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Salts of 4-aminobutyric acid and 6-aminohexanoic acid behaving as molecular Velcro†

M. Rademeyer * and B. van der Westhuizen

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The crystal structures of eight novel carboxyalkylammonium salts, ($^+H_3N(CH_2)nCOOH)X^-$, are reported, with n = 4 and X = Cl, Br and I in structures **1**, **2** and **3**, respectively, and n = 6 and X = Cl, Br·0.5H_2O, Cl·0.5H_2O, NO_3 and ClO_4 in structures **4**, **5**, **6**, **7** and **8**. The members of this family of compounds were found to display significant structural diversity, and a careful analysis of the structures employing the principles of crystal engineering was done to explain the observed trends and differences, specifically also the interdigitation or non-interdigitation of alkyl chains. It was found that a primary hydrogen bonding network formed between the ammonium groups and halide or oxo-anions, which plays a major structure-directing role. The structures may be likened to molecular Velcro, in which secondary hydrogen bonding interactions involving the carboxylic acid groups act as "hooks" to link primary networks.

Introduction

Long chain *n*-alkane molecules typically crystallise in layered structures,[1] with the cohesion of the alkyl chains achieved by van der Waals interactions. The introduction of a terminal functional group to the alkyl chain may potentially affect the ideal close packing of the alkyl chains. Due to the conformational flexibility of the alkyl chain, deviations of molecular conformations from the ideal all-*trans* conformation, and *gauche* bonds, are possible. Depending on the size of the terminal functional group, the chains may pack to form a bilayer, or the alkyl chains may interdigitate.[2]

In the case of primary long chain *n*-alkylammonium salts, a counter anion is incorporated into the structure to ensure charge neutrality, in addition to the terminal ammonium head group. The resulting structure balances the strong ionic interactions and hydrogen bonding between the charged ammonium groups and anions, and the van der Waals interactions between the alkyl chains, in addition to close packing requirements.

A search of the Cambridge Crystallographic Database[3] (CSD, version 5.38, May 2017 update) reveals that a number of structures of primary, mono-*n*-alkylammonium halides (CSD refcodes: DEAMMC01-02,[4,5] DODAMB,[6] KAKSIA,[7] ZZZLWK02,[5] ZZZLWK03,[8] ZZZLWK04 (ref. 9)) and primary mono-*n*-alkylammonium halide monohydrates (CSD refcodes: HUZBOT,[10] KUTSAU,[11] QUMWOL,[12] QUMWUR,[12] QUMXAY,[12] QUMXEC,[12] QUMXIG,[12] TABLAJ,[13] ULIJAB[14]) have been reported.

Both the anhydrous and the monohydrate salts typically form layered, interdigitated structures in which the alkyl chains do not contain any *gauche* bonds. No structures of primary, mono-*n*-alkylammonium nitrates or -perchlorates could be located in the CSD.

In the reported primary *n*-alkylammonium halide structures, a hydrogen bonding network is formed between the ammonium group and the hydrogen bond accepting anion, X^-. Bond[15] classified the hydrogen bonding networks of these structures according to the principles of ring-stacking and ring-laddering.

In the current study, the effect of the introduction of a terminal carboxylic functional group at the opposite end of the ammonium group in a primary mono-*n*-alkylammonium cation, to form a carboxyalkylammonium cation, ($^+H_3N(CH_2)$-*n*COOH), and the structures of the salts obtained, are investigated. This introduces further hydrogen bonding capability compared to the *n*-alkylammonium cation. In these salts, the carboxylic acid functional group can act as both a hydrogen bond donor or acceptor, resulting in two hydrogen bonding donors (the ammonium group and the carboxylic acid group) and two hydrogen bonding acceptors (the anion and the carboxylic acid group). If the carboxyalkylammonium salt is hydrated, water molecules may act as both hydrogen bonding donors or acceptors. In the case of the anhydrous carboxyalkylammonium salts, a hydrogen bonding network that combines all the hydrogen bonding donors and acceptors in a single hydrogen bonding network may theoretically be formed.

Department of Chemistry, University of Pretoria, cnr Lynnwood Road &, Roper Street, Hatfield, Pretoria 0002, South Africa. E-mail: melanie.rademeyer@up.ac.za

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Etter[16] noted that the strongest hydrogen bonding donor often interacts with the strongest hydrogen bonding acceptor. If this approach is applied to the carboxyalkylammonium salts, the strongest hydrogen bonding donor, the charged ammonium group, and the strongest hydrogen bond acceptor, the charged anion, are expected to interact *via* hydrogen bonding, while the second strongest donor and acceptor, both carboxylic acid groups, will form hydrogen bonds.

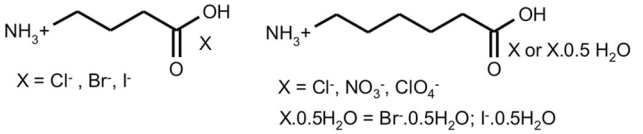
Here we report the structural characteristics and hydrogen bonding interactions in a series of carboxyalkylammonium salts, $(^{+}H_3N(CH_2)nCOOH)X^{-}$ where X^{-} = Cl^{-}, Br^{-}, I^{-}, NO_3^{-} and ClO_4^{-} and n = 4 or 6. A minimum of four carbon atoms in the alkyl chain allows van der Waals interactions between the *n*-alkyl portions in the cations. By restricting the number of carbon atoms in the chain to the even numbers 4 and 6, the well-known odd–even effect, often observed in compounds containing alkyl portions,[17] is expected to be negated.

Salt formation is achieved *via* the protonation of the amine group of 4-aminobutyric acid (also known as γ-aminobutyric acid or GABA), and the longer chain 6-aminohexanoic acid, with a strong acid, HX. GABA is a commercially available supplement against anxiety,[18] while 6-aminohexanoic acid is prescribed as a treatment for bleeding disorders.[19] Many drugs used today are marketed in the form of a salt,[20] with the active ingredient as cation or anion, due to potentially improved properties like solubility and chemical stability of the salt compared to the neutral compound. Considering these potential improvements, the investigation of salt formation of pharmaceutically important compounds is also of interest.

When the active pharmaceutical ingredient is a cation, inorganic anions like chloride and phosphate are commonly employed in salt formation because of their abundant occurrence in the body.[20] Bromide and nitrate anions are used to a lesser extent due to the respective risks of bromism and nitrosamine formation.[20] At the same time iodide anions may lead to iodism.[21] In the current study, the pharmaceutically important chloride, bromide, iodide and nitrate salts are considered, and even though the perchlorate anion is not used in salt formation in the pharmaceutical industry, perchlorate salts were included here due to their hydrogen bonding capability.

Two salt structures related to those in the current study have been reported in the literature, and these structures will be included in the current comparison. Firstly, the crystal structure of 4-aminobutyric acid hydrochloride, has been reported twice (CSD refcodes: GAMBAC01,[22] GAMBAC10 (ref. 23)), but additional symmetry was observed for this structure in the current study. Previously the space group was reported as $P2_1$, while in this study we found it to be $P2_1/m$, with the cation lying on a mirror plane. This warrants the inclusion of structure **1** here. The structure of the bromide salt of the much longer chain 11-aminoundecanoic acid, a hemihydrate, was reported by Sim[24] (CSD refcode: AUNDBH).

In the current study, eight novel carboxyalkylammonium salt structures have been determined, as illustrated in Scheme 1. The salts under investigation will be abbreviated C*n*X for the anhydrous salts, or C*n*X·0.5H_2O for the hemihydrate salts, where *n* indicates the number of carbon atoms in the cation and X indicates the anion (X = Cl^{-}, Br^{-}, I^{-}, NO_3^{-} or ClO_4^{-}).



Scheme 1 Novel structures determined in the current investigation.

Results

Crystallographic discussion of structures

The crystallographic parameters of structures **1** to **8** are listed in Table 1, their asymmetric units are illustrated in Fig. 1 and strong hydrogen bonding interactions are given in Table 2.

One carboxybutylammonium cation and one chloride anion comprise the asymmetric unit of **1**, C4Cl, and there are two asymmetric units in the unit cell. The whole cation, including the carboxylic acid group, lies on a mirror plane, and the alkyl portion adopts the low energy, all-*trans* conformation, with torsion angles close to 180°. A layered structure is formed parallel to the *ab*-plane, with the cations packing in an interdigitated fashion, as shown in Fig. 2(a). The ammonium groups, chloride anions and carboxylic acid groups comprise the inorganic layer, while the parallel alkyl and carboxylic acid portions of the cation form the organic layer. When viewed down the *b*-axis, the cations in a layer are parallel and tilted at an angle of 62.6(1)° relative to the layer plane, as shown in Fig. 2(a).

In the inorganic layer, the ammonium groups, chloride anions and carboxylic acid groups all interact through hydrogen bonding to form a single, two-dimensional hydrogen bonded network. However, even though only one hydrogen bonding network is present, this network can be divided into two parts, namely a two-dimensional primary hydrogen bonding network, consisting of charge-assisted hydrogen bonds between the strongest hydrogen bonding donor, the ammonium group, and the strongest hydrogen bonding acceptor, the chloride anion, and a secondary hydrogen bonding network, involving hydrogen bonds which anchor the carboxylic acid groups of the interdigitated cations to the primary hydrogen bonding network.

In the primary hydrogen bonding network, each ammonium group interacts with three chloride anions through three classic, charge-assisted N^{+}–H···Cl^{-} hydrogen bonds, while each chloride anion, in turn, is hydrogen bonded to three ammonium groups. Employing the description of Bond,[15] the hydrogen bonding interactions in the primary hydrogen bonding network result in the formation of a one-dimensional *transoid* hydrogen bonded ladder, as illustrated in Fig. 2(b), with both the ladder sides and rungs formed by

Table 1 Crystal data for structures **1** to **8**

	1	**2**	**3**	**4**
Empirical formula	$HOOC(CH_2)_3NH_3^+Cl^-$	$HOOC(CH_2)_3NH_3^+Br^-$	$HOOC(CH_2)_3NH_3^+I^-$	$HOOC(CH_2)_5NH_3^+Cl^-$
Abbreviation	C4Cl	C4Br	C4I	C6Cl
M (g mol^{-1})	139.58	184.04	231.03	167.63
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic
Space group (no.)	$P2_1/m$	$Pbca$	$Pnma$	$P2_1/c$
T (K)	150(2)	150(2)	150(2)	150(2)
a/Å	5.9059(3)	13.3778(13)	9.5887(4)	11.2287(6)
b/Å	6.3964(3)	6.4784(6)	6.0522(3)	8.5257(4)
c/Å	8.9893(4)	15.7657(15)	12.6513(6)	9.1381(5)
α/°	90	90	90	90
β/°	100.064(2)	90	90	101.510(2)
γ/°	90	90	90	90
V/Å^3	334.36(3)	1366.4(2)	734.19(6)	857.22(8)
Z	2	8	4	4
D (calc)/g cm^{-3}	1.386	1.789	2.090	1.299
μ/mm^{-1}	0.487	5.935	4.286	0.383
F(000)	148	736	440	0.392
Scan range (θ)/°	2.301–33.303	2.584–27.216	2.665–28.398	3.023–27.194
Total reflections	16 556	36 170	21 535	24 417
Unique reflections	1386	1521	1010	1897
[R(int)]	0.0441	0.0660	0.0329	0.0383
Parameters	71	114	72	107
R_1 [$I > 2\sigma(I)$]	0.0288	0.0152	0.0110	0.0244
wR_2 (all data)	0.0781	0.0365	0.0252	0.0638

	5	**6**	**7**	**8**
Empirical formula	$HOOC(CH_2)_5NH_3^+Br^-\cdot0.5H_2O$	$HOOC(CH_2)_5NH_3^+I^-\cdot0.5H_2O$	$HOOC(CH_2)_5NH_3^+NO_3^-$	$HOOC(CH_2)_5NH_3^+ClO_4^-$
Abbreviation	C6Br·0.5H_2O	C6Br·0.5H_2O	C6NO_3	C6ClO_4
M (g mol^{-1})	442.20	536.18	194.19	231.63
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group (no.)	$C2/c$	$C2/c$	$P2_1/c$	$P\bar{1}$
T (K)	150(2)	150(2)	150(2)	150(2)
a/Å	29.6835(16)	30.237(2)	4.8399(5)	5.2863(3)
b/Å	4.9623(3)	5.0915(3)	8.3511(7)	5.6138(3)
c/Å	12.5219(6)	12.8358(9)	23.167(2)	17.4559(9)
α/°	90	90	90	82.962(2)
β/°	92.194(2)	93.163(2)	91.273(4)	86.746(2)
γ/°	90	90	90	88.924(2)
V/Å^3	1843.10(17)	1973.1(2)	936.14(15)	513.26(5)
Z	4	4	4	2
D (calc)/g cm^{-3}	1.594	1.805	1.378	1.499
μ/mm^{-1}	4.418	3.207	0.119	0.378
F(000)	904	1048	416	244
Scan range (θ)/°	2.747–27.157	2.699–27.301	2.593–27.519	2.355–27.264
Total reflections	25 382	24 581	24 903	13 688
Unique reflections	2047	2222	2150	2284
[R(int)]	0.0447	0.0369	0.0813	0.0298
Parameters	155	155	116	184
R_1 [$I > 2\sigma(I)$]	0.0166	0.0132	0.1366	0.0286
wR_2 (all data)	0.0407	0.0324	0.4188	0.0726

N^+–H$\cdots Cl^-$ hydrogen bonds. Neighbouring ladders are connected *via* a $N^+\cdots Cl^-$ close contact to form a corrugated, two-dimensional 4^4 net,[15] as illustrated in Fig. 2(c).

The same hydrogen bonding network has been reported by Bond[15] for primary alkyl- and arylammonium chloride and bromide salts where the hydrocarbon parts of the cations comprise alkyl chains or small aromatic moieties. In this net, the hydrocarbon parts of the cations across the net diagonal are in a *transoid* arrangement while those lying along the N$\cdots$X net directions are in a *cisoid* arrangement relative to each other.[15]

In structure **1**, carboxylic acid groups hydrogen bond to the primary hydrogen bonded sheet from above and below *via* an O–H$\cdots Cl^-$ hydrogen bonding interaction to the chloride anions in the primary network, to form an interdigitated structure. Here the –OH moiety of the carboxylic acid group hydrogen bonds to a chloride anion at the apex of the sawtooth geometry on each side of the primary hydrogen bonding network, as shown in Fig. 2(a). The resulting overall hydrogen bonding network comprises the strong charge-assisted interactions between the ammonium groups and chloride anions in the primary network as well as the weaker

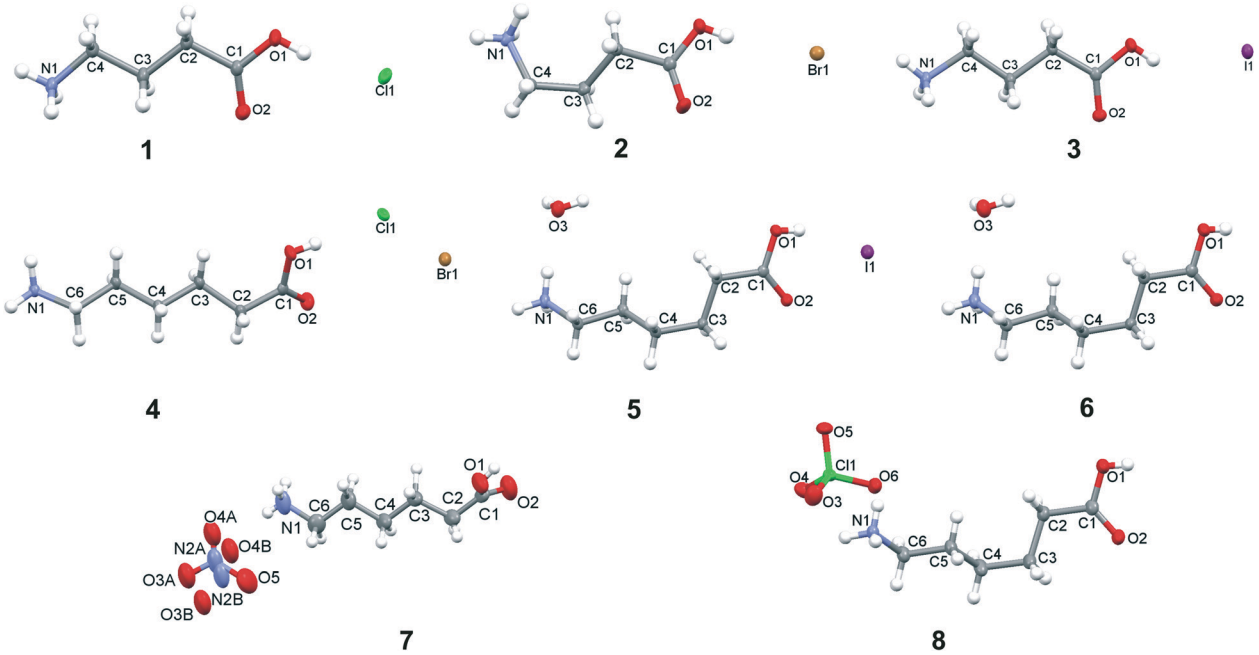


Fig. 1 Asymmetric units of structures **1** to **8**, illustrating the atomic numbering scheme. Ellipsoids are drawn at the 50% probability level.

O–H···Cl^- interactions anchoring the carboxylic acid groups to the primary network.

The asymmetric unit of structure **2**, C4Br, contains one carboxybutylammonium cation and one isolated bromide anion, with eight asymmetric units in the unit cell, and this structure is not isostructural to structure **1**. The cation does not exhibit the low energy, all-*trans* geometry, instead the C(2)–C(3)–C(4)–N(1) section adopts a *gauche* conformation with a torsion angle of −61.5(3)°, as shown in Fig. 2(d). The C(1)–C(2)–C(3)–C(4) portion of the cation has a torsion angle of −162.5(2)°, indicating a much smaller deviation from the all-*trans* geometry compared to the C(2) to N(1) portion.

The layered packing of **2**, parallel to the *ab*-plane, is illustrated in Fig. 2(d). The ammonium groups, bromide anions and carboxylic acid functional groups all comprise an inorganic layer, while the alkyl portions and carboxylic acid groups form the organic layer. When viewed down the *b*-axis, pairs of cations pointing in the same direction alternate with pairs of cations adopting an opposite orientation, as illustrated in Fig. 2(d).

The ammonium groups, bromide anions and carboxylic acid groups interact *via* hydrogen bonds to form a single hydrogen bonding network, but this network can again be divided into a two-dimensional primary hydrogen bonding network consisting of charge-assisted hydrogen bonds between ammonium groups and bromide anions, and a secondary hydrogen bonding network in which the carboxylic acid groups hydrogen bond to the primary hydrogen bonding network from above and below. In the primary hydrogen bonding network, each ammonium group interacts with three bromide anions, through three conventional, charge-assisted N^+–H···Br^- hydrogen bonds to form a *transoid* hydrogen bonded ladder, shown in Fig. 2(e). Neighbouring ladders are linked *via* a close N^+···Br^- contact to form a 4^4 net,[15] shown in Fig. 2(f).

The alkyl chains of the cations across the net diagonal in a ladder adopt a *transoid* arrangement, and those along the N^+···Br^- net directions a *cisoid* arrangement similar to what was found in structure **1**, but due to the pairwise packing of cations, the cations across the net diagonal between ladders are *cisoid* relative to each other, and the primary hydrogen bonded network exhibits a sinusoidal conformation rather than the saw-tooth conformation seen in structure **1**.

Carboxylic acid functional groups are hydrogen bonded to the primary network *via* hydrogen bonds, but unlike structure **1**, where only the –OH portion of the carboxylic acid group hydrogen bonds to the primary network, in structure **2** both the –OH group and the =O group of the carboxylic acid functional group anchor the carboxylic acid group of the cation to the primary hydrogen bonding network, with a bromide anion and an ammonium group acting as a hydrogen bond acceptor and donor to the –COOH group, respectively, as shown in Fig. 2(d). This means that the bromide anion and the ammonium group in the primary hydrogen bonding network are suitably positioned for hydrogen bonding to and from the carboxylic acid group, allowing the –COOH group to straddle the species in the primary network. Anchoring occurs to an ammonium group and a bromide anion that belong to neighbouring ladders, hence the hydrogen bonds involving the carboxylic acid group further link the *transoid* ladders defined earlier. The combination of the primary hydrogen bonded network with the hydrogen bonding interactions involving the terminal carboxylic acid groups results in a two-dimensional hydrogen bonded sheet parallel to the *ab*-plane in which pairs of cations linked through their

Table 2 Strong hydrogen bonding parameters [Å, °] for compounds **1** to **8**

Structure	D–H···A (Å)	*d*(D–H) (Å)	*d*(H···A) (Å)	*d*(D···A) (Å)	∠ (DHA) (°)	Symmetry operator
1	O(1)–H(1)···Cl(1)	0.85(3)	2.25(3)	3.0820(11)	167(2)	
	N(1)–H(1A)···Cl(1)$^{\#1}$	0.87(2)	2.29(2)	3.1521(12)	169.5(18)	$^{\#1}$ $x-1, y, z+1$
	N(1)–H(1B)···Cl(1)$^{\#2}$	0.879(16)	2.508(16)	3.2790(3)	146.9(13)	$^{\#2}$ $-x+1, -y+2, -z+1$
2	O(1)–H(1)···Br(1)	0.77(2)	2.54(2)	3.2977(12)	169(2)	
	N(1)–H(1A)···Br(1)$^{\#1}$	0.87(2)	2.48(2)	3.3337(14)	164.5(17)	$^{\#1}$ $-x+3/2, -y, z-1/2$
	N(1)–H(1B)···Br(1)$^{\#2}$	0.84(2)	2.91(2)	3.5729(15)	137.0(18)	$^{\#2}$ $x-1/2, y, -z+1/2$
	N(1)–H(1B)···O(2)$^{\#3}$	0.84(2)	2.19(2)	2.7680(18)	125.8(19)	$^{\#3}$ $x, -y+1/2, z-1/2$
	N(1)–H(1C)···Br(1)$^{\#4}$	0.95(2)	2.62(2)	3.3315(14)	132.6(17)	$^{\#4}$ $-x+3/2, -y+1, z-1/2$
	N(1)–H(1C)···Br(1)$^{\#3}$	0.95(2)	2.91(2)	3.5453(15)	125.2(17)	
3	O(1)–H(1)···I(1)	0.79(3)	2.79(3)	3.4476(14)	142(3)	
	N(1)–H(1A)···O(2)$^{\#1}$	0.86(3)	2.11(3)	2.961(2)	173(2)	$^{\#1}$ $x+1/2, y, -z+3/2$
	N(1)–H(1B)···I(1)$^{\#2}$	0.89(2)	2.77(2)	3.6295(10)	164.7(14)	$^{\#2}$ $-x+1, -y+2, -z+1$
4	O(1)–H(1)···Cl(1)	0.818(18)	2.255(18)	3.0589(9)	167.9(16)	
	N(1)–H(1A)···Cl(1)$^{\#1}$	0.893(17)	2.399(17)	3.2678(11)	164.2(13)	$^{\#1}$ $-x+1, -y+1, -z+1$
	N(1)–H(1B)···Cl(1)$^{\#2}$	0.911(17)	2.535(17)	3.2312(11)	133.6(13)	$^{\#2}$ $x-1, -y+3/2, z+1/2$
	N(1)–H(1C)···Cl(1)$^{\#3}$	0.933(17)	2.265(17)	3.1932(11)	173.7(13)	$^{\#3}$ $x-1, y, z$
5	O(1)–H(1)···O(2)$^{\#1}$	0.75(2)	1.93(2)	2.6749(15)	175(2)	$^{\#1}$ $-x+3/2, -y+5/2, -z+1$
	N(1)–H(1A)···O(3)	0.89(2)	2.02(2)	2.8939(18)	166.2(18)	
	N(1)–H(1B)···Br(1)$^{\#2}$	0.90(2)	2.80(2)	3.4437(16)	129.7(16)	$^{\#2}$ $-x, -1+y, 1/2-z$
	N(1)–H(1B)···Br(1)$^{\#3}$	0.90(2)	2.77(2)	3.4483(15)	133.2(17)	$^{\#3}$ $x, 1-y, -1/2+z$
	N(1)–H(1C)···Br(1)$^{\#4}$	0.91(2)	2.44(2)	3.3422(14)	174.3(17)	$^{\#4}$ $-x+1, -y+1, -z$
6	O(1)–H(1)···O(2)$^{\#1}$	0.68(2)	2.00(2)	2.6822(17)	177(3)	$^{\#1}$ $-x+3/2, -y+5/2, -z+1$
	N(1)–H(1A)···O(3)	0.90(2)	2.03(2)	2.9026(18)	162.5(19)	
	N(1)–H(1B)···I(1)$^{\#2}$	0.87(2)	2.96(2)	3.6265(16)	135.0(17)	$^{\#2}$ $x, -y, -1/2+z$
	N(1)–H(1C)···I(1)$^{\#3}$	0.90(2)	2.64(2)	3.5460(16)	176.3(19)	$^{\#3}$ $-x+1, -y+1, -z$
7	O(1)–H(1)···O(2)$^{\#1}$	0.78(8)	1.85(9)	2.626(10)	173(7)	$^{\#1}$ $-x+2, -y, -z+1$
	N(1)–H(1A)···O(5)$^{\#2}$	0.91	2.1	2.823(8)	135.1	$^{\#2}$ $x+1, y, z$
	N(1)–H(1B)···O(4A)	0.91	2.14	2.829(7)	131.5	
	N(1)–H(1C)···O(3A)$^{\#3}$	0.91	2.15	3.011(8)	157.7	$^{\#3}$ $-x+1, y-1/2, -z+1/2$
	N(1)–H(1C)···O(4A)$^{\#3}$	0.91	2.14	2.798(6)	128.5	
8	O(1)–H(1)···O(2)$^{\#1}$	0.75(2)	1.91(2)	2.6515(16)	176(2)	$^{\#1}$ $-x-1, -y+1, -z+1$
	N(1)–H(1A)···O(5)$^{\#2}$	0.89(2)	2.28(2)	3.0245(17)	141.4(18)	$^{\#2}$ $x, y+1, z$
	N(1)–H(1B)···O(4)$^{\#4}$	0.83(2)	2.22(2)	3.0091(17)	159(2)	$^{\#4}$ $x-1, y, z$
	N(1)–H(1C)···O(4)$^{\#5}$	0.81(2)	2.32(2)	2.9824(17)	140(2)	$^{\#5}$ $x-1, y+1, z$
	N(1)–H(1C)···O(5)$^{\#5}$	0.81(2)	2.52(3)	3.2755(18)	157(2)	

Hydrogen bonding definition: strong hydrogen bonding donors and acceptors, d_{min}(D···A) = *R*(D) + *R*(A) − 0.50 Å; d_{max}(D···A) = *R*(D) + *R*(A), D–H···A > 120.0°.

carboxylic acid functional groups to the primary hydrogen bonded sheet alternate with pairs of cations that form part of the primary hydrogen bonding sheet, on both sides of the layer, as shown in Fig. 2(d).

The asymmetric unit of structure C4I, **3**, contains one cation and one isolated iodide anion. The cation adopts the low energy, all-*trans* conformation, with all torsion angles close to 180°, and lies on a mirror plane.

As illustrated in Fig. 2(g) to (i), the layered type packing observed for structures **1** and **2** is not exhibited by this structure. Instead rows of iodide anions pack in a channel formed by six cations, in the *b*-direction. Each ammonium group acts as hydrogen bond donor to two iodide anions, thereby anchoring the iodide ions in the channel. The ammonium group also interacts with the =O atom on the carboxylic acid group, a hydrogen bonding interaction which connects the cations forming the channel. An additional hydrogen bonding interaction with the =O atom on the carboxylic acid group as the donor anchors the iodide anion inside the channel, thus each iodide anion accepts three hydrogen bonds from groups on the surface of the channel. The combination of these hydrogen bonding interactions results in a three-dimensional hydrogen bonding network, involving all the hydrogen bonding donors and acceptors, which extends throughout the structure.

One isolated chloride anion and one carboxypentylammonium cation comprise the asymmetric unit of **4**, C6Cl, with four asymmetric units in the unit cell. This structure is not homologous to the other chloride salt structure, structure **1**, or to structures **2** or **3**. The cation adopts the low energy, all-*trans* conformation with the carbon atoms approximately planar, as shown in Fig. 2(j). The ammonium group and carboxylic acid group, however, deviate slightly from the plane formed by the C(3)–C(6) atoms.

A structure consisting of layers parallel to the *bc*-plane is formed with the alkyl parts of the cation all packing parallel in an organic layer, while the hydrogen bonded ammonium groups, carboxylic acid groups and chloride anions comprise the inorganic layer, as illustrated in Fig. 2(j). When viewed down the *c*-axis, the chloride anions pack in layers, surrounded by layers of carboxylic acid and ammonium groups. The carbon zig-zag plane through atoms C(1)–C(6) of the cation makes an angle of 65.3(2)° with the layer plane.

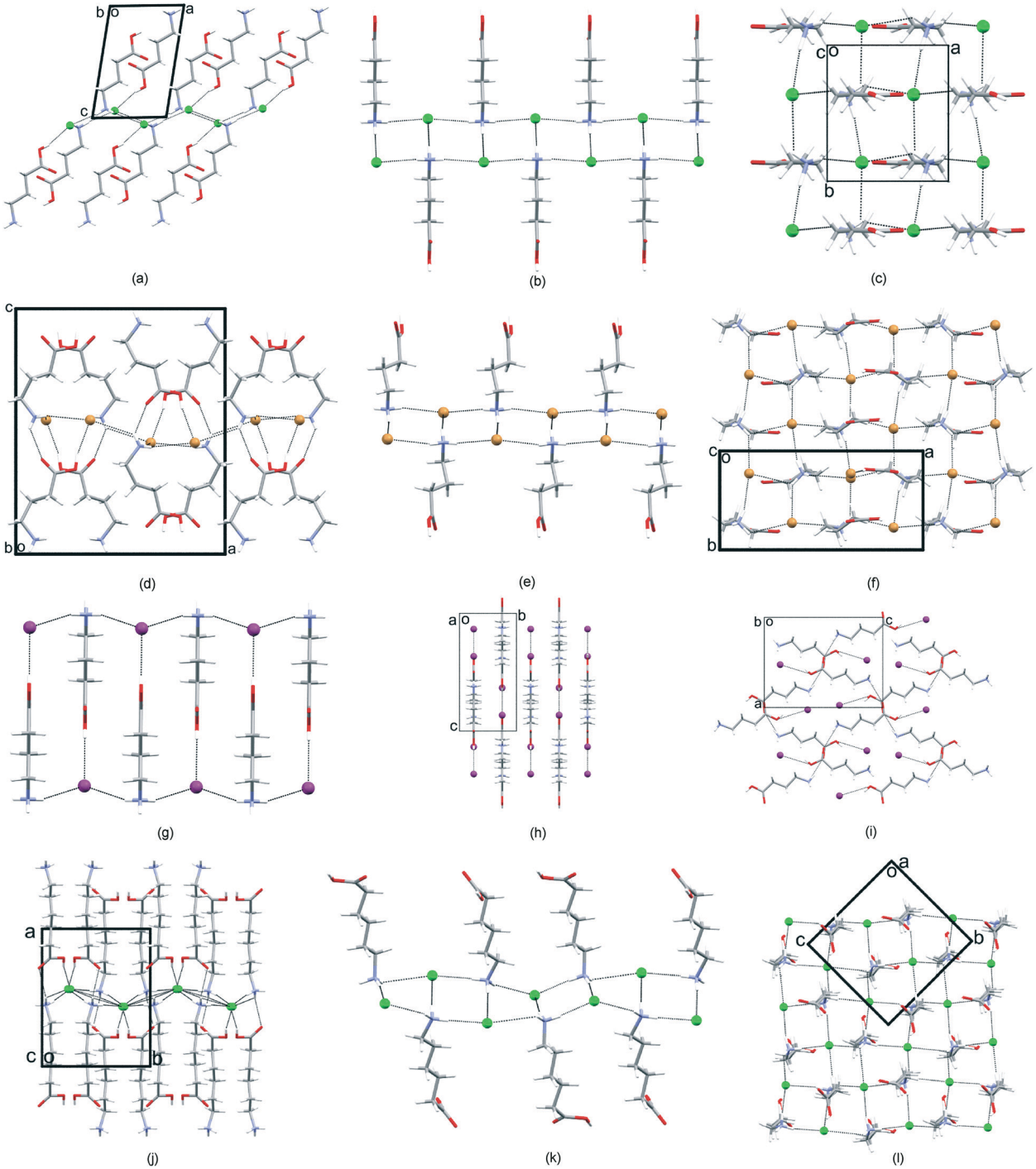


Fig. 2 (a) Interdigitated, layered packing in C4Cl, **1**. (b) *Transoid* ladder and primary hydrogen bonded layer viewed down the *a*-axis. (c) 4^4 net in **1**. (d) Layered packing in C4Br, **2**. (e) *Transoid* ladder viewed down the *a*-axis. (f) 4^4 net in **2**. (g). Hydrogen bonding in C4I, **3**. (h) Packing in **3**. (i) Iodide anions packing in the channel formed by the cations. (j) Layered packing in C6Cl, **4**. (k) Hydrogen bonded ladder in C6Cl, **4**. (l) 4^4 net in **4**. In all figures, hydrogen bonds are shown as dotted lines.

In the inorganic layer, the ammonium groups, chloride anions and carboxylic acid groups interact through hydrogen bonding to form a single hydrogen bonding network, but as done previously for structures **1** and **2**, this network can be divided into a primary network comprising the ammonium groups and chloride anions, and a secondary network that links the carboxylic acid groups to the primary network.

In the primary network, each ammonium group forms three strong, charge-assisted N^+–H···Cl^- hydrogen bonds to three Cl^- hydrogen bonding acceptors to form a *transoid* hydrogen bonded ladder, as shown in Fig. 2(k). Neighbouring ladders are connected through N^+···Cl^- close contacts to form a 4^4 net,[15] as illustrated in Fig. 2(l). This is the same net as that formed for structure **1**, except that it does not adopt a

saw-tooth conformation due to the non-planarity of the hydrogen bonded ladder.

The –OH group of the carboxylic acid group forms a hydrogen bond to a chloride anion in the primary hydrogen bonding network, and at the same time, the =O group accepts a hydrogen bond from an ammonium group in the primary network, thus, the carboxylic acid group straddles an ammonium group and a chloride ion in a ladder. In contrast to what was observed in structure **2**, where the carboxylic acid group straddles groups across ladder rungs, in this structure, the orientation of carboxylic acid groups alternates by approximately 90° as they alternately bridge ammonium and chloride groups across the ladder rung, then across the ladder rail, on the same side of the ladder. Neighbouring ladders are straddled by the carboxylic acid groups from opposite sides of the primary network, as shown in Fig. 2(j).

Structures **5**, C6Br·0.5H_2O, and **6**, C6I·0.5H_2O, are isostructural, with the unit cell of **6** slightly larger than that of structure **5**, due to the larger size of the iodide anion compared to the bromide anion, and these structures will be discussed together. Even though water molecules were available as the solvent during the crystallisation of all the compounds, water molecules are only incorporated in structures **5** and **6**. The asymmetric unit consists of one carboxypentylammonium cation, one halide anion and half a water molecule, with the oxygen atom of the water molecule lying on a two-fold rotation axis. In both structures, the C(3)–N(1) portion of the cation adopts an all-*trans* conformation, but the C(2)–C(3)–C(4)–C(5) torsion angles display values of 71.4(2)° and 70.1(3)° in structures **5** and **6**, respectively, indicating a *gauche* bond, hence a deviation from the all-*trans* geometry in this part of the alkyl chain. A layered structure is displayed by compounds **5** and **6**, parallel to the *bc*-plane, but a different type of structure is formed compared to the other layered structures **1**, **2** and **4** discussed previously. In structures **5** and **6**, the packing is such that the carboxylic acid groups pack in a layer, which is separated from a layer containing the ammonium groups, halide anions and water molecules, by alkyl chains, as shown in Fig. 3(a). This means that the cation chains are not interdigitated, as was observed in structures **1**, **2** and **4**. Structures **5** and **6** can be considered to consist of two layers, an inorganic layer containing the ammonium groups, halide anions and water molecules and an organic layer comprising the alkyl chains and carboxylic acid groups. In structures **5** and **6**, the *trans*-part of the alkyl chains is tilted by 64.4° and 68.3°, respectively, relative to the layer plane.

While a single hydrogen bonding network is formed in structures **1**, **2** and **4**, hydrogen bonding occurs in two separate regions of the structure in **5** and **6**, due to the non-interdigitation of the cation chains, with a two-dimensional hydrogen bonding network involving the ammonium groups, water molecules and halide anions present in the inorganic layer, and a second zero-dimensional network comprising carboxylic acid dimers in the organic layer.

In the inorganic layer, a *transoid* hydrogen bonded ladder is formed between ammonium groups and halide anions, as shown in Fig. 3(b). This ladder differs from the hydrogen bonded ladders described for structures **1**, **2** and **4** where all three hydrogen atoms of the ammonium group are involved in the hydrogen bonding interactions forming the ladder, since in structures **5** and **6** only two ammonium hydrogen atoms participate in hydrogen bonding interactions to form the ladder, requiring one of the interactions to be a bifurcated hydrogen bond. The third hydrogen atom of each ammonium group forms a hydrogen bond to the oxygen atom of a water molecule, and is thus not available to participate in ladder formation. The water molecule links neighbouring ladders by accepting a hydrogen bond from an ammonium group in a neighbouring ladder, and by making a hydrogen bond to a halide anion in a neighbouring ladder, as shown in Fig. 3(c). A two-dimensional hydrogen bonding network parallel to the *ab*-plane is formed.

The same hydrogen bonding network is observed in the homologous structure 11-aminoundecanoic acid bromide hemihydrate[24] (CSD refcode: AUNDBH). However, in AUNDBH, the alkyl chains do not exhibit the *gauche* bond observed in structures **5** and **6**. Interestingly, the same hydrogen bonding network is also displayed di-*n*-alkylammonium salt structures, including 1,8-diaminooctane dihydrochloride monohydrate[25] (CSD refcode: GINJUJ) and 1,12-diaminododecane dihydrochloride monohydrate[26] (CSD refcode: BENTET01).

This means that in structures **5**, **6** and AUNBDH, the carboxylic acid hydrogen bonding dimers can be considered to link two carboxyalkylammonium cations into a larger "supramolecular cation", which effectively has two terminal ammonium groups, similar to the di-alkylammonium cations in the BENTET01 and GINJUJ structures.

Another interesting feature of structures **5** and **6**, as well as the literature structures AUNBDH, BENTET01 and GINJUJ, which all display the same hydrogen bonding network, is that the alkyl chains in the organic layer pack with crossed alkyl chains. Thus, it seems to imply that this specific type of hydrogen bonding network requires the alkyl chains to adopt a crossed chain packing. Pascher *et al.*[2] commented that the energetics driving crossed alkyl chain packing is not well understood.

One carboxypentylammonium cation and one nitrate anion comprise the asymmetric unit of C6NO_3, structure **7**. The nitrate anion was found to be disordered over two positions, with occupancies of 0.58 and 0.42, respectively. The hydrogen bonding analysis was performed by considering only the anion with the highest occupancy. The cation adopts the all-*trans* conformation, with torsion angle values close to 180°, and the nitrate anion geometry is trigonal planar. Similar to structures **5** and **6**, a non-interdigitated layered structure is formed. The inorganic layer containing the ammonium groups and nitrate anions is separated from the carboxylic acid groups by alkyl chains, with the alkyl chains and carboxylic acid groups forming the organic layer. Carboxylic acid hydrogen bonded dimers link two cations to form an extended di-*n*-alkylammonium-like supramolecular dication, which is tilted by approximately 29°

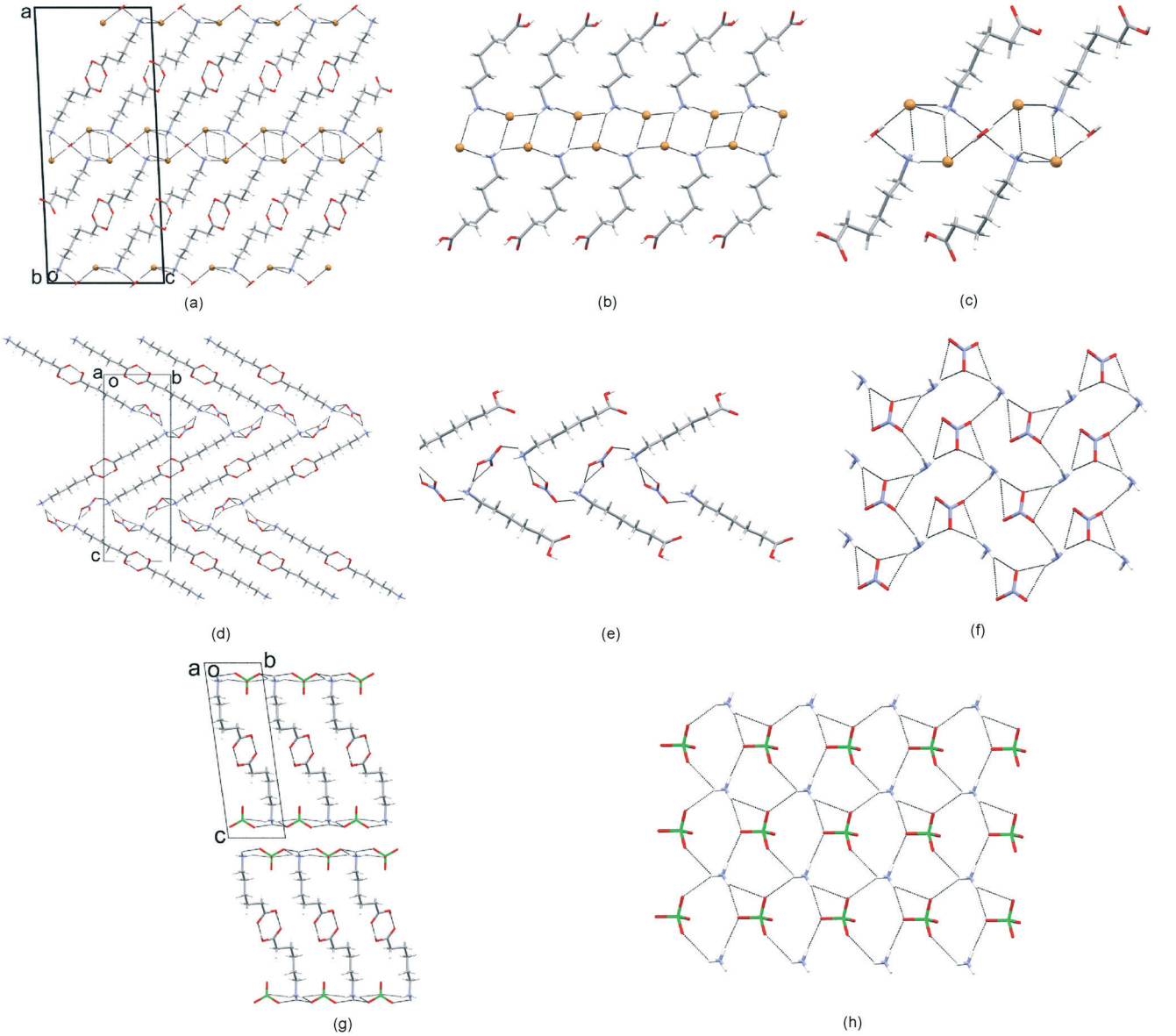


Fig. 3 (a) Layered packing in C6Br·0.5H_2O, **5** (also representative of C6I·0.5H_2O, **6**). (b) Hydrogen bonded ladder in **5**. (c) Hydrogen bonds involving water molecules in **5**. (d) Layered packing in C6NO_3, **7**. (e) Two-dimensional hydrogen bonding network in **7**. (f) Hydrogen bonding interactions between ammonium groups and nitrate anions in **7**. (g) Layered packing in C6ClO_4, **8**. (h) Hydrogen bonding between ammonium groups and perchlorate anions in **8**.

relative to the layer plane. In neighbouring layers, the supramolecular cations alternate in tilted-orientation, as shown in Fig. 3(d).

Strong, charge-assisted hydrogen bonds between the ammonium groups and nitrate anions in the inorganic layer result in a corrugated, two-dimensional hydrogen bonded sheet parallel to the *ab*-plane, as illustrated in Fig. 3(e). In this sheet, each ammonium group forms three hydrogen bonds to three different nitrate anions, of which two are bifurcated and one is a classical hydrogen bond, as shown in Fig. 3(f). Each nitrate anion is hydrogen bonded to three different ammonium groups. The same hydrogen bonding network is observed in *p*-toluidinium nitrate (CSD refcode: FUGTOR,[27] FUGTOR01 (ref. 28)), *m*-toluidinium nitrate (QUZHOJ[29]), *m*-nitroanilinium nitrate (PAJFEM[30]) and adamantine-ammonium nitrate (ELIMIV[31]).

The asymmetric unit of **8**, C6ClO_4, contains one carboxypentylammonium cation and one tetrahedral perchloride anion. The N(1)–C(6)–C(5)–C(4)–C(3) portion of the cation adopts the planar, all-*trans* conformation, with torsion angles close to 180°, while the O(1)–C(1)–C(2)–C(3)–C(4) section forms a planar, all-*trans* section. However, the planes through the two *trans* sections are at an angle of 58.4(2)°, which is expressed as a *gauche* C(2)–C(3)–C(4)–C(5) torsion angle of 66.0(4)°, indicating a kinked conformation.

Similar to what was observed in structures **5**–**7**, two types of layers, parallel to the *ab*-plane, are formed, as shown in Fig. 3(g). Perchlorate anions and ammonium groups pack in

the inorganic layer, and the alkyl chains and carboxylic acid groups form the organic layer. In the organic layer, hydrogen bonds link the carboxylic acid groups into zero-dimensional carboxylic acid dimers, effectively linking the cations to form an extended supramolecular di-*n*-alkylammonium-like cation, with a tilt angle of approximately 56° relative to the layer plane. Alkyl chains in neighbouring layers display the same orientation, as shown in Fig. 3(g).

In the inorganic layer, strong, charge-assisted N–H$^{+}\cdots^{-}$O–Cl hydrogen bonds link each ammonium group to four different perchlorate anions through one classical and two bifurcated hydrogen bonds, to form a two-dimensional hydrogen bonded sheet parallel to the *ab*-plane, as illustrated in Fig. 3(h). Two of these sheets are present in the inorganic layer, as shown in Fig. 3(g), with the ammonium groups of one sheet stacking on top of the perchloride groups in the second sheet, thus interacting through electrostatic interactions.

The same hydrogen bonding network is observed in the structure of 1,4-diammoniumbutane bis (perchlorate) (CSD refcode: URAKEE[32]), which again illustrates the similarity between the hydrogen bonding network in a carboxyalkylammonium salt structure and an alkyldiammonium salt structure, and the role of the carboxylic acid dimer hydrogen bonds that connect the carboxyalkylammonium cations into a supramolecular cation that resembles a alkyldiammonium cation.

Structural comparison

All the compounds except compound **3**, C4I, the only anhydrous iodide salt, form structures in which the alkyl chains pack in layers distinct from layers containing the ammonium groups, anions and water molecules where present.

A comparison of the layered structures **1**, **2** and **4** to **8** can thus be made. Of interest is the fact that only structures **5** and **6** are isostructural, even though long chain compounds are known to often form homologous series in which the members with an even or odd number of carbon atoms in the chain exhibit similar structures, the only differences being those required by the increase in the carbon chain length. In the current series, the structures C4Cl, **1**, and C6Cl, **4**, are not homologous. This observation may be attributed to the fact that, unlike in long chain compounds that do not contain head groups and counter ions, where van der Waals interactions are the major intermolecular interactions between the alkyl chains, both hydrogen bonding and van der Waals interactions are structure-directing in the current family of structures, and the final structure obtained represents a balance between the two. The fact that more than one stable hydrogen bonding network containing the strong hydrogen bond donors and acceptors in the current family of structures can be obtained, may thus contribute to the formation of non-homologous structures.

Water molecules are incorporated into only two of the structures, **5** and **6**, despite water being available as solvent in all cases.

In all the layered structures, a primary hydrogen bonding network containing the strongest hydrogen bonding donors and acceptors (the ammonium groups and anions, with the possible inclusion of water molecules into this network) can be identified. This underlines the statement by Etter[16] that the strongest hydrogen bonding donors and acceptors are likely to be involved in hydrogen bonding to each other. The weaker carboxylic acid hydrogen bonding groups may either anchor to the primary network resulting in interdigitation of the alkyl chains, as is observed in structures **1**, **2** and **4**, or form hydrogen bonded carboxylic acid dimers, separated from the primary network by alkyl chains, as seen in structures **5** to **8**.

In the case of the halide anion containing structures, the primary networks correspond to networks previously reported for arylammonium halides,[15] *n*-alkylammonium halides[15] and di-*n*-alkylammonium halides,[25,26] indicating the important structure-directing role of the strong, charge-assisted N^{+}–H$\cdots$X^{-} hydrogen bonding interactions. The fact that the same hydrogen bonding networks are formed, even though an additional hydrogen bonding capability is present in the carboxyalkylammonium halides compared to *n*-dialkylammonium and arylammonium halides, highlights the degree of molecular recognition taking place between the ammonium groups and halide anions, as well as the stability of the observed charge-assisted hydrogen bonding networks and the robustness of the hydrogen bonding synthons comprising these hydrogen bonding networks.

Interdigitation of alkyl chains. One of the most striking differences between the structures in the series is the fact that in certain structures (**1**, **2** and **4**, all containing halide anions, but no water molecules) the alkyl chains are interdigitated, with the carboxylic acid group anchoring to the primary hydrogen bonding network, while structures **5** to **8** (containing either halide anions and water molecules or larger oxo-anions) are non-interdigitated, with hydrogen bonded dimers forming between carboxylic acid groups, separate from the primary hydrogen bonding network. Bond[15] showed that in related *n*-alkylammonium halides, the small diameter of the *n*-alkylammonium cation does not affect the hydrogen bonding in the primary hydrogen bonding network on interdigitation, thus interdigitation can easily occur without disruption of the primary hydrogen bonding network. In analogy, in the current family of structures, the small cross section of the carboxyalkylammonium cations should still allow interdigitation to occur in all the structures.

The question why interdigitation of the alkyl chains can now be asked, and thus anchoring of the carboxylic group to the primary network to form a single hydrogen bonding network occurs in structures **1**, **2** and **4**, but not in structures **5** to **8**.

In structure **1**, the all-*trans* alkyl chains alternate above and below the primary network, as shown in Fig. 2(a) and (b), and this leaves the halide anions open to accept additional hydrogen bonds, which allows a carboxylic acid group from a neighbouring primary network to anchor

to the primary network, and thus interdigitation of the alkyl chains. In structure **2**, even though the kinked alkyl chain has a larger "average cross section" than that of an all-*trans* alkyl chain, and is thus expected to inhibit access of a neighbouring carboxylic acid group to the primary network, the fact that the alkyl chains alternate above and below the primary network in pairs, as shown in Fig. 2(d) and (e), means that again the halide anions are accessible to the neighbouring carboxylic acid groups, and alkyl chain interdigitation occurs. Alternation of the all-*trans* cations above and below the primary network is also observed in structure **4**, making the chloride anions accessible, and allowing interdigitation, as illustrated in Fig. 2(j) and (k). The primary hydrogen bonding network formed in structures **5** and **6** does not show alternation of the cations above and below the primary hydrogen bonding network, as illustrated in Fig. 3(a) and (b). Instead, in these structures, all the positions above and below the primary hydrogen bonding network are occupied by alkyl chains, effectively blocking access to the halide anion. Hence, the formation of carboxylic acid dimers in a second hydrogen bonding layer occurs, which is the only other route available to satisfy the hydrogen bonding capability of all the functional groups. Even though alternation of the alkyl chains above and below the primary network occurs in structure **7**, as shown in Fig. 3(d) and (e), the corrugation of the primary hydrogen bonding network, as well as the large tilt angle of the cations, prevents access of neighbouring carboxylic acid groups to the nitrate anions in the primary network, and a non-interdigitated structure is formed. The fact that alkyl chains occupy all positions above and below the primary hydrogen bonding network, shown in Fig. 3(g), explains the non-interdigitation of alkyl chains in structure **8**.

In the interdigitated structures, one may imagine the primary network being formed *via* strong, charge-assisted hydrogen bonds, and the alkyl chains of one such a network slotting into the spaces between the alkyl chains of a neighbouring network, with a good fit between the chains. The carboxylic acid groups then anchor the two networks together.

In the case of the non-interdigitated structures, no space is available for the slotting of the alkyl chains of neighbouring primary networks to occur, preventing interdigitation, but since the terminal ends of the chains contain the carboxylic acid groups, hydrogen bonded dimers are formed.

The type of primary hydrogen bonding network formed thus determines if alternation of alkyl chains above and below the primary layer occurs or not, and this determines the accessibility of a hydrogen bond acceptor in the primary network to accept a hydrogen bond from a neighbouring carboxylic acid group, which in turn determines the interdigitation, or not, of the alkyl chains. However, even if alternation of alkyl chains above and below the primary hydrogen bonding network occurs, corrugation of the primary network and/or a large alkyl chain tilt angle may prevent chain interdigitation, as is seen in structure **7**. This again emphasises the structure-directing role of the strong, charge-assisted hydrogen bonding species in the current family of structures, not only on the primary hydrogen bonding network formed, but also on the type of layered structure that ultimately results.

The two types of structures, interdigitated and non-interdigitated, may be viewed as two different types of "molecular Velcro", where the primary hydrogen bonded layer represents the nylon Velcro strip. In the case of the interdigitated structures, the carboxylic acid "hooks" of a primary layer anchor it onto a neighbouring primary layer, as shown in Fig. 4(a) and (b), through interdigitation of the layers. When interdigitation does not occur, the carboxylic acid groups "hook" together, and zipper the layers together, forming a non-interdigitated structure, as shown in Fig. 4(c) and (d).

Cation geometry and tilt angle. The final structure obtained has to allow optimal electrostatic interactions between the charged anions and ammonium groups, as well as appropriate interactions of the alkyl chains through van der Waals interactions, and secondary hydrogen bonding interactions involving the carboxylic acid groups, with a balance being achieved between these driving forces. Strong, charge-assisted hydrogen bonds anchor the ammonium head groups of the cation in the primary network, and determine the positions of the ammonium groups in the structure. The alkyl chains then adapt their geometry to obtain the best close packing *via* van der Waals interactions, while also satisfying the hydrogen bonding requirements of the carboxylic acid functional groups at the other end of the cation. Since the alkyl chains, ammonium groups and carboxylic acid groups all form a part of the same cation, optimum packing may often only be achieved *via* distortion of the cation geometry from the ideal, low energy all-*trans* geometry, or through tilting of the cation relative to the layer plane, or both. Thus, the nature of the primary network not only dictates the

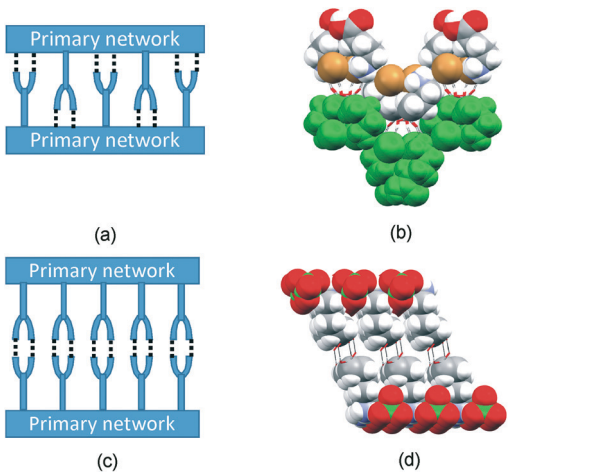


Fig. 4 "Molecular Velcro": (a) schematic of interdigitated structures, (b) space-fill depiction of structure C4Br, **2**, showing two primary layers and the carboxylic acid hydrogen bonds acting as "hooks", (c) schematic of non-interdigitated structures, and (d) space-fill depiction of structure $C6ClO_4$, **8**, showing two primary layers and the carboxylic acid hydrogen bonds acting as "hooks".

interdigitation or non-interdigitation of the alkyl chains as described previously, it also affects the geometry and/or tilt angle of the alkyl chains relative to the layer plane in the layered structures.

Because the ammonium ends of the cations form part of the primary hydrogen bonding network, the distances between these ends of the cations, and thus the alkyl chains bonded to the ammonium groups, are fixed by the relative positions of ammonium groups, anions and possibly water molecules in the primary network. If the primary networks were planar, and the alkyl chains packed perpendicular to this network, the alkyl chain cross section would exceed the ideal cross-sectional area of 18–20 $Å^2$,[33] which corresponds to ideal close packing of alkyl chains.

However, there are different ways to bring the alkyl chains closer together to obtain a better close packing of chains, and improve the van der Waals interactions between the chains. The first is to reduce the tilt angle of the alkyl chains relative to the layer plane to a value smaller than 90°, which brings the alkyl chains closer together. The effective diameter of an alkyl chain can be increased by the introduction of a *gauche* bond in the alkyl chain. Interdigitation of the chains of a primary layer with the chains of a neighbouring primary layer also results in a closer packing of alkyl chains, provided interdigitation is possible. None of the above impacts on the primary hydrogen bonding network, and involves only the packing and/or geometry of the cation. A structure may exhibit more than one of these features to improve close packing of the alkyl chains when the cross-sectional area of the primary network, as defined by the placement of the ammonium groups in the primary network, exceeds the ideal alkyl chain cross-sectional area. In addition, when the ammonium group anchors a cation to the primary hydrogen bonding network, the cation geometry may also be distorted in order to correctly position the carboxylic acid group of the cation to form a hydrogen bond, either to a neighbouring primary network or to the carboxylic acid group of a cation bonded to a neighbouring primary network.

It should be noted that corrugation of the primary network also brings the alkyl chains closer together compared to a planar primary network, by shortening the distance between ammonium groups, and thus also decreasing the distance between the alkyl chains. As discussed in the following section, the novel layered structures reported here show a number of the features listed above, with the final structure obtained the result of a delicate balance between strong and weaker hydrogen bonding interactions, van der Waals interactions, and close packing of the species.

In all the interdigitated structures in the series (structures **1**, **2** and **4**), the packing is such that the anions and ammonium groups in the inorganic layer pack approximately above their counterparts in successive inorganic layers. Thus, they roughly overlay when viewed perpendicular to the layer plane. The carboxyalkylammonium cation then adopts the required geometry to position the carboxylic acid groups correctly to hydrogen bond to the halide anions in neighbouring primary networks. As such, the distances between the carboxylic acid groups are similar to the distances between the halide anions in the primary network, allowing the alkyl chains to slot between each other (interdigitate) and anchor to the primary network. This means that the halide anions in the primary network have a structure-directing effect, as hydrogen bonding acceptors, and force the cation to adopt a geometry which allows the correct positioning of carboxylic acid group for hydrogen bonding.

In structure **1**, the carboxylic acid groups of the cations can be correctly positioned for hydrogen bonding to the neighbouring inorganic layers by adopting a tilted position relative to the zig-zag primary layer, while maintaining the low energy, all-*trans* cation geometry, as shown in Fig. 5(a) and (b), which illustrate how the cation "stretches" in the direction of the chloride anion it is hydrogen bonded to in the neighbouring primary layer. The reduced tilt angle, and the fact that interdigitation occurs between the chains of two neighbouring layers, results in an ideal packing of alkyl chains in structure **1**. The corrugation of the primary network also makes the chloride anion accessible to accept a hydrogen bond from the carboxylic acid group.

A *gauche* bond is required to position the carboxylic acid group in the correct position to hydrogen bond to the bromide anion in a neighbouring inorganic layer in structure **2**, as shown in Fig. 5(c) and (d). In this structure, the hydrogen bonded layer is slightly corrugated, and the alkyl chains are tilted relative to the layer plane.

The cations in structure **4** maintain the all-*trans* geometry while hydrogen bonding to the chloride anion in a neighbouring layer (Fig. 5(e)). However, the carboxylic acid group is twisted out of the carbon zig-zag plane to allow hydrogen bonding, as illustrated in Fig. 5(f). The primary network is corrugated in structure **4**, making the chloride anion more accessible to the carboxylic acid group.

Cation geometries observed in the non-interdigitated structures can be explained in the same way, but here a supramolecular cation formed *via* the carboxylic acid dimer, which results in an "*n*-alkyldiammonium-type supramolecule", is considered. The ammonium groups of the "supramolecule" have to be positioned in such a way to fit into two primary hydrogen bonding networks, while maintaining the carboxylic acid dimers and close packing between the alkyl chains. This can be achieved by adopting the correct tilt angle, or the introduction of a *gauche* bond in the alkyl chain, or both. In structures **5** and **6**, the cations are tilted relative to the layer plane, and a *gauche* bond is introduced to achieve the correct positioning of the hydrogen bonding groups of the supramolecular cation in consecutive inorganic layers, as well as close packing of the alkyl chains (Fig. 6(a)). Note that in structures **5** and **6**, the cation "stretches" across a water molecule in the primary network to reach a halide anion in a neighbouring primary network, as shown in Fig. 6(b). When projecting this stretch on the lower primary network, the cation stretch corresponds to a "long" ammonium···halide distance, as shown in Fig. 6(b).

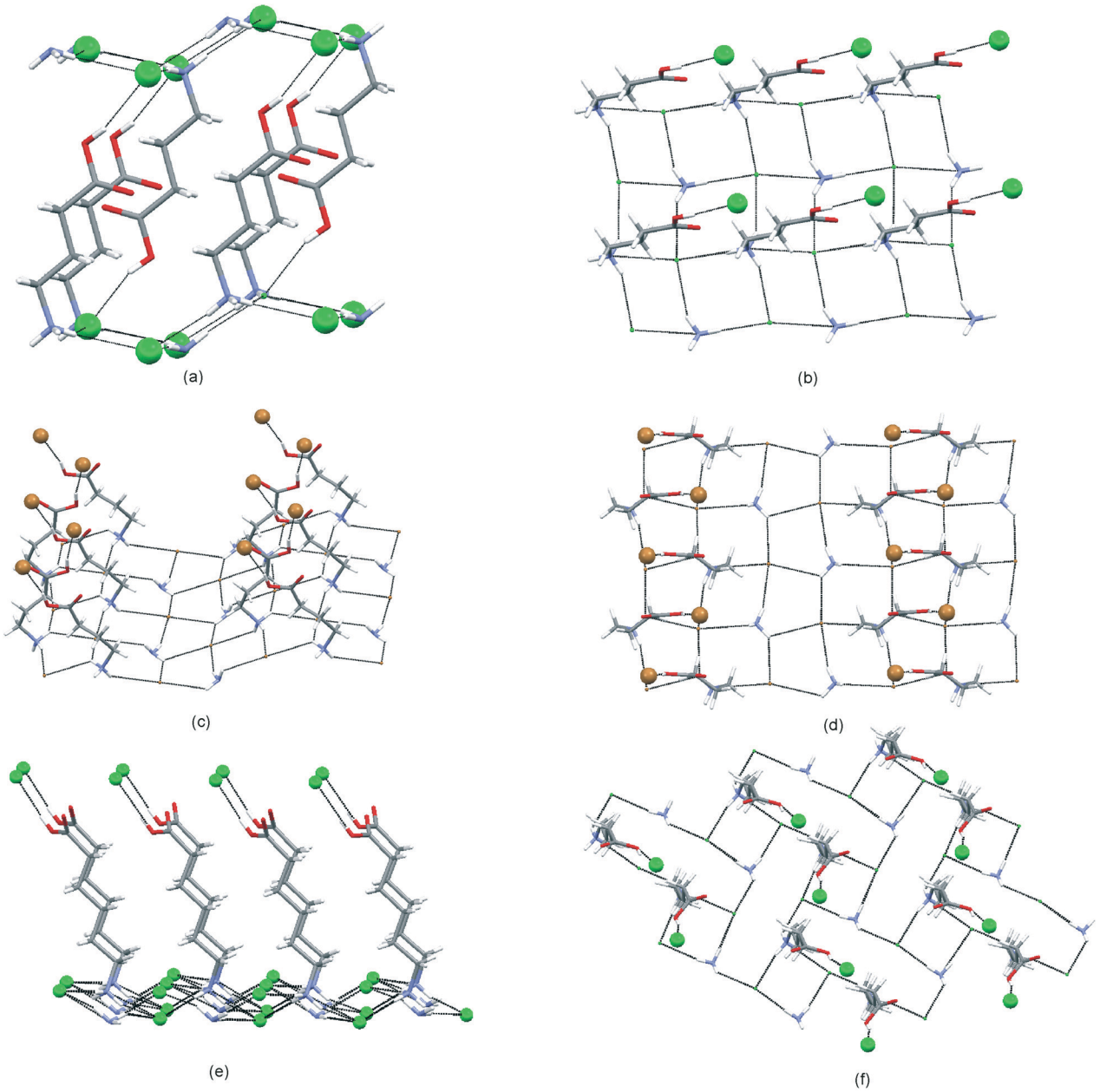


Fig. 5 (a) Tilted, all-*trans* cations and zig-zag primary layer in C4Cl, **1**. (b) Tilted cation "stretching" to reach a hydrogen bonding acceptor in C4Cl, **1**. (c) Kinked cations hydrogen bonding to bromide acceptors in C4Br, **2**. (d) Kinked cations bonding to bromide anions, viewed normal to a layer plane in C4Br, **2**. (e) Tilted, all-*trans* cation and primary network in C6Cl, **4**. (f) Cations hydrogen bonding to chloride anions in a neighbouring primary layer in C6Cl, **4**, viewed normal to the layer plane.

In structure **7**, the supramolecular cation displays a high tilt angle (Fig. 6(c)), and corrugation is observed in the primary network, both structural features which bring the alkyl chains closer together. It this structure, the cation stretches over a "trough" in the corrugated primary network (Fig. 6(c)), thus also a region with a long ammonium···anion distance, as was observed in structures **5** and **6**.

A *gauche* bond is also observed in structure **8** (Fig. 6(e)). However, here the tilt angle is smaller than in structures **5** and **6**. The primary network (Fig. 6(f)) is not corrugated.

It is interesting to note the position of the *gauche* bond in the carboxyalkylammonium cations. A *gauche* bond is observed in structures **2**, **5**, **6** and **7**, and in all these structures the *gauche* bond involves the C(2)–C(3)–C(4)–C(5)/N(1) atoms, with atom C(1) being the carboxylic acid group carbon atom. This means that the distortion from the ideal all-*trans* geometry occurs close to the carboxylic acid group, while the portion of the cation closer to the ammonium group retains its all-*trans* geometry better, at least in the case of the longer chain salts.

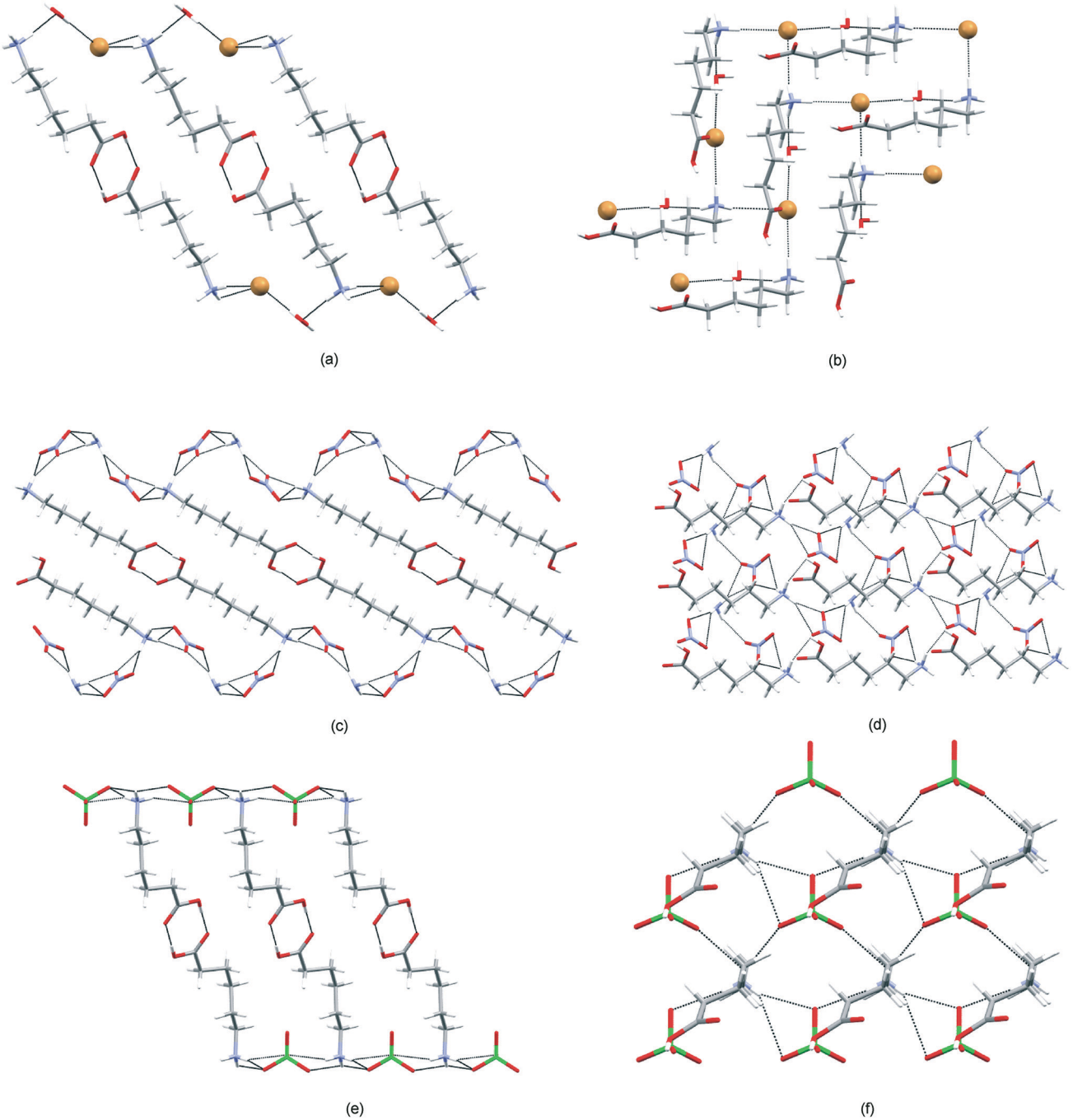


Fig. 6 (a) Kinked cation forming a "supramolecular diammonium cation" in C6Br·0.5H_2O, **5** (also representative of structure C6I·0.5H_2O, **6**). (b) Kinked cations stretching across a water molecule to hydrogen bond to a bromide anion in a neighbouring primary layer in structure C6Br·0.5H_2O, **5**, viewed normal to the layer plane. (c) Tilted "supramolecular diammonium cation" in structure C6NO_3, **7**. (d) Cation hydrogen bonded to nitrate anions in a neighbouring primary layer in structure C6NO_3, **7**, viewed normal to the layer plane. (e) Tilted "supramolecular diammonium cation" in structure C6ClO_4, **8**. (f) Cation stretching to hydrogen bond to a perchlorate anion in structure C6ClO_4, **8**, viewed normal to the layer plane.

Conclusions

In summary, a two-dimensional primary hydrogen bonding network involving the strongest hydrogen bonding donors and acceptors, namely the ammonium groups and halide/oxo-anions, is formed in all the layered structures **1**, **2**, **4** and **5** to **8**. The robustness of the primary network is shown by the fact that a number of the networks observed in the current study correspond to networks reported for primary alkyl- and arylammonium halide and nitrate structures in the literature, as well as for *n*-alkyl-diammonium salts. Secondary hydrogen bonding interactions involving the carboxylic acid groups link neighbouring primary networks, either through the formation of carboxylic acid dimers in non-interdigitated

structures, or through hydrogen bonding of the carboxylic acid group to a primary network in interdigitated structures.

The type of primary hydrogen bonding network is pivotal in determining whether or not interdigitation occurs between neighbouring layers, with one important feature of the network being whether the alkyl chains alternate above and below the primary network or not. Various factors affect the conformation adopted by the cation, and in the end, the final structure obtained represents a delicate balance between strong and weak hydrogen bonds, van der Waals interactions and close packing effects.

Experimental

Chemicals and reagents

All chemicals were used as-purchased without further purification: 4-aminobutyric acid (Sigma, 99%), 6-aminohexanoic acid (Fluka, ≥98.5%), HCl (Sigma-Aldrich, 37%), HBr (Sigma-Aldrich, 48%), HI (Sigma-Aldrich, 57%), HNO_3 (Promark Chemicals, 55%), $HClO_4$ (Sigma-Aldrich, 70%) and chloroform (Sigma-Aldrich, ≥99.8%).

Synthesis

No attempts were made to optimise the yields of the reactions. Due to risk of explosion, elemental analysis determinations were not performed for the perchlorate and nitrate salts, **7** and **8**. The calculated and experimental powder X-ray diffraction powder patterns are compared in the ESI.†

Synthesis of C4Cl, 1. 4-Aminobutyric acid (1.0052 g, 9.747 mmol) was dissolved in a 250 ml beaker in 40 ml distilled water. To this solution, 1.7 ml HCl (19.49 mmol) was added. The solution was left open to the atmosphere, at room temperature, until colourless crystals of the product were formed. The crystals were filtered off from the mother liquor. Yield: 98.1%. Elemental analysis: calculated: C: 34.42%, H: 7.22%, N: 10.03%; found: C: 34.30%, H: 7.16%, N: 10.02%.

Synthesis of C4Br, 2. 4-Aminobutyric acid (0.9817 g, 9.520 mmol) was dissolved in 40 ml chloroform in a 250 ml beaker. To this solution, 2.2 ml (19.55 mmol) HBr was added. The solution was left open to the atmosphere. Colourless crystals of **2** formed on partial evaporation of the solvent, and were filtered off from the mother liquor. Better quality crystals were obtained on crystallisation of the product from water. Yield: 57.9%. Elemental analysis: calculated: C: 26.11%, H: 5.48%, N: 7.61%; found: C: 26.11%, H: 5.51%, N: 7.58%.

Synthesis of C4I, 3. 4-Aminobutyric acid (0.5052 g, 4.899 mmol) was dissolved in 10 ml water in a 50 ml beaker. 0.65 ml HI (4.921 mmol) was added to this solution, and the beaker was heated on a hot plate at 60 °C to reduce the solution volume to approximately 4 ml. The solution was removed from the heat, and a white product crystallised on cooling. Crystals of **3** suitable for single crystal X-ray diffraction were obtained by re-crystallisation of the product from distilled water at room temperature. Yield: 95.2%. Elemental analysis: calculated: C: 20.79%, H: 4.36%, N: 6.06%; found: C: 20.76%, H: 4.38%, N: 6.04%.

Synthesis of C6Cl, 4. 6-Aminohexanoic acid (1.0099 g, 7.699 mmol) was dissolved in 50 ml distilled water in a 250 ml beaker, and 1.3 ml of HCl (15.08 mmol) was added. The solution was left to evaporate at room temperature, and crystals of **4** were filtered off from the mother liquor. Yield: 31.7%. Elemental analysis: calculated: C: 42.99%, H: 8.42%, N: 8.36%; found: C: 43.17%, H: 8.46%, N: 8.34%.

Synthesis of C6Br·0.5H_2O, 5. 6-Aminohexanoic acid (0.9960 g, 7.593 mmol) was dissolved in 50 ml water in a 250 ml beaker. To this solution, 1.7 ml (15.1 mmol) HBr was added. The solution was left open to the atmosphere. Colourless crystals of **5** formed on partial evaporation of the solvent, and were filtered off from the mother liquor. Yield: 64.6%. Elemental analysis: calculated: C: 32.59%, H: 6.84%, N: 6.34%; found: C: 32.75%, H: 6.87%, N: 6.36%.

Synthesis of C6I·0.5H_2O, 6. 6-Aminohexanoic acid (1.0091 g, 7.693 mmol) was dissolved in a 250 ml beaker in 20 ml distilled water. To this solution 1.1 ml of HI (8.327 mmol) was added. The solution was left open to air, at room temperature. A cream coloured product crystallised, and was filtered off. Re-crystallisation of the product from distilled water at room temperature yielded crystals suitable for single crystal X-ray diffraction. Yield: 88.2%. Elemental analysis: calculated: C: 26.88%, H: 5.64%, N: 5.22%; found: C: 26.85%, H: 5.68%, N: 5.19%.

Synthesis of C6NO_3, 7. 6-Aminohexanoic acid (0.9902 g, 7.5489 mmol) was dissolved in 20 ml distilled water in a 50 ml beaker. To this solution, 1.0 ml HNO_3 (16.0 mmol) was added. The solution was left open to the atmosphere. On partial evaporation of the solvent, colourless crystals of **7** formed. The crystals were filtered off from the mother liquor. Yield: 47.6%.

Synthesis of C6ClO_4, 8. 6-Aminohexanoic acid (0.9951 g, 7.5863 mmol) was dissolved in 20 ml water in a 50 ml beaker. To this solution, 1.3 ml of $HClO_4$ (15.1 mmol) was added. The solution was left open to the atmosphere. Colourless crystals of **8** formed on partial evaporation of the solvent, and were filtered off. Yield: 37.7%.

Crystallographic studies

X-ray structure analysis. The X-ray diffraction data for all compounds were collected using a Bruker D8 Venture diffractometer, with a Photon 100 CMOS detector, at 150(2) K, employing a combination of ϕ and ω scans. Monochromatic MoKα radiation with a wavelength λ of 0.71073 Å, from an IμS source, was used as the irradiation source. Data reduction and absorption corrections were performed using SAINT+[34] and SADABS[35] as part of the APEXII[36] suite. The structures were solved by direct methods using SHELXS[37] as part of the WinGX[38] suite. Structure refinements were carried out using SHELXL[39] in WinGX[38] as GUI. In structures **1**, **2**, **3**, **5**, **6** and **8**, non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed as observed in the difference map and refined isotropically. Hydrogen atoms in structure **3** involved in hydrogen bonding, were refined isotropically, while the rest

of the hydrogen atoms were placed geometrically, and non-hydrogen atoms refined fully. For structure 7, all hydrogens atoms were placed geometrically, except the hydroxide hydrogen atom, while non-hydrogen atoms were refined anisotropically, and the nitrate anion was modelled to be disordered over two positions. Graphics were generated using Mercury 3.9.[40] Even though structure 7, $C6NO_3$, is of a poorer quality than the rest due to the disorder displayed by the nitrate anion, it adds value to the paper, and the authors felt that it should be included for comparative purposes, especially since the cation shows no disorder, and its conformation is clear. Single crystal X-ray diffraction analysis of a number of crystals of compound 7 was carried out, but improved data could not be obtained, indicating that the disorder is the cause of the lower *R* value.

Powder X-ray diffraction. Powder X-ray diffraction patterns were measured on a Bruker D2 Phaser powder diffractometer employing a Si low-background sample holder, and experimental powder patterns were compared with powder patterns calculated from single crystal structure data using the software DiffractWD.[41]

Conflicts of interest

There are no conflicts to declare.

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