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The hydrogen-bonding patterns of 3-phenylpropylammonium benzoate and 3-phenylpropylammonium 3-iodobenzoate: generation of chiral crystals from achiral molecules

Andreas Lemmerer

Centre for Supramolecular Chemistry Research, Department of Chemistry, University of Cape Town, Rondebosch 7701, South Africa
Correspondence e-mail: andreas.lemmerer@uct.ac.za

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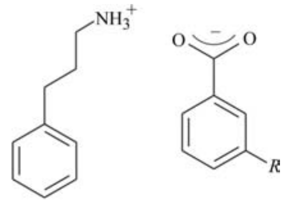
The crystal structures and hydrogen-bonding patterns of 3-phenylpropylammonium benzoate, $C_9H_{14}N^+\cdot C_7H_5O_2^-$, (I), and 3-phenylpropylammonium 3-iodobenzoate, $C_9H_{14}N^+\cdot C_7H_4IO_2^-$, (II), are reported and compared. The addition of the I atom on the anion in (II) produces a different hydrogen-bonding pattern to that of (I). In addition, the supramolecular heterosynthon of (II) produces a chiral crystal packing not observed in (I). Compound (I) packs in a centrosymmetric fashion and forms achiral one-dimensional hydrogen-bonded columns through charge-assisted $N-H\cdots O$ hydrogen bonds. Compound (II) packs in a chiral space group and forms helical one-dimensional hydrogen-bonded columns with 2_1 symmetry, consisting of repeating $R^3_4(10)$ hydrogen-bonded rings that are commonly observed in ammonium carboxylate salts containing chiral molecules. This hydrogen-bond pattern, which has been observed repeatedly in ammonium carboxylate salts, thus provides a means of producing chiral crystal structures from achiral molecules.

Comment

Supramolecular heterosynthons are defined as intermolecular interactions that exist between different but compatible functional groups (Walsh *et al.*, 2003; Bis & Zaworotko, 2005; Bis *et al.*, 2006). If one wishes to combine two or more molecules in the solid state, heterosynthons increase the number of possible combinations when compared to homosynthons, which only occur between the same functional group. Examples of neutral heterosynthons are the carboxylic acid–pyridine and carboxylic acid–amide dimers (Aakeröy & Schultheiss, 2007).

One of the aims of supramolecular chemistry is to identify and exploit those heterosynthons that behave predictably in the solid state. Desiraju and others have called the phenomenon of predictability 'synthon robustness', with respect to those synthons that occur repeatedly in crystal structures (Banerjee, Mondal *et al.*, 2006). If the intermolecular interaction is between charged species, the electrostatic attractive force strengthens the heterosynthon and a greater robustness is expected (Banerjee, Saha *et al.*, 2006). Robustness of a heterosynthon refers to how a desired synthon changes under the influence of steric or electronic effects of functional groups on the molecules interacting in the crystal structures. To this end, we have investigated the heterosynthon formed between carboxylic acids and amines. More specifically, the compounds we have used all transfer the carboxylic acid H atom to the amine to form ammonium carboxylate salts (Lemmerer *et al.*, 2008*a*,*b*,*c*).



(I) *R* = H
(II) *R* = I

A data analysis of $(R\text{–}NH_3^+)\cdot(R'\text{–}CO_2^-)$ ammonium carboxylate salt structures in the Cambridge Structural Database (CSD, Version 5.29, November 2007 release; Allen, 2002) revealed the three most frequently occurring heterosynthons described using graph-set notation (Bernstein *et al.*, 1995): (i) one-dimensional columns of $R^3_4(10)$ hydrogen-bonded rings (75/126), (ii) one-dimensional columns of alternating $R^2_4(8)$ and $R^4_4(12)$ hydrogen-bonded rings (26/126), and (iii) two-dimensional layers built up with $R^5_6(16)$ hydrogen-bonded rings (19/126) (Lemmerer *et al.*, 2008*b*). The one-dimensional columns of $R^3_4(10)$ rings are also called type-II columns by Kinbara *et al.* (1996) and are shown schematically in Fig. 1. In fact, this motif occurs even more frequently with increasing robustness if the cation containing the ammonium group is chiral, such as 1-phenylethylammonium. In those ammonium carboxylate salts, the type-II heterosynthon is formed in 69 out of 83 structures located in the CSD. This paper describes an attempt to determine if the type-II motif occurs in a related salt using achiral 3-phenylpropyl-

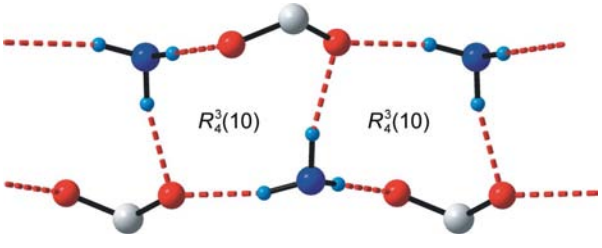


Figure 1
The type-II supramolecular heterosynthon commonly observed in ammonium carboxylate salts.

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ammonium as the cation and benzoate and 3-iodobenzoate as the anion.

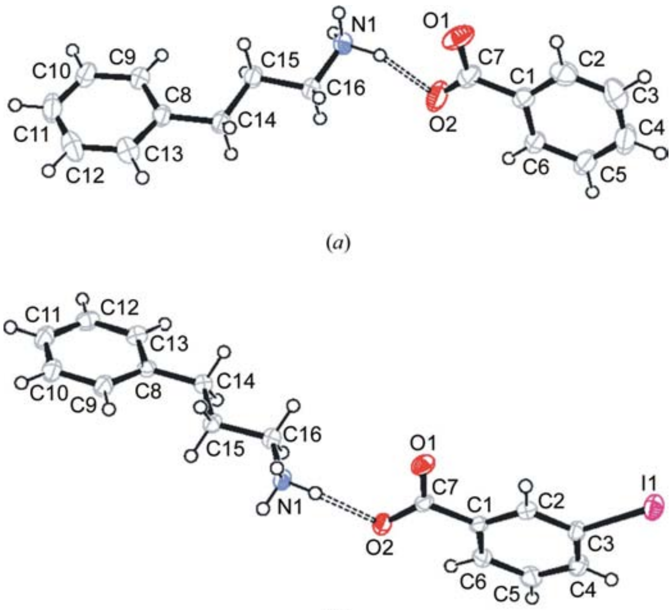

Figure 2
The asymmetric unit of (*a*) (I) and (*b*) (II). Displacement ellipsoids are shown at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

The molecular structure and atomic numbering scheme of (I) are shown in Fig. 2(*a*). The asymmetric unit consists of one 3-phenylpropylammonium cation and one benzoate anion. The propylammonium chain is parallel to the aromatic ring, with the mean deviation of a least-squares plane being less than 0.209 (1) Å. The ammonium group forms three charge-assisted N—H⋯O hydrogen bonds to the benzoate group. Atoms H1*A* and H1*B* form a 12-membered hydrogen-bonded ring, $R_4^4(12)$, connecting two cations and two anions. This ring is parallel to the *ab* plane. Adjacent $R_4^4(12)$ rings are joined through a hydrogen bond from H1*C* to O2 in the direction of the crystallographic *c* axis (Fig. 3). This means that O2 functions as a bifurcated hydrogen-bond acceptor. Ultimately, this results in one-dimensional hydrogen-bonded columns made up of four cations and four anions. Compound (I) does not form the type-II column. Adjacent columns are connected *via* a C—H⋯π interaction from the cation of adjacent columns [C14—H14*A*⋯*Cg*: $d = 2.64$ Å, $D = 3.563$ (2) Å and $\theta = 155°$; *Cg* is the centroid of the benzoate ring at $(1 - x, 1 - y, 1 - z)$].

The molecular structure and atomic numbering scheme of the asymmetric unit of (II) are shown in Fig. 2(*b*). The molecular geometries of the propylammonium cation and 3-iodobenzoate anion are similar to those of (I). The ammonium group forms three charge-assisted hydrogen bonds to form a ring, with graph-set notation $R_4^3(10)$, consisting of two ammonium cations and two carboxylate anions, one involving both O atoms (O1 and O2) and the second involving only the

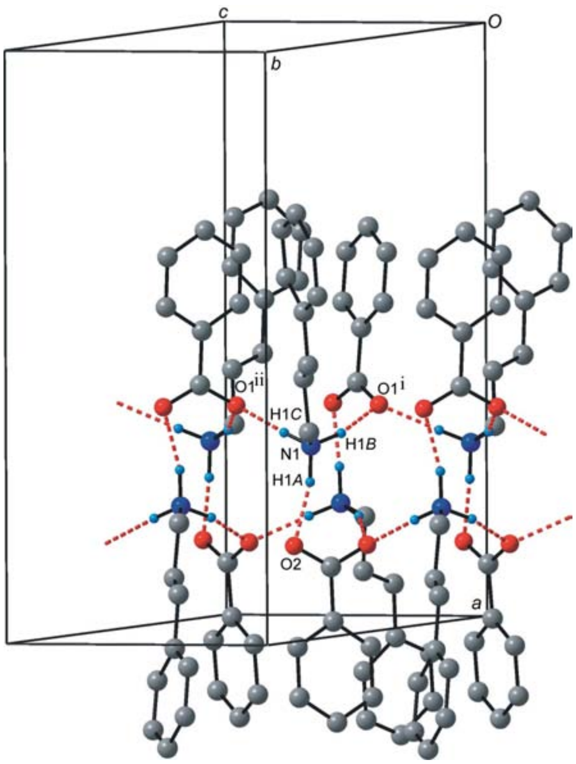

Figure 3
The hydrogen-bonding pattern of (I). H atoms not involved in hydrogen bonding have been omitted for clarity. [Symmetry codes: (i) $-x + \frac{3}{2}, -y + \frac{1}{2}, z$; (ii) $-x + \frac{3}{2}, y, z + \frac{1}{2}$.]

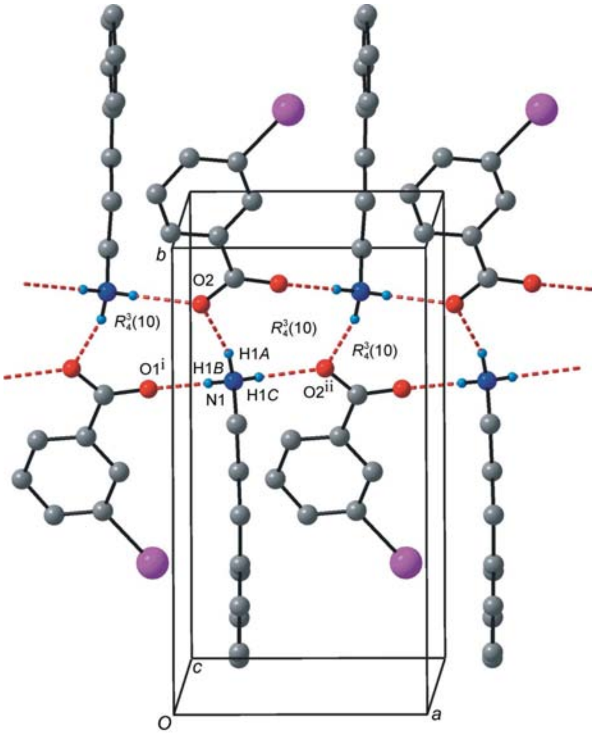

Figure 4
The type-II hydrogen-bonding pattern of (II), generating a 2_1 helical pattern. H atoms not involved in hydrogen bonding have been omitted for clarity. [Symmetry codes: (i) $x - \frac{1}{2}, -y + \frac{3}{2}, -z + 1$; (ii) $x + \frac{1}{2}, -y + \frac{3}{2}, -z + 1$.]

O1 atom (see Fig. 1). This hydrogen-bonded pattern has translational symmetry *via* a twofold screw axis inherent in the space group and is repeated along the *a* axis [6.9616 (2) Å]. All three ammonium H atoms are used to form the ring and atom O2 acts as a bifurcated hydrogen-bond acceptor. Compound (II) thus forms the type-II hydrogen-bonded column with two cations and two anions (Fig. 4). The columns are connected by a pair of C—H$\cdots\pi$ interactions through both H atoms on the benzylic position to the aromatic ring of adjacent cations [C14*A*—H14*A*$\cdots$*Cg*^{i}: d = 2.73 Å, D = 3.550 (3) Å and θ = 141°; C14*B*—H14*B*$\cdots$*Cg*^{ii}: d = 2.70 Å, D =3.522 (3) Å and θ = 141°] (Fig. 5) [*Cg*^{i} and *Cg*^{ii} are the centroids of the 3-iodobenzoate ring at ($\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$) and ($-\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$), respectively]. Adjacent columns are further stabilized by a C3—I1$\cdots$O1^{iii} [symmetry code: (iii) $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$] halogen bond (Ramasubbu *et al.*, 1986; Corradi *et al.*, 2000; Aakerōy *et al.*, 2007) with d(I1$\cdots$O1) = 3.050 (2) Å and θ (C3—I1$\cdots$O1) = 165.04 (8)° along the [011] and [01$\overline{1}$] directions to create a chicken-wire-shaped mesh of columns (Fig. 5).

Neither (I) nor (II) contain a cation or anion that is chiral and the type-II synthon is not formed in (I). However, the I atom attached to the anion in (II) causes the type-II column to be formed and the compound crystallizes in the chiral space group $P2_12_12_1$. In supramolecular chemistry, the creation of chiral crystals from constituents that do not possess a chirality centre is a much studied phenomenon (Mateos-Timoneda *et al.*, 2004). Chiral helices are created when the molecules interact to create an arrangement with 2_1 symmetry (Tanaka *et al.*, 2007). The type-II supramolecular heterosynthon of (II) is such a 'helical' generating interaction (Koshima, 2000).

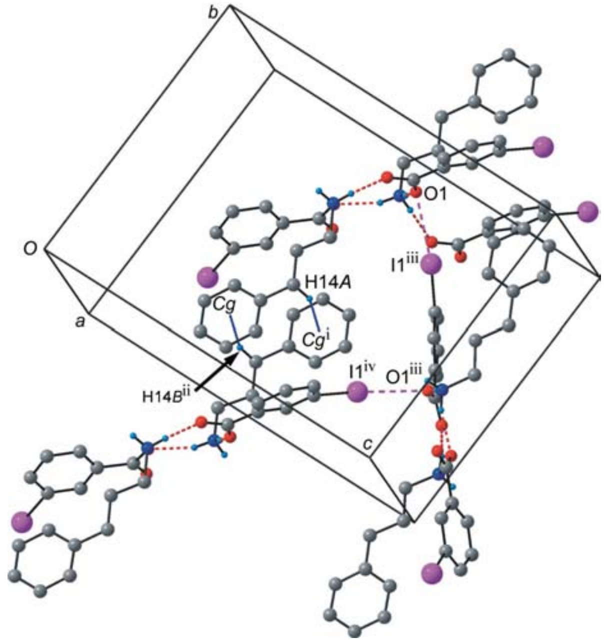

Figure 5
The packing diagram of (II), showing the two C—H$\cdots\pi$ interactions and C—I$\cdots$O halogen bonds that connect adjacent helical columns. H atoms not involved in hydrogen bonding have been omitted for clarity. [Symmetry codes: (i) $x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (ii) $x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (iii) $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$; (iv) $x, y - 1, z$.]

Experimental

All chemicals were purchased from commercial sources and used as received. Compound (I) was prepared by slow evaporation of a solution of 3-phenylpropylamine (0.100 g, 0.704 mmol) and benzoic acid (0.0904 g, 0.704 mmol) in methanol (5 ml). Compound (II) was prepared by slow evaporation of a solution of 3-phenylpropylamine (0.100 g, 0.704 mmol) and *m*-iodobenzoic acid (0.183 g, 0.704 mmol) in methanol (10 ml).

Compound (I)

Crystal data

$C_9H_{14}N^+\cdot C_7H_5O_2^-$
M_r = 257.32
Orthorhombic, *Pccn*
a = 16.2963 (2) Å
b = 23.3235 (5) Å
c = 7.4094 (7) Å
V = 2816.2 (3) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.08 mm^{-1}
T = 173 (2) K
0.5 × 0.13 × 0.10 mm

Data collection

Nonius KappaCCD area-detector diffractometer
Absorption correction: integration (*XPREP*; Bruker, 1999) T_{min} = 0.966, T_{max} = 0.992
16169 measured reflections
3401 independent reflections
2087 reflections with $I > 2\sigma(I)$
R_{int} = 0.107

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.133
S = 0.92
3401 reflections
181 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}

Compound (II)

Crystal data

$C_9H_{14}N^+\cdot C_7H_4IO_2^-$
M_r = 383.21
Orthorhombic, $P2_12_12_1$
a = 6.9616 (2) Å
b = 12.8517 (3) Å
c = 17.7512 (3) Å
V = 1588.17 (6) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 2.02 mm^{-1}
T = 173 (2) K
0.38 × 0.11 × 0.1 mm

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*$\cdots$O2	1.00 (2)	1.85 (2)	2.806 (2)	161 (2)
N1—H1*B*$\cdots$O1^{i}	1.01 (2)	1.86 (2)	2.809 (2)	157 (2)
N1—H1*C*$\cdots$O1^{ii}	0.94 (2)	1.81 (2)	2.746 (2)	175 (2)

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

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*$\cdots$O2	0.86 (3)	1.94 (3)	2.767 (3)	161 (3)
N1—H1*B*$\cdots$O1^{i}	0.87 (4)	1.95 (4)	2.811 (3)	175 (3)
N1—H1*C*$\cdots$O2^{ii}	0.84 (4)	2.03 (4)	2.856 (3)	172 (3)

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

Data collection

Nonius KappaCCD area-detector diffractometer
Absorption correction: integration (*XPREP*; Bruker, 1999)
$T_{\min} = 0.594$, $T_{\max} = 0.845$
22976 measured reflections
3826 independent reflections
3554 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.044$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.023$
$wR(F^2) = 0.051$
$S = 1.08$
3826 reflections
190 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max} = 0.59$ e Å^{-3}
$\Delta\rho_{\min} = -0.74$ e Å^{-3}
Absolute structure: Flack (1983); 1625 Friedel pairs
Flack parameter: −0.023 (18)

For both compounds, all C-bound H atoms were refined using a riding model, with C—H = 0.95 (aromatic) or 0.99 Å (CH_2) and $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(C). Ammonium H atoms were located in a difference Fourier map and their coordinates refined freely, with $U_{\rm iso}$(H) = $1.5U_{\rm eq}$(N).

For both compounds, data collection: *COLLECT* (Nonius, 2000); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; 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, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG3065). Services for accessing these data are described at the back of the journal.

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