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(*S*)-Alanine–(*S*)-mandelic acid (1/1)

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Key indicators

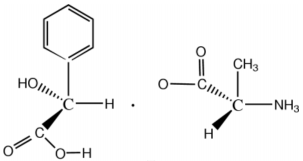
Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.005 Å
Disorder in main residue
R factor = 0.054
wR factor = 0.154
Data-to-parameter ratio = 10.9

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

Crystals of the title molecular complex, $C_8H_8O_3 \cdot C_3H_7NO_2$, were obtained from the remaining filtrate after separating the crystals of a molecular complex of (*S*)-alanine–(*R*)-mandelic acid in an optical resolution experiment using (*S*)-alanine. Each (*S*)-alanine is hydrogen bonded to three (*S*)-mandelic acid molecules (and *vice versa*). The carboxylate of (*S*)-alanine is nearly coplanar with the carboxyl group of (*S*)-mandelic acid, a situation that is very different from that found in the reported (*S*)-alanine–(*R*)-mandelic acid.

Comment

In the investigation of the optical resolution of racemic mandelic acid by (*S*)-alanine, crystals of the molecular complex of (*S*)-alanine and (*R*)-mandelic acid [(*S*)A/(*R*)M] were obtained from the solution of racemic mandelic acid and (*S*)-alanine, and the crystal structure has been reported (Hu *et al.*, 2002). After several days separating the (*S*)A/(*R*)M crystals from the solution, new crystals appeared in the remaining filtrate. An X-ray structure analysis revealed that the new crystals are (*S*)-alanine–(*S*)-mandelic acid (1/1) [(*S*)A/(*S*)M], (I), a diastereomer of (*S*)A/(*R*)M. We present here the structure of (I), for comparison with the reported (*S*)A/(*R*)M.



(I)

The title molecular complex consists of (*S*)-alanine and (*S*)-mandelic acid in a 1:1 ratio. The ordered (*S*)-alanine displays the normal inner-salt structure (Table 1) and links with three neighboring (*S*)-mandelic acid molecules *via* N—H···O and O···H—O hydrogen bonds (Table 2). The phenyl ring of (*S*)-mandelic acid is disordered, three different orientations being observed in the crystal (Fig. 1); this is due to the space around the phenyl group, as shown in the molecular packing diagram (Fig. 2).

There are several distinct structural differences between (I) and the reported (*S*)A/(*R*)M. The asymmetric unit contains one (*S*)-alanine and one (*S*)-mandelic acid molecule in (I), but two (*S*)-alanine, two (*R*)-mandelic acid and one water molecule in (*S*)A/(*R*)M, which is a hydrate. Strong hydrogen bonding occurs between the carboxylate group of alanine and the carboxyl group of mandelic acid in both (I) and (*S*)A/(*R*)M, the O···O separation being 2.461 (4) Å in (I), and 2.494 (3) and 2.554 (3) Å in (*S*)A/(*R*)M. The O—H bond of the carboxyl group is *anti* to the C═O bond in (I), but *syn* to the C═O bond in (*S*)A/(*R*)M. The carboxylate plane is

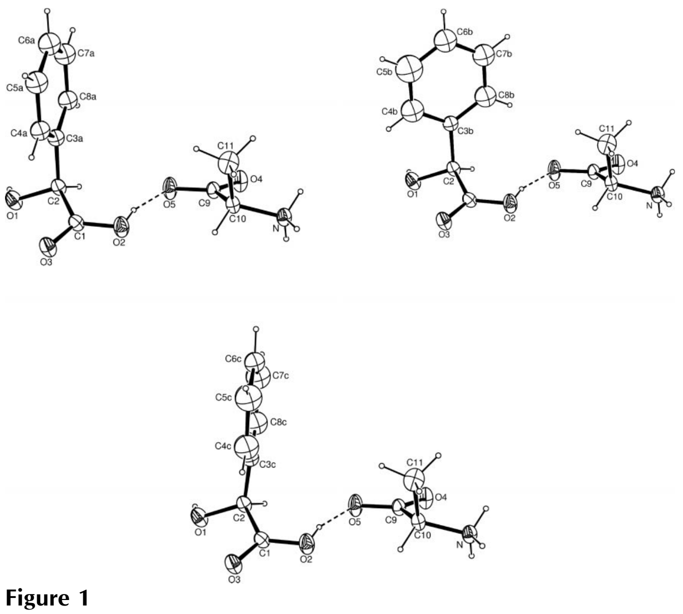


Figure 1
The structure of (I), with 30% probability displacement ellipsoids, the dashed lines showing the hydrogen bond between (*S*)-alanine and (*S*)-mandelic acid [symmetry codes: (ii) $1 - x, y, -z$; (iii) $x - \frac{1}{2}, \frac{1}{2} + y, z$]. Three components of the disordered mandelic acid molecule are illustrated.

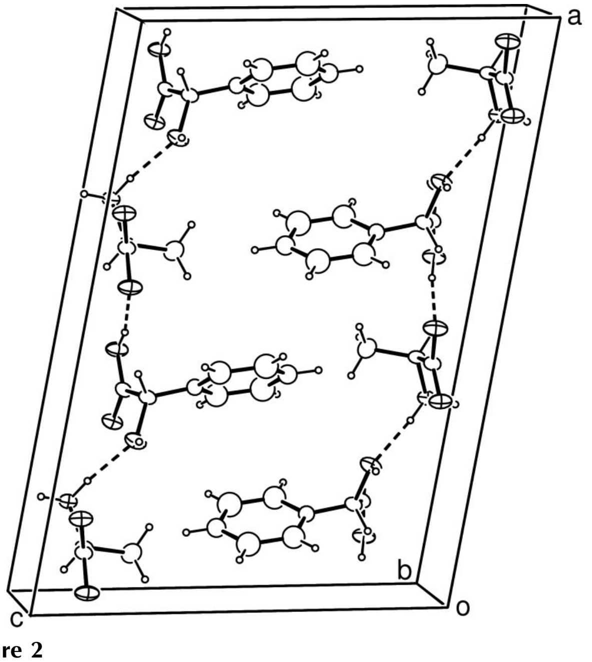


Figure 2
A molecular packing diagram, showing the intermolecular hydrogen bonding (as dashed lines) and the space around the phenyl ring.

roughly coplanar with the carboxyl plane in (I), the dihedral angle being 26.4 (3)°, but in (*S*)A/(*R*)M they are nearly perpendicular to each other, the dihedral angles being 56.8 (3) and 59.6 (3)°, respectively, for the two independent molecules.

Experimental

Racemic mandelic acid (1.5 g, 10 mmol) and (*S*)-alanine (0.90 g, 10 mmol) were dissolved in hot water (10 ml) and the solution was kept at room temperature. After 2 d, crystals (0.85 g) of (*S*)A/(*R*)M·H_2O were separated from the solution (Hu *et al.*, 2002). The remaining filtrate was kept at room temperature to obtain more crystals. The fine crystals of the title compound (0.45 g) were obtained from the remaining filtrate after a further 3 d. The CHN content was analyzed using an Eager 200 elemental analysis instrument. Analysis calculated for $C_{11}H_{15}NO_5$: C 54.8, H 6.3, N 5.8%; found: C 54.7, H 6.3, N 5.9%. The specific optical rotation $[\alpha]_D$ of +80.2° (H_2O) was determined using a Wzz-1S instrument. Recrystallization from an aqueous solution was performed to obtain well shaped single crystals of the title compound.

Crystal data

$C_8H_8O_3{\cdot}C_3H_7NO_2$
$M_r = 241.24$
Monoclinic, *C*2
$a = 17.795\ (4)$ Å
$b = 5.394\ (2)$ Å
$c = 12.431\ (2)$ Å
$\beta = 100.650\ (10)°$
$V = 1172.7\ (5)$ Å^3
$Z = 4$
$D_x = 1.366$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 20 reflections
$\theta = 5.5$–$9.8°$
$\mu = 0.11$ mm^{-1}
$T = 295\ (2)$ K
Prism, colorless
0.4 × 0.4 × 0.2 mm

Data collection

Rigaku AFC-7*S* diffractometer
$\omega/2\theta$ scans
1928 measured reflections
1484 independent reflections
1276 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.017$
$\theta_{\rm max} = 27.5°$
$h = -1 \rightarrow 22$
$k = -7 \rightarrow 1$
$l = -16 \rightarrow 15$
3 standard reflections every 150 reflections intensity decay: 0.6%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.054$
$wR(F^2) = 0.154$
$S = 1.06$
1484 reflections
136 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0812P)^2 + 1.03P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.35$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.33$ e Å^{-3}

Table 1
Selected geometric parameters (Å).

O1—C2	1.422 (4)	O5—C9	1.272 (4)
O2—C1	1.270 (4)	N—C10	1.479 (4)
O3—C1	1.230 (4)	C9—C10	1.521 (4)
O4—C9	1.224 (4)	C10—C11	1.514 (5)

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

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
O1—H1*A*⋯O3$^{\rm i}$	0.82	1.98	2.797 (4)	171
O2—H2*A*⋯O5	0.82	1.67	2.461 (4)	163
N—H3*A*⋯O4$^{\rm iv}$	0.89	1.87	2.763 (4)	176
N—H3*B*⋯O1$^{\rm iii}$	0.89	1.99	2.877 (4)	173
N—H3*C*⋯O3$^{\rm ii}$	0.89	2.12	3.000 (4)	169

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

Three different orientations for the phenyl ring were found in a difference Fourier map. Isotropic rigid-group refinement for the phenyl rings was performed. The three occupancies were initially refined and then fixed in the final cycles of refinement. H atoms on the N atom were located in a difference Fourier map, then refined as a group with N—H = 0.89 Å and $U_{\rm iso}({\rm H}) = 1.5U_{\rm eq}({\rm N})$. Other H atoms were placed in calculated positions, with C—H = 0.93–0.98 Å and O—H = 0.82 Å, and treated as riding, with U_{iso}(H) = $1.2U_{eq}$ or $1.5U_{eq}$ of the carrier atoms. The absolute configuration was assigned on the basis of the *S* configuration of the starting (*S*)-alanine and was not determined directly from the X-ray data; Friedel pairs were averaged.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1985); program(s) used to solve structure: *SIR*-2 (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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