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7-Hydroxy-3-(4-nitrophenyl)-2*H*-chromen-2-one

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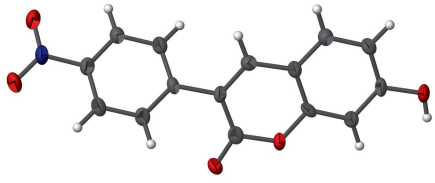
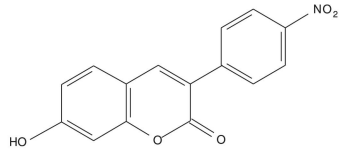
In the title compound, $C_{15}H_9NO_5$, the coumarin ring system is essentially planar, with a dihedral angle of 1.42 (10)° between the two fused rings. The mean plane of the coumarin ring system forms a dihedral angle of 36.10 (1)° with the nitro-substituted benzene ring. The nitro group is almost coplanar with the benzene ring to which it is bonded, with a maximum deviation of 0.014 (6) Å for all atoms in the nitrobenzene group. As in other reported coumarin compounds, there is asymmetry with respect to the O—C═O bond angles, with values of 113.6 (5) and 128.0 (5)°. In a similar way, the O—C—C and C—C—C angles at the junction of the two fused rings have values of 117.6 (5) and 123.7 (5)°, respectively. In the crystal, molecules are linked by O—H···O hydrogen bonds, forming chains along [010]. In addition, weak C—H···O hydrogen bonds link these chains, forming a three-dimensional network.

3D view



Chemical scheme



Structure description

A recent study reveals that many coumarin fluorophores have shown enhanced pure blue efficient electroluminescence with 2.7 and 4.1% of external quantum efficiency, respectively (Chen *et al.*, 2003). Also certain high-efficiency blue electroluminescence based on coumarin derivatives is found as blue-emitting OLEDs and laser dyes (Yu *et al.*, 2009; Serin *et al.*, 2002). Based on the photo-physical properties of coumarins and as a part of our ongoing research on these molecules (Harishkumar *et al.*, 2012; Mahadevan *et al.*, 2013; Rajesha *et al.*, 2012), the synthesis and crystal structure determination of the title compound are reported herein. The compound is currently being assessed for its photo-physical properties.

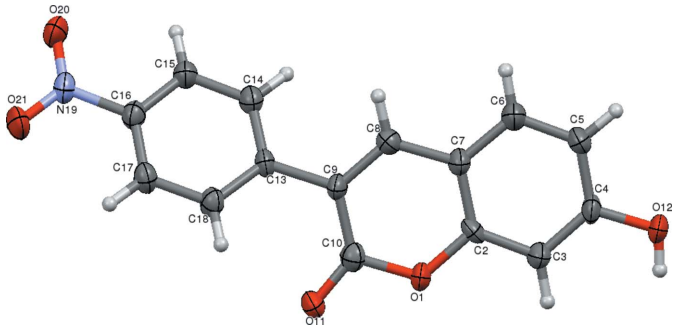


Figure 1
The molecular structure of the title compound, with displacement ellipsoids for non-H atoms drawn at the 50% probability level.

The molecular structure of the title compound is shown in Fig. 1. The coumarin ring system is essentially planar with a dihedral angle of 1.42 (10)° between the two fused rings. The mean plane of the coumarin ring system forms a dihedral angle of 36.10 (1)° with the nitro-substituted benzene ring. This value differs slightly from the reported value of 25.27 (9) Å for 8-ethoxy-3-(4-nitrophenyl)-2*H*-chromen-2-one (Walki *et al.*, 2015). The nitro group is almost coplanar with the phenyl ring with a maximum deviation in the nitrobenzene group of 0.014 (6) Å for C16. Electron localization is indicated by the C8═C9 bond with a length of 1.360 (7) Å. As in other coumarin compounds reported there is an asymmetry in the O—C═O bond angles with values for O1—C10—O11 of 113.6 (5)° and O11—C10—C9 of 128.0 (5)°. The bond angles, O1—C2—C3 and C8—C7—C6, at the junction of the two rings in the coumarin moiety are 117.6 (5)° and 123.7 (5)° respectively.

In the crystal, molecules are linked by O—H···O hydrogen bonds, forming chains along [010]. In addition weak C—H···O hydrogen bonds link these chains, forming a three-dimensional network (Fig. 2, Table 1).

Synthesis and crystallization

A mixture of 0.43 g m (3.08 mmol) of 2,4-dihydroxy benzaldehyde and 0.5 g m (3.08 mmol) of 4-nitro phenylacetonitrile

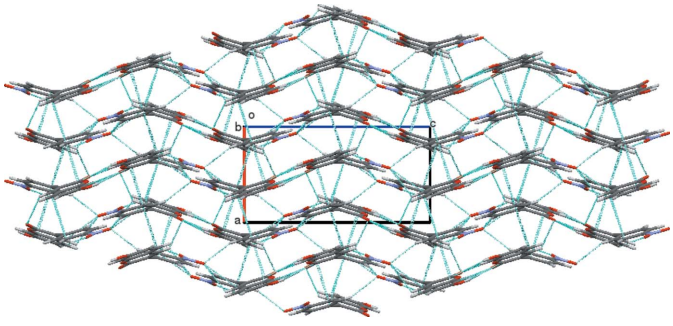


Figure 2
The crystal packing of the title compound, viewed along the *b* axis. Hydrogen bonds are shown as blue lines.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O12—H12···O11^{i}	0.82	1.89	2.704 (6)	172
C3—H3···O11^{i}	0.93	2.53	3.209 (7)	130
C5—H5···O21^{ii}	0.93	2.47	3.244 (7)	141
C8—H8···O11^{iii}	0.93	2.58	3.253 (6)	130
C14—H14···O20^{iv}	0.93	2.40	3.325 (7)	170
C18—H18···O20^{v}	0.93	2.49	3.370 (7)	158

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

was dissolved in ethanol (25 ml), followed by the addition of 0.525 g m (6.16 mmol) of piperidine. The reaction mixture was then stirred at room temperature for 3 h. The completion of the reaction was monitored by thin layer chromatography [petroleum ether and ethyl acetate (8:2 *v*/*v*)]. After the completion of the reaction, the reaction mixture was filtered and washed with diethylether to yield a brown precipitate. The crude product obtained was refluxed with 10% acetic acid for 2 h and was filtered and washed with water. The product obtained was further purified by recrystallization using glacial acetic acid as solvent to form brown crystals, m.p. = 535–537 K, yield 91.6%.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{15}H_9NO_5$
M_r	283.23
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	296
a, *b*, *c* (Å)	7.0087 (9), 13.0242 (13), 13.6761 (17)
V (Å^3)	1248.4 (3)
Z	4
Radiation type	Cu *Kα*
μ (mm^{-1})	0.98
Crystal size (mm)	0.29 × 0.26 × 0.25
Data collection	
Diffractometer	Bruker X8 Proteum
Absorption correction	Multi-scan (*SADABS*; Bruker, 2013)
T_{min}, T_{max}	0.765, 0.792
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	6307, 2037, 1279
R_{int}	0.124
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.587
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.068, 0.181, 0.98
No. of reflections	2037
No. of parameters	190
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.29, −0.35

Computer programs: *APEX2* (Bruker, 2013), *SAINT* (Bruker, 2013), *SHELXS97* (Sheldrick, 2008), *SHELXL97* (Sheldrick, 2008), *Mercury* (Macrae *et al.*, 2008).

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full crystallographic data

IUCrData (2016). **1**, x160329 [doi:10.1107/S2414314616003291]

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7-Hydroxy-3-(4-nitrophenyl)-2*H*-chromen-2-one

Crystal data

$C_{15}H_9NO_5$
M_r = 283.23
Orthorhombic, $P2_12_12_1$
Hall symbol: P 2ac 2ab
a = 7.0087 (9) Å
b = 13.0242 (13) Å
c = 13.6761 (17) Å
V = 1248.4 (3) Å^3
Z = 4
$F(000)$ = 584
D_x = 1.507 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54178 Å
Cell parameters from 2037 reflections
θ = 4.7–64.9°
μ = 0.98 mm^{-1}
T = 296 K
Rectangle, brown
0.29 × 0.26 × 0.25 mm

Data collection

Bruker X8 Proteum diffractometer
Radiation source: Bruker MicroStar microfocus rotating anode
Helios multilayer optics monochromator
Detector resolution: 18.4 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2013)
T_{min} = 0.765, T_{max} = 0.792
6307 measured reflections
2037 independent reflections
1279 reflections with $I > 2\sigma(I)$
R_{int} = 0.124
θ_{max} = 64.9°, θ_{min} = 4.7°
h = −7→8
k = −15→14
l = −15→14

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.068
$wR(F^2)$ = 0.181
S = 0.98
2037 reflections
190 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-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0812P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.35 e Å^{-3}

Special details

Experimental. ^{1}H NMR(400 MHz, DMSO-d_6 δ p.p.m.)10.79 (s, 1H), 8.40 (s, 1H), 8.28–8.29 (m, 2H), 8.0–8.02(m, 2H), 7.65(d, J= 8.40 Hz, 1H), 6.84–6.85 (m, 1H), 6.78 (d, J= 2.0 Hz, 1H).
IR (KBr) (ν_{max}/cm^{-1}): 3180 (C—OH), 2925 (C—H), 1678 (C=O), 1346 (N—O), 1127 (C—O—C).
Mass spectra of the compound showed molecular ion peak at m/z = 282.4 [M^+].

Geometry. Bond distances, angles *etc*. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement on F^2 for ALL reflections except those flagged by the user for potential systematic errors. Weighted *R*-factors *wR* and all goodnesses 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 observed criterion of $F^2 > \sigma(F^2)$ is used only for calculating -*R*-factor-obs *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	0.4270 (5)	0.6104 (2)	0.3410 (3)	0.0301 (11)
O11	0.4770 (5)	0.7766 (2)	0.3319 (3)	0.0322 (11)
O12	0.3610 (6)	0.2463 (2)	0.3452 (3)	0.0409 (15)
O20	0.4326 (6)	1.0871 (3)	0.7822 (3)	0.0447 (16)
O21	0.3441 (6)	1.1717 (3)	0.6546 (3)	0.0472 (15)
N19	0.3856 (6)	1.0912 (3)	0.6965 (4)	0.0340 (18)
C2	0.3786 (7)	0.5216 (4)	0.3899 (4)	0.0253 (19)
C3	0.3933 (7)	0.4300 (4)	0.3393 (5)	0.0307 (17)
C4	0.3449 (8)	0.3408 (4)	0.3889 (5)	0.0303 (19)
C5	0.2816 (8)	0.3427 (4)	0.4851 (4)	0.035 (2)
C6	0.2686 (8)	0.4342 (4)	0.5349 (5)	0.035 (2)
C7	0.3205 (8)	0.5259 (4)	0.4875 (4)	0.0290 (18)
C8	0.3137 (7)	0.6256 (4)	0.5334 (4)	0.0287 (19)
C9	0.3675 (7)	0.7127 (4)	0.4860 (4)	0.0277 (19)
C10	0.4251 (7)	0.7064 (4)	0.3859 (4)	0.0307 (19)
C13	0.3718 (7)	0.8134 (4)	0.5380 (4)	0.0267 (18)
C14	0.4250 (7)	0.8149 (4)	0.6359 (4)	0.0313 (19)
C15	0.4280 (7)	0.9056 (4)	0.6883 (4)	0.0313 (19)
C16	0.3772 (8)	0.9957 (4)	0.6398 (4)	0.0300 (19)
C17	0.3265 (8)	0.9975 (4)	0.5432 (4)	0.0310 (19)
C18	0.3210 (7)	0.9055 (4)	0.4914 (4)	0.0310 (19)
H3	0.43400	0.42830	0.27460	0.0370*
H5	0.24780	0.28180	0.51610	0.0420*
H6	0.22590	0.43540	0.59930	0.0420*
H8	0.27110	0.63050	0.59770	0.0340*
H12	0.40080	0.25340	0.28920	0.0610*
H14	0.45900	0.75380	0.66660	0.0370*
H15	0.46290	0.90660	0.75390	0.0370*
H17	0.29620	1.05920	0.51260	0.0370*
H18	0.28390	0.90510	0.42610	0.0370*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.042 (2)	0.0174 (16)	0.031 (2)	−0.0023 (15)	0.0015 (18)	−0.0052 (16)
O11	0.043 (2)	0.0205 (17)	0.033 (2)	−0.0011 (16)	0.0050 (19)	0.0039 (18)
O12	0.072 (3)	0.0176 (17)	0.033 (3)	−0.0035 (18)	0.007 (2)	−0.0074 (16)

O20	0.071 (3)	0.027 (2)	0.036 (3)	−0.004 (2)	−0.007 (2)	−0.0086 (18)
O21	0.077 (3)	0.0196 (19)	0.045 (3)	0.005 (2)	−0.004 (2)	0.002 (2)
N19	0.044 (3)	0.020 (2)	0.038 (4)	−0.002 (2)	0.001 (2)	−0.006 (2)
C2	0.027 (3)	0.020 (3)	0.029 (4)	−0.004 (2)	0.000 (2)	0.009 (2)
C3	0.040 (3)	0.023 (3)	0.029 (3)	0.002 (3)	0.005 (3)	−0.001 (3)
C4	0.039 (3)	0.016 (3)	0.036 (4)	0.000 (3)	−0.001 (3)	−0.006 (2)
C5	0.051 (4)	0.021 (3)	0.032 (4)	−0.003 (3)	0.006 (3)	0.003 (3)
C6	0.050 (4)	0.024 (3)	0.031 (4)	−0.001 (3)	0.000 (3)	−0.001 (3)
C7	0.037 (3)	0.020 (2)	0.030 (4)	0.001 (2)	0.003 (3)	−0.001 (2)
C8	0.034 (3)	0.026 (3)	0.026 (4)	−0.003 (2)	0.001 (2)	0.001 (2)
C9	0.036 (3)	0.019 (3)	0.028 (4)	−0.005 (2)	0.003 (2)	−0.005 (2)
C10	0.031 (3)	0.026 (3)	0.035 (4)	0.004 (2)	−0.002 (3)	−0.001 (3)
C13	0.032 (3)	0.015 (2)	0.033 (4)	−0.001 (2)	0.000 (2)	0.000 (2)
C14	0.037 (3)	0.023 (3)	0.034 (4)	0.001 (2)	0.002 (3)	0.000 (2)
C15	0.041 (3)	0.023 (3)	0.030 (4)	−0.001 (3)	−0.001 (3)	−0.001 (2)
C16	0.034 (3)	0.024 (3)	0.032 (4)	−0.002 (2)	−0.002 (3)	−0.004 (2)
C17	0.033 (3)	0.021 (3)	0.039 (4)	0.001 (2)	−0.005 (3)	0.001 (3)
C18	0.035 (3)	0.024 (3)	0.034 (4)	0.006 (3)	−0.005 (3)	−0.002 (3)

Geometric parameters (Å, º)

O1—C2	1.378 (6)	C9—C10	1.430 (8)
O1—C10	1.393 (6)	C9—C13	1.492 (7)
O11—C10	1.230 (6)	C13—C18	1.404 (7)
O12—C4	1.373 (6)	C13—C14	1.390 (8)
O20—N19	1.219 (7)	C14—C15	1.382 (7)
O21—N19	1.230 (6)	C15—C16	1.394 (7)
O12—H12	0.8200	C16—C17	1.368 (8)
N19—C16	1.467 (7)	C17—C18	1.393 (7)
C2—C3	1.383 (8)	C3—H3	0.9300
C2—C7	1.397 (8)	C5—H5	0.9300
C3—C4	1.387 (8)	C6—H6	0.9300
C4—C5	1.389 (9)	C8—H8	0.9300
C5—C6	1.376 (8)	C14—H14	0.9300
C6—C7	1.407 (8)	C15—H15	0.9300
C7—C8	1.443 (7)	C17—H17	0.9300
C8—C9	1.360 (7)	C18—H18	0.9300
C2—O1—C10	122.5 (4)	C14—C13—C18	119.6 (5)
C4—O12—H12	109.00	C9—C13—C14	118.5 (5)
O20—N19—O21	123.3 (4)	C13—C14—C15	121.0 (5)
O21—N19—C16	117.9 (5)	C14—C15—C16	118.0 (5)
O20—N19—C16	118.8 (4)	N19—C16—C15	116.9 (5)
O1—C2—C7	120.1 (5)	N19—C16—C17	120.4 (5)
C3—C2—C7	122.3 (5)	C15—C16—C17	122.7 (5)
O1—C2—C3	117.6 (5)	C16—C17—C18	118.9 (5)
C2—C3—C4	117.4 (6)	C13—C18—C17	119.8 (5)
O12—C4—C5	117.0 (5)	C2—C3—H3	121.00

C3—C4—C5	121.8 (5)	C4—C3—H3	121.00
O12—C4—C3	121.2 (6)	C4—C5—H5	120.00
C4—C5—C6	120.4 (5)	C6—C5—H5	120.00
C5—C6—C7	119.4 (6)	C5—C6—H6	120.00
C2—C7—C6	118.8 (5)	C7—C6—H6	120.00
C2—C7—C8	117.5 (5)	C7—C8—H8	119.00
C6—C7—C8	123.7 (5)	C9—C8—H8	119.00
C7—C8—C9	122.3 (5)	C13—C14—H14	119.00
C8—C9—C10	119.1 (5)	C15—C14—H14	120.00
C10—C9—C13	120.1 (5)	C14—C15—H15	121.00
C8—C9—C13	120.8 (5)	C16—C15—H15	121.00
O1—C10—C9	118.5 (5)	C16—C17—H17	121.00
O11—C10—C9	128.0 (5)	C18—C17—H17	121.00
O1—C10—O11	113.6 (5)	C13—C18—H18	120.00
C9—C13—C18	122.0 (5)	C17—C18—H18	120.00

C10—O1—C2—C3	−177.3 (4)	C2—C7—C8—C9	−2.3 (8)
C10—O1—C2—C7	1.6 (7)	C7—C8—C9—C10	2.8 (8)
C2—O1—C10—O11	178.3 (4)	C7—C8—C9—C13	−175.6 (5)
C2—O1—C10—C9	−1.1 (7)	C8—C9—C13—C14	35.2 (7)
O20—N19—C16—C17	−179.5 (5)	C8—C9—C13—C18	−143.7 (5)
O20—N19—C16—C15	−1.2 (7)	C10—C9—C13—C14	−143.1 (5)
O21—N19—C16—C15	178.9 (5)	C10—C9—C13—C18	37.9 (7)
O21—N19—C16—C17	0.7 (7)	C8—C9—C10—O1	−1.1 (7)
O1—C2—C3—C4	179.8 (5)	C8—C9—C10—O11	179.7 (5)
C3—C2—C7—C8	178.9 (5)	C13—C9—C10—O1	177.3 (4)
C3—C2—C7—C6	−2.3 (8)	C13—C9—C10—O11	−2.0 (8)
C7—C2—C3—C4	1.0 (8)	C9—C13—C14—C15	−178.7 (5)
O1—C2—C7—C6	178.8 (5)	C18—C13—C14—C15	0.3 (8)
O1—C2—C7—C8	0.1 (7)	C9—C13—C18—C17	179.7 (5)
C2—C3—C4—C5	0.9 (8)	C14—C13—C18—C17	0.8 (7)
C2—C3—C4—O12	−178.0 (5)	C13—C14—C15—C16	−0.4 (8)
O12—C4—C5—C6	177.6 (5)	C14—C15—C16—N19	−178.7 (5)
C3—C4—C5—C6	−1.3 (9)	C14—C15—C16—C17	−0.5 (8)
C4—C5—C6—C7	−0.2 (9)	N19—C16—C17—C18	179.7 (5)
C5—C6—C7—C2	1.9 (8)	C15—C16—C17—C18	1.5 (8)
C5—C6—C7—C8	−179.4 (5)	C16—C17—C18—C13	−1.6 (8)
C6—C7—C8—C9	179.0 (5)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O12—H12···O11^{i}	0.82	1.89	2.704 (6)	172
C3—H3···O11^{i}	0.93	2.53	3.209 (7)	130
C5—H5···O21^{ii}	0.93	2.47	3.244 (7)	141
C8—H8···O11^{iii}	0.93	2.58	3.253 (6)	130
C14—H14···O20^{iv}	0.93	2.40	3.325 (7)	170

C18—H18···O11	0.93	2.51	2.962 (6)	110
C18—H18···O20^{v}	0.93	2.49	3.370 (7)	158

Symmetry codes: (i) −*x*+1, *y*−1/2, −*z*+1/2; (ii) *x*, *y*−1, *z*; (iii) *x*−1/2, −*y*+3/2, −*z*+1; (iv) −*x*+1, *y*−1/2, −*z*+3/2; (v) −*x*+1/2, −*y*+2, *z*−1/2.