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(*R*)-1-Phenyl-1-ethylammonium (*R*)-2-hydroxymethyl-2-(2-naphthyl)propanoate

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Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.011 Å
Disorder in main residue
R factor = 0.048
wR factor = 0.102
Data-to-parameter ratio = 7.6

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

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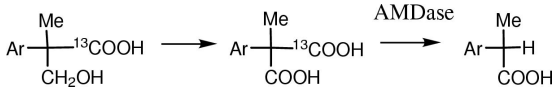
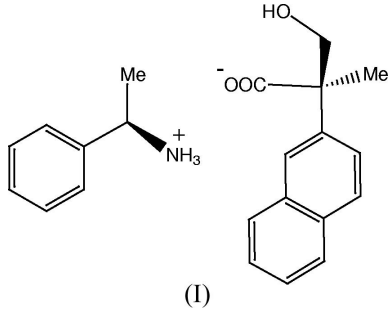
The title compound, $C_8H_{12}N^+\cdot C_{14}H_{13}O_3^-$, is the less soluble diastereomeric salt of 2-hydroxymethyl-2-(2-naphthyl)-propanoic acid with (*R*)-(+)-phenylethylamine. The ammonium group of the cation and the carboxylate group of the anion are linked *via* N—H···O hydrogen bonds, forming ribbons along the *b* axis.

Comment

Arylmalonate decarboxylase (AMDase) catalyzes the enantioselective decarboxylation of arylmethylmalonic acid. Recently, Ijima *et al.* (2005) have succeeded in preparing a mutant enzyme of arylmalonate decarboxylase, which gives the opposite enantiomer compared with the product of the native enzyme. To investigate the stereochemical course of the reaction catalyzed by the mutant enzyme, both enantiomers of methyl-2-naphthylmalonic acid, which contain ^{13}C in either one of the two carboxyl groups, were prepared.



The aim of the present paper is to assign the absolute configuration of the enantiomers of the methyl-2-naphthylmalonic acid labeled with ^{13}C. The title compound, (I), is a diastereomeric salt of the optically resolved synthetic intermediate 2-hydroxymethyl-2-(2-naphthyl)propanoic acid with phenylethylamine. An X-ray structure analysis of (I) has been carried out to determine the absolute configuration of (+)-2-hydroxymethyl-2-(2-naphthyl)propanoic acid based on the known absolute configuration of (*R*)-(+)-phenylethylamine.



(I)

As shown in Fig. 1, compound (I) consists of organic ions as the result of deprotonation of the carboxylic acid group. All three H atoms of the ammonium group are involved in hydrogen bonding to the carboxylate group (Table 2). The cations and anions are arranged alternately and connected *via*

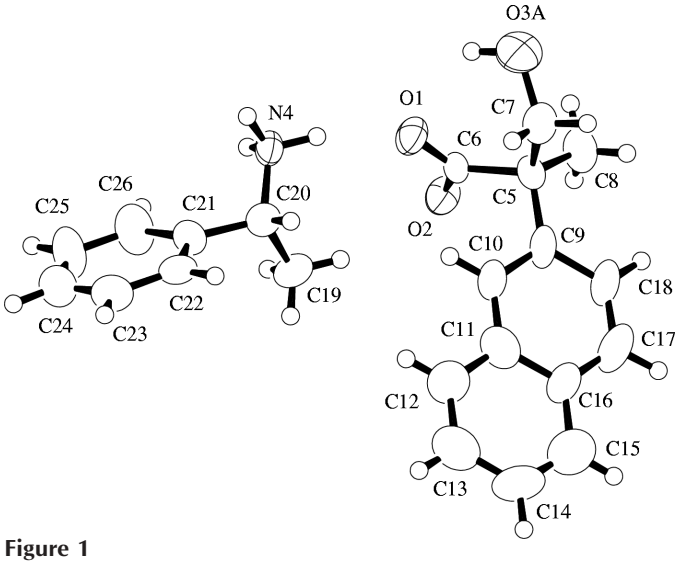


Figure 1
Molecular structure of (I), with the atom-labeling scheme and displacement ellipsoids drawn at the 50% probability level. One of the two possible positions of atom O3 has been omitted for clarity.

N—H···O hydrogen bonds to form ribbons that extend along the *b* axis (Fig. 2). The crystals of (I) grown from methanol, ethanol or aqueous solutions are fiber-like. As expected, the elongated direction of the needle specimen is the *b* axis.

Experimental

(±)-2-Hydroxymethyl-2-(2-naphthyl)propanoic acid was prepared as described previously (Miyamoto *et al.*, 1992). The optical resolution was carried out with (*R*)-(+)- phenylethylamine in acetone solution. The less soluble diastereomeric salts were recrystallized several times and dissolved in 2 *M* NaOH solution, each enantiomer being extracted by ethyl acetate (94–98% enantiomeric excess). Compound (I) is the less soluble diastereomeric salt, which consists of (*R*)-(+)-phenylethylamine and (+)-2-hydroxymethyl-2-(2-naphthyl)-propanoic acid. The specific rotation, $[\alpha]_D$, of (+)-2-hydroxymethyl-2-(2-naphthyl)propanoic acid at 293 K is +27.7 (1)° (*c* = 1.0, EtOH, where *c* is a concentration of units grams per 100 cm^{-3}). Crystals of (I) suitable for X-ray study were grown from an aqueous solution by slow evaporation.

Crystal data

$C_8H_{12}N^+\cdot C_{14}H_{13}O_3^-$
M_r = 351.44
Monoclinic, $P2_1$
a = 12.791 (2) Å
b = 6.4448 (16) Å
c = 12.068 (3) Å
β = 104.741 (16)°
V = 962.1 (4) Å^3
Z = 2
D_x = 1.213 Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 25 reflections
θ = 10.1–11.8°
μ = 0.08 mm^{-1}
T = 298 K
Needle, colorless
0.9 × 0.1 × 0.05 mm

Data collection

Rigaku AFC-7*R* diffractometer
ω–2θ scans
Absorption correction: integration (*ABSCOR*; Higashi, 1999)
T_{min} = 0.992, T_{max} = 0.996
2165 measured reflections
1854 independent reflections
698 reflections with $I > 2\sigma(I)$
R_{int} = 0.024
θ_{max} = 25.0°
h = −6 → 15
k = 0 → 7
l = −14 → 13
3 standard reflections
every 150 reflections
intensity decay: none

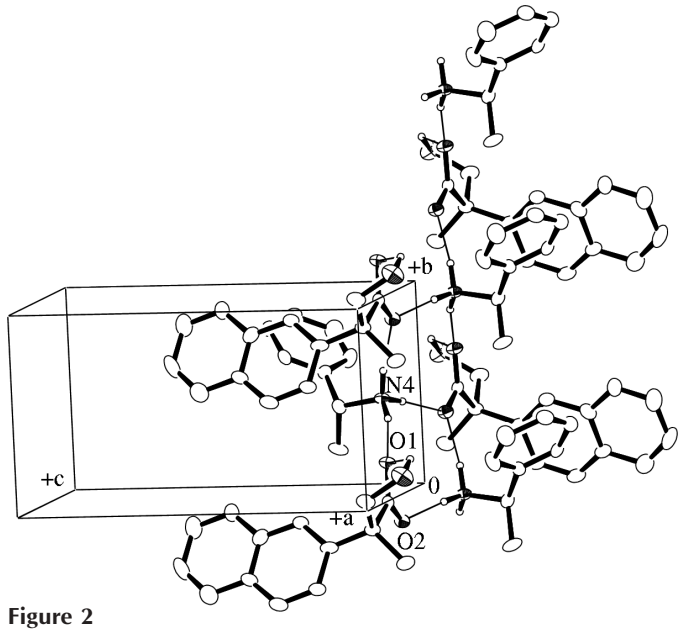


Figure 2
Hydrogen-bonded chain around the 2_1 screw axis parallel to the *b* axis. The thin lines indicate hydrogen bonds. H atoms not involved in hydrogen bonding have been omitted for clarity. The atom labels O1, O2 and N4 at (*x*, *y*, *z*) are indicated.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.102
S = 0.97
1854 reflections
244 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0179P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.016
$\Delta\rho_{max}$ = 0.16 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C6	1.255 (9)	O2—C6	1.280 (8)
O1—C6—C5—C9	106.1 (7)	N4—C20—C21—C26	51.3 (9)
O3*A*—C7—C5—C9	−170.3 (6)	C6—C5—C9—C10	−40.6 (8)
O3*B*—C7—C5—C9	57 (1)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3*A*—H3*A*···O1	0.95	2.07	2.743 (9)	126
O3*B*—H3*B*···O3*A*^{i}	0.95	1.82	2.71 (2)	154
N4—H4*A*···O1	0.95	1.84	2.769 (7)	166
N4—H4*B*···O2^{ii}	0.95	1.86	2.801 (6)	172
N4—H4*C*···O2^{iii}	0.95	1.85	2.791 (7)	172

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

Due to the low scattering power of the crystal, only 38% of the measured reflections were observed. There is a positional disorder of the alcohol atom O3, the site occupation factors of O3*A* and O3*B* being 70 and 30%, respectively. H atoms bonded to C atoms were positioned with idealized geometry and were refined with fixed isotropic displacement parameters [U_{iso}(H) = 1.2U_{eq}(C)] using a

riding model, with C—H = 0.95 Å. The positions of the N-bound H atoms were idealized on the basis of the position of one H atom, which was identified in a difference map. The O-bound H atoms were positioned with idealized geometry in the direction of the nearest appropriate hydrogen-bonding acceptor. The N- and O-bound H atoms were refined with fixed isotropic displacement parameters [U_{iso}(H) = 1.2U_{eq}(parent atom)] using a riding model with bond distances of 0.95 Å. The absolute configuration was assigned on the basis of the known absolute configuration of (*R*)-(+)-phenylethylamine (Eliel, 1962; Nassimbeni *et al.*, 1986). Because of negligible anomalous scattering effects, Friedel pairs were averaged in the refinement.

Data collection: *WinAFC Diffractometer Control Software* (Rigaku, 1999); cell refinement: *WinAFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 2001); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

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