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2-Amino-6-methoxy-4-(4-methoxyphenyl)-9,10-dihydro-4*H*-benzo[*f*]chromene-3-carbonitrile

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Key indicators

Single-crystal X-ray study
T = 297 K
Mean σ(C–C) = 0.003 Å
R factor = 0.039
wR factor = 0.092
Data-to-parameter ratio = 13.4

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

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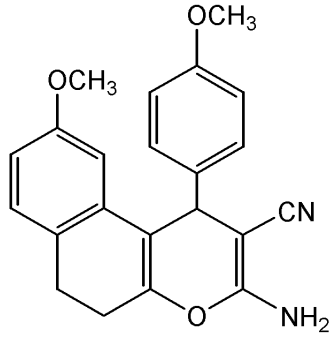
The title compound, $C_{22}H_{20}N_2O_3$, was synthesized by the reaction of 4-methoxybenzaldehyde, 7-methoxy-2-tetralone and malononitrile in the presence of triethylbenzylammonium chloride in an aqueous medium. X-ray analysis reveals that the pyran ring and the fused six-membered ring adopt boat and skew-boat conformations, respectively.

Comment

4*H*-Chromene is a building block of some natural products. 4*H*-Chromenes with amino and cyano groups are also the synthons of some special natural products (Hatokeyama *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 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 and present its crystal structure here.



(I)

A molecular view of (I) is shown in Fig. 1. The bond lengths and angles have the usual values found for related molecules in the Cambridge Structural Database (CSD; Version 5.24; Allen, 2002).

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 0.111 (2) and 0.239 (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 skew-boat conformation: atoms C2, C1, C10 and C9 are coplanar, while atoms C3 and C4 deviate from the plane by 0.701 (2) and 0.254 (3) Å, respectively.

The dihedral angle between the two *p*-methoxyphenyl rings is 90.9 (2)°. In addition, because of the existence of a conju-

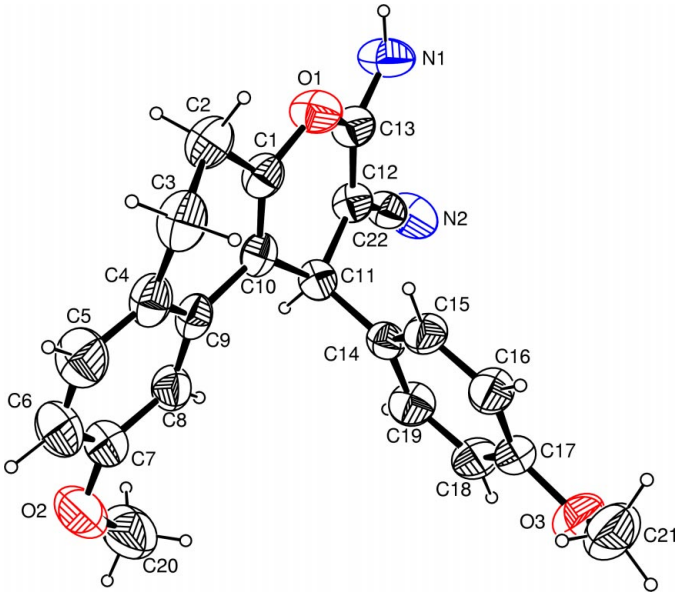


Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms are shown as small spheres of arbitrary radii.

gated system, the C13—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 (359.8°) indicates a planar geometry.

Intermolecular hydrogen bonds are formed between the amino group and both atom O3 of the carbonyl group and atom N2 of the cyano group of symmetry-related molecules (Table 1), forming chains which extend parallel to *a* (Fig. 2).

Experimental

The title compound was prepared by the reaction of 4-methoxybenzaldehyde (0.27 g, 2 mmol), 7-methoxy-2-tetralone (0.35 g, 2 mmol) and malononitrile (0.13 g, 2mmol) in the presence of triethylbenzylammonium chloride (0.2 g) in water (10 ml) at 298 K for 25 h. Yield 83%, m.p. 464–466 K. Analysis: IR (KBr, ν, cm^{-1}): 3407, 3315 (NH_2), 2190 (CN), 1643, 1603, 1503, 1455, 840, 769 (phenyl ring); ^{1}H NMR ($CDCl_3$, δ, p.p.m.): 2.56–2.63 (2H, *m*, CH_2), 2.85–2.96 (2H, *m*, CH_2), 3.63 (3H, *s*, CH_3O), 3.76 (3H, *s*, CH_3O), 4.39 (2H, *s*, NH_2), 4.47 (1H, *s*, CH), 6.55–6.58 (2H, *m*, ArH), 6.82 (2H, *d*, J = 8.4 Hz, ArH), 6.98 (1H, *d*, J = 8.0 Hz, ArH), 7.21–7.27 (2H, *m*, ArH). Single crystals of (I) suitable for X-ray diffraction were obtained by slow evaporation of an ethanol solution.

Crystal data

$C_{22}H_{20}N_2O_3$
M_r = 360.40
Monoclinic, $P2_1/c$
a = 10.267 (2) Å
b = 7.011 (1) Å
c = 26.352 (3) Å
β = 93.94 (1)°
V = 1892.4 (5) Å^3
Z = 4
D_x = 1.265 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 38 reflections
θ = 3.0–13.4°
μ = 0.09 mm^{-1}
T = 297 (2) K
Block, colourless
0.50 × 0.36 × 0.32 mm

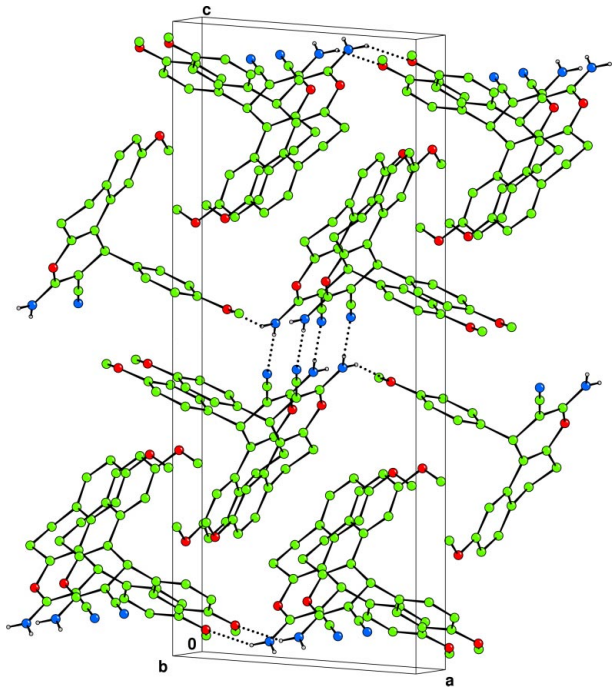


Figure 2
A view of the molecular packing for (I), with the N—H···O and N—H···N hydrogen-bonding interactions indicated by dotted lines. H atoms not involved in hydrogen bonding have been omitted.

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: none
4089 measured reflections
3424 independent reflections
1982 reflections with $I > 2\sigma(I)$
R_{int} = 0.012
θ_{max} = 25.3°
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 8$
$l = -31 \rightarrow 31$
3 standard reflections
every 97 reflections
intensity decay: 6.7%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.092
S = 0.85
3424 reflections
255 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0443P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.13 e Å^{-3}
$\Delta\rho_{min}$ = −0.12 e Å^{-3}
Extinction correction: *SHELXTL* (Sheldrick, 1997)
Extinction coefficient: 0.0110 (9)

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1B···O3^{i}	0.861 (9)	2.199 (11)	3.038 (2)	164.8 (19)
N1—H1A···N2^{ii}	0.873 (9)	2.174 (10)	3.034 (2)	168.4 (18)

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

Amino H 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 = 0.93–0.98 Å and U_{iso}(H) = 1.2U_{eq}(C).

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: *ORTEP*III (Burnett & Johnson, 1996), *ORTEP*-3 *for Windows* (Farrugia, 1997) and *CAMERON* (Watkin *et al.*, 1993); software used to prepare material for publication: *SHELXTL*.

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