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7-Diethylamino-3-dimethylamino-2*H*-1-benzopyran-2-one

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Key indicators

Single-crystal X-ray study
T = 123 K
Mean σ(C–C) = 0.004 Å
R factor = 0.057
wR factor = 0.162
Data-to-parameter ratio = 9.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the title compound, $C_{15}H_{20}N_2O_2$, the N atom of the diethylamine group has a planar environment, whereas the N atom of the dimethylamine group is pyramidal. Intermolecular C—H$\cdots\pi$ and C—H$\cdots$O interactions are observed in the crystal structure.

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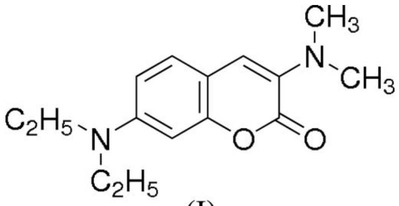
Comment

Materials containing a coumarin (2*H*-1-benzopyran-2-one) component have been useful in many fields, such as fluorescence materials and laser dyes, nonlinear optical materials, photorefractive materials, photo resists, intermediates for drug synthesis, luminescence materials and analytical reagents (Tian *et al.*, 2000). Although the fluorescence of coumarin itself is weak, the introduction of substituent groups into coumarin increases the fluorescence intensity (Murov *et al.*, 1993). We have previuosly reported some coumarin derivatives, such as 4-(7-diethylaminocoumarin-3-yl)benzene-isocyanate (Takechi *et al.*, 2001), 3-azoyl-7-diethylamino-coumarin (Takechi *et al.*, 2000), 3-[4-(bromomethyl)phenyl]-7-(diethylamino)-2*H*-1-benzopyran-2-one (Takechi *et al.*, 1996), 4-(7-diethylaminocoumarin-3-yl)benzoyl cyanide (Takechi *et al.*, 1998), and α-chymotrypsin having a coumarinyl-substituted sulfonium pendant group (Ishihara *et al.*, 2000). However, these studies have not clarified the relationship between the crystal structure and fluorescence behaviour of coumarin derivatives. Therefore, the elucidation of the crystal structures of coumarin moieties has attracted much attention. We now report the crystal structure of the title compound, 7-diethylamino-3-dimethylaminocoumarin, (I), which was determined in order to elucidate the effect of substituents at the 3- and 7-positions of coumarin on the strucuture and crystal packing.



(I)

A molecular view of the molecule of (I) is shown in Fig. 1. The C—C bond lengths, apart from the C6—C7 bond of the coumarin ring, agree with those of coumarin itself (Gavuzzo *et al.*, 1974), as shown in Table 2. The N atom of the diethylamine group has a planar environment, whereas the N atom of the dimethylamine group is pyramidal: the C7—N2 bond length is

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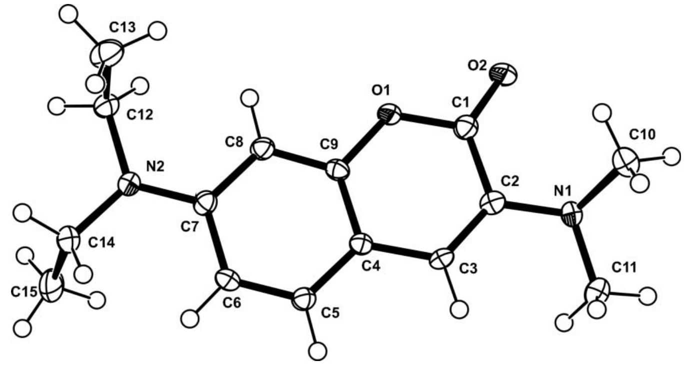

Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme.

close to the value of 1.355 Å observed for a Csp^2—Nsp^2 bond, while the C2—N1 bond length is similar to the value of 1.416 Å observed for a Csp^2—Nsp^3 bond (Lide, 2000). The respective deviations of each atom from the least-squares plane *A* defined by atoms C7, C12, C14 and N2 are 0.030 (2), 0.012 (1), 0.014 (1) and 0.014 (1) Å. The dihedral angle between the coumarin ring system (O1/O2/C1–C9) and the dimethylamine group (atoms N1, C10 and C11) is 44.24 (2)°. This means that the diethylamine groups substituted at the C7-position affects the conjugation system of coumarin.

An intermolecular C—H$\cdots\pi$ interaction is observed in (I) (Table 1). The distance between atom H2 and the centroid of the pyran ring (O1/C1–C4/C9) is 3.0878 Å, which agrees with the intramolecular C—H$\cdots\pi$ interaction [3.084 Å] observed in 2,5-bis(diphenylmethyl)hydroquinone (Guo *et al.*, 2005).

There are some intermolecular C—H$\cdots$O hydrogen bonds in (I) (Table 1). The H1$\cdots$O2$^{\rm i}$ and H19$\cdots$O1$^{\rm ii}$ [symmetry codes: (i) $x-1, y, z$; (ii) $-x+\frac{1}{2}, -y+2, z-\frac{1}{2}$] distances are similar to those of 7,16-bis(1-pyrenylmethyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (2.58 Å; Kubo *et al.*, 1997; Meadows *et al.*, 2000) and 2,7-dibromotropone (2.51 Å; Kubo *et al.*, 2005). The occurrence of these weak C—H$\cdots\pi$ and C—H$\cdots$O interactions builds up a three-dimensional network, as shown in Fig. 2.

Experimental

Compound (I) was synthesized by the reaction of glycine betaine and 4-(diethylamino)salicylaldehyde (Mahara *et al.*, 1997). Crystals of (I) were grown from an ethanol solution by slow evaporation.

Crystal data

$C_{15}H_{20}N_2O_2$
$M_r = 260.34$
Orthorhombic, $P2_12_12_1$
$a = 6.596$ (3) Å
$b = 14.360$ (6) Å
$c = 14.549$ (6) Å
$V = 1378.0$ (10) Å^3
$Z = 4$
$D_x = 1.255$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 4379 reflections
$\theta = 3.1$–27.5°
$\mu = 0.08$ mm^{-1}
$T = 123.1$ K
Prism, orange
0.15 × 0.14 × 0.10 mm

Data collection

Rigaku Saturn diffractometer
ω scans
Absorption correction: multi-scan (*REQAB*; Jacobson, 1998)
$T_{\rm min} = 0.987$, $T_{\rm max} = 0.992$
11200 measured reflections
1823 independent reflections
1467 reflections with $F^2 > 2\sigma(F^2)$
$R_{\rm int} = 0.138$
$\theta_{\rm max} = 27.5°$
$h = -8 \rightarrow 8$
$k = -18 \rightarrow 18$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.057$
$wR(F^2) = 0.163$
$S = 1.00$
1817 reflections
194 parameters
H-atom parameters constrained
$w = 1/[0.937\sigma(F_o^2)]/(4F_o^2)$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.31$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.31$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

Cg is the centroid of the pyran ring.

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C3—H1$\cdots$O2$^{\rm i}$	0.95	2.45	3.380 (3)	166 (1)
C5—H2$\cdots$O1$^{\rm i}$	0.95	2.71	3.599 (3)	157 (1)
C11—H9$\cdots$O2$^{\rm i}$	0.95	2.71	3.230 (4)	115 (1)
C15—H19$\cdots$O1$^{\rm ii}$	0.95	2.59	3.479 (4)	155 (1)
C5—H2$\cdots Cg^{\rm iii}$	0.95	3.09	3.44	104

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

Table 2
A comparison of selected bond lengths in (I) with related distances in coumarin (Å).

Bond length	Compound (I)	Coumarin†
C1—C2	1.460 (3)	1.448 (5)
C2—C3	1.352 (3)	1.344 (5)
C3—C4	1.435 (3)	1.432 (5)
C4—C5	1.401 (3)	1.390 (5)
C4—C9	1.392 (3)	1.395 (4)
C5—C6	1.373 (3)	1.369 (5)
C6—C7	1.419 (3)	1.368 (6)
C7—C8	1.405 (3)	1.392 (5)
C8—C9	1.378 (3)	1.383 (5)
O1—C1	1.378 (3)	1.367 (4)
O1—C9	1.373 (3)	1.378 (4)
O2—C1	1.209 (3)	1.205 (5)
N1—C2	1.407 (3)	
N1—C10	1.486 (3)	
N1—C11	1.446 (3)	
N2—C7	1.378 (3)	
N2—C12	1.459 (3)	
N2—C14	1.455 (3)	
C12—C13	1.529 (4)	
C14—C15	1.536 (4)	

† Gavuzzo *et al.* (1974).

H atoms bonded to C atoms were included in the refinement in calculated positions as riding atoms, with C—H = 0.95 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C). In the absence of significant anomalous dispersion effects, Friedel pairs were averaged. Six low-angle reflections were excluded from the refinement, as they were probably obscured by the beam stop.

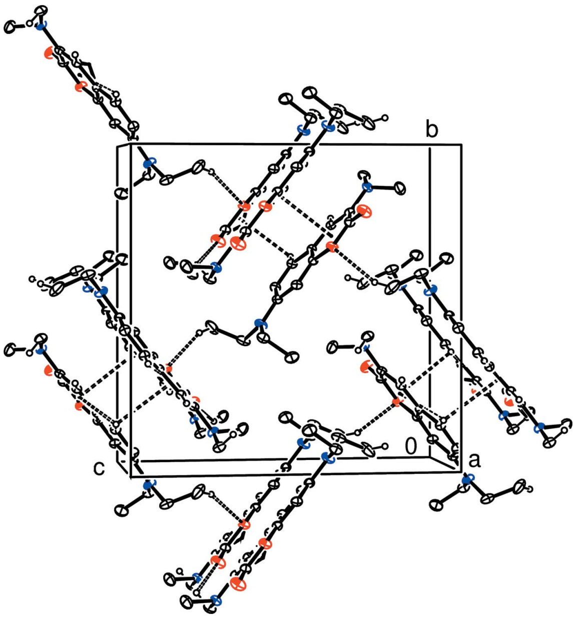

Figure 2

A packing diagram for (I), showing the hydrogen-bond network built from C—H$\cdots\pi$ and C—H$\cdots$O interactions (dashed lines). H atoms not involved in the hydrogen bonding have been omitted for clarity.

Data collection: *CrystalClear* (Rigaku, 1999); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku/MSC & Rigaku, 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 *ORTEPIII for Windows* (Farrugia, 1997); software used to prepare material for publication: *CrystalStructure*.

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