

Philippe Fernandes,^a Alastair J. Florence,^{a*} Kenneth Shankland,^b Panagiotis G. Karamertzanis,^c Ashley T. Hulme^c and R. Parathy Anandamanoharan^d

^aStrathclyde Institute of Pharmacy and Biomedical Sciences, John Arbuthnot Building, University of Strathclyde, 27 Taylor Street, Glasgow G4 0NR, Scotland, ^bISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX11 0QX, England, ^cChristopher Ingold Laboratory, Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, England, and ^dDepartment of Chemical Engineering, University College London, Torrington Place, London WC1E 7JE, England

Correspondence e-mail:
alastair.florence@strath.ac.uk

Key indicators

Powder X-ray study
 $T = 298$ K
Mean $\sigma(\text{C}-\text{C}) = 0.003$ Å
 R factor = 0.026
 wR factor = 0.031

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

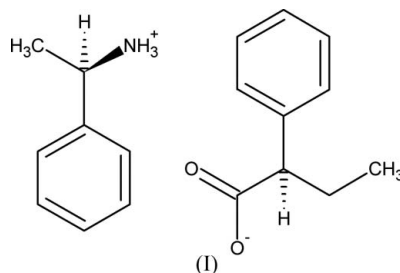
Powder study of (*R*)-1-phenylethylammonium (*R*)-2-phenylbutyrate form 3

The crystal structure of a new polymorph of the title compound, $\text{C}_8\text{H}_{12}\text{N}^+\cdot\text{C}_{10}\text{H}_{11}\text{O}_2^-$, 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 0.030. The compound crystallizes with one (*R*)-1-phenylethylammonium cation and one (*R*)-2-phenylbutyrate anion in the asymmetric unit.

Received 17 November 2006
Accepted 1 December 2006

Comment

The title compound is known to crystallize in at least two polymorphic forms, form 1 (Briano, 1978) and form 2 (Fernandes *et al.*, 2006). A third polymorph, form 3, (I), was produced *in situ* by heating a polycrystalline sample of form 2 to 393 K. The sample remained stable upon cooling to 295 K and the powder data were collected at this temperature.



The compound crystallizes in the monoclinic space group $P2_1$ with one (*R*)-1-phenylethylammonium cation and one

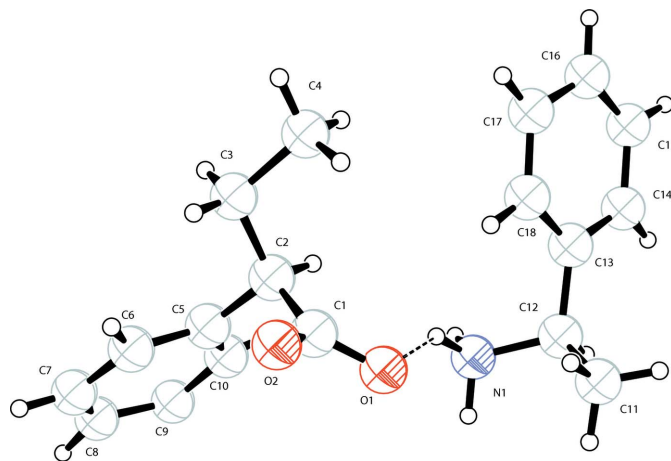
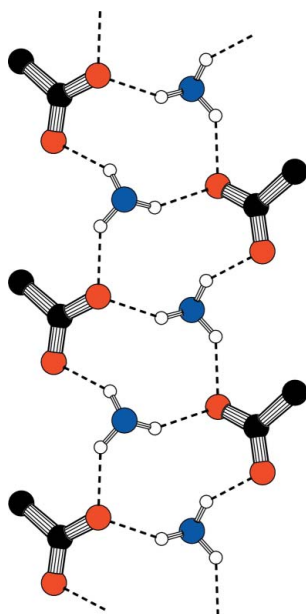


Figure 1

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

**Figure 2**

The hydrogen-bonded (dashed lines) ladder motif running parallel to the *b* axis in (I). Atoms not directly involved in hydrogen-bond contacts are omitted for clarity.

(*R*)-2-phenylbutyrate anion in the asymmetric unit (Fig. 1). The structure contains four N—H···O hydrogen bonds between the NH₃⁺ and COO[−] groups on adjacent ions. The ions pack to form a hydrogen-bonded ladder motif, similar to that observed in form 2 (Table 1, Fig. 2).

Experimental

A polycrystalline sample of (I) was prepared *in situ* by heating form 2 from 295 to 393 K until all the sample transformed. The sample was then cooled to 295 K and held at that temperature for the duration of the data collection. The sample was held in a rotating 0.7 mm borosilicate glass capillary and the temperature controlled using an Oxford Cryosystems Cryostream 700 series device. 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).

Crystal data

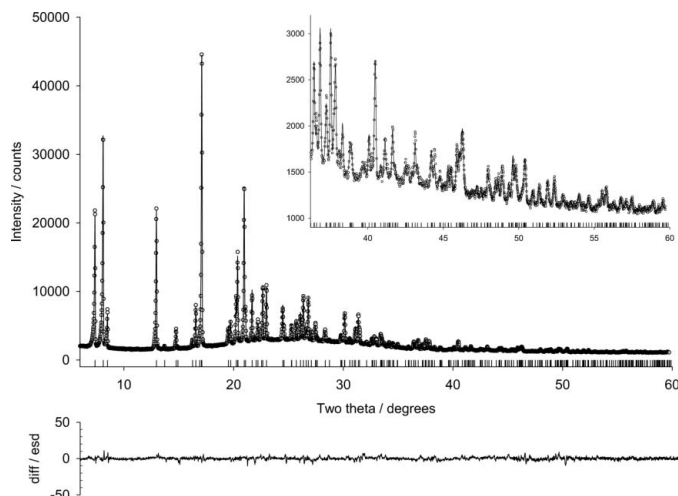
C₈H₁₂N⁺·C₁₀H₁₁O₂[−]
M_r = 285.37
 Monoclinic, *P*2₁
a = 11.88215 (15) Å
b = 5.97647 (8) Å
c = 13.07499 (15) Å
 β = 113.510 (1)°
V = 851.43 (2) Å³
Z = 2

D_x = 1.113 Mg m^{−3}
 Cu K α ₁ radiation
 μ = 0.57 mm^{−1}
T = 298 K
 Specimen shape: cylinder
 12 × 0.7 × 0.7 mm
 Specimen prepared at 393 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
 Wavelength of incident radiation: 1.54056 Å
 Absorption correction: none
 $2\theta_{\min}$ = 3.0, $2\theta_{\max}$ = 60.0°
 Increment in 2θ = 0.017°

**Figure 3**

Final observed (points), calculated (line) and difference [(*y*_{obs} − *y*_{calc})/ σ (*y*_{obs})] profiles for the Rietveld refinement of the title compound.

Refinement

R_p = 0.026
R_{wp} = 0.031
R_{exp} = 0.016
R_B = 0.0223%
S = 1.96
 Profile function: Fundamental parameters with axial divergence correction.
 145 parameters

Only H-atom coordinates refined
 $w = 1/\sigma(Y_{\text{obs}})^2$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 Preferred orientation correction: A spherical harmonics-based preferred orientation correction (Järvinen, 1993) was applied with *TOPAS* during the Rietveld refinement

Table 1

Hydrogen-bond geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N1—H1N <i>A</i> ···O1 ⁱ	0.963 (7)	2.585 (8)	3.457 (3)	150.7 (5)
N1—H1N <i>A</i> ···O2 ⁱ	0.963 (7)	1.827 (7)	2.683 (3)	146.6 (6)
N1—H1N <i>B</i> ···O1	0.978 (7)	1.927 (8)	2.754 (3)	140.7 (5)
N1—H1N <i>C</i> ···O1 ⁱⁱ	0.976 (7)	1.958 (9)	2.840 (5)	149.1 (9)

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

The diffraction pattern indexed to a monoclinic cell [*M*(20) = 95.7 F(20) = 253.2; *DICVOL-9I*; Boultif & Louër, 1991] and space group *P*2₁ 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 59.8° 2θ for Pawley (1981) fitting ($\chi^2_{\text{Pawley}} = 5.10$) 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 290 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 $\chi^2_{\text{SA}}/\chi^2_{\text{Pawley}}$ ratio of 1.83 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 3–59.7° 2 θ using a restrained Rietveld (1969) method as implemented in *Topas* (Coelho, 2003), with the R_{wp} falling to 0.030 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. U_{iso} values for H atoms were constrained to equal 0.1013 Å².

The restraints were set such that bond lengths and angles did not deviate more than 0.01 Å and 0.8°, respectively, from their initial values during the refinement. Atoms C13–C18 and H14–H18 (phenylethylammonium) and atoms C5–C10 and H6–H10 (phenylbutyrate) were restrained to be planar. A spherical harmonics (fourth order) correction of intensities for preferred orientation was applied in the final refinement (Järvinen, 1993). 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: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Version 011105; Spek, 2003); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004).

We thank the Basic Technology programme of the UK Research Councils for funding under the project Control and

Prediction of the Organic Solid State (<http://www.cpos-s.org.uk>).

References

- Allen, F. H., Johnson, O., Shields, G. P., Smith, B. R. & Towler, M. (2004). *J. Appl. Cryst.* **37**, 335–338.
- Boultif, A. & Louër, D. (1991). *J. Appl. Cryst.* **24**, 987–993.
- Brianso, M.-C. (1978). *Acta Cryst.* **B34**, 679–680.
- Coelho, A. A. (2003). *Topas User Manual*. Version 3.1. Bruker AXS GmbH, Karlsruhe, Germany.
- David, W. I. F., Shankland, K., Cole, J., Maginn, S., Motherwell, W. D. S. & Taylor, R. (2001). *DASH*. Version 3.0 User Manual. Cambridge Crystallographic Data Centre, England.
- David, W. I. F., Shankland, K. & Shankland, N. (1998). *Chem. Commun.* pp. 931–932.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Fernandes, P., Florence, A. J., Shankland, K., Karamertzanis, G. P., Hulme, A. T. & Anandamohan, R. P. (2006). *Acta Cryst.* **E62**. In the press.
- Hill, R. J. & Madsen, I. C. (2002). *Structure Determination from Powder Diffraction Data*, edited by W. I. F. David, K. Shankland, L. B. McCusker & Ch. Baerlocher, pp. 114–116. Oxford University Press.
- Järvinen, M. (1993). *J. Appl. Cryst.* **26**, 525–531.
- Kienle, M. & Jacob, M. (2003). *DIFFRAC plus XRD Commander*. Version 2.3. Bruker AXS GmbH, Karlsruhe, Germany.
- Markvardsen, A. J., David, W. I. F., Johnson, J. C. & Shankland, K. (2001). *Acta Cryst.* **A57**, 47–54.
- Pawley, G. S. (1981). *J. Appl. Cryst.* **14**, 357–361.
- Rietveld, H. M. (1969). *J. Appl. Cryst.* **2**, 65–71.
- Shankland, K., David, W. I. F. & Sivia, D. S. (1997). *J. Mater. Chem.* **7**, 569–572.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.