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Synthesis and crystal structure of 7-chloro-2-(ethylsulfinyl)-6-fluoro-3-(1*H*-pyrazole-1-yl)-4*H*-thiochromen-4-one, C₁₃H₁₀FN₃OS₂

Table 1: Data collection and handling.

Crystal:	Colourless plate
Size:	0.20 × 0.10 × 0.10 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.55 mm ⁻¹
Diffraction, scan mode:	Nonius CAD4, ω
$\theta_{\max}$, completeness:	25.4°, 99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	2833, 2726, 0.100
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1337
$N(\text{param})_{\text{refined}}$:	199
Programs:	Nonius [1], SHELX [2, 3]

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl	0.87045(10)	1.5192(4)	0.45350(7)	0.0833(6)
F	0.7419(2)	1.4501(8)	0.53321(14)	0.0823(11)
S1	0.66542(9)	0.7729(4)	0.29775(6)	0.0571(4)
N1	0.4426(3)	0.4308(10)	0.3373(2)	0.0554(12)
C1	0.5679(3)	0.5940(12)	0.2978(2)	0.0485(13)
O1	0.5105(2)	0.7378(9)	0.44957(16)	0.0723(12)
S2	0.53942(9)	0.3785(4)	0.22436(7)	0.0600(4)
C2	0.6814(3)	0.9647(12)	0.3688(2)	0.0468(13)
N2	0.3953(3)	0.3693(13)	0.2748(2)	0.0781(17)
O2	0.6258(2)	0.3740(10)	0.20319(17)	0.0764(13)
C3	0.7555(3)	1.1460(13)	0.3808(2)	0.0559(14)
H3A	0.7904	1.1608	0.3506	0.067*
C4	0.7768(3)	1.3016(12)	0.4367(3)	0.0542(15)
C5	0.7214(4)	1.2899(14)	0.4801(2)	0.0599(16)
C6	0.6496(3)	1.1123(14)	0.4691(2)	0.0621(16)
H6A	0.6141	1.1037	0.4991	0.075*
C7	0.6278(3)	0.9417(12)	0.4134(2)	0.0508(13)
C8	0.5506(3)	0.7544(13)	0.4054(2)	0.0553(15)
C9	0.5216(3)	0.5938(12)	0.3455(2)	0.0464(13)
C10	0.4087(4)	0.2976(14)	0.3823(3)	0.0741(19)
H10A	0.4306	0.3093	0.4280	0.089*
C11	0.3367(4)	0.1434(17)	0.3478(3)	0.087(2)
H11A	0.2988	0.0305	0.3646	0.105*
C12	0.3326(4)	0.1918(16)	0.2832(3)	0.088(2)
H12A	0.2899	0.1086	0.2482	0.105*
C13	0.4677(4)	0.6216(14)	0.1691(3)	0.0735(18)
H13A	0.4184	0.6828	0.1873	0.088*
H13B	0.5040	0.7791	0.1639	0.088*
C14	0.4282(5)	0.4893(19)	0.1037(3)	0.134(3)
H14A	0.3900	0.6175	0.0741	0.201*
H14B	0.3919	0.3347	0.1092	0.201*
H14C	0.4773	0.4304	0.0858	0.201*

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Abstract

C₁₄H₁₀ClFN₂O₂S₂, monoclinic, $P2_1/n$ (no. 14), $a = 15.070(3)$ Å, $b = 4.9050(10)$ Å, $c = 21.018(4)$ Å, $\beta = 105.59(3)^\circ$, $V = 1496.5(5)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0667$, $wR_{\text{ref}}(F^2) = 0.1363$, $T = 293(2)$ 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

To a stirred solution of the appropriate Cs₂CO₃ (25.0 mmol) and α -azole-*o*-chloroacetophenone (10.0 mmol) in DMF

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(20 mL) at 40 °C, carbon disulfide (13.0 mmol) was added dropwise. The reaction mixture was stirred at 40 °C for 2 h and room temperature for 30 min, then bromoethane (13.0 mmol) was added dropwise, with stirring continuous for 3 h. After completion of the reaction, the mixture was poured into ice water, filtered, washed with water. The compound obtained above was dissolved in acetic acid (30 mL) at 60 °C, immediately, 30% aq. H₂O₂ (12 mmol) was added dropwise to the solution at same temperature. The reaction mixture was stirred at 60 °C for 2–3 h then the mixture was slowly poured into ice water, filtered, washed with water and dried. A share of 20 mg of the obtained white title compound was dissolved in a mixed solution of ethyl acetate and methanol (about 5 mL). The colorless crystals of the title compound were obtained after seven days by slow evaporation.

Experimental details

Hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms, with constrained isotropic displacement parameters.

Comment

Thiochromone compounds are considered very important in medical chemistry, and they are extensively applied in antibacterial [4], antifungal [4], anticarcinogenic [5] and anti-malarial [6]. So far, the current research reports are focused on the synthesis of thiochromone derivatives [7–10], but the crystal data are rarely published.

Our newly synthesized crystal 7-chloro-2-(ethylsulfinyl)-6-fluoro-3-(1*H*-pyrazole-1-yl) thiochromone is shown in the figure. The crystal belongs to the monoclinic system crystal-lizing in the space group *P*2₁/*n*. The structure shows that the benzo moiety and the six-membered sulfur heterocycle in the molecule are almost in the same plane. Bond lengths and angles are in the expected ranges [11].

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References

1. Enraf-Nonius. CAD-4 Software (or CAD-4 EXPRESS). Enraf-Nonius, Delft, The Netherlands.
2. Sheldrick, G. M.: SHELXS97. Program for the Solution of Crystal Structures. University of Göttingen, Germany (1997).
3. Sheldrick, G. M.: Crystal structure refinement with SHELX. *Acta Crystallogr.* **C71** (2015) 3–8.
4. Nakazumi, H.; Ueyama, T.; Kitao, T. J.: Synthesis and antibacterial activity of 2-phenyl-4*H*-benzo[*b*]thiopyran-4-ones (Thioflavones) and related compounds. *J. Heterocycl. Chem.* **21** (1984) 193–196.
5. Holshouser, M. H.; Loeffler, L. J.; Hall, I. H.: Synthesis and antitumor activity of a series of sulfone analogues of 1, 4-naphthoquinone. *Med. Chem.* **24** (1981) 853–858.
6. Razdan, R. K.; Bruni, R. J.; Mehta, A. C.; Weinhardt, K. K.; Papanastassiou, Z. B.: A new class of antimalarial drugs: derivatives of benzothiopyrans. *Med. Chem.* **21** (1978) 643–649.
7. Xu, J.; Zhang, F.; Zhang, S.; Zhang, L.; Yu, X.; Yan, J.; Song, Q.: Radical promoted C(sp²)–S formation and C(sp³)–S bond cleavage: access to 2-substituted thiochromones. *Org. Lett.* **21** (2019) 1112–1115.
8. Sangeetha, S.; Sekar, G.: Copper-catalyzed one-pot synthesis of 2-arylthiochromenones: an *in situ* recycle of waste byproduct as useful reagent. *Org. Lett.* **21** (2019) 75–79.
9. Zhu, F.; Wu, X.-F.: Carbonylative synthesis of 3-substituted thiochromenones *via* rhodium-catalyzed [3+2+1] cyclization of different aromatic sulfides, alkynes, and carbon monoxide. *Org. Chem.* **83** (2018) 13612–13617.
10. Kim, H. Y.; Song, E.; Oh, K.: Unified approach to (thio)chromenones *via* one-pot Friedel–Crafts acylation/cyclization: distinctive mechanistic pathways of β-chlorovinylketones. *Org. Lett.* **19** (2017) 312–315.
11. Li, Y.; Xiao, T.; Liu, D.-L.; Yu, G.-Y.: Methyl 7-chloro-2-ethylsulfinyl-6-fluoro-4-oxo-4*H*-thiochromene-3-carboxalate. *Acta Crystallogr.* **E66** (2010) o694.