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2-Amino-3-cyano-4-(2,4-dichlorophenyl)-8-methylpyrano[3,2-*c*]pyran-5(4*H*)-one ethanol solvate

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Key indicators

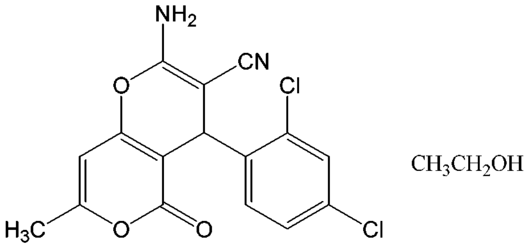
Single-crystal X-ray study
T = 193 K
Mean σ(C–C) = 0.004 Å
H-atom completeness 69%
Disorder in solvent or counterion
R factor = 0.050
wR factor = 0.147
Data-to-parameter ratio = 13.2

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

The title compound, $C_{16}H_{10}Cl_2N_2O_3 \cdot C_2H_6O$, was synthesized by the reaction of 4-hydroxy-6-methylpyran-2-one, 2,4-dichlorobenzaldehyde and malononitrile in the presence of triethylbenzylammonium chloride in an aqueous medium. X-ray analysis reveals that the pyranone ring is almost planar, while the pyran ring adopts a flattened boat conformation.

Comment

4*H*-Chromene is a building unit of some natural products. 4*H*-Chromenes with amino and cyano groups are also the synthons of some special natural products (Hatakeyama *et al.*, 1998; O'Callaghan & McMurry, 1995). We have recently reported the synthesis of some 4*H*-chromene derivatives (Shi *et al.*, 2002; Zhuang *et al.*, 2002; Wang *et al.*, 2004). 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 the title compound, (I), in an aqueous medium. We report here the synthesis and the X-ray crystal structure of (I).



(I)

The pyranone ring (C4–C8/O3) is almost planar. The pyran ring adopts a flattened boat conformation; atoms O1 and C3 deviate from the mean plane of the atoms C1/C2/C4/C5 by 0.036 (2) and 0.088 (3) Å, respectively. A similar conformation was observed in the structure of 2-amino-4-(2-chlorophenyl)-3-ethoxycarbonyl-4*H*-benzo[*f*]chromene (Zhuang *et al.*, 2003). The dihedral angle between the pyranone ring and the 2,4-dichlorophenyl ring is 89.6 (3)°. In addition, because of the existence of a conjugated system, the C1—N1 bond length of 1.327 (3) Å is shorter than the typical C*sp*^{2}—N bond distance (Lorente *et al.*, 1995). An intermolecular hydrogen bond is formed between the amino group and cyano atom N2 (Fig. 2 and Table 2). The ethanol solvent molecule also forms hydrogen bonds with the amino group and carbonyl atom O2.

Experimental

The title compound, (I), was prepared by the reaction of 4-hydroxy-6-methylpyran-2-one (0.25 g, 2 mmol), 2,4-dichlorobenzaldehyde

(0.35 g, 2 mmol) and malononitrile (0.13 g, 2 mmol) in the presence of triethylbenzylammonium chloride (0.2 g) in water (10 ml) at 363 K for 6 h (yield 89%, m.p. 503–504 K). Crystals of (I) suitable for X-ray diffraction were obtained by slow evaporation of an aqueous ethanol solution. IR (KBr, cm^{-1}): 3495, 3330 (NH$_2$), 2200 (CN), 1700 (CO), 1650, 1575, 1475, 9750, 850 (phenyl ring); ^{1}H NMR (CDCl$_3$, δ): 2.24 (3H, *s*, CH$_3$), 4.80 (1H, *s*, CH), 6.29 (1H, *s*, ArH), 7.27 (2H, *s*, NH$_2$), 7.29 (1H, *d*, J = 8.4 Hz, ArH), 7.38 (1H, *d*, J = 8.4 Hz, ArH), 7.56 (1H, *s*, ArH).

Crystal data

$C_{16}H_{10}Cl_2N_2O_3{\cdot}C_2H_6O$
$M_r = 395.23$
Triclinic, $P\overline{1}$
a = 9.2879 (12) Å
b = 10.4526 (12) Å
c = 11.0678 (10) Å
α = 63.905 (10)°
β = 75.826 (14)°
γ = 80.288 (15)°
V = 933.29 (18) Å^3
$Z = 2$
D_x = 1.406 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3571 reflections
θ = 3.0–25.3°
μ = 0.37 mm^{-1}
T = 193 (2) K
Block, colorless
0.50 × 0.31 × 0.20 mm

Data collection

Rigaku Mercury CCDd iffractometer
ω scans
Absorption correction: multi-scan (Jacobson, 1998)
$T_{\min}$ = 0.835, $T_{\max}$ = 0.929
9269 measured reflections
3403 independent reflections
2985 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.019
$\theta_{\max}$ = 25.4°
$h = -10 \rightarrow 11$
$k = -12 \rightarrow 12$
$l = -11 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.147$
$S = 1.08$
3403 reflections
258 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0852P)^2 + 0.4955P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max}$ = 0.65 e Å^{-3}
$\Delta\rho_{\min}$ = −0.43 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C5	1.366 (3)	O3—C6	1.387 (3)
O1—C1	1.377 (3)	N1—C1	1.327 (3)
O2—C6	1.215 (3)	N2—C9	1.150 (3)
O3—C7	1.367 (3)		
C5—O1—C1—C2	−2.5 (3)	C7—O3—C6—C4	3.9 (3)
O1—C1—C2—C3	−4.2 (4)	C5—C4—C6—O3	−4.3 (3)
C1—C2—C3—C4	7.9 (3)	C6—O3—C7—C8	−1.5 (4)
C2—C3—C4—C5	−5.8 (3)	O3—C7—C8—C5	−0.6 (4)
C3—C4—C5—O1	0.1 (4)	C4—C5—C8—C7	0.0 (4)
C1—O1—C5—C4	4.6 (3)		

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

D—H···A	D—H	H···A	D···A	D—H···A
C14—H14···N2$^{\rm i}$	0.95	2.52	3.439 (4)	164
O4—H4···O2	0.87 (5)	2.42 (4)	3.020 (3)	127 (3)
O4—H4···O2$^{\rm ii}$	0.87 (5)	2.15 (5)	2.894 (3)	143 (4)
N1—H1B···N2$^{\rm iii}$	0.78 (3)	2.26 (3)	3.026 (3)	172 (3)
N1—H1A···O4$^{\rm iv}$	0.87 (3)	1.99 (3)	2.856 (3)	175 (3)

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

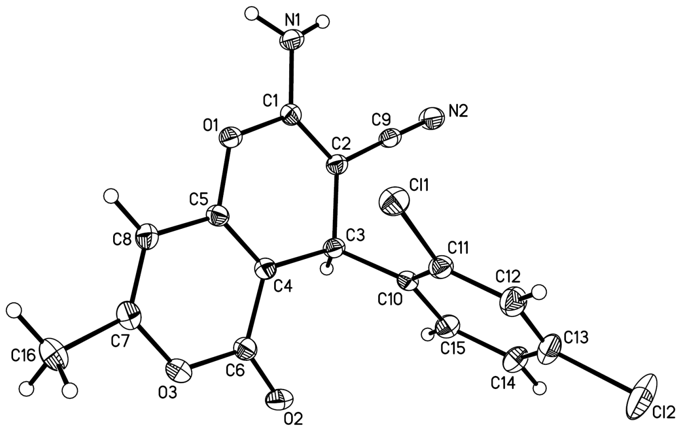


Figure 1
The molecular structure drawing of (I), showing 30% probability displacement ellipsoids and the atom-numbering scheme.

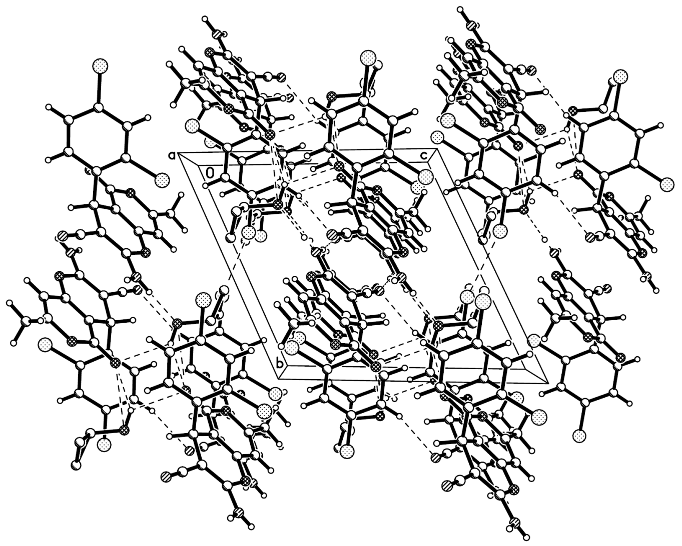


Figure 2
A molecular packing diagram of the crystal of (I). Dashed lines indicate hydrogen bonds.

There is a positional disorder of terminal atom C18 of the ethanol solvent molecule. The site-occupation factors of C18A and C18B were assumed to be 0.45 and 0.55, respectively. (The site occupation of atom C18A was assumed to be X, while that of C18B was assumed to be $1 - X$; X was refined by full-matrix least-squares techniques with anisotropic displacement paremeters to give a value of X of 0.45, so the site occupation of C18B was 0.55.) The H atoms bonded to C atoms in the pyranone molecule were positioned geometrically and treated as riding, with C—H bond distances of 0.95–1.00 Å and $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$ or $1.5U_{\rm eq}({\rm C}_{\rm methyl})$. H atoms bonded to C atoms in the ethanol solvent molecule were not included. The amino and hydroxyl H atoms were located in difference Fourier maps and refined isotropically. The N—H and O—H bond lengths are 0.78 (3)–0.87 (3) and 0.87 (5) Å, respectively.

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*.

o1996 Daqing Shi *et al.* • $C_{16}H_{10}Cl_2N_2O_3{\cdot}C_2H_6O$ *Acta Cryst.* (2004). E**60**, o1995–o1997

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