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Ethyl 2-amino-3-ethoxycarbonyl-7,8-dimethyl-4-[4-(methylsulfanyl)phenyl]-5-oxo-4*H*-pyrano[3,2-*c*]chromene-3-carboxylate

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In the title compound, $C_{24}H_{23}NO_5S$, the pyran ring bearing the amino group adopts a flattened boat conformation. In the crystal structure, the molecules are linked by N—H···O hydrogen bonds.

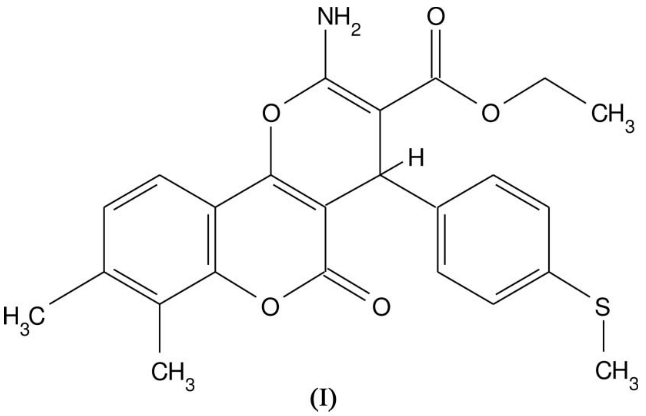
Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.003 Å
R factor = 0.046
wR factor = 0.137
Data-to-parameter ratio = 12.6

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

Comment

4-Hydroxycoumarin forms the nucleus of many natural products and drugs. It is a key intermediate for the widely used oral anticoagulants and rodenticides. There is interest in fused pyranochromenes because chromene derivatives can be used as immunomodulators and for the treatment of different diseases of connective tissues, diabetes, *etc*. We present here the synthesis and crystal structure of the title compound, (I). The molecule is being assessed for biological activity.



(I)

In (I), the pyran ring (O1/C2/C3/C8/C9/C14) of the coumarin nucleus is planar, while the other pyran ring adopts a flattened boat conformation; in the latter, atoms C4 and O7 deviate by 0.086 (2) and 0.069 (2) Å, respectively, from the plane defined by the atoms C3, C5, C6 and C8. Similar conformations were observed in the structures of ethyl 2-amino-5-oxo-4-(*p*-tolyl)-4H,5*H*-pyrano[3,2-*c*]chromene-8-carboxylate (Wang *et al.*, 2004) and ethyl 2-amino-4-(2,4-dichlorophenyl)-4*H*-benzo[*f*]chromene-3-carboxylate (Shi *et al.*, 2003). The dihedral angle between the pyran ring (C3/C4/C5/C6/O7/C8) and the methylsulfanylphenyl ring is 89.52 (6)°. The C6—C5—C19—C20 torsion angle of 6.4 (4)° indicates that the carbonyl group is oriented in the (+)synperiplanar conformation about the C6═C5 bond.

The structure exhibits both inter- and intramolecular hydrogen bonds (Table 1 and Fig. 2), which help to stabilize the crystal structure. The intermolecular hydrogen bond N18—H18*B*···O17[i] links the molecules into chains (symmetry code as in Table 1).

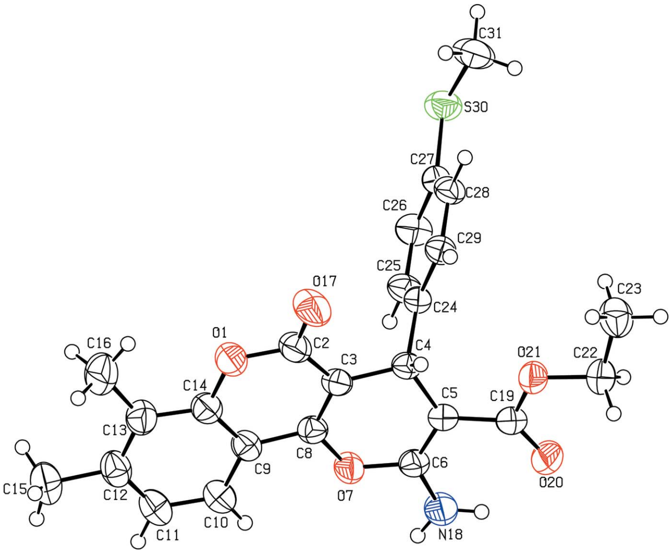


Figure 1
View of (I), with displacement ellipsoids drawn at the 50% probability level..

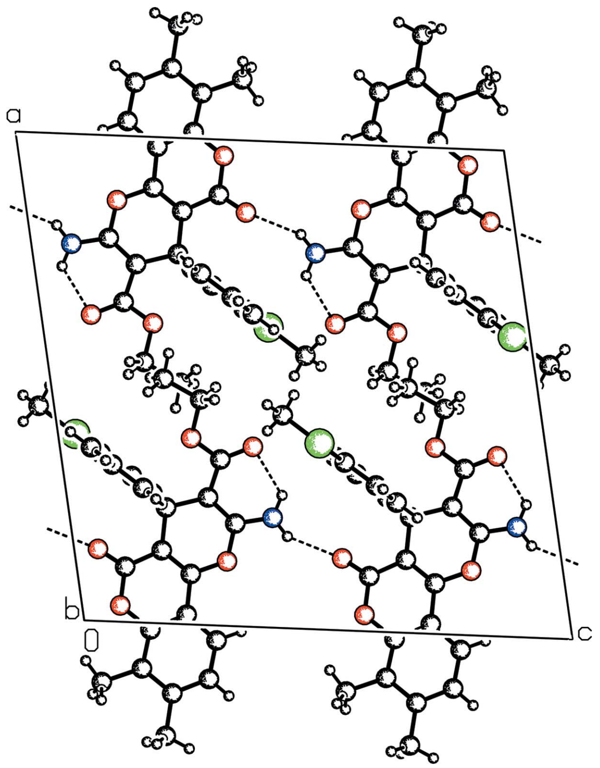


Figure 2
The crystal packing in (I), viewed down the *b* axis. Dashed lines indicate hydrogen bonds.

Experimental

A mixture of 4-hydroxy-7,8-dimethylcoumarin (0.01 mol) and ethyl 2-cyano-3-(4-thiophenyl)acrylate (0.01 mol) in methanol (45 ml) and piperidine (6–8 drops as a base catalyst) was refluxed on a steam bath for 10–11 h. The product was separated, washed with methanol and filtered. Crystallization from dimethylformamide gave a yield of 28% (m.p. 469 K; analysis calculated: C 65.89, H 5.30, N 3.2%). 1.0 g of the compound was taken up in 20 ml of dimethylformamide. Charcoal (2 g) was added and the mixture heated for 5–6 min. The solution was filtered while hot through Whatman 42 filter paper. The solution was kept in a slightly open stoppered conical flask; pale-yellow crystals grew by solvent evaporation.

Crystal data

$C_{24}H_{23}NO_5S$
$M_r = 437.50$
Monoclinic, $P2_1/c$
$a = 17.295$ (5) Å
$b = 7.494$ (4) Å
$c = 17.127$ (9) Å
$\beta = 100.220$ (3)°
$V = 2184.6$ (18) Å^3
$Z = 4$
$D_x = 1.330$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.18$ mm^{-1}
$T = 295$ (2) K
Block, pale yellow
0.25 × 0.22 × 0.22 mm

Data collection

MacScience DIPLabo 32001 diffractometer
ω scans
Absorption correction: none
6677 measured reflections
3585 independent reflections
3119 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.022$
$\theta_{\rm max} = 25.0°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.137$
$S = 1.16$
3585 reflections
285 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0787P)^2 + 0.3836P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.35$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.29$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.034 (3)

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

D—H···A	D—H	H···A	D···A	D—H···A
N18—H18A···O20	0.86	2.09	2.694 (2)	127
N18—H18B···O17$^{\rm i}$	0.86	2.13	2.838 (2)	139
C16—H16A···O1	0.96	2.29	2.765 (3)	110

Symmetry code: (i) $x, -y + \frac{3}{2}, z + \frac{1}{2}$.

H atoms were placed at idealized positions and allowed to ride on their parent atoms, with C—H = 0.92—0.98 Å and N—H = 0.86 Å; $U_{\rm iso}$(H) values were set equal to $xU_{\rm eq}$(carrier atom), where $x = 1.5$ for methyl H atoms and $x = 1.2$ for all other H atoms.

Data collection: *XPRESS* (MacScience, 2002); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003) and *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *PLATON*.

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