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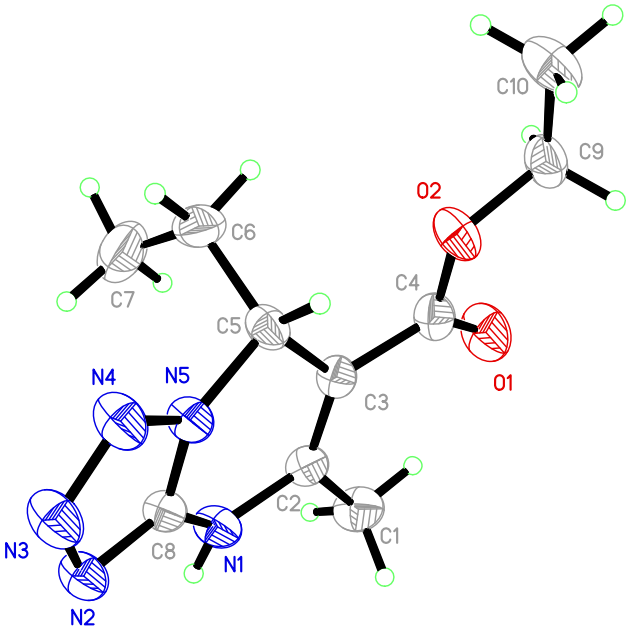
The crystal structure of ethyl 7-ethyl-5-methyl-4,7-dihydrotetrazolo[1,5-*a*]pyrimidine-6-carboxylate, $C_{10}H_{15}N_5O_2$



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Abstract

$C_{10}H_{15}N_5O_2$, triclinic, $P\bar{1}$ (no. 2), a = 8.0501(16) Å, b = 8.6163(17) Å, c = 9.6654(19) Å, α = 69.74(3)°, β = 75.79(3)°, γ = 87.43(3)°, V = 609.1(2) Å^3, Z = 2, $R_{gt}(F)$ = 0.0593, w$R_{ref}(F^2)$ = 0.1821, T = 293 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.

Table 1: Data collection and handling.

Crystal:	Colorless prism
Size:	0.36 × 0.16 × 0.14 mm
Wavelength:	Mo*K*α radiation (0.71073 Å)
μ:	0.09 mm^{-1}
Diffractometer, scan mode:	Rigaku SCXmini, ω
θ_{max}, completeness:	27.5°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	6372, 2794, 0.034
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1667
$N(param)_{refined}$:	157
Programs:	Rigaku [1], Olex2 [2], Shelx [3, 4], Diamond [5]

Source of materials

In a 25 mL reaction vessel, a solution of propionaldehyde (10 mmol), ethyl 3-oxobutanoate (10 mmol), and 5-aminotetrazole (10 mmol) in 7.5 mL propane-1,2-diol and 2 mL water was sealed, and kept at 120 °C for 12 h before it was cooled to room temperature. The reaction solution was poured into 50 mL distilled water, stirred vigorously for 10 min, and then the solid of crude tetrazolopyrimidine was filtered out. Recrystallization with methanol and DMF gave the crystal product. **IR** (KBr, ν, cm^{-1}) for $C_{10}H_{15}N_5O_2$: 3475, 3247, 3176, 3100, 2947, 2932, 1707, 1651, 1574, 1450, 1318, 1262, 1227, 1150, 1095, 1018, 990, 878, 844, 788, 672, 565, 472 [8]. **^{1}H NMR** (300 MHz, $CDCl_3$) (δ, ppm) for $C_{10}H_{15}N_5O_2$: 11.08(s, 1H, NH), 5.82(s, 1H, CH), 4.26(s, 2H,CH_2), 2.62(s, 3H, CH_3), 2.08(s, 1H, CH_2), 1.88(s, 1H, CH_2), 1.34(s, 3H, CH_3), 0.80(s, 3H, CH_3) [9]. **ESI–MS** for $C_{10}H_{15}N_5O_2$[$(M-1)^-$]: 236.46.

Experimental details

All the hydrogen atoms were calculated geometrically and with C–H distances ranging from 0.96 to 0.98 Å, with U_{iso}(H) = 1.2–1.5U_{eq}(C). N—H = 0.86 Å, with U_{iso}(H) = 1.2U_{eq}(N).

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
O1	0.2143 (3)	−0.0977 (2)	−0.0208 (2)	0.0810 (6)
O2	0.2386 (2)	0.17728 (19)	−0.13123 (17)	0.0613 (5)
N1	0.3790 (2)	−0.0114 (2)	0.3407 (2)	0.0510 (5)
H1	0.381700	−0.087596	0.425638	0.061*
N2	0.5110 (2)	0.2062 (2)	0.3884 (2)	0.0534 (5)
N3	0.5291 (3)	0.3720 (2)	0.3096 (2)	0.0650 (6)
N4	0.4616 (3)	0.4124 (2)	0.1947 (2)	0.0619 (6)
N5	0.3968 (2)	0.26838 (19)	0.19599 (19)	0.0465 (5)
C1	0.3115 (3)	−0.2336 (3)	0.2645 (3)	0.0639 (7)
H1A	0.267821	−0.255143	0.188694	0.096*
H1B	0.235484	−0.285120	0.362843	0.096*
H1C	0.423139	−0.277980	0.264019	0.096*
C2	0.3243 (3)	−0.0501 (2)	0.2301 (2)	0.0450 (5)
C3	0.2910 (2)	0.0717 (2)	0.1086 (2)	0.0429 (5)
C4	0.2454 (3)	0.0358 (3)	−0.0168 (3)	0.0511 (6)
C5	0.2969 (3)	0.2544 (2)	0.0916 (2)	0.0496 (6)
H5	0.357781	0.318492	−0.012910	0.059*
C6	0.1201 (4)	0.3247 (3)	0.1267 (4)	0.0792 (9)
H6A	0.135169	0.441321	0.110442	0.095*
H6B	0.058023	0.316591	0.055050	0.095*
C7	0.0121 (4)	0.2404 (4)	0.2860 (4)	0.0990 (11)
H7A	−0.000446	0.124075	0.304976	0.149*
H7B	−0.098979	0.286977	0.296298	0.149*
H7C	0.066917	0.256673	0.357906	0.149*
C8	0.4279 (3)	0.1465 (2)	0.3140 (2)	0.0431 (5)
C9	0.1833 (3)	0.1674 (3)	−0.2597 (3)	0.0629 (7)
H9A	0.071200	0.111089	−0.225923	0.076*
H9B	0.263831	0.106900	−0.312147	0.076*
C10	0.1757 (4)	0.3407 (4)	−0.3626 (3)	0.0843 (9)
H10A	0.093509	0.398292	−0.310088	0.126*
H10B	0.142096	0.339835	−0.450999	0.126*
H10C	0.286641	0.395780	−0.393031	0.126*

Comment

Tetrazolo[1,5-*a*]pyrimidines and their partially hydrogenated derivatives are very important chemical intermediates [6]. To address green chemistry principles for the synthesis of dihydro tetrazolo pyrimidines, one may concern carrying out these reactions under solvothermal conditions with propane-1,2-diol and water as mixture solvents [7].

There is one crystallographically independent molecule in the asymmetric unit. Almost all non-hydrogen atoms are coplanar except C(6) and C(7) from propionaldehyde [10]. Distance between N1–C2 (1.393 Å) is shorter than C5–N2 (1.473 Å). The tetrazole conjugated system extends to C3 from N1. The pyrimidine ring is in a flattened boat conformation [11]. Two adjacent molecules are connected by N(1)—H···N(2) intermolecular hydrogen bonds. Bond lengths and angles are as expected [12–14].

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References

1. Rigaku. *CrystalClearSM Expert*; Rigaku Corporation: Tokyo, Japan, 2005.
2. Bourhis L. J., Dolomanov O. V., Gildea R. J., Howard J. A. K., Puschmann H. The anatomy of a comprehensive constrained, restrained refinement program for the modern computing environment–olex2 dissected. *Acta Crystallogr.* 2015, *A71*, 59–75.
3. Sheldrick G. M. *SHELXT* – integrated space-group and crystal structure determination. *Acta Crystallogr.* 2015, *A71*, 3–8.
4. Sheldrick G. M. Crystal structure refinement with *SHELXL*. *Acta Crystallogr.* 2015, *C71*, 3–8.
5. Brandenburg K. *Diamond. Visual Crystal Structure Information System. Ver. 4.0*; Crystal Impact: Bonn, Germany, 2015.
6. Shaik A., Shaik F. B., Tangella N. P., Veera B. G., Vadiga S. K., Naveen M. An efficient, multicomponent, green protocol to access 4, 7-dihydrotetrazolo [1, 5-*a*] pyrimidines and 5, 6, 7, 9-tetrahydrotetrazolo[5, 1-*b*]quinazolin-8(4*H*)-ones using PEG-400 under microwave irradiation. *Synth. Commun.* 2019, *49*, 3181–3190.
7. Wang W. X., Cai H. L., Xiong R. G. Hydrothermal synthesis method of 5-(4′-methylbiphenyl-2-yl)-1*H*-tetrazole. *Chin. Chem. Lett.* 2013, *24*, 783–785.
8. Kour P., Singh V. P., Khajuria B., Singh T., Kumar A. Al (III) chloride catalyzed multi-component domino strategy: synthesis of library of dihydrotetrazolo[1, 5-*a*]pyrimidines and tetrahydrotetrazolo[1, 5-*a*]quinazolinones. *Tetrahedron Lett.* 2017, *58*, 4179–4185.
9. Irina G. T., Sergey A. K., Vladimir I. M., Svitlana V. S., Viktoriya V. D., Vladimir N. S., Mikhail V. D., Valentyn A. C., Sergey M. D. In water multicomponent synthesis of low-molecular-mass 4, 7-dihydrotetrazolo[1, 5-*a*]pyrimidines. *Beilstein J. Org. Chem.* 2019, *15*, 2390–2397.
10. Fang B., Meng J. P., Luo Y. Crystal structure of methyl 2-(4-(pyrazolo[1, 5-*a*] pyrimidin-6-yl)phenyl)acetate, $C_{15}H_{13}N_3O_2$. *Z. Kristallogr. N. Cryst. Struct.* 2019, *234*, 395–396.
11. Shen S. D., Feng X. D., Yang W. H., Yao C. S. Ethyl 7-(4-bromophenyl)-5-trifluoromethyl-4, 7-dihydrotetrazolo[1, 5-*a*] pyrimidine-6-carboxylate. *Acta Crystallogr.* 2010, *E66*, o2421.
12. Price I. K., Rougeot C., Hein J. E. Crystal structure of 5, 7-diphenyl-4, 7-dihydrotetrazolo[1, 5-*a*]pyrimidine. *Acta Crystallogr.* 2015, *E71*, o220.
13. Wang W. The crystal structure of ethyl 5-methyl-7-(4-(phenylthio)phenyl)-4, 7-dihydrotetrazolo[1, 5-*a*] pyrimidine-6-carboxylate, $C_{20}H_{19}N_5O_2S$. *Z. Kristallogr. N. Cryst. Struct.* 2021, *236*, 781–783.
14. Haleel A. K., Rafi U. M., Jayathuna M. A., Rahiman A. K. Theoretical, single crystal and molecular docking analysis of tetrazolo[1, 5-*a*] pyrimidine-6-carboxylate derivatives. *J. Mol. Struct.* 2022, *1250*, 131706.