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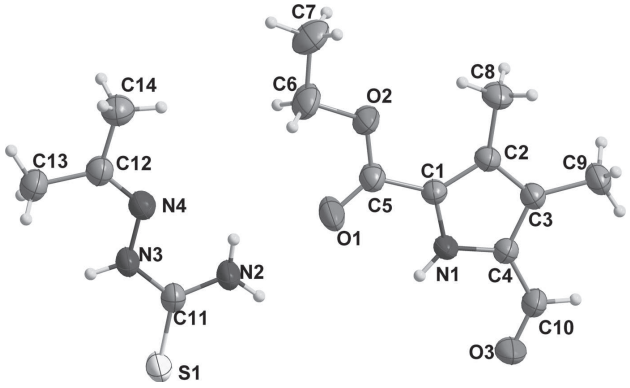
Crystal structure of ethyl 5-formyl-3,4-dimethylpyrrole-2-carboxylate–1-(propan-2-ylidene)thiosemicarbazide (1/1), $C_{14}H_{22}N_4O_3S$



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Abstract

$C_{13}H_{17}N_3OS$, triclinic, $P\bar{1}$ (no. 2), $a = 6.9906(9)$ Å, $b = 8.0075(11)$ Å, $c = 16.057(2)$ Å, $\alpha = 81.822(2)°$, $\beta = 89.151(2)°$, $\gamma = 70.735(2)°$, $V = 839.4(2)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0444$, $wR_{ref}(F^2) = 0.1299$, $T = 296(2)$ K.

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The asymmetric unit of the title 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

Ethyl 5-formyl-2,4-dimethylpyrrole-3-carboxylate (0.390 g, 2 mmol) and thiosemicarbazide (0.091 g, 1 mmol) were dissolved in acetone (10 mL). The mixture was stirred for 1 h under refluxing. The resulting solution was left in air for a few days, yielding colorless block-shaped crystals.

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Table 1: Data collection and handling.

Crystal:	Block, colorless
Size:	0.20 × 0.18 × 0.16 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.21 mm^{-1}
Diffractometer, scan mode:	Bruker SMART, φ and ω-scans
θ_{max}, completeness:	25°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	4412, 2938, 0.014
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2341
$N(param)_{refined}$:	204
Programs:	Bruker programs [1], SHELX [2]

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

Atom	x	y	z	U_{iso}*/U_{eq}
S1	1.03937(12)	−0.06446(8)	−0.37095(4)	0.0675(3)
O1	0.7242(3)	0.4375(2)	−0.17547(10)	0.0720(6)
O2	0.6332(3)	0.72001(19)	−0.14989(9)	0.0554(4)
O3	1.0119(3)	−0.0173(2)	0.11150(10)	0.0681(5)
N1	0.8341(3)	0.3153(2)	−0.00592(10)	0.0403(4)
H1	0.866051	0.228980	−0.035393	0.048*
N2	0.8885(3)	0.2275(3)	−0.29905(11)	0.0597(6)
H2A	0.830903	0.341024	−0.301183	0.072*
H2B	0.921847	0.160435	−0.251145	0.072*
N3	0.8688(3)	0.2703(2)	−0.44204(10)	0.0473(5)
H3	0.889395	0.232314	−0.489961	0.057*
N4	0.7759(3)	0.4510(2)	−0.43706(11)	0.0464(4)
C1	0.7474(3)	0.4913(2)	−0.03652(12)	0.0391(5)
C2	0.7177(3)	0.5904(3)	0.02966(12)	0.0410(5)
C3	0.7901(3)	0.4678(3)	0.10292(12)	0.0430(5)
C4	0.8624(3)	0.2976(3)	0.07912(12)	0.0417(5)
C5	0.7020(3)	0.5434(3)	−0.12715(13)	0.0458(5)
C6	0.5835(5)	0.7851(3)	−0.23865(15)	0.0695(8)
H6A	0.482558	0.739195	−0.258090	0.083*
H6B	0.703533	0.746150	−0.271503	0.083*
C7	0.5027(5)	0.9842(4)	−0.24833(17)	0.0790(9)
H7A	0.379470	1.021278	−0.218333	0.119*
H7B	0.475701	1.031844	−0.306908	0.119*
H7C	0.600834	1.027718	−0.225975	0.119*
C8	0.6252(4)	0.7886(3)	0.02710(15)	0.0553(6)
H8A	0.729003	0.837939	0.037466	0.083*
H8B	0.525566	0.813641	0.069515	0.083*
H8C	0.561693	0.841346	−0.027313	0.083*
C9	0.7889(4)	0.5149(3)	0.19010(14)	0.0607(7)
H9A	0.854398	0.408651	0.228885	0.091*

Table 2 (continued)

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
H9B	0.651507	0.567555	0.205952	0.091*
H9C	0.860194	0.598555	0.191259	0.091*
C10	0.9512(4)	0.1308(3)	0.13234(13)	0.0540(6)
H10	0.963968	0.136369	0.189369	0.065*
C11	0.9257(3)	0.1561(3)	−0.36944(12)	0.0462(5)
C12	0.7206(3)	0.5610(3)	−0.50505(13)	0.0458(5)
C13	0.7457(4)	0.5155(3)	−0.59216(14)	0.0598(6)
H13A	0.886266	0.453851	−0.600452	0.090*
H13B	0.699340	0.623267	−0.631883	0.090*
H13C	0.667730	0.440024	−0.600338	0.090*
C14	0.6217(4)	0.7537(3)	−0.49573(16)	0.0602(6)
H14A	0.607477	0.765180	−0.437065	0.090*
H14B	0.490327	0.798036	−0.523586	0.090*
H14C	0.703962	0.821470	−0.520562	0.090*

Experimental details

The hydrogen atoms were placed at calculated positions and refined as riding atoms with isotropic displacement parameters.

Discussion

Cocrystals are an important class of crystalline materials, which can enhance physicochemical properties of drugs such as solubility and bioavailability [3, 4]. Our previous work shows that the pyrrole moiety is an excellent hydrogen bond donor, and there exist different weak interactions in the crystals of its derivaties [5, 6]. As part of our ongoing studies, the title compound was synthesized and characterized by X-ray diffraction.

In the title structure, there are two independent and different molecules with the 1:1 ratio in the asymmetric unit, namely ethyl 5-formyl-3,4-dimethylpyrrole-2-carboxylate and 1-(propan-2-ylidene)thiosemicarbazide, respectively. As previously reported, two pyrrole aldehyde molecules are linked into a centrosymmetric dimer by pairs of intermolecular N—H···O hydrogen bonds, forming a $R_2^2(10)$ ring motif [3, 4]. Similar dimer could be observed in the case of 1-(propan-2-ylidene)thiosemicarbazide with a $R_2^2(8)$ ring motif. Dimers are connected alternately *via* classic intermolecular N—H···O hydrogen bonds, forming an one-dimensional chain along c axis. The structure is also stabilized by weak N—H···O and C—H···S interactions.

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