(+)- and (±)-ketopinic acid: hydrogen-bonding patterns in a β-keto acid in its enantiomeric and racemic forms and enantiomeric disordering in the racemate

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Abstract

Crystal structures have been determined for both (+)- and (±)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptane-1-carboxylic acid, C$_{10}$H$_{14}$O$_3$. The asymmetric unit of the (+)-form, (I), contains two molecules paired by mutual hydrogen bonding of their carboxyl groups, without ketone involvement. Both carboxyl groups are disordered and the conformation of each relative to its own molecule differs by 46.3 (4)° for the two halves of the dimer. In the racemate, (II), the asymmetric unit also contains two molecules, each of which dimerizes with a centrosymmetric counterpart by mutual hydrogen bonding of carboxyl groups across the **a** or **b** cell edge, also without ketone involvement. Besides disorder of the carboxyl C—O lengths and angles, each half of the asymmetric unit of (II) displays extensive enantiomeric disorder, corresponding to transposition of the ethylene and methylene bridges, with the carboxyl and ketone C atoms plus the *anti*-methyl C atom exactly coinciding. Each contributor to the structure of (II) has a different rotational conformation for its carboxyl group, none corresponding to those found in (I).

Comment

Among crystalline organic compounds, keto carboxylic acids occupy a cusp of behavioral territory where relatively minor structural differences may produce marked changes in hydrogen-bonding patterns. Our continuing interest in the solid-state structures of keto acids lies in

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mapping the molecular characteristics that control the five known hydrogen-bonding modes. The most common of these is acid dimerization without ketone involvement (Lalancette, Thompson & Coté, 1997), but carboxyl-to-ketone chains (catemers) constitute a sizable minority of cases (Brunskill *et al.*, 1997). The remaining three types of mode, namely intramolecular hydrogen bonds (Thompson *et al.*, 1996), acid-to-acid catemers (Lalancette *et al.*, 1998) and carboxyl-to-ketone dimers (Kosela *et al.*, 1995), are all comparatively rare. Several cases also exist of hydrates with more complex hydrogen-bonding patterns (Lalancette *et al.*, 1990, 1998; Lalancette, Brunskill & Thompson, 1997). We have previously referenced numerous examples and discussed factors that appear to govern the choice of hydrogen-bonding mode (Brunskill *et al.*, 1999; Lalancette *et al.*, 1999).

The geometry of β-keto acids appears attractive for internal hydrogen bonding (Toffoli *et al.*, 1988, and reference therein), consistent with the six-centered internal hydrogen transfer known to underlie their facile thermal decarboxylation (Logue *et al.*, 1975). However, there is scant crystallographic evidence for this hydrogen-bonding mode in β-keto acids (Thompson *et al.*, 1996), although it is found in several γ-keto acids (Griffe *et al.*, 1972; Sheldrick & Trowitzsch, 1983; Halfpenny, 1990; Coté, Lalancette & Thompson, 1996) and one ε-keto acid (Abell *et al.*, 1990), requiring larger hydrogen-bonding rings. Among those β-keto acids adequately stable for isolation and study, previous X-ray work has found carboxyl pairing (Martuscelli & Avitabile, 1967; Avitabile *et al.*, 1969, 1971; Thompson *et al.*, 1992; Coté, Thompson & Lalancette, 1996) and catemers (Lalancette *et al.*, 1991), plus one instance of internal hydrogen bonding (Thompson *et al.*, 1996).

We present here the crystal structures of the title β-keto acid, 7,7-dimethyl-2-oxobicyclo[2.2.1]heptane-1-carboxylic acid, in both its (+)-enantiomeric form, (I), and its racemic form, (II). We wished both to define the hydrogen bonding for this compound and to see whether its mode would be altered by the packing changes forced by the presence *versus* the absence of the enantiomer (Eliel & Kofron, 1953; Walborsky *et al.*, 1961; Simpson & Marsh, 1966; Lalancette *et al.*, 1991).
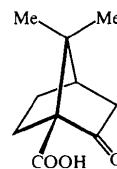
(I), the (+) form
(II), the (±) form

Fig. 1 presents a view of (I), using the established numbering for camphor systems. The asymmetric unit consists of a pair of conformationally distinct mol-

ecules of identical handedness, (I) and (I'), mutally hydrogen-bonded through their carboxyl groups with no ketone participation in the hydrogen bonding. Except for the O and H atoms of the carboxyl groups, the rigidity of the bicyclic framework fixes the position of every atom present, so that all distances and angles not involving carboxyl O or H are identical for (I) *versus* (I'), within experimental error. However, in (I), the C2—C1—C10—O2 torsion angle, specifying the conformation of the carboxyl group relative to the rest of the molecule, is 96.9 (4)°, while in (I'), this angle is 50.6 (4)°.
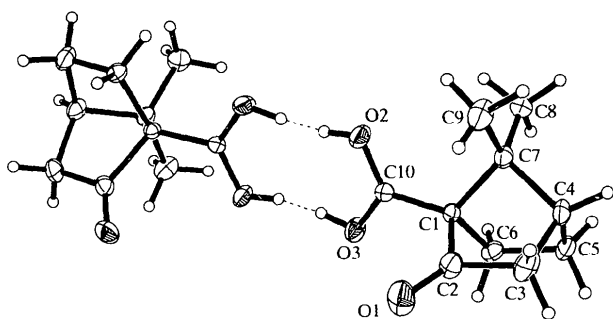

Fig. 1. A view of the asymmetric unit of the (+)-enantiomer, (I), with its numbering scheme. Numbering is shown only for the unprimed molecule. Ellipsoids are shown at the 20% probability level and H atoms are drawn as spheres of arbitrary radii.

Averaging of the C—O bond lengths and C—C—O angles, by either static or dynamic disorder, is often encountered in dimeric carboxylic acids (Leiserowitz, 1976), and is seen here in both halves of the asymmetric unit. Electron density resulting from disordered carboxyl H atoms was found near each carboxyl O atom and these were modeled as H atoms with half occupancy, as shown in Fig. 1. In (I), the disorder is essentially complete, as evidenced by O2—C10 and O3—C10 lengths of 1.255 (4) and 1.249 (4) Å, respectively, with O2—C10—C1 and O3—C10—C1 angles of 118.3 (3) and 119.3 (3)°, respectively. In (I'), similar residual differences were found, still within experimental error: O2'—C10' = 1.263 (4) and O3'—C10' = 1.251 (4) Å, and O2'—C10'—C1' = 118.6 (3) and O3'—C10'—C1' = 119.1 (3)°. These values may be contrasted with lengths and angles cited as typical for highly ordered carboxyl dimers: 1.21 and 1.31 Å (for C=O and C—O, respectively), and 123 and 112° (for C—C=O and C—C—O, respectively) (Borthwick, 1980).

Fig. 2 illustrates the packing of the cell, with the dimer centers located at non-crystallographic sites. The four asymmetric units of the cell (Z = 8) are all screw-related and adopt two contrasting alignments, resulting in a herring-bone-like pattern lying in the *bc* plane.

Figs. 3 and 4 show the two halves of the asymmetric unit for the racemate, (II), with 'ghost' atoms to
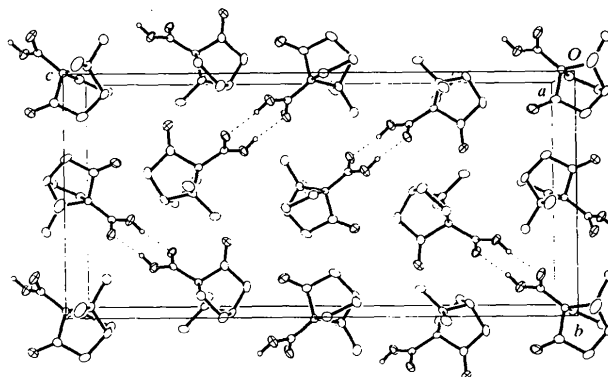

Fig. 2. A packing diagram for (I), with extracellular molecules. Ellipsoids are shown at the 20% probability level.

illustrate the disorder found to arise from the occupation of each molecular site by both enantiomers. The two components of the asymmetric unit are not joined as a dimer, rather, each constitutes half of a separate dimer, pairing with its own centrosymmetric complement. The numbering and priming scheme used for (I) is supplemented here with 'D' and 'L' to show the chirality of each molecular entity. Thus, in the (II) component (Fig. 3) the major site occupant is the (+)-species, designated D, and the torsion angles C2D—C1D—C10D—O2D = 72 (1)° and C2D—C1D—C10D—O2L = −86 (1)° specify the conformation of the rotationally disordered carboxyl group relative to the rest of this (+)-molecule. The corresponding data for the minor, levorotatory, occupant at the same site is C2D—C1L—C10D—O2L = −35 (1)° and C2D—C1L—C10D—O2D = 113 (1)°. The labeling of the disordered carboxyl group for (II) is arbitrary and is not meant to specify which component of the carboxyl belongs to which component of the skeletal framework. For the (II') component (Fig. 4), the major site occupant is the (−)-species, and C2L'—C1L'—C10L'—O2L' = 99 (1)°. For the minor, dextrorotatory, species in (II'), C2L'—C1D'—C10L'—O2L' = 45 (1)°. It is noteworthy that none of these values or their complements corresponds to the values found for either (I) or (I'). Hence, each of the eight contributors to both structures is conformationally distinct. This suggests that, apart from packing forces, the barriers to carboxyl rotation are quite small within this torsional range. The rotational sweep of the planar carboxyl group is approximately 60°, including conformers in which the carboxyl is close to coplanarity with C10—C1—C6 and with C10—C1—C7, whereas the exclusion zone centers around coplanarity with C10—C1—C2, and presumably involves dipolar repulsions with the ketone. Semi-empirical molecular (*AM*1) modeling of this carboxyl rotation using *SPARTAN* (Wavefunction, 1995; Dewar *et al.*, 1985) gives results in agreement with this, showing energy maxima of about 2 and 3 kcal mol⁻¹ for the regions near the closest approach of the ketone oxygen to O3 and O2, respectively.
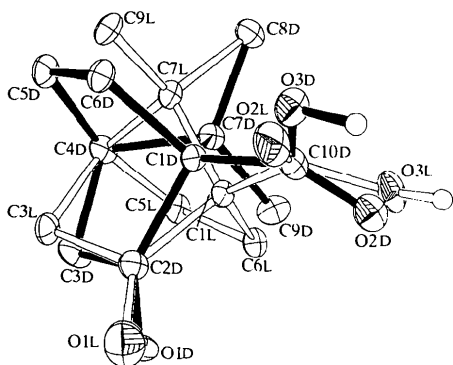
Fig. 3. A view of one-half of the asymmetric unit, (II), for the racemate. The major component (D) is shown with dark bonds and the minor component (L) with open bonds. Ellipsoids are set at the 20% probability level. All non-carboxyl H atoms have been omitted for clarity.
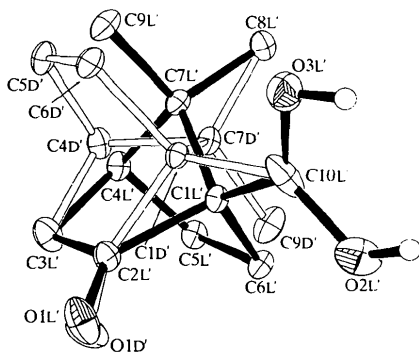

Fig. 4. A view of the second half of the asymmetric unit, (II'), for the racemate. The major component (L') is shown with dark bonds and the minor component (D') with open bonds. Ellipsoids are set at the 20% probability level. All non-carboxyl H atoms have been omitted for clarity.

The carboxyl C—O bond lengths of (II') were found to be completely averaged by disorder [O2L'—C10L' = 1.255 (2) and O3L'—C10L' = 1.245 (2) Å]. However, the C—C—O angles are somewhat distorted (ranging from 103 to 133°) from the usual values, since the model includes a single position for the 'C10 pair'. These angular distortions are governed to some extent by the C1L'—C10L'—C1D' angle of 31.3 (1)°, which describes the differences in orientation between the C1—C10 bonds in the two conformers. The high anisotropy of C10L' may also be a result of modeling the 'C10 pair' as a single atom. For (II), partial ordering of the C—O lengths was shown after the two carboxyl conformations were resolved [C10D—O2D = 1.189 (10), C10D—O3D = 1.288 (6), C10D—O2L = 1.194 (8) and C10D—O3L = 1.350 (10) Å]. Again, modeling difficulties produce somewhat distorted C—C—O angles, ranging from 99 to 134°, and the C1D—C10D—C1L angle is 26.9 (2)°. Electron density resulting from disordered carboxyl H atoms was found on each side of the carboxyl group for both (II) and (II') and these were modeled as H atoms with half occupancy.

Figs. 3 and 4 show that the enantiomeric disordering corresponds to transposition of the C5—C6 and C7 bridges for both (II) and (II'), and illustrate that in both cases several atoms (C2, C8 and C10) coincide so closely that they were not separable in our treatment. This is reflected in the numbering, where each coinciding pair of atoms bears the number for the higher-occupancy component of the pair, e.g. the pair C2D/C2L is designated C2D. The ketone O atoms (O1) were only marginally resolvable, and the carboxyl O atoms of molecule (II) were separable, while those of (II') were not. Although C3 was resolvable for (II) but not for (II'), the reverse was true for C4. This enantiomeric disorder evidently arises from the relatively undifferentiated shape of the non-polar portion of the bicyclic framework of the molecule. So long as the ketone and carboxyl dipoles occupy their correct lattice positions, the remainder of the molecule offers such slight enantiomeric shape and polarity distinctions that, with some rotational adjustment of the carboxyl units, the D/L dimer easily tolerates end-for-end transposition. We have no evidence either for or against participation by D/D or L/L dimers in the disordering.

The two halves of the asymmetric unit were found to differ in the apparent extent of this enantiomeric disorder. For the occupancy pair of (II) in Fig. 3, refinement indicated an occupancy of 76.4 (3)% for the (+)-enantiomer (D), which is therefore shown with dark bonds. An occupancy of 54.0 (3)% for the (−)-enantiomer (L', dark bonds) was found for the Fig. 4 pair of (II'). In each instance, the minor enantiomer is shown with open bonds in the figures. The strikingly different enantiomer occupancy values for (II) and (II'), if correct, require that the two types of dimers, which differ as to carboxyl conformation, also differ in their extent of disorder. The disordering for (II') is so close to 50:50 that for all practical purposes we may describe its dimer as having complete enantiomeric disorder, i.e. in the crystal its D/L unit is transposed end-for-end in an entirely random fashion. The more interesting case is (II), which would require a significant (75:25) alignment bias within the crystal, with transposition only 25% of the time. An alternative description is that, on average, the type (II) dimer is completely disordered half the time and enantiomerically aligned half the time. Because the occupancy values were obtained by averaging the unequal occupancies of the disordered atoms, some of whose resolvabilities were problematic, it is unclear what confidence one should place in the assigned errors, the occupancy values or the differences found between (II) and (II'). However, it is far from unknown to find some lack of randomness in supposedly random crystallization processes (Kondepudi et al., 1990) or to find that a single chosen crystal is not representative (Pasteur, 1848).

Fig. 5 illustrates the packing of the cell. The strikingly similar melting points of the racemic and non-racemic materials (see *Experimental*) might suggest some similarity in packing. However, the packing arrangements for (I) and (II), along with the space groups and crystal systems, are found to be quite different. In (I), the ketone dipoles are arrayed in a '*cisoid*' fashion within the dimer unit, while for (II), the dimer has the '*transoid*' deployment of the ketone dipoles required by the centrosymmetry of the space group (*P*1̄). Each of the molecules from Figs. 3 and 4 can be seen here to constitute half of a separate centrosymmetric dimer centered on a crystallographic site, with type (II) dimers centered on the **b** cell edge and type (II') on the **a** edge. As Fig. 5 shows, the packing has the axes for all carboxyl pairings lying parallel, like rods stacked in a bundle, in contrast to (I), whose herring-bone pattern has axes with two different orientations at 73° to one another.
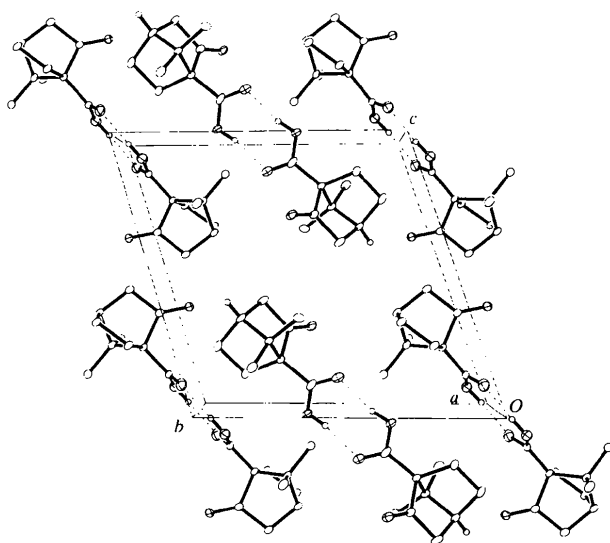

Fig. 5. A packing diagram for (II), with extracellular molecules to illustrate the dimers formed across the **b** and **a** edges of the chosen cell by (II) and (II') type species, respectively. Only the major occupancy components of (II) and (II') are shown for clarity, but the H4 atom is included for (II) and omitted for (II') to allow visual differentiation. Ellipsoids are set at the 20% probability level.

The solid-state (KBr) IR spectrum of (I) displays normal C=O stretching absorptions at 1752 (ketone) and 1691 cm^{-1} (carboxyl), with Raman frequencies of 1749 cm^{-1} for the ketone and 1641 cm^{-1} for the carboxyl group. The 50 cm^{-1} frequency difference between IR and Raman in the latter case is exactly average for those carboxyl dimers we have studied; this, combined with the small frequency difference for carboxyl groups involved in catemeric hydrogen-bonding patterns (typically *ca* 4 cm^{-1}), has been shown to be a reliable experimental diagnostic for hydrogen-bonding modes in solid-state keto carboxylic acids (Vanderhoff *et al.*, 1990). The

corresponding values for (II) are: 1750 and 1691 cm^{-1} (IR), and 1744 and 1650 cm^{-1} (Raman), yielding an IR–Raman frequency difference of 41 cm^{-1} for the carboxyl. In CHCl$_3$ solution, both (I) and (II) have their C=O absorptions at 1758 and 1718 cm^{-1}.

Experimental

Both the (+)-enantiomer, (I), of known absolute stereochemistry (m.p. *ca* 508 K; Kokke & Varkevisser, 1974), prepared as described by Bartlett & Knox (1973), and the racemate, (II) (m.p. *ca* 511 K), prepared by the same method, were crystallized from ethanol–water. Ketopinic acid both sublimes and partially decomposes below its melting point, so that the value of the melting point obtained with a given sample is very technique-sensitive and exact literature values should be mistrusted. For the racemate, Bartlett & Knox (1973) give a melting point of 506–507 K, while the checkers of the very same procedure report a value of 513–515 K. Literature values as low as 499–501 K and as high as 507 K have been reported for the (+)-enantiomer.

Compound (I)

Crystal data

C$_{10}$H$_{14}$O$_3$	Mo *K*α radiation
M$_r$ = 182.21	λ = 0.71073 Å
Orthorhombic	Cell parameters from 30
*P*2$_1$2$_1$2$_1$	reflections
a = 7.363 (1) Å	θ = 8.67–15.12°
b = 11.299 (1) Å	μ = 0.091 mm^{-1}
c = 23.502 (3) Å	*T* = 298 (2) K
V = 1955.2 (4) Å^3	Prism
Z = 8	0.6 × 0.5 × 0.5 mm
D$_x$ = 1.238 Mg m^{-3}	Colorless
D$_m$ not measured	

Data collection

Siemens *P*4 diffractometer	θ$_{max}$ = 25°
2θ/θ scans	*h* = −8 → 8
Absorption correction: none	*k* = −1 → 13
3993 measured reflections	*l* = −1 → 27
3443 independent reflections	3 standard reflections
2122 reflections with	every 97 reflections
I > 2σ(*I*)	intensity variation: <2%
R$_{int}$ = 0.031	

Refinement

Refinement on *F^2*	Δρ$_{max}$ = 0.128 e Å^{-3}
R[*F^2* > 2σ(*F^2*)] = 0.060	Δρ$_{min}$ = −0.144 e Å^{-3}
wR(*F^2*) = 0.130	Extinction correction:
S = 1.04	*SHELXL*97 (Sheldrick,
3443 reflections	1997*a*)
241 parameters	Extinction coefficient:
H atoms: see below	0.0064 (8)
w = 1/[σ^2(*F$_o^2$*) + (0.0361*P*)^2	Scattering factors from
+ 0.3835*P*]	*International Tables for*
where *P* = (*F$_o^2$* + 2*F$_c^2$*)/3	*Crystallography* (Vol. C)
(Δ/σ)$_{max}$ < 0.001	

Table 1. *Selected geometric parameters (Å, °) for (I)*

O1—C2	1.192 (5)	O1'—C2'	1.205 (4)
O2—C10	1.255 (4)	O2'—C10'	1.263 (4)
O3—C10	1.249 (4)	O3'—C10'	1.251 (4)
O3—C10—C1	119.3 (3)	O3'—C10'—C1'	119.1 (3)
O2—C10—C1	118.3 (3)	O2'—C10'—C1'	118.6 (3)

Table 2. *Hydrogen-bonding and close-contact geometry for (I) (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3···O2'	0.82	1.87	2.667 (3)	166
O3'—H3'···O2	0.82	1.84	2.634 (3)	162
O2—H2···O3'	0.82	1.83	2.634 (3)	167
O2'—H2'···O3	0.82	1.87	2.667 (3)	165
C4—H4A···O1'^{i}	0.98	2.54	3.301 (5)	135
C5—H5B···O3'^{ii}	0.97	2.71	3.633 (5)	160
C8—H8A···O3'^{ii}	0.96	2.71	3.523 (5)	143

Symmetry codes: (i) $\frac{1}{2} - x, 2 - y, z - \frac{1}{2}$; (ii) $\frac{1}{2} + x, \frac{3}{2} - y, -z$.

Compound (II)

Crystal data

C$_{10}$H$_{14}$O$_3$
M_r = 182.21
Triclinic
$P\bar{1}$
a = 7.0947 (3) Å
b = 11.8316 (6) Å
c = 12.1662 (6) Å
α = 72.013 (1)°
β = 77.019 (1)°
γ = 86.546 (1)°
V = 946.47 (8) Å^3
Z = 4
D_x = 1.279 Mg m^{-3}
D_m = 1.26 (1) Mg m^{-3}
D_m measured by flotation in cyclohexane/CCl$_4$

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 4280 reflections
θ = 1.8–25.0°
μ = 0.093 mm^{-1}
T = 123 (2) K
Prism
0.40 × 0.30 × 0.28 mm
Colorless

Data collection

Siemens SMART CCD diffractometer
10 s per frame, 1321 frames, 0.3° ω oscillation scans
Absorption correction: none
5796 measured reflections
4161 independent reflections
3710 reflections with $I > 2\sigma(I)$

R_{int} = 0.025
θ_{max} = 28.23°
h = −9 → 9
k = −14 → 14
l = −1 → 16
Intensity decay: negligible

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.137
S = 1.07
4161 reflections
381 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0615P)^2 + 0.3444P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.275 e Å^{-3}
$\Delta\rho_{min}$ = −0.342 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 3. *Selected geometric parameters (Å, °) for (II)*

O1D—C2D	1.195 (5)	O3L—C10D	1.350 (10)
O1L—C2D	1.26 (2)	O1L'—C2L'	1.216 (8)
O2D—C10D	1.189 (10)	O1D'—C2L'	1.183 (9)
O3D—C10D	1.288 (6)	O2L'—C10L'	1.255 (2)
O2L—C10D	1.194 (8)	O3L'—C10L'	1.245 (2)
O2D—C10D—C1D	120.5 (5)	O3L'—C10L'—C1L'	132.46 (19)
O3D—C10D—C1D	116.6 (3)	O2L'—C10L'—C1L'	103.78 (19)
O2L—C10D—C1L	133.7 (4)	O3L'—C10L'—C1D'	102.8 (2)
O3L—C10D—C1L	98.8 (5)	O2L'—C10L'—C1D'	133.3 (2)

Table 4. *Hydrogen-bonding for (II) (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
O3D—H3D···O2D^i	0.84	1.81	2.636 (11)	167
O3L—H3L···O2L^i	0.84	1.84	2.650 (12)	163
O3L'—H3L'···O2L'^{iii}	0.84	1.84	2.653 (2)	164
O2L'—H2L'···O3L'^{iii}	0.84	1.82	2.653 (2)	169

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

For (I), of the unique data, there were 1448 Friedel pairs; these were not merged. All non-carboxyl H atoms, although found in electron-density difference maps, were replaced in calculated positions and allowed to refine as riding models on their appropriate C atoms. Methyl groups were allowed to rotate freely. The displacement parameters of the methine, methylene and methyl H atoms on both (I) and (I') were refined as groups. The disordered carboxyl H atoms were found in electron-density difference maps but replaced in calculated positions with occupancies fixed at 50%; their isotropic displacement parameters were allowed to refine as a group.

For (II), atoms C2D, C4D, C8D and C10D were unresolvable from the enantiomeric couple and were assigned full occupancy. The occupancies of O1D, C1D, C3D, C5D, C6D, C7D and C9D were refined as a group, leading to a group occupancy of 76%. The site occupancies for atoms O1L, C1L, C3L, C5L, C6L, C7L and C9L of the antipode were refined such that the total site occupancy for D/L pairs summed to unity. Rotational disorder of the carboxyl group for (II) was initially apparent as both high anisotropy and residual electron density around the O atoms when modeled as a single rotamer. New O-atom positions were located at the areas of highest residual electron density and assigned occupancies of 50%, with displacement parameters initially fixed at 0.08 Å^2. Refinement of positional parameters led to a partial ordering of the carboxyl bond lengths, and half-H atoms were added in calculated positions to those O atoms with the longer C—O distance. The displacement parameters of the O atoms were then allowed to refine, first isotropically and then anisotropically. Attempts to refine O-atom occupancies for the carboxyl rotamers resulted in a high correlation with the displacement parameters and so occupancies were fixed at 50%.

For (II'), atoms C2L', C3L', C8L' and C10L' were unresolvable from the enantiomeric couple and were assigned full occupancy. The occupancies of O1L', C1L', C4L', C5L', C6L', C7L' and C9L' were refined as a group, leading to a group occupancy of 54%. The site occupancies for atoms O1D', C1D', C4D', C5D', C6D', C7D' and C9D' of the antipode were refined such that the total site occupancy for D/L pairs summed to unity. The carboxyl group was found to be disordered but no significant residual electron density was apparent in the difference maps. Disordered carboxyl H atoms were apparent in the difference maps and were added in calculated positions at 50% occupancy.

For both (II) and (II'), many H atoms were apparent in the difference maps but the calculated positions were used for refinement. Partial H atoms were added to resolvable C atoms with occupancies equal to those of the C atoms. For unresolvable C atoms, partial H atoms were added in the correct geometry to accord with the respective D or L framework and the occupancies set to the respective group occupancies. Isotropic displacement parameters for carboxyl and methyl H atoms were set to 1.5 times, and for methine and methylene H atoms were set to 1.2 times the equivalent isotropic displacement parameters of the atoms upon which they were riding.

Data collection: *XSCANS* (Siemens, 1996) for (I); *SMART* (Siemens, 1995) for (II). Cell refinement: *XSCANS* for (I); *SAINT* (Siemens, 1995) for (II). Data reduction: *XSCANS* for (I); *SAINT* for (II). For both compounds, program(s) used to solve structures: *SHELXS*97 (Sheldrick, 1997b); program(s) used to refine structures: *SHELXL*97 (Sheldrick, 1997a); molecular graphics: *SHELXL*97; software used to prepare material for publication: *SHELXL*97.

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(2S,SR)-*tert*-Butyl 2-(*p*-tolylsulfinylacetyl)-pyrrolidine-1-carboxylate†

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Abstract

The title compound, $C_{18}H_{25}NO_4S$, is the single adduct obtained from the reaction between the *N*-(*tert*-butoxy-

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