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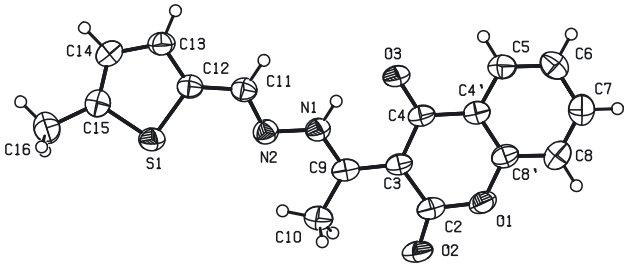
The crystal structure of 3-(1-(2-((5-methylthiophen-2-yl)methylene)hydrazinyl) ethylidene)chroman-2,4-dione, $C_{17}H_{14}N_2O_3S$



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Abstract

$C_{17}H_{14}N_2O_3S$, monoclinic, $P2_1/c$ (no. 14), a = 9.8966(5) Å, b = 9.4360(4) Å, c = 16.7115(7) Å, β = 92.245(4)°, V = 1559.39(12) Å^3, Z = 4, $R_{gt}(F)$ = 0.0358, $wR_{ref}(F^2)$ = 0.1013, T = 170 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.

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Table 1: Data collection and handling.

Crystal:	Yellow irregular
Size:	0.53 × 0.46 × 0.26 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.22 mm^{-1}
Diffractometer, scan mode:	Gemini R ultra, ω
θ_{max}, completeness:	26.4°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	32946, 3188, 0.036
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2792
$N(param)_{refined}$:	215
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], PLATON [4]

Source of material

The synthesis was performed according to the previously reported procedure [5]. The reaction of 3-acetyl-4-hydroxycoumarin with hydrazine hydrate gives a corresponding hydrazone. Condensation of the obtained hydrazone with 5-methylthiophene-2-carbaldehyde afforded the target compound 3-(1-(2-((5-methylthiophen-2-yl)methylene) hydrazinyl)ethylidene)chroman-2,4-dione. The obtained yellow solid was dissolved in acetone and allowed to slowly evaporate to form the crystals of the title compound.

Experimental details

Coordinates of carbon-bonded hydrogen atoms were introduced in idealized positions and refined using riding model. Their U_{iso} values are aproximated as $U_{iso} = kU_{eq}$ of the parent atom (k = 1.2 for sp^2 and 1.5 for sp^3 hybridized atoms).

Comment

Azines are compounds formed by the reaction of two different or the same carbonyl compounds (mostly aldehydes or ketones) with hydrazine [6, 7]. It is well known that they possess antibacterial [8], antifungal [9],

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
S1	0.87812 (4)	0.67596 (4)	0.36715 (2)	0.04671 (14)
O1	0.43999 (11)	0.06147 (11)	0.66941 (5)	0.0505 (3)
O2	0.60654 (13)	0.20437 (14)	0.69839 (6)	0.0685 (4)
O3	0.39687 (11)	0.20110 (12)	0.43885 (6)	0.0552 (3)
N1	0.59360 (12)	0.36706 (13)	0.46404 (7)	0.0429 (3)
H1	0.5290 (18)	0.3197 (18)	0.4343 (11)	0.065(5)*
N2	0.67878 (12)	0.46785 (12)	0.43386 (7)	0.0444 (3)
C2	0.52581 (15)	0.16768 (15)	0.64641 (8)	0.0452 (3)
C3	0.51281 (13)	0.22073 (14)	0.56514 (7)	0.0391 (3)
C4	0.41183 (13)	0.16285 (14)	0.51051 (7)	0.0401 (3)
C4′	0.32269 (13)	0.05342 (14)	0.54086 (8)	0.0405 (3)
C5	0.21898 (15)	−0.00668 (17)	0.49305 (9)	0.0500 (3)
H5	0.204646	0.024035	0.439251	0.060*
C6	0.13748 (16)	−0.11000 (18)	0.52334 (10)	0.0573 (4)
H6	0.066792	−0.150188	0.490601	0.069*
C7	0.15857 (17)	−0.15553 (18)	0.60176 (11)	0.0592 (4)
H7	0.102092	−0.227134	0.622364	0.071*
C8	0.26002 (17)	−0.09842 (17)	0.64997 (10)	0.0566 (4)
H8	0.274617	−0.130236	0.703544	0.068*
C8′	0.34080 (14)	0.00667 (14)	0.61892 (8)	0.0433 (3)
C9	0.60231 (14)	0.32835 (14)	0.54005 (8)	0.0415 (3)
C10	0.70383 (18)	0.40300 (19)	0.59326 (10)	0.0635 (4)
H10A	0.777992	0.337998	0.607877	0.095*
H10B	0.660589	0.434974	0.641838	0.095*
H10C	0.739597	0.485039	0.565023	0.095*
C11	0.65823 (14)	0.49418 (15)	0.35937 (8)	0.0431 (3)
H11	0.588580	0.445543	0.329849	0.052*
C12	0.73950 (13)	0.59656 (14)	0.32004 (8)	0.0412 (3)
C13	0.72116 (15)	0.64599 (16)	0.24346 (8)	0.0480 (3)
H13	0.650260	0.615188	0.207619	0.058*
C14	0.81824 (16)	0.74708 (16)	0.22345 (9)	0.0512 (4)
H14	0.819254	0.791784	0.172536	0.061*
C15	0.91036 (15)	0.77500 (16)	0.28349 (9)	0.0475 (3)
C16	1.02682 (18)	0.8761 (2)	0.28408 (11)	0.0647 (4)
H16A	1.020505	0.935234	0.235864	0.097*
H16B	1.111840	0.822800	0.285089	0.097*
H16C	1.024386	0.936586	0.331686	0.097*

anticonvulsant [10], anti-neuroinflammatory [11], anticancer [12], and antioxidant activities [13].

Coumarins are known to possess a wide spectrum of pharmacological activities, such as antimicrobial [14], antioxidant [15], anticancer [16], anti-inflammatory [17]. The coumarin core is a good scaffold for the synthesis of analogs with an aim to study and improve their biological properties. Prompted by all of the above mentioned we decided to contribute to the structural diversity of these compounds by preparing the unsymmetrical azine of the 3-substituted coumarin core and the heterocyclic aldehyde. In this paper, we present the crystal structure of this compound.

The asymmetric unit contains one molecule of 3-(1-(2-((5-methylthiophen-2-yl)methylene)hydrazinyl)ethylidene) chroman-2,4-dione. The whole molecule is quite planar, as the rms deviation of all non-hydrogen atoms from the mean plane amounts 0.075 Å. All bond lengths and angles are within the expected range, and are comparable to those found in the structurally related coumarin compound [18]. The molecular structures of the compound appear to be different in the crystalline state and solution, transformed one into another by virtue of prototropic tautomerism. According to NMR spectra [5], oxygen atom O3 is protonated, while a tautomer in which proton transfer from O3 to N1 occurred exists in the crystalline state. The location of the hydrogen atom H1 in the crystal structure is unequivocally confirmed by difference electron density map, and unrestrained refinement of H1.

The only classical hydrogen bond donor is involved in an intramolecular hydrogen bond N1—H1···O3 with the following parameters: d(D—H) = 0.911(18) Å, d(H···A) = 1.725(18) Å, d(D···A) = 2.5211(16) Å, α(D—H···A) = 144.2(16)°. It appears that the dominant intermolecular interaction is the stacking of molecules, the geometry of which can be described by following parameters: d(Cg1···Cg2^i) = 3.6863(8) Å, δ(Ω1,Ω2) = 4.18(7)°, and d(Cg1···Cg3^i) = 3.7641(8) Å, δ(Ω1,Ω3) = 3.70(6)°, where Cg1 is centroid of the five membered tiophene ring Ω1, Cg2 is centroid of the six-membered lactone ring Ω2, and Cg3 is centroid of the 10-membered coumarine ring Ω3; δ is dihedral angle between ring mean planes; symmetry operation (i): $-x + 1, -y + 1, -z + 1$.

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Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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