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Powder study of (*R*)-1-phenylethylammonium (*R*)-2-phenylbutyrate form 2

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The crystal structure of a new polymorph of the title compound, $C_8H_{12}N^+\cdot C_{10}H_{11}O_2^-$, was solved by simulated annealing from laboratory X-ray powder diffraction data, collected at 295 K. Subsequent Rietveld refinement using data collected to 1.54 Å resolution yielded an R_{wp} of 0.029. The compound crystallized with one (*R*)-1-phenylethylammonium cation and one (*R*)-2-phenylbutyrate anion in the asymmetric unit.

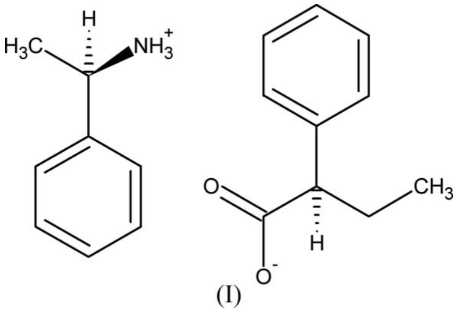
Key indicators

Powder X-ray study
T = 295 K
Mean σ(C–C) = 0.002 Å
R factor = 0.025
wR factor = 0.029

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The structure of the title compound, (I), was first reported by Brianso (1978), hereafter referred to as form 1. Crystallization from ethanol yielded a second polymorph, which is reported here.



(I)

The crystal structure of the new form (form 2) was solved by simulated annealing using laboratory capillary X-ray powder diffraction data. The compound crystallizes in the orthorhombic space group $P2_12_12_1$ with one (*R*)-1-phenylethylammonium cation and one (*R*)-2-phenylbutyrate anion in the asymmetric unit (Fig. 1).

The ion pairs in this new polymorph pack to form a hydrogen-bonded ladder parallel to the *a* axis (Fig. 2). Each ladder consists of $R_4^3(10)$ (Etter, 1990) hydrogen-bonded rings comprising four alternating ammonium and carboxylate groups linked by N—H···O=C contacts (Table 1). O1 forms a bifurcated hydrogen bond to H1N*B* and H1N*C*, while O2 forms just one hydrogen bond to H1N*A*. All strong hydrogen-bond donors and acceptors are satisfied.

Form 1 shows the same hydrogen-bonded ring motif, albeit with different packing of the ladders in the crystal structure. This arises because the orientation of the 2-phenylbutyrate ion with respect to the 1-phenylethylammonium ion is different. Also, the conformation of the terminal methyl group differs between the two forms – adopting a *gauche* conformation with respect to the carboxylate group in form 2, while in form 1 the groups are in an *anti* conformation.

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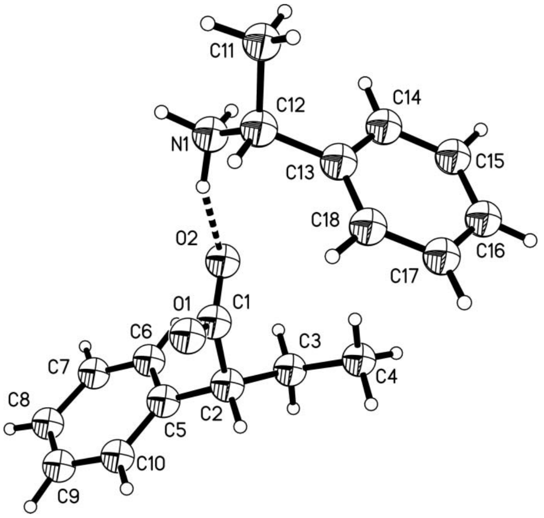

Figure 1
The asymmetric unit of (I), with the atom-numbering scheme. Displacement spheres are shown at the 50% probability level (Bruker, 2000). The dashed line indicates a hydrogen bond.

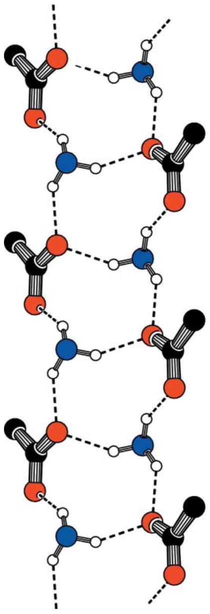

Figure 2
The hydrogen-bonded ladder motif observed in form 2. Atoms not directly involved in hydrogen-bond contacts have been omitted for clarity.

Experimental

(R)-2-phenylbutyric acid (Lancaster, 97% purity) and (R)-1-phenylethylammine (Alfa Aesar, 99+% purity) were used without further purification. The product was crystallized as a fine powder byevaporation of an ethanol solution with a starting ratio of 2:1 acid:base.

The sample was loaded into a 0.7 mm borosilicate glass capillary and rotated throughout the data collection to minimize preferred orientation effects. Data were collected using a variable count time (VCT) scheme in which the step time is increased with 2θ (Shankland *et al.*, 1997; Hill & Madsen, 2002).

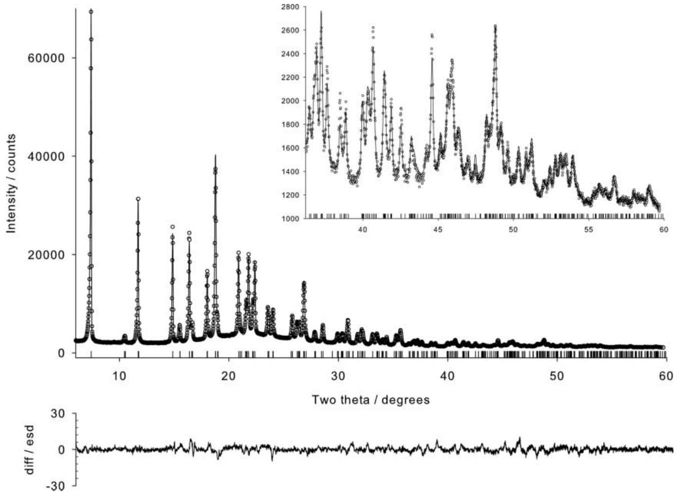

Figure 3
Final observed (points), calculated (line) and difference [($y_{\rm obs} - y_{\rm calc}$)/$\sigma$($y_{\rm obs}$)] profiles for the Rietveld refinement of the title compound.

Crystal data

$C_8H_{12}N^+\cdot C_{10}H_{11}O_2^-$
M_r = 285.37
Orthorhombic, $P2_12_12_1$
a = 6.0620 (1) Å
b = 16.7794 (3) Å
c = 16.8881 (4) Å
V = 1717.80 (6) Å^3
Z = 4
D_x = 1.104 Mg m^{-3}
Cu $K\alpha_1$ radiation
Wavelength of incident radiation: 1.54056 Å
μ = 0.56 mm^{-1}
T = 295 K
Specimen shape: cylinder
12 × 0.7 × 0.7 mm
Specimen prepared at 380 K
Particle morphology: needle, white

Data collection

Bruker AXS D8 Advance diffractometer
Specimen mounting: 0.7 mm borosilicate capillary
Specimen mounted in transmission mode
Scan method: step
Absorption correction: none
$2\theta_{\rm min}$ = 6.0, $2\theta_{\rm max}$ = 60.0°
Increment in 2θ = 0.017°

Refinement

$R_{\rm p}$ = 0.025
$R_{\rm wp}$ = 0.029
$R_{\rm exp}$ = 0.015
$R_{\rm B}$ = 0.022
S = 2.03
Profile function: Fundamental parameters with axial divergence correction.
161 parameters
Only H-atom coordinates refined
$w = 1/\sigma(Y_{\rm obs})^2$
$(\Delta/\sigma)_{\rm max}$ = 0.005
Preferred orientation correction: A spherical harmonics-based preferred orientation correction (Järvinen, 1993) was applied with *TOPAS* (Coelho, 2003) during the Rietveld refinement

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1NA···O2	0.964 (5)	1.863 (6)	2.732 (3)	148.5 (5)
N1—H1NB···O1$^{\rm i}$	0.976 (6)	1.907 (7)	2.744 (3)	142.2 (5)
N1—H1NC···O1$^{\rm ii}$	0.956 (5)	1.932 (7)	2.797 (5)	149.4 (6)
C10—H10···O2$^{\rm iii}$	0.953 (5)	2.492 (6)	3.426 (3)	166.8 (4)

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

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The diffraction pattern indexed to a monoclinic cell [$M(19) = 30.7$, $F(19) = 63.0$; *DICVOL91*; Boultif & Louër, 1991] and the space group $P2_12_12_1$ was assigned from volume considerations and a statistical consideration of the systematic absences (Markvardsen *et al.*, 2001). The data set was background subtracted and truncated to 59.5° 2θ for Pawley fitting (Pawley, 1981; $\chi^2_{\rm Pawley} = 6.10$) and the structure solved using the simulated annealing (SA) global optimization procedure, described previously (David *et al.*, 1998), that is now implemented in the *DASH* computer program (David *et al.*, 2001). The SA structure solution used 311 reflections and involved the optimization of two fragments totaling 14 degrees of freedom (six positional and orientational for each fragment present in the asymmetric unit plus a torsion angle for each fragment). All degrees of freedom were assigned random values at the start of the simulated annealing. The best SA solution had a favourable $\chi^2_{\rm SA}/\chi^2_{\rm Pawley}$ ratio of 3.41 and a chemically reasonable packing arrangement, with no significant misfit to the diffraction data.

The solved structure was then refined against the data in the range 6–59.7° 2θ using a restrained Rietveld (1969) method as implemented in *TOPAS* (Coelho, 2003), with $R_{\rm wp}$ falling to 0.029 during the refinement. All atomic positions (including H atoms) for the structure of (I) were refined, subject to a series of restraints on bond lengths, bond angles and planarity. The refined C—H distances were 0.949 (5)–0.973 (5) Å. $U_{\rm iso}$ values for H atoms were constrained to equal 0.076 Å^2.

The restraints were set such that bonds and angles did not deviate more than 0.01 Å and 0.8°, respectively, from their initial values during the refinement. Atoms C16, C15, C14, C13, C18, C17, H16, H15, H14, H18 and H17 (phenylethylammonium) and atoms C5, C6, C7, C8, C9, C10, H6, H7, H8, H9 and H10 (phenylbutyrate) were restrained to lie in respective planar groups. A spherical harmonics (fourth order) correction of intensities for preferred orientation was applied in the final refinement (Järvinen, 1993). The refined final spherical harmonics coefficients were consistent with mild preferred orientation effects in the sample. The observed and calculated diffraction patterns for the refined crystal structure are shown in Fig. 3.

Data collection: *DIFFRAC plus XRD Commander* (Kienle & Jacob, 2003); cell refinement: *TOPAS* (Coelho, 2003); data reduction: *DASH* (David *et al.*, 2001); program(s) used to solve structure: *DASH*; program(s) used to refine structure: *TOPAS*; molecular graphics: *Mercury* (Macrae *et al.*, 2006) and *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *enCIFer* (Version 1.1; Allen *et al.*, 2004).

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