

2-Amino-4-(3,4-dichlorophenyl)-4*H*-pyrano[3,2-*c*]-
coumarin-3-carbonitrile *N,N*-dimethylformamide
solvateDaqing Shi,^{a,b*} Nan Wu,^a Qiya
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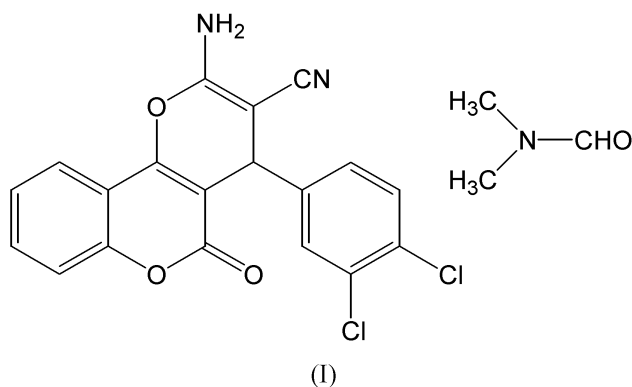
Key indicators

Single-crystal X-ray study
T = 193 K
Mean $\sigma(\text{C}-\text{C})$ = 0.002 Å
R factor = 0.039
wR factor = 0.094
Data-to-parameter ratio = 16.2For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound [systematic name: 2-amino-4-(3,4-dichlorophenyl)-5-oxo-4*H*,5*H*-pyrano[3,2-*c*]chromene-3-carbonitrile *N,N*-dimethylformamide solvate], C₁₉H₁₀Cl₂N₂O₃·C₃H₇NO, was synthesized by the reaction of 4-hydroxycoumarin and 3',4'-dichlorobenzylidenemalononitrile, catalysed by KF-montmorillonite. In the crystal structure, the amino group is involved in intermolecular N—H···O hydrogen bonds.

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 7*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).



In (I), the pyran ring of coumarin is almost planar, with deviations less than 0.017 (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/C5 by 0.065 (2) and 0.096 (3) Å, respectively. Similar conformations were observed in the structure 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-(tolyl)-4*H*,5*H*-pyrano[3,2-*c*]chromene-8-carboxylate (Wang *et al.*, 2004*b*). The dihedral angle between coumarin pyran ring O3/C6/C4/C5/C12/C7 and the fused benzene ring is 1.2 (3)°, and that between the coumarin pyran ring and the 3,4-dichlorophenyl ring is 84.0 (3)°. The sum of the bond angles (360.0°) around

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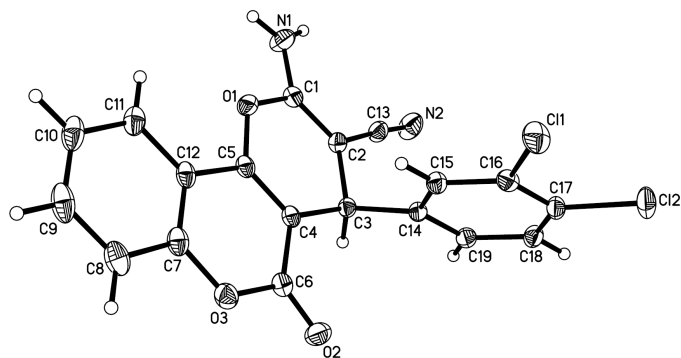


Figure 1
The molecular structure of (I), showing 40% probability displacement ellipsoids and the atom-numbering scheme.

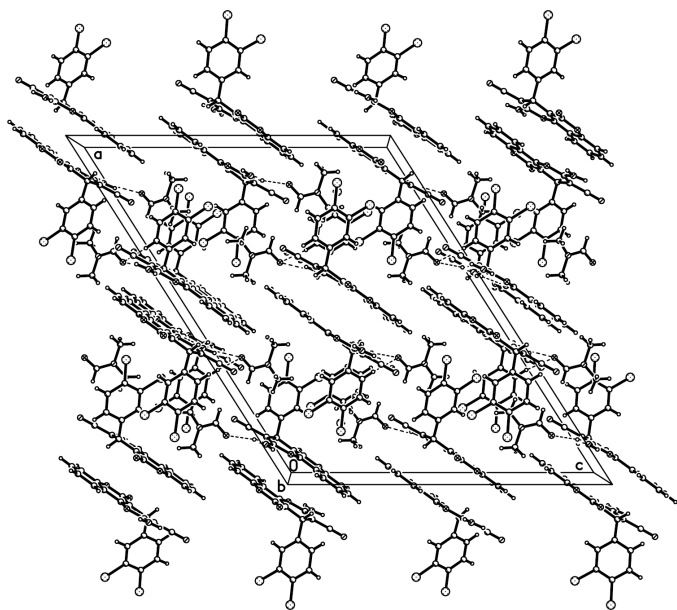


Figure 2
The molecular packing of (I). Dashed lines indicate hydrogen bonds.

N1 indicates a planar geometry. As a result of the existence of conjugation, the N1—C1 [1.333 (2) Å] distance is significantly shorter than the typical Csp^2-N bond distance (1.426 Å; Lorente *et al.*, 1995).

The amino group is involved in intermolecular N—H...O hydrogen bonds with atom O2 of the carbonyl group and atom O4 of the *N,N*-dimethylformamide (DMF) solvent molecule (Table 2 and Fig. 2). There is a short contact between the cyano N2 and C20ⁱ of DMF [2.992 (2) Å; symmetry code: (i) $x, 1 - y, \frac{1}{2} + z$].

Experimental

The title compound, (I), was prepared by the reaction of 4-hydroxycoumarin (0.41 g, 2.5 mmol) and 3',4'-dichlorobenzylidene-malononitrile (0.56 g, 2.5 mmol), catalysed by KF-montmorillonite (0.2 g) in *N,N*-dimethylformamide at 353 K for 6 h (yield 80%, m.p. 520–521 K). Crystals of (I) suitable for X-ray diffraction were obtained by slow evaporation of an *N,N*-dimethylformamide–ethanol solution. ¹H NMR (DMSO-*d*₆, δ): 4.49 (1H, *s*, CH), 7.31 (2H, *d*, *J* =

8.4 Hz, ArH), 7.37 (2H, *d*, *J* = 8.4 Hz, ArH), 7.45 (2H, *s*, NH₂), 7.47–7.52 (1H, *m*, ArH), 7.70–7.74 (1H, *m*, ArH), 7.90 (1H, *d*, *J* = 8.0 Hz, ArH).

Crystal data

$C_{19}H_{10}Cl_2N_2O_3 \cdot C_3H_7NO$
 $M_r = 458.29$
Monoclinic, $C2/c$
 $a = 28.126$ (6) Å
 $b = 7.8824$ (13) Å
 $c = 22.096$ (5) Å
 $\beta = 122.493$ (3)°
 $V = 4131.8$ (14) Å³
 $Z = 8$

$D_x = 1.473$ Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 8932 reflections
 $\theta = 3.1$ –27.5°
 $\mu = 0.35$ mm⁻¹
 $T = 193$ (2) K
Block, colorless
0.65 × 0.55 × 0.24 mm

Data collection

Rigaku Mercury diffractometer
 ω scans
Absorption correction: multi-scan (Jacobson, 1998)
 $T_{min} = 0.804$, $T_{max} = 0.921$
22202 measured reflections
4722 independent reflections

4404 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.023$
 $\theta_{max} = 27.5^\circ$
 $h = -36 \rightarrow 36$
 $k = -10 \rightarrow 10$
 $l = -28 \rightarrow 28$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.094$
 $S = 1.11$
4722 reflections
291 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0398P)^2 + 3.5942P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.28$ e Å⁻³
 $\Delta\rho_{min} = -0.23$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

| | | | |
|--------------|-------------|--------------|-------------|
| O1—C5 | 1.3583 (17) | N1—C1 | 1.333 (2) |
| O1—C1 | 1.3784 (17) | N2—C13 | 1.150 (2) |
| O2—C6 | 1.2091 (19) | C1—C2 | 1.357 (2) |
| O3—C7 | 1.3815 (19) | C2—C3 | 1.5232 (19) |
| O3—C6 | 1.3830 (17) | C3—C4 | 1.5086 (18) |
| C5—O1—C1—C2 | −5.82 (19) | C1—O1—C5—C4 | 6.98 (19) |
| O1—C1—C2—C3 | −2.1 (2) | C7—O3—C6—C4 | 1.67 (19) |
| C1—C2—C3—C4 | 7.97 (18) | C5—C4—C6—O3 | −3.28 (19) |
| C2—C3—C4—C5 | −6.91 (17) | C6—O3—C7—C12 | 0.7 (2) |
| C3—C4—C5—O1 | 0.0 (2) | O3—C7—C12—C5 | −1.5 (2) |
| C6—C4—C5—C12 | 2.6 (2) | C4—C5—C12—C7 | −0.2 (2) |

Table 2

Hydrogen-bonding geometry (Å, °).

| $D-H \cdots A$ | $D-H$ | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|---|----------|--------------|--------------|----------------|
| N1—H1B ⁱ ...O4 ⁱ | 0.88 (2) | 2.04 (2) | 2.888 (2) | 163 (2) |
| N1—H1A ⁱ ...O2 ⁱⁱ | 0.85 (2) | 2.20 (2) | 3.036 (2) | 169 (2) |
| C19—H19 ⁱ ...O4 ⁱⁱⁱ | 0.95 | 2.55 | 3.445 (2) | 158 |

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

Amino H atoms were located in difference density maps and refined isotropically. The positions of the other H atoms were calculated and refined as riding, with C—H = 0.95–1.00 Å and $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *CrystalClear* (Rigaku, 2000); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku/MSK, 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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