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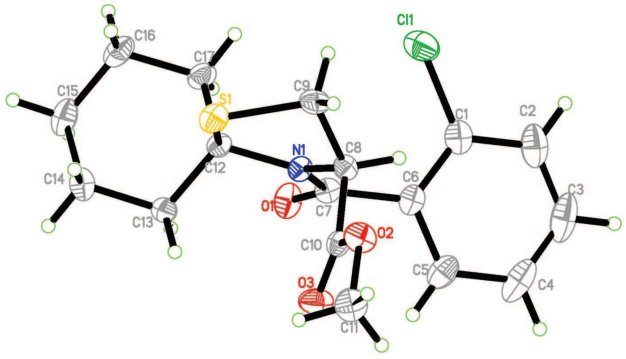
Crystal structure of methyl (*R*)-4-(*o*-chlorobenzoyl)-1-thia-4-azaspiro[4.5]decane-3-carboxylate, $C_{17}H_{20}ClNO_3S$



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Abstract

$C_{17}H_{20}ClNO_3S$, orthorhombic, $P2_12_12_1$ (no. 19), $a = 6.1984(2)$ Å, $b = 14.3940(5)$ Å, $c = 18.9651(6)$ Å, $V = 1692.06(10)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0263$, $wR_{ref}(F^2) = 0.0683$, $T = 293(2)$ K.

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The asymmetric unit of the title crystal structure is shown in the figure. Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.13 × 0.12 × 0.10 mm
Wavelength:	Cu $K\alpha$ radiation (1.54178 Å)
μ:	32.7 cm^{-1}
Diffractometer, scan mode:	D8 Venture Photon II, φ and ω
$2\theta_{max}$, completeness:	136.4°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	8944, 3042, 0.035
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2976
$N(param)_{refined}$:	210
Programs:	CrysAlis^{PRO} [1], SHELX [2], DIAMOND [3]

Source of materials

L-cysteine methyl ester hydrochloride (4.29 g, 25 mmol), cyclohexanone (2.45 g, 25 mmol) and Et_3N (5.05 g, 50 mmol) were stirred for 2 h in toluene (20 mL) at 65 °C under a nitrogen atmosphere. *o*-Chlorobenzoyl chloride (4.38 g, 25 mmol) was dropwise added to the reaction mixture at 0 °C and then reacted for 1 h. The mixture was washed with saturated NaCl solution (3 times 20 mL) and dried using anhydrous sodium sulfate. The solvent was removed under reduced pressure to yield crude title compound. The title compound was purified by column chromatography to yield 6.7 g (76%) of a white solid. Single crystals were obtained from ethyl acetate and *n*-hexane by slowly evaporating the solvent at room temperature.

Experimental details

The C—H atoms were constrained to an ideal geometry, with C—H distances of 0.93–0.98 Å. The U_{iso} values of the hydrogen atoms of methyl groups were set to 1.5 $U_{eq}(C_{methyl})$ and the U_{iso} values of all other hydrogen atoms were set to 1.2 $U_{eq}(C)$. A Flack-Parsons parameter is 0.050(6) based on 1191 quotients.

Comment

Thiazolidine derivatives are important intermediates for the synthesis of many pharmaceutical compounds, which exhibited biological importance in many fields, such as medicine [4, 5], plant protection [6]. Recently, it was shown that some thiazolidine derivatives had superior safener activities [7]. Therefore, thiazolidine derivatives are considered to be new generation herbicide safeners and are promising alternatives to some commercial products. Based on active subunit combinations and bioisosterism [8–10], methyl (*R*)-4-(*o*-chlorobenzoyl)-1-thia-4-azaspiro[4.5]decane-3-carboxylate was designed and synthesized to protect maize from herbicide injury.

Crystal structure analysis showed that the three rings, thiazolidane ring (C8/C9/S1/C12/N1), chlorophenyl

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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}
C1	0.6229(4)	0.37442(17)	0.41523(11)	0.0454(6)
N1	0.6930(3)	0.57346(11)	0.33722(8)	0.0301(3)
O1	0.9396(3)	0.55611(11)	0.42518(8)	0.0457(4)
S1	0.48528(9)	0.70955(4)	0.27335(3)	0.04108(17)
C2	0.6169(6)	0.27880(19)	0.42294(14)	0.0635(8)
H2	0.5021	0.2505	0.4461	0.076*
Cl1	0.41335(12)	0.44100(5)	0.44965(4)	0.0627(2)
O2	0.5836(3)	0.52343(12)	0.15470(8)	0.0460(4)
C3	0.7821(8)	0.22632(19)	0.39603(16)	0.0723(10)
H3	0.7798	0.1621	0.4015	0.087*
O3	0.8978(3)	0.54158(13)	0.21032(9)	0.0509(4)
C4	0.9509(7)	0.2675(2)	0.36108(15)	0.0689(9)
H4	1.0610	0.2312	0.3425	0.083*
C5	0.9573(5)	0.36366(17)	0.35344(12)	0.0510(6)
H5	1.0723	0.3914	0.3300	0.061*
C6	0.7927(4)	0.41821(14)	0.38075(10)	0.0371(5)
C7	0.8155(3)	0.52242(14)	0.38206(10)	0.0323(4)
C8	0.5693(3)	0.53352(13)	0.27917(10)	0.0318(4)
H8	0.5267	0.4698	0.2908	0.038*
C9	0.3708(3)	0.59423(16)	0.27211(13)	0.0409(5)
H9A	0.2723	0.5850	0.3112	0.049*
H9B	0.2955	0.5822	0.2282	0.049*
C10	0.7059(3)	0.53394(13)	0.21172(10)	0.0324(4)
C11	0.6937(5)	0.5281(2)	0.08768(12)	0.0553(6)
H11A	0.7656	0.5869	0.0835	0.083*
H11B	0.5907	0.5217	0.0502	0.083*
H11C	0.7978	0.4789	0.0848	0.083*
C12	0.6773(3)	0.67701(13)	0.34371(10)	0.0310(4)
C13	0.8920(3)	0.72515(14)	0.33014(11)	0.0355(4)
H13A	0.9421	0.7098	0.2831	0.043*
H13B	0.9982	0.7028	0.3636	0.043*
C14	0.8705(5)	0.83019(16)	0.33698(13)	0.0479(6)
H14A	1.0101	0.8590	0.3296	0.057*
H14B	0.7727	0.8532	0.3011	0.057*
C15	0.7856(5)	0.85626(17)	0.40944(14)	0.0551(7)
H15A	0.7670	0.9231	0.4120	0.066*
H15B	0.8901	0.8383	0.4450	0.066*
C16	0.5715(5)	0.80891(17)	0.42468(14)	0.0541(6)
H16A	0.4625	0.8332	0.3929	0.065*
H16B	0.5273	0.8233	0.4725	0.065*
C17	0.5851(4)	0.70318(16)	0.41594(11)	0.0416(5)
H17A	0.6761	0.6775	0.4527	0.050*
H17B	0.4422	0.6765	0.4210	0.050*

ring (C1/C2/C3/C4/C5/C6) and cyclohexane ring (C12/C13/C14/C15/C16/C17), are not parallel to each other. The cyclohexane ring is in the stable chair conformation and the dihedral angle between the best planes of the cyclohexane and thiazolidine moiety is 81.28°. The dihedral angle between the best planes of the thiazolidane ring and benzene ring is 68.82°. It has been indicated that the target compound contained a chiral carbon C8, with the *R* configuration. In the crystal structure, molecules are connected by van der Waals forces and non-classical intermolecular hydrogen bonds.

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