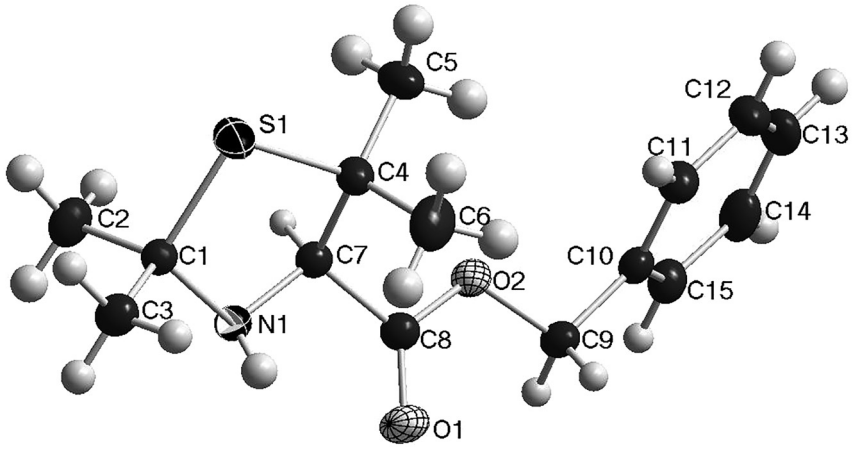
Lingli Shao, Shuping Cai, Zhiming Li, Yutao Feng, Mengting Chen, Kaining Xu and Zhenxiang Liu*

The crystal structure of benzyl 2,2,5,5-tetramethylthiazolidine-4-carboxylate, $C_{15}H_{21}NO_2S$



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Abstract

$C_{15}H_{21}NO_2S$, monoclinic, $P2_1/n$ (no. 62), a = 12.0769(6) Å, b = 6.1507(3) Å, c = 20.4335(11) Å, β = 90.710(2)°, V = 1517.71(13) Å^3, Z = 4, T = 170 K, $R_{gt}(F)$ = 0.0341, w$R(F^2)$ = 0.0376.

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1 Source of materials

A mixture consisting of 149.2 mg (1.0 mmol) penicillamine, 165.8 mg (1.2 mmol) K_2CO_3 and 5 ml acetone were added to a Schlenk-tube equipped with a magnetic stir bar and stirred at room temperature (20–40 °C) for 30 min, then 118.8 µl (1.0 mmol) benzyl bromide and the phase transfer catalyst 55.6 mg (0.2 mmol) tetra-butylammonium chloride were added dropwise to the mixture and was further stirred for 16 h. The resulted solution was treated by 10 ml water and was extracted 3 times with ethyl acetate, combined the organic phases and dried with sodium sulphate anhydrous, after evaporated by rotary evaporation, the obtained mixture was subjected to chromatography using a silica gel column (an eluent was petroleum ether: ethyl acetate = 10:1 to 5:1), and 166.2 mg of the pure yellow product was obtained with a yield of 59.5 %. ^{1}H NMR (400 MHz, chloroform-d) δ 7.37 (d, J = 5.4 Hz, 5H), 5.20 (s, 2H), 3.93 (s, 1H), 3.21 (s, 1H), 1.66 (s, 3H), 1.60 (s, 3H), 1.55 (s, 3H), 1.15 (s, 3H). ^{13}C NMR (101 MHz, chloroform-d) δ 169.61, 135.25, 128.89, 128.79, 128.75, 72.98, 72.81, 67.22, 61.36, 33.58, 32.12, 29.09, 27.95. HRMS (ESI): m/z calcd for $C_{15}H_{21}NO_2S$ $[M^+H]^+$: 279.3980. Found: 280.1377.

Preparing of the crystals of benzyl 2,2,5,5-tetramethylthiazolidine-4-carboxylate was obtained through a volatile compound saturated solution method. Dissolve the compound (5.0 mg) in 15 ml mixed solvent (petroleum ether:ethyl acetate = 5:1) to obtain a pale-yellow transparent solution. Yellow needle crystals was obtained.

2 Experimental details

After absorption correction, the crystal structure was solved using the Olex2 software[2] and the programs SHELXT[3] program and refined with SHELXL[4] and the molecular graphics were drawn by using DIAMOND software.[5] All hydrogens were generated geometrically (C–H bond fixed at 0.96 Å), assigned

***Corresponding author: Zhenxiang Liu**, College of Pharmaceutical Engineering, Jinhua University of Vocational Technology, Jinhua, 321016, People's Republic of China, E-mail: liuzhenxiang86@163.com. https://orcid.org/0009-0000-7001-3833
Lingli Shao, Shuping Cai, Mengting Chen and Kaining Xu, College of Pharmaceutical Engineering, Jinhua University of Vocational Technology, Jinhua, 321016, People's Republic of China
Zhiming Li, Zhejiang Shengtai Safety Technology CO., LTD., Hangzhou, 310000, People's Republic of China
Yutao Feng, The College of Biochemical Engineering, Beijing Union University, Beijing, 100021, People's Republic of China

isotropic thermal parameters, and allowed to ride on their parent carbon atoms before the final cycle of refinement.

3 Comment

The introduction of heteroatoms into heteroycles are widely distributed in nature. Moreover, most compounds associated with biological functions are heterocycles, including nucleic acids, certain vitamins, hormones, and the like. Due to their distinctive structure and properties, heterocyclic compounds exhibit a broad spectrum of applications across various sectors.[6–8]

Thiazole derivatives are a class of nitrogen-containing heterocyclic compounds characterized by the presence of a thiazole ring, which is a five-membered ring incorporating sulfur and nitrogen atoms. These compounds hold a significant position in drug design because they can serve as the fundamental scaffolds for a variety of bioactive molecules.[9] For instance, penicillin, which was the first antibacterial drug applied clinically, the immunomodulator piduomode, the antidiabetic drug pioglitazone, and so on, all belong to thiazolidine compounds.[10]

The article describes the synthesis of a new compound, benzyl 2,2,5,5-tetramethylthiazole-4-carboxylate, using penicillamine, acetone, and benzyl bromide as raw materials. The synthesis is carried out in a one-pot method under the presence of a phase transfer catalyst.

In the structure of the crystal, most bond lengths and angles within the molecule are normal (Tables 1 and 2). The C4–S1 bond length is 1.8375(11) Å, which is basically the same as the bond length.[11–14] The newly formed C1–S1 bond length after condensation with acetone is 1.8702(10) Å, which is the same as the bond length of the analogue and larger than those found in thiazolidine-4-carboxylic acid because the steric requirement of the methyl groups.

Table 1: Data collection and handling.

Crystal:	Colourless needle
Size:	0.09 × 0.03 × 0.03 mm
Wavelength:	GaKα radiation (1.34139 Å)
μ:	1.23 mm^{-1}
Diffractometer, scan mode:	Bruker D8 VENTURE Metaljet, PHOTON, φ and ω scans
θ_{max}, completeness:	60.8°, 100 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	49,178, 3,486, 0.040
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 3,141
$N(param)_{refined}$:	179
Programs:	Bruker,[1] SHELX[2,3], Diamond[4], OLEX2[5]

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

	x	y	z	U_{iso}*/U_{eq}
S1	0.20321 (2)	0.97036 (6)	0.63686 (2)	0.03833 (11)
O1	0.46416 (7)	0.75826 (14)	0.47468 (4)	0.0375 (2)
O2	0.31712 (6)	0.53949 (13)	0.46129 (4)	0.02911 (18)
N1	0.40714 (7)	0.86284 (15)	0.59863 (4)	0.02594 (19)
C1	0.35434 (8)	0.94915 (17)	0.65692 (5)	0.0250 (2)
C2	0.36888 (11)	0.7940 (2)	0.71430 (6)	0.0386 (3)
H2A	0.327517	0.848599	0.751842	0.058*
H2B	0.447615	0.783384	0.726060	0.058*
H2C	0.340896	0.649933	0.701988	0.058*
C3	0.40140 (10)	1.17068 (18)	0.67408 (6)	0.0325 (2)
H3A	0.391008	1.269398	0.636865	0.049*
H3B	0.480601	1.156876	0.684245	0.049*
H3C	0.363003	1.228990	0.712238	0.049*
C4	0.21509 (9)	0.84531 (19)	0.55558 (5)	0.0301 (2)
C5	0.12003 (10)	0.6851 (3)	0.54518 (6)	0.0451 (3)
H5A	0.125840	0.567964	0.577559	0.068*
H5B	0.123914	0.623506	0.501040	0.068*
H5C	0.049286	0.760903	0.550275	0.068*
C6	0.21486 (12)	1.0213 (2)	0.50300 (7)	0.0454 (3)
H6A	0.147641	1.109462	0.506658	0.068*
H6B	0.216677	0.953160	0.459670	0.068*
H6C	0.280124	1.114256	0.508883	0.068*
H1	0.4340 (14)	0.969 (3)	0.5750 (8)	0.055*
C7	0.33009 (8)	0.72958 (17)	0.56116 (5)	0.0253 (2)
H7	0.319860	0.589087	0.584954	0.030*
C8	0.37977 (8)	0.68032 (17)	0.49491 (5)	0.0266 (2)
C9	0.35527 (9)	0.49053 (19)	0.39538 (5)	0.0301 (2)
H9A	0.427235	0.413639	0.397517	0.036*
H9B	0.365027	0.626671	0.370259	0.036*
C10	0.26958 (9)	0.34979 (18)	0.36286 (5)	0.0268 (2)
C11	0.16061 (9)	0.4196 (2)	0.35581 (6)	0.0343 (3)
H11	0.139298	0.557537	0.372346	0.041*
C12	0.08315 (10)	0.2884 (3)	0.32474 (6)	0.0434 (3)
H12	0.008545	0.335805	0.320451	0.052*
C13	0.11402 (12)	0.0883 (3)	0.29990 (6)	0.0457 (3)
H13	0.060574	−0.001238	0.278598	0.055*
C14	0.22234 (12)	0.0186 (2)	0.30602 (6)	0.0399 (3)
H14	0.243760	−0.117837	0.288469	0.048*
C15	0.29986 (10)	0.14900 (19)	0.33796 (5)	0.0315 (2)
H15	0.374149	0.100207	0.342778	0.038*

In the crystal structure, intermolecular hydrogen bonds are found between the O2 atom and the H6c (x, $-1 + y$, z) atom of adjacent molecule, H6c atom and another adjacent O2 (x, $1 + y$, z) atom with d(C–H···O) = 2.8279(8) Å and 008736(C–H···O) = 128.88(7)°. These weak C–H···O hydrogen-bonding interactions form a one-dimensional chain and the supramolecular contact $\pi\cdots\pi$ stacking result a three-dimensional network structure.

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