Crystal structure of 3-(5-bromo-2,4-dioxo-3,4-dihydropyrimidin-1(2*H*)yl) propionic acid methyl ester, $C_8H_9BrN_2O_4$

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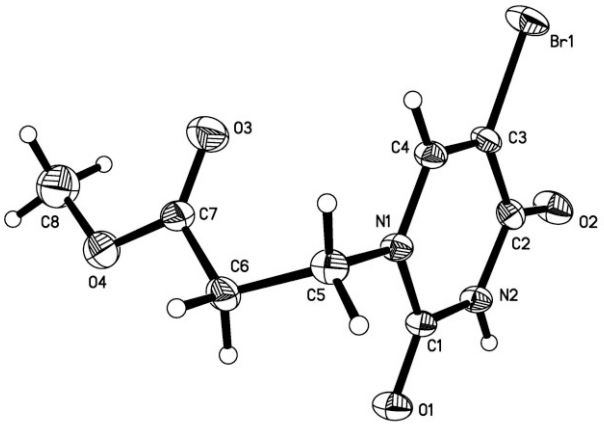
Received December 26, 2011, accepted July 06, 2012, available online July 26, 2012, CCDC no. 1267/3784



Abstract

$C_8H_9BrN_2O_4$, triclinic, $P\bar{1}$ (no. 2), a = 6.1027(9) Å, b = 7.933(1) Å, c = 10.855(2) Å, α = 81.154(3)°, β = 85.118(3)°, γ = 83.093(3)°, V = 514.3 Å^3, Z = 2, $R_{gt}(F)$ = 0.0402, $wR_{ref}(F^2)$ = 0.1847, T = 298 K.

Table 1. Data collection and handling.

Crystal:	colourless prisms, size 0.16×0.21×0.25 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	39.92 cm^{-1}
Diffractometer, scan mode:	Bruker APEX II area-detector, φ and ω
$2\theta_{max}$:	50.98°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4414, 1900
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1770
$N(param)_{refined}$:	138
Programs:	SHELXS-97 [8]

Source of material

5-Bromouracil (1.9 g, 10 mmol), methyl acrylate (1.36 mL, 15 mmol), triethyl amine (0.25 mL) and DMF (30 mL) were added into a flask and stirred at 333 K for 2 hours under continuous thin-layer chromatography (TLC) detection. The solid was obtained after removal of DMF by reduced pressure distillation and washing by ethyl acetate (30 mL). The purified product was dissolved in ethanol and the single crystals were separated after a few days by suction.

Experimental details

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

Discussion

The Michael reaction is one of the most important addition reactions applied widespread in organic synthesis and drug synthesis [1,2]. Also the synthesis of N-alkylated uracils and their precursors is a Michael-type addition (in this case aza-Michael reaction) [1-4] of uracil anions to acceptors possessing activated double bonds. Based on the interest in modification of 5-substituted uracils at N-1 position by an aza-Michael addition approach, we report here the synthesis of a 5-bromouracil derivative, namely 3-(5-bromo-2,4-dioxo-3,4-dihydropyrimidin-1(2*H*)-yl) propionic acid methyl ester, and the determination of its crystal structure. The bond lengths and angles in the title molecule are within normal ranges. The N1–C4 and N1–C1 bond distance [1.374(5) Å and 1.378(5) Å] and N2–C1 and N2–C2 bond distance [1.364(5) Å and 1.400(5) Å] are shorter than the N1–C5 single bond of 1.475(4) Å . The C2–C3 bond length of 1.443(5) Å is shorter than a typical C–C bond length [1.499(6) Å], but longer than a typical C=C double bond [1.344(6) Å] . The C1–O1 and C2–O2 bond lengths [1.218(5) Å and 1.206(5) Å] are shorter than a typical C–O bond length [1.447(7) Å], but longer than a typical C=O double bond [1.201(6) Å] [5-7]. The partial double bond character of the structure is presumed as a result of the electron delocalization. The atoms (C1, C2, C3, C4, N1 and N2) in the heterocyclic ring are slightly puckered,with an r.m.s. deviation of 0.0011 Å. The adjacent molecules are linked by intermolecular N2–H2···O1^{i} hydrogen bond interactions to form dimers stabilizing the crystal structure.

Symmetry code **i**: -x+2, -y+1, -z+2

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

Atom	Site	x	y	z	U_{iso}
H(2)	2*i*	0.8064	0.5789	0.9492	0.037
H(4)	2*i*	0.4979	0.2473	0.7321	0.037
H(5A)	2*i*	0.7242	0.0105	0.8084	0.041
H(5B)	2*i*	0.8339	0.0139	0.9333	0.041
H(6A)	2*i*	1.1540	0.0950	0.8233	0.045
H(6B)	2*i*	1.0987	–0.0776	0.7866	0.045
H(8A)	2*i*	1.2439	0.1244	0.4169	0.102
H(8B)	2*i*	1.4555	0.2017	0.4455	0.102
H(8C)	2*i*	1.2233	0.3096	0.4534	0.102

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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}
Br(1)	2*i*	0.22805(7)	0.56825(5)	0.68153(4)	0.0376(4)	0.0487(4)	0.0706(5)	0.0050(2)	–0.0273(3)	–0.0080(3)
O(1)	2*i*	0.9962(5)	0.2919(3)	0.9729(3)	0.042(2)	0.031(1)	0.046(2)	–0.001(1)	–0.020(1)	–0.007(1)
O(2)	2*i*	0.4999(6)	0.7456(4)	0.8461(3)	0.047(2)	0.030(2)	0.074(2)	0.008(1)	–0.020(2)	–0.013(1)
O(3)	2*i*	0.9038(6)	0.1734(6)	0.5865(3)	0.045(2)	0.093(3)	0.044(2)	0.003(2)	–0.010(2)	–0.002(2)
O(4)	2*i*	1.2686(6)	0.1255(5)	0.5980(3)	0.041(2)	0.061(2)	0.049(2)	–0.008(2)	0.000(1)	–0.012(1)
N(1)	2*i*	0.7392(5)	0.2501(4)	0.8446(3)	0.031(2)	0.023(1)	0.032(1)	–0.002(1)	–0.008(1)	–0.006(1)
N(2)	2*i*	0.7455(5)	0.5159(4)	0.9072(3)	0.032(2)	0.027(2)	0.036(2)	–0.006(1)	–0.009(1)	–0.007(1)
C(1)	2*i*	0.8381(6)	0.3498(5)	0.9123(3)	0.026(2)	0.030(2)	0.030(2)	–0.005(1)	–0.007(1)	–0.004(1)
C(2)	2*i*	0.5640(6)	0.5965(5)	0.8421(3)	0.028(2)	0.029(2)	0.037(2)	–0.005(1)	–0.000(1)	–0.002(1)
C(3)	2*i*	0.4722(6)	0.4818(5)	0.7744(3)	0.022(2)	0.038(2)	0.035(2)	–0.000(1)	–0.008(1)	–0.003(1)
C(4)	2*i*	0.5603(6)	0.3177(5)	0.7773(3)	0.028(2)	0.033(2)	0.035(2)	–0.007(2)	–0.007(1)	–0.007(1)
C(5)	2*i*	0.8261(7)	0.0679(4)	0.8471(4)	0.041(2)	0.021(2)	0.041(2)	–0.002(2)	–0.009(2)	–0.004(1)
C(6)	2*i*	1.0508(8)	0.0443(5)	0.7807(4)	0.037(2)	0.032(2)	0.044(2)	0.007(2)	–0.009(2)	–0.008(2)
C(7)	2*i*	1.0616(7)	0.1213(5)	0.6459(4)	0.037(2)	0.042(2)	0.040(2)	–0.001(2)	–0.010(2)	–0.015(2)
C(8)	2*i*	1.301(1)	0.196(1)	0.4674(5)	0.063(4)	0.085(4)	0.055(3)	–0.013(3)	0.004(3)	–0.005(3)

Acknowledgments. We acknowledge financial support by Zhejiang Provincial Technology Innovation Project Foundation (no. 2011R424023), and Wenzhou Techonlogy Project Foundation (no. Y20100003).

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