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4-Methyl-7-(salicylideneamino)coumarin

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Key indicators

Single-crystal X-ray study
T = 173 K
Mean σ(C–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.

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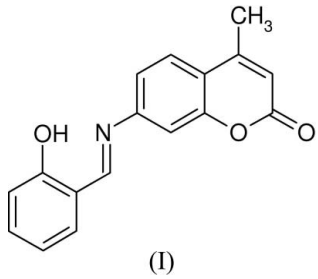
The title compound, $C_{17}H_{13}NO_3$, consists of a methyl-substituted coumarin group fused to a 2-hydroxyphenyl ring *via* an azomethine linkage. The coumarin and benzene ring planes form a dihedral angle of 24.0 (1)°. Intramolecular O—H···N hydrogen bonding is present and the crystal structure includes intermolecular C—H···O interactions.

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 2*H*chromen-2-one (Kachkovski *et al.*, 2004). We report here the crystal structure of (I) (Fig. 1).



(I)

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

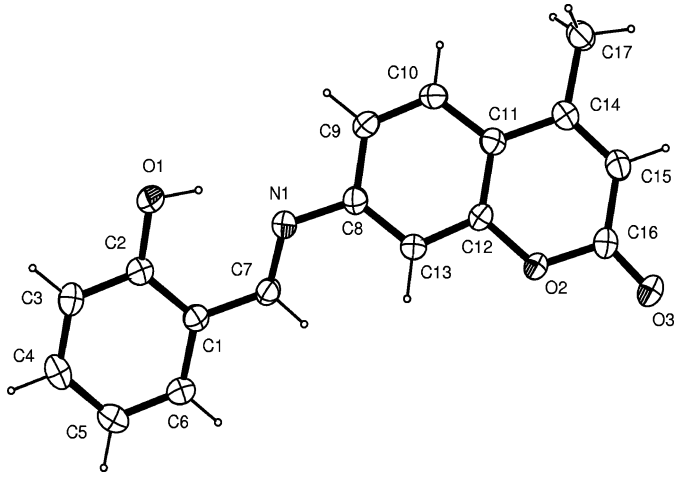


Figure 1
The molecular structure of (I), showing displacement ellipsoids at the 50% probability level for non-H atoms.

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

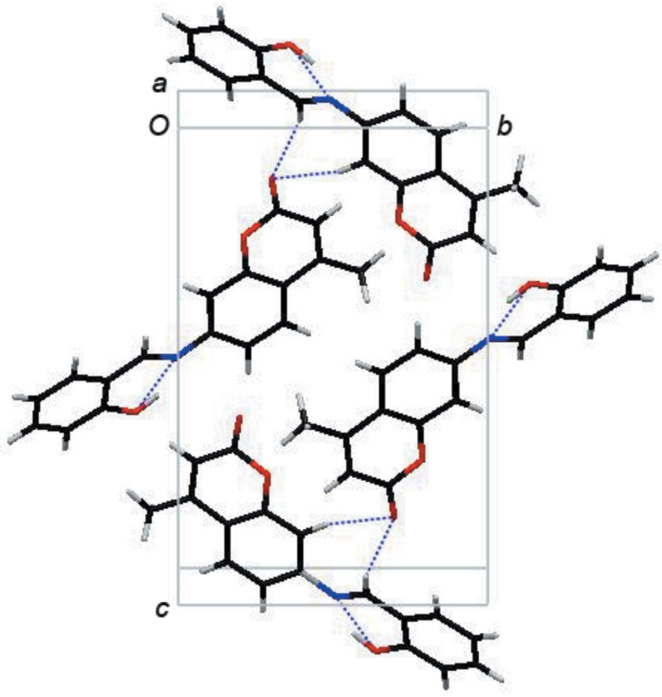


Figure 2
View of the unit-cell contents of (I), showing intramolecular O—H···N hydrogen bonds and intermolecular C—H···O interactions as dashed lines.

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). ^{1}H 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*, H17*A*–*C*), 8.65 (1H, *s*, H7), 12.79 (1H, *s*, H1); ^{13}C 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

$C_{17}H_{13}NO_3$
M_r = 279.28
Monoclinic, $P2_1/c$
a = 8.7209 (3) Å
b = 9.9919 (3) Å
c = 15.3906 (4) Å
β = 97.853 (2)°
V = 1328.53 (7) Å^3
Z = 4
D_x = 1.396 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 173 (2) K
Prism, orange
0.25 × 0.2 × 0.2 mm

Data collection

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

Refinement

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

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_{iso}(H) = 1.2U_{eq}(C) for Csp^2, and C—H = 0.98 Å and U_{iso}(H) = 1.5U_{eq}(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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supporting information

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Crystal data

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Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 8.7209$ (3) Å
$b = 9.9919$ (3) Å
$c = 15.3906$ (4) Å
$\beta = 97.853$ (2)°
$V = 1328.53$ (7) Å^3
$Z = 4$
$F(000) = 584$
$D_x = 1.396$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 7644 reflections
$\theta = 3.4$–26.0°
$\mu = 0.10$ mm^{-1}
$T = 173$ K
Prism, orange
0.25 × 0.2 × 0.2 mm

Data collection

Nonius KappaCCD diffractometer
Radiation source: Enraf Nonius FR590
Graphite monochromator
Detector resolution: 9 pixels mm^{-1}
ω and φ scans
12760 measured reflections
2600 independent reflections
2213 reflections with $I > 2\sigma(I)$
$R_{int} = 0.033$
$\theta_{max} = 26.0°$, $\theta_{min} = 3.5°$
$h = -10 \rightarrow 10$
$k = -12 \rightarrow 9$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.099$
$S = 1.02$
2600 reflections
195 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0498P)^2 + 0.3959P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.20$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.96556 (10)	−0.13858 (10)	0.67129 (6)	0.0321 (2)
H1	0.934 (2)	−0.069 (2)	0.6335 (13)	0.068 (6)*
O2	0.60263 (10)	0.21112 (9)	0.27394 (5)	0.0286 (2)
O3	0.51133 (12)	0.30134 (10)	0.14659 (6)	0.0422 (3)
N1	0.80250 (12)	−0.00876 (10)	0.54404 (7)	0.0270 (3)
C1	0.73582 (14)	−0.22881 (12)	0.58642 (8)	0.0233 (3)
C2	0.86395 (14)	−0.23980 (13)	0.65290 (8)	0.0251 (3)
C3	0.88635 (15)	−0.35761 (13)	0.70148 (9)	0.0300 (3)
H3	0.9725	−0.3655	0.7462	0.036*
C4	0.78415 (16)	−0.46272 (13)	0.68494 (9)	0.0322 (3)
H4	0.801	−0.5427	0.7183	0.039*
C5	0.65646 (16)	−0.45341 (13)	0.62004 (9)	0.0310 (3)
H5	0.5861	−0.5261	0.6093	0.037*
C6	0.63358 (15)	−0.33729 (12)	0.57154 (8)	0.0272 (3)
H6	0.5468	−0.3307	0.5272	0.033*
C7	0.70922 (14)	−0.10920 (12)	0.53335 (8)	0.0250 (3)
H7	0.6211	−0.1047	0.4897	0.03*
C8	0.77850 (14)	0.10553 (12)	0.48957 (8)	0.0257 (3)
C9	0.84691 (16)	0.22489 (14)	0.52279 (8)	0.0322 (3)
H9	0.9039	0.2264	0.58	0.039*
C10	0.83234 (16)	0.34013 (13)	0.47339 (8)	0.0302 (3)
H10	0.8783	0.4205	0.4974	0.036*
C11	0.75108 (14)	0.34116 (12)	0.38847 (8)	0.0242 (3)
C12	0.68437 (14)	0.22046 (12)	0.35694 (8)	0.0233 (3)
C13	0.69678 (14)	0.10337 (12)	0.40544 (8)	0.0250 (3)
H13	0.6503	0.023	0.3817	0.03*
C14	0.73364 (14)	0.45777 (12)	0.33190 (8)	0.0250 (3)
C15	0.65366 (14)	0.44444 (13)	0.25094 (8)	0.0282 (3)
H15	0.6425	0.5206	0.2136	0.034*
C16	0.58430 (15)	0.32011 (13)	0.21838 (8)	0.0293 (3)
C17	0.80358 (16)	0.58880 (13)	0.36292 (9)	0.0323 (3)
H17A	0.9165	0.5835	0.3664	0.048*
H17B	0.7758	0.6093	0.4211	0.048*
H17C	0.7644	0.6595	0.3216	0.048*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0291 (5)	0.0327 (5)	0.0317 (5)	−0.0064 (4)	−0.0055 (4)	0.0040 (4)
O2	0.0346 (5)	0.0253 (5)	0.0230 (5)	−0.0008 (4)	−0.0057 (4)	0.0015 (4)

O3	0.0530 (7)	0.0380 (6)	0.0300 (5)	−0.0041 (5)	−0.0139 (5)	0.0056 (4)
N1	0.0311 (6)	0.0259 (6)	0.0232 (5)	−0.0020 (4)	0.0007 (4)	0.0025 (4)
C1	0.0247 (6)	0.0245 (6)	0.0213 (6)	0.0005 (5)	0.0049 (5)	−0.0011 (5)
C2	0.0237 (6)	0.0270 (6)	0.0250 (6)	−0.0003 (5)	0.0054 (5)	−0.0005 (5)
C3	0.0284 (7)	0.0330 (7)	0.0282 (7)	0.0048 (5)	0.0023 (5)	0.0050 (5)
C4	0.0373 (7)	0.0257 (7)	0.0353 (7)	0.0053 (5)	0.0113 (6)	0.0071 (6)
C5	0.0325 (7)	0.0255 (6)	0.0365 (8)	−0.0033 (5)	0.0102 (6)	−0.0015 (6)
C6	0.0262 (6)	0.0291 (7)	0.0262 (6)	−0.0014 (5)	0.0032 (5)	−0.0030 (5)
C7	0.0264 (6)	0.0276 (6)	0.0204 (6)	0.0003 (5)	0.0005 (5)	0.0002 (5)
C8	0.0269 (6)	0.0262 (6)	0.0236 (6)	−0.0010 (5)	0.0024 (5)	0.0029 (5)
C9	0.0387 (8)	0.0331 (7)	0.0227 (6)	−0.0088 (6)	−0.0037 (5)	0.0011 (5)
C10	0.0362 (7)	0.0270 (7)	0.0265 (7)	−0.0085 (5)	0.0006 (5)	−0.0019 (5)
C11	0.0249 (6)	0.0245 (6)	0.0239 (6)	−0.0007 (5)	0.0054 (5)	−0.0004 (5)
C12	0.0234 (6)	0.0263 (6)	0.0197 (6)	0.0012 (5)	0.0011 (5)	−0.0005 (5)
C13	0.0275 (6)	0.0224 (6)	0.0245 (6)	−0.0014 (5)	0.0017 (5)	−0.0012 (5)
C14	0.0241 (6)	0.0243 (6)	0.0278 (7)	0.0018 (5)	0.0079 (5)	0.0015 (5)
C15	0.0294 (7)	0.0259 (6)	0.0293 (7)	0.0017 (5)	0.0038 (5)	0.0054 (5)
C16	0.0313 (7)	0.0290 (7)	0.0262 (7)	0.0024 (5)	−0.0004 (5)	0.0048 (5)
C17	0.0408 (8)	0.0252 (7)	0.0314 (7)	−0.0030 (6)	0.0068 (6)	0.0013 (5)

Geometric parameters (Å, º)

O1—C2	1.3489 (15)	C7—H7	0.95
O1—H1	0.92 (2)	C8—C13	1.3902 (17)
O2—C12	1.3784 (14)	C8—C9	1.3987 (18)
O2—C16	1.3804 (15)	C9—C10	1.3761 (18)
O3—C16	1.2119 (15)	C9—H9	0.95
N1—C7	1.2882 (16)	C10—C11	1.3990 (18)
N1—C8	1.4152 (15)	C10—H10	0.95
C1—C6	1.4024 (17)	C11—C12	1.3969 (17)
C1—C2	1.4124 (17)	C11—C14	1.4500 (17)
C1—C7	1.4483 (17)	C12—C13	1.3841 (17)
C2—C3	1.3940 (18)	C13—H13	0.95
C3—C4	1.3785 (19)	C14—C15	1.3488 (18)
C3—H3	0.95	C14—C17	1.4947 (17)
C4—C5	1.394 (2)	C15—C16	1.4413 (18)
C4—H4	0.95	C15—H15	0.95
C5—C6	1.3793 (18)	C17—H17A	0.98
C5—H5	0.95	C17—H17B	0.98
C6—H6	0.95	C17—H17C	0.98
C2—O1—H1	107.5 (12)	C8—C9—H9	119.7
C12—O2—C16	121.47 (10)	C9—C10—C11	121.27 (12)
C7—N1—C8	120.88 (10)	C9—C10—H10	119.4
C6—C1—C2	118.73 (11)	C11—C10—H10	119.4
C6—C1—C7	119.76 (11)	C12—C11—C10	116.87 (11)
C2—C1—C7	121.51 (11)	C12—C11—C14	118.73 (11)
O1—C2—C3	118.73 (11)	C10—C11—C14	124.40 (11)

O1—C2—C1	121.71 (11)	O2—C12—C13	115.79 (10)
C3—C2—C1	119.55 (11)	O2—C12—C11	121.24 (10)
C4—C3—C2	120.31 (12)	C13—C12—C11	122.98 (11)
C4—C3—H3	119.8	C12—C13—C8	118.78 (11)
C2—C3—H3	119.8	C12—C13—H13	120.6
C3—C4—C5	120.97 (12)	C8—C13—H13	120.6
C3—C4—H4	119.5	C15—C14—C11	118.29 (11)
C5—C4—H4	119.5	C15—C14—C17	121.23 (11)
C6—C5—C4	119.10 (12)	C11—C14—C17	120.48 (11)
C6—C5—H5	120.4	C14—C15—C16	123.08 (11)
C4—C5—H5	120.4	C14—C15—H15	118.5
C5—C6—C1	121.34 (12)	C16—C15—H15	118.5
C5—C6—H6	119.3	O3—C16—O2	116.39 (11)
C1—C6—H6	119.3	O3—C16—C15	126.41 (12)
N1—C7—C1	121.41 (11)	O2—C16—C15	117.19 (11)
N1—C7—H7	119.3	C14—C17—H17A	109.5
C1—C7—H7	119.3	C14—C17—H17B	109.5
C13—C8—C9	119.50 (11)	H17A—C17—H17B	109.5
C13—C8—N1	123.69 (11)	C14—C17—H17C	109.5
C9—C8—N1	116.77 (11)	H17A—C17—H17C	109.5
C10—C9—C8	120.59 (12)	H17B—C17—H17C	109.5
C10—C9—H9	119.7		

C6—C1—C2—O1	−179.16 (11)	C16—O2—C12—C13	−178.79 (11)
C7—C1—C2—O1	1.41 (18)	C16—O2—C12—C11	0.50 (17)
C6—C1—C2—C3	0.41 (17)	C10—C11—C12—O2	−179.69 (11)
C7—C1—C2—C3	−179.01 (11)	C14—C11—C12—O2	−0.29 (18)
O1—C2—C3—C4	179.50 (12)	C10—C11—C12—C13	−0.45 (19)
C1—C2—C3—C4	−0.09 (19)	C14—C11—C12—C13	178.95 (11)
C2—C3—C4—C5	−0.4 (2)	O2—C12—C13—C8	179.63 (11)
C3—C4—C5—C6	0.5 (2)	C11—C12—C13—C8	0.35 (19)
C4—C5—C6—C1	−0.14 (19)	C9—C8—C13—C12	−0.51 (19)
C2—C1—C6—C5	−0.30 (18)	N1—C8—C13—C12	−178.09 (11)
C7—C1—C6—C5	179.13 (11)	C12—C11—C14—C15	−0.11 (17)
C8—N1—C7—C1	177.58 (11)	C10—C11—C14—C15	179.24 (12)
C6—C1—C7—N1	−178.58 (12)	C12—C11—C14—C17	−179.81 (11)
C2—C1—C7—N1	0.84 (18)	C10—C11—C14—C17	−0.46 (19)
C7—N1—C8—C13	−24.41 (19)	C11—C14—C15—C16	0.33 (19)
C7—N1—C8—C9	157.94 (12)	C17—C14—C15—C16	−179.98 (12)
C13—C8—C9—C10	0.8 (2)	C12—O2—C16—O3	179.55 (11)
N1—C8—C9—C10	178.54 (12)	C12—O2—C16—C15	−0.29 (17)
C8—C9—C10—C11	−0.9 (2)	C14—C15—C16—O3	−179.95 (13)
C9—C10—C11—C12	0.73 (19)	C14—C15—C16—O2	−0.13 (19)
C9—C10—C11—C14	−178.64 (12)		