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Key indicators

Single-crystal X-ray study
 $T = 150$ K
Mean $\sigma(\text{C}-\text{C}) = 0.003$ Å
 R factor = 0.057
 wR factor = 0.173
Data-to-parameter ratio = 15.7For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.7-Diethylamino-2-oxo-2H-chromene-3-carboxylic
acid

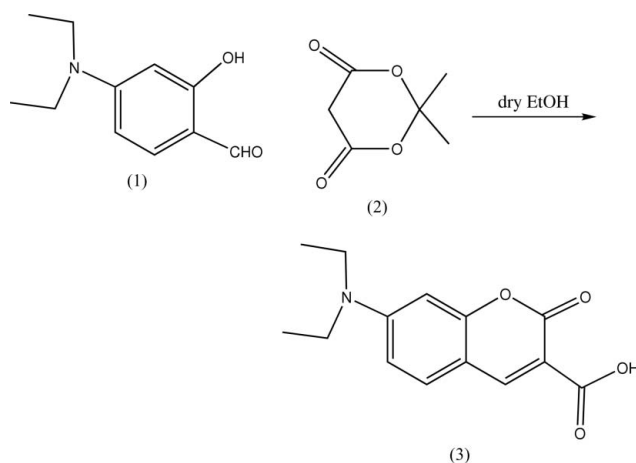
In the title molecular structure, $\text{C}_{14}\text{H}_{15}\text{NO}_4$, all non-H atoms, except for the C atoms of the terminal methyl groups of the diethylamino substituents, are essentially coplanar. In the crystal structure, a two-dimensional network is formed *via* weak intermolecular $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds and $\pi-\pi$ stacking interactions.

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Comment

Coumarins (2H-1-benzopyran-2-ones) are well known fluorescent organic dyes, displaying a broad range of biological activities (Murray *et al.*, 1982). Coumarin derivatives have been used as therapeutic agents (Kessler, 1991; O'Kennedy & Thornes, 1997), optical bleaching agents (Jusinski & Taatjes, 2001), triplet sensitizers (Sharov *et al.*, 1998; Urano *et al.*, 1998) and luminescent probes (Hemmila, 1989). For example, linear furocoumarins, commonly known as psoralens, are widely used as photosensitizing agents in photochemotherapy to treat skin diseases such as psoriasis (Parrish *et al.*, 1982; Cimino *et al.*, 1985) and in photopheresis to treat cutaneous T-cell lymphoma (Edelson *et al.*, 1987; Gasparro, 1994) and various autoimmune diseases (Morison *et al.*, 1996). In addition, some groups have focused on the fundamental photochemical and photophysical properties of coumarin laser dyes. A special interest has been the use of polymeric media in which dyes may be doped or bound in microdomains in water (Jones II *et al.* 1985; Jones II & Rahman, 1992, 1994). We report here the crystal structure of the title coumarin, (3), derived from the reaction of 4-(diethylamino)salicylaldehyde, (1), and 2,2-dimethyl-1,3-dioxane-4,6-dione, (2), in ethanol as solvent.



A view of the molecular structure of (3) is shown in Fig. 1 and selected bond lengths and angles are given in Table 1. All non-H atoms, except for C12 and C14, are essentially coplanar,

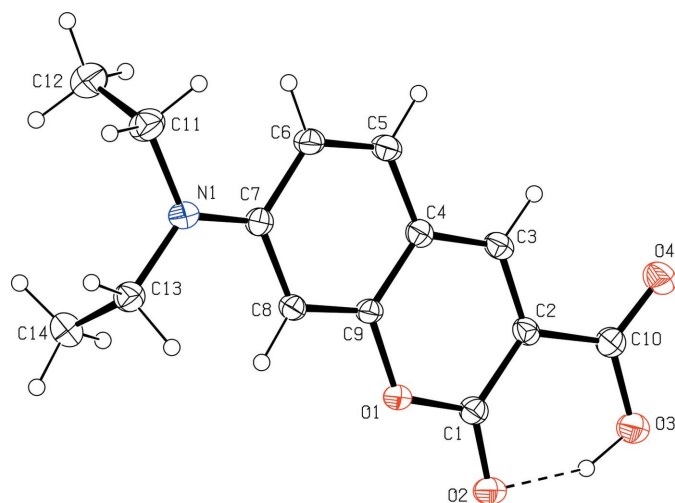


Figure 1
The molecular structure of (3), showing 30% probability displacement ellipsoids. The intramolecular hydrogen bond is shown as a dashed line.

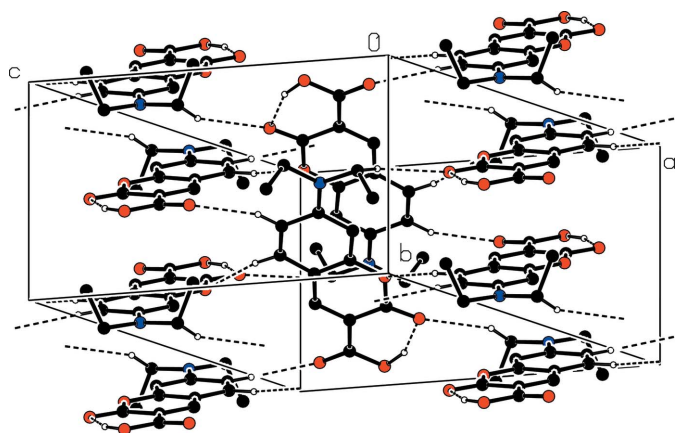


Figure 2
A partial packing plot (Spek, 2003) of (3), showing hydrogen bonds as dashed lines. Colour codes: red O, blue N and black C.

with an r.m.s deviation of 0.0244 Å for the fitted atoms. The sum of the angles at atom N1 is 359.6°, indicating sp^2 hybridization. The formation of an intramolecular O—H...O hydrogen bond (Table 2) may influence the conformation of the carboxylic acid substituent with respect to a rotation about the C2—C10 bond, although the widening (on the basis of hybridization principles) of the O2—C1—C2 angle appears to suggest some steric interaction in this part of the molecule.

In the crystal structure, weak intermolecular C—H...O hydrogen bonds (Table 2) and π - π stacking interactions [where $Cg1 \cdots Cg1(1-x, 2-y, 1-z) = 3.4510$ (13) Å and $Cg1 \cdots Cg2(1-x, 1-y, 1-z) = 3.5266$ (13) Å; $Cg1$ and $Cg2$ are the centroids defined by ring atoms O1/C1—C4/C9 and C4—C9, respectively, with perpendicular distances of 3.35 Å, in both cases] connect molecules, forming a two-dimensional network perpendicular to the a axis (Fig. 2).

Experimental

4-(Diethylamino)salicylaldehyde, (1) (5 g, 25.9 mmol), and 2,2-dimethyl-1,3-dioxane-4,6-dione, (2) (3.73 g, 25.9 mmol), were dissolved in 10 ml of dry ethanol. A catalytic amount of piperidine (two drops) and a drop of glacial acetic acid were added to the solution. The mixture was stirred at room temperature for 48 h and then refluxed for 4 h. Compound (3) (yield 89%, m.p. 502–504 K) was obtained by filtration of the orange crystalline solid that formed during the reaction. X-ray quality crystals were obtained by slow recrystallization of a chloroform solution at 269 K.

Crystal data

| | |
|----------------------------------|---|
| $C_{14}H_{15}NO_4$ | $Z = 4$ |
| $M_r = 261.27$ | $D_x = 1.402 \text{ Mg m}^{-3}$ |
| Monoclinic, $P2_1/c$ | Mo $K\alpha$ radiation |
| $a = 14.1207$ (4) Å | $\mu = 0.10 \text{ mm}^{-1}$ |
| $b = 7.7519$ (4) Å | $T = 150$ (1) K |
| $c = 12.6348$ (5) Å | Plate, orange |
| $\beta = 116.482$ (2)° | $0.14 \times 0.12 \times 0.04 \text{ mm}$ |
| $V = 1237.92$ (9) Å ³ | |

Data collection

| | |
|--|--|
| Bruker–Nonius KappaCCD diffractometer | 9549 measured reflections |
| φ scans and ω scans with κ offsets | 2810 independent reflections |
| Absorption correction: multi-scan (SORTAV; Blessing, 1995) | 1517 reflections with $I > 2\sigma(I)$ |
| $T_{\min} = 0.720$, $T_{\max} = 0.997$ | $R_{\text{int}} = 0.075$ |
| | $\theta_{\max} = 27.5^\circ$ |

Refinement

| | |
|---------------------------------|--|
| Refinement on F^2 | H atoms treated by a mixture of independent and constrained refinement |
| $R[F^2 > 2\sigma(F^2)] = 0.057$ | $w = 1/[\sigma^2(F_o^2) + (0.0876P)^2]$ |
| $wR(F^2) = 0.173$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.00$ | $(\Delta/\sigma)_{\max} < 0.001$ |
| 2810 reflections | $\Delta\rho_{\max} = 0.28 \text{ e \AA}^{-3}$ |
| 179 parameters | $\Delta\rho_{\min} = -0.26 \text{ e \AA}^{-3}$ |

Table 1

Selected geometric parameters (Å, °).

| | | | |
|------------|-------------|-----------|-------------|
| O1—C1 | 1.369 (2) | O4—C10 | 1.214 (2) |
| O1—C9 | 1.383 (2) | N1—C7 | 1.358 (3) |
| O2—C1 | 1.230 (2) | N1—C13 | 1.468 (3) |
| O3—C10 | 1.343 (3) | N1—C11 | 1.479 (3) |
| C7—N1—C13 | 121.05 (18) | O2—C1—C2 | 126.4 (2) |
| C7—N1—C11 | 121.48 (18) | O1—C1—C2 | 118.16 (18) |
| C13—N1—C11 | 117.07 (18) | O3—C10—C2 | 117.04 (18) |
| O2—C1—O1 | 115.39 (17) | | |

Table 2

Hydrogen-bond geometry (Å, °).

| $D-H \cdots A$ | $D-H$ | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|------------------------------|----------|--------------|--------------|----------------|
| O3—H1O...O2 | 0.97 (3) | 1.70 (3) | 2.609 (2) | 153 (3) |
| C5—H5A...O1 ⁱ | 0.95 | 2.49 | 3.393 (2) | 160 |
| C6—H6A...O4 ⁱⁱ | 0.95 | 2.40 | 3.228 (3) | 146 |
| C13—H13B...O2 ⁱⁱⁱ | 0.99 | 2.57 | 3.468 (3) | 150 |

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

H atoms bonded to C atoms were placed in calculated positions, with C—H distances of 0.95 (aromatic), 0.99 (methylene) and 0.98 Å (methyl), and were included in the refinement in a riding-model approximation, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{methyl C})$. The

hydroxyl H atom (H1O) was refined independently with an isotropic displacement parameter.

Data collection: *COLLECT* (Nonius, 2002); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXTL* (Sheldrick, 2001); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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