Crystal structure of *tert*-butyl-3-(4-oxo-2-thioxo-3,4-dihydropyrimidin-1(2*H*)-yl)propanoate, $C_{11}H_{15}N_2O_3S$

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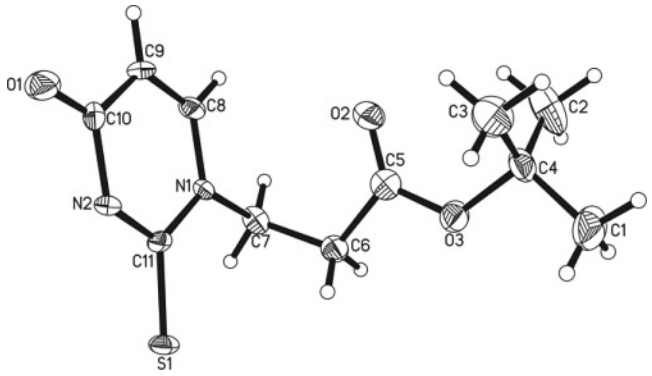

Abstract

$C_{11}H_{15}N_2O_3S$, monoclinic, $P2_1/c$ (no. 14), a = 11.852(2) Å, b = 7.467(1) Å, c = 15.548(2) Å, β = 103.983(2)°, V = 1335.2 Å^3, Z = 4, $R_{gt}(F)$ = 0.1500, $wR_{ref}(F^2)$ = 0.2809, T = 298 K.

Table 1. Data collection and handling.

Crystal:	colourless blocks, size 0.22×0.28×0.35 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	2.41 cm^{-1}
Diffractometer, scan mode:	Bruker APEX area-detector, φ and ω
$2\theta_{max}$:	50.04°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	6766, 2356
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2261
$N(param)_{refined}$:	157
Programs:	SHELX [14]

Source of material

2-thiouracil (1.28g, 10mmol), tert-butyl acrylate (2.2ml, 15mmol), and 0.06g boric acid (1mmol) [13] were placed into a flask. After the addition of water (40ml) the mixture was stirred at 333 K for several hours. The progress of the reaction was monitored by thin-layer chromatography (TLC). The solvent was removed under reduced pressure. Then the solid material was washed with ethyl acetate (40 ml) and the solution was filtered to afford the pure product. The purified product was dissolved in the mixture of methanol and acetone (v/v = 2/1). The resulting solution was left in air for a few days, yielding colourless crystals.

Experimental details

All H atoms were positioned geometrically and allowed to ride on their parent atoms with distances of Csp^2–H = 0.93 Å with U_{iso} = 1.2U_{eq} (parent atom) and N–H = 0.86 Å with U_{iso} = 1.2U_{eq} (parent atom).

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Discussion

2-thiouracil (TU), an established antithyroid drug and melanoma-seeker [1], has shown therapeutic properties, especially antiviral, antithyroid [2-4], and antitumor activities was found to selectively inhibit neuronal nitric oxide synthase (nNOS) in a competitive manner (Ki =20WM) [5]. Therefore many derivatives of 2-thiouracil have been developed to improve its topical delivery and reduce the side effects. On the other hand, compounds containing thiophene aromatic ring are ubiquitous in nature, thiophene oligomers and polymers have received great attention due to their potential anti-cancer and anti-inflammatory properties [6]. In recent years, more and more attention has been focused on synthesis and properties of thiophene carboxylic acid derivatives, which not only play an important role in constructing coordination polymers with attractive topological structures but which also have been found application in a large number of organic reactions and are widely employed in organic synthesis [7-9]. *tert*-butyl-3-(4-oxo-2-thioxo-3,4-dihydropyrimidin-1(2*H*)-yl)propanoate was synthesized and its crystal structure determined. The bond lengths and angles in the title molecule (Fig. 1) are within normal ranges. The N1–C8 and N1–C11 bond distance [1.370(9)Å and 1.363(9)Å] and N2–C10 and N2–C11 bond distance [1.389(10)Å and 1.363(9)Å] are shorter than a N–C single bond (1.443(4)Å), but longer than a typical N=C double bond (1.269(2)Å). The C9–C10 and C8–C9 bond lengths [1.433(11)Å and 1.315(11)Å] are shorter than a typical C–C bond [1.530(6)Å], but longer than a typical C=C double bond [1.433(11)Å]. The C10–O1 bond lengths [1.203(9)Å] are short than a typical C–O bond length [1.439(2)Å], but longer than a typical C=O double bond [1.173(5)Å]. The C11–S1 bond distance [1.679(8)Å] are both shorter than a typical C–S bond length [1.817(2)Å], but longer than a typical C=S double bond [1.571(1)Å] [10-12]. The partial double bond character of the structure is presumed as a result of the electron delocalization. The atoms (C11, C10, C9, C8, N1 and N2) in the heterocyclic ring are slightly puckered, with an r.m.s. deviation of 0.0298Å. The dihedral angle formed by the heterocyclic ring and The flat (C5/C6/C7) is 78.23(0.37)°. It should be noted that the hydrogen bonding interactions plays an important role in the crystal structure of the title compound.

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1A)	4*e*	0.6883	0.5507	0.2130	0.147
H(1B)	4*e*	0.7746	0.7122	0.2375	0.147
H(1C)	4*e*	0.7397	0.6412	0.1398	0.147
H(2A)	4*e*	0.6625	0.9279	0.0751	0.150
H(2B)	4*e*	0.7026	1.0196	0.1682	0.150
H(2C)	4*e*	0.5724	1.0324	0.1151	0.150
H(3A)	4*e*	0.5079	0.9068	0.2419	0.109
H(3B)	4*e*	0.6363	0.8866	0.2979	0.109
H(3C)	4*e*	0.5539	0.7194	0.2804	0.109

Table 2. continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(6A)	4*e*	0.3473	0.507	0.0461	0.050
H(6B)	4*e*	0.3752	0.604	–0.0357	0.050
H(7A)	4*e*	0.2109	0.789	–0.0472	0.047
H(7B)	4*e*	0.1750	0.5866	–0.0581	0.047
H(8)	4*e*	0.1548	0.9586	0.0550	0.045
H(9)	4*e*	0.0612	1.0021	0.1608	0.046

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	4*e*	0.1356(2)	0.3350(3)	0.0578(1)	0.047(1)	0.023(1)	0.044(1)	0.0005(9)	0.0088(9)	–0.0064(9)
O(1)	4*e*	0.0069(6)	0.7479(8)	0.2589(4)	0.070(4)	0.039(3)	0.064(4)	–0.004(3)	0.042(3)	–0.007(3)
O(2)	4*e*	0.3837(5)	0.8988(9)	0.0928(5)	0.049(4)	0.050(4)	0.081(5)	–0.002(3)	0.001(3)	–0.019(4)
O(3)	4*e*	0.5223(5)	0.6877(8)	0.1101(4)	0.044(3)	0.058(4)	0.053(4)	0.002(3)	0.006(3)	–0.015(3)
N(1)	4*e*	0.1575(5)	0.6922(8)	0.0567(4)	0.029(3)	0.028(3)	0.042(4)	–0.004(3)	0.009(3)	0.002(3)
N(2)	4*e*	0.0715(5)	0.5732(8)	0.1627(4)	0.035(3)	0.022(3)	0.035(3)	0.003(3)	0.009(3)	–0.004(3)
C(1)	4*e*	0.7127(9)	0.662(2)	0.1924(9)	0.054(7)	0.12(1)	0.102(9)	0.012(7)	–0.016(6)	–0.054(9)
C(2)	4*e*	0.640(1)	0.957(2)	0.1287(8)	0.088(9)	0.13(1)	0.079(8)	–0.060(9)	0.008(7)	0.006(8)
C(3)	4*e*	0.5743(9)	0.829(2)	0.2557(6)	0.073(7)	0.085(8)	0.052(6)	–0.001(6)	–0.002(5)	–0.015(6)
C(4)	4*e*	0.6133(7)	0.789(1)	0.1723(6)	0.036(5)	0.062(6)	0.045(5)	–0.009(4)	–0.001(4)	–0.010(4)
C(5)	4*e*	0.4166(7)	0.755(1)	0.0764(5)	0.051(5)	0.052(5)	0.023(4)	–0.001(4)	0.018(4)	–0.001(4)
C(6)	4*e*	0.3431(7)	0.621(1)	0.0155(5)	0.044(5)	0.048(5)	0.035(4)	–0.004(4)	0.012(4)	–0.008(4)
C(7)	4*e*	0.2156(7)	0.675(1)	–0.0163(5)	0.046(5)	0.038(4)	0.033(4)	–0.008(4)	0.007(3)	0.001(4)
C(8)	4*e*	0.1329(7)	0.860(1)	0.0833(5)	0.045(4)	0.022(4)	0.051(5)	–0.005(3)	0.021(4)	–0.004(3)
C(9)	4*e*	0.0795(7)	0.8861(9)	0.1472(5)	0.043(4)	0.014(4)	0.061(5)	0.003(3)	0.015(4)	–0.009(3)
C(10)	4*e*	0.0492(6)	0.739(1)	0.1961(5)	0.025(4)	0.036(4)	0.049(5)	–0.005(3)	0.011(4)	0.001(4)
C(11)	4*e*	0.1206(6)	0.544(1)	0.0932(5)	0.022(4)	0.029(4)	0.038(4)	0.004(3)	–0.005(3)	0.005(3)

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