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Key indicators

Single-crystal X-ray study
 $T = 123$ K
Mean $\sigma(\text{C}-\text{C}) = 0.005$ Å
 R factor = 0.046
 wR factor = 0.135
Data-to-parameter ratio = 9.5For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

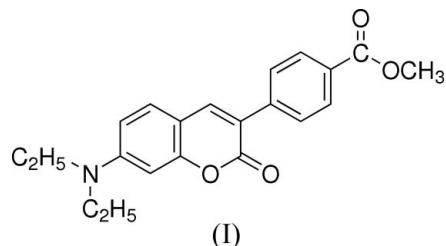
Methyl 4-(7-diethylamino-2-oxo-2H-1-benzopyran-3-yl)benzoate

In the title compound, $\text{C}_{21}\text{H}_{21}\text{NO}_4$, the non-fused benzene ring makes angles of 16.0 (1) and 5.6 (2)° with the coumarin ring and the methoxycarbonyl group, respectively. Intermolecular $\pi-\pi$, $\text{C}-\text{H}\cdots\pi$ and $\text{C}-\text{H}\cdots\text{O}$ interactions are observed in the crystal structure.

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Comment

Coumarin derivatives have been found to be very useful as fluorescence materials and laser dyes, nonlinear optical materials, photorefractive materials, photo resists, intermediates for drug synthesis, luminescence materials, analytical reagents, *etc.* (Takahashi *et al.*, 2005). Recently, we have reported the synthesis and fluorescence properties of 7-diethylaminocoumarin derivatives as fluorophores accessible for analytical purposes in the fields of analytical and biological chemistry (Takechi *et al.*, 2000). The crystal structure analyses of 7-diethylaminocoumarin (Yufit *et al.*, 1991), 7-diethylamino-3-dimethylaminocoumarin (Takahashi *et al.*, 2005) and 7-diethylamino-4-methyl-3-phenylcoumarin (Patalakha *et al.*, 1991) have been reported. We now report the crystal structure of the title compound, (I).



A view of the molecular structure of (I) is shown in Fig. 1. The C—C bond lengths of the coumarin ring of (I) are similar to those of 7-diethylaminocoumarin (Yufit *et al.*, 1991) and 7-diethylamino-3-dimethylaminocoumarin (Takahashi *et al.*, 2005) and differ from those of coumarin itself (Gavuzzo *et al.*, 1974). The C6—C7 bond length of (I) is longer than that of coumarin itself [1.368 (6) Å; Gavuzzo *et al.*, 1974]. The C7—N1 bond length is close to that of 7-diethylamino-3-dimethylaminocoumarin [1.378 (3) Å; Takahashi *et al.*, 2005]. The respective deviations of each atom from the least-squares plane defined by atoms C7, C18, C20 and N1 are 0.025 (1), 0.028 (2), 0.026 (1) and 0.053 (3) Å. The two ethyl groups of the diethylamine group are *syn* with respect to one another.

The dihedral angle between the coumarin ring system and the benzene ring is 16.0 (1)°, which differs from that of 7-diethylamino-4-methyl-3-phenylcoumarin [112.7 (1)°; Patalakha *et al.*, 1991]. The dihedral angle between the unfused

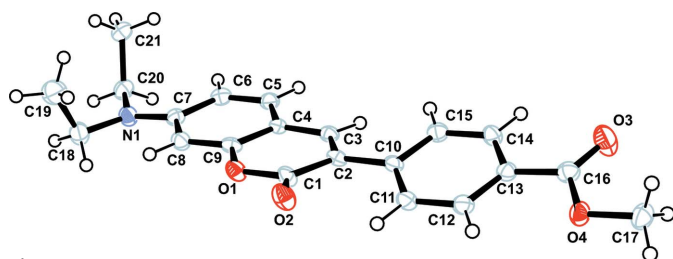


Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids.

benzene ring and the methoxycarbonyl group is $5.6(2)^\circ$, resembling that of methyl *p*-aminobenzoate [$6.9(1)^\circ$; Dorignetto *et al.*, 2004].

Intermolecular π - π interactions between the coumarin and benzene planes of (I) are observed (Fig. 2). The intermolecular distance is $3.194(5) \text{ \AA}$ for $C5 \cdots C15^i$ [symmetry code: (i) $x - 1, y, z$], which is shorter than the intermolecular distance between the two coumarin rings of ethyl 8-methoxycoumarin-3-carboxylate [$3.2611(16) \text{ \AA}$; Takahashi *et al.*, 2006].

Intermolecular $C-H \cdots \pi$ and $C-H \cdots O$ interactions are observed in the crystal structure of (I) (Table 2 and Fig. 2), with distances typical for these types of interactions: $C-H \cdots \pi = 2.8\text{--}3.1 \text{ \AA}$ (Kubo *et al.*, 2005, 2006) and $C-H \cdots O = 2.5\text{--}2.7 \text{ \AA}$ (Kubo *et al.*, 2005; Takahashi *et al.*, 2005, 2006)

The combination of intermolecular $C-H \cdots \pi$ and $C-H \cdots O$ interactions and π - π stacking interactions in (I) builds up a three-dimensional network.

Experimental

Compound (I) was synthesized by the reaction of 4-(diethylamino)-2-hydroxybenzaldehyde, 4-carbomethoxyphenyl acetate and piperidine (Takechi *et al.*, 1996). Crystals of (I) were grown from a chloroform solution by slow evaporation.

Crystal data

$C_{21}H_{21}NO_4$	$Z = 4$
$M_r = 351.40$	$D_x = 1.358 \text{ Mg m}^{-3}$
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
$a = 6.332(2) \text{ \AA}$	$\mu = 0.09 \text{ mm}^{-1}$
$b = 12.103(4) \text{ \AA}$	$T = 123.1 \text{ K}$
$c = 22.424(8) \text{ \AA}$	Platelet, yellow
$V = 1718.5(10) \text{ \AA}^3$	$0.12 \times 0.12 \times 0.03 \text{ mm}$

Data collection

Rigaku Saturn diffractometer	14109 measured reflections
ω scans	2249 independent reflections
Absorption correction: multi-scan (REQAB; Jacobson, 1998)	1207 reflections with $F^2 > 2\sigma(F^2)$
$T_{\min} = 0.884, T_{\max} = 0.997$	$R_{\text{int}} = 0.072$
	$\theta_{\max} = 27.5^\circ$

Refinement

Refinement on F^2	$w = 1/[0.7250\sigma(F_o^2)]/(4F_o^2)$
$R[F^2 > 2\sigma(F^2)] = 0.046$	$(\Delta/\sigma)_{\max} < 0.001$
$wR(F^2) = 0.135$	$\Delta\rho_{\max} = 0.34 \text{ e \AA}^{-3}$
$S = 1.01$	$\Delta\rho_{\min} = -0.41 \text{ e \AA}^{-3}$
2249 reflections	Extinction correction: Larson
236 parameters	(1970), equation 22
H-atom parameters constrained	Extinction coefficient: 111 (33)

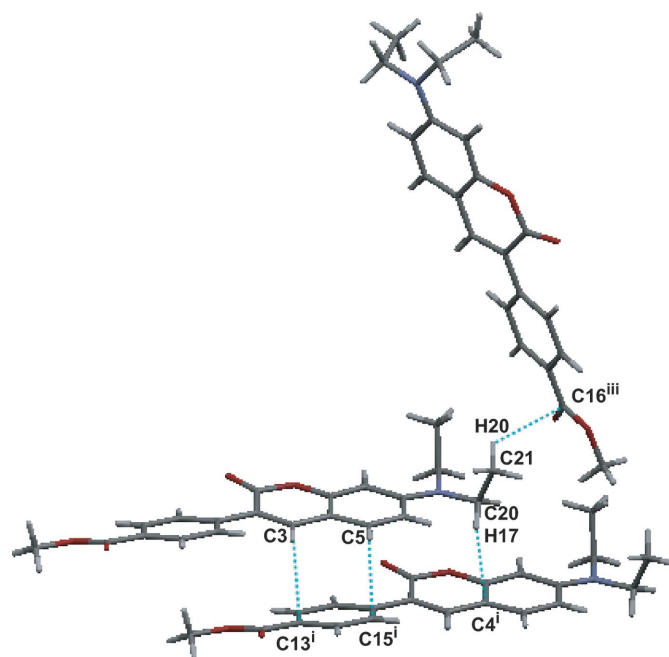


Figure 2
Three molecules of (I), showing the close intermolecular contacts mediated by the intermolecular π - π and $C-H \cdots \pi$ interactions (dashed lines). [Symmetry codes: (i) $x - 1, y, z$; (iii) $\frac{1}{2} - x, -y, z - \frac{1}{2}$]

Table 1

Selected geometric parameters (\AA , $^\circ$).

O1—C1	1.398 (4)	C2—C10	1.480 (5)
O1—C9	1.375 (4)	C3—C4	1.413 (4)
O2—C1	1.209 (4)	C4—C5	1.397 (5)
N1—C7	1.376 (4)	C4—C9	1.402 (5)
N1—C18	1.462 (5)	C5—C6	1.367 (5)
N1—C20	1.464 (5)	C6—C7	1.421 (5)
C1—C2	1.457 (5)	C7—C8	1.405 (5)
C2—C3	1.363 (5)	C8—C9	1.368 (5)
C3 \cdots C13 ⁱ	3.354 (5)	C5 \cdots C15 ⁱ	3.194 (5)
C7—N1—C18	120.9 (3)	C18—N1—C20	117.4 (3)
C7—N1—C20	120.8 (3)		
C17—O4—C16—C13	$-179.8(3)$	C3—C2—C10—C15	16.3 (5)
C7—N1—C18—C19	78.4 (4)	C12—C13—C16—O4	6.5 (5)
C7—N1—C20—C21	$-75.3(4)$	C14—C13—C16—O3	4.2 (5)
C3—C2—C10—C11	$-164.9(3)$		

Symmetry code: (i) $x - 1, y, z$.

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C3—H1 \cdots O2 ⁱⁱ	0.95	2.49	3.070 (4)	120 (1)
C20—H17 \cdots C4 ⁱ	0.95	2.86	3.476 (5)	124 (1)
C21—H20 \cdots C16 ⁱⁱⁱ	0.95	2.88	3.493 (5)	123 (1)

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

H atoms were included in the refinement in calculated positions as riding atoms, with C—H = 0.95 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. Due to the absence of any anomalous scatterers, the absolute configuration could not be determined and Friedel pairs were merged.

Data collection: *CrystalClear* (Rigaku, 1999); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku/MSC, 2004); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *MERCURY* (Version 1.3; Macrae *et al.*, 2006); software used to prepare material for publication: *CrystalStructure*.

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