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Hydrogen-Bonded Urea–Anion Host Lattices. Part 2. Crystal Structures of Inclusion Compounds of Urea with Tetraalkylammonium Bicarbonates

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Abstract. New inclusion complexes $(C_2H_5)_4N^+HCO_3^- \cdot (NH_2)_2CO \cdot 2H_2O$ (**1**) and $(n\text{-}C_4H_9)_4N^+HCO_3^- \cdot 3(NH_2)_2CO$ (**2**) have been prepared and characterized by X-ray crystallography. Crystal data, MoK_α radiation: **1**, space group $P2_1/n$, $Z = 8$, $a = 9.356(1)$, $b = 29.156(4)$, $c = 12.161(1)$ Å, $\beta = 90.03(1)°$, $R_F = 0.062$ for 2214 observed data; **2**, space group $P\bar{1}$, $Z = 2$, $a = 8.404(2)$, $b = 12.352(2)$, $c = 14.377(4)$ Å, $\alpha = 88.20(2)$, $\beta = 89.56(2)$, $\gamma = 71.68(1)°$, $R_F = 0.052$ for 3092 observed data. In both compounds the tetraalkylammonium ions are sandwiched between puckered layers, which are constructed from $[((NH_2)_2CO)_2(HCO_3^-)_2]_\infty$, ribbons, each composed of centrosymmetric hydrogen-bonded urea dimers and bicarbonate dimers, by lateral linkage through water molecules in **1**, and by direct cross-linkage of an alternate, parallel arrangement of the urea/bicarbonate and complementary urea ribbons in **2**.

Key words. Urea, tetraalkylammonium ion, bicarbonate, hydrogen bonding, inclusion compound.

Supplementary Data relating to this article have been deposited with the British Library as Supplementary Publication No. SUP 82201 (40 pages).

1. Introduction

The chemistry of urea and thiourea inclusion compounds has received much attention (and is still a subject of continuing interest) since their discovery about fifty years ago [1, 2]. Urea is a good host molecule because it has a well-defined trigonal planar geometry and can form at least six hydrogen bonds [3]. The guest molecules in the channel-type urea inclusion compounds comprise straight-chain hydrocarbons such as paraffins, olefins, carboxylic acids, ketones and esters, and the host lattice contains linear, parallel, non-intersecting channels within which the guest molecules are accommodated [4–12]. However, the periodic repeat distance of the guest molecules, in most cases, is incommensurate with that of the host structure along the channel direction [13, 14]. Recently, a very interesting new mode of inter-channel ordering of guest molecules in n-alkane/urea inclusion compounds has been experimentally and theoretically studied by Harris and coworkers [15–18].

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We became interested in the generation of new host lattices by the combined use of urea and other molecular species as the building blocks. In the series of isomorphous urea–tetraethylammonium salt hydrate complexes, namely $(C_2H_5)_4N^+X^-\cdot(NH_2)_2CO\cdot 2H_2O$, (X = Cl, Br, CN), the cations are sandwiched between puckered layers constructed from the cross-linkage of planar zigzag chains of hydrogen-bonded urea molecules by the water molecules and halide/pseudohalide anions [19]. The planar zigzag urea chain in these structure contrasts with the relatively open framework in tetragonal urea [20] and the helical spirals in both the urea channel adducts [1, 2] and the isomorphous series $(n\text{-}C_3H_7)_4N^+X^-\cdot 3(NH_2)_2CO\cdot H_2O$, (X = F, Cl, Br, I) [21, 22].

In the rational design of new urea–anion host lattices that can accommodate peralkylated ammonium cations of different sizes, we consider the bicarbonate ion which can easily form O—H· · ·O and O· · ·H—N hydrogen bonds with another bicarbonate ion and with urea, respectively. In the present work, we report the preparation and structural characterization of the following crystalline inclusion compounds:

$$(C_2H_5)_4N^+HCO_3^-\cdot(NH_2)_2CO\cdot 2H_2O \qquad (1)$$

$$(n\text{-}C_4H_9)_4N^+HCO_3^-\cdot 3(NH_2)_2CO \qquad (2)$$

2. Experimental

Tetraethylammonium hydroxide (25 wt.-% aqueous solution) and tetra-*n*-butylammonium hydroxide (40 wt.-% aqueous solution) were obtained from Eastman Kodak. Each hydroxide was mixed with urea in a molar ratio of 1 : 2, and a minimum quantity of water was added to dissolve the solid. After compressed air was allowed to bubble through the solution for about 3–4 h, the latter was subjected to slow evaporation at room temperature in a desiccator charged with Drierite. Colorless crystals appeared in the form of small polyhedra for **2**, but complex **1** initially deposited from solution as very thin needles, and was recrystallized from 50% alcohol to yield larger plates that could be used for X-ray analysis.

Information concerning crystallographic data and structure refinement of the two compounds is summarized in Table I. Intensities were collected in the variable ω-scan technique [23] on a Siemens R3m/V diffractometer using MoK_α radiation (λ = 0.71073 Å) at 291 K. The raw data were processed with a learnt-profile procedure [24], and empirical absorption correction based on ψ-scan data was also applied.

All calculations were performed on a PC 486 computer with the SHELXTL PC program package [25]. All non-hydrogen atoms were located by direct methods and all of them were assigned anisotropic thermal parameters. The amido, methylene, and methyl H atoms were generated geometrically (C—H distance fixed at 0.96 Å) and allowed to ride on their respective parent atoms. The hydrogen atoms of the

Table I. Data collection and processing parameters of urea–tetraalkylammonium bicarbonate complexes.

Complex	**1**	**2**
Molecular formula	$(C_2H_5)_4N^+HCO_3^-$ $\cdot CO(NH_2)_2 \cdot 2H_2O$	$(C_4H_9)_4N^+HCO_3^-$ $\cdot 3CO(NH_2)_2$
Molecular weight	287.4	483.7
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No.2)
Unit cell parameters		
a, Å	9.356(1)	8.404(2)
b, Å	29.156(4)	12.352(2)
c, Å	12.161(1)	14.377(3)
α, °	90	88.20(2)
β, °	90.03(1)	89.56(2)
γ, °	90	71.68(1)
V, Å^3	3317.5(6)	1416.1(5)
Z	8	2
$F(000)$	1264	532
Density (flotation in n-hexane/CCl_4), g cm^{-3}	1.181	1.123
Density (calcd.), g cm^{-3}	1.151	1.134
Absorption coefficient, cm^{-1}	0.093	0.084
Crystal size, mm	0.30 × 0.42 × 0.50	0.55 × 0.60 ×0.65
Mean μr	0.021	0.027
Transmission factors	0.927–0.954	0.944–0.972
Scan speed (deg min^{-1})	6.0–60.0	3.0–29.3
Scan range (below K_{α_1} to above K_{α_2})	0.60–0.60	0.80–0.80
Background counting	Stationary counts for one-half of scan time at each end of scan	
$2\theta_{max}$, °	48	55
Unique data measured	4599	6421
Observed data	$\vert F_o\vert > 4\sigma(\vert F_o\vert)$, 2214	$\vert F_o\vert > 4\sigma(\vert F_o\vert)$, 3092
Number of variables, p	344	299
$R_F = \sum \Vert F_o\vert - \vert F_c\Vert / \sum \vert F_o\vert$	0.062	0.052
Constant g in weighting scheme $\omega = [\sigma^2(F_o) + g\vert F_o\vert^2]^{-1}$	0.0003	0.002
$R_G = [\sum \omega(\vert F_o\vert - \vert F_c\vert)^2/\vert F_o\vert^2]^{1/2}$	0.070	0.074
$S = [\sum \omega(\vert F_o\vert - \vert F_c\vert)^2/(n-p)]^{1/2}$	1.88	1.21
Residual extrema in final difference map, e Å^{-3}	+0.18 to −0.19	+0.33 to −0.19
Largest and mean Δ/σ	0.000, 0.000	0.000, 0.000

bicarbonate ions in the two complexes were located from subsequent difference Fourier syntheses. The hydrogen atoms of the water molecules in **1** failed to appear in the difference map, and their positions were derived from the scheme of hydrogen bonding. All hydrogen atoms were assigned appropriate isotropic temperature factors and included in the structure-factor calculations. Analytic expressions of atomic scattering factors were employed, and anomalous dispersion corrections were incorporated [26]. The refinement of the coordinates and anisotropic thermal parameters of the non-hydrogen atoms was carried out by the full-matrix least-squares method, and the final R indices and other parameters are listed in Table I.

3. Results and Discussion

The final positional and equivalent isotropic thermal parameters of **1** and **2** are listed in Tables II and III, respectively. Anisotropic temperature factors, hydrogen coordinates, and structure factors have been deposited as Supplementary Data.

3.1. THE UREA–BICARBONATE LAYER STRUCTURES OF 1 AND 2

Compounds **1** and **2** have closely related crystal structures in which the cations are separated by urea–anion puckered layers to generate a sandwich-like packing mode. In compound **1** the layer structure may be conveniently described with reference to the hydrogen bonding scheme shown in Figure 1 and Table IV. Two independent urea molecules **C(1)** [for simplicity the urea molecule composed of atoms C(1), O(1), N(1) and N(2) is designated as **C(1)**] and **C(2)** are connected by pairs of N—H· · ·O hydrogen bonds to form a dimer, and likewise the bicarbonate ions **C(3)** [composed of atoms C(3), O(3), O(4) and O(5)] and **C(4)** occur as a cyclic dimer consolidated by a pair of O—H· · ·O hydrogen bonds. These two kinds of dimeric units are alternately linked by pairs of N—H· · ·O hydrogen bonds to form an approximately planar ribbon oriented parallel to the c axis; its deviation from coplanarity is shown by the torsion angles C(1)—N(2)· · ·O(7b)—C(4b) = 25.4, C(1)—N(1)· · ·O(2)—C(2) = −7.7, and C(2)—N(4)· · ·O(4)—C(3) = 31.1, and C(3)—O(5)· · ·O(6)—C(4) = 2.6°. The water molecules lie in between the ribbons, and hydrogen bonds of the types N—H· · ·O(water) and O(water)—H· · ·O link them together to form a puckered layer normal to the b axis (Figure 1). Urea–bicarbonate–water layers of this type are located at $y = 1/8, 3/8, 5/8$ and $7/8$ (Figure 2).

The tetraethylammonium cations, which are well ordered and nearly attain idealized $\bar{4}2m$ molecular symmetry, are arranged in a column running parallel to the [100] direction. Adjacent columns are arranged side by side, separated by a distance of $c/2$ but shifted by $a/2$ in the [100] direction, to generate a cationic layer parallel to the (010) family of planes. These layers are located at $y = 0, \frac{1}{4}$,

Table II. Atomic coordinates ($\times 10^4$) and thermal parameters[a] ($Å^2 \times 10^3$) of $(C_2H_5)_4N^+HCO_3^- \cdot CO(NH_2)_2 \cdot H_2O$ (**1**).

Atom	x	y	z	U_{eq} or U
Urea–bicarbonate–water host lattice				
O(1)	1561(4)	1442(1)	5215(2)	76(1)
C(1)	1584(5)	1409(2)	6225(4)	56(1)
N(1)	2764(4)	1260(1)	6752(3)	67(1)
N(2)	479(4)	1508(1)	6863(3)	71(1)
O(2)	5382(4)	1109(1)	5521(3)	75(1)
C(2)	5312(5)	1139(2)	4489(4)	59(1)
N(3)	4148(4)	1287(1)	3963(3)	68(1)
N(4)	6428(4)	1016(2)	3866(3)	83(1)
C(3)	5315(5)	1174(2)	1069(4)	58(1)
O(3)	4135(3)	1193(1)	1590(2)	76(1)
O(4)	6490(4)	1182(2)	1513(3)	93(1)
O(5)	5237(4)	1142(1)	−2(3)	78(1)
C(4)	1587(5)	1252(2)	−360(4)	62(1)
O(6)	2747(4)	1208(2)	−873(3)	89(1)
O(7)	397(4)	1287(2)	−810(3)	95(1)
O(8)	1642(4)	1271(1)	724(2)	77(1)
O(1W)	9298(4)	927(1)	1903(3)	79(1)
O(2W)	9524(4)	850(1)	4233(3)	83(1)
O(3W)	7351(4)	1685(1)	6539(3)	86(1)
O(4W)	7603(4)	1532(1)	8842(3)	82(1)
Tetraethylammonium ion				
N(5)	9332(4)	2363(1)	3013(3)	65(1)
C(5)	10589(5)	2034(2)	3000(4)	72(1)
C(6)	12021(5)	2248(2)	2741(5)	101(1)
C(7)	9577(6)	2738(2)	3867(4)	81(1)
C(8)	9697(7)	2569(2)	5043(4)	114(1)
C(9)	8025(6)	2078(2)	3275(5)	97(1)
C(10)	6615(6)	2350(2)	3342(6)	139(1)
C(11)	9178(5)	2599(2)	1915(4)	81(1)
C(12)	8990(6)	2286(2)	931(4)	126(1)
N(6)	7504(4)	134(1)	7558(3)	55(1)
C(13)	8690(5)	465(2)	7249(4)	71(1)
C(14)	10161(5)	257(2)	7101(4)	93(1)
C(15)	6141(5)	413(2)	7659(4)	73(1)
C(16)	4810(5)	144(2)	7955(4)	99(1)
C(17)	7382(5)	−236(2)	6698(4)	73(1)
C(18)	7097(6)	−72(2)	5529(4)	99(1)
C(19)	7823(5)	−105(2)	8621(4)	74(1)
C(20)	8022(6)	213(2)	9628(4)	102(1)

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[a] For non-hydrogen atoms, equivalent isotropic temperature factor U_{eq} defined as 1/3 of the trace of the orthogonalised **U** matrix.
The exponent of the isotropic temperature factor takes the form $-8\pi^2 U \sin^2 \theta / \lambda^2$.

Table III. Atomic coordinates ($\times 10^4$) and thermal parameters[a] ($Å^2 \times 10^3$) of $(C_4H_9)_4N^+ HCO_3^- \cdot 3CO(NH_2)_2$ (**2**).

Atom	x	y	z	U_{eq} or U
Urea-bicarbonate host lattice				
O(1)	10071(3)	−151(2)	1246(1)	77(1)
C(1)	10201(3)	829(2)	1204(2)	55(1)
N(1)	10297(3)	1386(2)	1975(1)	60(1)
N(2)	10268(3)	1365(2)	391(1)	72(1)
O(2)	9643(3)	296(2)	3738(1)	64(1)
C(2)	9413(3)	−649(2)	3746(2)	51(1)
N(3)	9215(3)	−1178(2)	4540(1)	66(1)
N(4)	9294(3)	−1166(2)	2954(2)	72(1)
O(3)	8658(3)	6446(2)	4530(2)	93(1)
C(3)	8860(4)	5925(3)	3794(2)	73(1)
N(5)	9940(4)	4872(2)	3711(2)	82(1)
N(6)	8051(4)	6425(3)	3016(2)	97(1)
C(4)	9604(3)	4295(2)	1190(2)	58(1)
O(4)	10413(3)	3751(2)	531(1)	74(1)
O(5)	9413(3)	3880(2)	1962(1)	78(1)
O(6)	8886(3)	5419(2)	1063(1)	86(1)
Tetra-n-butylammonium ion				
N(7)	5009(3)	2733(2)	2275(1)	56(1)
C(5)	3912(3)	2104(2)	2732(2)	65(1)
C(6)	4795(4)	877(3)	3032(2)	76(1)
C(7)	3714(4)	400(3)	3615(3)	104(2)
C(8)	4392(6)	−829(3)	3869(3)	118(2)
C(9)	3888(3)	3938(2)	2018(2)	68(1)
C(10)	4754(4)	4697(3)	1532(2)	86(1)
C(11)	3504(6)	5810(3)	1148(3)	120(2)
C(12)	2498(8)	6545(4)	1818(3)	155(3)
C(13)	6389(3)	2771(2)	2936(2)	62(1)
C(14)	5838(4)	3290(3)	3858(2)	88(1)
C(15)	7236(5)	3175(4)	4489(2)	98(2)
C(16)	6857(5)	3658(3)	5248(3)	111(2)
C(17)	5853(3)	2127(2)	1416(2)	63(1)
C(18)	4715(4)	2054(3)	640(2)	80(1)
C(19)	5692(5)	1440(3)	−173(2)	91(2)
C(20)	4584(7)	1484(4)	−1015(3)	142(3)

[a] For non-hydrogen atoms, equivalent isotropic temperature factor U_{eq} defined as 1/3 of the trace of the orthogonalised **U** matrix.

The exponent of the isotropic temperature factor takes the form $-8\pi^2 U \sin^2\theta/\lambda^2$.

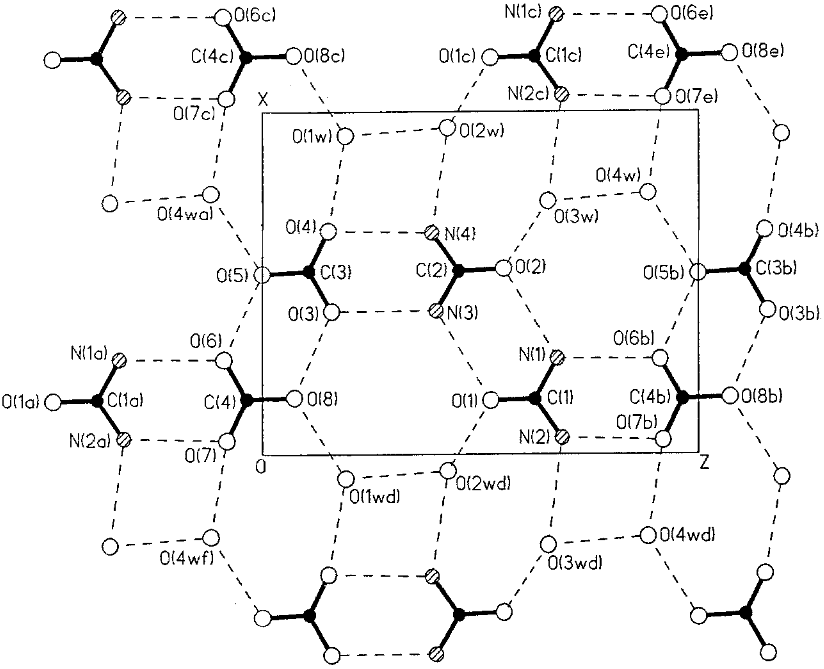

Figure 1. Hydrogen-bonded layer in $(C_2H_5)_4N^+HCO_3^- \cdot (NH_2)_2CO \cdot 2H_2O$ (**1**) formed by urea dimers and bicarbonate dimers bridged by water molecules. The atom labels correspond to those given in Tables II and IV. Broken lines represent hydrogen bonds. Symmetry transformations: (a) x, y, $-1+z$; (b) x, y, $1+z$; (c) $1+x$, y, z; (d) $-1+x$, y, z; (e) $1+x$, y, $1+z$; (f) $-1+x$, y, $-1+z$.

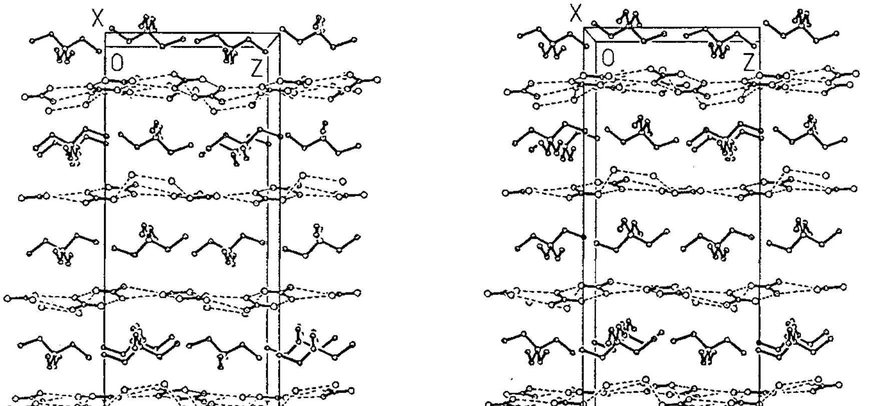

Figure 2. Stereodrawing of the crystal structure of **1**. The origin of the unit cell lies at the upper left corner, with a towards the reader, b downwards, and c pointing from left to right. Broken lines represent hydrogen bonds, and atom types are distinguished by size and shading.

Table IV. Selected bond distances (Å), bond angles (°) and torsion angles (°) in the urea–bicarbonate systems[a].

$(C_2H_5)_4N^+HCO_3^-\cdot CO(NH_2)_2\cdot 2H_2O$ (**1**)

(i) *Urea and bicarbonate molecules*

C(1)—O(1)	1.240 (7)	C(1)—N(1)	1.340 (8)
C(1)—N(2)	1.325 (8)	C(2)—O(2)	1.256 (7)
C(2)—N(3)	1.331 (8)	C(2)—N(4)	1.337 (8)
C(3)—O(3)	1.274 (7)	C(3)—O(4)	1.230 (8)
C(3)—O(5)	1.308 (7)	C(4)—O(6)	1.249 (8)
C(4)—O(7)	1.248 (9)	C(4)—O(8)	1.315 (7)
O(1)—C(1)—N(1)	120.9(5)	O(1)—C(1)—N(2)	122.6(6)
N(1)—C(1)—N(2)	116.6(5)	O(2)—C(2)—N(3)	122.5(5)
O(2)—C(2)—N(4)	120.4(5)	N(3)—C(2)—N(4)	117.1(5)
O(3)—C(3)—O(4)	123.5(5)	O(3)—C(3)—O(5)	116.9(5)
O(4)—C(3)—O(5)	119.6(6)	O(6)—C(4)—O(7)	123.9(5)
O(6)—C(4)—O(8)	118.6(6)	O(7)—C(4)—O(8)	117.4(6)

(ii) *Hydrogen bonding (donor atom listed first)*

N(1)···O(2)	2.903	N(1)···O(6b)	2.891
N(2)···O(7b)	2.906	N(2)···O(3Wd)	2.995
N(3)···O(1)	2.903	N(3)···O(3)	2.905
N(4)···O(4)	2.905	N(4)···O(2W)	2.967
O(2W)···O(1c)	2.837	O(3W)···O(2)	2.783
O(8)···O(3)	2.572	O(5)···O(6)	2.561
O(4W)···O(5b)	2.854	O(1W)···O(4)	2.771
O(1W)···O(8c)	2.810	O(4W)···O(7e)	2.754
O(2W)···O(1W)	2.845	O(3W)···N(2c)	2.995
C(1)—N(1)···O(2)—C(2)	−7.7	C(1)—N(2)···O(7b)—C(4b)	25.4
C(2)—N(3)···O(1)—C(1)	6.7	C(2)—N(3)···O(3)—C(3)	−25.0
C(2)—N(4)···O(4)—C(3)	31.1	C(3)—O(5)···O(6)—C(4)	2.6
C(4)—O(8)···O(3)—C(3)	6.3	O(2)—C(2)—N(4)···O(2W)	−16.7
O(2W)···O(1c)—C(1c)—N(2c)	−62.6	O(1W)···O(4)—C(3)—O(3)	136.1
O(1W)···O(8c)—C(4c)—O(6c)	−149.7	O(3W)···O(2)—C(2)—N(3)	115.2
O(4W)···O(5b)—C(3b)—O(3b)	−151.3	O(4W)···O(7e)—C(4e)—O(6e)	−150.3

$\frac{1}{2}$, and $\frac{3}{4}$ in the unit cell, each being sandwiched between two hydrogen-bonded urea-bicarbonate-water layers (Figure 2).

In the urea–bicarbonate layer structure of **2** (Figure 3), centrosymmetric, hydrogen-bonded dimers of independent urea molecules **C(1)** and **C(2)** (the same kind of symbolic abbreviations are used here as for **1**) are alternately linked by additional pairs of N—H···O hydrogen bonds to form an approximately planar ribbon oriented parallel to the *c* axis. Likewise the bicarbonate ions C(4) occur as centrosymmetric cyclic dimers each consolidated by a pair of O—H···O

Table IV. Continued.

$(n\text{-}C_4H_9)_4N^+HCO_3^- \cdot 3CO(NH_2)_2$ (**2**)

(i) *Urea and bicarbonate molecules*

C(1)—O(1)	1.218 (1)	C(1)—N(1)	1.339 (3)
C(1)—N(2)	1.335 (3)	C(2)—O(2)	1.242 (4)
C(2)—N(3)	1.333 (3)	C(2)—N(4)	1.342 (3)
C(3)—O(3)	1.239 (4)	C(3)—N(5)	1.340 (4)
C(3)—N(6)	1.311 (4)	C(4)—O(4)	1.247 (3)
C(4)—O(5)	1.238 (3)	C(4)—O(6)	1.336 (3)
O(1)—C(1)—N(1)	121.1 (2)	O(1)—C(1)—N(2)	121.7 (2)
N(1)—C(1)—N(2)	116.9 (3)	O(2)—C(2)—N(3)	121.5 (2)
O(2)—C(2)—N(4)	121.1 (2)	N(3)—C(2)—N(4)	117.0 (3)
O(3)—C(3)—N(5)	123.0 (3)	O(3)—C(3)—N(6)	120.6 (3)
N(5)—C(3)—N(6)	116.3 (3)	O(4)—C(4)—O(5)	125.3 (2)
O(4)—C(4)—O(6)	117.9 (2)	O(5)—C(4)—O(6)	116.8 (2)

(ii) *Hydrogen bonding (donor atom listed first)*

N(4)···O(1)	2.886	N(2g)···O(1)	2.893
N(1)···O(2)	2.963	N(3a)···O(2)	3.016
N(5b)···O(3)	3.002	N(3e)···O(3)	3.114
N(2)···O(4)	3.001	N(1)···O(5)	2.933
N(5)···O(5)	2.928	O(4f)···O(6)	2.619
N(6)···O(6)	3.095		
C(1)—N(1)···O(2)—C(2)	4.7	C(1)—N(1)···O(5)—C(4)	26.8
C(1)—N(2)···O(1g)—C(1g)	2.9	C(1)—N(2)···O(4)—C(4)	34.6
C(2)—N(3)···O(2a)—C(2a)	17.1	C(2)—N(3)···O(3d)—C(3d)	10.2
C(2)—N(4)···O(1)—C(1)	13.4	C(3)—N(5)···O(5)—C(4)	62.8
C(3)—N(5)···O(3b)—C(3b)	12.9	C(3)—N(6)···O(6)—C(4)	−24.6
C(4)—O(6)···O(4f)—C(4f)	−5.6		

[a] *Symmetry transformations:*
1, a $(x, y, -1+z)$; b $(x, y, 1+z)$; c $(1+x, y, z)$; d $(-1+x, y, z)$; e $(1+x, y, 1+z)$; f $(-1+x, y, -1+z)$.
2, a $(2-x, -y, 1-z)$; b $(2-x, 1-y; 1-z)$; c $(x, y, 1+z)$; d $(x, -1+y, z)$; e $(x, 1+y, z)$; f $(2-x, 1-y, -z)$; g $(2-x, -y, -z)$.
Standard deviations in hydrogen bond lengths and bond angles:
1, $\sigma(l) \approx 0.009$ Å, $\sigma(\theta) \approx 0.5$ °;
2, $\sigma(l) \approx 0.004$ Å, $\sigma(\theta) \approx 0.3$ °.

hydrogen bonds, and together with centrosymmetric cyclic C(**3**) urea dimers they form a highly puckered zigzag $[((NH_2)_2CO)_2(HCO_3^-)_2]_\infty$ ribbon running parallel to the *c* axis. For these two types of ribbons, the extent of deviation from planarity can be seen from the relevant torsion angles: C(1)—N(1)···O(2)—C(2) = 4.7, C(1)—N(2)···O(1g)—C(1g) = −2.9, C(2)—N(3)···O(2a)—C(2a) = 17.1;

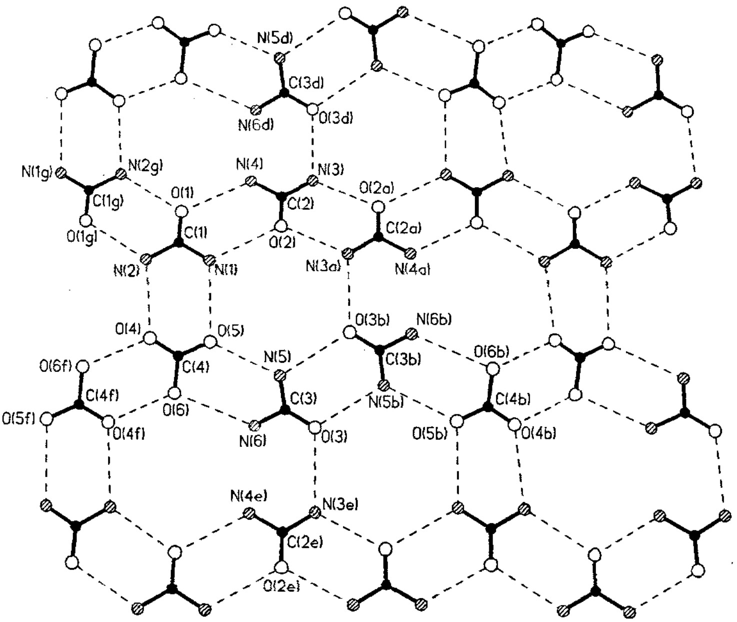

Figure 3. Hydrogen-bonded layer in $(n\text{-}C_4H_9)_4N^+HCO_3^-\cdot(NH_2)_2CO$ (**2**) formed by the cross-linkage of urea ribbons and $[(HCO_3^-)_2((NH_2)_2CO)_2]_\infty$ ribbons. The atom labels correspond to those given in Tables III and IV. Broken lines represent hydrogen bonds. Symmetry transformations: (a) $2 - x, -y, 1 - z$; (b) $2 - x, 1 - y, 1 - z$; (c) $x, y, 1 + z$; (d) $x, -1 + y, z$; (e) $x, 1 + y, z$; (f) $2 - x, 1 - y, -z$; (g) $2 - x, -y, -z$.

but C(3)—N(5)· · ·O(5)—C(4) = 62.8, C(3b)—N(5b)· · ·O(5b)—C(4b) = −45.1°, respectively. The parallel, alternate arrangement of these two kinds of complementary ribbons facilitates cross-linkage by N—H· · ·O hydrogen bonds to form a puckered anionic layer normal to the *a* axis; note that there is a mismatch between atoms N(4) and N(6d) belonging to different ribbons.

Figure 4 shows a perspective view of the crystal structure of **2** along the *b* axial direction. The distance separating two adjacent urea–bicarbonate layers is $a = 8.40$ Å, and between them there is a layer composed of the stacked columns of ordered tetrahedral $(n\text{-}C_4H_9)_4N^+$ cations.

3.2. STRUCTURAL FEATURES AND RELATIONSHIPS

The layer-type host structures of **1** and **2** are similar to those formed in our previous studies on urea-water-tetraethylammonium halide inclusion complexes [19] and adducts of thiourea and peralkylated ammonium salts [27]. Both **1** and **2** contain a hydrogen-bonded ribbon built of alternating urea dimers and cyclic dimeric bicarbonate moieties, but different additional molecular components, namely water molecules in **1** and urea ribbons in **2**, are used in the construction of the hydrophilic layer.

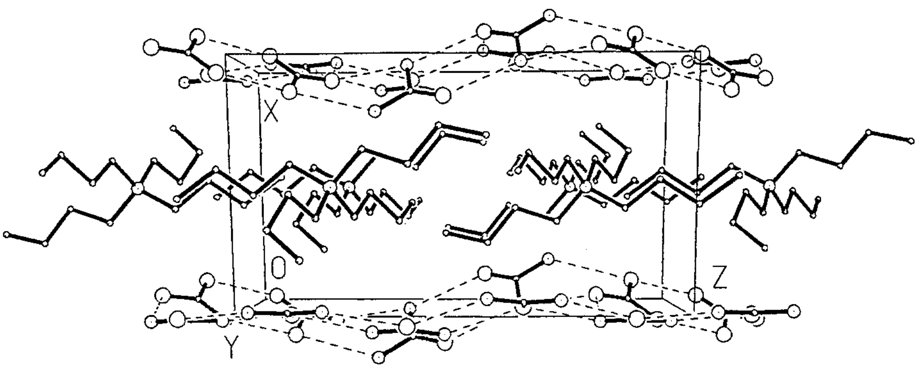

Figure 4. Perspective view of the crystal structure of **2**. Broken lines represent hydrogen bonds, and atom types are distinguished by size and shading.

The tetraethylammonium cations in **1** are sandwiched between two layers formed by bicarbonate dimers and molecules of urea and water. The interlayer spacing of $b/4 = 7.29$ Å is slightly smaller than the corresponding value for a similar layer structure with tetraethylammonium cations accommodated in the thiourea-bicarbonate-water lattice [$b/2 = 7.47$ Å] [27] (which is consistent with the difference in size between urea and thiourea), but in good agreement with those in the urea-water-halide lattice ($b/2 = 7.28$ Å) in monoclinic $(C_2H_5)_4N^+Cl^- \cdot (NH_2)_2CO \cdot 2H_2O$ [19] and the acetate-water lattice ($1/b* = 7.39$ Å) in triclinic $(C_2H_5)_4N^+CH_3COO^- \cdot 4H_2O$ [28].

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