2924 measured reflections
2763 independent reflections
2537 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.072$

3 standard reflections
every 200 reflections
frequency: 120 min
intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.118$
$S = 1.079$
2763 reflections
260 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.012$
$\Delta\rho_{\rm max} = 0.13$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.17$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

C11—O20	1.233 (2)	C13—C14	1.472 (2)
C11—C12	1.481 (2)	N21—O23	1.218 (2)
C12—C13	1.325 (2)	N21—O22	1.216 (2)
C3—C2—C11	121.87 (13)	C12—C11—C2	118.40 (14)
O20—C11—C12	120.72 (14)	C13—C12—C11	123.2 (2)
O20—C11—C2	120.88 (13)	C12—C13—C14	124.83 (15)
C1—C2—C11—O20	−1.0 (2)	O20—C11—C12—C13	−14.9 (3)
C3—C2—C11—O20	179.1 (1)	C2—C11—C12—C13	165.7 (2)
C1—C2—C11—C12	178.4 (1)	C11—C12—C13—C14	−176.7 (1)
C3—C2—C11—C12	−1.5 (2)	C12—C13—C14—C19	12.8 (2)

Data collection: *SDP* (Frenz, 1978). Cell refinement: *SDP*. Data reduction: *SDP*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: MU1335). Services for accessing these data are described at the back of the journal.

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4-Methyl-7,10-dihydrobenzo[*h*]coumarin and 4-Methyl-7,8,9,10-tetrahydro-8,9-epoxybenzo[*h*]coumarin

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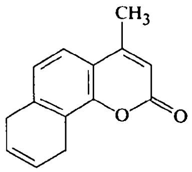
Abstract

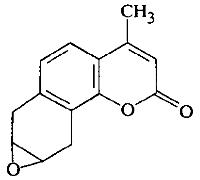
The coumarin rings in the title molecules, $C_{14}H_{12}O_2$ and $C_{14}H_{12}O_3$, are planar. In the epoxide derivative, the tetrahydrobenzene ring adopts a boat conformation and the oxirane plane is nearly perpendicular to the coumarin moiety.

Comment

Coumarin derivatives are used as laser dyes (Maeda, 1984). Some of them are found in natural products and exhibit antifungal and anticoagulant properties (Parrish *et al.*, 1974; Troste & Toste, 1996). The role of arene oxides in biological systems continues to attract attention due to their cytotoxicity, mutagenicity and carcinogenicity (Boyd & Sharma, 1996; Boyd & Jerina, 1985). The crystal structure determination of the title compounds, 4-methyl-7,10-dihydrobenzo[*h*]coumarin [$C_{14}H_{12}O_2$, (I)] and 4-methyl-7,8,9,10-tetrahydro-8,9-epoxybenzo[*h*]coumarin [$C_{14}H_{12}O_3$, (II)], was undertaken as part of structural studies on coumarin derivatives.



(I)



(II)

Bond lengths and angles in the coumarin rings are normal and are in agreement with those observed in other coumarin derivatives (Chinnakali *et al.*, 1992; Yip *et al.*, 1996). In (I), C13—C14 [1.324 (3) Å] shows double-bond character and the bond lengths C12—C13 [1.459 (3) Å] and C14—C15 [1.474 (2) Å] are shorter

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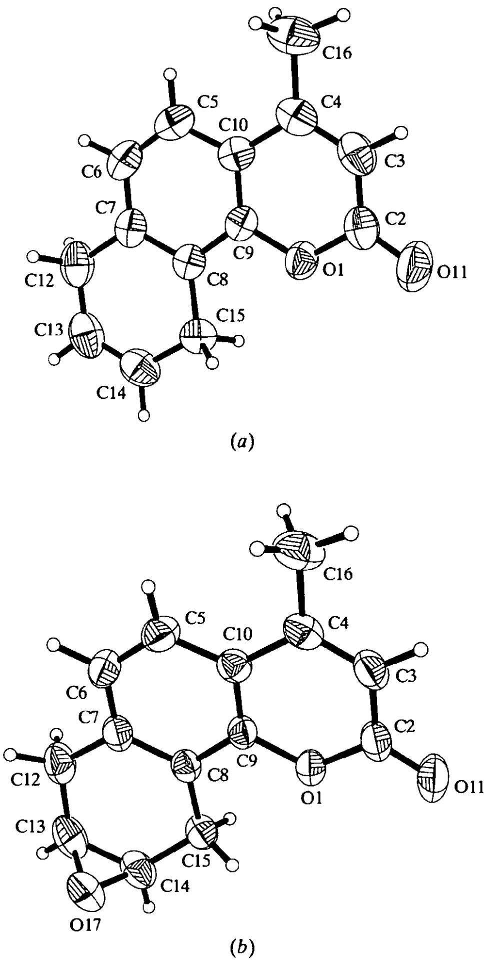

Fig. 1. The structures of (*a*) (I) and (*b*) (II) showing 50% probability displacement ellipsoids.

compared with C7—C12 [1.491 (2) Å] and C8—C15 [1.493 (2) Å]. The C_{sp^3}—C_{sp^3} and C_{sp^3}—O distances in (II) agree with values reported for oxirane ring systems (Allen *et al.*, 1987).

In (I), the dihydrobenzene ring is planar, with a maximum deviation of −0.031 (2) Å for C12; the plane makes a dihedral of 3.08 (4)° with the coumarin plane. The tetrahydrobenzene ring in (II) is in a boat conformation, with asymmetry parameters ΔC_s(C15) = 0.007 (1) and ΔC_s(C8—C7) = 0.013 (1) (Nardelli, 1983*a*); in this ring, atoms C12 and C15 deviate from the best plane by −0.233 (2) and −0.173 (2) Å, respectively. The oxirane plane is nearly perpendicular [86.62 (9)°] to the coumarin plane.

In the crystal, the molecules of (I) are stacked as two sets of parallel layers, each with an interlayer distance of 3.506 (2) Å, whereas in (II), they are packed as layers parallel to (102) planes, with an interlayer distance of 3.338 (2) Å. The crystal structures of both compounds are stabilized by weak C—H···O interactions.

Experimental

Condensation of 5,8-dihydro-1-naphthol with ethyl acetoacetate resulted in compound (I). Epoxidation of (I) with *m*-chloroperbenzoic acid furnished (II) (Sriraghavan & Ramakrishnan, 1997). Single crystals were grown by slow evaporation of the respective compounds from a chloroform and methanol solvent system.

Compound (I)

Crystal data

$C_{14}H_{12}O_2$
M_r = 212.24
Monoclinic
$P2_1/n$
a = 8.2178 (8) Å
b = 13.345 (1) Å
c = 9.7934 (9) Å
β = 96.781 (9)°
V = 1066.4 (2) Å^3
Z = 4
D_x = 1.322 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 39 reflections
θ = 5.45–12.42°
μ = 0.088 mm^{-1}
T = 293 (2) K
Rectangular tablet
0.56 × 0.42 × 0.22 mm
Colourless

Data collection

Siemens *P*4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
3194 measured reflections
2451 independent reflections
1286 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.025

$\theta_{\rm max}$ = 27.49°
$h = -1 \rightarrow 10$
$k = -1 \rightarrow 17$
$l = -12 \rightarrow 12$
3 standard reflections every 97 reflections intensity decay: <3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.104
S = 0.852
2451 reflections
194 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0505P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$

$\Delta\rho_{\rm max}$ = 0.133 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.115 e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0036 (14)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Intermolecular interactions (Å, °) for (I)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3···O11$^{\rm i}$	0.94 (2)	2.64 (2)	3.509 (2)	154 (1)
C12—H12*B*···O11$^{\rm ii}$	0.98 (2)	2.62 (2)	3.519 (2)	152 (2)

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

Compound (II)

Crystal data

$C_{14}H_{12}O_3$
M_r = 228.24

Mo $K\alpha$ radiation
λ = 0.71073 Å

Monoclinic
$P2_1/c$
$a = 10.959$ (1) Å
$b = 12.963$ (1) Å
$c = 7.9905$ (8) Å
$\beta = 106.081$ (9)°
$V = 1090.7$ (2) Å^3
$Z = 4$
$D_x = 1.390$ Mg m^{-3}
D_m not measured

Cell parameters from 39 reflections
$\theta = 5.38$–$12.49°$
$\mu = 0.098$ mm^{-1}
$T = 293$ (2) K
Needle
$0.50 \times 0.24 \times 0.18$ mm
Colourless

Data collection

Siemens *P*4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
3279 measured reflections
2499 independent reflections
1257 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.025$

$\theta_{\rm max} = 27.50°$
$h = -14 \rightarrow 13$
$k = -16 \rightarrow 1$
$l = -1 \rightarrow 10$
3 standard reflections every 97 reflections intensity decay: <3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.105$
$S = 0.828$
2499 reflections
203 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0484P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$

$\Delta\rho_{\rm max} = 0.178$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.136$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0131 (17)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 2. *Intermolecular interactions (Å, °) for (II)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3···O11$^{\rm i}$	0.94 (2)	2.64 (2)	3.495 (3)	152 (1)
C6—H6···O17$^{\rm ii}$	1.01 (2)	2.59 (2)	3.295 (2)	127 (1)

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

Table 3. *Selected geometric parameters (Å, °) for (I) and (II)*

	(I)	(II)
C3—C4	1.337 (2)	1.338 (2)
C7—C12	1.491 (2)	1.509 (2)
C12—C13	1.459 (3)	1.490 (3)
C13—C14	1.324 (3)	1.451 (3)
C14—C15	1.474 (2)	1.493 (2)
C8—C15	1.493 (2)	1.503 (2)
C13—O17	–	1.448 (2)
C14—O17	–	1.443 (2)
C3—C2—O11	126.9 (2)	127.0 (2)
O1—C2—O11	115.7 (2)	116.2 (2)
O1—C9—C8	115.2 (1)	114.7 (1)
C4—C10—C5	124.6 (2)	124.7 (2)
C13—O17—C14	–	60.3 (1)

Data collection, cell refinement and data reduction: *XSCANS* (Siemens, 1994). Structure solution and molecular graphics: *SHELXTL/PC* (Sheldrick, 1990). Structure refinement: *SHELXL*93 (Sheldrick, 1993). Geometrical calculations: *PARST* (Nardelli, 1983*b*).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1186). Services for accessing these data are described at the back of the journal.

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Two Dyotropomers Resulting from Irreversible Thermal ($4\sigma + 2\pi$) 2H Group Transfer

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Abstract

The structures of two compounds, (1D) (*endo*-*endo*-1,5,6,7,8,12,13,14,15,15-decachloropentacyclo[10.2.1.1^{3,10}.0^{2,11}.0^{4,9}]hexadeca-4(9),5,7-triene, $C_{16}H_8Cl_{10}$) and (2D) (13,14-benzo-3,4,5,6-tetrachlorotetracyclo[6.4.2.2^{9,12}.0^{2,7}]hexadeca-2(7),3,5-triene, $C_{20}H_{16}Cl_4$), are reported. Both compounds are products of an irre-