Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

(*S*)-(−)-1-Phenylethylaminium 3,5-dinitrosalicylate

Graham Smith,[a]* Urs D. Wermuth[a] and Jonathan M. White[b]

[a]School of Physical and Chemical Sciences, Queensland University of Technology, GPO Box 2434, Brisbane 4001, Australia, and [b]School of Chemistry, University of Melbourne, Parkville, 3052, Australia

Correspondence e-mail: g.smith@qut.edu.au

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.007 Å
R factor = 0.045
wR factor = 0.107
Data-to-parameter ratio = 7.2

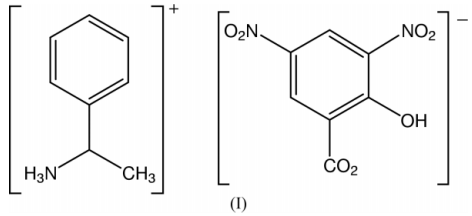
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 21 October 2003
Accepted 27 October 2003
Online 22 November 2003

The crystal structure of the 1:1 proton-transfer compound of 3,5-dinitrosalicylic acid with the optically active amine (*S*)-(−)-1-phenylethylamine, *viz*. (*S*)-(−)-1-phenylethylaminium 3,5-dinitrosalicylate, $C_8H_{12}N^+\cdot C_7H_3N_2O_7^-$, shows the presence of two pseudo-centrosymmetrically related and conformationally similar carboxylate anions and two chiral but conformationally different (*S*)-aminium cations in the crystallographic repeat unit. In these cations, the protonated amine-N atoms have a number of hydrogen-bonding associations with carboxyl, phenol and nitro O atoms of the acid [N···O = 2.824 (4)–3.245 (5) Å]. These, together with peripheral hydrogen-bonding associations and some weak cation–anion π–π interactions, result in a three-dimensional network polymer structure.

Comment

We have previously reported the crystal structures of a number of proton-transfer compounds of 3,5-dinitrosalicylic acid (DNSA) with Lewis bases (Smith *et al.*, 1995, 2003*a*,*b*; Smith, Wermuth, Bott *et al.*, 2002; Smith, Wermuth & Healy, 2002). This acid is sufficiently strong (pK_a = 2.2) to protonate most amines and, with primary amines particularly, the resultant alkylaminium cation often gives hydrogen-bonding interactions with up to six acceptor atoms, *e.g.* with methylamine (1:1) (Smith, Wermuth, Bott *et al.*, 2002). Only in rare examples with very weak bases does protonation not occur, *e.g.* with phenazine (pK_a = 1.2) (Kumar *et al.*, 2002). In addition, aryl substitution in the alkylamine often aids crystallization with these compounds, *e.g.* with benzylamine (1:1) (Smith, Wermuth & Healy, 2002), although rarely through π–π interactions. However, to date no compounds of DNSA with optically active bases have been reported, so the reaction with (*S*)-(−)-α-methylbenzylamine [*S*-(−)-1-phenylethylamine (PHEA)] was tried, resulting in the isolation of good crystals of the title compound, *S*-(−)-1-phenylethylaminium 3,5-dinitrosalicylate, (I).



(I)

Although the structure determination of (I) does not confirm with any certainty the (*S*) absolute configuration of the two unique 1-(−)-phenylethylaminium cations on the basis of the Flack (1983) parameter, the configuration is assumed from chemical evidence. The two PHEA cation

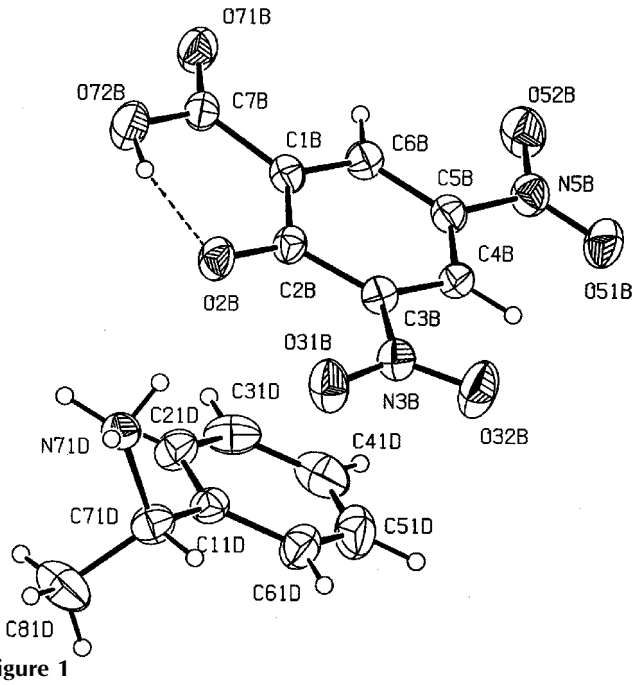


Figure 1
The molecular configuration and atom-naming scheme for one of the PHEA cation–DNSA anion pairs (molecules *D* and *B*) in (I). Atoms are shown as 30% probability ellipsoids

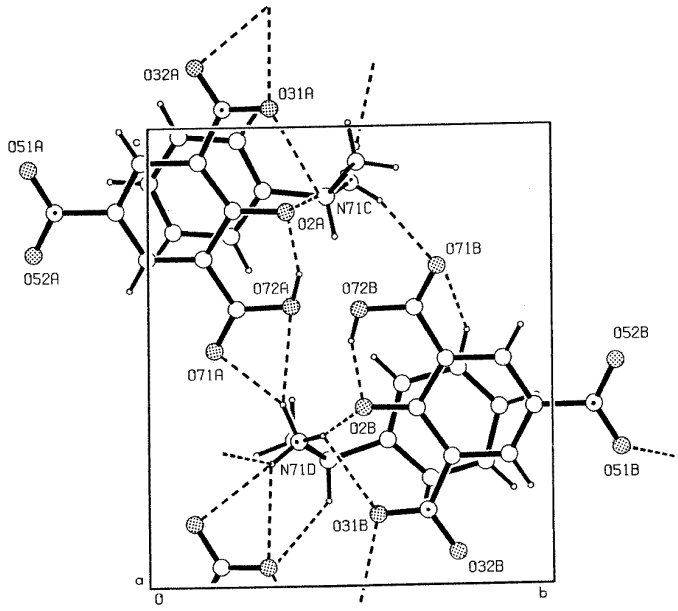


Figure 2
Perspective view of the packing in the unit cell, viewed down the *a* axis, showing hydrogen-bonding associations as broken lines.

molecules (*C* and *D*) which, with the two DNSA anions (molecules *A* and *B*), comprise the unit-cell contents and the asymmetric unit in the space group *P*1, exhibit in (I) pseudocentrosymmetry. However, the two chiral PHEA cations possess, as expected, the same (*S*) configuration, but there are significant conformational differences between the *C* and *D* cation pairs, as discussed later. Fig. 1 shows one of the two cation–anion pairs (molecules *D* and *B*). The two $DNSA^-$ anions are only slightly different conformationally, the corresponding torsion angles in the carboxyl and nitro substituent groups (C2—C1—C7—O71, C2—C3—N3—O32 and C4—C5—N5—O52) for *A* and *B* being 179.6 (4)/178.6 (4), 160.0 (4)/−168.7 (4) and 176.7 (4)/−177.0 (4)°, respectively. However, the $PHEA^+$ cations, although both have the same (*S*) configuration, are conformationally different, as indicated by the magnitude of the side-chain torsion angle C21—C11—C71—N71 [−89.6 (5)° (*C*) and −54.1 (5)° (*D*)]. These differences are probably responsible for the failure of the compound to crystallize in a higher symmetry space group. In addition, there is significantly more thermal motion for some of the aromatic ring atoms of the PHEA cations (particularly *C*) than for the DNSA anions.

The protonated N atom in each PHEA cation is involved in a number of hydrogen-bonding interactions (Table 1), including one four-centred association about H74*D* (completing seven in all about N41*D*), while about N41*C* there are only four. These include *A*···*C* and *B*···*D* interactions between the stacks along the *a*-axis direction (Fig. 2), as well as inter-stack associations. The result is an extended three-dimensional network polymer structure (Fig. 2). Some weak π–π interactions are in evidence between the cation–anion pairs in the stacks [Cg(C1*A*—C6*A*)···Cg(C1*C*—C6*C*) = 3.640 (7) Å and Cg(C1*B*···C6*B*)···Cg(C1*D*—C6*D*) = 3.738 (7) Å; *Cg* is the centroid of each ring]. The previously mentioned high thermal motion of atoms of the cation rings might be considered analogous to phenomena observed for a number of π–π associated compounds involving 2,4,6-trinitrobenzene and similar aromatic compounds (Herbstein, 1971; Herbstein & Kaftory, 1975; Smith, Wermuth & White, 2002), where the aromatic ring atoms of the adduct molecule are disordered.

With (I), the usual intramolecular hydrogen bond is found between the phenolic O atom and a carboxylate group in each of the DNSA anions [O2···H72—O72 = 2.467 and 2.482 (4) Å], with the proton located on the carboxyl oxygen, as is more often the case with DNSA proton-transfer compounds (Smith, Wermuth & Healy, 2002; Smith *et al.* 2003*a*,*b*).

Experimental

The synthesis of the title compound was carried out by heating, under reflux, 1 mmol quantities of 3,5-dinitrosalicylic acid (DNSA) and (*S*)-(−)-1-phenylethylamine [(*S*)-(−)-α-methylbenzylamine = PHEA] (Aldrich) in 50 ml of 50% ethanol/water for 10 min. After concentration to *ca* 30 ml, partial room-temperature evaporation of the hot-filtered solution gave yellow crystals (m.p. 447–450 K); $[\alpha]_D^{20}$ = −2° (in ethanol) [*cf* −39° for PHEA (neat)].

Crystal data

$C_8H_{12}N^+\cdot C_7H_3N_2O_7^-$
M_r = 349.30
Triclinic, *P*1
a = 7.5177 (8) Å
b = 9.6277 (10) Å
c = 11.1566 (12) Å
α = 89.008 (2)°
β = 79.373 (2)°
γ = 87.054 (2)°
V = 792.57 (15) Å^3
Z = 2
D_x = 1.464 Mg m^{-3}
Mo *K*α radiation
Cell parameters from 1643 reflections
θ = 2.8–26.0°
μ = 0.12 mm^{-1}
T = 293 (2) K
Block, yellow
0.25 × 0.15 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer	$R_{int} = 0.041$
φ and ω scans	$\theta_{max} = 27.5^\circ$
5055 measured reflections	$h = -7 \rightarrow 9$
3494 independent reflections	$k = -12 \rightarrow 12$
2511 reflections with $I > 2\sigma(I)$	$l = -14 \rightarrow 14$

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.045$	$w = 1/[\sigma^2(F_o^2) + (0.0612P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.107$	$(\Delta/\sigma)_{max} = 0.013$
$S = 0.93$	$\Delta\rho_{max} = 0.20$ e Å^{-3}
3494 reflections	$\Delta\rho_{min} = -0.19$ e Å^{-3}
485 parameters	

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

D—H···A	D—H	H···A	D···A	D—H···A
O72A—H72A···O2A	0.94 (5)	1.64 (6)	2.467 (4)	145 (5)
O72B—H72B···O2B	0.81 (4)	1.71 (4)	2.482 (4)	157 (4)
N71C—H72C···O2A^{i}	0.94 (6)	1.98 (5)	2.840 (4)	151 (5)
N71C—H72C···O31A^{i}	0.94 (6)	2.53 (6)	2.940 (4)	106 (4)
N71D—H72D···O71A	0.95 (6)	2.08 (6)	2.956 (5)	153 (5)
N71D—H72D···O72A	0.95 (6)	2.40 (7)	3.245 (5)	148 (5)
N71C—H73C···O71B^{i}	0.85 (4)	2.04 (4)	2.865 (4)	161 (3)
N71D—H73D···O2B	0.92 (4)	1.94 (4)	2.824 (4)	162 (3)
N71D—H73D···O31B	0.92 (4)	2.41 (4)	3.000 (4)	122 (3)
N71C—H74C···O31B^{ii}	0.93 (4)	2.17 (4)	3.099 (4)	178 (4)
N71D—H74D···O31A^{iii}	0.80 (4)	2.52 (3)	3.098 (5)	131 (3)
N71D—H74D···O32A^{iii}	0.80 (4)	2.46 (4)	3.196 (5)	153 (4)
N71D—H74D···O51B^{iv}	0.80 (4)	2.46 (4)	2.958 (5)	121 (3)
C31D—H31D···O52A^{v}	0.93	2.58	3.321 (6)	137
C71D—H71D···O31A^{iii}	0.98	2.55	3.245 (5)	128
C81C—H81C···O2A	0.96	2.57	3.506 (7)	164

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

H atoms involved in hydrogen-bonding interactions [H72A, H72B, H72–H74 (C and D)] were located by difference methods and their positional and isotropic displacement parameters were refined. Others were included in the refinement at calculated positions [0.93 Å (aromatic) and 0.96 Å (aliphatic)] as riding atoms, with $U_{iso} = 1.2U_{eq}$(parent atom). For refined amine H atoms, the mean N—H distance is 0.90 (6) Å. Because of the identified pseudosymmetry for the structure (96%), an attempt to refine the structure in the space group $P\overline{1}$ (assuming the high improbability of racemization) gave a residual R of no better than 0.11 (*cf.* 0.045 reported for $P1$). The small specific rotation for (I) (−2°) is consistent with the crystallographic observations, which include the hydrogen-bonding interactions associated with both of the (*S*)-aminium groups in cations C and D. In the absence of significant anomalous scattering effects, Friedel pairs were merged.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1999); program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *PLATON for Windows* (Spek, 1999); software used to prepare material for publication: *PLATON for Windows*.

The authors acknowledge financial support from The School of Physical and Chemical Sciences of the Queensland University of Technology and The University of Melbourne.

References

Bruker (1997). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (1999). *SAINT*. Version 6.02. Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (2000). *SMART*. Version 5.55. Bruker AXS Inc., Madison, Wisconsin, USA.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Herbstein, F. H. (1971). Persp. *Struct. Chem.* **4**, 166–395.

Herbstein, F. H. & Kaftory, M. (1975). *Acta Cryst.* B**31**, 60–67.

Kumar, V. S. S., Kuduva, S. S. & Desiraju, G. R. (2002). *Acta Cryst.* E**58**, o865–o866.

Smith, G., Lynch, D. E., Byriel, K. A. & Kennard, C. H. L. (1995). *Aust. J. Chem.* **48**, 1133–1149.

Smith, G., Wermuth, U. D., Bott, R. C., Healy, P. C. & White, J. M. (2002). *Aust. J. Chem.* **55**, 349–356.

Smith, G., Wermuth, U. D. & Healy, P. C. (2002). *Acta Cryst.* E**58**, o845–o847.

Smith, G., Wermuth, U. D., Healy, P. C. & White, J. M. (2003*a*). *Aust. J. Chem.* **56**, 707–713.

Smith, G., Wermuth, U. D., Healy, P. C. & White, J. M. (2003*b*). *J. Chem. Crystallogr.* Submitted.

Smith, G., Wermuth, U. D. & White, J. M. (2002). *Acta Cryst.* E**58**, o1130–o1132.

Spek, A. L. (1999). *PLATON for Windows*. September 1999 Version. University of Utrecht, The Netherlands.