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Crystal structure of (*E*)-ethyl 2-((4-oxo-4*H*-chromen-3-yl)methyleneaminoxy)acetate, $C_{14}H_{13}NO_5$

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Abstract

$C_{14}H_{13}NO_5$, monoclinic, $P2_1$ (no. 4), $a = 4.6967(7)$ Å, $b = 10.7175(16)$ Å, $c = 12.945(2)$ Å, $\beta = 94.827(8)^\circ$, $V = 649.30(17)$ Å³, $Z = 2$, $R_{gt}(F) = 0.0577$, $wR_{ref}(F^2) = 0.1302$, $T = 223(2)$ 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

The starting material 4-oxo-4*H*-chromene-3-carbaldehyde (522 mg, 3 mmol), purchased from Aldrich, was dissolved in

Table 1: Data collection and handling.

Crystal:	Colourless plate
Size:	0.14 × 0.12 × 0.05 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	0.11 mm ⁻¹
Diffractometer, scan mode:	PHOTON 100 CMOS, φ and ω
θ_{max} , completeness:	28.4°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	26,931, 3254, 0.137
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 1835
$N(param)_{refined}$:	182
Programs:	Bruker [1], SHELX [2, 3], Olex2 [4]

40 mL of methanol to give a clear solution. Two equivalents of hydroxyl amine (6 mmol, 420 mg) and sodium acetate (6 mmol, 490 mg) in 15 mL of water were added to the above solution, and reaction mixture was stirred at 70 °C for 5 h. The reaction mixture was cooled down to room temperature to furnish precipitation of the corresponding oxime compound. The solid was filtered and washed with cold methanol. The oxime compound (2 mmol, 380 mg) and K_2CO_3 (3 mmol, 415 mg) were dissolved in 30 mL of DMF to give a clear solution. To the solution, was added ethyl-bromoacetate (3 mmol, 0.4 mL) and the reaction mixture was stirred at 50 °C. After the completion of the reaction (checked by TLC), the reaction mixture was cooled down to room temperature and poured into 100 mL of ice-water to form a precipitate. Crystals of the title compound were obtained by recrystallization from an ethanol solution.

Experimental details

Data collections and reduction were carried out using the Bruker software APEX2 and SAINT including SADABS [1]. Hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms.

Comment

Oxime esters are one of the most important moiety in a large number of bioactive compounds with a wide range of

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
C1	0.1748 (6)	0.0642 (3)	0.4571 (2)	0.0320 (7)
O1	0.2163 (4)	0.1571 (2)	0.51261 (16)	0.0406 (5)
C2	−0.0446 (7)	0.0647 (3)	0.3685 (2)	0.0344 (7)
C3	−0.2081 (6)	0.1703 (3)	0.3418 (2)	0.0401 (8)
H3	−0.1774	0.2444	0.3801	0.048*
C4	−0.4142 (7)	0.1666 (4)	0.2598 (3)	0.0491 (9)
H4	−0.5247	0.2379	0.2426	0.059*
C5	−0.4597 (8)	0.0588 (4)	0.2025 (3)	0.0532 (10)
H5	−0.6013	0.0576	0.1466	0.064*
C6	−0.3004 (8)	−0.0470 (4)	0.2259 (3)	0.0487 (9)
H6	−0.3307	−0.1204	0.1867	0.058*
C7	−0.0941 (6)	−0.0423 (3)	0.3090 (2)	0.0375 (8)
O2	0.0594 (5)	−0.1498 (2)	0.32907 (18)	0.0441 (6)
C8	0.2634 (7)	−0.1500 (3)	0.4085 (3)	0.0417 (8)
H8	0.3667	−0.2243	0.4213	0.050*
C9	0.3316 (6)	−0.0519 (3)	0.4714 (2)	0.0326 (7)
C10	0.5677 (7)	−0.0726 (3)	0.5499 (3)	0.0368 (8)
H10	0.6522	−0.1522	0.5534	0.044*
N1	0.6678 (6)	0.0101 (3)	0.6143 (2)	0.0397 (7)
O3	0.9037 (5)	−0.0459 (2)	0.67441 (19)	0.0482 (6)
C11	1.0344 (7)	0.0452 (3)	0.7422 (2)	0.0410 (8)
H11A	1.0473	0.1242	0.7047	0.049*
H11B	1.2291	0.0185	0.7651	0.049*
C12	0.8707 (8)	0.0653 (4)	0.8346 (3)	0.0517 (9)
O4	0.6764 (6)	0.0028 (3)	0.8604 (2)	0.0822 (10)
O5	0.9754 (7)	0.1624 (3)	0.88836 (19)	0.0763 (9)
C13	0.8423 (15)	0.1892 (6)	0.9839 (4)	0.129 (3)
H13A	0.6413	0.1638	0.9753	0.155*
H13B	0.9369	0.1397	1.0404	0.155*
C14	0.8570 (19)	0.3090 (6)	1.0096 (5)	0.158 (3)
H14A	1.0552	0.3325	1.0258	0.237*
H14B	0.7513	0.3231	1.0698	0.237*
H14C	0.7752	0.3591	0.9521	0.237*

activities [5, 6]. In addition they have been known as photoinitiators in the field of photochemistry [7, 8]. Chromenon is an indispensable structure in flavonoids which have demonstrated diverse biological activities in medicinal chemistry [9–12]. Isoflavonoids have substituent at three-position of the chromenone structure and they have shown structural difference from other flavonoids which have substituent at two-position. Because of the critical structural differences, isoflavones exhibit physiological functions that are different to those of other flavonoids [13]. Recent research has shown that isoflavones have broad biological activities including an influence on osteoporosis [14], cardiovascular diseases [15], and it has been shown that an inhibition of thyroid peroxidase is possible [16]. In an extension of our previous studies on isoflavones [17–19],

chromenone was combined with an oxime ester to obtain isoflavone analogs.

In the title compound (see the Figure), the chromenone ring (C1–C9/O2) is almost planar, with a maximum deviation of 0.023 Å at C1 (r.m.s. deviation = 0.010 Å). The chromenone ring and the C10=N1 double bond of the oxime unit lie in the same plane [N1–C10–C9–C1 = −1.3(5)]. The C10=N1 imine double bond adopts an *E*-configuration, which was defined by a dihedral angle of −177.6(3)° for C9–C10–N1–O3. In the oxime unit, the ethylacetate group attached to the oxygen forms an *anti*-conformation with the imine C10=N1 double bond as it moves away from the hydrogen attached to the imine carbon [C11–O3–N1–C10 = 176.0(3)°]. In the crystal, the carbonyl oxygen (O1) forms weak and branched C(10)–H(10)⋯O(1) and C(8)–H(8)⋯O(1) hydrogen bonds to form a six-membered ring, which propagates along the *b*-axis by a C(11)–H(11A)⋯O(2) hydrogen bond. The chain is further stabilized by additional C(11)–H(11B)⋯O(4) interactions.

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