

(2*R*,3*R*)-2-[(4-Chlorophenyl)hydroxy-methyl]cyclopentanone

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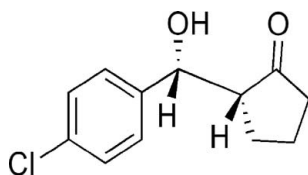
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Key indicators: single-crystal X-ray study; $T = 150$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.046; wR factor = 0.168; data-to-parameter ratio = 13.3.

The title compound, $\text{C}_{12}\text{H}_{13}\text{ClO}_2$, was prepared by the direct asymmetric intermolecular aldol reaction of cyclopentanone and 4-chlorobenzaldehyde catalysed by L-tryptophan in water. The absolute molecular structure was determined to be a racemic twin with 91% (2*R*,3*R*) isomer and 9% of the (2*S*,3*S*) form. In the crystal structure, the molecules are connected into a one-dimensional chain along the a axis through the formation of intermolecular $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds. Further, non-conventional $\text{C}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\pi$ contacts are observed in the structure, which consolidate the crystal packing.

Related literature

For the structure of 2-[hydroxy(4-nitrophenyl)methyl]-4-methylcyclohexanone, see: Li (2007). For a structure with $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds, see: Nangia (2002). For a database study of $\text{C}-\text{H}\cdots\pi$ interactions in the conformation of peptides, see: Umezawa *et al.* (1999). For direct intermolecular aldol reactions catalysed by acyclic amino acids, see: Córdova *et al.* (2006); Deng & Cai (2007). For asymmetric direct aldol reaction assisted by water and a proline-derived tetrazole catalyst, see: Torii *et al.* (2004). For the development of direct catalytic asymmetric aldol, Mannich, Michael and Diels–Alder reactions, see: Notz *et al.* (2004).



Experimental

Crystal data

$\text{C}_{12}\text{H}_{13}\text{ClO}_2$
 $M_r = 224.67$
 Orthorhombic, $P2_12_12_1$
 $a = 5.7401$ (1) Å
 $b = 10.4549$ (2) Å
 $c = 18.2135$ (3) Å
 $V = 1093.03$ (3) Å³
 $Z = 4$
 Cu $K\alpha$ radiation
 $\mu = 2.90$ mm⁻¹
 $T = 150$ (2) K
 $0.43 \times 0.31 \times 0.25$ mm

Data collection

Bruker APEXII CCD diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.336$, $T_{\max} = 0.484$
 3762 measured reflections
 1936 independent reflections
 1865 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.040$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.046$
 $wR(F^2) = 0.168$
 $S = 1.14$
 1936 reflections
 146 parameters
 H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.34$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.52$ e Å⁻³
 Absolute structure: Flack (1983), 572 Friedel pairs
 Flack parameter: 0.09 (3)

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O1}-\text{H1}\cdots\text{O2}^{\text{i}}$	0.92 (7)	1.89 (7)	2.793 (4)	165 (7)
$\text{C10}-\text{H10A}\cdots\text{O2}^{\text{ii}}$	0.99	2.53	3.328 (5)	138
$\text{C5}-\text{H5A}\cdots\text{Cg2}^{\text{iii}}$	0.95	2.96	3.818 (4)	150

Symmetry codes: (i) $x - \frac{1}{2}, -y + \frac{1}{2}, -z$; (ii) $x + \frac{1}{2}, -y + \frac{1}{2}, -z$; (iii) $-x, y + \frac{1}{2}, -z + \frac{1}{2}$. Cg2 is the centroid of the C1–C5, C12 ring.

Data collection: APEX2 (Bruker, 2004); cell refinement: SAINT (Bruker, 2004); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL and PLATON (Spek, 2003).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SI2143).

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supplementary materials

Acta Cryst. (2009). E65, o164-o165 [doi:10.1107/S160053680804261X]

(2*R*,3*R*)-2-[(4-Chlorophenyl)hydroxymethyl]cyclopentanone

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Comment

The direct asymmetric aldol reaction is one of the most important C—C bond-forming reactions (Notz *et al.*, 2004.). It is not surprising that a large number of catalysts and methods have been developed to achieve efficient adducts with high diastereo- and enantioselectivities (Córdova *et al.* 2006; Torii *et al.* 2004.). Our primary results demonstrating that acyclic amino acids could catalyze the direct stereoselective aldol reaction in water micelles (Deng & Cai, 2007). In this contribution, as an extension to our previous studies, we report the synthesis and crystal structure of the title compound.

In the title compound (Fig. 1.), the bond lengths and angles are within ranges as reported by Li (2007). The structural analysis reveals that the absolute molecular structure was a (2*R*, 3*R*)- isomer. The most striking feature of the title compound is the interesting arrangement of the title molecules, which connect each other to form a one-dimension chain along the *a* axis by intermolecular O—H...O hydrogen bonds (Fig. 2). Furthermore, the weak non-conventional intermolecular C—H... π contact is observed, in which C5—H5A is donor and the chlorophenyl ring Cg2 (C1, C2, C3, C4, C12, C5) is π acceptor (Umezawa *et al.*, 1999). This contact, with additional intermolecular C—H...O interactions (Nangia *et al.* 2002), further consolidate the crystal packing. Details of hydrogen bonds are given in Table 1.

Experimental

4-chlorobenzaldehyde (71 mm g, 0.5 mmol) and cyclopentanone (0.5 ml) was added to a solution of L-tryptophan (30.6 mg, 0.15 mmol) and pure water (0.5 ml) at room temperature. The mixture was stirred, monitored by TLC. The mixture was quenched with a saturated aqueous NaHCO₃ solution and extracted by ethyl acetate (3× ml). The resulting solvent was removed *in vacuo* to yield the crude product. Purification by silica gel chromatography using 100 ~200 mesh ZCX II eluted by hexane-ethyl acetate (3:1, *v/v*) gave the yellow solid (70 mg, yield 63%). The crystalline compound was obtained through the slow volatilization of ethyl acetate containing the title compound.

Refinement

All H atoms were positioned geometrically and treated as riding, with C—H bond lengths constrained to 0.95 Å (aromatic CH), 0.99 Å (methylene CH₂), or 0.92 Å (hydroxy), and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{methylene C})$. Moreover, the Flack parameter was refined as 0.09 (3) and indicates a possible racemic twin of about 10%. This may be because the number of measured Friedel pairs is relatively low. 572 Friedel pairs were measured, which is a fraction of measured Friedel pairs of 0.419, as indicated in the check.cif of *PLATON* (Spek, 2003).

Figures

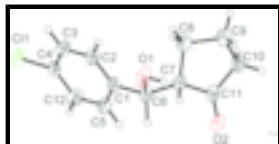


Fig. 1. View of the title molecular structure with atom numbering scheme and 30% probability displacement ellipsoids for non-hydrogen atoms.

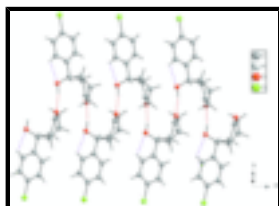


Fig. 2. View of the one-dimension chain along the *a* axis by intermolecular O—H...O hydrogen bonds.

(2*R*,3*R*)-2-[(4-Chlorophenyl)hydroxymethyl]cyclopentanone

Crystal data

$C_{12}H_{13}ClO_2$

$M_r = 224.67$

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Hall symbol: P 2ac 2ab

$a = 5.7401$ (1) Å

$b = 10.4549$ (2) Å

$c = 18.2135$ (3) Å

$V = 1093.03$ (3) Å³

$Z = 4$

$F_{000} = 472$

$D_x = 1.365$ Mg m⁻³

Cu $K\alpha$ radiation

$\lambda = 1.54178$ Å

Cell parameters from 2189 reflections

$\theta = 4.9$ – 76.7°

$\mu = 2.90$ mm⁻¹

$T = 150$ (2) K

Block, colorless

$0.43 \times 0.31 \times 0.25$ mm

Data collection

Bruker APEXII CCD
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 150$ (2) K

φ and ω scans

Absorption correction: multi-scan
(SADABS; Sheldrick, 1996)

$T_{\min} = 0.336$, $T_{\max} = 0.484$

3762 measured reflections

1936 independent reflections

1865 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.040$

$\theta_{\max} = 76.7^\circ$

$\theta_{\min} = 4.9^\circ$

$h = -7 \rightarrow 5$

$k = -9 \rightarrow 12$

$l = -22 \rightarrow 17$

Refinement

Refinement on F^2

Least-squares matrix: full

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$R[F^2 > 2\sigma(F^2)] = 0.046$	$w = 1/[\sigma^2(F_o^2) + (0.0962P)^2 + 1.0311P]$
$wR(F^2) = 0.168$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.14$	$(\Delta/\sigma)_{\max} < 0.001$
1936 reflections	$\Delta\rho_{\max} = 0.34 \text{ e } \text{\AA}^{-3}$
146 parameters	$\Delta\rho_{\min} = -0.52 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Extinction correction: none
Secondary atom site location: difference Fourier map	Absolute structure: Flack (1983), 572 Friedel pairs
	Flack parameter: 0.09 (3)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.0477 (5)	0.4383 (3)	0.06246 (17)	0.0418 (7)
O2	0.5454 (4)	0.3133 (2)	-0.01098 (14)	0.0355 (6)
C3	-0.0344 (7)	0.7839 (4)	0.1635 (2)	0.0361 (8)
H3A	-0.1615	0.7951	0.1962	0.043*
C11	0.5311 (6)	0.3306 (3)	0.0549 (2)	0.0303 (7)
C2	0.0105 (6)	0.6644 (3)	0.1340 (2)	0.0324 (7)
H2A	-0.0858	0.5940	0.1469	0.039*
C6	0.2476 (6)	0.5168 (3)	0.05323 (19)	0.0291 (7)
H6A	0.283 (8)	0.528 (4)	-0.005 (2)	0.035*
C10	0.5749 (7)	0.2346 (3)	0.1141 (2)	0.0388 (8)
H10A	0.7174	0.1845	0.1036	0.047*
H10B	0.4415	0.1751	0.1188	0.047*
C12	0.2900 (8)	0.8713 (4)	0.0969 (2)	0.0423 (9)
H12A	0.3851	0.9420	0.0837	0.051*
C5	0.3327 (7)	0.7509 (3)	0.0683 (2)	0.0373 (8)
H5A	0.4601	0.7397	0.0356	0.045*
C1	0.1955 (6)	0.6465 (3)	0.08574 (18)	0.0288 (7)
C7	0.4634 (6)	0.4583 (4)	0.08953 (19)	0.0322 (7)
H7A	0.595 (8)	0.518 (5)	0.075 (2)	0.039*
C4	0.1048 (6)	0.8865 (3)	0.1455 (2)	0.0330 (7)
C9	0.6046 (7)	0.3132 (4)	0.1835 (2)	0.0443 (9)
H9A	0.7683	0.3411	0.1894	0.053*
H9B	0.5573	0.2637	0.2273	0.053*

supplementary materials

C8	0.4435 (8)	0.4280 (4)	0.1717 (2)	0.0415 (9)
H8A	0.4946	0.5019	0.2017	0.050*
H8B	0.2810	0.4063	0.1850	0.050*
C11	0.05251 (19)	1.03468 (8)	0.18560 (5)	0.0445 (3)
H1	0.075 (14)	0.358 (6)	0.044 (4)	0.08 (2)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0210 (11)	0.0328 (14)	0.0716 (18)	-0.0039 (11)	0.0011 (12)	-0.0157 (13)
O2	0.0268 (11)	0.0352 (13)	0.0444 (13)	0.0035 (11)	0.0001 (11)	-0.0124 (10)
C3	0.0272 (15)	0.042 (2)	0.0396 (17)	0.0004 (16)	0.0043 (14)	-0.0058 (15)
C11	0.0170 (13)	0.0257 (16)	0.0481 (18)	-0.0006 (13)	-0.0004 (13)	-0.0017 (13)
C2	0.0253 (15)	0.0308 (17)	0.0410 (17)	-0.0021 (13)	0.0015 (13)	-0.0030 (14)
C6	0.0192 (13)	0.0277 (17)	0.0403 (17)	-0.0022 (13)	-0.0007 (12)	-0.0057 (14)
C10	0.0382 (19)	0.0217 (16)	0.056 (2)	0.0033 (15)	0.0023 (17)	0.0028 (15)
C12	0.042 (2)	0.035 (2)	0.050 (2)	-0.0024 (17)	0.0116 (18)	0.0000 (17)
C5	0.0322 (17)	0.0246 (17)	0.055 (2)	-0.0013 (14)	0.0142 (17)	-0.0003 (16)
C1	0.0244 (14)	0.0285 (17)	0.0334 (16)	0.0043 (13)	-0.0034 (13)	-0.0020 (13)
C7	0.0235 (14)	0.0342 (18)	0.0388 (16)	0.0018 (16)	-0.0015 (13)	-0.0035 (14)
C4	0.0350 (17)	0.0255 (16)	0.0384 (16)	0.0065 (14)	0.0005 (14)	0.0027 (13)
C9	0.0403 (19)	0.046 (2)	0.047 (2)	0.0113 (18)	-0.0042 (17)	0.0053 (18)
C8	0.0411 (19)	0.044 (2)	0.0390 (17)	0.0109 (18)	-0.0030 (16)	-0.0057 (15)
C11	0.0542 (6)	0.0270 (4)	0.0522 (5)	0.0076 (4)	0.0046 (4)	-0.0052 (3)

Geometric parameters (\AA , $^\circ$)

O1—C6	1.420 (4)	C10—H10B	0.9900
O1—H1	0.92 (7)	C12—C5	1.384 (6)
O2—C11	1.216 (4)	C12—C4	1.392 (5)
C3—C4	1.378 (5)	C12—H12A	0.9500
C3—C2	1.384 (5)	C5—C1	1.383 (5)
C3—H3A	0.9500	C5—H5A	0.9500
C11—C10	1.494 (5)	C7—C8	1.534 (5)
C11—C7	1.528 (5)	C7—H7A	1.01 (5)
C2—C1	1.392 (5)	C4—C11	1.739 (4)
C2—H2A	0.9500	C9—C8	1.530 (5)
C6—C1	1.510 (5)	C9—H9A	0.9900
C6—C7	1.531 (5)	C9—H9B	0.9900
C6—H6A	1.08 (4)	C8—H8A	0.9900
C10—C9	1.517 (6)	C8—H8B	0.9900
C10—H10A	0.9900		
C6—O1—H1	111 (5)	C1—C5—H5A	119.0
C4—C3—C2	120.2 (3)	C12—C5—H5A	119.0
C4—C3—H3A	119.9	C5—C1—C2	118.3 (3)
C2—C3—H3A	119.9	C5—C1—C6	120.4 (3)
O2—C11—C10	126.9 (3)	C2—C1—C6	121.3 (3)
O2—C11—C7	123.7 (3)	C11—C7—C6	112.1 (3)

C10—C11—C7	109.3 (3)	C11—C7—C8	104.0 (3)
C3—C2—C1	120.5 (3)	C6—C7—C8	116.3 (3)
C3—C2—H2A	119.7	C11—C7—H7A	104 (3)
C1—C2—H2A	119.7	C6—C7—H7A	104 (3)
O1—C6—C1	108.2 (3)	C8—C7—H7A	115 (2)
O1—C6—C7	111.8 (3)	C3—C4—C12	120.3 (3)
C1—C6—C7	110.4 (3)	C3—C4—C11	119.6 (3)
O1—C6—H6A	109 (2)	C12—C4—C11	120.1 (3)
C1—C6—H6A	109 (2)	C10—C9—C8	103.9 (3)
C7—C6—H6A	108 (2)	C10—C9—H9A	111.0
C11—C10—C9	104.9 (3)	C8—C9—H9A	111.0
C11—C10—H10A	110.8	C10—C9—H9B	111.0
C9—C10—H10A	110.8	C8—C9—H9B	111.0
C11—C10—H10B	110.8	H9A—C9—H9B	109.0
C9—C10—H10B	110.8	C9—C8—C7	104.7 (3)
H10A—C10—H10B	108.8	C9—C8—H8A	110.8
C5—C12—C4	118.6 (4)	C7—C8—H8A	110.8
C5—C12—H12A	120.7	C9—C8—H8B	110.8
C4—C12—H12A	120.7	C7—C8—H8B	110.8
C1—C5—C12	122.0 (3)	H8A—C8—H8B	108.9
C4—C3—C2—C1	-0.3 (5)	O2—C11—C7—C8	173.9 (4)
O2—C11—C10—C9	163.5 (4)	C10—C11—C7—C8	-6.1 (4)
C7—C11—C10—C9	-16.5 (4)	O1—C6—C7—C11	63.0 (4)
C4—C12—C5—C1	0.8 (7)	C1—C6—C7—C11	-176.4 (3)
C12—C5—C1—C2	-0.4 (6)	O1—C6—C7—C8	-56.5 (4)
C12—C5—C1—C6	179.9 (4)	C1—C6—C7—C8	64.1 (4)
C3—C2—C1—C5	0.1 (5)	C2—C3—C4—C12	0.7 (6)
C3—C2—C1—C6	179.8 (3)	C2—C3—C4—C11	-177.7 (3)
O1—C6—C1—C5	-163.3 (3)	C5—C12—C4—C3	-1.0 (6)
C7—C6—C1—C5	74.0 (4)	C5—C12—C4—C11	177.4 (3)
O1—C6—C1—C2	17.0 (4)	C11—C10—C9—C8	32.5 (4)
C7—C6—C1—C2	-105.7 (4)	C10—C9—C8—C7	-36.6 (4)
O2—C11—C7—C6	47.5 (4)	C11—C7—C8—C9	26.1 (4)
C10—C11—C7—C6	-132.5 (3)	C6—C7—C8—C9	149.8 (3)

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1 \cdots O2 ⁱ	0.92 (7)	1.89 (7)	2.793 (4)	165 (7)
C10—H10A \cdots O2 ⁱⁱ	0.99	2.53	3.328 (5)	138
C5—H5A \cdots Cg2 ⁱⁱⁱ	0.95	2.96	3.818 (4)	150

Symmetry codes: (i) $x-1/2, -y+1/2, -z$; (ii) $x+1/2, -y+1/2, -z$; (iii) $-x, y+3/2, -z+1/2$.

Fig. 1

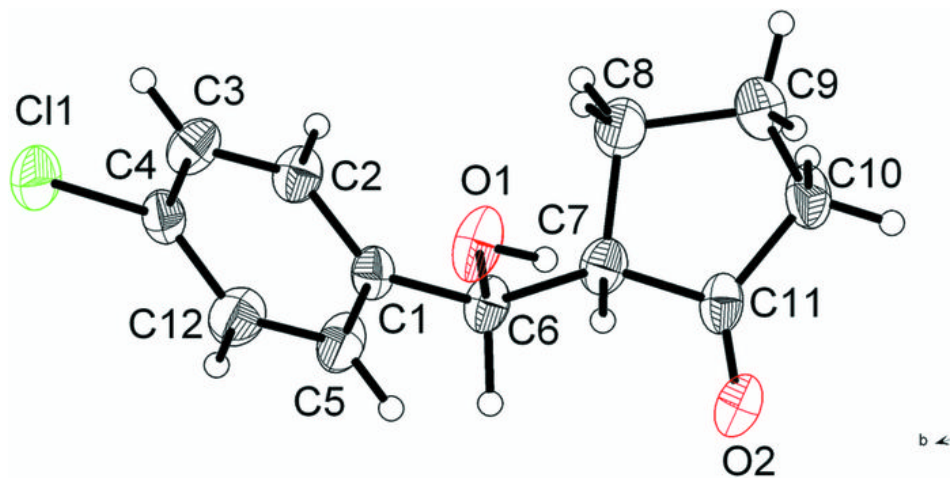


Fig. 2

