Monoclinic
$P2_1/c$
$a = 6.3603$ (1) Å
$b = 17.8106$ (3) Å
$c = 9.3363$ (1) Å
$\beta = 99.036$ (1)°
$V = 1044.50$ (3) Å^3
$Z = 2$
$D_x = 1.274$ Mg m^{-3}

Cell parameters from 4336 reflections
$\theta = 1$–25°
$\mu = 0.301$ mm^{-1}
$T = 143$ K
Plate
0.40 × 0.20 × 0.05 mm
Colourless

Data collection

Siemens CCD three-circle diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996*a*)
$T_{\min} = 0.874$, $T_{\max} = 1.000$
13687 measured reflections
2122 independent reflections

1531 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.082$
$\theta_{\max} = 26.43°$
$h = -7 \rightarrow 7$
$k = -19 \rightarrow 21$
$l = -11 \rightarrow 11$
130 standard reflections frequency: 600 min intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.123$
$S = 1.048$
2122 reflections
108 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0438P)^2 + 1.5197P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.460$ e Å^{-3}
$\Delta\rho_{\min} = -0.394$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

The data collection nominally covered a sphere of reciprocal space, by a combination of eight, for (I), and seven, for (II), sets of exposures; each set had a different φ angle for the crystal and each exposure covered 0.3° in ω. The crystal-to-detector distance was 5.95 cm. Coverage of the unique set is over 99% complete to at least 26° in θ. Crystal decay was monitored by repeating the initial frames at the end of data collection and analyzing the duplicate reflections. The data were corrected for Lorentz and polarization effects. All H atoms were located by difference Fourier synthesis and refined with fixed individual displacement parameters [U(H) = 1.2$U_{\rm eq}$(C)] using a riding model with C—H(aromatic) = 0.95 and C—H(secondary) = 0.99 Å.

For both compounds, data collection: *SMART* (Siemens, 1995); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structures: *SHELXS*96 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*96 (Sheldrick, 1996*b*); molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 1991).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1227). Services for accessing these data are described at the back of the journal.

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A Tetragonal-Looking But Twinned Orthorhombic Structure

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Abstract

2,2′-Methylenebis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-one), $C_{17}H_{24}O_4$, forms crystals which appear tetragonal, but are actually orthorhombic. They are twinned on (110). The asymmetric unit consists of two very similar molecules, each with exact crystallographic C_2 symmetry. Each molecule forms two strong intramolecular hydrogen bonds connecting the two cyclohexenone rings.

Comment

Recently we determined the crystal structure of (1) (see Scheme), which appeared to be twinned (Bolte, Degen & Rühl, 1997). The title compound, (2), was synthesized in order to compare it with (1) and to find out whether it was similarly twinned. The two independent half molecules in the asymmetric unit of (2) are very similar in geometry; a least-squares fit of all non-H atoms shows

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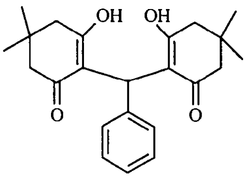
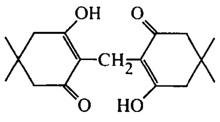
an r.m.s.d. of 0.097 Å. The cyclohexenone rings display envelope conformations [$q2$ = 0.394, $\varphi2$ = 181.6, $q3$ = −0.234 and $q2$ = 0.400, $\varphi2$ = 179.0, $q3$ = −0.230 (Cremer & Pople, 1975) for (1) and (2), respectively]. The two cyclohexenone rings of each molecule are connected by two strong hydrogen bonds [H16···O12^{i} 1.80 (3) Å, O16—H16···O12^{i} 164 (2)° and O16···O12^{i} 2.644 (2) Å; H26···O22^{ii} 1.60 (3) Å, O26—H26···O22^{ii} 169 (2)° and O26···O22^{ii} 2.636 (2) Å; symmetry codes: (i) $\frac{1}{2}-x$, $\frac{3}{2}-y$, z; (ii) $\frac{1}{2}-x$, $\frac{1}{2}-y$, z] so that two additional eight-membered rings are formed. The geometrical parameters of the moieties O12—C12—C11—C16—O16 and O22—C22—C21—C26—O26 indicate that each of these is a conjugated π system. No significant intermolecular contacts can be found.



(1)



(2)

The geometry of (2) is also very similar to that of (1) (Bolte *et al.*, 1997) except that in (2) the angles C11—C1—C11^{i} and C21—C2—C21^{ii} of 115.8 (2) and 116.6 (2)°, respectively, are slightly wider than the corresponding angles in (1) [114.0 (1) and 113.0 (1)°]; this difference is obviously due to the steric effect of the phenyl ring in (1). While in (1) the apex of one of the four cyclohexenone rings is bent upwards away from the phenyl ring, in (2) all the apices are bent downwards to the methylenic H atoms at C1 or C2.

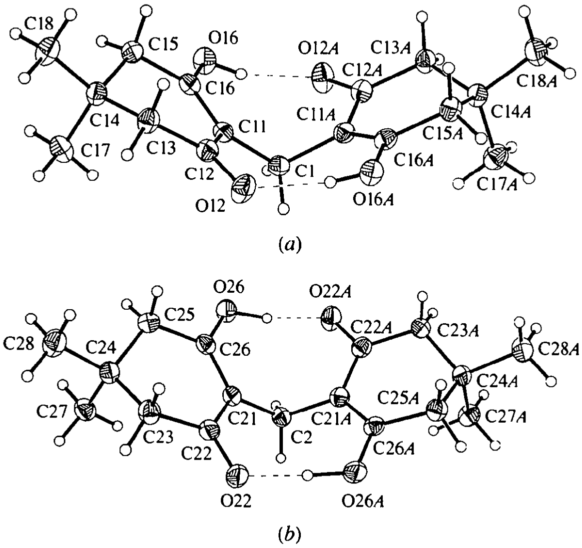


Fig. 1. Perspective views of (*a*) molecule 1 and (*b*) molecule 2 with the atom numbering. Displacement ellipsoids are drawn at the 50% probability level.

Experimental

Compound (2) was obtained by mixing a solution of 0.6 g (4.3 mmol) 5,5-dimethyl-1,3-cyclohexanedione in 8 ml 50% ethanol with 0.2 ml (2 mmol) formaldehyde. After addition of a catalytic quantity of piperidine, the reaction mixture was heated to boiling. After 10 min of reflux, the solution was cooled to 273 K. The white crystalline solid which formed was collected by filtration. The crude product was purified by recrystallization from ethanol–water (1:1). Suitable crystals were obtained by slow evaporation of a diethyl ether solution.

Crystal data

$C_{17}H_{24}O_4$
M_r = 292.36
Orthorhombic
Pccn
a = 18.9237 (2) Å
b = 18.9167 (2) Å
c = 8.7226 (1) Å
V = 3122.46 (6) Å^3
Z = 8
D_x = 1.244 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 8192 reflections
θ = 1–25°
μ = 0.087 mm^{-1}
T = 143 K
Block
0.80 × 0.70 × 0.50 mm
Colourless

Data collection

Siemens CCD three-circle diffractometer
ω scans
Absorption correction: empirical ψ scans (*SADABS*; Sheldrick, 1996*a*)
$T_{\min}$ = 0.824, $T_{\max}$ = 1.000
40539 measured reflections
3218 independent reflections

3077 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.036
$\theta_{\max}$ = 26.47°
$h = -23 \rightarrow 22$
$k = -23 \rightarrow 23$
$l = -10 \rightarrow 10$
863 standard reflections frequency: 540 min intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.092
S = 1.062
3218 reflections
201 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0537P)^2 + 0.709P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.001

$\Delta\rho_{\max}$ = 0.260 e Å^{-3}
$\Delta\rho_{\min}$ = −0.162 e Å^{-3}
Extinction correction: *SHELXL*96 (Sheldrick, 1996*b*)
Extinction coefficient: 0.0068 (8)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
C1	1/4	3/4	0.1921 (2)	0.0213 (4)
C11	0.19170 (7)	0.78464 (7)	0.09970 (15)	0.0198 (3)
C12	0.19733 (8)	0.85886 (7)	0.06655 (17)	0.0223 (3)
O12	0.25218 (6)	0.89292 (6)	0.09864 (14)	0.0308 (3)
C13	0.13820 (8)	0.89644 (8)	−0.01624 (19)	0.0235 (3)
C14	0.06546 (9)	0.86025 (9)	−0.00462 (17)	0.0224 (3)
C15	0.07568 (8)	0.78157 (8)	−0.04274 (17)	0.0232 (3)
C16	0.13544 (7)	0.74778 (8)	0.04239 (16)	0.0211 (3)

O16	0.12907 (6)	0.67770 (5)	0.05336 (13)	0.0268 (3)
C17	0.03518 (8)	0.86878 (8)	0.15669 (18)	0.0288 (4)
C18	0.01514 (8)	0.89366 (8)	−0.1213 (2)	0.0304 (3)
C2	1/4	1/4	0.6847 (2)	0.0227 (4)
C21	0.28394 (7)	0.30885 (7)	0.59361 (16)	0.0215 (3)
C22	0.35723 (8)	0.30388 (8)	0.55471 (17)	0.0239 (3)
O22	0.39212 (6)	0.24824 (6)	0.58010 (15)	0.0335 (3)
C23	0.39409 (8)	0.36404 (8)	0.4753 (2)	0.0255 (4)
C24	0.35912 (9)	0.43620 (9)	0.49982 (17)	0.0233 (3)
C25	0.27962 (8)	0.42880 (8)	0.46599 (18)	0.0251 (3)
C26	0.24608 (8)	0.36683 (8)	0.54397 (17)	0.0221 (3)
O26	0.17696 (6)	0.37239 (6)	0.56006 (14)	0.0293 (3)
C27	0.37060 (8)	0.46200 (8)	0.66484 (18)	0.0289 (4)
C28	0.39077 (9)	0.49060 (9)	0.3884 (2)	0.0327 (4)

The data collection nominally covered over a sphere of reciprocal space, by a combination of six sets of exposures; each set had a different φ angle for the crystal and each exposure covered 0.3° in ω. The crystal-to-detector distance was 6.0 cm. Coverage of the unique set was over 99% complete to at least 26° in θ. Crystal decay was monitored by repeating the initial frames at the end of data collection and analyzing the duplicate reflections. Despite the excellent reflection profiles and promising $R_{\rm int}$ and $R_{\rm sigma}$ of 0.068 and 0.016, respectively, it was impossible to solve the structure in the tetragonal space group $P4_2/ncm$. As a result, the symmetry was lowered to the orthorhombic space group *Pccn*, for which the same extinction conditions are valid; $R_{\rm int}$ and $R_{\rm sigma}$ for this space group are only slightly better: 0.036 and 0.015, respectively. Now the structure could be solved with difficulty by direct methods using *SHELXS*86 (Sheldrick, 1990), but anisotropic refinement with *SHELXL*96 (Sheldrick, 1996*b*) by full-matrix least-squares methods remained stuck at $R1 = 0.21$, yielding non-sensible anisotropic displacement parameters. Taking into account our experiences with (1) (Bolte *et al.*, 1997), we assumed that this crystal was twinned also, and applying the twin law (010/100/00$\bar{1}$) provided the ultimate success ($R1$ dropped below 0.1). All H atoms could be located by difference Fourier synthesis. While the two hydroxyl H atoms were refined isotropically, the others were refined with fixed individual displacement parameters [$U(\mathrm{H}) = 1.5U_{\rm eq}(\mathrm{C_{methyl}})$ or $U(\mathrm{H}) = 1.2\ U_{\rm eq}(\mathrm{C})$] using a riding model with C—H(methyl) = 0.98 or C—H(secondary) = 0.99 Å. The twin ratio refined to 0.424 (2).

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SMART*. Data reduction: *SAINT* (Siemens, 1995). Molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 1991).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: HA1194). Services for accessing these data are described at the back of the journal.

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Methyl 3′,6′-Bis(chloromethyl)-2,2′-dimethoxy-1,1′-binaphthalene-3-carboxylate

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Abstract

The dihedral angle between the naphthalene ring systems in the title compound, $C_{26}H_{22}Cl_2O_4$, is 97.0 (1)°. The methoxycarbonyl group is disordered over two positions and is twisted out of the plane of the attached binaphthyl ring system in both cases. The molecules are joined together through weak C4′—H4′···O2 and C4′—H4′···O2A($-x+\frac{1}{2}$, $y+\frac{1}{2}$, $-z+\frac{1}{2}$) hydrogen bonds, and by stacking interactions between the methoxycarbonyl groups along the **a** direction.

Comment

Chemists have long sought ways to control the molecular structure of synthetic high-molecular weight compounds at a level comparable to that realised in biological macromolecules. With such methods available, it may be possible to fine tune the properties of materials thus obtained.

One method discovered recently has already resulted in a new set of materials called starburst dendrimers as seen in numerous review articles (Stibor & Lellek, 1994; Tomalia, Naylor & Goddard, 1990; Mekelburger, Jaworek & Voegtle, 1992; Newkome, Moorefield & Baker, 1992; Tomalia & Durst, 1993; Issberner, Moors & Voegtle, 1994; Newkome & Moorefield, 1996; Bell, 1996). Starburst dendrimers, as highly ordered polymers, are believed to provide solutions to a wide variety of technological and ecological problems, from the removal of heavy metal pollutants from industrial waste to highly efficient drug-delivery systems and even the formation of artificial chemical cells and tissues (Tomalia & Durst, 1993; Newkome & Moorefield, 1996).

The extraordinary activity in the field of dendrimers and within chiral dendrimers in particular, prompted us to develop a modular preparative approach to inherently axially chiral dendrimers (Lellek & Stibor, 1997). One of the leading structures of our design is the title molecule, (I), shown with the atom-numbering scheme in Fig. 1.