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2,6-Dimethyl-4-*m*-tolylcyclohex-3-enecarboxylic acid

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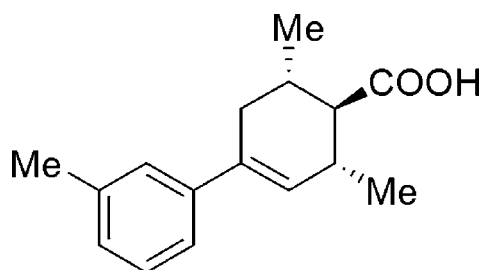
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 Key indicators: single-crystal X-ray study; $T = 150$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.049; wR factor = 0.137; data-to-parameter ratio = 18.4.

The title compound, $\text{C}_{16}\text{H}_{20}\text{O}_2$, was synthesized to study the hydrogen-bonding interaction of the two enantiomers in the solid state. The racemate is made up of carboxylic acid *RS* dimers. Intermolecular $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds produce centrosymmetric $R_2^2(8)$ rings which dimerize the two chiral enantiomers through their carboxyl groups. The chirality of this compound is generated by the presence of the double bond in the cyclohexene ring and a chiral axis due to the *meta*-methyl substituent on the aromatic ring.

Related literature

In similar compounds previously reported (Xie *et al.*, 2002, 2007*a*, 2008), the racemates also consist of carboxylic acid *RS* dimers. For related literature, see: Xie *et al.* (2007*b*, 2004); Bernstein *et al.* (1995).



Experimental

Crystal data

 $\text{C}_{16}\text{H}_{20}\text{O}_2$
 $M_r = 244.32$

 Orthorhombic, *Pbca*
 $a = 11.2581$ (10) Å

 $b = 8.1055$ (7) Å
 $c = 29.857$ (3) Å
 $V = 2724.5$ (4) Å³
 $Z = 8$

 Mo $K\alpha$ radiation
 $\mu = 0.08$ mm⁻¹
 $T = 150$ (2) K
 $0.20 \times 0.18 \times 0.05$ mm

Data collection

 Bruker Kappa APEXII
 diffractometer
 Absorption correction: multi-scan
 (*SADABS*; Sheldrick, 1996)
 $T_{\min} = 0.985$, $T_{\max} = 0.996$

 18515 measured reflections
 3120 independent reflections
 2265 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.043$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.049$
 $wR(F^2) = 0.136$
 $S = 1.03$
 3120 reflections
 170 parameters

 H atoms treated by a mixture of
 independent and constrained
 refinement
 $\Delta\rho_{\text{max}} = 0.50$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.20$ e Å⁻³

Table 1
 Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O1}-\text{H1O}\cdots\text{O2}^i$	1.05 (3)	1.62 (3)	2.6628 (18)	174 (3)

 Symmetry code: (i) $-x + 1, -y, -z + 1$.

Data collection: *APEX2* (Bruker, 2007); cell refinement: *S SAINT* (Bruker, 2007); data reduction: *S SAINT*; program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: OM2254).

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supplementary materials

Acta Cryst. (2008). E64, o1869 [doi:10.1107/S1600536808027542]

2,6-Dimethyl-4-*m*-tolylcyclohex-3-enecarboxylic acid

S. Xie, H. J. Stein and M. Pink

Comment

The title carboxylic acid was prepared to study the interaction of the two enantiomers in the solid state. We have previously reported the structure of its precursor, which is achiral and forms hydrogen-bonded dimers (Xie *et al.*, 2007*b*). The chirality of the title compound is generated by the presence of the double bond in the cyclohexene ring (Xie *et al.*, 2004). The resultant racemate is made up of carboxylic acid *RS* dimers (Xie *et al.*, 2002, 2007*a*, 2008). The structure and atom numbering are shown in Fig. 1, which illustrates the half-chair conformation of the cyclohexene ring. The torsion angles involving atoms C4, C5, C6, C1, and C2 are all near 180°, as are those involving atoms C13, C2, C3, C4, and C15. The carboxyl group is almost perpendicular to the cyclohexene ring with an angle of 86.5° between the O1—C14—O2 plane and the C1—C6 ring. The double bond between C5—C6 is not fully conjugated with the aromatic ring as shown by the C1—C6—C5 plane to benzene ring angle of 42.4°. Unlike other previously reported *para* substituted analogs, the molecule also has a chiral axis due to the *meta* methyl substituent on the aromatic ring.

Fig. 2 shows the hydrogen bonding scheme. Atom O1 acts as a donor in an intermolecular hydrogen bond to atom O2, producing an R₂²(8) ring (Bernstein *et al.*, 1995), thus creating a hydrogen-bonded dimer. There is no evidence to suggest that weak directional interactions interconnect the dimers. Hydrogen bond geometry is given in Table 1.

Experimental

The title carboxylic acid was synthesized following the similar method reported by Xie *et al.*, 2002. The purified compound was recrystallized from hexane-dichloromethane as colorless plates (m.p. 412–415 K).

Refinement

The hydrogen atoms not involved in hydrogen bonding were placed in idealized positions and refined as riding atoms with relative isotropic displacement parameters; they were positioned geometrically and refined using a riding model with C—H = 0.95 Å and $U_{\text{iso}}(\text{H}) = 1.2$ times $U_{\text{eq}}(\text{C})$. H1O was refined freely with individual displacement parameters.

Figures

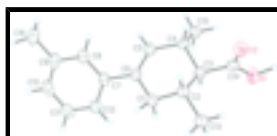


Fig. 1. The molecular structure and atom numbering scheme.

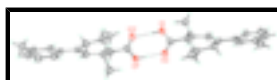


Fig. 2. Hydrogen bonded dimer. Dashed lines represent hydrogen bonds. [Symmetry code: #1 -x + 1, -y, -z + 1.]

2,6-Dimethyl-4-*m*-tolylcyclohex-3-enecarboxylic acid

Crystal data

$C_{16}H_{20}O_2$	$F_{000} = 1056$
$M_r = 244.32$	$D_x = 1.191 \text{ Mg m}^{-3}$
Orthorhombic, <i>Pbca</i>	Mo $K\alpha$ radiation
Hall symbol: -P 2ac 2ab	$\lambda = 0.71073 \text{ \AA}$
$a = 11.2581 (10) \text{ \AA}$	Cell parameters from 3951 reflections
$b = 8.1055 (7) \text{ \AA}$	$\theta = 3.2\text{--}25.9^\circ$
$c = 29.857 (3) \text{ \AA}$	$\mu = 0.08 \text{ mm}^{-1}$
$V = 2724.5 (4) \text{ \AA}^3$	$T = 150 (2) \text{ K}$
$Z = 8$	Plate, colorless
	$0.20 \times 0.18 \times 0.05 \text{ mm}$

Data collection

Bruker Kappa APEXII diffractometer	3120 independent reflections
Radiation source: fine-focus sealed tube	2265 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.043$
Detector resolution: $8.3 \text{ pixels mm}^{-1}$	$\theta_{\text{max}} = 27.5^\circ$
$T = 150(2) \text{ K}$	$\theta_{\text{min}} = 1.4^\circ$
ω and φ scans	$h = -14 \rightarrow 12$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$k = -10 \rightarrow 10$
$T_{\text{min}} = 0.985$, $T_{\text{max}} = 0.996$	$l = -38 \rightarrow 36$
18515 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.049$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.136$	$w = 1/[\sigma^2(F_o^2) + (0.066P)^2 + 0.9686P]$
$S = 1.03$	where $P = (F_o^2 + 2F_c^2)/3$
3120 reflections	$(\Delta/\sigma)_{\text{max}} < 0.001$
170 parameters	$\Delta\rho_{\text{max}} = 0.50 \text{ e \AA}^{-3}$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{\text{min}} = -0.19 \text{ e \AA}^{-3}$
	Extinction correction: none

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)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.47404 (12)	0.21830 (16)	0.50798 (4)	0.0403 (3)
H1O	0.477 (3)	0.103 (4)	0.5238 (11)	0.113 (11)*
O2	0.51225 (11)	0.06571 (15)	0.44750 (4)	0.0362 (3)
C1	0.56818 (15)	0.5618 (2)	0.38758 (6)	0.0333 (4)
H1A	0.5723	0.6504	0.4104	0.040*
H1B	0.6339	0.5799	0.3661	0.040*
C2	0.58687 (14)	0.3953 (2)	0.41086 (6)	0.0308 (4)
H2	0.5978	0.3087	0.3873	0.037*
C3	0.47402 (14)	0.3553 (2)	0.43738 (5)	0.0274 (4)
H3	0.4578	0.4494	0.4582	0.033*
C4	0.36497 (13)	0.3349 (2)	0.40608 (5)	0.0272 (3)
H4	0.3711	0.2262	0.3904	0.033*
C5	0.36254 (14)	0.4705 (2)	0.37130 (6)	0.0309 (4)
H5	0.2923	0.4822	0.3540	0.037*
C6	0.45258 (14)	0.57605 (19)	0.36300 (5)	0.0262 (3)
C7	0.43895 (13)	0.7170 (2)	0.33124 (5)	0.0282 (4)
C8	0.37328 (15)	0.7010 (2)	0.29151 (5)	0.0316 (4)
H8	0.3374	0.5979	0.2846	0.038*
C9	0.35932 (15)	0.8328 (2)	0.26180 (6)	0.0354 (4)
C10	0.41173 (16)	0.9834 (2)	0.27251 (7)	0.0413 (5)
H10	0.4038	1.0740	0.2525	0.050*
C11	0.47524 (17)	1.0027 (2)	0.31192 (7)	0.0421 (5)
H11	0.5088	1.1070	0.3191	0.051*
C12	0.49008 (15)	0.8706 (2)	0.34103 (6)	0.0351 (4)
H12	0.5351	0.8843	0.3677	0.042*
C13	0.69806 (14)	0.4001 (2)	0.43992 (6)	0.0360 (4)
H13A	0.7662	0.4336	0.4216	0.054*
H13B	0.7127	0.2903	0.4525	0.054*
H13C	0.6868	0.4795	0.4643	0.054*
C14	0.48878 (13)	0.2002 (2)	0.46525 (6)	0.0284 (4)
C15	0.25044 (15)	0.3372 (2)	0.43369 (6)	0.0333 (4)
H15A	0.1820	0.3237	0.4137	0.050*
H15B	0.2440	0.4427	0.4496	0.050*

supplementary materials

H15C	0.2520	0.2468	0.4555	0.050*
C16	0.2881 (2)	0.8129 (3)	0.21924 (6)	0.0483 (5)
H16A	0.2877	0.6965	0.2103	0.072*
H16B	0.3240	0.8793	0.1954	0.072*
H16C	0.2064	0.8500	0.2244	0.072*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0541 (8)	0.0364 (7)	0.0303 (7)	0.0076 (6)	0.0021 (6)	0.0048 (6)
O2	0.0399 (6)	0.0362 (7)	0.0327 (7)	0.0045 (5)	0.0002 (5)	0.0041 (5)
C1	0.0313 (8)	0.0340 (9)	0.0346 (9)	-0.0030 (7)	0.0007 (7)	0.0049 (7)
C2	0.0261 (8)	0.0334 (9)	0.0330 (9)	-0.0012 (6)	-0.0007 (7)	0.0037 (7)
C3	0.0260 (7)	0.0288 (8)	0.0273 (8)	0.0012 (6)	0.0000 (6)	0.0012 (7)
C4	0.0251 (7)	0.0273 (8)	0.0292 (8)	-0.0019 (6)	-0.0039 (6)	0.0038 (7)
C5	0.0287 (8)	0.0330 (9)	0.0310 (9)	0.0013 (6)	-0.0041 (7)	0.0052 (7)
C6	0.0298 (7)	0.0267 (8)	0.0222 (8)	0.0020 (6)	0.0022 (6)	-0.0003 (6)
C7	0.0275 (7)	0.0306 (8)	0.0264 (8)	0.0031 (6)	0.0068 (6)	0.0046 (7)
C8	0.0346 (8)	0.0319 (9)	0.0282 (8)	0.0042 (7)	0.0046 (7)	0.0032 (7)
C9	0.0339 (8)	0.0419 (10)	0.0305 (9)	0.0081 (7)	0.0059 (7)	0.0096 (8)
C10	0.0366 (9)	0.0398 (10)	0.0474 (11)	0.0026 (8)	0.0077 (8)	0.0184 (9)
C11	0.0384 (9)	0.0328 (9)	0.0551 (12)	-0.0057 (8)	0.0049 (9)	0.0107 (9)
C12	0.0329 (8)	0.0356 (9)	0.0368 (9)	-0.0041 (7)	0.0029 (7)	0.0054 (8)
C13	0.0257 (8)	0.0414 (10)	0.0410 (10)	-0.0020 (7)	-0.0027 (7)	0.0061 (8)
C14	0.0199 (7)	0.0289 (8)	0.0365 (9)	0.0000 (6)	-0.0029 (6)	0.0017 (7)
C15	0.0293 (8)	0.0363 (9)	0.0344 (9)	0.0007 (7)	-0.0020 (7)	0.0023 (7)
C16	0.0602 (12)	0.0509 (12)	0.0338 (10)	0.0090 (10)	-0.0029 (9)	0.0125 (9)

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

O1—C14	1.295 (2)	C7—C8	1.404 (2)
O1—H10	1.05 (3)	C8—C9	1.398 (2)
O2—C14	1.241 (2)	C8—H8	0.9500
C1—C6	1.499 (2)	C9—C10	1.393 (3)
C1—C2	1.533 (2)	C9—C16	1.511 (3)
C1—H1A	0.9900	C10—C11	1.386 (3)
C1—H1B	0.9900	C10—H10	0.9500
C2—C13	1.524 (2)	C11—C12	1.390 (3)
C2—C3	1.532 (2)	C11—H11	0.9500
C2—H2	1.0000	C12—H12	0.9500
C3—C14	1.517 (2)	C13—H13A	0.9800
C3—C4	1.552 (2)	C13—H13B	0.9800
C3—H3	1.0000	C13—H13C	0.9800
C4—C5	1.512 (2)	C15—H15A	0.9800
C4—C15	1.530 (2)	C15—H15B	0.9800
C4—H4	1.0000	C15—H15C	0.9800
C5—C6	1.349 (2)	C16—H16A	0.9800
C5—H5	0.9500	C16—H16B	0.9800
C6—C7	1.493 (2)	C16—H16C	0.9800

C7—C12	1.402 (2)		
C14—O1—H10	109.7 (18)	C9—C8—H8	119.2
C6—C1—C2	114.13 (13)	C7—C8—H8	119.2
C6—C1—H1A	108.7	C10—C9—C8	118.46 (16)
C2—C1—H1A	108.7	C10—C9—C16	120.77 (16)
C6—C1—H1B	108.7	C8—C9—C16	120.77 (17)
C2—C1—H1B	108.7	C11—C10—C9	120.85 (16)
H1A—C1—H1B	107.6	C11—C10—H10	119.6
C13—C2—C3	113.10 (14)	C9—C10—H10	119.6
C13—C2—C1	110.39 (14)	C10—C11—C12	120.39 (18)
C3—C2—C1	107.85 (13)	C10—C11—H11	119.8
C13—C2—H2	108.5	C12—C11—H11	119.8
C3—C2—H2	108.5	C11—C12—C7	120.30 (17)
C1—C2—H2	108.5	C11—C12—H12	119.9
C14—C3—C2	111.58 (13)	C7—C12—H12	119.9
C14—C3—C4	109.18 (13)	C2—C13—H13A	109.5
C2—C3—C4	111.55 (13)	C2—C13—H13B	109.5
C14—C3—H3	108.1	H13A—C13—H13B	109.5
C2—C3—H3	108.1	C2—C13—H13C	109.5
C4—C3—H3	108.1	H13A—C13—H13C	109.5
C5—C4—C15	110.23 (13)	H13B—C13—H13C	109.5
C5—C4—C3	110.51 (13)	O2—C14—O1	123.21 (15)
C15—C4—C3	109.93 (13)	O2—C14—C3	121.15 (15)
C5—C4—H4	108.7	O1—C14—C3	115.63 (15)
C15—C4—H4	108.7	C4—C15—H15A	109.5
C3—C4—H4	108.7	C4—C15—H15B	109.5
C6—C5—C4	124.97 (14)	H15A—C15—H15B	109.5
C6—C5—H5	117.5	C4—C15—H15C	109.5
C4—C5—H5	117.5	H15A—C15—H15C	109.5
C5—C6—C7	121.65 (14)	H15B—C15—H15C	109.5
C5—C6—C1	120.91 (14)	C9—C16—H16A	109.5
C7—C6—C1	117.33 (13)	C9—C16—H16B	109.5
C12—C7—C8	118.32 (15)	H16A—C16—H16B	109.5
C12—C7—C6	120.32 (15)	C9—C16—H16C	109.5
C8—C7—C6	121.34 (15)	H16A—C16—H16C	109.5
C9—C8—C7	121.65 (16)	H16B—C16—H16C	109.5
C6—C1—C2—C13	-172.47 (14)	C1—C6—C7—C12	-35.8 (2)
C6—C1—C2—C3	-48.44 (19)	C5—C6—C7—C8	-38.1 (2)
C13—C2—C3—C14	-52.09 (19)	C1—C6—C7—C8	145.50 (15)
C1—C2—C3—C14	-174.45 (14)	C12—C7—C8—C9	0.7 (2)
C13—C2—C3—C4	-174.51 (14)	C6—C7—C8—C9	179.46 (15)
C1—C2—C3—C4	63.12 (17)	C7—C8—C9—C10	-0.4 (2)
C14—C3—C4—C5	-168.20 (13)	C7—C8—C9—C16	-179.91 (16)
C2—C3—C4—C5	-44.41 (18)	C8—C9—C10—C11	-0.7 (3)
C14—C3—C4—C15	69.91 (17)	C16—C9—C10—C11	178.81 (18)
C2—C3—C4—C15	-166.30 (13)	C9—C10—C11—C12	1.5 (3)
C15—C4—C5—C6	133.15 (17)	C10—C11—C12—C7	-1.2 (3)
C3—C4—C5—C6	11.4 (2)	C8—C7—C12—C11	0.1 (2)

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C4—C5—C6—C7	-173.87 (15)	C6—C7—C12—C11	-178.63 (15)
C4—C5—C6—C1	2.4 (3)	C2—C3—C14—O2	-59.64 (19)
C2—C1—C6—C5	17.0 (2)	C4—C3—C14—O2	64.14 (18)
C2—C1—C6—C7	-166.55 (14)	C2—C3—C14—O1	121.08 (15)
C5—C6—C7—C12	140.62 (17)	C4—C3—C14—O1	-115.15 (15)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1O \cdots O2 ⁱ	1.05 (3)	1.62 (3)	2.6628 (18)	174 (3)

Symmetry codes: (i) $-x+1, -y, -z+1$.

Fig. 1

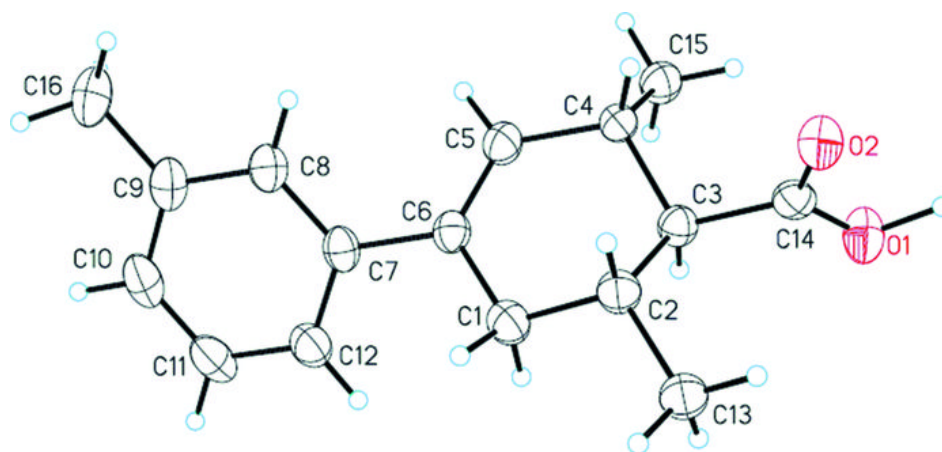


Fig. 2

