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Crystal Structure
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Ethyl (6a*RS*,8*RS*,12b*RS*)-6-oxo-8-phenyl-6a,7,8,12b-tetrahydro-6*H*-benzo[*b*]naphtho[1,2-*d*]pyran-6a-carboxylate

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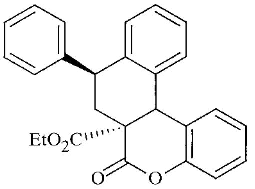
In the title compound, $C_{26}H_{22}O_4$, the pyranone ring adopts a twisted boat conformation, while the cyclohexane ring is close to an envelope conformation. The dihedral angle between the mean planes of the coumarin and naphthalene systems is 78.8 (1)°. The attached phenyl ring is in an equatorial position with respect to the cyclohexane ring.

Comment

The photoinduced reactions of coumarin derivatives have been widely investigated (Lewis & Barancyk, 1989). However, the photoinduced reactions of coumarins with phenylethenes have not been investigated to any great extent. In order to extend the scope of photoinduced reactions of coumarin derivatives, we have conducted the photoinduced reaction of 3-ethoxycarbonylcoumarin with 1,1-diphenylethene. It was found unexpectedly that the coumarin ring was annulated in this reaction to give the title compound, (I). An X-ray crystal structure analysis of (I) was undertaken to confirm its novel four-ring structure. The crystal structure is a racemate.



(I)

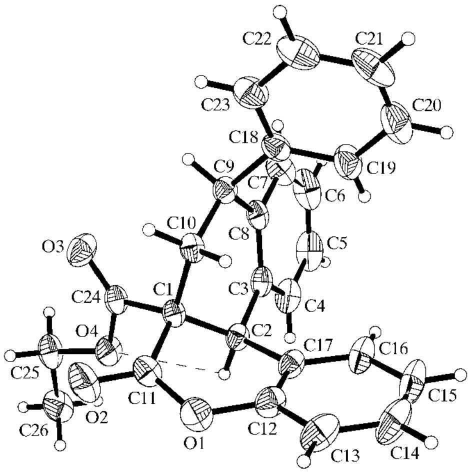


Figure 1
The structure of (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme. The intramolecular C—H···O hydrogen bond is shown as a dashed line.

In the structure of (I) (Fig. 1), the pyranone ring adopts a twisted boat conformation, with atoms C1 and C2 deviating by ±0.300 (3) Å, and puckering parameters (Cremer & Pople, 1975) Q_2 = 0.445 (3) Å, Q_3 = 0.192 (3) Å, Q_T = 0.484 (3) Å, θ = 66.7 (4)° and φ_2 = 151.0 (4)°. The cyclohexane ring is close to an envelope conformation, with atom C1 deviating by −0.358 (2) Å, and puckering parameters Q_2 = 0.413 (3) Å, Q_3 = −0.290 (3) Å, Q_T = 0.505 (3) Å, θ = 125.1 (3)° and φ_2 = 170.2 (4)°. The dihedral angle between the mean planes through the pyranone and cyclohexane rings is 69.7 (2)°, while these two rings make dihedral angles of 15.9 (2) and 10.2 (1)° with the benzene rings in the coumarin and naphthalene moieties, respectively. The coumarin and naphthalene

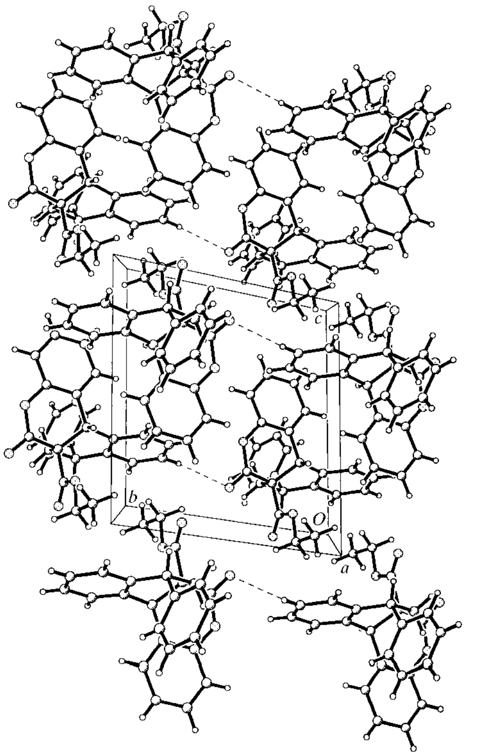


Figure 2
Packing diagram of the structure of (I) viewed down the *a* axis.

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moieties make a dihedral angle of 78.8 (1)° with one another, corresponding to a synclinal configuration.

The bond lengths and angles within (I) are normal (Allen *et al.*, 1987). Except for the C3—C8 and C12—C17 bonds, all the C—C bond distances in the pyranone and cyclohexane rings have typical Csp^3—Csp^3 single-bond values. The average C—C bond distances within the benzene and phenyl rings are 1.377 (4), 1.381 (4) and 1.387 (4) Å.

The phenyl-ring substituent attached to the cyclohexane ring moiety at C9 is twisted by 68.1 (2)° with respect to the mean plane of the cyclohexane ring, corresponding to an equatorial position with respect to the cyclohexane ring. The ketone O2 atom deviates by 0.286 (2) Å from the cyclohexane ring. The ethoxycarbonyl group is nearly planar, with atom O3 deviating by 0.261 (2) Å. This plane makes a dihedral angle of 85.4 (3)° with the cyclohexane ring.

In the title structure, an intramolecular C—H···O interaction forms an O4—C24—C1—C2—H2*A* closed ring. The molecules are stacked in columns nearly along the *c* axis (Fig. 2). One weak intermolecular C—H···O interaction (symmetry code: *x*, *y* + 1, *z*) was also observed, interconnecting the molecules into infinite molecular sheets along the *b* axis. These interactions, as well as van der Waals interactions, stabilize the molecular and packing structure in the crystal.

Experimental

The title compound, (I), was prepared by photolysis of 3-ethoxycarbonylcoumarin (50 mmol) in benzene solution with an excess of 1,1-diphenylethylene using light of wavelength longer than 300 nm. Single crystals suitable for X-ray diffraction analysis were recrystallized by slow evaporation from a petroleum ether–ethyl acetate solution.

Crystal data

$C_{26}H_{22}O_4$
$M_r = 398.44$
Triclinic, $P\bar{1}$
$a = 10.5692$ (2) Å
$b = 10.6982$ (2) Å
$c = 10.7687$ (1) Å
$\alpha = 94.848$ (1)°
$\beta = 99.091$ (1)°
$\gamma = 119.064$ (1)°
$V = 1032.43$ (3) Å^3
$Z = 2$
$D_x = 1.282$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4216 reflections
$\theta = 2.0$–28.3°
$\mu = 0.09$ mm^{-1}
$T = 293$ (2) K
Slab, colourless
0.36 × 0.30 × 0.14 mm

Table 1
Selected geometric parameters (Å, °).

O1—C11	1.356 (3)	C2—C17	1.513 (3)
O1—C12	1.399 (3)	C3—C8	1.404 (4)
C1—C11	1.518 (4)	C8—C9	1.518 (3)
C1—C10	1.537 (3)	C9—C18	1.527 (3)
C1—C2	1.548 (3)	C9—C10	1.535 (3)
C2—C3	1.504 (4)		
C11—C1—C24	105.24 (18)	C3—C2—C17	113.8 (2)
C11—C1—C10	107.43 (19)	C8—C9—C18	112.33 (19)
C24—C1—C10	112.1 (2)	C8—C9—C10	114.9 (2)

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.970$, $T_{\max} = 0.988$
6894 measured reflections
4425 independent reflections
2402 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.084$
$\theta_{\max} = 27.0°$
$h = -12 \rightarrow 13$
$k = -12 \rightarrow 13$
$l = -13 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.075$
$wR(F^2) = 0.209$
$S = 0.87$
4425 reflections
272 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0916P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.57$ e Å^{-3}
$\Delta\rho_{\min} = -0.59$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.226 (15)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2*A*···O4	0.98	2.44	2.815 (3)	102
C6—H6*A*···O2$^{\rm i}$	0.93	2.58	3.449 (4)	156

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

After checking their presence in the difference map, all H atoms were fixed geometrically and allowed to ride on their parent C atoms (C—H = 0.93–0.98 Å).

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, PARST* (Nardelli, 1995) and *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1509). Services for accessing these data are described at the back of the journal.

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