2-Amino-7-methyl-4-(3,4-methylenedioxy-phenyl)-5-oxopyrano[3,2-c]pyran-3-carbonitrile N,N-dimethylformamide solvate

Da-Qing Shi,[a,b]* Li-Hui Niu,[a] Xiang-Shan Wang,[a,b] Qi-Ya Zhuang[a,b] and Yong Zhang[c]

[a]Department of Chemistry, Xuzhou Normal University, Xuzhou 221116, People's Republic of China, [b]The Key Laboratory of Biotechnology for Medical Plants of Jiangsu Province, Xuzhou 221116, People's Republic of China, and [c]School of Chemistry and Chemical Engineering, Suzhou University, Suzhou 215006, People's Republic of China

Correspondence e-mail: dqshi@263.net

The title compound, $C_{17}H_{12}N_2O_5 \cdot C_3H_7NO$, was synthesized by the reaction of 4-hydroxy-6-methylpyran-2-one and 3,4-methylenedioxybenzylidenemalononitrile in the presence of triethylbenzylammonium chloride in an aqueous medium. The pyranone ring is almost planar, while the pyran ring adopts a boat conformation.

Comment

4*H*-Chromene is a construction unit of some natural products. 4*H*-Chromenes with amino and cyano groups are also a synthon 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 crystal structure of (I).


(I)
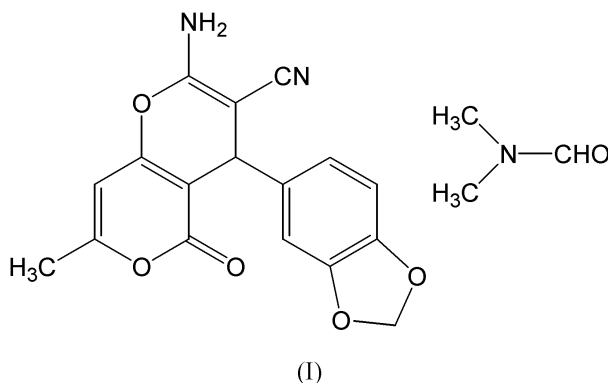
In (I), the pyranone ring is almost planar, with deviations of less than 0.022 (2) Å (Fig. 1). The pyran ring adopts a boat conformation: atoms C3, C4, C5 and O1 are coplanar, while atoms C1 and C2 deviate from the plane by 0.329 (2) and 0.417 (2) Å, respectively. A similar conformation was observed 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 and the substituted benzene ring is 81.5 (3)°. Because of the existence of a conjugated system, the C1—N1 bond length of 1.336 (2) Å is shorter than the typical Csp^2—N bond distance (Lorente *et al.*, 1995). The sum of the bond angles around N1 indicates a planar geometry. Intermolecular hydrogen bonds are formed between the amino group and both atom N2 of the cyano group and atom O6 of the carbonyl group in the *N*,*N*-dimethylformamide solvent molecule (Fig. 2 and Table 2).

organic papers
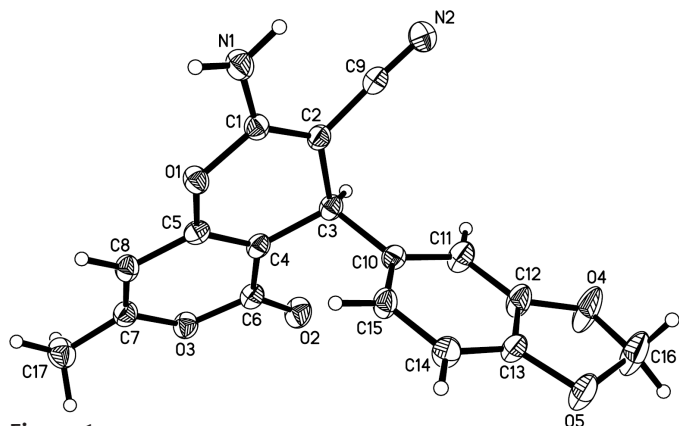
Figure 1
The molecular structure of (I), showing 45% probability displacement ellipsoids and the atom-numbering scheme.
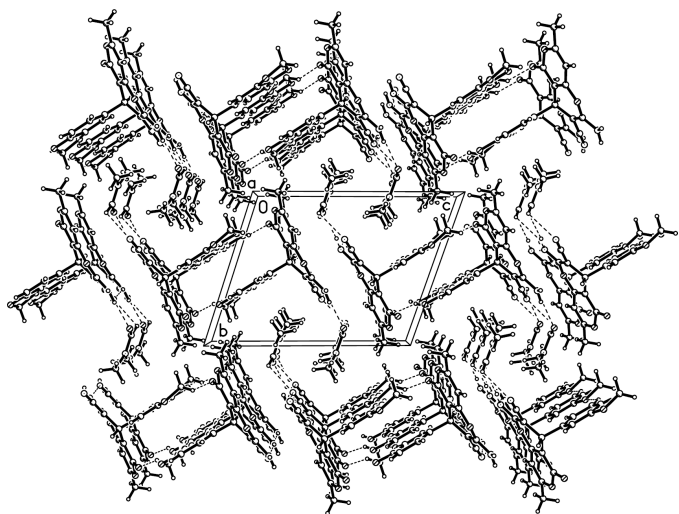
Figure 2
A molecular packing diagram for (I). Dashed lines indicate hydrogen bonds.

Experimental

The title compound, (I), was prepared by the reaction of 4-hydroxy-6-methylpyran-2-one (0.25 g, 2 mmol) and 3,4-methylenedioxybenzyl-idenemalononitrile (0.40 g, 2 mmol) in the presence of triethyl-benzylammonium chloride (0.2 g) in water (10 ml) at 363 K for 12 h (yield 94%, m.p. 501–503 K). Crystals suitable for X-ray diffraction were obtained by slow evaporation of an aqueous N,N-dimethyl-formamide solution. ^{1}H NMR (DMSO-d_6, δ): 2.23 (3H, s, CH$_3$), 4.22 (1H, s, CH), 5.99 (2H, s, OCH$_2$O), 6.26 (1H, s, ArH), 6.66 (1H, d, J = 8.0 Hz, ArH), 6.72 (1H, s, ArH), 6.84 (1H, d, J = 8.0 Hz, ArH), 7.16 (2H, s, NH$_2$).

Crystal data

C$_{17}$H$_{12}$N$_2$O$_5$·C$_3$H$_7$NO	$Z = 2$
$M_r = 397.38$	$D_x = 1.413$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 6.7513$ (18) Å	Cell parameters from 3676
$b = 11.010$ (3) Å	reflections
$c = 13.740$ (4) Å	$\theta = 3.1$–25.3°
$\alpha = 107.117$ (5)°	$\mu = 0.11$ mm^{-1}
$\beta = 93.142$ (3)°	$T = 193$ (2) K
$\gamma = 104.813$ (5)°	Block, yellow
$V = 934.2$ (5) Å^3	0.60 × 0.36 × 0.18 mm

Data collection

Rigaku Mercury diffractometer	3042 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.017$
Absorption correction: multi-scan	$\theta_{max} = 25.3°$
(Jacobson, 1998)	$h = -8 \rightarrow 7$
$T_{min} = 0.924$, $T_{max} = 0.981$	$k = -13 \rightarrow 13$
9243 measured reflections	$l = -16 \rightarrow 15$
3391 independent reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0516P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.039$	$+ 0.295P]$
$wR(F^2) = 0.102$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} < 0.001$
3391 reflections	$\Delta\rho_{max} = 0.18$ e Å^{-3}
274 parameters	$\Delta\rho_{min} = -0.20$ e Å^{-3}
H atoms treated by a mixture of	
independent and constrained	
refinement	

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.3762 (16)	N2—C9	1.1552 (19)
O1—C5	1.3791 (16)	C1—C2	1.3592 (19)
O2—C6	1.2096 (17)	C2—C3	1.5200 (19)
O3—C7	1.3694 (17)	C3—C4	1.5028 (19)
O3—C6	1.3905 (17)	C4—C5	1.3518 (19)
N1—C1	1.3364 (19)		
C5—O1—C1—C2	−12.22 (18)	C1—O1—C5—C4	16.98 (18)
O1—C1—C2—C3	−7.5 (2)	C7—O3—C6—C4	−4.61 (18)
C1—C2—C3—C4	20.08 (17)	C5—C4—C6—O3	3.21 (18)
C2—C3—C4—C5	−15.53 (17)	C6—O3—C7—C8	2.92 (19)
C3—C4—C5—O1	−1.7 (2)	O3—C7—C8—C5	0.3 (2)
C6—C4—C5—C8	−0.3 (2)	C4—C5—C8—C7	−1.5 (2)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$B\cdots$O6^i	0.92 (2)	1.98 (2)	2.862 (2)	160 (2)
N1—H1$A\cdots$N2^{ii}	0.87 (2)	2.32 (2)	3.147 (2)	158 (2)
C18—H18$\cdots$N2^i	0.95	2.57	3.135 (2)	118
C16—H16$A\cdots$O2^{iii}	0.99	2.38	3.262 (2)	148
C14—H14$\cdots$O4^{ii}	0.95	2.55	3.212 (2)	127

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

H atoms on carbon were positioned geometrically and treated as riding on their parent C atoms, with C—H distances in the range 0.95–1.00 Å, and with U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(C$_{methyl}$). The amino H atoms were located in difference Fourier maps and refined isotropically.

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*.

References

Hatakeyama, S., Ochi, N., Numata, H. & Takano, S. (1998). *J. Chem. Soc. Chem. Commun.* pp. 1202–1204.

Jacobson, R. (1998). Private communication to the Rigaku Corporation.

Lorente, A., Galan, C., Fonseca, I. & Sanz-Aparicio, J. (1995). *Can. J. Chem.* **73**, 1546–1555.

O'Callaghan, C. N. & McMurry, T. B. H. (1995). *J. Chem. Res. (S)*, pp. 214–215.

Rigaku (2000). *CrystalClear.* Rigaku Corporation, Tokyo, Japan.

Rigaku/MSC (2003). *CrystalStructure.* Rigaku/MSC, 9009 New Trails Drive, The Woodlands, TX 77381–5209, USA.

Sheldrick, G. M. (1997). *SHELXTL.* Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.

Shi, D. Q., Chen, J., Zhuang, Q. Y. & Hu, H. W. (2003). *J. Chem. Res. (S).* pp. 674–675.

Shi, D. Q., Wang, X. S. & Tu, S. J. (2002). *Chin. J. Org. Chem.* **22**, 1053–1056.

Wang, J., Shi, D.-Q. & Wang, X.-S. (2004). *Acta Cryst.* E**60**, o1401–o1402.

Zhuang, Q. Y., Shi, D. Q., Tu, S. J. & Wang, X. S. (2002). *Chin. J. Appl. Chem.* **19**, 1019–1020.

Zhuang, Q.-Y., Shi, D.-Q. & Wang, X.-S. (2003). *Acta Cryst.* E**59**, o1474–o1475.