organic compounds

Six two- and three-component ammonium carboxylate salt structures with a ladder-type hydrogen-bonding motif, three incorporating neutral carboxylic acid molecules

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Six ammonium carboxylate salts are synthesized and reported, namely 2-propylammonium benzoate, $C_3H_{10}N^+ \cdot C_7H_5O_2^-$, (I), benzylammonium ($R$)-2-phenylpropionate, $C_6H_{10}N^+ \cdot C_9H_9 O_2^-$, (II), ($RS$)-1-phenylethylammonium naphthalene-1-carboxylate, $C_8H_{12}N^+ \cdot C_{11}H_7O_2^-$, (III), benzylammonium–benzoate–benzoic acid (1/1/1), $C_6H_{10}N^+ \cdot C_7H_5O_2^- \cdot C_7H_6O_2$, (IV), cyclopropylammonium–benzoate–benzoic acid (1/1/1), $C_3H_8N^+ \cdot C_7H_5O_2^- \cdot C_7H_6O_2$, (V), and cyclopropylammonium–*ea-cis*-cyclohexane-1,4-dicarboxylate–*ee-trans*-cyclohexane-1,4-dicarboxylic acid (2/1/1), $2C_3H_8N^+ \cdot C_8H_{10}O_4^{2-} \cdot C_8H_{12}O_4$, (VI). Salts (I)–(III) all have a 1:1 ratio of cation to anion and feature three $N^+ - H \cdots O^-$ hydrogen bonds which form one-dimensional hydrogen-bonded ladders. Salts (I) and (II) have type II
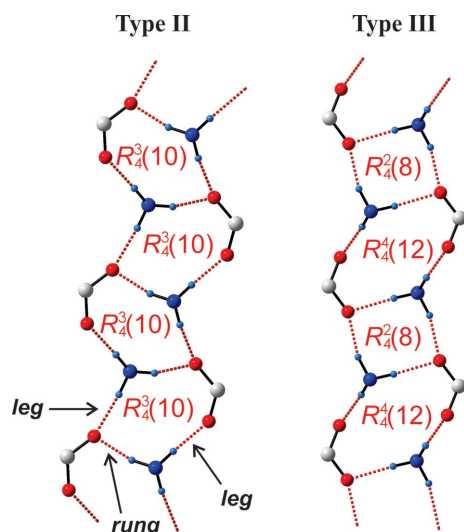
ladders, consisting of repeating $R_4^3(10)$ rings, while (III) has type III ladders, in this case consisting of alternating $R_4^2(8)$ and $R_4^4(12)$ rings. Salts (IV) and (V) have a 1:1:1 ratio of cation to anion to benzoic acid. They have type III ladders formed by three $N^+ - H \cdots O^-$ hydrogen bonds, while the benzoic acid molecules are pendant to the ladders and hydrogen bond to them *via* $O - H \cdots O^-$ hydrogen bonds. Salt (VI) has a 2:1:1 ratio of cation to anion to acid and does not feature any hydrogen-bonded ladders; instead, the ionized and un-ionized components form a three-dimensional network of hydrogen-bonded rings. The two-component 1:1 salts are formed from a 1:1 ratio of amine to acid. To create the three-component salts (IV)–(VI), the ratio of amine to acid was reduced so as to deprotonate only half of the acid molecules, and then to observe how the un-ionized acid molecules are incorporated into the ladder motif. For (IV) and (V), the ratio of amine to acid was reduced to 1:2, while for (VI) the ratio of amine to acid required to deprotonate only half the diacid molecules was 1:1.

Comment

Ammonium carboxylate salts of the general formula $(RNH_3^+) \cdot (R'COO^-)$ are known to form hydrogen-bonded one-dimensional ladders in the solid state, among other motifs (Lemmerer *et al.*, 2008*a*, 2010). The ladders are composed of hydrogen-bonded rings formed from four $N - H \cdots O$ hydrogen bonds and consist of two cation–anion pairs (Odendal *et al.*, 2010). The ladders are predominantly of two types, as classified by Nagahama *et al.* (2003): type II consists of repeating hydrogen-bonded rings, described using graph-set notation (Bernstein *et al.*, 1995) as $R_4^3(10)$, and type III consists of the repetition of two differently sized rings, described as $R_4^2(8)$ and $R_4^4(12)$ (Fig. 1). Together with the ladder concept used to describe the hydrogen-bonded pattern of ammonium carboxylate salts, the four hydrogen bonds forming the rings can be divided into legs and rungs (Fig. 1). These two ladders have also been described as robust heterosynthons (Lemmerer *et al.*, 2008*b*), as they form even in the presence of other hydrogen-bonding functional groups. The type of ladder observed is also dependent on the presence of a chiral ion. If either of the ions is present as the optically active enantiomer only (either R or S), then a type II ladder is formed almost exclusively, while if the ion is present as the racemate (RS), type III ladders form (with a minority of type II) (Lemmerer *et al.*, 2008*a*).

When combining an amine and an acid, the difference in pK_a can be indicative of whether a salt or a neutral complex is formed. Generally, a difference of three units should result in a salt (Bhogala *et al.*, 2005). However, it has been observed that salts formed with succinic and fumaric acids often include un-ionized acid molecules, even with large differences in pK_a (Haynes & Pietersen, 2008). We have observed the inclusion of un-ionized acid molecules together with ionized acid and amine molecules in the salt (4-pyridylmethyl)ammonium–*m*-iodobenzoate–*m*-iodobenzoic acid (1/1/1) (Lemmerer *et al.*, 2008*c*). In this salt, the peripheral un-ionized *m*-iodobenzoic
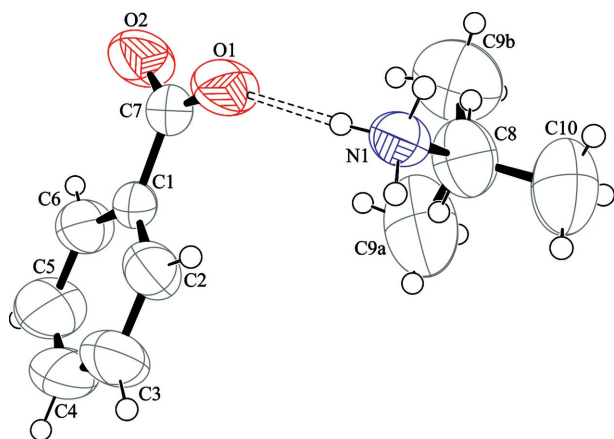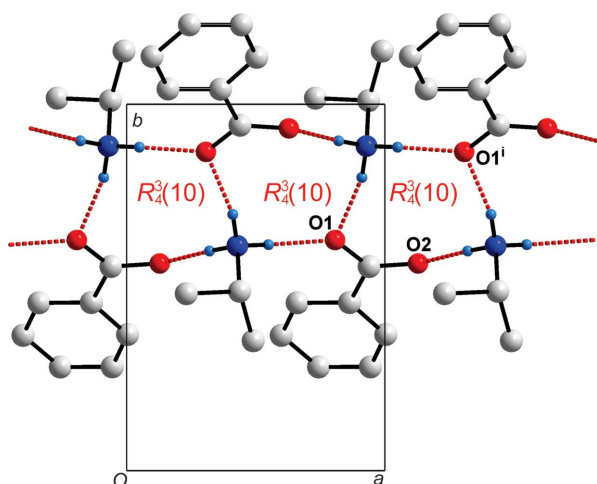

Figure 1
The two types of ladder formed by ammonium carboxylate salts. Type II (left) has repeating $R_4^3(10)$ rings, whereas type III (right) has alternating $R_4^2(8)$ and $R_4^4(12)$ rings. The three hydrogen bonds from the $-NH_3^+$ cation consist of two legs and one rung.

Figure 2
A perspective view of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The 2-propylammonium cation is disordered and both occupied sites are shown. The dashed line indicates the symmetry-independent $N^+-H\cdots O^-$ hydrogen bond.

different types of ladders and how their formation is controlled. The six salts synthesized and reported here are 2-propylammonium benzoate, (I), benzylammonium (R)-2-phenylpropionate, (II), (RS)-1-phenylethylammonium naphthalene-1-carboxylate, (III), benzylammonium–benzoate–benzoic acid (1/1/1), (IV), cyclopropylammonium–benzoate–benzoic acid (1/1/1), (V), and cyclopropylammonium–*ea-cis*-cyclohexane-1,4-dicarboxylate–*ee-trans*-cyclohexane-1,4-dicarboxylic acid (2/1/1), (VI).
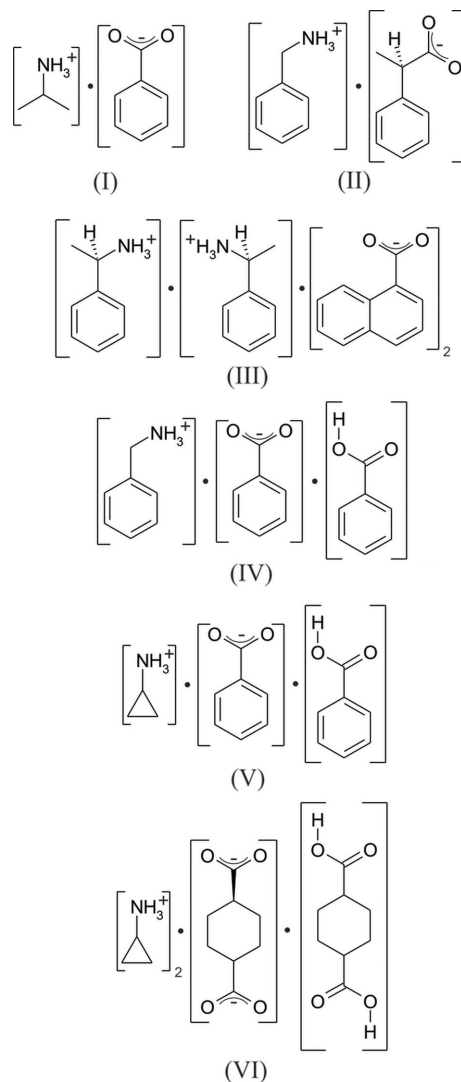

acid molecule forms hydrogen bonds to the pyridine N atom of the (4-pyridylmethyl)ammonium cation, thus forming a type II salt. This 1:1:1 salt was synthesized from a 1:1 ratio of amine to acid (with a large difference in pK_a), and the 1:1 salt (containing no un-ionized acid) was not obtained. The 1:1:1 salt was successfully synthesized using a 1:2 ratio of amine to acid, by having an excess of acid available which is then unable to undergo proton transfer to the amine. This had led us to believe that we might selectively prepare these three-component salts by controlling the molecular ratio in the crystallization synthesis. In this study, we wished to include un-ionized acid molecules into the salt structure in order to observe if the ladders are still formed and how the un-ionized acid molecule becomes incorporated. In addition, three related 1:1 salts have been synthesized that illustrate the
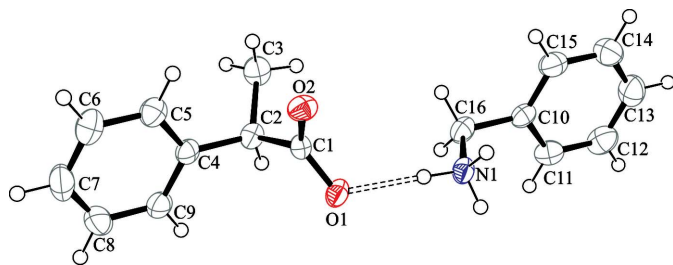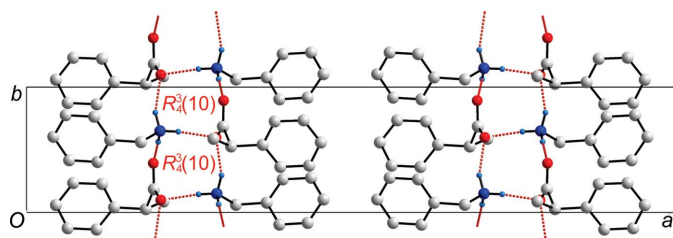

Figure 3
A partial packing diagram of the type II ladder for (I). $N^+-H\cdots O^-$ hydrogen bonds are shown as dashed lines. The 2-propylammonium cation is disordered and only the major occupied site is shown. H atoms not involved in hydrogen bonding have been omitted for clarity. [Symmetry code: (i) $x + \frac{1}{2}, -y + \frac{3}{2}, -z + 1$.]

The molecular structure and atomic numbering scheme of the asymmetric unit of the 1:1 salt (I) are shown in Fig. 2. The asymmetric unit consists of one disordered 2-propyl-ammonium cation and one benzoate anion, both on general positions. The ammonium group forms three charge-assisted hydrogen bonds to form a ring [graph-set notation $R_4^3(10)$] consisting of two ammonium cations and two carboxylate anions, one involving both atoms O1 and O2 and the second involving only atom O1 (see Fig. 3). This hydrogen-bonded pattern has translational symmetry *via* a twofold screw axis along the crystallographic a axis inherent in the space group $P2_12_12_1$. All three ammonium H atoms are used to form the ring and atom O1 acts as a bifurcated hydrogen-bond

Figure 4
A perspective view of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The dashed line indicates the symmetry-independent $N^+-H\cdots O^-$ hydrogen bond.
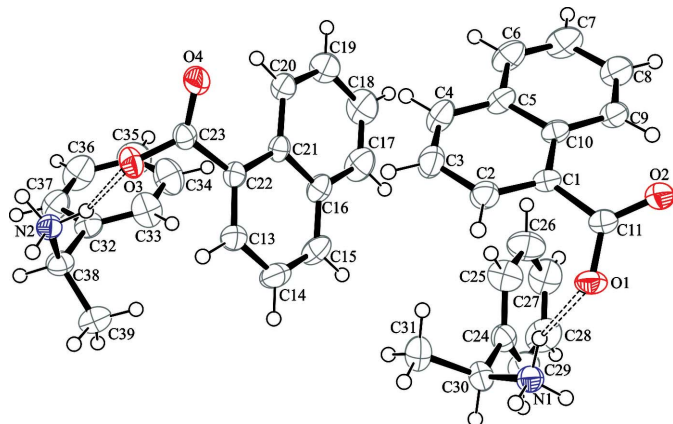

Figure 5
A partial packing diagram of the type II ladder for (II). $N^+-H\cdots O^-$ hydrogen bonds are shown as dashed lines. H atoms not involved in hydrogen bonding have been omitted for clarity.

Figure 7
A partial packing diagram of the type III ladder for (III). $N^+-H\cdots O^-$ hydrogen bonds are shown as dashed lines. H atoms not involved in hydrogen bonding have been omitted for clarity. [Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $-x + 1, -y + 2, -z + 1$; (iii) $x, y + 1, z$; (iv) $-x + 2, -y + 1, -z + 1$; (v) $x + 1, y, z$.]
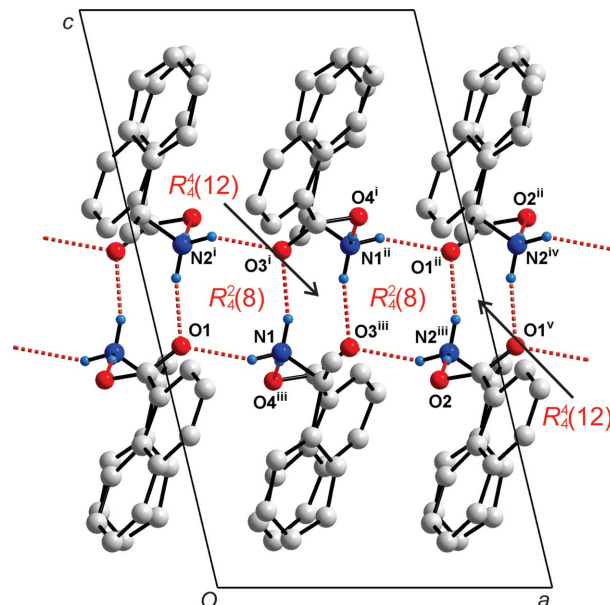
acceptor. Salt (I) thus forms a type II hydrogen-bonded ladder.

The molecular structure and atomic numbering scheme of the asymmetric unit of the 1:1 salt (II) are shown in Fig. 4. The asymmetric unit consists of one benzylammonium cation and one (R)-2-phenylpropionate anion, both on general positions. The salt crystallizes in the chiral space group $C2$ and features a type II ladder, extending along the twofold rotation axis in the direction of the b axis (Fig. 5).

The molecular structure and atomic numbering scheme of the asymmetric unit of the 1:1 salt (III) are shown in Fig. 6. The asymmetric unit consists of one (S)-1-phenylethyl-ammonium cation (labelled N1), one (R)-1-phenylethyl-

ammonium cation (N2) and two naphthalene-1-carboxylate anions, labelled O1/O2 and O3/O4, all on general positions. Both N1 and N2 cations form two charge-assisted hydrogen bonds to form a ring [graph-set notation $R_4^2(8)$] consisting of the two ammonium cations and the two carboxylate anions, involving atoms O1 and O3 (see Fig. 7). A second type of ring is formed by two N1 cations and two O3/O4 anions, again using four $N^+-H\cdots O^-$ hydrogen bonds, to generate an $R_4^4(12)$ ring. Another similar $R_4^4(12)$ ring is present, this time involving two N2 cations and two O1/O2 anions. The sequence
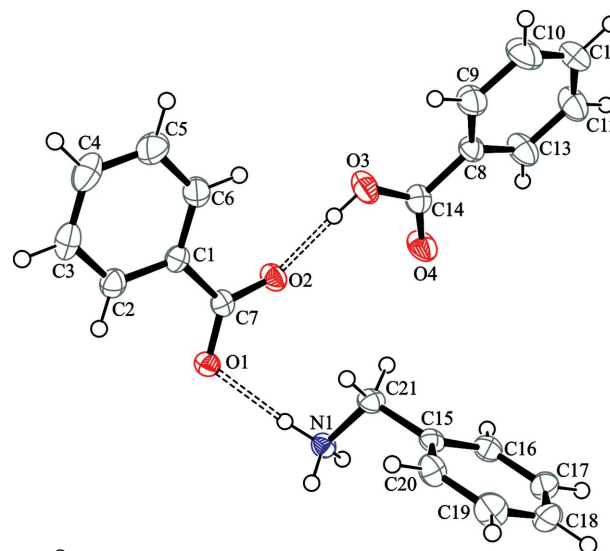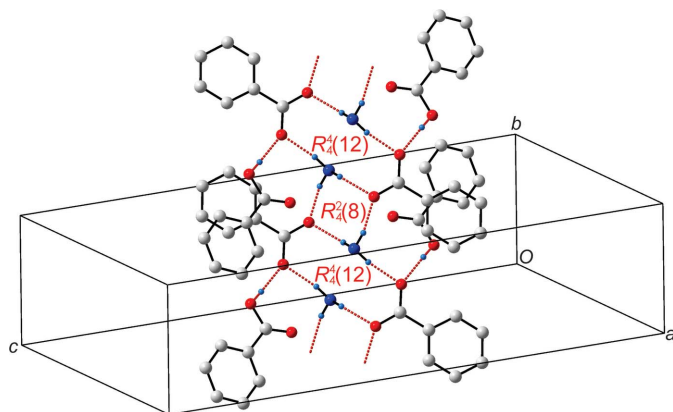

Figure 6
A perspective view of (III), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The dashed lines indicate the symmetry-independent $N^+-H\cdots O^-$ hydrogen bonds.

Figure 8
A perspective view of (IV), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The dashed lines indicate the symmetry-independent $O-H\cdots O^-$ and $N^+-H\cdots O^-$ hydrogen bonds.
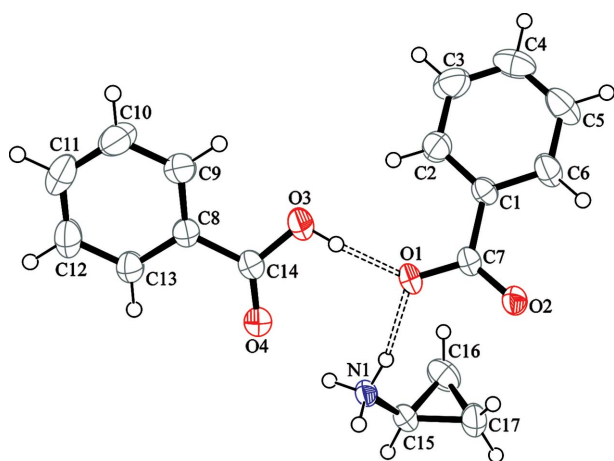
Figure 9
A partial packing diagram of the type III ladder for (IV). $N^+-H\cdots O^-$ and $O-H\cdots O^-$ hydrogen bonds are shown as dashed lines. H atoms not involved in hydrogen bonding have been omitted for clarity, together with the hydrocarbon part of the ammonium cation.

Figure 11
A partial packing diagram of the type III ladder for (V). $N^+-H\cdots O^-$ and $O-H\cdots O^-$ hydrogen bonds are shown as dashed lines. H atoms not involved in hydrogen bonding have been omitted for clarity, together with the hydrocarbon part of the ammonium cation.
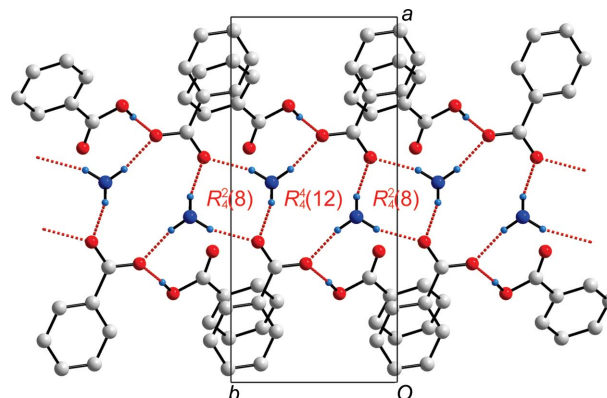
of these three unique rings generates a type III hydrogen-bonded ladder along the a axis.

The molecular structure and atomic numbering scheme of the asymmetric unit of the 1:1:1 salt (IV) are shown in Fig. 8. The asymmetric unit consists of one (un-ionized) benzoic acid molecule, one benzylammonium cation and one benzoate anion, all on general positions. The cation and anion form a type III ladder *via* $N^+-H\cdots O^-$ hydrogen bonds along the b axis. The benzoic acid molecule forms $O-H\cdots O^-$ hydrogen bonds to one of the carboxylate O atoms of the ladder (Fig. 9).

The molecular structure and atomic numbering scheme of the asymmetric unit of the 1:1:1 salt (V) are shown in Fig. 10. The asymmetric unit consists of one neutral benzoic acid molecule, one cyclopropylammonium cation and one benzoate anion, all on general positions. The cation and anion form a type III ladder *via* $N^+-H\cdots O^-$ hydrogen bonds along the b

axis. The benzoic acid molecule forms $O-H\cdots O^-$ hydrogen bonds to one of the carboxylate O atoms of the ladder (Fig. 11).

The molecular structure and atomic numbering scheme of the asymmetric unit of the 2:1:1 salt (VI) are shown in Fig. 12. The asymmetric unit consists of one neutral *ee-trans*-cyclohexane-1,4-dicarboxylic acid molecule, two cyclopropylammonium cations and one *ea-cis*-cyclohexane-1,4-dicarboxylate anion, all on general positions. The hydrogen-bonding pattern does not correspond to any of the three ring motifs for the other structures. Each of the two cyclopentylammonium cations forms hydrogen bonds to two separate cations (to one of their O atoms). The third hydrogen bond from the cations is to a carbonyl O atom of the neutral dicarboxylic acid molecule. In addition, the neutral dicarboxylic acid molecule forms hydrogen bonds to the carboxylate anion *via* an $O-H\cdots O^-$ hydrogen bond. A number of larger hydrogen-bonded rings are formed through this combination of un-ionized and ionized species (Fig. 13). Rings $R_6^4(16)$ and $R_5^5(21)$ are formed using all three species, whereas the $R_4^4(22)$
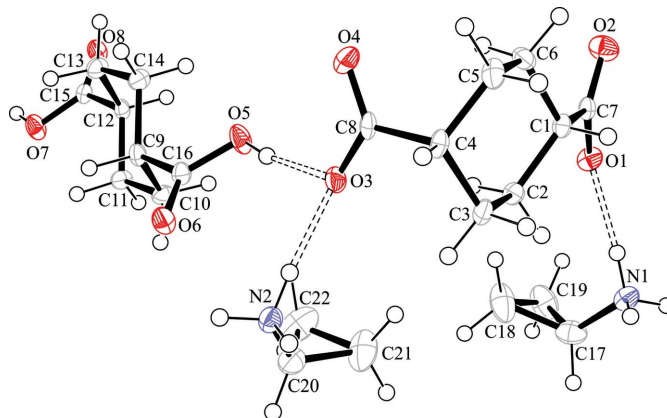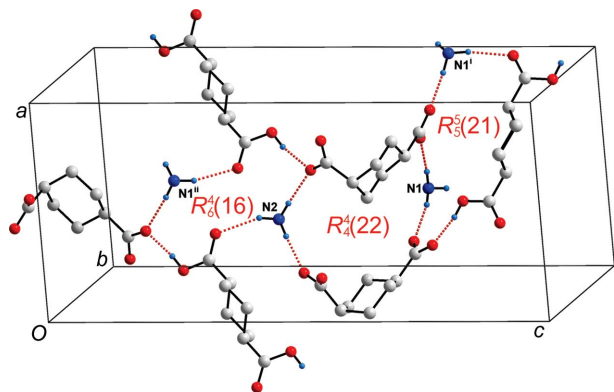

Figure 10
A perspective view of (V), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The dashed lines indicate the symmetry-independent $O-H\cdots O^-$ and $N^+-H\cdots O^-$ hydrogen bonds.

Figure 12
A perspective view of (VI), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The dashed lines indicate the symmetry-independent $O-H\cdots O^-$ and $N^+-H\cdots O^-$ hydrogen bonds.

Figure 13
A partial packing diagram of the hydrogen-bonded interactions for (VI). $N^+-H\cdots O^-$ and $O-H\cdots O^-$ hydrogen bonds are shown as dashed lines. H atoms not involved in hydrogen bonding have been omitted for clarity, together with the hydrocarbon part of the ammonium cation. [Symmetry codes: (i) $x + \frac{1}{2}, -y + \frac{3}{2}, z$; (ii) $-x + 1, -y + 1, z - \frac{1}{2}$.]

ring is formed using only the ionized species. A three-dimensional network is generated by these interactions.

The 1:1 salts (I)–(III) form type II and III ladders in accordance with previous studies (Lemmerer, 2008). The type II ladder was found to be the most common motif observed in general ammonium carboxylate salts deposited in the Cambridge Structural Database (CSD; Version 5.27; Allen, 2002). According to a detailed CSD analysis of 317 primary ammonium carboxylate salts performed by Yuge *et al.* (2008), 185 of the salts have a type II ladder (58%). Type II ladders are helical in nature and frequently crystallize in space groups with twofold screw axes. This is also observed for (I). If any of the ions are chiral in nature, and only the optically active enantiomer is present, then the chance of forming a type II ladder increases considerably (Lemmerer *et al.*, 2010, and references therein), and hence a type II ladder is again observed in salt (II), which has the *R* enantiomer of the 2-phenylpropionate cation. In salt (III), which contains the racemate of the 1-phenylethylammonium cation, a type III ladder forms, and the hydrogen-bonded rings are all centrosymmetric. It was observed previously that the racemate of the 1-phenylethylammonium cation often produces a type III ladder (Lemmerer *et al.*, 2008a).

The 1:1:1 salts (IV) and (V) and the 2:1:1 salt (VI) were prepared by including un-ionized acid molecules in the crystallization solution. This does not necessarily guarantee that they will be incorporated into the crystallized salts, but nonetheless they were incorporated in all three. A reason for this is the increased acceptor potential of the O atoms on the carboxylate anions. As they are now negatively charged, the electrostatic interaction is stronger between the un-ionized acid molecules and the ionized anions hydrogen bonding to each other. In salts (IV) and (V), the ladder motif is still observed, in this case a type III ladder. The benzoic acid molecules form hydrogen bonds to the O atoms of the carboxylate anions, as they are the only acceptor atoms available, and they are arranged as pendant molecules to the ladders. In the 2:1:1 salt (VI), the un-ionized and ionized acid

molecules have different conformations. The cyclohexane-1,4-dicarboxylic acid used consisted of a *cis/trans* mixture. In (VI), while the *cis* conformer underwent proton transfer to the two cyclopropylamine molecules, the *trans* conformer remained un-ionized. It is not clear at this stage why the *cis* conformer underwent proton transfer and the *trans* isomer did not. In contrast with the 1:1:1 salts of (IV) and (V), no ladder motif is formed in (VI) and the un-ionized acid molecules are incorporated into the rings formed by the ionized species. Previous work has shown that ammonium carboxylate salts that have two carboxylate groups on one ion form two-dimensional networks by joining two ladders together (Lemmerer *et al.*, 2008a; Lemmerer, 2011). It was hoped that the two-dimensional network would be retained and that the un-ionized diacid species would connect the two-dimensional networks into three-dimensional networks.

In conclusion, we have shown that is it possible to create three-component salt structures with a ladder motif by reducing the ratio of amine to acid in the synthesis.

Experimental

Compound (I)

Crystal data

$C_3H_{10}N^+ \cdot C_7H_5O_2^-$	$V = 1130.57\ (16)$ Å^3
$M_r = 181.23$	$Z = 4$
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
$a = 6.3823\ (7)$ Å	$\mu = 0.07$ mm^{-1}
$b = 9.0629\ (5)$ Å	$T = 243$ K
$c = 19.5457\ (13)$ Å	$0.26 \times 0.16 \times 0.1$ mm

Data collection

Bruker APEXII CCD area-detector diffractometer	9482 measured reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996) $T_{min} = 0.981$, $T_{max} = 0.993$	1232 independent reflections
	869 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.081$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.061$	23 restraints
$wR(F^2) = 0.181$	H-atom parameters constrained
$S = 1.04$	$\Delta\rho_{max} = 0.20$ e Å^{-3}
1232 reflections	$\Delta\rho_{min} = -0.19$ e Å^{-3}
133 parameters	

Table 1
Hydrogen-bond geometry (Å, °) for (I).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$A\cdots$O1	0.9	1.88	2.781 (4)	177
N1—H1$B\cdots$O1^i	0.9	1.88	2.763 (4)	167
N1—H1$C\cdots$O2^{ii}	0.9	1.79	2.681 (4)	174

Symmetry codes: (i) $x-\frac{1}{2}, -y+\frac{3}{2}, -z+1$; (ii) $x-1, y, z$.

Table 2
Hydrogen-bond geometry (Å, °) for (II).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$A\cdots$O1	0.91	1.91	2.8152 (16)	174
N1—H1$B\cdots$O1^i	0.91	1.91	2.7652 (18)	157
N1—H1$C\cdots$O2^{ii}	0.91	1.76	2.6651 (18)	178

Symmetry codes: (i) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+1$; (ii) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+1$.

Table 3
Hydrogen-bond geometry (Å, °) for (III).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$A\cdots$O1	0.91	1.92	2.7305 (19)	147
N1—H1$B\cdots$O4^i	0.91	1.86	2.7650 (17)	178
N1—H1$C\cdots$O3^{ii}	0.91	1.89	2.7716 (18)	162
N2—H2$A\cdots$O3	0.91	1.91	2.7232 (18)	147
N2—H2$B\cdots$O1^{ii}	0.91	1.89	2.7695 (19)	163
N2—H2$C\cdots$O2^{iii}	0.91	1.86	2.7678 (18)	175

Symmetry codes: (i) $x, y+1, z$; (ii) $-x+1, -y+1, -z+1$; (iii) $x+1, y-1, z$.

Table 4
Hydrogen-bond geometry (Å, °) for (IV).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O3—H3$\cdots$O2	0.84	1.79	2.6255 (16)	177
N1—H1$A\cdots$O1	0.91	1.99	2.8399 (18)	155
N1—H1$B\cdots$O1^i	0.91	1.87	2.7620 (18)	168
N1—H1$C\cdots$O2^{ii}	0.91	1.88	2.7835 (17)	171

Symmetry codes: (i) $-x+1, -y, -z+1$; (ii) $-x+1, -y+1, -z+1$.

Compound (II)

Crystal data

$C_7H_{10}N^+\cdot C_9H_9O_2^-$	$V = 1404.63\ (16)$ Å^3
$M_r = 257.32$	$Z = 4$
Monoclinic, $C2$	Mo $K\alpha$ radiation
$a = 30.970\ (2)$ Å	$\mu = 0.08$ mm^{-1}
$b = 5.8832\ (4)$ Å	$T = 173$ K
$c = 7.8239\ (5)$ Å	$0.63 \times 0.26 \times 0.09$ mm
$\beta = 99.825\ (2)°$	

Data collection

Bruker APEXII CCD area-detector diffractometer	16064 measured reflections
	1863 independent reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	1660 reflections with $I > 2\sigma(I)$
$T_{min} = 0.951$, $T_{max} = 0.993$	$R_{int} = 0.068$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$	1 restraint
$wR(F^2) = 0.086$	H-atom parameters constrained
$S = 1.09$	$\Delta\rho_{max} = 0.21$ e Å^{-3}
1863 reflections	$\Delta\rho_{min} = -0.15$ e Å^{-3}
174 parameters	

Compound (III)

Crystal data

$C_8H_{12}N^+\cdot C_{11}H_7O_2^-$	$\gamma = 90.652\ (5)°$
$M_r = 293.35$	$V = 1640.5\ (3)$ Å^3
Triclinic, $P\bar{1}$	$Z = 4$
$a = 8.8979\ (9)$ Å	Mo $K\alpha$ radiation
$b = 12.0013\ (8)$ Å	$\mu = 0.08$ mm^{-1}
$c = 16.0498\ (15)$ Å	$T = 173$ K
$\alpha = 100.213\ (5)°$	$0.51 \times 0.35 \times 0.12$ mm
$\beta = 103.102\ (3)°$	

Data collection

Bruker APEXII CCD area-detector diffractometer	27233 measured reflections
	7082 independent reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	3917 reflections with $I > 2\sigma(I)$
$T_{min} = 0.962$, $T_{max} = 0.991$	$R_{int} = 0.075$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.050$	401 parameters
$wR(F^2) = 0.135$	H-atom parameters constrained
$S = 1.00$	$\Delta\rho_{max} = 0.22$ e Å^{-3}
7082 reflections	$\Delta\rho_{min} = -0.25$ e Å^{-3}

Compound (IV)

Crystal data

$C_7H_{10}N^+\cdot C_7H_5O_2^-\cdot C_7H_6O_2$	$V = 1847.4\ (3)$ Å^3
$M_r = 351.39$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 12.3249\ (11)$ Å	$\mu = 0.09$ mm^{-1}
$b = 6.0804\ (6)$ Å	$T = 173$ K
$c = 24.7669\ (17)$ Å	$0.5 \times 0.08 \times 0.06$ mm
$\beta = 95.526\ (5)°$	

Data collection

Bruker APEXII CCD area-detector diffractometer	22843 measured reflections
	4004 independent reflections
Absorption correction: integration (*XPREP*; Bruker, 2004)	2214 reflections with $I > 2\sigma(I)$
$T_{min} = 0.957$, $T_{max} = 0.995$	$R_{int} = 0.094$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$	237 parameters
$wR(F^2) = 0.114$	H-atom parameters constrained
$S = 0.96$	$\Delta\rho_{max} = 0.21$ e Å^{-3}
4004 reflections	$\Delta\rho_{min} = -0.22$ e Å^{-3}

Compound (V)

Crystal data

$C_3H_8N^+\cdot C_7H_5O_2^-\cdot C_7H_6O_2$	$V = 1603.33\ (16)$ Å^3
$M_r = 301.33$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 15.3307\ (10)$ Å	$\mu = 0.09$ mm^{-1}
$b = 6.3703\ (3)$ Å	$T = 173$ K
$c = 17.9989\ (11)$ Å	$0.34 \times 0.2 \times 0.1$ mm
$\beta = 114.199\ (2)°$	

organic compounds

Table 5
Hydrogen-bond geometry (Å, °) for (V).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O3—H3$\cdots$O1	0.84	1.75	2.5881 (16)	173
N1—H1$A\cdots$O1	0.91	1.89	2.7901 (16)	168
N1—H1$B\cdots$O2^{i}	0.91	1.97	2.8573 (16)	165
N1—H1$C\cdots$O2^{ii}	0.91	1.91	2.7743 (15)	158

Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $x, y + 1, z$.

Table 6
Hydrogen-bond geometry (Å, °) for (VI).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O5—H5$\cdots$O3	0.84	1.68	2.511 (2)	168
O7—H7$\cdots$O1^{i}	0.84	1.66	2.490 (2)	169
N1—H1$A\cdots$O1	0.91	1.91	2.822 (2)	175
N1—H1$B\cdots$O6^{ii}	0.91	2.05	2.933 (2)	162
N1—H1$C\cdots$O2^{iii}	0.91	1.9	2.779 (2)	163
N2—H2$A\cdots$O3	0.91	1.91	2.812 (2)	174
N2—H2$B\cdots$O4^{iii}	0.91	1.85	2.709 (2)	158
N2—H2$C\cdots$O8^{iv}	0.91	2.1	2.944 (2)	153

Symmetry codes: (i) $-x + 2, -y + 1, z - \frac{1}{2}$; (ii) $-x + 1, -y + 1, z + \frac{1}{2}$; (iii) $x - \frac{1}{2}, -y + \frac{3}{2}, z$; (iv) $x - 1, y, z$.

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.970$, $T_{max} = 0.991$

9730 measured reflections
3876 independent reflections
2461 reflections with $I > 2\sigma(I)$
$R_{int} = 0.028$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.11$
$S = 1.00$
3876 reflections

200 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.19$ e Å^{-3}
$\Delta\rho_{min} = -0.19$ e Å^{-3}

Compound (VI)

Crystal data

$2C_3H_8N^+ \cdot C_8H_{10}O_4^{2-} \cdot C_8H_{12}O_4$
$M_r = 458.54$
Orthorhombic, $Pna2_1$
$a = 10.2478$ (4) Å
$b = 9.6134$ (4) Å
$c = 23.8354$ (9) Å

$V = 2348.17$ (16) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.10$ mm^{-1}
$T = 173$ K
$0.56 \times 0.4 \times 0.07$ mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.947$, $T_{max} = 0.993$

27099 measured reflections
2909 independent reflections
2735 reflections with $I > 2\sigma(I)$
$R_{int} = 0.037$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.094$
$S = 1.04$
2909 reflections
293 parameters

1 restraint
H-atom parameters constrained
$\Delta\rho_{max} = 0.33$ e Å^{-3}
$\Delta\rho_{min} = -0.18$ e Å^{-3}

For compound (I), the C-bound H atoms were positioned geometrically, with C—H = 0.99 (methine), 0.97 (methyl) or 0.94 Å

(aromatic), and refined as riding, with $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl groups or $1.2U_{eq}(C)$ otherwise. The N-bound H atoms were positioned geometrically, with N—H = 0.91 Å, and refined as riding with the orientation of the group being allowed to rotate to optimally fit the observed electron density, with $U_{iso}(H) = 1.5U_{eq}(N)$. The disorder of the 2-propylammonium cation was resolved by finding alternative positions for atom C9 in the difference Fourier map. These two atoms, C9*A* and C9*B*, were then refined anisotropically together with their site occupancy, such that the sum of the occupancies summed to one. The atomic displacement parameters of atoms C8, C9*A*, C9*B* and C10 were restrained using similarity and 'rigid bond' restraints with effective standard deviations of 0.02 and 0.005 Å^2, respectively.

For compounds (II)–(VI), the C-bound H atoms were positioned geometrically, with C—H = 1.00 (methine), 0.99 (methylene), 0.98 (methyl) or 0.95 Å (aromatic), and refined as riding, with $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl groups or $1.2U_{eq}(C)$ otherwise. The N-bound H atoms were positioned geometrically, with N—H = 0.91 Å, and refined as riding with the orientation of the group being allowed to rotate to optimally fit the observed electron density, with $U_{iso}(H) = 1.5U_{eq}(N)$.

In (I) and (VI), the absolute structure was chosen arbitrarily, whereas in (II), the absolute structure was chosen in accordance with the known configuration of the amine starting material. For these three structures, refinement of the absolute structure parameter (Flack & Bernardinelli, 2000) led to values whose precision was too poor to enable conclusions to be drawn about the absolute structure, so the Friedel pairs of reflections were merged prior to the final refinements.

For all compounds, data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT-Plus* (Bruker, 2004); data reduction: *SAINT-Plus* and *XPREP* (Bruker, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2009).

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