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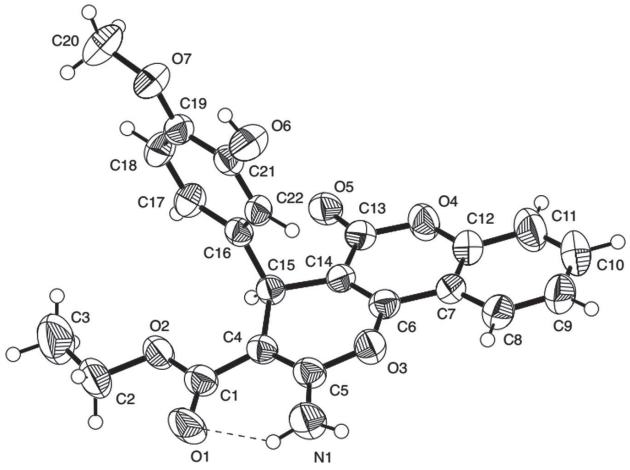
Crystal structure of ethyl 2-amino-4-(3-hydroxy-4-methoxyphenyl)-5-oxo-4*H*,5*H*-pyrano[3,2-c] chromene-3-carboxylate, $C_{22}H_{19}NO_7$



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Abstract

$C_{22}H_{19}NO_7$, monoclinic, $P2_1/c$ (no. 14), $a = 9.292(5)$ Å, $b = 13.230(3)$ Å, $c = 17.115(4)$ Å, $\beta = 106.04(5)°$, $V = 2022.1(14)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0441$, $wR_{ref}(F^2) = 0.1156$, $T = 293(2)$ K.

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The crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

A mixture of 4-hydroxycoumarin (10 mmol), 4-methoxy-3-hydroxy-benzaldehyde (10 mmol), ethyl cyanoacetate (10 mmol) and 4-(dimethylamino)pyridine (DMAP) (1 mmol)

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Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.26 × 0.21 × 0.17 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.10 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω-scans
θ_{max}, completeness:	25°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	9575, 3545, 0.053
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2422
$N(param)_{refined}$:	276
Programs:	Bruker programs [1], SHELX [2], OLEX2 [3]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
N1	0.37739(19)	0.22910(14)	−0.09055(9)	0.0680(5)
H1A	0.454562	0.197290	−0.096259	0.082*
H1B	0.318954	0.260025	−0.131310	0.082*
O1	0.62435(13)	0.08891(10)	0.12659(7)	0.0581(4)
O2	0.60726(16)	0.11426(12)	−0.00619(8)	0.0728(5)
O3	0.21916(13)	0.28623(10)	−0.02442(7)	0.0541(4)
O4	0.19830(13)	0.20025(10)	0.24259(7)	0.0540(4)
O5	0.00619(13)	0.27437(11)	0.15738(8)	0.0602(4)
O6	0.78606(13)	0.48778(10)	0.32840(7)	0.0588(4)
O7	0.60742(18)	0.54015(11)	0.18141(9)	0.0645(4)
C1	0.8186(3)	0.0013(3)	0.21988(17)	0.1226(12)
H1C	0.909765	−0.036119	0.226885	0.184*
H1D	0.837722	0.060055	0.254155	0.184*
H1E	0.745486	−0.040469	0.234352	0.184*
C2	0.7611(2)	0.03309(18)	0.13369(13)	0.0733(7)
H2A	0.834017	0.075368	0.118271	0.088*
H2B	0.741357	−0.025617	0.098376	0.088*
C3	0.5577(2)	0.12786(15)	0.05236(11)	0.0515(5)
C4	0.42644(18)	0.18663(13)	0.05266(10)	0.0436(4)
C5	0.3484(2)	0.23048(14)	−0.01861(11)	0.0481(5)
C6	0.15629(18)	0.28150(13)	0.03908(10)	0.0434(4)
C7	0.22544(17)	0.24035(13)	0.11173(10)	0.0408(4)
C8	0.38501(17)	0.20304(13)	0.13204(10)	0.0400(4)
H8	0.391033	0.138050	0.160236	0.048*
C9	0.14842(19)	0.23563(14)	0.17463(11)	0.0457(4)
C10	−0.0612(2)	0.31983(15)	0.08299(12)	0.0549(5)
C11	0.00879(19)	0.32583(13)	0.02177(11)	0.0465(5)
C12	−0.0658(2)	0.37428(15)	−0.05158(12)	0.0591(5)
H12	−0.020063	0.379295	−0.093380	0.071*
C13	−0.2060(2)	0.41400(17)	−0.06122(15)	0.0724(7)

Table 2 (continued)

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
H13	−0.255085	0.446773	−0.109264	0.087*
C14	−0.2743(2)	0.40502(19)	0.00127(17)	0.0853(8)
H14	−0.370039	0.431131	−0.005972	0.102*
C15	−0.2036(2)	0.35845(19)	0.07343(15)	0.0795(7)
H15	−0.250180	0.352987	0.114844	0.095*
C16	0.48983(17)	0.27794(13)	0.18823(9)	0.0390(4)
C17	0.57893(18)	0.24937(14)	0.26417(10)	0.0478(5)
H17	0.572204	0.183833	0.282492	0.057*
C18	0.67800(19)	0.31702(15)	0.31329(10)	0.0508(5)
H18	0.736644	0.296821	0.364184	0.061*
C19	0.68936(17)	0.41454(14)	0.28639(10)	0.0450(5)
C20	0.59896(18)	0.44494(13)	0.21065(10)	0.0429(4)
C21	0.50009(17)	0.37731(13)	0.16279(10)	0.0431(4)
H21	0.439137	0.398231	0.112659	0.052*
C22	0.8763(2)	0.46398(18)	0.40787(12)	0.0715(7)
H22A	0.937872	0.521066	0.430042	0.107*
H22B	0.813132	0.447741	0.442003	0.107*
H22C	0.938879	0.407061	0.405224	0.107*
H7	0.677(2)	0.5736(18)	0.2113(15)	0.084(8)*

in ethanol (100 mL) was refluxed for 2–3 h and then cooled to room temperature. After filtering the precipitates, they were sequentially washed with ice-cooled water and ethanol and then dried under a vacuum.

Experimental details

H atoms bonded to C and N atoms were positioned geometrically and refined using a riding model, with C—H = 0.93 or 0.96 Å and N—H = 0.86 Å with U_{iso}(H) = 1.2 times U_{eq}(C) and 1.2 times U_{eq}(N).

Discussion

Coumarins possess diverse pharmacological and biological activities such as antitumor, analgesic and ulcerogenic, anti-inflammatory, anticoagulant, phototriggering, and fungicidal properties, and can act as anticoagulants in the production of pesticides [4–7]. In particular, the antitumor activity of coumarin compounds has received considerable attention among researchers because of their cytotoxic activity against numerous types of cancers, including malignant melanoma, leukemia, renal cell carcinoma, prostate and breast cancer cell progression [8].

In the crystal structures of the title compound (*cf*. the figure), the pyran ring and the adjacent coumarin ring are essentially parallel to each other. However, the 3-hydroxy-4-methoxyphenyl ring makes a torsion angle to the pyran ring in the compound. Bond lengths and angles are all in the expected ranges.

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