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Ethyl 2-amino-4-(4-methoxyphenyl)-7-methyl-5-oxopyrano[3,2-c]pyran-3-carboxylate

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Key indicators

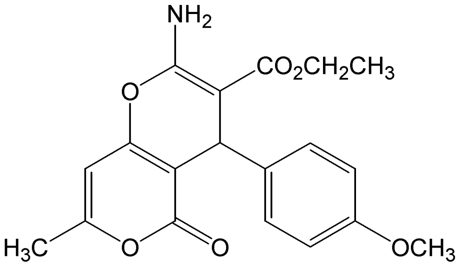
Single-crystal X-ray study
T = 193 K
Mean σ(C–C) = 0.003 Å
H-atom completeness 74%
Disorder in main residue
R factor = 0.059
wR factor = 0.163
Data-to-parameter ratio = 15.5

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

The title compound, $C_{19}H_{19}NO_6$, was synthesized by the reaction of 4-hydroxy-6-methylpyran-2-one and ethyl 4′-methoxy-2-cyanocinnamate in the presence of triethylbenzylammonium chloride in an aqueous medium. The pyranone ring is almost planar, while the fused pyran ring adopts a flattened boat conformation. The amino group is involved in both intra- and intermolecular N—H···O hydrogen bonds.

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 report here the crystal structure of the title compound, (I).



(I)

In (I), the pyranone ring is almost planar, with deviations less than 0.014 (2) Å. The fused pyran ring adopts a flattened boat conformation: atoms O1, C1, C2 and C3 are coplanar, while atoms C4 and C5 deviate from the plane by 0.177 (3) and 0.137 (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 phenyl ring is 84.5 (3)°. In addition, because of the existence of a conjugated system, the C1—N1 bond length of 1.339 (2) Å is shorter than the typical Csp^2—N bond distance (Lorente *et al.*, 1995). In the crystal structure, the amino group (N1) is involved in both intra- and intermolecular N—H···O hydrogen bonds (Fig. 2 and Table 2).

Experimental

The title compound, (I), was prepared by the reaction of 4-hydroxy-6-methylpyran-2-one (0.25 g, 2 mmol) and ethyl 4′-methoxy-2-cyanocinnamate (0.46 g, 2 mmol) in the presence of triethylbenzylammonium chloride (0.2 g) in water (10 ml) at 363 K for 18 h (yield 87%, m.p. 445–447 K). Crystals suitable for X-ray diffraction were obtained by slow evaporation of an aqueous ethanol solution. ^{1}H NMR (DMSO-d_6, δ): 1.09 (3H, *t*, J = 7.2 Hz, CH$_3$), 2.21 (3H, *s*, CH$_3$), 3.69 (3H, *s*, CH$_3$O), 3.97 (2H, *q*, J = 7.2 Hz, CH$_2$O), 4.48 (1H, *s*, CH), 6.28 (1H, *s*, ArH), 6.79 (2H, *d*, J = 6.8 Hz, ArH), 7.07 (2H, *d*, J = 6.8 Hz, ArH), 7.66 (2H, *s*, NH$_2$).

Crystal data

$C_{19}H_{19}NO_6$
M_r = 357.35
Monoclinic, $P2_1/c$
a = 10.720 (4) Å
b = 8.934 (3) Å
c = 18.167 (6) Å
β = 94.636 (7)°
V = 1734.2 (10) Å^3
Z = 4
D_x = 1.369 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7929 reflections
θ = 3.1–27.5°
μ = 0.10 mm^{-1}
T = 193 (2) K
Block, colorless
0.75 × 0.65 × 0.45 mm

Data collection

Rigaku Mercury diffractometer
ω scans
Absorption correction: multi-scan (Jacobson, 1998)
$T_{\min}$ = 0.914, $T_{\max}$ = 0.955
18 580 measured reflections
3947 independent reflections
3575 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.022
$\theta_{\max}$ = 27.5°
$h = -13 \rightarrow 13$
$k = -10 \rightarrow 11$
$l = -23 \rightarrow 23$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.059
$wR(F^2)$ = 0.163
S = 1.08
3947 reflections
255 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0836P)^2 + 0.9423P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max}$ = 0.69 e Å^{-3}
$\Delta\rho_{\min}$ = −0.29 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C5	1.373 (2)	N1—C1	1.339 (2)
O1—C1	1.376 (2)	C1—C2	1.369 (3)
O2—C6	1.214 (2)	C2—C3	1.529 (2)
O3—C7	1.372 (2)	C3—C4	1.512 (2)
O3—C6	1.394 (2)		
C5—O1—C1—C2	−7.7 (3)	C1—O1—C5—C4	5.3 (3)
O1—C1—C2—C3	1.5 (3)	C7—O3—C6—C4	−0.2 (3)
C1—C2—C3—C4	6.1 (2)	C5—C4—C6—O3	−1.4 (3)
C2—C3—C4—C5	−8.5 (2)	C6—O3—C7—C8	0.6 (3)
C3—C4—C5—O1	3.3 (3)	O3—C7—C8—C5	0.7 (3)
C6—C4—C5—C8	2.7 (3)	C4—C5—C8—C7	−2.4 (3)

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

D—H···A	D—H	H···A	D···A	D—H···A
C18—H18C···O4$^{\rm i}$	0.98	2.52	3.344 (3)	142
C19—H19C···O6$^{\rm ii}$	0.98	2.57	3.410 (3)	144
N1—H1A···O4	0.88 (3)	1.95 (3)	2.651 (3)	136 (3)
N1—H1B···O2$^{\rm iii}$	0.88 (3)	2.11 (3)	2.834 (2)	139 (2)

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

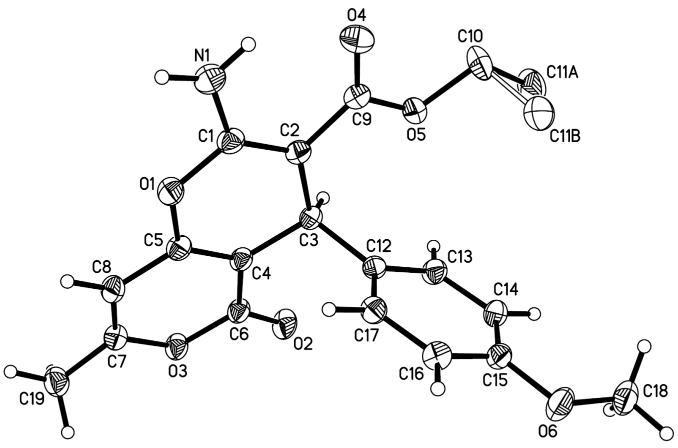


Figure 1
The molecular structure of (I), showing 40% probability displacement ellipsoids and the atom-numbering scheme. Both disorder components are shown for C11; H atoms were not located for C10 and C11..

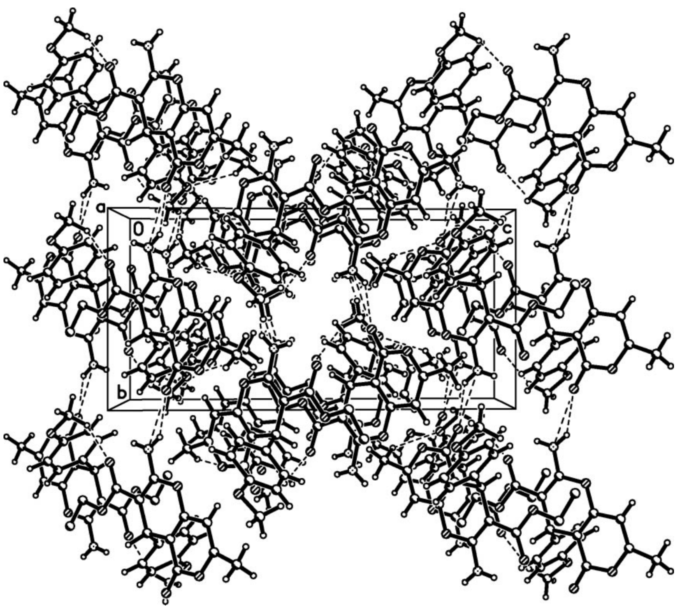


Figure 2
A molecular packing diagram for (I). One of two possible positions of atom C11 has been omitted for clarity. The dashed lines indicate short contacts.

Atom C11 is disordered over two sites, C11A and C11B. The site-occupancy factors were estimated to be 0.72 and 0.28, respectively. H atoms bonded to C atoms were positioned geometrically, except for the disordered ethyl group (C10, C11A and C11B), and were treated as riding, with C—H distances in the range 0.95–1.00 Å, and with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C) or 1.5$U_{\rm eq}$(C$_{\rm methyl}$). The amino H atoms were located from difference Fourier maps and refined isotropically, with N—H distances restrained to 0.88 (3) Å. The maximum residual electron density is located 0.97 Å from C10, but this could not easily be treated as an H atom in view of the disorder.

Data collection: *CrystalClear* (Rigaku, 2000); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku/MSC, 2003); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997);

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program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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