

Elham S. Aazam,^{a*} Amel Fawazy^a
 and Peter B. Hitchcock^b

^aDepartment of Chemistry, University of King Abdulaziz, PO Box 6171, Jeddah 21442, Saudi Arabia, and ^bThe Chemistry Laboratory, School of Chemistry, Physics and Environmental Science, University of Sussex, Brighton BN1 9QJ, England

Correspondence e-mail: eazam@kaau.edu.sa

Key indicators

Single-crystal X-ray study
 $T = 173$ K
 Mean $\sigma(\text{C}-\text{C}) = 0.002$ Å
 R factor = 0.036
 wR factor = 0.099
 Data-to-parameter ratio = 13.3

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

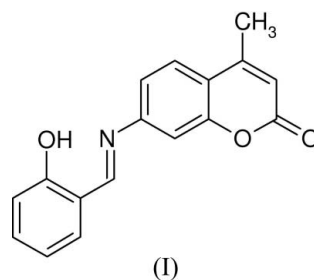
4-Methyl-7-(salicylideneamino)coumarin

The title compound, $\text{C}_{17}\text{H}_{13}\text{NO}_3$, consists of a methyl-substituted coumarin group fused to a 2-hydroxyphenyl ring *via* an azomethine linkage. The coumarin and benzene ring planes form a dihedral angle of $24.0(1)^\circ$. Intramolecular $\text{O}-\text{H}\cdots\text{N}$ hydrogen bonding is present and the crystal structure includes intermolecular $\text{C}-\text{H}\cdots\text{O}$ interactions.

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Comment

Coumarin derivatives are used as fluorescent dyes for synthetic fibres and daylight fluorescent pigments. The absorption spectrum of the title compound, (I), is comparable to that of azomethine dyes such as 6-substituted derivatives of 2Hchromen-2-one (Kachkovski *et al.*, 2004). We report here the crystal structure of (I) (Fig. 1).



Planar molecules of Schiff bases are usually stabilized by intermolecular $\pi-\pi$ interactions (Wozniak *et al.* 2000). However, (I) is not planar [the dihedral angle between the coumarin and benzene ring planes is $24.0(1)^\circ$], indicating an

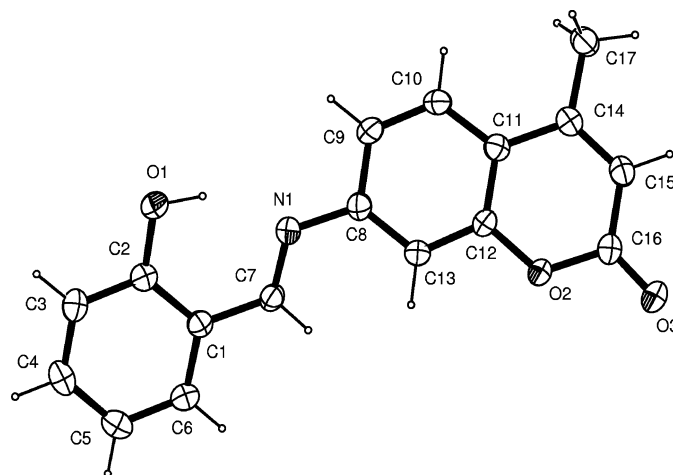


Figure 1
 The molecular structure of (I), showing displacement ellipsoids at the 50% probability level for non-H atoms.

absence of π - π coupling. Compound (I) shows no photochromic effect in the solid state at ambient temperature, which is attributed to the presence of an intramolecular O—H \cdots N hydrogen bond. Such an interaction is considered to be vital for determining lightfastness properties (that is, retention of colour strength over time under exposure to sunlight) by providing electronic protection of the chromophore towards photochemical degradation (Chang *et al.*, 2003).

Adjacent molecules of (I) are linked *via* intermolecular C—H \cdots O interactions (Fig. 2) between the carbonyl atom O3 and two C—H groups (C13—H13 and C7—H7) from a neighbouring molecule [C13 \cdots O3ⁱ = 3.5565 (16) Å and C13—H13 \cdots O3ⁱ = 165°, and C7 \cdots O3ⁱ = 3.2733 (15) Å and C7—H7 \cdots O3ⁱ = 146°; symmetry code: (i) 1 - x, -½ + y, ½ - z]. Similar interactions are present in 7-methoxy-3-(salicylideneamino)coumarin, which is a planar molecule (Khoo *et al.*, 2000).

Experimental

Salicylaldehyde (1.22 ml, 10 mmol) dissolved in 15 ml absolute ethanol was added to a warm stirred solution of 7-amino-4-methylcoumarin (1.75 g, 10 mmol) in absolute ethanol (15 ml), and the mixture was refluxed for 1 h. The resulting yellow–orange precipitate was removed, washed with ethanol followed by diethyl ether and then dried *in vacuo*. Suitable single crystals were grown by slow evaporation from either chloroform/methanol (1:1) or 10–15 ml ethanol (yield 85%, m.p 459–460 K). ¹H NMR (400 MHz, DMSO-*d*⁶, 298 K, TMS): δ 6.28 (1H, *s*, H15), 7.41–7.45 (2H, *m*, H9,H10), 7.64 (1H, *d*, H13), 7.00–7.26 (4H, *m*, aromatic), 2.46 (3H, *s*, H17A–C), 8.65 (1H, *s*, H7), 12.79 (1H, *s*, H1); ¹³C NMR (100.6 MHz, DMSO-*d*⁶, 298 K, TMS): δ 108.75–160.16 (aromatic C), 18.79 (C17), 164 (C16), 154 (C7). UV/Vis (ethanol, λ , nm): 210, 229, 269, 285, 350. Elemental analysis found: C 73.11, H 4.69, N 5.02%; calculated: C 72.78, H 4.55, N 5.11%. IR (ν , cm⁻¹): 3459 (O—H), 1718 (C=O), 1639 (C=N), 1570 (C=C), 1215 (C—O).

Crystal data

C ₁₇ H ₁₃ NO ₃	Z = 4
M _r = 279.28	D _x = 1.396 Mg m ⁻³
Monoclinic, P2 ₁ /c	Mo K α radiation
a = 8.7209 (3) Å	μ = 0.10 mm ⁻¹
b = 9.9919 (3) Å	T = 173 (2) K
c = 15.3906 (4) Å	Prism, orange
β = 97.853 (2)°	0.25 × 0.2 × 0.2 mm
V = 1328.53 (7) Å ³	

Data collection

Nonius KappaCCD diffractometer	2600 independent reflections
ω and φ scans	2213 reflections with $I > 2\sigma(I)$
Absorption correction: none	R _{int} = 0.033
12760 measured reflections	θ_{\max} = 26.0°

Refinement

Refinement on F ²	$w = 1/[\sigma^2(F_o^2) + (0.0498P)^2 + 0.3959P]$
$R[F^2 > 2\sigma(F^2)] = 0.037$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.099$	$(\Delta/\sigma)_{\max} < 0.001$
S = 1.02	$\Delta\rho_{\max} = 0.20 \text{ e } \text{Å}^{-3}$
2600 reflections	$\Delta\rho_{\min} = -0.21 \text{ e } \text{Å}^{-3}$
195 parameters	
H atoms treated by a mixture of independent and constrained refinement	

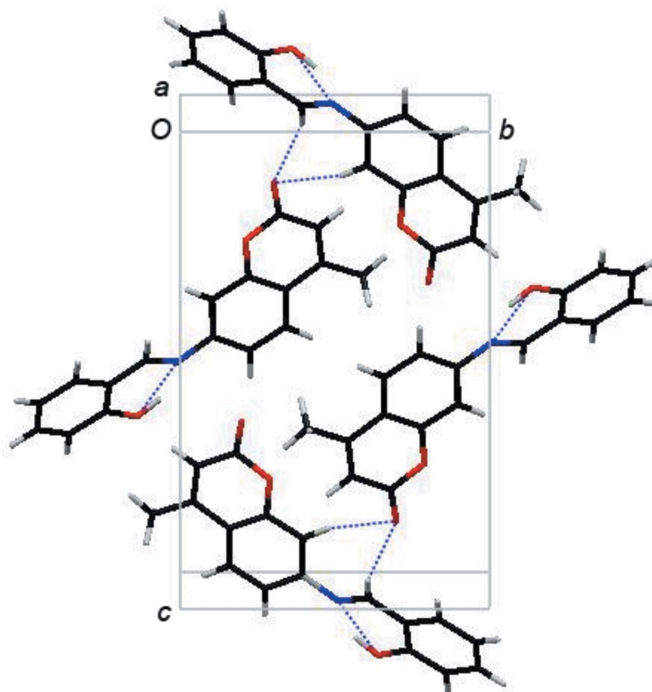


Figure 2

View of the unit-cell contents of (I), showing intramolecular O—H \cdots N hydrogen bonds and intermolecular C—H \cdots O interactions as dashed lines.

H atoms bound to C atoms were placed in calculated positions and allowed to ride during subsequent refinement, with C—H = 0.95 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for Csp², and C—H = 0.98 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for the methyl group. The methyl group was allowed to rotate about its local threefold axis. Atom H1 of the hydroxyl group was located in a Fourier map and refined freely with an isotropic displacement parameter; the refined O—H distance is 0.92 (2) Å.

Data collection: COLLECT (Nonius, 2000); cell refinement: SCALEPACK (Otwinowski & Minor, 1997); data reduction: SCALEPACK and DENZO (Otwinowski & Minor, 1997); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: WinGX (Farrugia, 1999).

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