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(–)-Dimenthyl malonate

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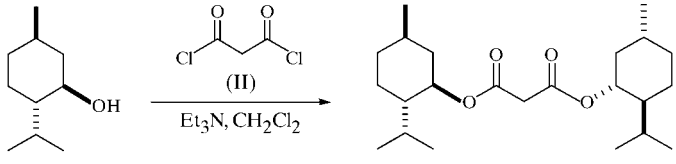
The title compound, bis(2-isopropyl-5-methylcyclohex-1-yl) malonate, $C_{23}H_{40}O_4$, crystallizes in the monoclinic space group $P2_1$. In the crystal, the molecule is not C_2 symmetric.

Comment

A large number of substituted malonic acid derivatives are known (Kanters & Kroon, 1972). Some attention has been focused on related keto (Adhikesavalu & Venkatesan, 1983) and aldehyde derivatives (Lundgren & Aurivillius, 1964), but little attention has been paid to the corresponding malonate ester derivatives. We were originally interested in the conformational preference of simple 1,3-dicarbonyl-containing molecules. To this aim, we synthesized the title C_2-symmetric dimenthyl malonate, (III), as our model compound. We chose enantiopure (−)-menthol, (I), as our ester scaffold, as this would lead directly to enantiopure C_2-symmetric (III) without contamination resulting from the formation of other stereoisomers. Addition of commercially available malonyl dichloride, (II), to a stirred solution of natural (−)-menthol and triethylamine in dichloromethane gave the required (−)-dimenthyl malonate, (III), as a cream-coloured precipitate in good yield (66%). The crude product was purified by flash column chromatography on silica gel, eluting with a light petroleum (313–333 K)–ether (19:1) mixture, and was then vapour recrystallized from hexane to give colourless needle-like crystals of (III).



(I) (III), 66%

X-ray diffraction of (III) revealed the structure illustrated in Fig. 1. The stereochemistry was assigned by reference to (−)-menthol. It was immediately evident that this molecule was not C_2 symmetric in its solid phase, due to the non-equivalence of the carbonyl groups, C1═O4 and C3═O3. By comparison, solution-phase NMR studies at room temperature are consistent with C_2 symmetry. We ascribe the conformation of this molecule in the crystal state to packing effects. The overall unit cell is pseudo-C_2-symmetric and contains two identical malonate molecules, as shown in Fig. 2.

The molecule is certainly not an enol derivative, with a C1—C2—C3 bond angle of 111.5 (5)° and not significantly different C1—C2 and C2—C3 bond lengths of 1.492 (7) and 1.497 (8) Å, respectively (Table 1). All the substituents on the cyclohexyl ring are in the expected equatorial positions.

The most striking structural feature is the relative conformation of both carbonyl groups, C1═O4 and C3═O3. They are clearly twisted away from each other, as shown by the torsion angles of 138.3 (6)° for O4—C1—C2—O3 and 102.6 (6)° for C1—C2—C3—O3. This is presumably due to a combination of hyperconjugation effects at C2—H with both

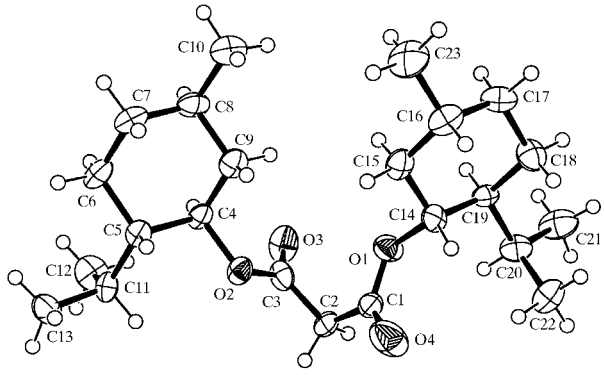


Figure 1
A view of the molecule of (III) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

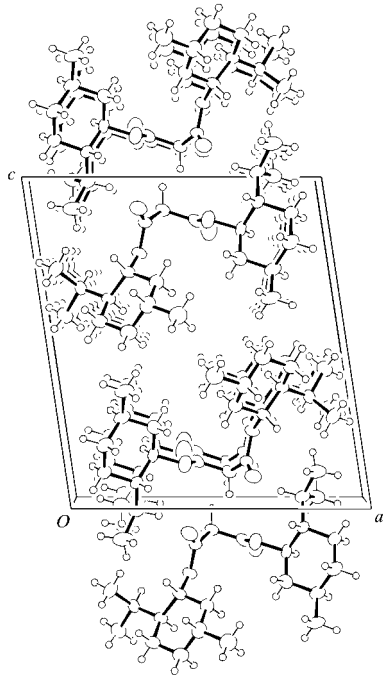


Figure 2
A packing diagram for (III), viewed along the *b* axis.

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carbonyl groups and a minimization of their relative dipole moments. This can also be seen in a related twist involving the other O atom in the ester motif, as shown by the torsion angles of −42.5 (6)° for O1—C1—C2—C3 and −73.4 (6)° for C1—C2—C3—O2. In contrast, both the ester groups strive for planarity [−9.5 (7)° for C4—O2—C3—O3 and −0.8 (8)° for C14—O1—C1—O4] through anomeric assistance (Table 1).

This type of antiparallel alignment has been reported in the structural arrangement of diimidazolines (Brennan & McKee, 1999), diones (Klein *et al.*, 1999) and related malonic acid derivatives (Kalsbeek, 1992). The effect of the non-equivalence of the menthyl groups is more interesting and can be seen more clearly by the non-equivalence of the ester groups. The C14—O1—C1—C2 torsion angle of the ester group is planar [−180.0 (4)°], whereas the related C4—O2—C3—C2 ester grouping certainly has a slight twist [166.6 (4)°] (Table 1). This is more than likely due to a combination of crystal-packing effects and the presence of a local pseudo-twofold axis (Table 2 and Fig. 2). This layer sequence is positioned in an *ABAB* system, with layer *B* oriented antiparallel to layer *A*.

Experimental

Malonyl dichloride (5.0 g, 3.45 ml, 35.5 mmol) was slowly added to a stirred solution of triethylamine (7.1 g, 9.90 ml, 70.9 mmol) and (−)-menthol (11.1 g, 70.9 mmol) in dichloromethane (100 ml), and the resulting solution was stirred for 1 h. The reaction was quenched slowly with water (30 ml) and the organic layer was extracted with diethyl ether (3 × 50 ml), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel, eluting with light petroleum (313–333 K)–ether (19:1) to give the title compound, (III) (9.0 g, 66%), as a light-cream solid. This solid was recrystallized using hexane to give colourless needle crystals (m.p. 327–328 K). Spectroscopic analysis: R_F [light petroleum (313–333 K)–ether (9:1)] 0.75; IR (ν_{max}, film, cm^{-1}): 1725 (CO); $[\alpha]_D$ −83.7 (*c* 2.7 in acetone); ^{1}H NMR (250 MHz, $CDCl_3$, δ, p.p.m.): 4.8 (2H, *td*, *J* = 10.8 and 4.4 Hz, CHO), 3.36 (2H, *s*, CH_2CO), 2.15–0.85 (18H, *m*, 6 × CH_2 and 6 × CH), 1.1–0.95 (6H, *m*, 2 × CH_3), 0.85 (3H, *d*, *J* = 7.0 Hz, $CHCH_3$); ^{13}C NMR (67 MHz, $CDCl_3$, δ, p.p.m.): 166.2, 75.5, 46.9, 42.4, 40.7, 34.2, 31.4, 26.1, 23.4, 22.0, 20.8, 16.3; analysis found: M^+ 381.3017; $C_{23}H_{41}O_4$ requires M^+ 381.3005; MS (*m*/*z*): 381 (80%, *M*), 243 (100, $M - C_{10}H_{18}$).

Crystal data

$C_{23}H_{40}O_4$
M_r = 380.55
Monoclinic, $P2_1$
a = 12.990 (2) Å
b = 6.092 (3) Å
c = 14.528 (2) Å
β = 98.55 (2)°
V = 1136.9 (6) Å^3
Z = 2
D_x = 1.112 Mg m^{-3}
Mo *K*α radiation
Cell parameters from 25 reflections
θ = 8.6–13.4°
μ = 0.07 mm^{-1}
T = 180 (2) K
Needle, colourless
0.4 × 0.2 × 0.2 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Non-profiled $\omega/2\theta$ scans
2285 measured reflections
2194 independent reflections
1234 reflections with $I > 2\sigma(I)$
R_{int} = 0.049
θ_{max} = 25°
$h = -15 \rightarrow 15$
$k = 0 \rightarrow 7$
$l = 0 \rightarrow 17$
2 standard reflections
frequency: 60 min
intensity decay: 7%

Table 1
Selected geometric parameters (Å, °).

C1—C2	1.492 (7)	C2—C3	1.497 (8)
C14—O1—C1—O4	−0.8 (8)	C4—O2—C3—O3	−9.5 (7)
C14—O1—C1—C2	−180.0 (4)	C4—O2—C3—C2	166.6 (4)
O4—C1—C2—C3	138.3 (6)	C1—C2—C3—O3	102.6 (6)
O1—C1—C2—C3	−42.5 (6)	C1—C2—C3—O2	−73.4 (6)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C15—H15*B*···O4^{i}	0.99	2.44	3.374 (8)	157
C20—H20···O3^{ii}	1.00	2.54	3.351 (7)	138

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

Refinement

Refinement on F^2
$R(F)$ = 0.058
$wR(F^2)$ = 0.163
S = 0.93
2194 reflections
251 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.096P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.003
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

H atoms were placed in geometrical positions, with C—H = 0.98–1.0 Å. U_{iso} values were refined for the H atoms on C2; all other H atoms were treated as riding, with U_{iso}(H) = 1.2 or 1.5U_{eq}(C).

Data collection: *CAD*-4-*PC Software* (Enraf–Nonius, 1994); cell refinement: *CAD*-4-*PC Software*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1538). Services for accessing these data are described at the back of the journal.

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