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The crystal structure of 4-(6-acetyl-5-methyl-4,7-dihydrotetrazolo[1,5-*a*]pyrimidin-7-yl) benzonitrile, C₁₄H₁₂N₆O

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Abstract

C₁₄H₁₂N₆O, monoclinic, *P*₂/c (no. 14), *a* = 17.827(4) Å, *b* = 11.021(2) Å, *c* = 7.0936(14) Å, β = 100.59(3)°, *V* = 1370.0(5) Å³, *Z* = 4, *R*_{gt}(*F*) = 0.0824, *wR*_{ref}(*F*²) = 0.2208, *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.

Source of material

4-Formylbenzonitrile (10 mmol), pentane-2,4-dione (10 mmol), 5-aminotetrazole (10 mmol), 7.5 mL propane-1,2-diol and 2 mL water were added successively into a 25 mL reaction vessel,

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Table 1: Data collection and handling.

Crystal:	Colorless prism
Size:	0.38 × 0.18 × 0.16 mm
Wavelength:	Mo Kα radiation (0.71073 Å)
μ:	0.09 mm ⁻¹
Diffractometer, scan mode:	Bruker P4, ω
θ _{max} , completeness:	27.5°, >99%
<i>N</i> (<i>hkl</i>) _{measured} , <i>N</i> (<i>hkl</i>) _{unique} , <i>R</i> _{int} :	13,141, 3109, 0.080
Criterion for <i>I</i> _{obs} , <i>N</i> (<i>hkl</i>) _{gt} :	<i>I</i> _{obs} > 2 σ(<i>I</i> _{obs}), 2098
<i>N</i> (<i>param</i>) _{refined} :	190
Programs:	CrystalClear [1], Olex2 [2], SHELX [3, 4], Diamond [5]

stirred well before the mixture was sealed in the vessel. The mixture was 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 from methanol and DMF gave the crystal product.

Experimental details

All the hydrogen atoms were calculated geometrically with C–H distances ranging from 0.93 to 0.98 Å. C_{aryl}–H = 0.93 Å, with *U*_{iso}(H) = 1.2*U*_{eq}(C). C_{methyl}–H = 0.96 Å, with *U*_{iso}(H) = 1.5*U*_{eq}(C).

Comment

Pyrimidines are a very important class of substances in life activities [6]. They are widely present in the human body and other organisms. For example, among the five most common nitrogen-containing basic components in nucleic acids, there are three pyrimidine-containing structures. Pyrimidine compounds have received widespread attention because of their strong biological activities [7]. Medicines containing pyrimidine rings mainly focus on anti-tumor [8] and virus aspects [9], including very important anti-hepatitis B virus varieties and anti-HIV varieties [10]. Pesticides containing pyrimidine rings have excellent performance in the three major fields of weed-ing, insecticide and sterilization and even plant growth regulators [11].

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	U _{iso} */U _{eq}
O1	0.18894 (17)	0.1203 (3)	0.3687 (4)	0.0760 (9)
N1	0.07279 (14)	−0.1021 (3)	1.0839 (4)	0.0456 (7)
N2	0.12557 (15)	−0.1869 (3)	1.1583 (4)	0.0500 (7)
N3	0.18428 (14)	−0.1836 (2)	1.0767 (4)	0.0442 (7)
N4	0.17045 (13)	−0.0947 (2)	0.9432 (3)	0.0337 (5)
N5	0.07367 (14)	0.0416 (2)	0.8264 (4)	0.0443 (7)
H5	0.033314	0.079874	0.842575	0.053*
N6	0.5348 (2)	0.1756 (3)	1.4104 (6)	0.0848 (12)
C1	0.10313 (15)	−0.0473 (3)	0.9500 (4)	0.0349 (6)
C2	0.0623 (2)	0.1581 (4)	0.5385 (5)	0.0603 (10)
H2A	0.015992	0.176678	0.583528	0.090*
H2B	0.090935	0.231224	0.532208	0.090*
H2C	0.050041	0.122390	0.413105	0.090*
C3	0.10891 (17)	0.0703 (3)	0.6738 (4)	0.0406 (7)
C4	0.17748 (16)	0.0227 (3)	0.6597 (4)	0.0367 (7)
C5	0.21355 (19)	0.0453 (3)	0.4905 (4)	0.0468 (8)
C6	0.2827 (2)	−0.0262 (4)	0.4709 (5)	0.0621 (10)
H6A	0.294985	−0.081117	0.577068	0.093*
H6B	0.272841	−0.071417	0.353251	0.093*
H6C	0.324780	0.027977	0.469608	0.093*
C7	0.22207 (15)	−0.0593 (3)	0.8137 (4)	0.0340 (6)
H7	0.237281	−0.132504	0.751895	0.041*
C8	0.29329 (15)	−0.0017 (3)	0.9321 (4)	0.0345 (6)
C9	0.35549 (16)	−0.0746 (3)	0.9999 (4)	0.0421 (7)
H9	0.355020	−0.155924	0.964883	0.051*
C10	0.41976 (17)	0.0936 (3)	1.1697 (4)	0.0439 (8)
C11	0.35837 (18)	0.1682 (3)	1.0986 (5)	0.0486 (8)
H11	0.359683	0.250051	1.130835	0.058*
C12	0.29525 (17)	0.1201 (3)	0.9795 (4)	0.0434 (7)
H12	0.254017	0.169791	0.931190	0.052*
C13	0.4846 (2)	0.1418 (4)	1.3034 (5)	0.0597 (10)
C28	0.41855 (17)	−0.0265 (3)	1.1201 (5)	0.0469 (8)
H28	0.460099	−0.075830	1.167074	0.056*

Under hydrothermal and solvothermal conditions, with special physical and chemical properties of various solvents in the subcritical or supercritical state [12], the activity of the reactants was greatly enhanced, the required reaction temperature was greatly reduced, the development of low-temperature synthetic chemistry was promoted, new chemical reactions were discovered.

In the title molecule, C₁₄H₁₂N₆O, all bond lengths are in normal ranges [13, 14]. The plane of the tetrazole ring forms dihedral angles of 77.56(9)° with the phenyl ring. The pyrimidine ring is in a flattened boat conformation. In the crystal, N–H...N hydrogen bonds stabilize the molecular structure.

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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. *SHELXTL* – 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. Gein V. L., Vladimirov I. N., Fedorova O. V., Kurbatova A. A., Nosova N. V., Krylova I. V., Vakhnin M. I. Synthesis of alkyl 5-aryl-7-methyl-1,5-dihydro-1,2,4-triazolo[1,5-a]pyrimidine-6-carboxylates. *Russ. J. Org. Chem.* 2010, *46*, 699–705.
7. Tkachenko I. G., Komykhov S. A., Musatov V. I., Shishkina S. V., Dyakonov V. V., Shvets V. N., Diachkov M. V., Chebanov V. A., Desenko S. M. In water multicomponent synthesis of low-molecular-mass 4,7-dihydro-1,2,4-triazolo[1,5-a]pyrimidines. *Beilstein J. Org. Chem.* 2019, *15*, 2390–2397.
8. Saira M., Yang J. Q., Tariq Q., Mei H. Z., Yang Z. L., Hu Y., Cao W. L., Valery P. S., Zhang J. G. Tetrazole and azido derivatives of pyrimidine: synthesis, mechanism, thermal behaviour & steering of azido–tetrazole equilibrium. *ChemistrySelect* 2020, *5*, 5414–5421.
9. Wang X. C., Wei Y., Da Y. X., Zhang Z., Quan Z. J. One-step synthesis of tetrazolo[1,5-a]pyrimidines by cyclization reaction of dihydropyrimidine-2-thiones with sodium azide. *Heterocycles* 2011, *83*, 2811–2822.
10. Shen S. D., Feng X. D., Yang W. H., Yao C. S. Ethyl 7-(4-bromophenyl)-5-trifluoromethyl-4,7-dihydro-1,2,4-triazolo[1,5-a]pyrimidine-6-carboxylate. *Acta Crystallogr.* 2010, *E66*, o2421.
11. Haleel A., Arthi P., Dastagiri Reddy N., Veena V., Sakthivel N., Arun Y., Perumal P. T., Rahiman A. K. DNA binding, molecular docking and apoptotic inducing activity of nickel(II), copper(II) and zinc(II) complexes of pyridine-based tetrazolo[1,5-a]pyrimidine ligands. *RSC Adv.* 2014, *4*, 60816–60830.
12. Li T. J., Yao C. S., Yu C. X., Wang X. S., Tu S. J. Ionic liquid-mediated one-pot synthesis of 5-(trifluoromethyl)-4,7-dihydro-1,2,4-triazolo[1,5-a]pyrimidine derivatives. *Synth. Commun.* 2012, *42*, 2728–2738.
13. Price I. K., Rougeot C., Hein J. E. Crystal structure of 5,7-diphenyl-4,7-dihydro-1,2,4-triazolo[1,5-a]pyrimidine. *Acta Crystallogr.* 2015, *E71*, o220.
14. Fang B., Meng J. P., Luo Y. Crystal structure of methyl 2-(4-(pyrazolo[1,5-a]pyrimidin-6-yl)phenyl)acetate, C₁₅H₁₃N₃O₂. *Z. Kristallogr. NCS* 2019, *234*, 395–396.