	0.0752 (2)	0.0589 (6)
C6	0.7899 (2)	0.2644 (2)	−0.0072 (2)	0.0603 (6)
C7	0.7238 (2)	0.2073 (2)	−0.0037 (2)	0.0639 (7)
C8	0.6759 (2)	0.1615 (2)	0.0786 (2)	0.0606 (6)
C9	0.6960 (2)	0.1727 (2)	0.1605 (2)	0.0590 (6)
C10	0.8444 (3)	0.3111 (3)	−0.0976 (2)	0.0749 (8)
O5	0.8168 (2)	0.3094 (2)	−0.1703 (1)	0.0980 (7)
O6	0.9140 (2)	0.3491 (3)	−0.0944 (2)	0.116 (1)
C11	0.6054 (3)	0.0991 (3)	0.0794 (2)	0.0754 (8)
O7	0.5799 (2)	0.0435 (2)	0.1560 (2)	0.1046 (7)
O8	0.5807 (2)	0.1020 (2)	0.0055 (2)	0.1164 (8)
O1*w*	0.8140 (2)	0.1779 (2)	−0.2693 (2)	0.0903 (7)
O2*w*	0.3826 (2)	0.8219 (2)	0.3050 (2)	0.0941 (7)
O3*w*	0.5015 (2)	0.1071 (2)	−0.1489 (2)	0.0912 (7)
O4*w*	0.5443 (2)	0.1758 (2)	0.4070 (2)	0.1004 (7)
O5*w*	0.4471 (2)	0.1050 (2)	0.3081 (2)	0.1082 (8)
O6*w*	0.3847 (3)	0.9402 (2)	0.4213 (2)	0.116 (1)
O7*w*	0.8602 (3)	0.4837 (2)	0.1508 (2)	0.122 (1)
O8*w*	0.9502 (6)	0.4894 (5)	−0.0251 (5)	0.136 (2)
N5	0.1805 (2)	0.1644 (2)	0.1068 (2)	0.0805 (8)
C12	0.2255 (4)	0.0843 (5)	0.1965 (4)	0.097 (2)
C13	0.1462 (7)	0.0810 (7)	0.2809 (5)	0.114 (3)
C14	0.2718 (4)	0.1560 (4)	0.0339 (4)	0.094 (2)
C15	0.241 (1)	0.234 (1)	−0.0592 (6)	0.141 (5)
C16	0.0819 (3)	0.1555 (4)	0.0867 (3)	0.082 (1)
C17	0.0969 (6)	0.0474 (6)	0.0734 (7)	0.115 (3)
C18	0.1376 (4)	0.2787 (4)	0.1274 (5)	0.100 (2)
C19	0.2265 (6)	0.3096 (6)	0.1500 (6)	0.150 (3)
C12′	0.193 (1)	0.0540 (8)	0.091 (1)	0.101 (4)
C13′	0.097 (2)	0.052 (2)	0.056 (2)	0.18 (2)
C14′	0.2985 (7)	0.143 (1)	0.112 (1)	0.094 (4)
C15′	0.311 (1)	0.242 (1)	0.120 (1)	0.129 (6)
C16′	0.094 (1)	0.194 (1)	0.1780 (7)	0.095 (4)
C17′	0.108 (2)	0.118 (2)	0.273 (1)	0.16 (1)
C18′	0.142 (1)	0.2416 (8)	0.0131 (6)	0.083 (3)
C19′	0.218 (2)	0.224 (2)	−0.072 (1)	0.125 (9)
N6	0.4991 (2)	0.5185 (2)	0.2504 (2)	0.0740 (7)
C20	0.5034 (3)	0.4199 (3)	0.2270 (3)	0.097 (1)
C21	0.3993 (4)	0.4272 (4)	0.1950 (4)	0.129 (2)
C22	0.6108 (3)	0.4922 (3)	0.2813 (3)	0.092 (1)

Table 2 (continued)

	x	y	z	U_{eq}
C23	0.6272 (3)	0.5804 (4)	0.3065 (3)	0.114 (1)
C24	0.4079 (3)	0.5486 (3)	0.3252 (2)	0.085 (1)
C25	0.4159 (4)	0.4635 (4)	0.4147 (3)	0.130 (2)
C26	0.4744 (3)	0.6132 (3)	0.1683 (2)	0.090 (1)
C27	0.5548 (4)	0.6001 (4)	0.0833 (3)	0.132 (2)
N7	0.8173 (2)	0.8452 (2)	0.3918 (2)	0.0718 (6)
C28	0.8480 (3)	0.7496 (3)	0.4726 (2)	0.085 (1)
C29	0.7703 (4)	0.7582 (4)	0.5591 (3)	0.124 (2)
C30	0.8163 (3)	0.9435 (3)	0.4142 (3)	0.093 (1)
C31	0.9241 (3)	0.9365 (3)	0.4394 (4)	0.120 (1)
C32	0.9023 (3)	0.8169 (3)	0.3125 (2)	0.084 (1)
C33	0.8906 (4)	0.9036 (4)	0.2233 (3)	0.127 (2)
C34	0.7020 (3)	0.8716 (3)	0.3673 (3)	0.096 (1)
C35	0.6830 (3)	0.7828 (4)	0.3459 (4)	0.127 (2)
(4)				
C1	0.3088 (3)	0.6266 (2)	0.4516 (7)	0.059 (1)
O1	0.3409 (2)	0.6564 (1)	0.5158 (7)	0.088 (2)
N1	0.2311 (2)	0.6265 (1)	0.4015 (7)	0.074 (2)
N2	0.3489 (3)	0.5913 (1)	0.4345 (6)	0.069 (2)
C2	0.1808 (3)	0.7368 (1)	0.4537 (7)	0.055 (1)
O2	0.1390 (2)	0.7057 (1)	0.4792 (5)	0.064 (1)
N3	0.2605 (2)	0.7353 (1)	0.4476 (7)	0.077 (2)
N4	0.1451 (2)	0.7733 (1)	0.4330 (7)	0.071 (2)
C3	0.2170 (3)	0.5195 (1)	0.2290 (6)	0.045 (1)
O3	0.1622 (2)	0.5437 (1)	0.2635 (5)	0.058 (1)
O4	0.2900 (2)	0.5234 (1)	0.2625 (6)	0.076 (1)
C4	0.1953 (2)	0.4820 (1)	0.1288 (6)	0.040 (1)
C5	0.1189 (2)	0.4778 (1)	0.0630 (5)	0.041 (1)
C6	0.0991 (2)	0.4437 (1)	−0.0283 (6)	0.041 (1)
C7	0.1566 (2)	0.4132 (1)	−0.0446 (6)	0.042 (1)
C8	0.2336 (2)	0.4168 (1)	0.0185 (6)	0.039 (1)
C9	0.2523 (3)	0.4515 (1)	0.1063 (6)	0.043 (1)
C10	0.0185 (2)	0.4384 (2)	−0.1024 (6)	0.045 (1)
O5	−0.0221 (2)	0.4721 (1)	−0.1261 (5)	0.059 (1)
O6	−0.0084 (2)	0.4057 (1)	−0.1452 (5)	0.062 (1)
C11	0.2984 (3)	0.3845 (1)	−0.0052 (6)	0.047 (1)
O7	0.3680 (2)	0.3907 (1)	0.0440 (5)	0.057 (1)
O8	0.2767 (2)	0.3539 (1)	−0.0827 (6)	0.077 (1)
O1*w*	0.4877 (2)	0.4486 (1)	0.0134 (6)	0.076 (1)
O2*w*	0.4545 (2)	0.5050 (1)	0.2509 (5)	0.071 (1)
O3*w*	0.0043 (2)	0.6780 (1)	0.3174 (6)	0.072 (1)
O4*w*	0.5101 (2)	0.6731 (1)	0.5605 (6)	0.070 (1)
O5*w*	−0.1609 (2)	0.6924 (1)	0.269 (1)	0.121 (2)
N5	0.4492 (2)	0.3703 (1)	−0.4773 (5)	0.047 (1)
C12	0.4092 (3)	0.4029 (1)	−0.3756 (6)	0.051 (1)
C13	0.3709 (3)	0.4375 (2)	−0.4686 (8)	0.073 (2)
C14	0.3340 (4)	0.4678 (2)	−0.354 (1)	0.084 (2)
C15	0.4848 (3)	0.3400 (1)	−0.3597 (7)	0.057 (2)
C16	0.5250 (4)	0.3038 (2)	−0.4361 (8)	0.076 (2)
C17	0.5618 (4)	0.2772 (2)	−0.308 (1)	0.094 (2)
C18	0.5144 (3)	0.3882 (2)	−0.5850 (6)	0.058 (1)
C19	0.5832 (3)	0.4093 (2)	−0.4992 (8)	0.076 (2)
C20	0.6394 (4)	0.4286 (2)	−0.618 (1)	0.109 (3)
C21	0.3877 (3)	0.3501 (2)	−0.5880 (6)	0.054 (1)
C22	0.3174 (3)	0.3291 (2)	−0.5077 (8)	0.076 (2)
C23	0.2622 (4)	0.3106 (2)	−0.633 (1)	0.114 (3)
N6	0.4482 (2)	0.1365 (1)	−0.6398 (5)	0.052 (1)
C24	0.5105 (3)	0.1168 (2)	−0.5303 (7)	0.059 (1)
C25	0.5779 (3)	0.0937 (2)	−0.6118 (7)	0.075 (2)
C26	0.6324 (4)	0.0742 (2)	−0.490 (1)	0.101 (2)
C27	0.3857 (3)	0.1559 (2)	−0.5316 (8)	0.066 (2)
C28	0.3181 (3)	0.1789 (2)	−0.613 (1)	0.083 (2)
C29	0.2613 (4)	0.1965 (2)	−0.493 (1)	0.130 (3)
C30	0.4092 (3)	0.1051 (1)	−0.7490 (6)	0.058 (1)
C31	0.3722 (4)	0.0688 (2)	−0.6662 (8)	0.077 (2)
C32	0.3378 (4)	0.0396 (2)	−0.7861 (8)	0.077 (2)
C33	0.4877 (3)	0.1673 (1)	−0.7488 (7)	0.058 (2)
C34	0.5267 (4)	0.2033 (2)	−0.6675 (8)	0.077 (2)
C35	0.5642 (4)	0.2307 (2)	−0.789 (1)	0.097 (2)

† C18–C25′ belong to a disordered tetraethylammonium cation; s.o.f. (site-occupancy factors) of C18–C25 are $\frac{3}{4}$ and those of C18′–C25′ are $\frac{1}{4}$. ‡ C12–C19′ belong to a disordered tetraethylammonium cation; s.o.f. of C12–C19 are 0.70 and those of C12′–C19′ are 0.30; O8*w* represents a disordered water molecule about an inversion center, s.o.f. is $\frac{1}{2}$.

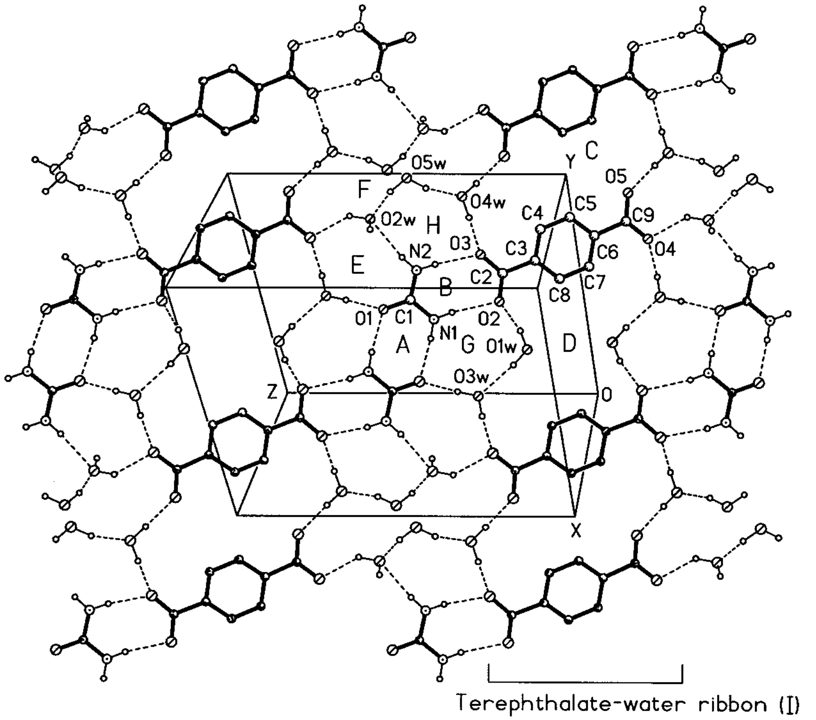

Figure 4
A section through the crystal structure of (2) viewed parallel to the normal of the (110) plane, showing a hydrogen-bonded layer formed by urea–terephthalate–water moieties.

of the terephthalate anion in a coplanar pattern [*B*, $N_2 = R_2^2(8)$] (Fig. 4), as indicated by the torsion angles C1—N1···O2—C2 0.6 and C1—N2···O3—C2 14.2°. Two of the urea–carboxylate cyclic heterodimers are centrosymmetrically connected through a pair of O—H···O hydrogen bonds from a bridging water molecule O4*w* with O atoms of different carboxylate groups, centered at (0, 0, 0), and form an antidromic hydrogen-bond ring motif [*C*, $N_3 = R_4^2(22)$]. The adjacent rings are analogously connected to similar rings through two pairs of O—H···O hydrogen bonds, centered at ($\frac{1}{2}$, $\frac{1}{2}$, 0), from two bridging water molecules O1*w* and O3*w* [*D*, $N_3 = R_6^6(26)$], and generate a hydrogen-bonded ribbon [*I*, $N_5 = C_5^5(14)$] running along the [110] direction. A pair of N—H_{syn}···O hydrogen bonds between urea molecules of neighboring ribbons centered at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) [*A*, $N_2 = R_2^2(8)$], and further hydrogen-bond ring motifs between adjacent ribbons *via* bridging water molecules, identified as *E*, $N_4 = R_4^3(10)$, *F*, $N_4R_8^8(20)$,

G, $N_5 = R_5^3(10)$ and H, $N_5 = R_5^3(10)$, build up an intricate scheme which leads to a hydrogen-bonded puckered layer orientated parallel to the ($\bar{1}10$) plane (Fig. 4). Note that the five independent water molecules in the asymmetric unit exhibit three different hydrogen-bonding patterns: each of O1*w* and O5*w* forms two donor hydrogen bonds only, each of O3*w* and O4*w* forms two donor and one acceptor hydrogen bond and serves as a 'three-way connector' in the hydrogen-bonding scheme, while O(2*w*) forms one donor and two acceptor hydrogen bonds and leaves one H atom free from bonding.

The disordered *N*(4) and well ordered *N*(3) tetraethylammonium cations in the asymmetric unit are arranged alternatively and constitute a cationic layer running parallel to the (110) family of planes, which is sandwiched between adjacent terephthalate–urea–water layers (Fig. 5). The interlayer distance is *ca* 8.0 Å.

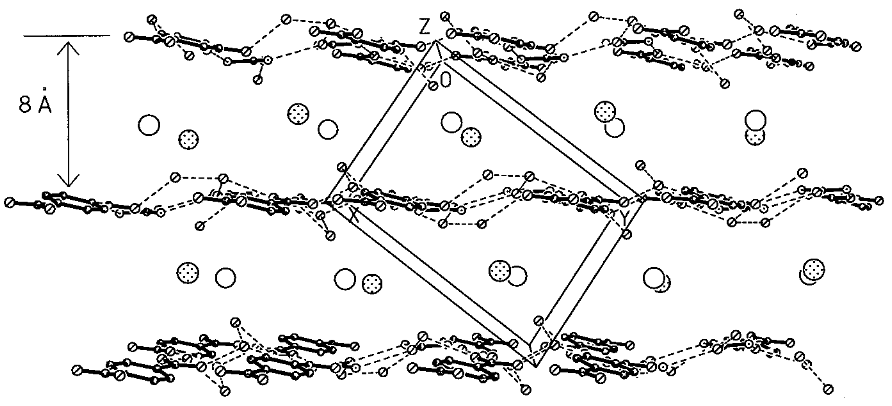

Figure 5
Perspective view along the *c* axis showing the stacking of anionic layers in (2). Large dotted circles represent well ordered Et_4N^+ ions *N*(3), while large open circles denote disordered *N*(4).

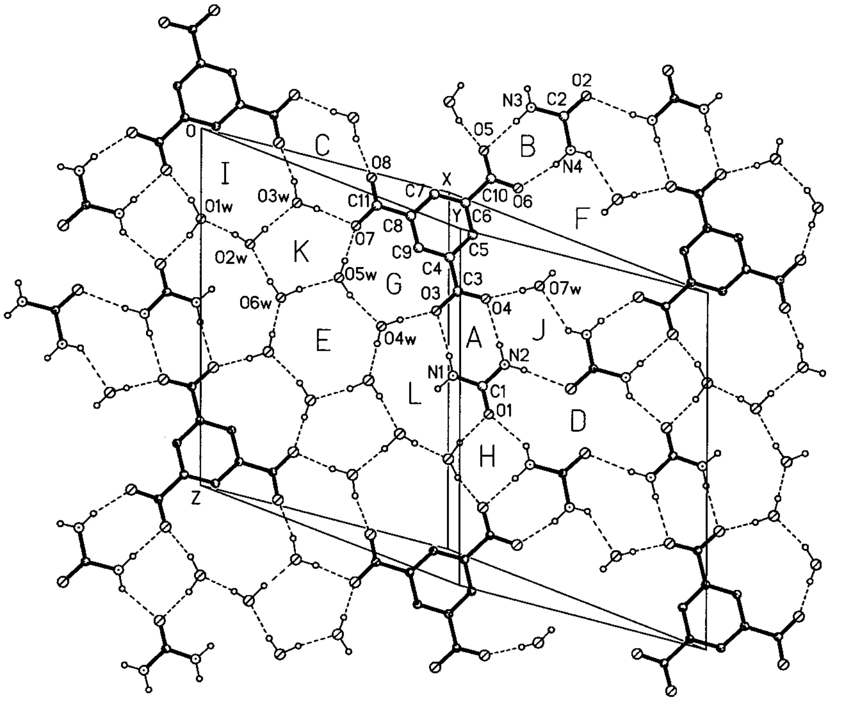

Figure 6
A section through the crystal structure of (3) viewed parallel to the normal of the ($\bar{1}10$) plane, showing a hydrogen-bonded anionic host layer.

3.3. Crystal structure of $[Et_4N^+]_3[1,3,5\text{-}C_6H_3(COO^-)_3]\cdot 2(NH_2)_2CO\cdot 7.5H_2O$ (3)

The asymmetric unit of (3) consists of a trimesate anion, two urea molecules, seven and a half water molecules and three independent tetraethylammonium cations. Water molecule O8*w* exhibits positional disorder about an inversion center (0, $\frac{1}{2}$, 0) and was assigned half site occupancy. The $[(C_2H_5)_4N5]^+$ ion is disordered about atom N5, which acts as a pseudo-inversion center, and the C atoms of each set of ethyl groups were refined to site occupancies of 0.7 and 0.3, respectively. Each of the two urea molecules, *C*(1) (composed of C1, O1, N1 and N2) and *C*(2) (composed of C2, O2, N3 and N4), is connected with one carboxylate group *C*(3) and *C*(10) of the trimesate anion, respectively, through a pair of $N—H_{anti}\cdots O$ hydrogen bonds [*A* and *B*, $N_2 = R_2^2(8)$; Fig. 6]. The third carboxylate group *C*(11) is centrosymmetrically coupled with a symmetry-equivalent carboxylate group of an adjacent trimesate anion *via* two bridging water molecules, O3*w* and O3*wa* centered at ($\frac{1}{2}$, 0, 0), the hydrogen bonding geometry being close to an elongated hexagon [*C*, $N_2 = R_4^4(12)$].

A cyclohexane-type puckered quasi-hexagonal ring motif is built up by hydrogen-bonded water molecules O4*w*, O5*w*, O6*w* and their symmetry equivalents in a chair conformation about the inversion center ($\frac{1}{2}, 0, \frac{1}{2}$) [*E*, $N_3 = R_6^6(12)$]. Each water molecule in the ring forms one donor and one acceptor hydrogen bond with neighboring water molecules, the remaining donor H atoms on O4*w* and O5*w* being linked in a 'chelate' fashion with the homodromic O atoms of carboxylates *C*(3) and *C*(11), resulting in a ring motif *G*. The remaining donor hydrogen bond on O6*w* connects water molecule O2*w* and forms a hydrogen-bonded pentagon O5*w*$\cdots$O6*w*$\cdots$O2*w*$\cdots$O3*w*$\cdots$O7 [*K*, $N_5 = R_5^4(10)$]. A further donor hydrogen bond is formed from O2*w* to O1*w*, while the latter bridges O atoms of urea *C*(1) and trimesate–carboxylate *C*(10) to generate a hydrogen-bonded quadrilateral [*H*, $N_4 = R_4^2(8)$]. The homodromically orientated adjacent urea–carboxylate cycles, *C*(1)—*C*(3) and *C*(2)—*C*(10), are

Table 3
Hydrogen-bonding parameters (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
(1)				
N1—H1*A*···O2	0.86	2.27	3.045 (3)	149.2
N1—H1*B*···O2^{i}	0.86	2.48	3.218 (3)	144.2
N2—H2*A*···O1^{ii}	0.86	2.11	2.951 (3)	164.4
N2—H2*B*···O3^{ii}	0.86	2.15	2.980 (3)	163.4
N3—H3*A*···O1	0.86	2.23	3.037 (3)	156.8
N3—H3*B*···O4	0.86	2.15	3.009 (2)	173.4
N4—H4*A*···O3^{iii}	0.86	2.14	2.962 (3)	160.7
N4—H4*B*···O5	0.86	1.95	2.805 (2)	174.2
N5—H5*A*···O2^{iv}	0.86	2.16	3.003 (3)	165.4
N5—H5*B*···O2^{v}	0.86	2.26	3.024 (2)	148.2
N6—H6*A*···O1*w*	0.86	2.55	3.219 (3)	135.1
N6—H6*B*···O1^{v}	0.86	2.11	2.955 (3)	168.8
O1*w*—H1*wA*···O3	0.85	2.12	2.879 (3)	148.6
O1*w*—H1*wb*···O4	0.85	2.06	2.898 (3)	167.0
(2)				
N1—H1*A*···O1^{vi}	0.86	2.09	2.915 (3)	159.4
N1—H1*B*···O2	0.86	2.14	2.980 (3)	166.1
N2—H2*A*···O2*w*^{vii}	0.86	2.19	3.037 (4)	166.7
N2—H2*B*···O3	0.86	2.09	2.916 (3)	161.6
O1*w*—H1*wA*···O3*w*	0.91	2.02	2.914 (3)	166.9
O1*w*—H1*wB*···O2^{viii}	0.97	1.86	2.802 (3)	164.0
O2*w*—H2*wA*···O4	0.96	1.96	2.766 (3)	140.0
O3*w*—H3*wA*···O1^{ix}	0.97	1.77	2.742 (3)	177.1
O3*w*—H3*wB*···O4	0.98	1.81	2.784 (3)	174.4
O4*w*—H4*wA*···O3^{x}	0.99	1.74	2.718 (3)	170.7
O4*w*—H4*wB*···O5	0.93	1.80	2.727 (3)	176.1
O5*w*—H5*wA*···O4*w*^{xi}	0.98	1.76	2.706 (4)	162.5
O5*w*—H5*wB*···O2*w*	0.97	1.98	2.873 (3)	150.9
O2*w*···O5*w*^{xi}			2.966 (4)	
(3)				
N1—H1*B*···O3	0.86	2.02	2.874 (3)	174.1
N2—H2*A*···O2^{xii}	0.86	2.18	3.025 (4)	169.2
N2—H2*B*···O4	0.86	2.08	2.941 (3)	177.1
N3—H3*A*···O1^{xiii}	0.86	2.30	2.864 (4)	123.0
N3—H3*B*···O5	0.86	1.96	2.791 (4)	163.5
N4—H4*A*···O7*w*^{xiv}	0.86	2.28	2.905 (6)	130.0
N4—H4*B*···O6	0.86	1.92	2.762 (5)	166.7
O1*w*—H1*wA*···O1^{xiii}	0.93 (2)	1.82 (2)	2.732 (3)	166 (4)
O1*w*—H1*wB*···O5	0.94 (2)	1.81 (2)	2.729 (4)	168 (4)
O2*w*—H2*wA*···O3*w*^{xv}	0.93 (2)	1.77 (2)	2.704 (3)	176 (5)
O2*w*—H2*wB*···O1*w*^{xv}	0.94 (2)	1.83 (2)	2.767 (3)	173 (4)
O3*w*—H3*wA*···O8	0.94 (2)	1.82 (2)	2.737 (3)	163 (4)
O3*w*—H3*wB*···O7^{xvi}	0.95 (2)	1.84 (2)	2.760 (3)	164 (3)
O4*w*—H4*wA*···O3	0.96 (2)	1.80 (2)	2.756 (3)	175 (5)
O4*w*—H4*wB*···O6*w*^{xvii}	0.96 (2)	1.81 (2)	2.763 (4)	171 (4)
O5*w*—H5*wA*···O7	0.94 (2)	1.82 (2)	2.754 (4)	172 (4)
O5*w*—H5*wB*···O4*w*	0.94 (2)	1.87 (3)	2.759 (4)	158 (4)
O6*w*—H6*wA*···O2*w*	0.94 (2)	1.87 (3)	2.782 (4)	162 (4)
O6*w*—H6*wB*···O5*w*^{xviii}	0.94 (2)	1.81 (2)	2.743 (4)	168 (5)
O7*w*—H7*wA*···O4	0.96 (2)	1.82 (2)	2.766 (4)	169 (5)
O7*w*—H7*wB*···O8*w*	0.96 (2)	1.91 (4)	2.698 (7)	138 (4)
O7*w*—H7*wB*···O8*w*^{xii}	0.96 (2)	2.03 (3)	2.914 (7)	153 (5)
O8*w*—H8*wA*···O7*w*	0.95 (2)	1.88 (6)	2.698 (7)	143 (7)
O8*w*—H8*wB*···O6	0.95 (2)	1.79 (3)	2.725 (7)	168 (9)
(4)				
N1—H1*A*···O2	0.86	2.25	3.096 (5)	170.2
N1—H1*B*···O3	0.86	2.33	3.182 (5)	173.5
N2—H2*A*···O1*w*^{xix}	0.86	2.29	3.070 (5)	150.9
N2—H2*B*···O4	0.86	1.99	2.839 (6)	169.3
N3—H3*A*···O1	0.86	2.13	2.983 (5)	174.7
N3—H3*B*···O5*w*^{xx}	0.86	2.31	3.103 (7)	153.7
N4—H4*A*···O4*w*^{xxi}	0.86	2.42	3.038 (6)	129.7
N4—H4*B*···O8^{xxii}	0.86	2.13	2.968 (5)	163.9
O5—H5*A*···O3^{xxiii}	0.82	1.73	2.539 (4)	168.0
O1*w*—H1*wA*···O7	0.84	1.94	2.762 (5)	164.3
O1*w*—H1*wB*···O2*w*	0.87	1.93	2.778 (6)	163.4
O2*w*—H2*wA*···O4	0.87	1.91	2.778 (4)	174.1
O2*w*—H2*wB*···O1*w*^{xix}	0.86	1.99	2.839 (6)	170.6
O3*w*—H3*wA*···O2	0.87	1.91	2.753 (5)	163.8
O3*w*—H3*wB*···O6^{xxiv}	0.85	2.01	2.791 (5)	151.9
O4*w*—H4*wA*···O1	0.88	2.00	2.864 (5)	164.9
O4*w*—H4*wB*···O7^{xix}	0.85	2.13	2.915 (4)	154.5
O5*w*—H5*wA*···O3*w*	0.88	1.93	2.791 (5)	166.9
O5*w*—H5*wB*···O8^{xxiv}	0.87	1.90	2.741 (6)	160.9
O3···O6^{xxiv}	–	–	3.130 (4)	–

Symmetry codes: (i) $2 - x, 1 - y, -z$; (ii) $2 - x, -y, -z$; (iii) $x, 1 + y, z$; (iv) $x, -1 + y, z$; (v) $1 - x, -y, -z$; (vi) $1 - x, 1 - y, 3 - z$; (vii) $x, y, 1 + z$; (viii) $1 - x, 1 - y, 2 - z$; (ix) $x, y, -1 + z$; (x) $-x, 2 - y, 2 - z$; (xi) $-x, 2 - y, 1 - z$; (xii) $-x + 2, -y + 1, -z$; (xiii) $x, y, z - 1$; (xiv) $-x + 2, -y + 1, -z$; (xv) $-x + 1, -y + 1, -z$; (xvi) $-x + 1, -y, -z$; (xvii) $-x + 1, -y + 1, -z + 1$; (xviii) $x, y + 1, z$; (xix) $1 - x, 1 - y, \frac{1}{2} + z$; (xx) $\frac{1}{2} + x, \frac{3}{2} - y, z$; (xxi) $-\frac{1}{2} + x, \frac{3}{2} - y, z$; (xxii) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z$; (xxiii) $-x, 1 - y, -\frac{1}{2} + z$; (xxiv) $-x, 1 - y, \frac{1}{2} + z$.

centrosymmetrically connected through a bridging water molecule O7*w* and a N—H$_{syn}$···O hydrogen bond from urea *C*(1) to *C*(2) that is attached to a different trimesate unit, generating a large cavity of dimensions *ca* 5.3 × 9.0 Å [*F*, $N_3 = R_6^6(24)$] around the inversion center at $(0, \frac{1}{2}, 0)$. The water molecule O8*w* fills this cavity and is disordered about the inversion center with hydrogen-bonding to O7*w*. A centrosymmetric urea tetramer, centered at $(0, \frac{1}{2}, \frac{1}{2})$, is generated from a hydrogen-bonded ring motif [*D*, $N_2 = R_4^4(16)$] , in which each urea molecule provides a donor and an acceptor hydrogen-bonding site. Further ring patterns, consisting of *G*, $N_3 = R_3^3(12)$, *I*, $N_4 = R_4^4(14)$, *J*, $N_4 = R_4^3(10)$ and *L*, $N_6 = R_6^5(14)$ in the intricate hydrogen-bonding scheme, generate a puckered layer structure running parallel to the $(\bar{1}10)$ family of planes (Fig. 6). Note that all well-ordered water molecules, O1*w* to O7*w*, have a similar hydrogen-bonding pattern in this structure, *i.e.* each forms two donor and one acceptor hydrogen bonds.

Three independent tetraethylammonium cations are arranged in two separate columns running parallel to the [001] direction. The columns of type $[(C_2H_5)_4N6]^+$ cations are located at $x \simeq 1/2$, $y \simeq 1/2$, and those columns located at $x \simeq 1/6$, $y \simeq 1/6$ and $x \simeq 5/6$, $y \simeq 5/6$ are composed of alternately arranged $[(C_2H_5)_4N5]^+$ and $[(C_2H_5)_4N7]^+$ cations along the [001] direction. The cationic layer is sandwiched between adjacent hydrogen-bonded layers with an inter-layer distance of *ca* 7.5 Å (Fig. 7).

3.4. Crystal structure of $[(n\text{-Pr})_4N^+]_2[1,3,5\text{-}C_6H_3(COO^-)_2(COOH)]\cdot 2(NH_2)_2CO\cdot 5H_2O$ (4)

The asymmetric unit of (4) consists of two tetra-*n*-propylammonium cations, a hydrogen trimesate anion, in which one carboxylate group *C*(10) retains an acidic H atom at O5, two urea molecules and five water molecules. Urea molecule *C*(1) (composed of C1, O1, N1 and N2) forms a pair of N—H$_{anti}$···O hydrogen bonds with carboxylate group *C*(3) of the hydrogen trimesate anion; the non-planar geometry is described by the dihedral angle of 14.9° between the urea molecule and the carboxylate group [*C*, $N_2 = R_2^2(8)$], with torsion angles C1—N2···O4—C3 −18.2 and C1—N1···O3—C3 −16.4°. As shown in the perspective view down the [010]

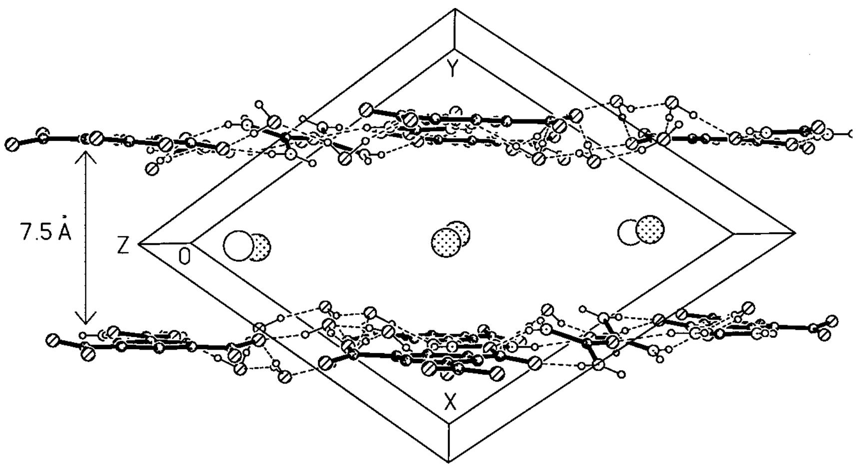

Figure 7
Perspective view along the *c* axis showing the stacking arrangement of layers in (3). Large dotted circles represent the well ordered Et_4N^+ ions *N*(6) and *N*(7), while large open circles denote disordered *N*(5).

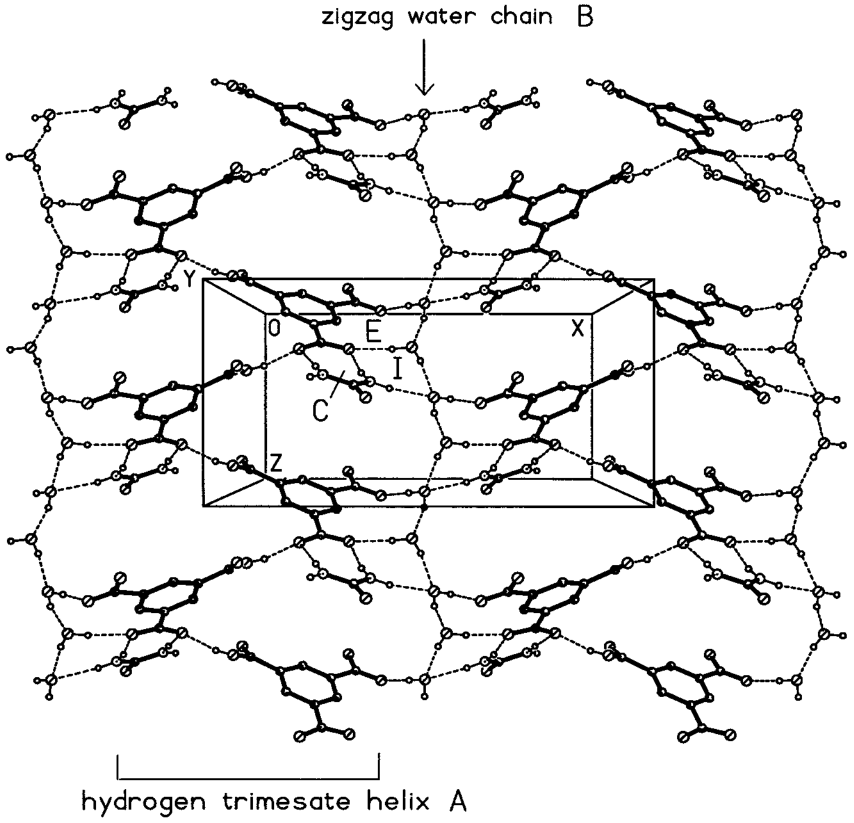

Figure 8
Perspective view along the [010] direction showing the hydrogen trimesate–urea helices (*A*) and zigzag water chains (*B*) in (4).

direction (Fig. 8), the hydrogen trimesate–urea heterodimers are arranged into a helix around the 2_1 screw axis along the *c* axial direction, *via* $O-H_{acid}\cdots O$ hydrogen bonds between the carboxylic group *C*(10) and carboxylate *C*(3) of symmetry-related trimesate anions [*A*, $N_1 = C(8)$]. Adjacent helices are connected laterally by a parallel zigzag water chain constituted from alternate linkage of O1*w* and O2*w* [*B*, $N_2 = C_2^2(4)$] through two hydrogen-bonded ring motifs *E* [$N_3 = R_3^3(12)$] and *I* [$N_4 = R_4^2(8)$].

Urea *C*(1) is further coupled with urea *C*(2) (composed of C2, O2, N3 and N4) *via* a pair of $N-H_{syn}\cdots O$ hydrogen bonds into a cyclic dimer [*D*, $N_2 = R_2^2(8)$], which adopts a twisted configuration, as indicated by the dihedral angle of 34.7° between the two urea molecules, and torsion angles C1—O1···N3—C2 43.7° and C1—N1···O2—C2 42.3° (Fig. 9). Urea molecule *C*(2) connects with the carboxylate group *C*(11) of a neighboring trimesate anion through one $N-H_{anti}\cdots O$ hydrogen bond and bridging water molecule O5*w*, resulting in a different ring pattern *F*, $N_3 = R_3^2(8)$. Other ring patterns *G*, $N_3 = R_3^3(8)$, *H*, $N_3 = R_3^3(12)$, *J*, $N_4 = R_4^3(10)$, *K*, $N_5 = R_5^3(12)$ and *L*, $N_6 = R_6^5(14)$ are illustrated in Fig. 9.

Nanoscale voids arise from the construction of the hydrogen-bonded network, leading to elongated hexagonal channels of cross sectional dimensions 8.3 × 17.9 Å that run parallel to the *a* axis (Fig. 10). The two independent tetra-*n*-propylammonium cations are arranged alternately in two columns within each channel in a well ordered pattern. Note that water molecules O2*w*, O3*w*, O4*w* and O5*w* each forms two donor and one acceptor hydrogen bond like a three-way connector in the hydrogen-bonding scheme, while O1*w* forms four (two donor and two acceptor) hydrogen bonds in a distorted tetrahedral geometry.

3.5. Hydrogen-bonding motifs

Scheme (II) illustrates some basic hydrogen-bonding motifs observed for (1)–(4). The urea–carboxylate pattern *I*, $N_2 = R_2^2(8)$ is found in all four compounds, as the rigid orientation of urea and terephthalate/trimesate moieties makes it the fundamental building block of the hydrogen-bonding network. In (1) carboxylate groups of terephthalate adopt pattern *I* with urea *C*(1) (1*C*[2]) and constitute the level portion of the layer structure; only one carboxylate group is found in this arrangement for (2) and (4) (2*A* and 4*C*); while in (3), two of the three carboxylate groups of the trimesate anion are connected with urea molecules in this pattern (3*A* and 3*B*). The urea dimer pattern *II*, $R_2^2(8)$ exists in the hydrogen-bonding

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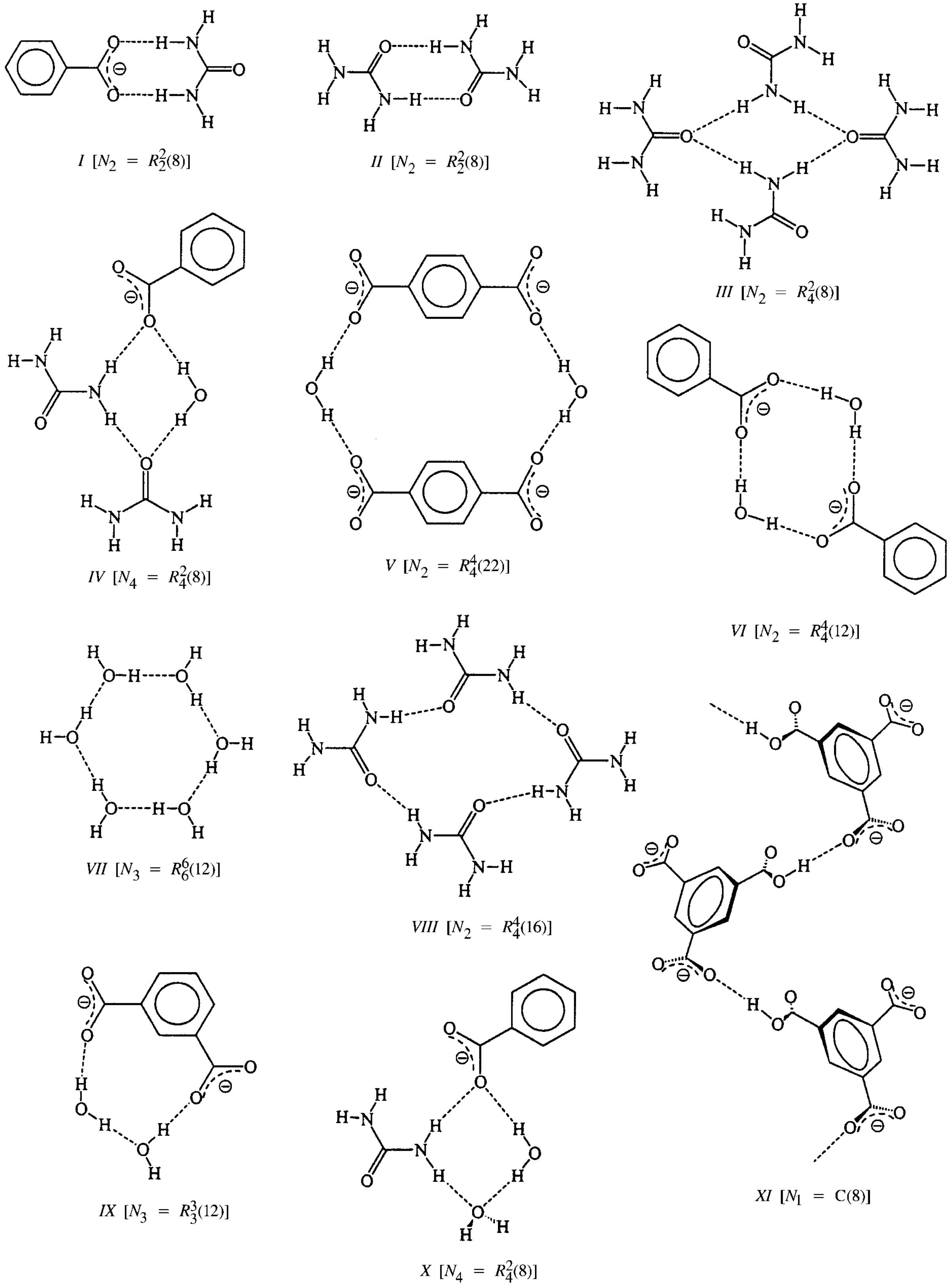
[2] This notation represents the corresponding pattern in each compound; here 1*C* represents pattern *C* in (1).

scheme in (1), (2) and (4) (1*A*, 1*B*, 2*A* and 4*D*). A head-to-head centrosymmetric arrangement of four urea molecules generating hydrogen-bonding pattern *III*, $R_4^2(8)$, which is the characteristic binary graph of primary amides (Bernstein *et al.*, 1995), is found in (1) and plays an important role in the formation of urea ribbon 1*E* {consisting of 1*A* and 1*D*,



(II)

$C_3^2(10)[R_2^2(8)R_4^2(8)]\}$ and the vertical portion of the latter structure (1*H*). Two unusual patterns consisting of unsymmetrically arranged urea, carboxylate and water moieties are found, namely *IV* (3*H*) and *X* (4*I*), in which chemically very different but functionally similar species, *e.g.* H_2O and H_2N—, can serve equally well as hydrogen-bonding donors. More examples of different patterns involving water molecules, *V* (2*C*), *VI* (3*C*), *VII* (3*E*) and *IX* (3*G*, 4*E*, 4*H*), which demonstrate the manifestation of some basic hydrogen-bonding functionality, together with the occurrence of more complicated patterns of water molecules in (1)–(4), imply a recognition process that takes place through the aqueous medium in the crystal nucleation process, which is an important aspect of hydrogen-bonding in biological systems (Jeffrey, 1994). Pattern *VIII* (3*D*) represents a centrosymmetrical cyclic urea tetramer consolidated by $N—H_{syn}\cdots O$ hydrogen bonds, while *XI* (4*A*) illustrates a helical chain of hydrogen trimesate anions.

The inter-layer spacing of (2) and (3), being 8.0 and 7.5 Å, respectively, are slightly larger than the corresponding values (average 7.0–7.5 Å) for similar layer structures with tetraethylammonium cations sandwiched in the urea–water–bicarbonate (Li *et al.*, 1995), urea–water–dihydrogen borate (Li *et al.*, 1999), urea–chloride (Li & Mak, 1997*a*), thiourea–water–bicarbonate (Li & Mak, 1995), thiourea–water–formate (Li & Mak, 1997*b*) and thiourea–oxalate (Li & Mak, 1997*c*) host lattices. This is to be expected in view of the higher molar ratio of water molecules used in the construction of the present layer structures; as flexible hydrogen-bonding connectors, some of the water molecules may deviate from the mean plane of the buckled layer.

The systematics of a wide variety of host lattices generated by the combined use of urea, thiourea or selenourea plus selected anionic and neutral species as building blocks have been recently reviewed (Li & Mak, 1998).

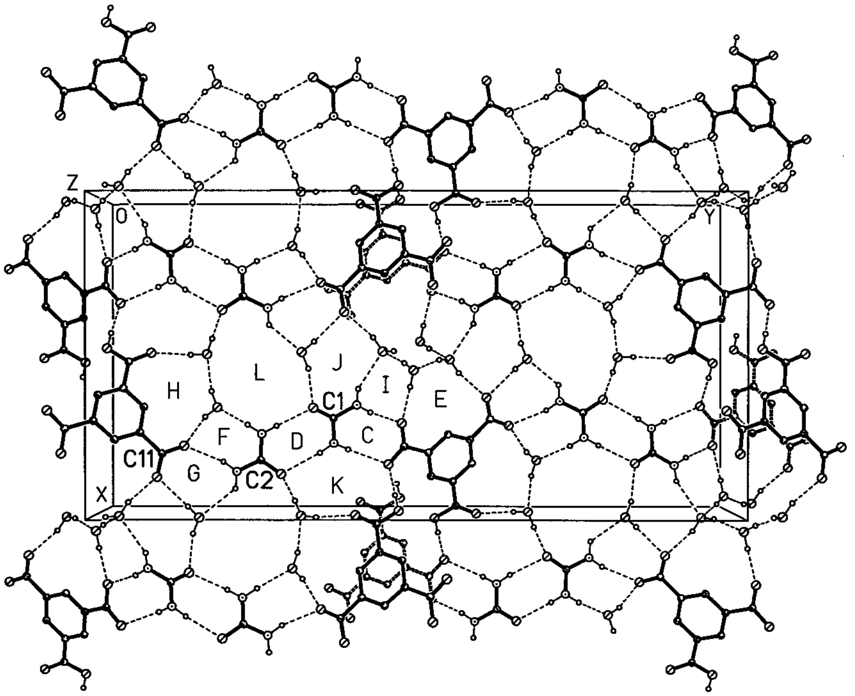


Figure 9
Perspective diagram viewed along the *c* axis showing the linkage of hydrogen-bonded patterns into a three-dimensional network in (4).

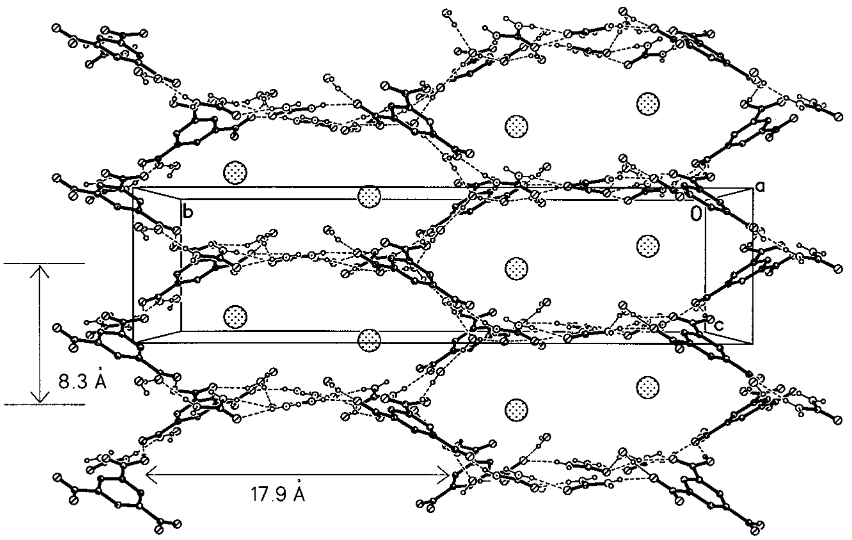


Figure 10
Perspective view along the *a* axis showing the channel-type structure of (4), with well ordered *n*-Pr_4N^+ cations (represented by large dotted circles) occupying each nanoporous channel in double columns.

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