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# A metastable modification of (*RS*)-mandelic acid

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**Key indicators**

Single-crystal X-ray study
*T* = 299 K
Mean σ(C–C) = 0.003 Å
*R* factor = 0.049
*wR* factor = 0.149
Data-to-parameter ratio = 13.0

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



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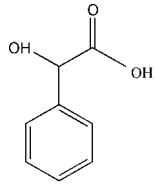
A metastable modification of (*RS*)-mandelic acid, $C_8H_8O_3$, was obtained from an aqueous solution. The structure features hydrogen-bonded double chains of acid molecules, which run along the *a* axis of the crystal. The structure shows a close relationship to that of the pure enantiomer and differs significantly from the structure of the stable modification of the racemate. There are two molecules in the asymmetric unit.

## Comment

Racemates in their crystalline form can belong to one of three classes. Two contain both enantiomers mixed in the crystal structure. These include racemic compounds that have an ordered *R*- and *S*-enantiomer distribution in the structure and solid solutions which have both enantiomers mixed randomly in the lattice. The third class of racemates, the racemic conglomerates, has an identical crystal lattice of that of the pure enantiomer, meaning that, although the whole crystalline mass is racemic, each crystal in itself is enantiomerically pure.

Most chiral organic compounds obtained in racemic form are reported to form true ordered racemic crystals, while only 5–10% are estimated to form racemic conglomerates and only very few form solid solutions. Simple resolution methods, such as direct crystallization, are applicable only to racemic conglomerates (Jacques *et al.*, 1994). The understanding of how two enantiomers interact in a solution upon crystallization is, however, still rather limited.




(I)

Mandelic acid is a chiral aromatic carboxylic acid, often used as a resolving agent in classical resolutions of pharmaceuticals. The crystal structures of the racemic and enantiomerically pure (*S*)-mandelic acid have been determined earlier by Cameron & Duffin (1974), Wei & Ward (1977) and Patil *et al.* (1987). A metastable mandelic acid racemate has been obtained previously upon cooling a melt (Rose, 1952; Kuhnert-Brandstätter & Ulmer, 1974), as well as from aqueous solutions (Profir *et al.*, 2002). The IR spectrum of this phase is almost identical to the spectrum of the pure mandelic acid enantiomer (Kuhnert-Brandstätter & Ulmer, 1974; Profir *et al.*, 2002). Furthermore, its melting point correlates well with the melting point of an artificially manufactured mandelic acid conglomerate (Fujita *et al.*, 1972). We grew crystals of the

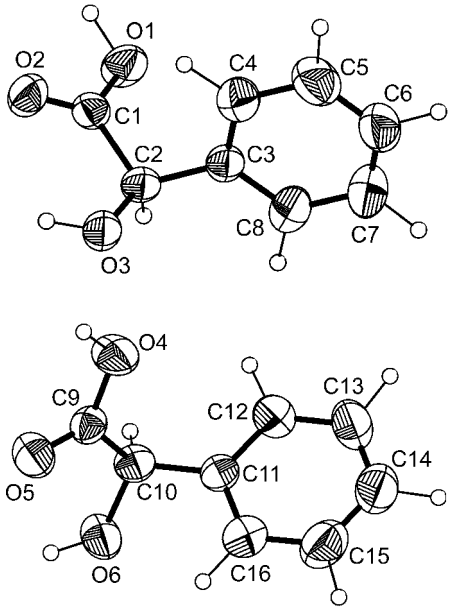



**Figure 1**
Two independent molecules in the asymmetric unit of (*RS*)-mandelic acid. Displacement ellipsoids are drawn at the 50% probability level.

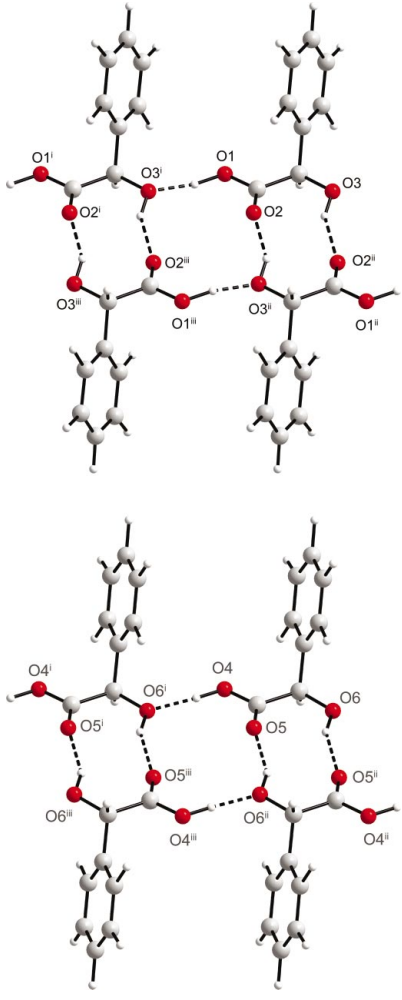



**Figure 2**
Fragments of two independent hydrogen-bonded double chains in the structure of (I). Hydrogen bonds are shown as dashed lines. [Symmetry codes: (i) $x-1, y, z$; (ii) $1-x, -y, 1-z$; (iii) $-x, -y, 1-z$.]

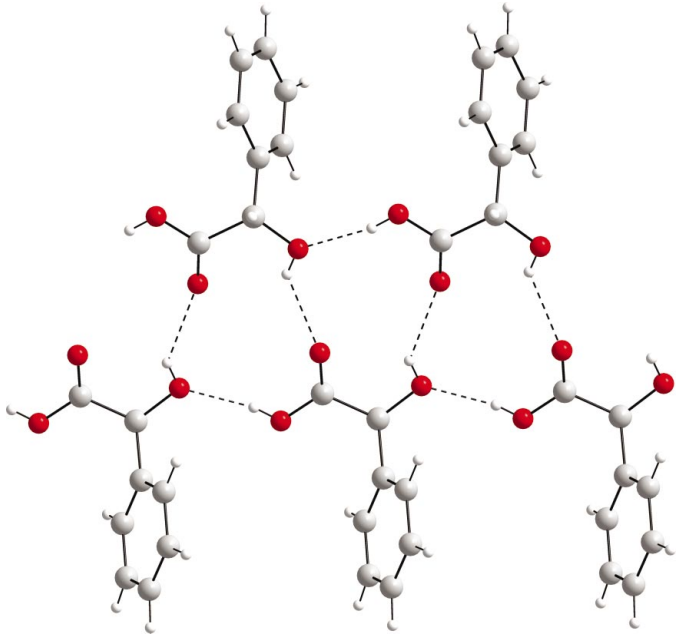


**Figure 3**
A fragment of the hydrogen-bonded double chain in structure of the *S*-enantiomer of mandelic acid (Patil *et al.*, 1987). Hydrogen bonds are shown as dashed lines.

metastable mandelic acid racemate, (I), in order to determine its structure and to find out to which of the above-mentioned racemate classes the metastable form belongs.

The metastable form of mandelic acid crystallizes with two acid molecules in the asymmetric unit. Fig. 1 shows their structures and atom labeling. Each of the molecules is connected to three neighboring molecules, as shown in Fig. 2, yielding double chains that run along the *a* axis, *i.e.* the direction of the shortest edge of the unit cell. Each of the two symmetry-independent molecules gives rise to a hydrogen-bonded double chain, which can be described as being made up of centrosymmetric dimers of mandelic acid molecules. Interestingly, this structure bears a striking resemblance to the structure of mandelic acid *S*-enantiomer (Patil *et al.*, 1987), which also features two symmetry-independent double chains running along the shortest axis of the crystal; as in the present structure, each of the two chains in the structure of the pure enantiomer is made up of only one kind of molecule. The difference between the two structures, however, lies in the fact that the single strings of molecules within the double chains in the structure of the racemic title compound, (I), are related by an inversion center, whereas in the structure of the pure enantiomer, the strings within the double chain are related by the screw axis parallel to the chain. Thus, these strings may be considered parallel in the structure of the enantiomer and 'anti-parallel' in the racemic structure. This difference becomes clear when the double chain in Fig. 2 is compared with that in Fig. 3, showing the fragment of one of the independent chains in the structure of (*S*)-mandelic acid (Patil *et al.*, 1987).

The packing diagrams of the metastable racemic crystal and the crystal of the *S*-enantiomer are compared in Fig. 4. The

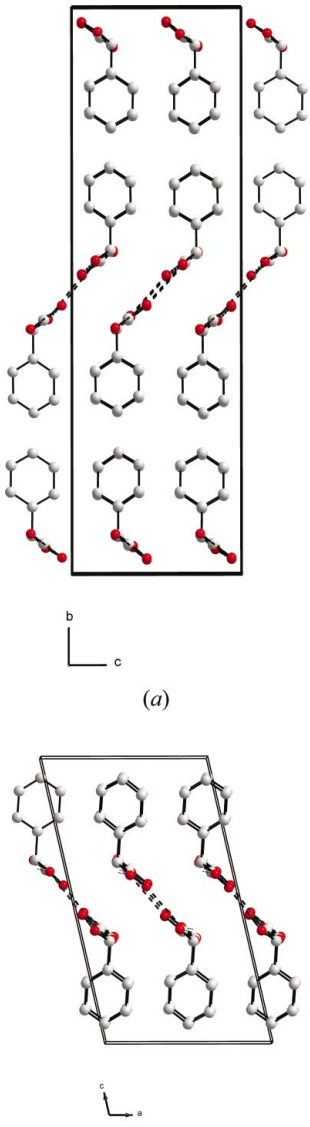



**Figure 4**
Crystal packing diagrams for (*a*) the metastable racemic form and (*b*) the pure *S*-enantiomeric form of mandelic acid.

two shorter edges of the unit cells are rather close in value in both structures, whereas the long axis of the racemate unit cell is approximately twice as long as in the pure enantiomer.

Upon heating at 318 K for nine days, the racemic metastable mandelic acid is transformed into the stable racemic form. The structure of the latter (Wei & Ward, 1977) differs from that of (I) quite significantly. In particular, instead of the above described one-dimensional chain motifs, in the stable modification, two-dimensional molecular aggregation is observed.

## Experimental

An undersaturated solution of (*RS*)-mandelic acid (Sigma, 99%) was filtered through a 0.2 µm membrane filter and distributed into five 10 ml flasks that were protected from light and allowed to evaporate slowly at room temperature. After several weeks, crystals of the metastable mandelic acid racemate precipitated in the three of the flasks. These crystals were used for diffraction experiments both by single-crystal and by powder methods; the latter was used to confirm the identity of the bulk material. In the remaining two flasks, the stable modification of the racemic acid crystallized.

*Crystal data*

$C_8H_8O_3$
$M_r$ = 152.15
Monoclinic, $P2_1/c$
$a$ = 5.8468 (1) Å
$b$ = 29.2410 (4) Å
$c$ = 8.7228 (1) Å
$\beta$ = 92.1651 (8)°
$V$ = 1490.24 (4) Å$^3$
$Z$ = 8
$D_x$ = 1.356 Mg m$^{-3}$
Cu $K\alpha$ radiation
Cell parameters from 7612 reflections
$\theta$ = 6.8–66.5°
$\mu$ = 0.88 mm$^{-1}$
$T$ = 299 K
Prism, colorless
0.30 × 0.30 × 0.10 mm

*Data collection*

Bruker–Nonius KappaCCD diffractometer
$\varphi$ and $\omega$ scans
Absorption correction: numerical (Herrendorf & Bärnighausen, 1997)
$T_{min}$ = 0.741, $T_{max}$ = 0.938
10243 measured reflections
2590 independent reflections
1884 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.048
$\theta_{max}$ = 66.5°
$h = -6 \rightarrow 6$
$k = -34 \rightarrow 34$
$l = -10 \rightarrow 9$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)]$= 0.049
$wR(F^2)$ = 0.149
$S$ = 1.06
2590 reflections
199 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0769P)^2 + 0.286P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.14 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.21 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O1—H1O···O3$^{i}$ | 1.08 | 1.58 | 2.6492 (18) | 170 |
| O3—H3O···O2$^{ii}$ | 0.94 | 2.00 | 2.8557 (16) | 150 |
| O4—H4O···O6$^{i}$ | 1.04 | 1.62 | 2.6419 (18) | 164 |
| O6—H6O···O5$^{iv}$ | 1.01 | 1.87 | 2.8089 (17) | 153 |

Symmetry codes: (i) $x-1, y, z$; (ii) $1-x, -y, 1-z$; (iv) $2-x, -y, 2-z$.

All H atoms were located in a difference map. They were refined in the riding model approximation, with $U_{iso}$ equal to $1.2U_{eq}$ of the carrier atom.

Data collection: *KappaCCD Software* (Nonius, 1997); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *maXus* (Mackay *et al.*, 1997).

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