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Crystal structure of ethyl 2,2-difluoro-2-(7-methoxy-2-oxo-2*H*-chromen-3-yl)acetate, $C_{14}H_{12}F_2O_5$

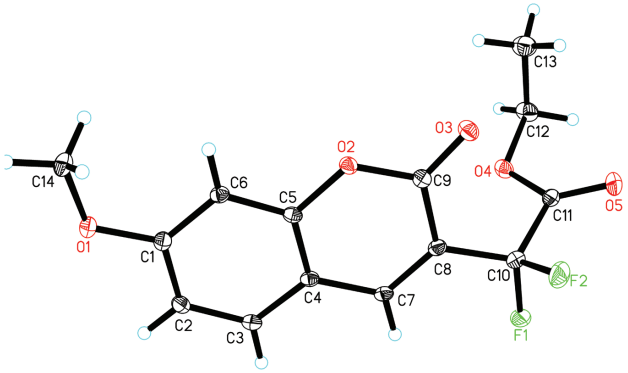

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.13 × 0.12 × 0.11 mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ:	1.17 mm^{-1}
Diffractometer, scan mode:	SuperNova, ω
θ_{max}, completeness:	73.5°, 99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	4640, 2504, 0.024
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2359
$N(param)_{refined}$:	193
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3]

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Abstract

$C_{14}H_{12}F_2O_5$, monoclinic, $P2_1/n$ (no. 14), $a = 6.8723(2)$ Å, $b = 27.0231(7)$ Å, $c = 7.3669(2)$ Å, $\beta = 109.235(3)°$, $Z = 4$, $V = 1291.75(7)$ Å^3, $R_{gt}(F) = 0.0484$, $wR_{ref}(F^2) = 0.1335$, $T = 100$ K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

To synthesize ethyl 2,2-difluoro-2-(7-methoxy-2-oxo-2*H*-chromen-3-yl) acetate, a 25 mL of Schlenk tube equipped with a Teflon septum were added $Ir(PPy)_3$, K_2HPO_4 (2.0 equiv) and 7-methoxycoumarin (0.40 mmol, 1.0 equiv) under Ar, followed by DMSO (3 mL) with stirring. Ethyl bromodifluoroacetate (0.80 mmol, 2.0 equiv) was added subsequently. The vial was then irradiated with a 12 W blue LEDs. After stirring for 24 h, the reaction mixture was diluted with ethyl acetate, washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified with silica gel chromatography to provide pure product. Crystals were obtained by slow evaporation from ethyl acetate/petroleum ether (2:1) solution at room temperature over a period of seven days.

Experimental details

The structure was solved by direct methods [2] and refined using the SHELX-2014 program package [3]. Hydrogen atoms were placed in geometrically idealized positions and refined using a riding model.

Comment

Coumarins, belonging to the benzo-alfa-pyrones family, are the common oxygen heterocyclic compounds in academic society. The great interest about these compounds is due to their biological activities against different pathologies, which motivate the development of several drugs that are mainly antithrombotics, such as warfarin and acenocoumarol. Based on this findings, these compounds are also used for preliminary studies of antibacterials [4], antivirals [5], antifungals [6]. Molecules containing fluorine atom(*s*) regularly exhibit beneficial effects in pharmaceuticals. The difluoromethylene (CF_2) group is considered abioisostere of oxygen atom and carbonyl groups and can modulate the pK_a value of neighboring functional groups such as amines. We reported a

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C1	0.4441(2)	0.55758(6)	0.1545(2)	0.0185(3)
C2	0.2658(2)	0.53332(6)	0.1619(2)	0.0198(3)
H2	0.138941	0.549270	0.116817	0.024*
C3	0.2775(2)	0.48627(6)	0.2351(2)	0.0191(3)
H3	0.158930	0.470909	0.241564	0.023*
C4	0.4675(2)	0.46099(5)	0.3004(2)	0.0166(3)
C5	0.6405(2)	0.48591(6)	0.2873(2)	0.0163(3)
C6	0.6343(2)	0.53371(6)	0.2193(2)	0.0173(3)
H6	0.753614	0.549505	0.216822	0.021*
C7	0.4939(2)	0.41213(6)	0.3791(2)	0.0174(3)
H7	0.381472	0.395103	0.391802	0.021*
C8	0.6818(2)	0.39064(6)	0.4350(2)	0.0180(3)
C9	0.8597(2)	0.41597(6)	0.4138(2)	0.0177(3)
C10	0.7260(3)	0.34009(6)	0.5229(2)	0.0234(4)
C11	0.8370(3)	0.30410(6)	0.4267(3)	0.0239(4)
C12	0.8743(3)	0.28252(6)	0.1287(3)	0.0286(4)
H12A	0.785234	0.280511	−0.004219	0.034*
H12B	0.898725	0.249190	0.180046	0.034*
C13	1.0737(3)	0.30599(7)	0.1386(3)	0.0352(5)
H13A	1.130154	0.289300	0.052249	0.053*
H13B	1.168427	0.303613	0.267457	0.053*
H13C	1.051033	0.340194	0.102593	0.053*
C14	0.5985(3)	0.63237(6)	0.0974(3)	0.0250(4)
H14A	0.674182	0.616688	0.024665	0.037*
H14B	0.683401	0.634408	0.229965	0.037*
H14C	0.558937	0.665079	0.048162	0.037*
F001	0.54671(17)	0.31792(4)	0.51913(18)	0.0339(3)
F004	0.84288(19)	0.34379(4)	0.71123(15)	0.0373(3)
O1	0.41707(18)	0.60385(4)	0.08168(17)	0.0237(3)
O2	0.83075(16)	0.46338(4)	0.34401(16)	0.0184(3)
O3	1.03115(17)	0.39876(4)	0.45494(17)	0.0232(3)
O4	0.77420(17)	0.31178(4)	0.23944(17)	0.0225(3)
O5	0.9564(2)	0.27354(5)	0.5157(2)	0.0409(4)

new compound, namely ethyl 2,2-difluoro-2-(7-methoxy-2-oxo-2*H*-chromen-3-yl) acetate, which may show high biological activity.

The crystal structure of the title compound was determined by X-ray crystallography. In the crystal structure of the title compound, the six-membered ring containing oxygen atom is nearly planar. The bond lengths of C9—O2 and C11—O4 are 1.3704(19) Å and 1.319(2) Å, respectively. The bond angle (F4—C10—C8) and (C8—C9—O3) are 109.98(14)° and 125.23(15)°, respectively. All geometric parameters are in the typical ranges and they are comparable with the parent structure [7] and other previously reported compounds [8, 9].

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