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2-Amino-4-(4-methoxyphenyl)-5-oxo-4*H*,5*H*-pyrano[3,2-*c*]chromene-3-carbonitrile *N*,*N*-dimethylformamide solvate

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Key indicators

Single-crystal X-ray study
T = 193 K
Mean σ(C–C) = 0.003 Å
R factor = 0.049
wR factor = 0.119
Data-to-parameter ratio = 13.0

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

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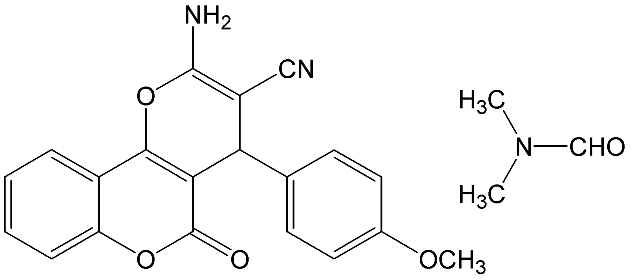
The title compound, $C_{20}H_{14}N_2O_4 \cdot C_3H_7NO$, was synthesized by the reaction of 4-hydroxycoumarin and 4′-methoxybenzylidenemalononitrile catalyzed by KF-montmorillonite. There are two independent molecules in the asymmetric unit, and the amino groups form N—H···O hydrogen bonds with *N*,*N*-dimethylformamide.

Comment

Coumarin and its derivatives are natural compounds and are important chemicals in the perfume, cosmetic and pharmaceutical industries (Soine, 1964). Recently, inorganic solid supports as catalysts, resulting in higher selectivity, milder conditions and easier work-up, have been reported as useful catalysts for many organic reactions (Gao *et al.*, 1998; Shi *et al.*, 2002). As part of our program aimed at developing new and environmentally friendly methodologies for the preparation of fine chemicals (Shi *et al.*, 2003), we have synthesized 4*H*-pyrano[3,2-*c*]coumarin derivatives by a two-component reaction catalyzed by KF-montmorillonite. We report here the synthesis and the crystal structure of the title compound, (I).



(I)

The asymmetric unit contains two molecules of coumarin and two molecules of DMF. In one coumarin molecule, the pyran ring is almost planar, with deviations of less than 0.033 (2) Å (Fig. 1). The other pyran ring adopts a flattened boat conformation; atoms O1 and C3 deviate from the plane defined by atoms C1/C2/C4/C5 by 0.043 (2) and 0.132 (3) Å, respectively. A similar conformation was observed in the structures of ethyl 9-amino-7-(4-methoxyphenyl)-7*H*-pyrano-[3,2-*c*]coumarin-8-carboxylate (Wang *et al.*, 2004*a*) and ethyl 2-amino-5-oxo-4-(*p*-tolyl)-4*H*,5*H*-pyrano[3,2-*c*]chromene-8-carboxylate (Wang *et al.*, 2004*b*). The dihedral angle between the coumarin pyran ring O3/C6/C4/C5/C12/C7 and the fused benzene ring is 2.5 (3)° and that between the coumarin pyran ring and the 4-methoxyphenyl ring is 89.8 (3)°. In the other independent molecule, the coumarin rings are almost coplanar, and the second pyran ring (C24–C28/O6) adopts a

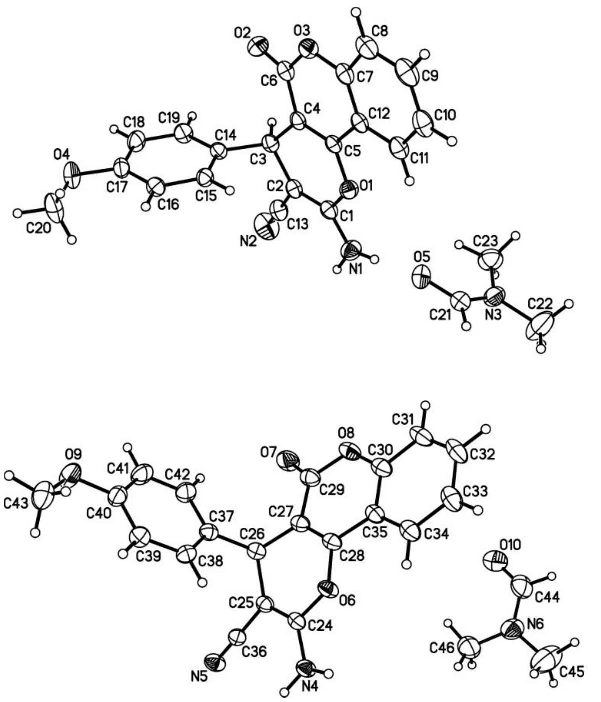


Figure 1
The asymmetric unit of (I), showing 40% probability displacement ellipsoids and the atom-numbering scheme.

half-chair conformation: atoms C26/C27/C28/O6 are coplanar, while atoms C24 and C25 deviate from this plane by 0.381 (2) and 0.455 (3) Å, respectively.

The sums of the bond angles around N1 or N4 indicate planar geometries. In addition, because of the existence of a conjugated system, the N1—C1 and N4—C24 bond distances (Table 1) are significantly shorter than the typical Csp^2—N distance (1.426 Å; Lorente *et al.*, 1995). The amino groups are involved in N—H···O hydrogen bonds with *N*,*N*-dimethylformamide molecules (Table 2 and Fig. 2).

Experimental

The title compound, (I), was prepared by the reaction of 4-hydroxycoumarin (0.49 g, 3 mmol) and 4′-methoxybenzylidenemalononitrile (0.55 g, 3 mmol) catalyzed by KF-montmorillonite (0.2 g) in *N*,*N*-dimethylformamide at 353 K for 6 h (yield 80%, m.p. 507–508 K). Crystals of (I) suitable for X-ray diffraction were obtained by slow evaporation of an *N*,*N*-dimethylformamide–ethanol (1:5) solution.

Crystal data

$C_{20}H_{14}N_2O_4 \cdot C_3H_7NO$
$M_r = 419.43$
Triclinic, $P\overline{1}$
$a = 12.472$ (3) Å
$b = 13.003$ (3) Å
$c = 13.620$ (3) Å
$\alpha = 99.799$ (4)°
$\beta = 95.399$ (4)°
$\gamma = 104.785$ (5)°
$V = 2082.5$ (8) Å^3
$Z = 4$
$D_x = 1.338$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7449 reflections
$\theta = 3.1$–25.3°
$\mu = 0.10$ mm^{-1}
$T = 193$ (2) K
Block, colorless
0.49 × 0.41 × 0.17 mm

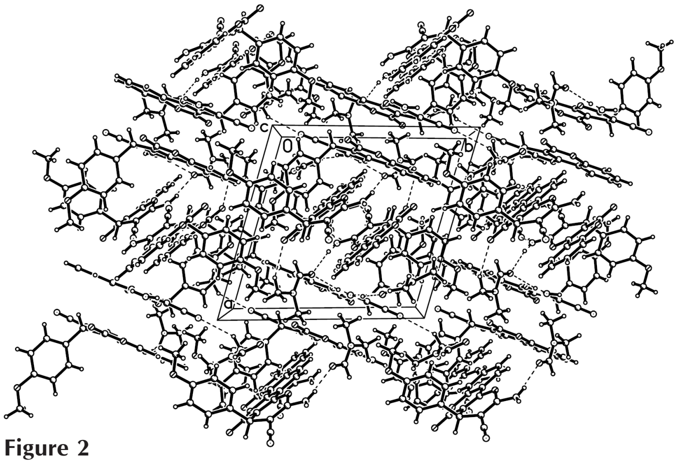


Figure 2
A molecular packing diagram for (I). The dashed lines indicate hydrogen bonds and short contacts.

Data collection

Rigaku Mercury diffractometer
ω scans
Absorption correction: multi-scan (Jacobson, 1998)
$T_{\min} = 0.955$, $T_{\max} = 0.984$
20798 measured reflections
7573 independent reflections
6262 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.024$
$\theta_{\max} = 25.4°$
$h = -15 \rightarrow 15$
$k = -14 \rightarrow 15$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.119$
$S = 1.10$
7573 reflections
582 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0527P)^2 + 0.4884P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.19$ e Å^{-3}
$\Delta\rho_{\min} = -0.21$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C5	1.365 (2)	O7—C29	1.208 (2)
O1—C1	1.381 (2)	O8—C30	1.376 (2)
O2—C6	1.204 (2)	O8—C29	1.384 (2)
O3—C7	1.380 (2)	N1—C1	1.340 (2)
O3—C6	1.387 (2)	N2—C13	1.147 (3)
O6—C28	1.366 (2)	N4—C24	1.336 (2)
O6—C24	1.3788 (19)	N5—C36	1.150 (2)
C5—O1—C1—C2	−4.5 (2)	C28—O6—C24—C25	−13.4 (2)
O1—C1—C2—C3	−3.2 (3)	O6—C24—C25—C26	−7.0 (3)
C1—C2—C3—C4	10.0 (2)	C24—C25—C26—C27	22.7 (2)
C1—O1—C5—C4	3.8 (2)	C24—O6—C28—C27	15.1 (2)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O5	0.92 (2)	2.01 (2)	2.921 (2)	171 (2)
N1—H1*B*···O10$^{\rm i}$	0.91 (3)	2.01 (3)	2.870 (3)	157 (2)
N4—H4*A*···O5	0.86 (2)	2.10 (2)	2.952 (2)	172 (2)
N4—H4*B*···N5$^{\rm ii}$	0.90 (2)	2.11 (2)	2.998 (2)	173 (2)
C22—H22*A*···O7$^{\rm iii}$	0.98	2.52	3.423 (3)	154
C46—H46*A*···N2$^{\rm iv}$	0.98	2.52	3.355 (3)	143

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

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Amino H atoms were refined isotropically. The positions of the other H atoms were calculated and refined as riding, with C—H = 0.95–1.00 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C) or 1.5$U_{\rm eq}$(C$_{\rm methyl}$).

Data collection: *CrystalClear* (Rigaku, 2000); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku/MSC, 2003); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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