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3-Amino-1-(3,4-methylenedioxyphenyl)-9-methoxy-5,6-dihydro-1*H*-benzo[*f*]chromene-2-carbonitrile

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Key indicators

Single-crystal X-ray study
T = 299 K
Mean σ(C–C) = 0.002 Å
R factor = 0.035
wR factor = 0.082
Data-to-parameter ratio = 13.1

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

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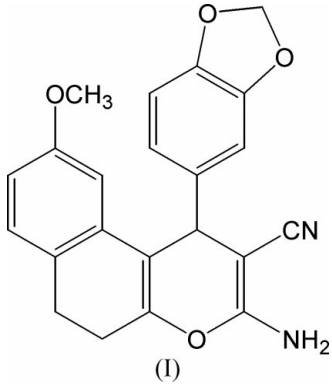
The title compound, $C_{22}H_{18}N_2O_4$, was synthesized by the reaction of 7-methoxy-2-tetralone and 3,4-methylenedioxybenzylidenemalononitrile in the presence of triethylbenzylammonium chloride in an aqueous medium. X-ray analysis reveals that the pyran ring and the fused six-membered ring adopt boat and screw-boat forms, respectively.

Comment

4*H*-Chromene is a building block of some natural products. 4*H*-Chromenes with amine 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 a 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 the title compound, (I), in an aqueous medium. We report here the synthesis and crystal structure of (I).



(I)

The molecular structure is shown in Fig. 1. Although nearly planar, the pyran ring can be regarded as having a boat conformation; atoms C1, C10, C12 and C13 are coplanar, while atoms O1 and C11 deviate from the plane by 0.098 (2) and 0.188 (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 fused six-membered ring (C1–C4/C9/C10) adopts a screw-boat conformation; atoms C2, C1, C10 and C9 are coplanar, while atoms C3 and C4 deviate from the plane by 0.681 (2) and 0.240 (3) Å, respectively. A similar conformation was observed in the structure of 2-amino-6-methoxy-4-(4-methoxyphenyl)-9,10-dihydro-4*H*-benzo[*f*]chromene-3-carbonitrile (Yu *et al.*, 2004). Because of the existence of a conjugated system, the C13—N2 bond length of 1.3434 (18) Å

is shorter than the typical Csp^2—N bond distance (Lorente *et al.*, 1995). Intermolecular hydrogen bonds (Table 2) are formed between the amine group and atom O2 of the methylenedioxy group, and between the amine group and atom N1 of the cyano group (Fig. 2).

Experimental

Compound (I) was prepared by the reaction of 7-methoxy-2-tetralone (0.35 g, 2 mmol) and 3,4-methylenedioxybenzylidenemalononitrile (0.40 g, 2 mmol) in the presence of triethylbenzylammonium chloride (0.2 g) in water (10 ml) at 313 K for 20 h (yield 87%, m.p. 502–504 K). Crystals of (I) suitable for X-ray diffraction were obtained by slow evaporation of an ethanol solution. IR (ν, cm^{-1}): 3434, 3325 (NH_2), 2185 (CN), 1634, 1605, 1489, 1409, 814, 763 (phenyl ring). ^{1}H NMR: δ 2.55–2.60 (2H, *m*, CH_2), 2.87–2.94 (2H, *m*, CH_2), 3.65 (3H, *s*, CH_3O), 4.40 (2H, *s*, NH_2), 4.44 (1H, *s*, CH), 5.90 (2H, *d*, J = 8.4 Hz, OCH_2O), 6.57–6.59 (2H, *m*, ArH), 6.72–6.74 (2H, *m*, ArH), 6.83 (1H, *d*, J = 8.4 Hz, ArH), 6.99 (1H, *d*, J = 8.0 Hz, ArH).

Crystal data

$C_{22}H_{18}N_2O_4$	D_x = 1.349 Mg m^{-3}
M_r = 374.38	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 34 reflections
a = 10.277 (1) Å	θ = 5.6–13.2°
b = 6.9852 (5) Å	μ = 0.09 mm^{-1}
c = 25.695 (3) Å	T = 299 (2) K
β = 92.512 (9)°	Block, colourless
V = 1842.8 (3) Å^3	0.56 × 0.38 × 0.24 mm
Z = 4	

Data collection

Siemens *P*4 diffractometer	θ_{max} = 25.3°
ω scans	$h = 0 \rightarrow 12$
Absorption correction: none	$k = 0 \rightarrow 8$
3993 measured reflections	$l = -30 \rightarrow 30$
3336 independent reflections	3 standard reflections
2127 reflections with $I > 2\sigma(I)$	every 97 reflections
R_{int} = 0.011	intensity decay: 4.2%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0419P)^2]$
$R[F^2 > 2\sigma(F^2)]$ = 0.035	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.082	$(\Delta/\sigma)_{max} < 0.001$
S = 0.86	$\Delta\rho_{max}$ = 0.15 e Å^{-3}
3336 reflections	$\Delta\rho_{min}$ = −0.12 e Å^{-3}
255 parameters	Extinction correction: *SHELXL*97
H-atom parameters constrained	Extinction coefficient: 0.0121 (9)

Table 1
Selected geometric parameters (Å, °).

O1—C13	1.3572 (17)	C1—C10	1.332 (2)
O1—C1	1.3902 (18)	C1—C2	1.483 (2)
N1—C22	1.1459 (19)	C11—C12	1.518 (2)
N2—C13	1.3434 (18)	C12—C22	1.411 (2)
C13—O1—C1	118.17 (13)	N2—C13—C12	127.89 (15)
C10—C1—O1	123.63 (14)	N2—C13—O1	110.05 (14)
C13—O1—C1—C10	−8.0 (2)	C11—C12—C13—O1	1.2 (2)
C1—C2—C3—C4	43.47 (19)	C1—O1—C13—C12	10.5 (2)
C8—C9—C10—C11	16.5 (2)		

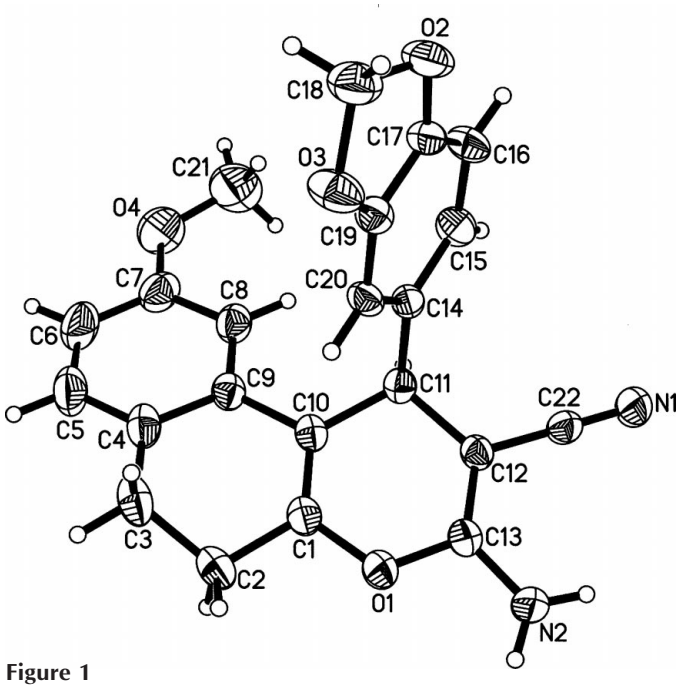


Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme.

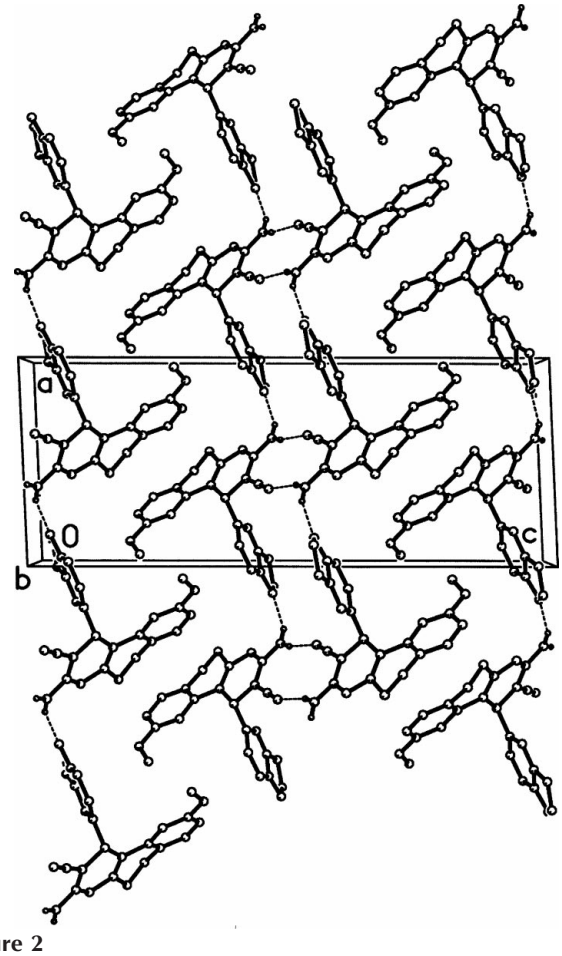


Figure 2
The molecular packing in the crystal structure of (I). Broken lines indicate hydrogen bonds. H atoms not involved in hydrogen bonds have been omitted.

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

	D—H	H···A	D···A	D—H···A
N2—H20A···N1^{i}	0.86	2.20	3.042 (2)	167
N2—H20B···O2^{ii}	0.86	2.24	3.043 (2)	155

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

H atoms were positioned geometrically and treated as riding on their parent atoms, with C—H distances in the range 0.93–0.98 Å and N—H distances of 0.86 Å; the U_{iso}(H) values were set at $1.2U_{eq}$(parent atom).

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Sheldrick, 1997); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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