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Hydrogen-bonded anionic layer structures constructed from 4,4′-biphenyldicarboxylate and water molecules, and also with urea as an additional component

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ABSTRACT: The crystal engineering of four new layer-type molecular solids is described. The anionic host layer in $2(Et_4N^+)\cdot[4,4'\text{-}(C_6H_4)_2(COO^-)_2]\cdot 4H_2O$ (1) is constructed from 4,4′-biphenyldicarboxylate (BPDC) and a square $(H_2O)_4$ cluster through O—H···O and C—H···O hydrogen bonds. A hydrogen-bonded $[(H_2O)_8O_4]$ cluster connects BPDC ions through O—H···O linkages to form an anionic layer in $2[(n\text{-Pr})_4N^+]\cdot[4,4'\text{-}(C_6H_4)_2(COO^-)_2]\cdot 8H_2O$ (2). In $2[(n\text{-Pr})_4N^+]\cdot[4,4'\text{-}(C_6H_4)_2(COO^-)_2]\cdot 2[(NH_2)_2CO]\cdot 4H_2O$ (3) and $2[(n\text{-Bu})_4N^+]\cdot[4,4'\text{-}(C_6H_4)_2(COO^-)_2]\cdot 2[(NH_2)_2CO]\cdot 4H_2O$ (4), BPDC forms analogous hydrogen-bonding patterns with urea and water molecules through N—H···O and O—H···O interactions, but the resulting anionic layers are pleated and nearly planar, respectively. Tetraalkylammonium cations are sandwiched between layers as guest species in all four structures. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: crystal engineering; hydrogen bonding; supramolecular chemistry; urea; 4,4′-biphenyldicarboxylate; anionic layer structure

INTRODUCTION

Recent efforts in the study of molecular solids are connected with structural design based on the exploitation of intermolecular interactions, which mediate crystal packing and direct the molecular orientation in supramolecular architecture.[1] Hydrogen bonding, as the most important non-covalent interaction, plays a central role in the rational control and predictability of molecular self-assembly processes in crystal engineering.[2–4] Conventional strong hydrogen bonds such as O—H···O and N—H···O are well known in this context, but weak interactions such as C—H···O and C—H···N have also attracted considerable interest because they occur frequently in organic crystal structures and share some of the characteristics of their stronger counterparts.[5,6] As the established principles of crystal engineering are still incapable of predicting solid-state structures unerringly,[7] a reasonable strategy for surmounting this obstacle is to use robust supramolecular modules or synthons, where ‘robust’ is defined as the ability of the synthon to maintain its dimensionality and general structural features in different crystalline environments that contain various ancillary functional groups and/or additional molecular species.[8]

An example of the interplay of strong and weak hydrogen bonding based on simple and robust structural elements in abstruse hydrogen-bonded motifs is provided by a recent study on molecular complexes of some 4,4′-disubstituted biphenyls with urea, thiourea and water.[9] It is anticipated that the 4,4′-biphenyldicarboxylate anion (BPDC), possessing a rigid molecular skeleton and strong acceptor groups at both ends, will serve as an effective building block for the construction of hydrogen-bonded molecular solids. Here we report the generation of four new hydrogen-bonded layer-type structures and their characterization by x-ray crystallography:

$$2(Et_4N^+)\cdot[4,4'-(C_6H_4)_2(COO^-)_2]\cdot\ 4H_2O\ (\mathbf{1})$$

$$2[(n\text{-Pr})_4N^+]\cdot[4,4'-(C_6H_4)_2(COO^-)_2]\cdot\ 8H_2O\ (\mathbf{2})$$

$$2[(n\text{-Pr})_4N^+]\cdot[4,4'-(C_6H_4)_2(COO^-)_2]\cdot\ 2[(NH_2)_2CO]\cdot\ 4H_2O\ (\mathbf{3})$$

$$2[(n\text{-Bu})_4N^+]\cdot[4,4'-(C_6H_4)_2(COO^-)_2]\cdot\ 2[(NH_2)_2CO]\cdot\ 4H_2O\ (\mathbf{4})$$

EXPERIMENTAL

Synthesis. Molecular adducts **1–4** were prepared by crystallizing 4,4′-biphenyldicarboxylic acid, and together with urea in a 1:2 molar ratio in the case of **3** and **4**, from

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Table 1. Crystallographic data and structure refinement parameters

	1	**2**	**3**	**4**
Formula	$C_{30}H_{56}N_2O_8$	$C_{38}H_{80}N_2O_{12}$	$C_{40}H_{80}N_6O_{10}$	$C_{48}H_{96}N_6O_{10}$
Formula weight	572.77	757.04	805.10	917.31
Crystal habit and size (mm^3)	Colorless needle 0.40 × 0.20 × 0.18	Colorless prism 0.50 × 0.40 × 0.30	Colorless plate 0.40 × 0.30 × 0.18	Yellow block 0.50 × 0.45 × 0.40
Crystal system	Triclinic	Orthorhombic	Monoclinic	Orthorhombic
Space group	$P1$ (No. 2)	$Pbcn$ (No. 60)	$P2_1/c$ (No. 14)	$Pca2_1$ (No. 29)
a (Å)	7.746(1)	16.955(1)	8.603(1)	31.622(1)
b (Å)	14.604(1)	16.452(1)	17.382(1)	9.384(1)
c (Å)	15.564(1)	16.403(1)	16.820(1)	18.511(1)
α (°)	108.62(1)	90	90	90
β (°)	94.03(1)	90	104.72(1)	90
γ (°)	94.43(1)	90	90	90
V (Å^3)	1655.1(3)	4575.5(5)	2432.7(3)	5493.0(7)
Z	2	4	2	4
$F(000)$	628	1672	884	2024
d_{calc} (g cm^{-3})	1.149	1.099	1.099	1.109
μ(mm^{-1})	0.082	0.080	0.078	0.077
Absorption	ABSCOR	ABSCOR	ABSCOR	ABSCOR
T_{max}, T_{min}	1.233–0.749	1.285–0.703	1.352–0.694	1.000–0.970
Diffractometer	RAXIS IIC	RAXIS IIC	RAXIS IIC	AFC7R
Scan type	Oscillation	Oscillation	Oscillation	ω-scan
$2\theta_{max}$ (°)	52	52	50	52
Index ranges	±9, 17, ±18	±20, ±19, 19	9, ±20, ±19	38, 11, 22
$N_{collected}$	4109	11045	5281	5571
N_{unique} (R_{int})	4109 (0.00)	3913 (0.0437)	3196 (0.0636)	5571 (0.00)
$N_{parameter}$	386	263	266	602
$R1$[a] [$I > 2\sigma(I)$]	0.0633	0.0861	0.0699	0.0497
$wR2$[b]	0.1670	0.2075	0.1917	0.1507
a/b[c]	0.0753/0.0614	0.0733/1.4817	0.0944/0.0307	0.0664/0.000
S (GOF)[d]	1.115	1.235	1.177	0.942
Max. Δ/σ	0.000	0.000	0.000	0.043
$\Delta\rho_{max}$ (e Å^{-3})	0.138, −0.155	0.289, −0.167	0.177, −0.205	0.155, −0.173
C_k[e]	0.675	0.658	0.640	0.659

[a] $R1 = \Sigma|F_o| - |F_c|/\Sigma|F_o|$ with observed reflections.

[b] $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/[\Sigma w(F_o^2)^2]\}^{1/2}$ with all unique reflections.

[c] Weighting scheme: $w^{-1} = \sigma^2(F_o^2) + (a \times P)^2 + b \times P$, where $P = (F_o^2 + 2F_c^2)/3$.

[d] $S = \mathrm{GOF} = \{[\Sigma w(F_o^2 - F_c^2)^2]/(N_{unique} - N_{parameter})\}^{1/2}$.

[e] C_k is the packing coefficient calculated using the program PLATON-99.[21]

an aqueous solution of the corresponding tetraalkylammonium hydroxide R_4NOH (40 wt% for R = *n*-Bu, 1 M for R = *n*-Pr, 35 wt% for R = Et). Diffraction-quality crystals were obtained in nearly quantitative yield in 2–3 weeks from slow evaporation of solvent at ambient temperature in a desiccator filled with Drierite.

X-ray crystallography. Information concerning crystallographic data collection and structure refinement of all four compounds is summarized in Table 1. Intensity data for **1–3** were collected at 294 K on an MSC/Rigaku RAXIS IIC imaging-plate detector system[10] using Mo Kα radiation (λ = 0.71073 Å) from a Rigaku RU-200 rotating-anode generator operating at 50 kV and 9 mA. Data collection and reduction were performed using bioteX software.[11] For **1**, the data were collected to 0.82 Å resolution (86% complete) by taking oscillation frames in the range 0–168°, $\Delta\varphi$ = 6°, exposure 10 min per frame; for **2**, the data were collected in a similar way with 90% completeness, $\Delta\varphi$ = 5° in the range 0–180°, exposure 8 min per frame; for **3**, the data were 82% complete, $\Delta\varphi$ = 4° in the range 0–168°, exposure 10 min per frame. A self-consistent semi-empirical absorption correction based on Fourier coefficient fitting of symmetry-equivalent reflections was applied by using the ABSCOR program.[12] Intensity data for **4** were collected at 294 K in the variable ω-scan mode on a Rigaku AFC7R four-circle diffractometer from the same Rigaku RU-200 generator. 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.[13]

Determination of the crystal structures of **1–4** by direct methods yielded the positions of all non-hydrogen atoms, which were refined with anisotropic thermal parameters. Hydrogen atoms attached to carbon atoms were gener-

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Table 2. Hydrogen bonding geometries: bond lengths (Å) and angles (°)

Adduct	D—H···A[a]	*d*(D—H)	*d*(H···A)	*d*(D···A)	∠(DHA)
1	O(1W)—H(1WA)···O(1)	0.902(11)	1.940(11)	2.839(3)	175(2)
	O(1W)—H(1WB)···O(3W)#1	0.904(11)	1.953(13)	2.790(3)	153(2)
	O(2W)—H(2WA)···O(1W)#2	0.911(11)	1.916(11)	2.818(3)	170(2)
	O(2W)—H(2WB)···O(2)	0.911(11)	1.843(12)	2.750(3)	174(2)
	O(3W)—H(3WA)···O(4W)#3	0.902(11)	1.937(14)	2.786(3)	156(3)
	O(3W)—H(3WB)···O(3)	0.906(11)	1.789(12)	2.695(3)	178(4)
	O(4W)—H(4WA)···O(4)	0.912(11)	1.891(11)	2.796(3)	171(2)
	O(4W)—H(4WB)···O(2W)#4	0.910(11)	2.002(14)	2.834(3)	151(2)
	C(4)—H(4)···O(4)#3	0.93	2.843	3.802	176
	C(9)—H(9)···O(1)#2	0.93	3.342	4.031	130
2	O(1W)—H(1WA)···O(2)#5	0.900(17)	1.932(17)	2.757(3)	152(3)
	O(1W)—H(1WB)···O(1)	0.899(17)	1.935(17)	2.806(3)	163(3)
	O(2W)—H(2WA)···O(1W)	0.899(16)	1.936(17)	2.790(3)	158(3)
	O(2W)—H(2WB)···O(2)#6	0.887(17)	2.232(17)	3.118(3)	176(3)
	O(3W)—H(3WA)···O(2W)#7	0.898(16)	2.102(19)	2.977(3)	164(3)
	O(3W)—H(3WB)···O(2)	0.908(17)	1.928(17)	2.833(3)	175(3)
	O(4W)—H(4WA)···O(3W)	0.895(17)	2.10(2)	2.964(3)	161(4)
	O(4W)—H(4WB)···O(1)#6	0.900(17)	1.998(18)	2.896(3)	175(4)
3	N(1)—H(1B)···O(2)	0.86	2.09	2.929(3)	165.6
	N(2)—H(2A)···O(1)#8	0.86	2.09	2.940(4)	170.9
	N(2)—H(2B)···O(3)	0.86	2.06	2.904(3)	165.3
	O(1W)—H(1WA)···O(2)	0.955(17)	1.841(18)	2.780(3)	168(3)
	O(1W)—H(1WB)···O(1)#9	0.950(17)	1.756(18)	2.689(3)	166(3)
	O(2W)—H(2WA)···O(1W)#10	0.950(19)	1.835(19)	2.776(3)	170(3)
	O(2W)—H(2WB)···O(3)	0.943(19)	1.94(2)	2.864(3)	168(3)
4	N(1)—H(1A)···O(2)#11	0.86	2.14	2.997(6)	171.6
	N(1)—H(1B)···O(3)	0.86	2.02	2.883(5)	175.5
	N(2)—H(2B)···O(4)	0.86	2.03	2.891(6)	178.7
	N(3)—H(3A)···O(1)#12	0.86	2.20	3.027(6)	160.5
	N(3)—H(3B)···O(5)	0.86	2.05	2.908(5)	176.1
	N(4)—H(4B)···O(6)	0.86	2.04	2.872(6)	164.1
	O(1W)—H(1WA)···O(2W)#13	0.86(2)	2.09(3)	2.940(6)	170(6)
	O(1W)—H(1WB)···O(3)	0.86(2)	2.04(3)	2.889(6)	171(7)
	O(2W)—H(2WA)···O(4)	0.86(2)	1.98(3)	2.818(5)	165(5)
	O(2W)—H(2WB)···O(2)#14	0.86(2)	2.06(4)	2.806(6)	145(5)
	O(3W)—H(3WA)···O(4W)#15	0.88(2)	2.09(3)	2.934(6)	162(5)
	O(3W)—H(3WB)···O(5)	0.87(2)	2.16(4)	2.981(6)	157(7)
	O(4W)—H(4WA)···O(1)#16	0.85(2)	2.04(3)	2.886(5)	169(6)
	O(4W)—H(4WB)···O(6)	0.85(2)	2.03(3)	2.864(5)	166(6)

[a] Symmetry transformations used to generate equivalent atoms: #1, $x-1, y-1, z$; #2, $x+1, y, z$; #3, $x-1, y, z$; #4, $x+1, y+1, z$; #5, $x, y-1, z$; #6, $-x+1, -y, -z+2$; #7, $x, y+1, z$; #8, $-x+1, -y+1, z$; #9, $-x, -y+1, -z$; #10, $x+1, y, z$; #11, $x, y-1, z-1$; #12, $x, y+1, z+1$; #13, $x, y-1, z$; #14, $x, y, z-1$; #15, $x, y+1, z$; #16, $x, y, z+1$.

ated assuming idealized geometry, assigned appropriate isotropic thermal parameters and allowed to ride on their parent carbon atoms. Hydrogen atoms involved in hydrogen bonding were unambiguously located from difference electron density maps, assigned isotropic thermal parameters 1.2–1.5 times those of their parent non-hydrogen atoms and refined using the riding model (N—H bond lengths refined to 0.86 Å and O—H bond lengths refined to 0.82–0.85 Å). All computations were performed on an IBM compatible PC with the SHELXL-97[14] for full-matrix least-squares refinement against F^2 and SHELXTL-PC program package[15] for preparing the diagrams. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated.[16] The atomic parameters of **1–4** have been deposited with the Cambridge Crystallographic Data Center as CCDC Ref. No. 138308–138311.

RESULTS AND DISCUSSION

Geometric parameters of the hydrogen-bonding schemes in **1–4** are listed in Table 2. Description of the anionic layer structures is facilitated by the use of graph set analysis to identify hydrogen-bonding motifs and patterns, and details of the definition, terminology and notation are given in papers by Bernstein and coworkers.[17]

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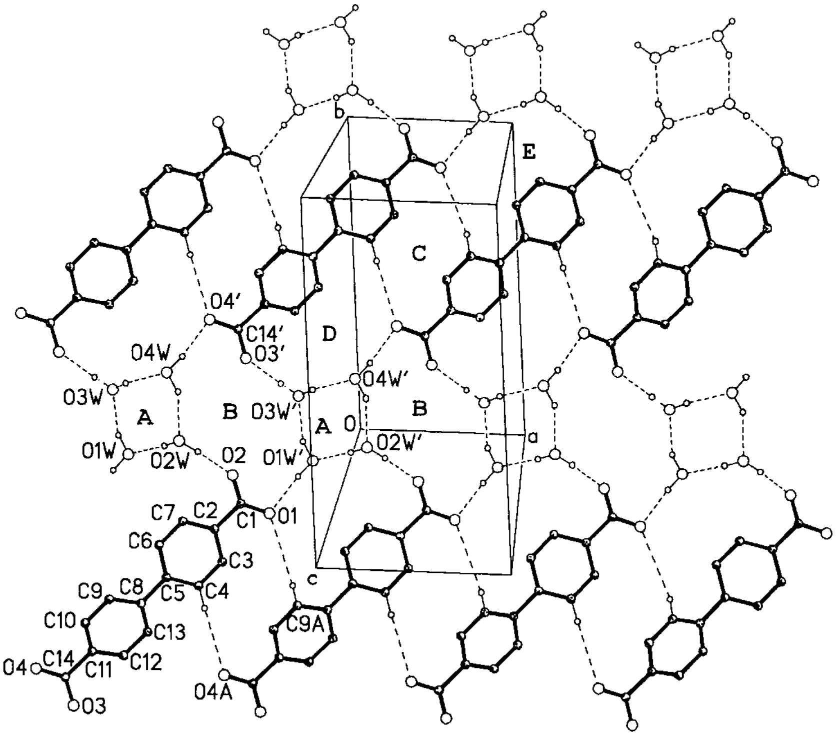

Figure 1. Hydrogen-bonded anionic layer in **1** shown as a projection viewed down the [001] direction. Atom types are differentiated by size and shading and hydrogen bonds are represented by broken lines. Various hydrogen-bonding motifs as discussed in the text are labeled by bold capital letters **A** to **E**, and similar labels are used in Figs 3, 6 and 8

$2(Et_4N^+)\cdot[4,4'{-}(C_6H_4)_2(COO^-)_2]\cdot 4H_2$ (1)

The asymmetric unit of **1** consists of one BPDC anion, four water molecules and two Et_4N^+ cations. As shown in Fig. 1, the four independent water molecules are almost coplanar with an average deviation of ca 0.06 Å, forming a hydrogen-bonded tetramer [**A** $N_4 = R_4^4(8)$] through four O—H···O interactions ($d_{O\cdots O} = 2.786$–2.834 Å, $\theta = 151$–170°). Each water molecule provides one hydrogen-bonding donor site and acts as an acceptor in building the tetrameric square. The remaining four *exo*-orientated water donor sites are linked to four distinct carboxylate-O atoms of adjacent BPDC ions through O_W—H···O hydrogen bonds ($d_{O\cdots O} = 2.695$–2.839 Å, $\theta = 171$–178°), thereby generating a hydrogen-bonding pattern **B** $N_6 = R_6^6(16)$ The alternating **A–B** motifs are arranged into an infinite one-dimensional ribbon running approximately parallel to the *a* axis. Each BPDC anion bridges neighboring **A–B** ribbons obliquely at an angle of 46.6° from the normal with its two phenyl rings slightly twisted at a dihedral angle of 34.8°, producing a slightly puckered layer parallel to the (001) set of planes. The network is further stabilized by C—H···O hydrogen bonding involving H atoms attached to C(4) and C(9) which point toward adjacent carboxylate-O atoms as a result of the offset parallel arrangement of BPDC ions, generating ring motifs **C** $N_2 = R_2^2(12)$, **D** $N_4 = R_4^3(15)$ and **E** $N_4 = R_4^3(15)$. Ordered Et_4N^+ cations are sandwiched between anionic layers with an inter-layer distance of ca 6.7 Å (Fig. 2).

$2[(n\text{-}Pr)_4N^+]\cdot[4,4'\text{-}(C_6H_4)_2(COO^-)_2]\cdot 8H_2O$ (2)

As shown in Fig. 3, the anionic layer in **2** can be described as a two-dimensional ladder-type structure. The BPDC ions are bridged through a pair of O_W—H···O hydrogen bonds (**A** $N_2 = R_4^4(12)$) by symmetry-related water molecules O(1W) and O(1WA) into an infinite chain running parallel to the [010] direction. The two phenyl rings of BPDC are twisted with a dihedral angle of 29°, and the pair of carboxylate groups that are connected by the double water-bridge make a dihedral angle of 32.5°. Neighboring chains are double-linked by two hydrogen-bonding patterns. Both O(1W)—O(2W) and O(3W)—O(4W) join O(1) and O(2) belonging to BPDC carboxylate groups of adjacent chains, generating two large centrosymmetric ring motifs **B** $N_3 = R_6^6(34)$ and **C** $N_3 = R_6^6(34)$ with an area of ca 69 Å^2, plus an unusual centrosymmetric $[(H_2O)_8O_4]$ cluster resembling a 'basketane' with an additional handle on the opposite side, which consists of hydrogen-bonding ring motifs **D** and **E** $N_4 = R_4^3(8)$, **F**, **G**, **H** and **I** $N_6 = R_6^4(12)$ ($d_{O\cdots O} = 2.757$–3.118 Å, $\theta = 152$–175°) (Fig. 4). The alternating arrangement of pattern **A** and $[(H_2O)_8O_4]$

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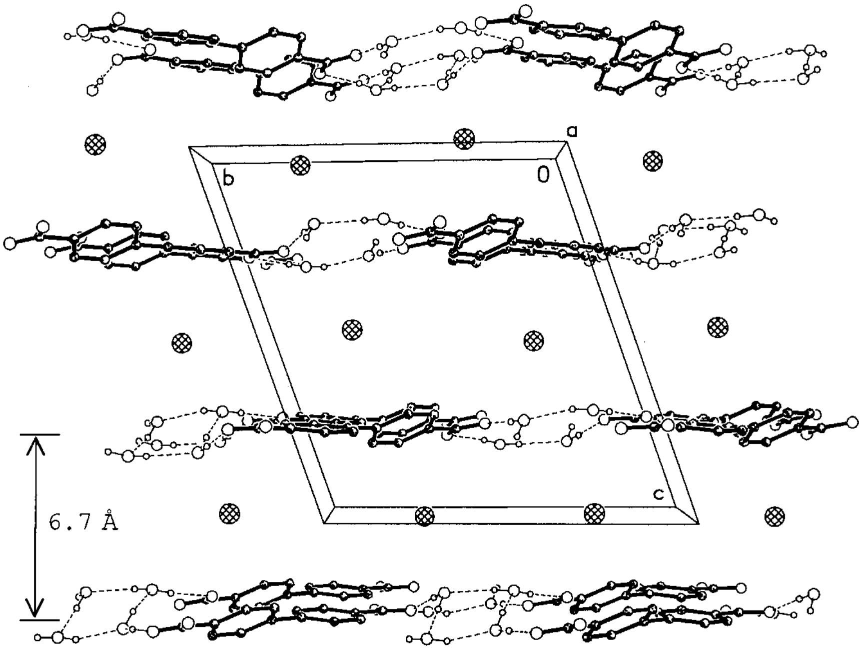

Figure 2. A perspective packing diagram viewed parallel to the (100) plane showing that the Et_4N^+ cations are sandwiched between anionic layers generated by BPDC and water molecules. Large cross-hatched circles represent cations

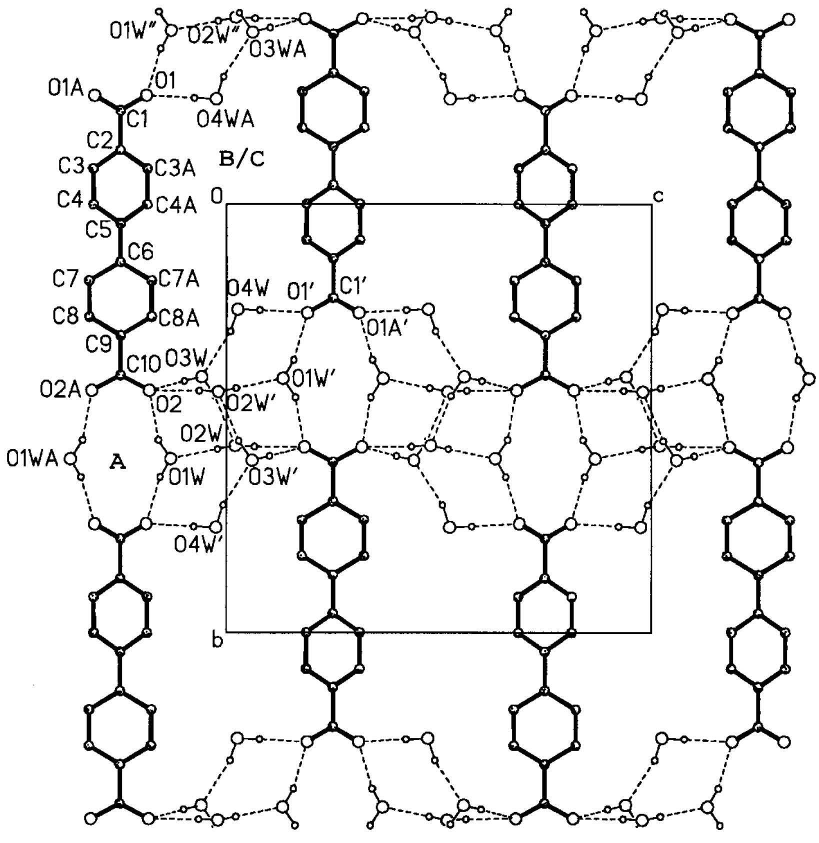

Figure 3. Projection down the *a* axis showing a hydrogen-bonded anionic layer constructed from BPDC and water cluster in **2**

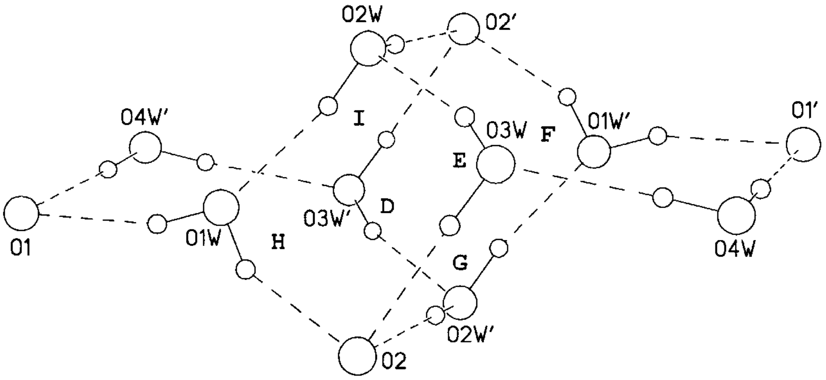

Figure 4. Highlight of hydrogen-bonded $[(H_2O)_8O_4]$ double basketane-like cluster that connects BPDC ions and consolidates the anionic layer in **2**

cluster along the [001] direction yields a zig-zag ribbon, which functions as a side bar of the ladder structure, and successive BPDC ions that constitute the steps are shifted laterally back and forth by *ca.* 2.95 Å parallel to the *b* axis. The resulting anionic layers that are oriented parallel to the *bc*-plane stack along the [100] direction with an inter-layer distance of $a/2 \approx 8.5$ Å, the void space being filled with cationic layers of ordered $(n\text{-Pr})_4N^+$ at $x = 1/4$ and 3/4 (Fig. 5).

$2[(n\text{-Pr})_4N^+]\cdot[4,4'\text{-}(C_6H_4)_2(COO^-)_2]\cdot2[(NH_2)_2CO]\cdot4H_2O$ (3)

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 reviewed recently.[18] As anionic layers are constructed by BPDC and a flexible water cluster in **1** and **2**, we reasoned that introduction of the rigid and topologically complementary urea molecule would likely lead to the creation of a BPDC–urea ribbon. This expectation was realized in the successful preparation of inclusion compound **3**.

As shown in Fig. 6, the planar urea dimer motif (**A** $N_1 = R_2^2(8)$) consolidated by a pair of $N—H_{anti}\cdots O$ hydrogen bonds is centered at (1/2, 0, 0). It interacts with the carboxylate groups of two symmetry-equivalent BPDC ions through a pair of $N—H_{syn}\cdots O$ hydrogen bonds [**B** $N_2 = R_2^2(8)$] to generate an infinite zig-zag chain running along the diagonal of the *ab*-plane. Two independent water molecules, O(1W) and O(2W), link the carboxylate-O atoms of BPDC belonging to neighboring chains through three $O_W—H\cdots O$ hydrogen bonds, resulting in the large ring motif **E** $N_3 = R_6^6(34)$with an area of *ca.* 67 Å^2. The excess donor

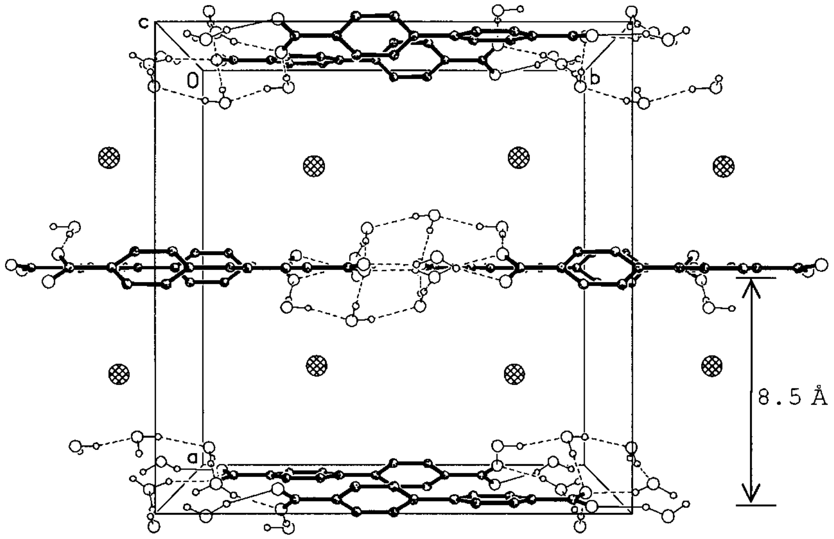

Figure 5. Crystal packing diagram viewed down the *c* axis showing $(n\text{—Pr})_4N^+$ cations sandwiched between BPDC-water layer in **2**

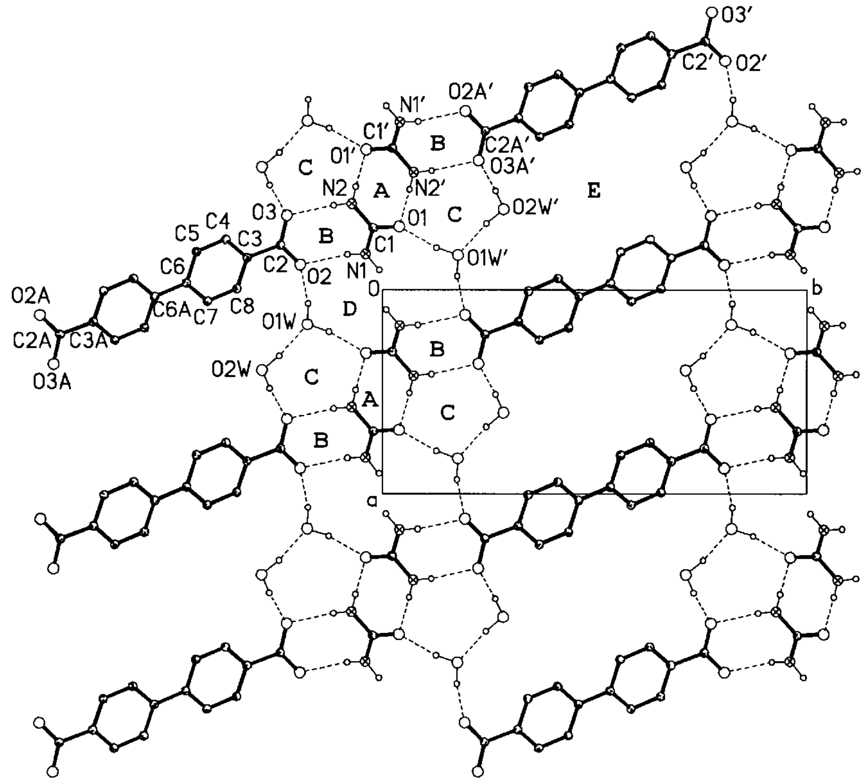

Figure 6. Projection down the *c* axis showing a hydrogen-bonded anionic layer constructed from BPDC, urea and water moieties in **3**. The axial label *a* stands for *a*sin*β*

site of O(1W) makes an O_W—H···O hydrogen bond to a urea molecule to generate hydrogen-bonded ring patterns **C** $N_5 = R_5^3(10)$and **D** $N_3 = R_6^4(16)$that strengthen the network. Repetition of patterns **A, B, C** and **D** leads to a wide ribbon running along the *a* axis, and adjacent ribbons are linked by pattern **E** to construct a ladder-type structure.

The two phenyl rings of centrosymmetric BPDC are necessarily coplanar, and each carboxylate group is slightly twisted out of the phenyl plane by 8.8°. However, the planar urea dimer is orientated at a dihedral angle of 52° to the BPDC phenyl plane. The geometries may be described by torsion angles C(1)—N(1)—O(2)—C(2) = −10.9° and C(1)—N(2)—O(3)—C(2) = 9.4°, thus gen-

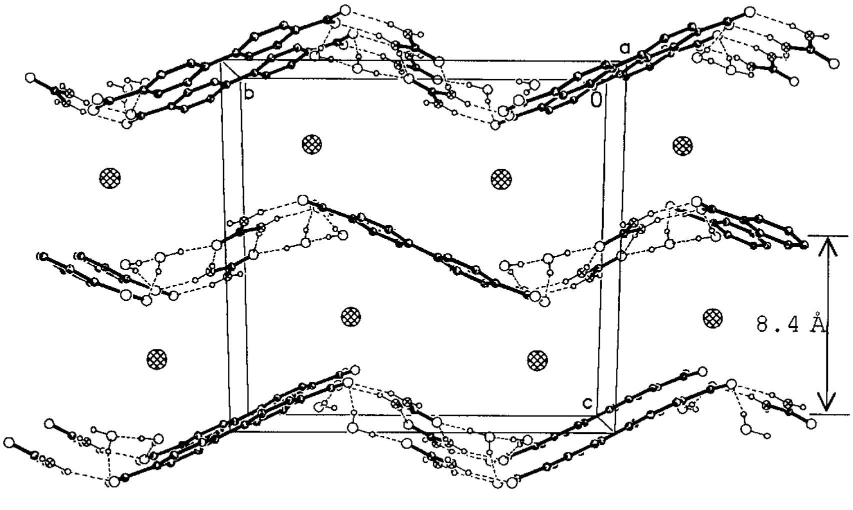

Figure 7. Packing diagram viewed down the *a* axis showing hydrogen-bonded anionic puckered layers in **3** sandwich $(n\text{—Pr})_4N^+$ cations

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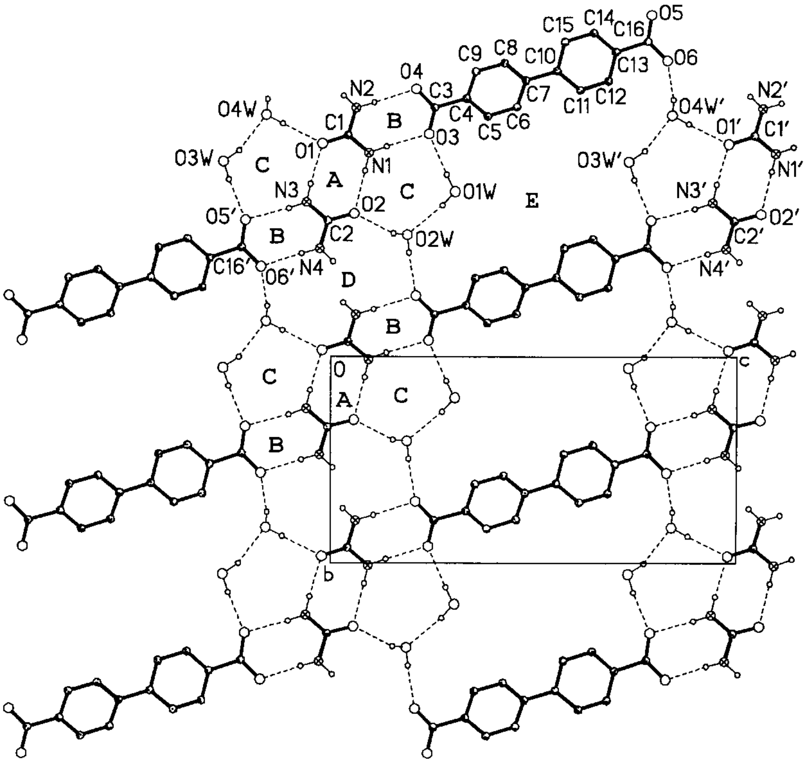

Figure 8. Projection down the *a* axis showing a hydrogen-bonded anionic layer constructed from BPDC, urea and water moieties in **4**. The axial labels *b* and *c* stand for *b*sinγ and *c*sinβ, respectively

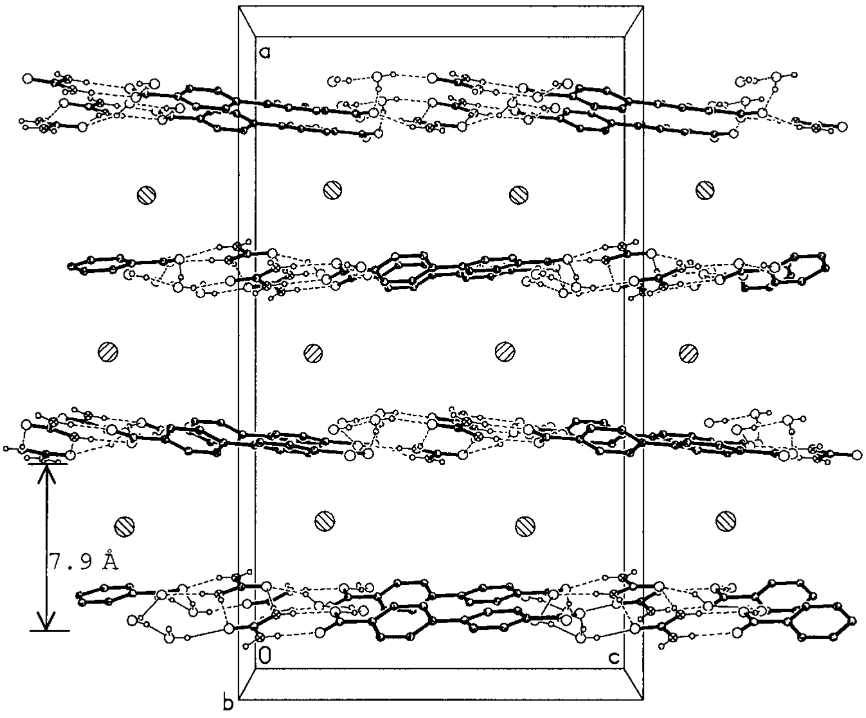

Figure 9. Crystal packing diagram viewed down the *b* axis showing $(n\text{—Bu})_4N^+$ cations sandwiched between hydrogen-bonded anionic layers in **4**. The two independent cations are arranged in separate layers

erating a hydrogen-bonded pleated layer oriented parallel to the (001) set of planes (Fig. 7). Ordered $(n\text{-Pr})_4N^+$ cations are sandwiched between the anionic layers with an inter-layer distance of $c/2 = 8.4$ Å, which is consistent with that of **2**.

$2[(n\text{-Bu})_4N^+]\cdot[4,4'\text{-}(C_6H_4)_2(COO^-)_2]\cdot2[(NH_2)_2CO]$ $4H_2O$ (4)

It is interesting that although **3** and **4** crystallize in different crystal systems, their anionic layers are remarkably similar, being constructed of the same hydrogen-bonding patterns (compare Fig. 6 with Fig. 8).

In **4**, BPDC is connected by urea dimer **A** $[N_2 = R_2^2(8)]$ through a pair of N—$H_{syn}\cdots$O hydrogen bonds **B** $[N_2 = R_2^2(8)]$ to form an infinite zig-zag chain running parallel to the *bc*-diagonal (Fig. 8). The water molecules link adjacent chains in patterns **C** $N_5 = R_5^3(10)$and **D** $N_6 = R_6^4(16)$ to generate a hydrogen-bonded ribbon along the *b* axis.

The resulting ribbons are then connected by large ring motif **E** $N_6 = R_6^6(34)$ with an area of ca 70 Å^2. The only difference of this overall scheme from the case in **3** is that here the hydrogen-bonding patterns **A, D** and **E** are non-centrosymmetric. However, 'iso-pattern' does not lead to isostructure, as the anionic layer in **4** is approximately planar, rather than pleated as in **3** (compare Fig. 7 with Fig. 9).

The BPDC phenyl rings make a dihedral angle of 17.2°, and the two independent urea molecules derivate from coplanarity with a dihedral angle of 8.0° and torsion angles C(1)—O(1)—N(2)—C(2) = −21.2° and C(1)—N(1)—O(2)—C(2) = 0.1°. The mean plane of the urea dimer is approximately coplanar with the BPDC mean plane, with a dihedral angle of 2.6° and maximum deviation of 0.3 Å, the corresponding torsion angles being C(1)—N(1)—O(3)—C(4) = 1.8°, C(1)—N(2)—O(4)—C(4) = 4.9°, C(2)—N(3)—O(5′)—C(16′) = −13.7° and C(2)—N(4)—O(6′)—C(16′) = −24.9°. Therefore, the resulting hydrogen-bonded anionic layer is oriented parallel to the *bc*-plane and stacks along the *a* axis, with an inter-layer distance of *ca*. $a/4 = 7.9$ Å (Fig. 9). Two independent $(n\text{-Bu})_4N^+$ cations are sandwiched between adjacent host layers, but arranged in separate layers located at $x = 1/4$ and 1/2, respectively.

CONCLUSION

The present series of four inclusion compounds substantiate the robustness of BPDC as a supramolecular building block to construct anionic host layers, exhibiting a strong tendency in generating a ladder-type structure owing to its rigidity and effectiveness as a bifunctional hydrogen-bond acceptor. The inter-layer spacings of all four compounds are consistent with corresponding values in similar structures with tetraalkylammonium cations sandwiched between layers.[19] The cooperativity of hydrogen bonding facilitates the construction and stabilization of hydrogen-bonded networks,[20] leading to the interplay of flexible (water cluster) and rigid (urea) supramolecular synthons in crystal engineering. The equal efficiency of close packing between the BPDC–water cluster and BPDC–urea-water motifs, as manifested by their comparable packing coefficients (calculated using the program PLATON-99[21]) (C_k, 0.64–0.68 in Table 1), indicates that multi-site hydrogen-bonding interactions readily stabilize crystal structures by including solvent molecules during supramolecular self-assembly, despite the fact that 85% of known organic crystals are unsolvated.[22]

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