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Methyl 2-amino-4-(4-chlorophenyl)-4*H*-pyrano-[3,2-*c*]coumarin-3-carboxylate *N*,*N*-dimethylformamide solvate

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Key indicators

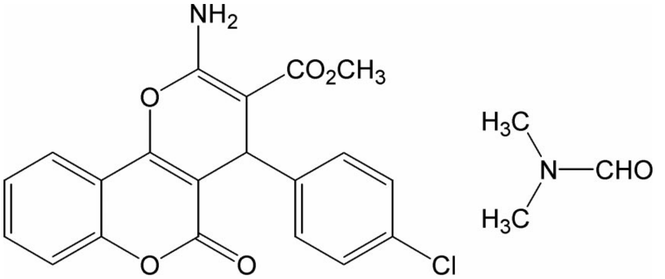
Single-crystal X-ray study
T = 193 K
Mean σ(C–C) = 0.002 Å
R factor = 0.038
wR factor = 0.102
Data-to-parameter ratio = 12.7

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

The title compound [systematic name: methyl 2-amino-4-(4-chlorophenyl)-5-oxo-4*H*,5*H*-pyrano[3,2-*c*]chromene-3-carboxylate *N*,*N*-dimethylformamide solvate], $C_{20}H_{14}ClNO_5 \cdot C_3H_7NO$, was synthesized by the reaction of 4-hydroxycoumarin and methyl 4′-chloro-2-cyanocinnamate catalyzed by KF-montmorillonite. There are N—H···O hydrogen bonds and C—H···O interactions in the crystal structure.

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 programme aimed at developing new and environmentally friendly methodologies for the preparation of fine chemicals (Shi *et al.*, 2003), we have synthesized 7*H*-pyrano[3,2-*c*]coumarin derivatives by a two-component reaction catalyzed by KF-montmorillonite. We report here the synthesis and crystal structure of the title compound, (I).



(I)

The molecular structure is shown in Fig. 1. The pyran ring of coumarin is almost planar, with deviations less than 0.021 (2) Å. The other pyran ring adopts a flattened boat conformation; atoms O1 and C3 deviate from the plane defined by atoms C1, C2, C4 and C5 by 0.119 (2) and 0.219 (3) Å, respectively. Similar conformations were 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*]coumarin-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 0.8 (3)° and that between the coumarin pyran ring and the 4-chlorophenyl ring is 84.3 (3)°. Because of the existence of a conjugated system, the N1—C1 [1.335 (2) Å] distance is significantly shorter than

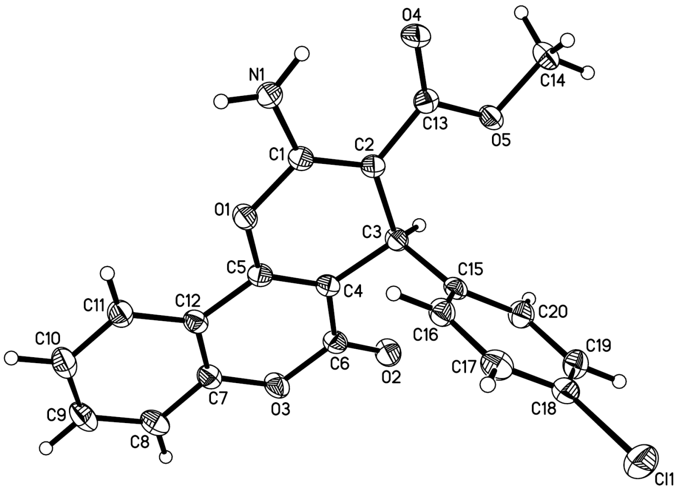


Figure 1
The molecular structure of (I), showing 40% probability displacement ellipsoids and the atom-numbering scheme. The solvent molecule has been omitted.

the typical Csp^2—N bond distance (1.426 Å; Lorente *et al.*, 1995). The amine group is involved in an intramolecular N—H···O hydrogen bond (Table 2) with atom O4 of the carbonyl group and also in an intermolecular hydrogen bond with atom O6 of the *N*,*N*-dimethylformamide group (Fig. 2).

Experimental

Compound (I) was prepared by the reaction of 4-hydroxycoumarin (0.32 g, 2 mmol) and methyl 4′-chloro-2-cyanocinnamate (0.45 g, 2 mmol) catalyzed by KF-montmorillonite (0.2 g) in *N*,*N*-dimethylformamide at 353 K for 4 h (yield 73%, m.p. 489–491 K). Crystals of (I) suitable for X-ray diffraction were obtained by slow evaporation of an *N*,*N*-dimethylformamide–ethanol solution. IR (KBr, cm^{-1}): 3380, 3268 (NH$_2$), 1726, 1700 (CO), 1614, 1520, 1490, 840, 748 (phenyl ring). ^{1}H NMR (DMSO-d_6): δ 3.56 (3H, *s*, CH$_3$O), 4.70 (1H, *s*, CH), 7.25–7.31 (4H, *m*, ArH), 7.44–7.51 (2H, *m*, ArH), 7.68–7.72 (1H, *m*, ArH), 7.88 (2H, *s*, NH$_2$), 7.97 (1H, *d*, *J* = 7.6 Hz, ArH).

Crystal data

$C_{20}H_{14}ClNO_5{\cdot}C_3H_7NO$
$M_r = 456.87$
Triclinic, $P\overline{1}$
$a = 7.5757$ (5) Å
$b = 12.7812$ (4) Å
$c = 12.9142$ (8) Å
$\alpha = 62.186$ (5)°
$\beta = 89.802$ (8)°
$\gamma = 74.080$ (6)°
$V = 1052.09$ (12) Å^3
$Z = 2$
$D_x = 1.442$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3920 reflections
$\theta = 3.1$–25.3°
$\mu = 0.23$ mm^{-1}
$T = 193$ (2) K
Block, colourless
0.69 × 0.50 × 0.38 mm

Data collection

Rigaku Mercury diffractometer
ω scans
Absorption correction: multi-scan (Jacobson, 1998)
$T_{\min} = 0.860$, $T_{\max} = 0.919$
10 329 measured reflections
3814 independent reflections
3463 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.016$
$\theta_{\max} = 25.4$°
$h = -9 \rightarrow 9$
$k = -14 \rightarrow 15$
$l = -15 \rightarrow 15$

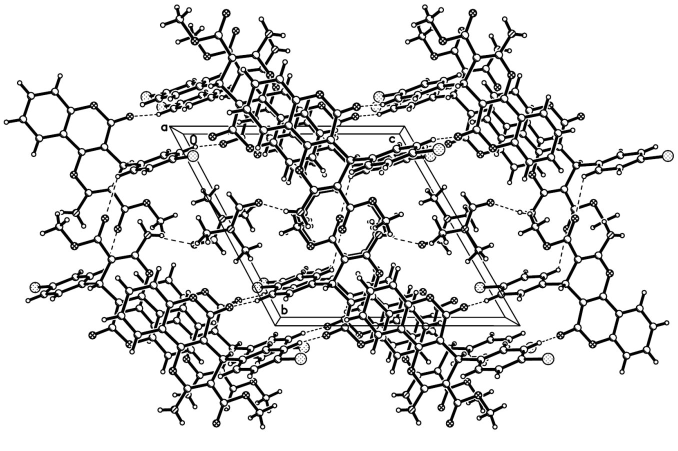


Figure 2
The molecular packing in the crystal structure of (I). Broken lines indicate hydrogen bonds.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.102$
$S = 1.06$
3814 reflections
301 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0561P)^2 + 0.3138P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.24$ e Å^{-3}
$\Delta\rho_{\min} = -0.26$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C5	1.3680 (17)	N1—C1	1.3352 (18)
O1—C1	1.3768 (16)	C1—C2	1.3655 (19)
O2—C6	1.2031 (18)	C2—C3	1.5176 (18)
O3—C7	1.3775 (18)	C3—C4	1.5074 (19)
O3—C6	1.3789 (17)		
C5—O1—C1	118.24 (11)	C2—C1—O1	122.32 (12)
C7—O3—C6	122.02 (11)	C4—C3—C2	108.85 (11)
N1—C1—C2	128.70 (13)	O2—C6—O3	117.12 (12)
N1—C1—O1	108.96 (12)	O2—C6—C4	125.10 (13)
C5—O1—C1—C2	−11.08 (19)	C7—O3—C6—C4	3.20 (19)
O1—C1—C2—C3	−4.7 (2)	C5—C4—C6—O3	−3.8 (2)
C1—C2—C3—C4	17.36 (18)	C6—O3—C7—C12	−0.7 (2)
C3—C4—C5—O1	3.1 (2)	O3—C7—C12—C5	−1.2 (2)
C1—O1—C5—C4	12.1 (2)	O1—C5—C12—C11	0.0 (2)

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

	D—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*B*···O6	0.86 (2)	2.11 (2)	2.9518 (19)	168 (2)
N1—H1*A*···O4	0.88 (2)	2.10 (2)	2.7173 (18)	127 (2)
C16—H16···O4$^{\rm i}$	0.95	2.52	3.1976 (17)	129
C19—H19···O2$^{\rm ii}$	0.95	2.44	3.2231 (19)	139

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+1, -y+2, -z$.

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Amine atoms H1*A* and H1*B* 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 Corporation, 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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