siti Sains Malaysia for a Visiting Postdoctoral Fellowship.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: HA1251). Services for accessing these data are described at the back of the journal.

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9-Hydroxy-4-methyl-8-phenylthio-7,8,9,10-tetrahydrobenzo[*h*]coumarin

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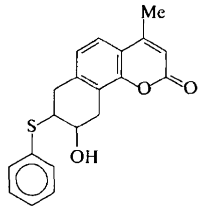
Abstract

The title molecule, $C_{20}H_{18}O_3S$, exists as an enantiomeric pair, the two halves of which are linked by mutual O—H···O hydrogen bonds involving the hydroxyl group and the carbonyl O atom. The tetrahydrobenzene ring adopts a half-chair conformation in one of the enantiomers, while in the other, it is in a conformation intermediate between sofa and half-chair. The coumarin moieties of the molecules are stacked along the *a* direction, with significant π–π interactions.

Comment

The coumarin subunit is of interest because it is found in many natural products displaying diverse biological properties. The range of compounds includes antifungal compounds, anticoagulants and compounds active against psoriasis (Parrish *et al.*, 1974). The amino and hydroxy derivatives of coumarin are widely used in dye lasers (Maeda, 1984). The crystal structure determination of the title compound, (I), one of these coumarin derivatives, was performed in order to elucidate its molecular conformation.



(I)

The molecules of (I) crystallize as an enantiomeric pair in the asymmetric unit of a non-centrosymmetric space group. This pair is linked by mutual O—H···O intermolecular hydrogen bonds involving the hydroxyl group and the carbonyl O atom, to form a dimer. The bond lengths and angles observed in the structure are comparable with those reported for other coumarin derivatives (Chinnakali *et al.*, 1998*a*,*b*; Kumar *et al.*, 1997). The coumarin rings of the two molecules are individually planar. The tetrahydrobenzene ring adopts a half-chair conformation [$\Delta C_2(C7A—C8A)$ = 3.7 (6)°] in one molecule, while in the other it is in a conformation intermediate between sofa and half-chair [$\Delta C_s(C8B)$ = 10.7 (5)° and $\Delta C_2(C7B—C8B)$ = 10.1 (6)°] (Duax *et al.*, 1976).

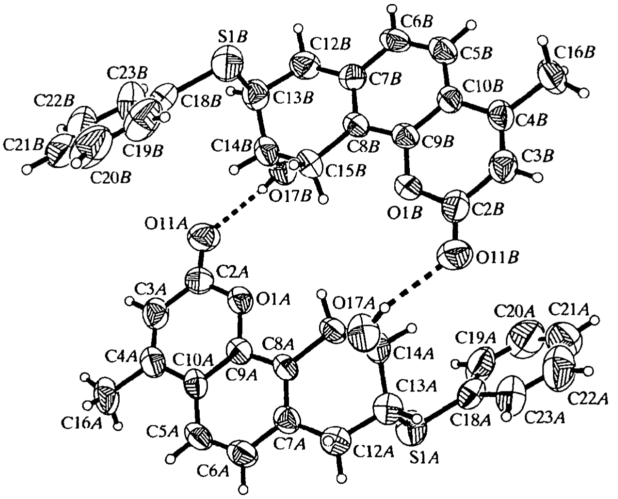


Fig. 1. The structure of (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms are shown as spheres of arbitrary radii.

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In one molecule of the enantiomeric pair, the mean plane through the tetrahydrobenzene ring forms dihedral angles of 1.6 (2) and 42.1 (3)°, respectively, with the coumarin moiety and the phenyl ring [4.0 (2) and 42.6 (3)° in the other molecule]. The dimeric pairs translated along the *a* direction are linked by weak C20*B*—H20*B*···O11*A*(*x* + 1, *y*, *z*) hydrogen bonds to form a molecular column. Also along the *a* direction, the coumarin moieties of the molecules are stacked alternately at distances of 3.332 (7) and 3.612 (7) Å, indicating significant π–π interactions. The crystal structure is further stabilized by a number of C—H···π interactions involving the phenyl rings (Ph_A and Ph_B) of the enantiomeric pair (Table 2). The packing of the molecules differs significantly from that observed for the regioisomeric compound 8-hydroxy-4-methyl-9-phenylthio-7,8,9,10-tetrahydro-7,8-benzocoumarin (Kumar *et al.*, 1997).

Experimental

Ring opening of 4-methyl-7,10-dihydro-8,9-epoxy-7,8-benzocoumarin with thiophenol gave two regioisomeric ring-opened compounds, namely, 8-hydroxy-4-methyl-9-phenylthio-7,8,9,10-tetrahydro-7,8-benzocoumarin and the title compound, (I). Single crystals of (I) were grown by slow evaporation from a chloroform/methanol (1:1) solution.

Crystal data

$C_{20}H_{18}O_3S$
$M_r = 338.40$
Orthorhombic
$P2_12_12_1$
$a = 7.5028\ (3)$ Å
$b = 17.3288\ (6)$ Å
$c = 26.1306\ (9)$ Å
$V = 3397.4\ (2)$ Å^3
$Z = 8$
$D_x = 1.323$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 3580 reflections
$\theta = 1.41$–$25.00°$
$\mu = 0.205$ mm^{-1}
$T = 293\ (2)$ K
Needle
0.50 × 0.16 × 0.08 mm
Colourless

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (empirical using *SADABS*; Sheldrick, 1996)
$T_{min} = 0.904$, $T_{max} = 0.984$
18 365 measured reflections
3410 independent reflections (plus 2543 Friedel-related reflections)

4005 reflections with $I > 2\sigma(I)$
$R_{int} = 0.050$
$\theta_{max} = 25°$
$h = -8 \rightarrow 8$
$k = 0 \rightarrow 20$
$l = 0 \rightarrow 31$
Intensity decay: negligible

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.065$
$wR(F^2) = 0.158$
$S = 1.132$
5953 reflections
437 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0517P)^2 + 1.7281P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.57$ e Å^{-3}
$\Delta\rho_{min} = -0.31$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.3 (1)

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

S1*A*—C18*A*	1.773 (6)	S1*B*—C18*B*	1.778 (5)
S1*A*—C13*A*	1.832 (6)	S1*B*—C13*B*	1.841 (5)
O1*A*—C2*A*	1.372 (5)	O1*B*—C2*B*	1.370 (5)
O1*A*—C9*A*	1.387 (5)	O1*B*—C9*B*	1.379 (5)
C2*A*—O11*A*	1.216 (5)	C2*B*—O11*B*	1.204 (5)
C3*A*—C4*A*	1.335 (7)	C3*B*—C4*B*	1.343 (6)
C5*A*—C6*A*	1.355 (7)	C5*B*—C6*B*	1.374 (6)
O11*A*—C2*A*—O1*A*	116.4 (4)	O11*B*—C2*B*—O1*B*	117.5 (4)
O11*A*—C2*A*—C3*A*	125.9 (5)	O1*B*—C2*B*—C3*B*	115.9 (5)
O1*A*—C9*A*—C8*A*	115.5 (4)	O1*B*—C9*B*—C8*B*	115.1 (4)
C5*A*—C10*A*—C4*A*	126.0 (4)	C5*B*—C10*B*—C4*B*	124.6 (4)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O17*A*—H17*A*···O11*B*	0.82	2.05	2.840 (5)	162
O17*B*—H17*B*···O11*A*	0.82	2.01	2.796 (5)	160
C20*B*—H20*B*···O11*A*^{i}	0.93	2.52	3.303 (9)	142
C12*A*—H12*A*···$\pi(Ph_A{}^{ii})$	0.97	2.92	3.705 (9)	138
C3*B*—H3*B*···$\pi(Ph_B{}^{iii})$	0.93	3.25	4.117 (9)	156
C13*B*—H13*B*···$\pi(Ph_B{}^{iv})$	0.98	3.25	4.058 (9)	140
C23*B*—H23*B*···$\pi(Ph_B{}^{iv})$	0.93	3.05	3.914 (9)	155

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

After checking their presence in the difference map, all H atoms were placed at geometrically calculated positions and a riding model was used for their refinement; rotating-group refinement was used for the methyl groups.

Data collection: *SMART* (Siemens, 1996). Cell refinement: *SAINT* (Siemens, 1996). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1273). Services for accessing these data are described at the back of the journal.

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Methyl (2*RS*,4a*RS*,8a*RS*)-2-(4-methylbenzyl)-3-oxoperhydronaphthalene-2-carboxylate

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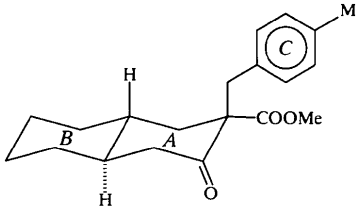
Abstract

In the title compound, $C_{20}H_{26}O_3$, the fused cyclohexane rings adopt the chair conformation. The dihedral angle between the two planes is 2.97 (8)°. The equatorially attached carboxylate group forms a dihedral angle of 69.97 (9)° with the cyclohexanone ring. The phenyl rings of the inversion-related molecules are involved in mutual C—H···π interactions.

Comment

The title compound, (I), was obtained during studies of stereoselectivity in cyclic β-ketoester alkylations (Surya Prakash Rao *et al.*, 1994). When methyl (4a*R*,8a*R*)-3-oxoperhydronaphthalene-2-carboxylate was alkylated with 4-methylbenzyl bromide in the presence of potassium carbonate, both *E*- and *Z*-benzylated products were obtained. The X-ray structure determination of one of these products was carried out in order to elucidate the molecular conformation.



(I)

In general, the geometry values of the fused-ring system are comparable with those observed in a related structure (Chadwick & Dunitz, 1979). The C2—C19 [1.526 (2) Å] and C2—C3 [1.546 (2) Å] distances are longer than the normal Csp^3—Csp^2 bond distance of 1.507 Å (Allen *et al.*, 1987). The *trans*-fused cyclohexanone and cyclohexane rings are in chair conformations, with a pseudo-twofold rotational axis bisecting the C2—C3, C6—C7 and C9—C10 bonds. The mean planes through the cyclohexanone and cyclohexane rings form a dihedral angle of 2.97 (8)°. The carboxylate group is attached equatorially and the C11—C2—C19—O2 torsion angle of 25.6 (2)° characterizes the synperiplanar conformation of the O2 and C11 atoms. The conformation of the attachment of the benzyl substituent to the decalin ring system is described by the torsion angle C3—C2—C11—C12 of −175.4 (1)°; the C2—C11—C12—C13 torsion angle of 86.0 (2)° shows how the phenyl ring of the benzyl moiety is oriented. A short intramolecular C1···O3 contact [2.713 (2) Å] is observed in this structure. The phenyl rings (*C*) of the

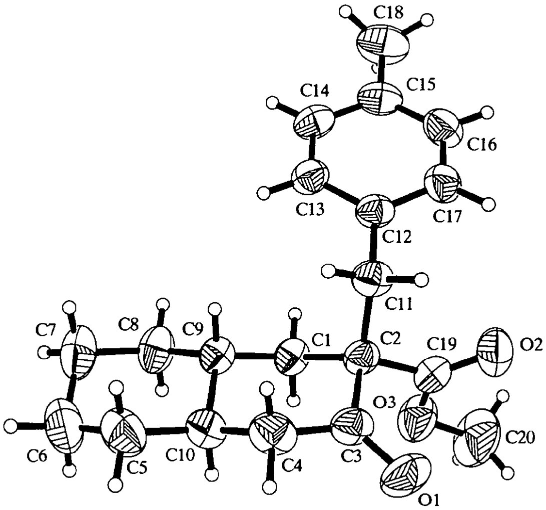


Fig. 1. The structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme.

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