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Steric effects in hydrogen bonded columns of salts of benzoic acid and 1adamantanecarboxylic acid with the cyclic amines $C_nH_{2n+1}NH_2$, n = 5, 6, 7, 8and 12^+

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The hydrogen bonded columns of salts of benzoic acid or adamantanecarboxylic acid and five cyclic amines are reported. During solution crystallization, the H from the carboxylic acid transfers to the amine to form ammonium carboxylate salts which feature three charge-separated $N^+-H\cdots O^-$ hydrogen bonds to form two types of 1-D hydrogen bonded columns. Of the ten structures, *viz.* (cyclopentylammonium · benzoate) (1), (cyclohexylammonium · benzoate) (2), (cycloddecylammonium · benzoate) (5), (cyclopentylammonium · adamantanecarboxylate) (6), (cyclohexylammonium · adamantanecarboxylate) (7) and

(cyclododecylammonium · adamantanecarboxylate) (10) form a type II hydrogen bonded column which consists of repeating $R_4^3(10)$ hydrogen bonded rings whereas (cycloheptylammonium · benzoate) (3), (cyclooctylammonium · benzoate) (4), (cycloheptylammonium · adamantanecarboxylate) (8), and (cyclooctylammonium · adamantanecarboxylate) (9) form a type III hydrogen bonded column, which consists of alternating $R_4^2(8)/R_4^4(12)$ hydrogen bonded rings. Even with two sterically different anions, the type of hydrogen bonded column formed is the same for each counter cation and hence it is the size of the cyclic ammonium rings that influences the type of hydrogen bonded column. From this we can gather clues about the effect of the steric size of the cation and anion and its effect on the overall packing.

Introduction

The rapidly growing field of crystal engineering¹ is still in its formative stages. Crystal engineering is a form of supramolecular/organic synthesis, where the individual synthons are discrete molecules that use molecular recognition through intermolecular interactions to form supramolecular entities.² The role of hydrogen bonding as the primary intermolecular interaction has been established through the work of amongst others Desiraju and Etter.³ The key is to identify robust hydrogen bonding synthons that behave predictably in different chemical environments.⁴ The question posed in this work is how do specific hydrogen bonding heterosynthons change when systematically varying two components in a binary system? In order to better analyze hydrogen bonding patterns, graph set (GS) notation has been a vital tool and will be used in this report.⁵ The hydrogen bonding properties of carboxylic acids, both protonated and

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unprotonated, are well established.⁶ In its unprotonated form, it can act as a four-fold acceptor due to its four lone pairs of electrons.⁶ As a donor, protonated amines are unrivaled as a three-fold donor of the three H atoms, used in both organic and inorganic systems.⁷ If combined in solution and with the correct difference in pK_{as} , the proton from the carboxylic acid is transferred to the amine to form three charge-assisted N⁺-H···O⁻ hydrogen bonds and crystallize out as ammonium carboxylate molecular salts.

Work on ammonium carboxylate salts of general formula (R– NH₃⁺)·(R'–CO₂⁻) has been used to investigate the formation of conglomerates of chiral primary amines with achiral monocarboxylic acids,⁸ 1,3-diene mono- and dicarboxylic acids and a range of naphthylmethyl and benzylamines for topochemical polymerization,⁹ α , β -unsaturated carboxylic acids with chiral and achiral aromatic amines for *E*/*Z* isomerization¹⁰ and photopolymerization of di(benzylammonium) (*Z*,*Z*)-muconates.¹¹ In all of the above mentioned studies, the strength and robustness of the hydrogen bonded interaction in the salts were crucial.

In their work with conglomerates, Kinbara *et al.*⁸ observed that the hydrogen bonded pattern formed different types of translational hydrogen bonded units that form a columnar structure around either a two-fold screw axis $(2_1$ -column) or inversion centers (*i*-column). These two categories of hydrogen

bonded columns were latter classified as type II (2_1 -column) and type III (i-column) (see Scheme 1).¹⁰ The type II column consists of repeating ten-membered hydrogen bonded rings, GS notation $R_4^3(10)$, and type III column of alternating eight-membered $R_4^2(8)$ and twelve-membered $R_4^4(12)$ rings. The columns can also be described as ladders, with rungs and legs formed by the individual N^+ – $H^{\dots}O^-$ hydrogen bonds. The type II column was consistently observed when the chiral ammonium cation consisted of only a single enantiomer and the type III column when both enantiomers (racemic mixture) of the ammonium cation were used. When the ammonium cation does not possess a chiral centre, what determines the type of hydrogen bonded column observed? It was suggested by Kinbara et al.8 that the type II bonding is more often observed in salts that have large R/R' hydrocarbon groups bonded to the ammonium or carboxylate functional groups. We want to determine if there is a steric motive in switching between the two different types of heterosynthons. Previously, we have had success in correlating the steric size of the ammonium cation with the resulting packing architecture in systems containing an inorganic component, of general formula $[(C_nH_{2n-1}NH_3)_xPbI_y]^{12}$ The amines used were cyclic hydrocarbons. For ring sizes from n = 3 to n = 6, a 2-D inorganic motif of corner-sharing PbI₆ octahedra was observed. For ring sizes greater than 6, 1-D motifs of corner-sharing PbI₆ chains (n = 7) and face-sharing PbI₆ chains (n = 8) resulted.

To this end, a similar series of cyclic hydrocarbon rings with a single amine group and two different hydrocarbons with a carboxylic acid functional group, benzoic acid and 1-adamantanecarboxylic acid were chosen (Scheme 2). The two acid



Scheme 1 The repeating pattern of the two hydrogen bonded heterosynthons observed in ammonium carboxylate salts.



Scheme 2 The five cationic and two anionic species chosen to investigate steric effects on the type of hydrogen bonding heterosynthons and packing of ammonium carboxylate salts 1–10.

molecules are sterically very different, benzoic acid with a flat aromatic ring and the latter with a symmetrical rounded shape. The crystal structures of the ammonium carboxylates with general formula $[C_6H_4CO_2 \cdot C_nH_{2n-1}NH_3]$ (n = 5, 6, 7, 8 and 12) and $[C_{10}H_{15}CO_2 \cdot C_nH_{2n-1}NH_3]$ (n = 5, 6, 7, 8 and 12) were synthesized and are described below.

Results

The ten ammonium carboxylate salts were all prepared in an identical manner. A 1 : 1 stoichiometric ratio of amine to acid was dissolved in methanol and crystals grown by slow evaporation at room temperature. Structure determination was carried out using single crystal X-ray diffraction and summarized in Tables 1 and 2. As a consequence of the known conformational flexibility of the hydrocarbon rings, all data collections were performed at 173 K. Powder X-ray diffraction of the bulk material confirmed in each case that the crystal structure was representative of the bulk material (see ESI[†]). The atomic

Table 1Crystal data for 1, 2, 3, 4 and 5

	1	2	3	4	5
Empirical formula	C ₁₂ H ₁₇ NO ₂	C ₁₃ H ₁₉ NO ₂	C ₁₄ H ₂₁ NO ₂	C15H23NO2	$C_{19}H_{31}NO_2$
Molecular weight	207.27	221.29	235.32	249.34	305.45
Crystal size/mm	0.68 imes 0.30 imes 0.08	0.48 imes 0.10 imes 0.04	0.50 imes 0.09 imes 0.05	$0.45 \times 0.20 \times 0.20$	0.57 imes 0.10 imes 0.10
Crystal system	Orthorhombic	Orthorhombic	Tetragonal	Triclinic	Monoclinic
Space group	$P2_{1}2_{1}2_{1}$	Fdd2	$I4_1/a$	$P\bar{1}$	$P2_1$
<i>Î</i> /K	173	173	173	173	173
a/Å	6.0786(4)	22.1824(12)	29.9735(5)	6.4482(1)	6.2730(5)
b/Å	10.5312(8)	35.8905(19)	29.9735(5)	9.0987(2)	27.265(2)
c/Å	17.6034(12)	6.3763(3)	6.0374(2)	12.4471(2)	10.4419(8)
$\alpha /^{\circ}$	90	90	90	86.603(1)	90
βI°	90	90	90	87.8990(1)	90.432(2)
γI°	90	90	90	77.976(1)	90
$V/Å^3$	1126.88(14)	5076.4(5)	5424.7(2)	712.78(2)	1785.9(2)
Ζ	4	16	16	2	4
Calc./g cm ⁻³	1.222(5)	1.158(3)	1.153(2)	1.162(4)	1.136(1)
μ/mm^{-1}	0.083	0.078	0.076	0.076	0.072
F(000)	448	1920	2048	272	672
Scan range $(\theta)/^{\circ}$	2.25 to 28.00	2.16 to 27.98	1.36 to 28.00	1.64 to 28.00	1.95 to 27.99
Total reflections	5870	6684	29 101	13 319	18 832
Unique reflections[<i>R</i> (int)]	1589 [0.0764]	1670 [0.1217]	3276 [0.0618]	3443 [0.0497]	4330 [0.1059]
No. data with $I \ge 2\sigma(I)$	1251	1231	2299	2958	3820
Parameters	137	165	174	164	399
$R1 \left[I > 2\sigma(I) \right]$	0.0487	0.0702	0.0442	0.0419	0.0559
wR2 (all data)	0.1241	0.2219	0.1117	0.1162	0.1384

Table 2Crystal data for 6, 7, 8, 9 and 10

	6	7	8	9	10
Empirical formula	C ₁₆ H ₂₇ NO ₂	C ₁₃ H ₁₉ NO ₂	C ₁₄ H ₂₁ NO ₂	C ₁₅ H ₂₃ NO ₂	C ₁₉ H ₃₁ NO ₂
Molecular weight	265.39	221.29	235.32	249.34	305.45
Crystal size/mm	$0.25 \times 0.17 \times 0.10$	0.49 imes 0.14 imes 0.07	$0.48 \times 0.15 \times 0.08$	0.50 imes 0.12 imes 0.04	$0.60 \times 0.53 \times 0.26$
Crystal system	Orthorhombic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_{1}2_{1}2_{1}$	$P\overline{1}$	C2/c	$P2_1/c$	C2/c
T/K	173	173	173	173	173
a/Å	6.4660(3)	6.5544(3)	23.4749(10)	6.4758(3)	28.9710(6)
b/Å	11.0130(4)	12.7542(4)	6.4309(2)	11.2016(6)	6.5850(1)
c/Å	21.0380(9)	19.7109(9)	21.8759(10)	24.5573(16)	23.0547(5)
αl°	90	76.690(3)	90	90	90
βl°	90	89.615(3)	96.802(2)	93.217(4)	102.386(1)
γl°	90	89.590(2)	90	90	90
V/Å ³	1498.20(10)	1602.30(15)	3279.2(2)	1778.56(16)	4295.87(15)
Ζ	4	4	8	4	8
Calc./g cm ⁻³	1.177	1.158	1.189	1.148	1.124
μ/mm^{-1}	0.076	0.074	0.076	0.073	0.070
F(000)	584	616	1296	680	1616
Scan range $(\theta)/^{\circ}$	1.94 to 28.00	1.06 to 25.50	1.75 to 28.00	1.66 to 28.00	1.44 to 28.00
Total reflections	7939	8569	9841	12 847	13 575
Unique reflections/R(int)	2099 [0.0660]	5824 [0.1169]	3669 [0.0525]	4267 [0.1404]	5186 [0.0681]
No. data with $I \ge 2\sigma(I)$	1685	4057	2792	1985	3835
Parameters/restraints	183/69	527/681	191/0	200/0	318/318
$R1 \left[I > 2\sigma(I) \right]$	0.0475	0.0915	0.0500	0.0650	0.0438
w $R2$ (all data)	0.1267	0.2709	0.1218	0.1470	0.1469

numbering scheme of the ammonium carboxylate salts of the benzoate series 1-5 is shown in Fig. 1 and of the adamantane carboxylate series 6-10 in Fig. 2. The distances and angles within the five compounds reported are generally as expected.¹³ Seeing that the hydrogen bonded interactions are central to this study, the hydrogen atoms on the ammonium group are all labelled consistently in order to make comparisons of the ten structures easier. H(1A) on the ammonium group is always *trans* to the methine H(8) on the cyclic hydrocarbon ring and forms a symmetry independent hydrogen bond to O(1) on the benzoate

anion or adamantane carboxylate anion (compound 7 is the exception and hydrogen bonds to O(2)). All structures have three simple $N^+-H\cdots O^-$ hydrogen bonds between the ammonium cation and carboxylate anion pairs that have been observed previously and their geometric values are listed in Tables 3 and 4.⁸ The packing of the columns can either be described as a square, hexagonal or checkerboard like arrangement, depending on the number of columns and relative positioning around a central column. The ten structures will be described briefly individually and then overall trends discussed.

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2



3



4

C(11) C(12) C(19) C(13 C(18) (20) C(21) 0(4 C(16) C(17) C(36) C(38) C(37) (15) C(25) C(23) C(35 C(27) C(24) C(28 C(34 C(30) C(5) C(31) CIA 5

Fig. 1 The asymmetric units of salts 1–5, showing the atomic numbering scheme. Displacement ellipsoids are shown at the 50% probability level. The H atoms on the C atoms are omitted for clarity in 3 and 5.

Crystallographic description of the ammonium carboxylate salts 1–5 with the benzoate anion

 $[C_5H_9NH_3 \cdot C_6H_5CO_2]$ (1). Salt 1 crystallized in the chiral space group $P_{2_12_12_1}$ and contains one crystallographically independent cyclopentylammonium cation and one benzoate anion. The cyclopentylammonium ring has an envelope conformation. The three unique N⁺-H···O⁻ hydrogen bonds form one unique hydrogen bonded ring. The ring consists of two ammonium groups, one benzoate anion using both O(1) and O(2) as acceptor and one benzoate anion using only O(1). The resulting graph set notation is $R_4^3(10)$. The ring is repeated along the *a*-axis with H(1C) common to adjacent rings to form the type **II** hydrogen bonded columns (Fig. 3a). The neighbouring columns are linked by C–H··· π interactions along the *b*-axis between H(11B) on the cyclopentylammonium ring and the benzoate anion (H(11B)···Cg: 2.81 Å; <C(11)–H(11B)···Cg: 148°) (Fig. 3b).

 $[C_6H_{11}NH_3 \cdot C_6H_5CO_2]$ (2). Salt 2 crystallized in the chiral space group *Fdd2* and contains one crystallographically independent cyclohexylammonium cation and one benzoate anion. The cyclohexylammonium ring has two disordered C atoms and





6





9



10

Fig. 2 The asymmetric units of salts 6–10, showing the atomic numbering scheme. Displacement ellipsoids are shown at the 50% probability level. The H atoms on the C atoms are omitted for clarity in 7. Only the major parts of the disordered adamantane carboxylate anions are shown in 7 and 10.

the predominant ring conformation is chair. The three unique $N^+-H\cdots O^-$ hydrogen bonds combine similarly as in salt 1 to form the type II hydrogen bonded column (Fig. 4a). The molecular packing is generated by interdigitation of the hydrogen bonded columns with neighbouring columns in both the *a* and *b*-axis directions (Fig. 4b). The columns are shaped like crosses and benzene and cyclohexane rings interdigitating with the neighbouring columns. There are no $C-H\cdots\pi$ interactions between neighbouring columns. A polymorph of this salt has been reported previously, and consists of three symmetry unique

type **II** hydrogen bonded columns in the asymmetric unit.¹⁸ The packing of the columns in that polymorph is hexagonal.

 $[C_7H_{13}NH_3 \cdot C_6H_5CO_2]$ (3). Salt 3 crystallized in the centrosymmetric space group $I4_1/a$ and contains one crystallographically independent cycloheptylammonium cation and one benzoate anion. Two C atoms are disordered in the ring and the predominant ring conformation is twist-chair. The three unique N⁺-H···O⁻ hydrogen bonds form two unique hydrogen bonded rings. Both hydrogen bonded rings are centrosymmetric. The

D–H···A	D–H/Å	H…A/Å	D…A/Å	<(D–H···A)/°	Symmetry transformations
1					
$N(1)-H(1A)\cdots O(1)$	0.91	1.95	2.817(3)	159	_
$N(1) - H(1B) \cdots O(2)$	0.91	1.82	2.726(3)	177	x - 1, y, z
$N(1) - H(1C) \cdots O(1)$	0.91	1.88	2.766(3)	165	$x - \frac{1}{2}, -y + \frac{3}{2}, -z + 1$
2					, , ,
$N(1)-H(1A)\cdots O(1)$	0.91	1.85	2.754(4)	174	_
$N(1) - H(1B) \cdots O(2)$	0.91	1.81	2.713(6)	169	-x + 1/2, -y + 1, z - 1/2
N(1) - H(1C) - O(1)	0.91	1.87	2.769(5)	171	-x + 1/2, -y + 1, z + 1/2
3					
$N(1)-H(1A)\cdots O(1)$	0.91	1.87	2.768(2)	167	
$N(1)-H(1B)\cdots O(2)$	0.91	1.82	2.724(2)	171	x, y, z - 1
$N(1)-H(1C)\cdots O(1)$	0.91	1.92	2.819(2)	169	-x + 1, -y + 1, -z + 1
4					
$N(1)-H(1A)\cdots O(1)$	0.91	1.91	2.782(1)	160	
$N(1)-H(1B)\cdots O(1)$	0.91	1.89	2.787(1)	171	-x + 1, -y + 1, -z + 1
$N(1)-H(1C)\cdots O(2)$	0.91	1.84	2.740(1)	170	x + 1, y, z
5					
$N(1)-H(1A)\cdots O(1)$	0.91	1.89	2.787(3)	167	
$N(1)-H(1B)\cdots O(2)$	0.91	1.82	2.718(3)	168	x - 1, y, z
$N(1)-H(1C)\cdots O(3)$	0.91	1.81	2.714(3)	170	
$N(2)-H(2A)\cdots O(3)$	0.91	1.89	2.782(3)	168	x + 1, y, z
$N(2)-H(2B)\cdots O(4)$	0.91	1.83	2.722(3)	167	_
$N(2)-H(2C)\cdots O(1)$	0.91	1.83	2.738(3)	172	_

Table 3 Hydrogen bonding details for benzoate salts 1-5

 Table 4
 Hydrogen bonding details for adamantane carboxylate salts 6–10

D–H···A	D–H/Å	H…A/Å	D…A/Å	<(D–H···A)/°	Symmetry transformations
6					
$N(1)-H(1A)\cdots O(1)$	0.91	1.89	2.773(2)	162	_
$N(1) - H(1B) \cdots O(1)$	0.91	1.86	2.767(3)	173	x + 1/2, -v + 1/2, -z + 1
N(1) - H(1C) - O(2)	0.91	1.80	2.706(3)	177	$x - \frac{1}{2}, -v + \frac{1}{2}, -z + 1$
7					, , ,
$N(1)-H(1A)\cdots O(2)$	0.91	1.87	2.754(4)	163	_
$N(1) - H(1B) \cdots O(3)$	0.91	1.81	2.708(4)	169	x - 1, v, z
$N(1) - H(1C) \cdots O(4)$	0.91	1.89	2.797(4)	173	
$N(2) - H(2A) \cdots O(4)$	0.91	1.85	2.743(4)	167	_
$N(2)-H(2B)\cdots O(1)$	0.91	1.80	2.712(4)	175	_
$N(2)-H(2C)\cdots O(2)$	0.91	1.89	2.797(4)	177	x + 1, v, z
8					
$N(1)-H(1A)\cdots O(1)$	0.91	1.89	2.768(2)	161	
$N(1) - H(1B) \cdots O(2)$	0.91	1.81	2.719(1)	175	x, y + 1, z
$N(1) - H(1C) \cdots O(1)$	0.91	1.93	2.830(2)	170	-x + 3/2, -y + 1/2, -z + 1
9					, <u>,</u> ,
$N(1)-H(1A)\cdots O(1)$	0.91	1.88	2.769(3)	164	_
$N(1) - H(1B) \cdots O(2)$	0.91	1.83	2.735(2)	177	x - 1, v, z
N(1) - H(1C) - O(2)	0.91	1.89	2.787(2)	169	-x + 1, -y + 1, -z + 1
10					, , ,
$N(1)-H(1A)\cdots O(1)$	0.91	1.87	2.753(1)	164	_
$N(1) - H(1B) \cdots O(2)$	0.91	1.89	2.769(1)	162	x, y - 1, z
$N(1)-H(1C)\cdots O(2)$	0.91	1.97	2.848(1)	163	-x + 3/2, y - 1/2, -z + 3/2

 $R_4^2(8)$ hydrogen bonded ring consists of charge assisted hydrogen bonds and has two ammonium groups and two benzoate anions using only one O atom, O(1); and the $R_4^4(12)$ ring consists of two ammonium groups and two benzoate anions, both using O(1) and O(2). The rings alternate along the *c*-axis with H(1C) common to both rings to form the type **III** hydrogen bonded column (Fig. 5a). The molecular packing is generated by interdigitation of the hydrogen bonded columns with neighbouring columns in both the *a* and *b*-axis directions (Fig. 5b). Each column is linked to its four neighbouring columns by intercolumnar C–H… π interactions along the *a*- and *b*-axis between H(10A) on the cycloheptylammonium ring and the benzoate anion $(H(10A)\cdots Cg: 2.69 \text{ Å}; <C(10)-H(10A)\cdots Cg: 155^{\circ}).$

 $[C_8H_{15}NH_3 \cdot C_6H_5CO_2]$ (4). Salt 4 crystallized in the centrosymmetric space group $P\bar{1}$ and contains one crystallographically independent cyclooctylammonium cation and one benzoate anion. No C atoms are disordered in the ring and the predominant ring conformation is boat-chair. The three unique N⁺-H···· O⁻ hydrogen bonds combine similarly as in salt 3 to form the type III hydrogen bonded column (Fig. 6a). Both hydrogen bonded rings are centrosymmetric. The rings alternate along the



Fig. 3 (a) The type **II** hydrogen bonded ring repeating along the *a*-axis of salt **1**. Shown are the D···A distances in Å. (b) Hexagonal arrangement of columns in **1**, viewed along the *a*-axis. Hydrogen bonds are shown as dashed red lines and C–H··· π interactions as dashed blue lines.

a-axis with H(1C) common to both rings. The molecular packing is generated by interdigitation of the hydrogen bonded columns with neighbouring columns in both the *b* and *c*-axis directions (Fig. 6b). There are no C-H $\cdots\pi$ interactions between neighbouring columns.

 $[C_{12}H_{23}NH_3 \cdot C_6H_5CO_2]$ (5). Salt 5 crystallized in centrosymmetric space group $P2_1$ and contains two crystallographically independent cyclododecylammonium cations and two benzoate anions. The two cyclododecylammonium rings are not disordered and their conformation is not classifiable. In contrast to the previous salt structures that have the type II column, the four molecules making up the ring are crystallographically different



Fig. 4 (a) The type **II** hydrogen bonded ring repeating along the *c*-axis of salt **2**. Shown are the $D \cdots A$ distances in Å. (b) Hexagonal arrangement of columns in **2**, viewed along the *c*-axis.

and hence there are six unique N⁺–H···O⁻ hydrogen bonds. The rings are repeated along the *a*-axis with H(1C) and H(2C) common to adjacent rings to form the type **II** hydrogen bonded columns with the $R_4^3(10)$ (Fig. 7a). The molecular packing is generated by interdigitation of the hydrogen bonded columns with neighbouring columns along the *c*-axis direction (Fig. 7b). The neighbouring chains are linked by intercolumnar C–H··· π interactions along the *c*-axis only between H(21A) on the cyclododecylammonium ring and the benzoate (H(21A)···Cg1: 2.81 Å; <C(21)–H(21A)···Cg1: 148°) and similarly by H(33A) (H(33A)···Cg2: 2.84 Å; <C(33)–H(33A)···Cg2: 148 Å). In addition, there exists a C–H··· π interaction within a column, using H(26A) (H(26A)···Cg1: 2.99 Å; <C(26)–H(26A)···Cg2: 132°).

Crystallographic description of the ammonium carboxylate salts 6–10 with the adamantane carboxylate anion

 $[C_5H_9NH_3 \cdot C_{10}H_{15}CO_2]$ (6). Salt 6 crystallized in the chiral space group $P2_12_12_1$ and contains one crystallographically independent cyclopentylammonium cation and one adamantane carboxylate anion. The cyclopentylammonium ring has an envelope conformation, such that one C atom is disordered over two positions. The three unique N⁺-H···O⁻ hydrogen bonds combine similarly as in salt 1 to form the type II hydrogen bonded column (Fig. 8a). The ring is repeated along the *a*-axis





with H(1A) common to adjacent rings. The molecular packing is generated by interdigitation of the hydrogen bonded columns with neighbouring columns in the *c*-axis direction (Fig. 8b). There are no possible C–H··· π interactions.

 $[C_6H_{11}NH_3 \cdot C_{10}H_{15}CO_2]$ (7). Salt 7 crystallized in the centrosymmetric space group $P\bar{1}$ and contains two crystallographically independent cyclohexylammonium cations and two adamantane carboxylate anions. The two cyclohexyl rings have the chair conformation. The two anions are rotationally disordered around their main molecular axis through C1 and C11. The two parts are rotated 60% to each other (see ESI† for Ortep-style representations of the disorder). The six unique N⁺− H···O⁻ hydrogen bonds combine similarly as in salt 5 to form the type II hydrogen bonded column (Fig. 9a). The rings are repeated along the *a*-axis with H(1A) and H(2A) common to adjacent rings to form $R_4^3(10)$ rings. The molecular packing is generated by interdigitation of the hydrogen bonded columns with neighbouring columns in both the *b*- and *c*-axis directions (Fig. 9b).



Fig. 6 (a) The type **III** hydrogen bonded ring repeating along the *a*-axis of salt **4**. (b) The checkerboard arrangement of columns of **4**, viewed along the *a*-axis.

 $[C_7H_{13}NH_3 \cdot C_{10}H_{15}CO_2]$ (8). Salt 8 crystallized in the centrosymmetric space group *C2/c* and contains one crystallographically independent cycloheptylammonium cation and one adamantane carboxylate anion. The three unique N⁺-H···O⁻ hydrogen bonds combine similarly as in salt 3 to form the type **III** hydrogen bonded column (Fig. 10a). Both hydrogen bonded rings are centrosymmetric. The rings alternate along the *b*-axis with H(1C) common to both rings. The molecular packing is generated by interdigitation of the hydrogen bonded columns with neighbouring columns in both the *a* and *c*-axis directions (Fig. 10b).

 $[C_8H_{15}NH_3 \cdot C_{10}H_{15}CO_2]$ (9). Salt 9 crystallized in the centrosymmetric space group $P2_1/c$ and contains one crystallographically independent cyclooctylammonium cation and one adamantane carboxylate anion. No C atoms are disordered in the ring and the predominant ring conformation is boat-chair. The three unique N⁺-H···O⁻ hydrogen bonds combine similarly as in salt 3 to form the type III hydrogen bonded column (Fig. 11a). Both hydrogen bonded rings are centrosymmetric. The rings alternate along the *a*-axis with H(1C) common to both rings The molecular packing is generated by interdigitation of the hydrogen bonded columns with neighbouring columns in both the *b* and *c*-axis directions (Fig. 11b).





Fig. 8 (a) The type **II** hydrogen bonded ring repeating along the *c*-axis of salt **6**. (b) Packing diagram of **6**, viewed along the *c*-axis.

Fig. 7 (a) The type II hydrogen bonded ring repeating along the *a*-axis of salt 5. (b) The checkerboard arrangement of columns of 5, viewed along the *a*-axis.

 $[C_{12}H_{23}NH_3 \cdot C_{10}H_{15}CO_2]$ (10). Salt 10 crystallized in centrosymmetric space group *C*2/*c* and contains one crystallographically independent cyclododecylammonium cation and one adamantane carboxylate anion. The cyclododecylammonium rings are not disordered and their conformation is not classifiable. The anion is rotationally disordered similarly to what is observed in salt 7 (see ESI†). The three unique N⁺–H···O⁻ hydrogen bonds combine similarly as in salt 1 to form the type II hydrogen bonded column (Fig. 12a). The ring is repeated along the *b*-axis with H(1C) common to adjacent rings. The molecular packing is generated by interdigitation of the hydrogen bonded columns with neighbouring columns in the *c*-axis direction (Fig. 12b).

Discussion

Overall, all ten ammonium carboxylate salts have either the type II or III heterosynthon, which confirms that that these two

heterosynthons are robust interactions and can be predicted to occur in general ammonium carboxylate salts.¹⁴ In a Cambridge Structural Database survey carried out on ammonium carboxylate salts showed that either the type **II** or **III** heterosynthon occurs in 80% of the reported structures.¹⁵ Within those structures, the type **II** motif occurs almost three times as

frequently as the type III motif.¹⁵

These statistics are borne out in the ten new ammonium carboxylates. The majority of the structures have the type II heterosynthon (six), while the remaining four have the type III. Tables 5 and 6 summarize the type of heterosynthon for each combination of cation and anion. Interestingly, the identity of the anion did not play a role in forming the type of heterosynthon, but rather the cation. This means that the same cation in each of the two series displayed the same synthon, II for cyclopentylammonium, cyclohexylammonium and cyclo-dodecylammonium; and III for cycloheptylammonium and cyclooctylammonium. Ammonium carboxylate salts that have a chiral cation (*i.e.* ammonium group) and only the optically active cation present frequently form the type II synthon, some 87% of the time, and hence also crystallize in chiral space



Fig. 9 (a) The type **II** hydrogen bonded ring repeating along the *c*-axis of salt **7**. (b) Hexagonal arrangement of columns in **7**, viewed along the *a*-axis.

groups.¹⁶ Due to the inherent helical nature of the type II column, it does crystallize in chiral space groups and has been used to make chiral helical assemblies from achiral molecules.¹⁷ In this work, four of the ten structures crystallized in chiral space groups (1, 2, 5 and 6), all of them with the type II column.

In the work by Kinbara and co-workers,¹⁰ they investigated the effect of the hydrogen bonded network on the reactivity of the photoisomerization of ammonium α , β -unsaturated carboxylates. To aid them in their discussions, they introduced four parameters to describe the packing of the hydrogen bonded columns formed in their salts. The first two parameters are the inter-columnar distances d_1 and d_2 to the nearest two columns, the angle between them (θ) and the repeat length of the column d_3 , which corresponds usually to one of the three unit cell parameters, whichever one is the smallest of the three. We adapted these parameters to our system, with the repeat length of



Fig. 10 (a) The type **III** hydrogen bonded ring repeating along the *b*-axis of salt **8**. (b) Checkerboard arrangement of columns in **8**, viewed along the *b*-axis.

the columns (or hydrogen bonded rings) being d_0 and the intercolumnar distances (from a central column to each of the closest columns, where there can be from four to eight neighbours) being d_1-d_8 , respectively, with increasing distance (Scheme 3). These values were measured for compounds **1–5**, listed in Table 5, and **6–10** (Table 6). Occasionally, the d_0 values correspond to half or exactly the value of the unit cell parameter the columns are parallel to, and are listed together with the d_{1-8} values. The d_{1-8} values help to monitor the packing effects of the columns as a function of the ring size of the cations and the shape of the two anions.

The packing of columns is based on the close packing principle of bumps in hollows. Since each individual column has its hydrogen bonding functional groups pointing inward and the hydrocarbon part pointing outward as crosses (X), the hydrocarbon parts interdigitate as best as possible. The interdigitation is stabilized in the benzoate series by C-H…interactions in 1, 3 and 5. For compounds 1, 2, 3, 6 and 9 the range of minimum to maximum intercolumnar d values is narrow, indicative of the hexagonal or square packing of the columns. For small ring sizes like cyclopentyl, the hexagonal is preferred, even when going to a bulkier anion such as adamantane. Unusual is the hexagonal packing in 9, which has a large ring cation and the bulky adamantane. The d value range for 9 is the largest for the salts with







Fig. 12 (a) The type II hydrogen bonded ring repeating along the *b*-axis of salt 10. (b) Checkerboard arrangement of columns in 10, viewed along the *b*-axis.

the hexagonal packing (~ 2.3 Å). The checkerboard packing is characterized by having eight neighbours, and has a much larger range of *d* values. For both anions, the largest cation features the checkerboard arrangement. Hence, we can propose that the

Table 5 Comparative geometric descriptors of hydrogen bonded columns in benzoate salts 1-5

Compound	1	2	3	4	5
Ζ'	1	1	1	1	2
Sequence of ring motifs found	$-R_4^3(10)-$	$-R_4^3(10)-$	$-R_4^2(8)-R_4^4(12)-$	$-R_4^2(8)-R_4^4(12)-$	$-R_4^3(10)-$
Presence of C– $H \cdots \pi$ hydrogen bonds	Yes	No	Yes	No	Yes
Type of column	II	II	III	III	II
Chiral space group	Yes	Yes	No	No	Yes
Average D-A distance/Å	2.77(5)	2.75(3)	2.77(5)	2.77(3)	2.74(3)
Packing of columns	Hexagonal	Hexagonal	Square	Checkerboard	Checkerboard
$d_0/\text{\AA}$	6.0786(4) <i>a</i> -axis	6.3763(3) <i>c</i> -axis	6.0374(2) <i>c</i> -axis	6.4482(1) c-axis	6.2730(5) a-axis
$d_1/\text{\AA}$	10.2565(6)	10.5481(4)	10.5979(1)	9.0987(2) b-axis	10.4419(8) c-axis
$d_2/\text{\AA}$	10.2565(6)	10.5481(4)	10.5979(1)	9.0987(2) b-axis	10.4419(8) c-axis
$d_{3}/\text{\AA}$	10.2565(6)	11.0912(6) ¹ / ₂ a-axis	10.5979(1)	12.4471(2) <i>c</i> -axis	13.827(1)
$d_4/\text{\AA}$	10.2565(6)	11.0912(6) ¹ / ₂ a-axis	10.5979(1)	12.4471(2) c-axis	13.827(1)
$d_5/\text{\AA}$	10.5312(8)	11.0912(6) ¹ / ₂ a-axis	_	14.9765(2)	15.8732(9)
$d_6/\text{\AA}$	10.5312(8)	11.0912(6) ¹ / ₂ a-axis	_	14.9765(2)	15.8732(9)
$d_7/\text{\AA}$		_	_	14.9765(2)	18.6676(10)
$d_8/\text{\AA}$	—	—	_	14.9765(2)	18.6676(10)

 Table 6
 Comparative geometric descriptors of hydrogen bonded columns in salts 6–10

Compound	6	7	8	9	10
Ζ'	1	2	1	1	1
Sequence of ring motifs found	$-R_4^3(10)-$	$-R_4^3(10)-$	$-R_4^2(8)-R_4^4(12)-$	$-R_4^2(8)-R_4^4(12)-$	$-R_4^3(10)-$
Presence of C– $H \cdots \pi$ hydrogen bonds	N/A	N/A	N/A	N/A	N/A
Type of column	II	II	III	III	II
Chiral space group	Yes	No	No	No	No
Average D–A distance/Å	2.75(4)	2.75(4)	2.77(6)	2.76(3)	2.79(5)
Packing of columns	Hexagonal	Hexagonal pairs	Checkerboard	Hexagonal	Checkerboard
$d_0/\text{\AA}$	6.4660(3) <i>a</i> -axis	6.5544(3) a-axis	6.4309(2) b-axis	6.4758(1) a-axis	6.5850(1) b-axis
$d_1/\text{\AA}$	10.0134(4) b-axis	8.9754(4)	10.9380(5)	11.2016(6) b-axis	11.5274(3) ¹ / ₂ c-axis
$d_2/\text{\AA}$	10.0134(4) <i>b</i> -axis	11.4823(5)	10.9380(5)	11.2016(6) b-axis	11.5274(3) ½ c-axis
$d_3/\text{\AA}$	11.8730(4)	12.7057(6)	11.7374(5) ¹ / ₂ a-axis	13.4957(6)	14.4855(3) 1/2 a-axis
$d_4/\text{\AA}$	11.8730(4)	12.7452(4)	11.7374(5) ¹ / ₂ a-axis	13.4957(6)	14.4855(3) 1/2 a-axis
$d_5/\text{\AA}$	11.8730(4)	12.7452(4)	15.0664(6)	13.4957(6)	16.4644(3)
$d_6/\text{\AA}$	11.8730(4)	15.0273(5)	15.0664(6)	13.4957(6)	16.4644(3)
$d_7/\text{\AA}$	_	16.1299(6)	16.9652(6)	_ ``	16.4644(3)
$d_8/\text{\AA}$	_	_	16.9652(6)		16.4644(3)



Scheme 3 The column parameters used to describe the relative distances of neighbouring columns around a central one. d_0 is the repeat distance of the hydrogen bonded rings in the central column and d_1-d_6 are the distances required for the hexagonal packing in this example of salt **2**. More distances need to be specified for different packing arrangements like checkerboard (d_1-d_8) .

hexagonal and checkerboard packing are observed at the extreme ends of the steric influence of the hydrocarbon parts. The packing arrangement of the columns in 7 is not easily classifiable relative to the other nine structures. An individual column is surrounded by an unsymmetrical arrangement of seven columns (Fig. 9b). There is however a larger packing motif. If one where to consider the two columns in the unit cell as a single unit, a pair of columns, then there are six pairs in a hexagonal arrangement around the central pair.

The d_0 spacing or the repeat distances of the hydrogen bonded columns are unpredictably affected by the type of hydrogen bonded column (II or III) and by the ring size of the cation. The lengths occur in a narrow range from 6.0374(2) to 6.5850(1) Å. This range falls neatly into the respective range observed by Kinbara et al.8 made in a large study of racemiccompound salts of chiral primary amines with achiral monocarboxylic acids (5.750(1) to 6.854(1) Å). Both the type II and III heterosynthons have similar minimum (1 and 3) and maximum values (7 and 10). What is noteworthy and in correspondence to the suggestion mentioned in the Introduction is that the steric size of the R/R' groups is better accommodated by the type II heterosynthon, which is what is observed for the two salts with the cyclododecyl ring. The eight-membered hydrogen bonded ring of the type III heterosynthon possibly does not allow for efficient separation between the hydrocarbon parts of the four molecules making up the ring, whereas the ten-membered ring of the type II heterosynthon is more accommodating. There is a slight average decrease in the rung length or width in the columns in the ten-membered rings of the type II heterosynthon (2.76 Å), over the average calculated for the eight-membered ring (2.81 A). However, the average D...A distances (calculated from the three $N^+ \cdots O^-$ distances of the rung and two legs of the columns) hardly deviate across all ten structures and all types of heterosynthons. Similar steric arguments have been made to explain the formation of 2-D nets or ladders or cubanes in ammonium carboxylate salts containing straight-chain alkyl and aromatic substituents.18

Conclusions

In summary, it is demonstrated that the hydrogen bonded columns formed by charge-assisted $N^+-H^{\dots}O^-$ hydrogen bonds form a robust synthon, of which there are two known types. What favours one type over the other for achiral ammonium cations and achiral carboxylate anions is as yet unknown and a more substantial investigation could shed light on this phenomenon. However, there are indications that large groups drive or promote type **II** formation. It was shown in this study that the type of hydrogen bonded column, either **II** or **III**, is dependent on subtle variations of the steric size of the

ammonium cation and independent of the steric size of the two anions used in this study. Having only two anions does not prove conclusively that they do not have an effect, and future work will systematically investigate both cation and anion sizes on the packing. A description of the geometrical arrangement of the hydrogen bonded columns in the solid state will hopefully be useful in analysing the structures. In future studies, we hope to closely monitor the influence of steric substituents *ortho* to the carboxylic acid group in a number of benzoic acid derivatives on the type of heterosynthon observed and *para* substituents on the packing of the columns.

Experimental

Synthesis

Crystals used in this study were obtained by slow evaporation of methanolic solutions. All chemicals were purchased from Aldrich and used without further purification. The procedure used for 1 was repeated for salts 2–10, unless otherwise indicated.

 $[C_5H_9NH_3 \cdot C_6H_5CO_2]$ (1). 0.086 g of benzoic acid (0.704 mmol) and 0.050 g of cyclopentylamine (0.70 mmol) were added to 6 ml of methanol and then dissolved using ultrasound and gentle heating. Crystals were grown by slow evaporation at ambient conditions.

 $[C_6H_{11}NH_3 \cdot C_6H_5CO_2]$ (2). 0.100 g of benzoic acid (0.819 mmol) and 0.081 g of cyclohexylamine (0.706 mmol) were added to 5 ml of MeOH.

The conformational disorder around the two carbon atoms, C(9) and C(11), was resolved by finding alternate positions from the difference Fourier map for the respective atoms. These atoms were then refined anisotropically together with their site occupancy such that the sum of the occupancies for the two alternate atom positions equalled one. The ratio of major to minor site occupancies was 0.789(9) to 0.211(9). The bond lengths and bond angles were restrained using the SADI instruction in SHELX and the thermal displacement parameters using SIMU and DELU. Hydrogen atom positions were then calculated for the respective atoms using ariding model.

 $[C_7H_{13}NH_3 \cdot C_6H_5CO_2]$ (3). 0.100 g of benzoic acid (0.819 mmol) and 0.093 g of cycloheptylamine (0.819 mmol) were added to 5 ml of MeOH.

The conformational disorder around the two carbon atoms, C(10) and C(13), was resolved by finding alternate positions from the difference Fourier map for the respective atoms. These atoms were then refined anisotropically together with their site occupancy such that the sum of the occupancies for the two alternate atom positions equalled one. The ratio of major to minor site occupancies was 0.864(2) to 0.136(2). The bond lengths and bond angles were restrained using the SADI instruction in SHELX. Hydrogen atom positions were then calculated for the respective atoms using a riding model.

 $[C_8H_{15}NH_3 \cdot C_6H_5CO_2]$ (4). 0.100 g of benzoic acid (0.819 mmol) and 0.104 g of cyclooctylamine (0.819 mmol) were added to 5 ml of MeOH.

 $[C_{12}H_{25}NH_3 \cdot C_6H_5CO_2]$ (5). 0.200 g of benzoic acid (1.64 mmol) and 0.300 g of cyclododecylamine (1.64 mmol) were added to 15 ml of MeOH.

 $[C_5H_9NH_3 \cdot C_{10}H_{15}CO_2]$ (6). 0.100 g of 1-adamantane carboxylic acid (0.555 mmol) and 0.047 g of cyclopentylamine (0.56 mmol) were added to 6 ml of methanol and then dissolved using ultrasound and gentle heating.

 $[C_6H_{11}NH_3 \cdot C_{10}H_{15}CO_2]$ (7). 0.100 g of 1-adamantane carboxylic acid (0.555 mmol) and 0.055 g of cyclohexylamine (0.56 mmol) were added to 5 ml of MeOH.

The conformational disorder around the two adamantane rings involving the carbon atoms C(2)-C(10) was resolved by finding alternate positions from the difference Fourier map for the respective atoms. These atoms were then refined anisotropically together with their site occupancy such that the sum of the occupancies for the two alternate atom positions equalled one. The ratio of major to minor site occupancies was 0.899(4) to 0.101(4). The bond lengths and bond angles were restrained using the SAME instruction and the thermal displacement parameters using SIMU and DELU. Hydrogen atom positions were then calculated for the respective atoms using a riding model.

 $[C_7H_{13}NH_3 \cdot C_{10}H_{15}CO_2]$ (8). 0.100 g of 1-adamantanecarboxylic acid (0.555 mmol) and 0.063 g of cycloheptylamine (0.56 mmol) were added to 5 ml of MeOH.

 $[C_8H_{15}NH_3 \cdot C_{10}H_{15}CO_2]$ (9). 0.100 g of 1-adamantane carboxylic acid (0.555 mmol) and 0.071 g of cyclooctylamine (0.56 mmol) were added to 5 ml of MeOH.

 $[C_{12}H_{25}NH_3 \cdot C_{10}H_{15}CO_2]$ (10). 0.100 g of 1-adamantane carboxylic acid (0.555 mmol) and 0.102 g of cyclododecylamine (0.555 mmol) were added to 10 ml of MeOH.

The conformational disorder around the adamantane ring involving the carbon atoms C(2)-C(10) was resolved similarly as in 7. The ratio of major to minor site occupancies was 0.928(2) to 0.072(2).

Crystal data and X-ray structure analysis

Intensity data were collected on a Bruker APEX II CCD area detector diffractometer with graphite monochromated Mo K_{α} radiation (50 kV, 30 mA) at 173 K. The collection method involved ω -scans of width 0.5°. Data reduction was carried out using the program *SAINT*+, version 6.02¹⁹ and face indexed absorption corrections were made using the program *XPREP*¹⁹ for all compounds except **3**. Compound **3** had empirical absorption corrections done using *SADABS*.²⁰

The crystal structure was solved by direct methods using $SHELXS-97.^{21}$ Non-hydrogen atoms were first refined isotropically followed by anisotropic refinement by full matrix least-squares calculations based on F^2 using $SHELXL-97.^{21}$ Hydrogen atoms were first located in the difference map then positioned geometrically and allowed to ride on their respective parent atoms. Diagrams and publication material were generated using

WinGX,²² *ORTEP*,²³ *PLATON*²⁴ and *DIAMOND*.²⁵ Further crystallographic data are summarised in Table 1.

Powder X-ray diffraction

Powder X-ray diffraction data for all compounds were collected at 293 K on a Bruker D8 Advance diffractometer which employs a sealed tube Cu X-ray source ($\lambda = 1.5406$ Å) operating at 40 kV and 30 mA, and is equipped with a primary beam Göbel mirror and Bruker Våntec-1 PSD detector using radial Soller slits and a secondary beam Ni filter.

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