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Key indicators

Single-crystal X-ray study
 $T = 120$ K
Mean $\sigma(\text{C}-\text{C}) = 0.003$ Å
 R factor = 0.048
 wR factor = 0.121
Data-to-parameter ratio = 9.3

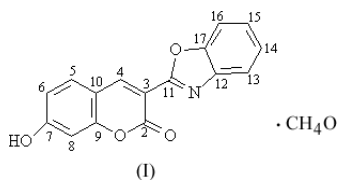
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

3-(Benzoxazol-2-yl)-7-hydroxychromen-2-one methanol solvate

The title compound, $\text{C}_{16}\text{H}_9\text{NO}_4 \cdot \text{CH}_4\text{O}$, is a coumarin derivative suitable for use as a laser dye. The coumarin and the benzoxazole ring systems in the molecule are planar. The angle between them is $8.03(7)^\circ$. The crystal packing is characterized by hydrogen bonds that form dimers which are, in turn, linked by $\text{C}-\text{H} \cdots \text{O}$ intermolecular interactions in the $[100]$ direction.

Comment

Coumarins are compounds extensively studied due to their practical applications (Krasovitskii, 1988; Dall'Acqua *et al.*, 1996). Biological and chemical sensors, fluorescent probes and laser dyes, are some of their applications (Christie & Lui, 1999; Chandrasekharan & Kelly, 2002). Additionally, coumarins that contains an electron-releasing group in the 7-position, and a heterocyclic electron-acceptor residue in the 3-position, are recognized as fluorescent dyes suitable for application to synthetic fibers (Sokodowska *et al.*, 2001).



The compound 3-benzoxazol-2-yl-7-hydroxy-chromen-2-one, (I), due to a dissociation equilibrium based on the hydroxyl group, results in neutral and anionic form in protic solvents. This coumarin is suitable for use as a laser dye, since it shows high fluorescence quantum yields in solvents of different polarities (Machado & Miranda, 2001). Even at low temperature (77 K), phosphorescence was not detected. Meanwhile, a quantum yield of 0.06 for singlet-oxygen generation was measured for the neutral species in chloroform, indicating the possibility of intersystem crossing (Machado & Miranda, 2001).

The X-ray analysis of (I) was undertaken as part of a study to elucidate the relationships between the characteristics of functional dyes containing the coumarin skeleton and their molecular structures.

An ORTEP-3 (Farrugia, 1997) drawing of the asymmetric unit, which is composed of one coumarin molecule and one methanol molecule of crystallization, is shown in Fig. 1. Selected geometric parameters are presented in Table 1.

The angle between the benzoxazole and coumarin moieties is $8.03(7)^\circ$, showing more deviation from planarity than another analog in which the angle is $5.24(8)^\circ$ (Guilardi *et al.*,

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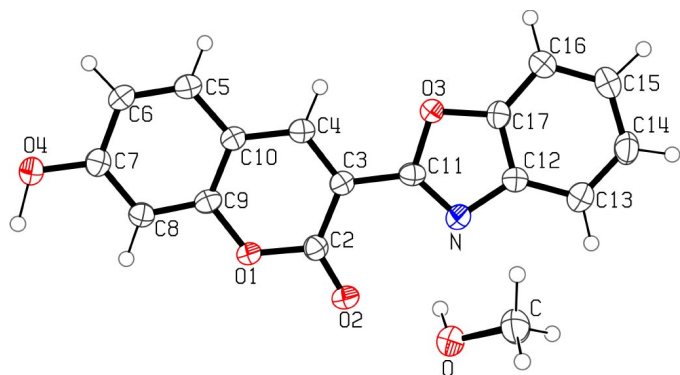


Figure 1
An ORTEP-3 view (Farrugia, 1997) of the asymmetric unit, showing displacement ellipsoids at the 50% probability level.

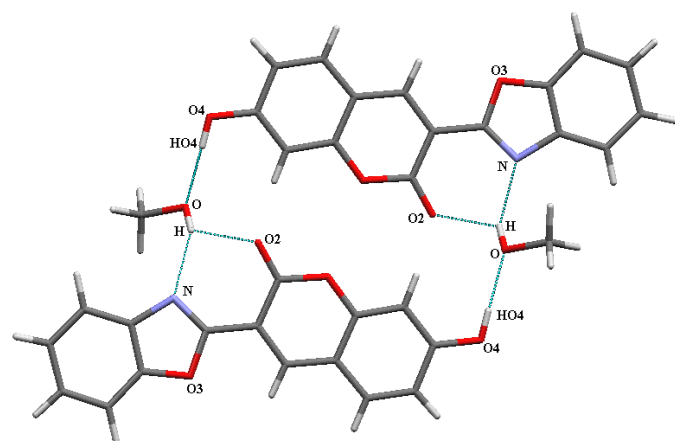


Figure 2
A MERCURY view (Cambridge Crystallographic Data Centre, 2003) of the hydrogen bonds in the methanol-linked dimers.

2002). Atom O4 deviates by 0.116 (2) Å from the coumarin plane, probably because of the hydrogen bonding.

The bond length C3—C11 is in good agreement, within experimental error, with those observed in 3-(benzoxazol-2-yl)chromen-2-one (Guilardi *et al.*, 2002) and 3-(2-benzothiazolyl)-7-(diethylamino)coumarin (Jasinski & Paight, 1995).

The bond C3—C4 has double-bond character. The bonds C2—C3 and C4—C10, adjacent to double bonds, are systematically longer than 1.40 Å. The bond angles C8—C9—O1 and C5—C10—C4 at the junction of the two rings are, respectively, smaller and greater than 120°. Similar behavior is observed for an unsubstituted coumarin (Gavuzzo *et al.*, 1974), a coumarin-3-carboxylic acid (Dobson & Gerkin, 1996) and a 3-(bromoacetyl)coumarin (Vasudevan *et al.*, 1991).

In comparison with coumarins having no substituent at the 7-position (Gavuzzo *et al.*, 1974; Guilardi *et al.*, 2002), the title compound shows an increase in the bond lengths C6—C7 and C7—C8, and a decrease in the C6—C7—C8 bond angle of ~2° that may be due to the presence of the hydroxyl group at the 7-position. Other hydroxycoumarins, such as 7-hydroxycoumarin (Ueno, 1985), 7-hydroxyphenylcoumarin (Honda *et al.*, 1995) and 7-hydroxy-4-methylcoumarin monohydrate (Jasinski & Woudenberg, 1994), exhibit similar behavior.

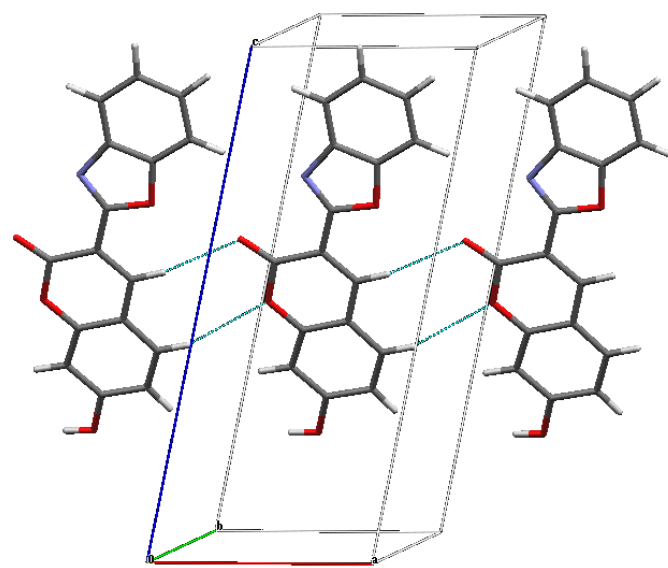


Figure 3
A MERCURY view (Cambridge Crystallographic Data Centre, 2003) of the C—H...O intermolecular interactions in the [100] direction.

The methanol O atom is involved in three hydrogen bonds. It is a donor in a two-centered bond to N and O2 and an acceptor from O4 such that solvent-bridged dimers are formed around an inversion center, involving two methanol molecules and two molecules of compound (I) (Table 2 and Fig. 2). The dimers are linked by C—H...O intermolecular interactions in the [100] direction (Fig. 3).

Experimental

The title compound was prepared, purified and crystallized as described by Luan *et al.* (2002).

Crystal data

C₁₆H₉NO₄·CH₄O
M_r = 311.28
 Triclinic, *P* $\bar{1}$
a = 6.5606 (3) Å
b = 7.3493 (3) Å
c = 15.3575 (7) Å
 α = 79.724 (2)°
 β = 78.980 (2)°
 γ = 74.194 (5)°
V = 693.1 (2) Å³

Z = 2
D_x = 1.492 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 11153 reflections
 θ = 2.9–27.5°
 μ = 0.11 mm⁻¹
T = 120 (2) K
 Prism, yellow
 0.23 × 0.14 × 0.03 mm

Data collection

Nonius KappaCCD diffractometer
 ω and ϕ scans with κ offsets
 11 153 measured reflections
 2424 independent reflections
 1844 reflections with *I* > 2σ(*I*)

*R*_{int} = 0.079
 θ_{max} = 25°
h = -7 → 7
k = -8 → 8
l = -18 → 18

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.048
wR (*F*²) = 0.121
S = 1.05
 2424 reflections
 260 parameters
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0613P)^2 + 0.2086P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.24 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.22 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

O1—C9	1.376 (2)	C3—C11	1.459 (3)
O1—C2	1.388 (2)	C4—C10	1.421 (3)
O2—C2	1.213 (3)	C6—C7	1.412 (3)
C2—C3	1.454 (3)	C7—C8	1.389 (3)
C3—C4	1.364 (3)		
O2—C2—O1	115.89 (17)	C8—C7—C6	120.7 (2)
O2—C2—C3	127.46 (19)	O1—C9—C8	116.82 (18)
O1—C2—C3	116.65 (18)	C5—C10—C4	124.49 (19)
C4—C3—C2	120.42 (19)		
C4—C3—C11—N	172.8 (2)	C4—C3—C11—O3	−5.1 (3)
C2—C3—C11—N	−5.5 (3)	C2—C3—C11—O3	176.62 (17)

Table 2

Hydrogen-bonding and intermolecular interaction geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O—H...N	1.06 (4)	1.99 (4)	2.926 (3)	145 (3)
O—H...O2	1.06 (4)	2.15 (4)	2.870 (2)	123 (3)
O4—HO4...O ⁱ	1.09 (3)	1.53 (3)	2.627 (3)	179 (3)
C5—H5...O1 ⁱⁱ	0.96 (2)	2.65 (3)	3.555 (3)	157 (2)
C4—H4...O2 ⁱⁱ	0.98 (2)	2.46 (2)	3.402 (3)	160 (2)

Symmetry codes: (i) $-x, 1 - y, 1 - z$; (ii) $1 + x, y, z$.

H atoms were located in a difference Fourier synthesis and refined freely. The final refined C—H distances ranged from 0.96 (2) to 1.11 (3) Å, and O—H distances ranged from 1.06 (4) to 1.09 (3) Å.

Data collection: *COLLECT* (Nonius, 1997–2000); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); 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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