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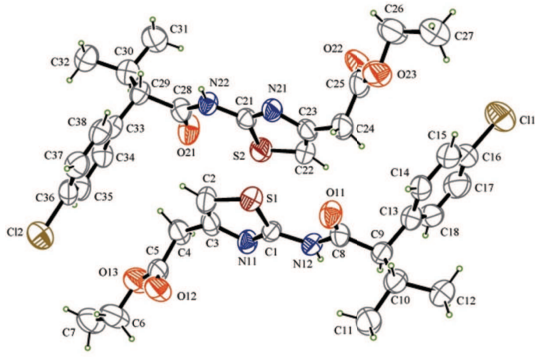
Crystal structure of ethyl 2-(2-(2-(4-chlorophenyl)-3-methylbutanamido)thiazol-4-yl)acetate, $C_{18}H_{21}ClN_2O_3S$



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Abstract

$C_{18}H_{21}ClN_2O_3S$, monoclinic, $P2_1/c$, $a = 12.582(4)$ Å, $b = 14.790(5)$ Å, $c = 21.406(8)$ Å, $\beta = 92.572(13)°$, $V = 3979(2)$ Å^3, $Z = 8$, $R_{gt}(F) = 0.0464$, $wR_{ref}(F^2) = 0.1298$, $T = 298(2)$ K.

CCDC no.: 1446499

Table 1: Data collection and handling.

Crystal:	Colorless, platelet, size 0.13×0.32×0.52 mm
Wavelength:	Mo K_α radiation (0.71075 Å)
μ:	3.15 cm^{-1}
Diffractometer, scan mode:	Rigaku RAXIS-RAPID, ω
$2\theta_{max}$:	54.96°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	36808, 8966
$N(param)_{refined}$:	493
Programs:	SHELX [9]

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(2)	4*e*	0.4721	0.0773	0.2292	0.106
H(9)	4*e*	−0.0046	0.3142	0.1497	0.083
H(10)	4*e*	0.0350	0.2737	0.0239	0.092
H(14)	4*e*	−0.0456	0.1223	0.0496	0.093
H(15)	4*e*	−0.1872	0.0221	0.0544	0.106
H(17)	4*e*	−0.2990	0.1642	0.1957	0.124
H(18)	4*e*	−0.1573	0.2613	0.1915	0.103
H(23)	4*e*	0.0437	0.0971	0.3058	0.118
H(29)	4*e*	0.5093	−0.1678	0.3555	0.082
H(30)	4*e*	0.5054	−0.1209	0.4840	0.103
H(34)	4*e*	0.5915	0.0119	0.4584	0.091
H(35)	4*e*	0.7158	0.1204	0.4377	0.101
H(37)	4*e*	0.7576	0.0094	0.2704	0.109
H(38)	4*e*	0.6303	−0.0984	0.2912	0.095
H(41)	4*e*	0.4192	0.2155	0.3608	0.109
H(42)	4*e*	0.5061	0.1465	0.3386	0.109
H(61)	4*e*	0.7083	0.3631	0.3343	0.158
H(62)	4*e*	0.6197	0.4334	0.3522	0.158
H(71)	4*e*	0.7463	0.3381	0.4408	0.166
H(72)	4*e*	0.7669	0.4392	0.4228	0.166
H(73)	4*e*	0.6633	0.4128	0.4566	0.166
H(101)	4*e*	0.1351	0.2822	0.2089	0.081
H(111)	4*e*	0.0942	0.4235	0.0197	0.145
H(112)	4*e*	0.1590	0.3711	0.0725	0.145
H(113)	4*e*	0.0679	0.4375	0.0900	0.145
H(121)	4*e*	−0.1433	0.3028	0.0218	0.124
H(122)	4*e*	−0.0878	0.3879	−0.0057	0.124
H(123)	4*e*	−0.1260	0.3896	0.0630	0.124
H(201)	4*e*	0.3681	−0.1222	0.3011	0.079
H(241)	4*e*	0.0798	−0.0034	0.1621	0.121
H(242)	4*e*	−0.0141	0.0409	0.1984	0.121
H(261)	4*e*	−0.0432	−0.2515	0.1178	0.165
H(262)	4*e*	−0.1280	−0.2234	0.1666	0.165
H(271)	4*e*	−0.1438	−0.1911	0.0380	0.172
H(272)	4*e*	−0.2221	−0.1475	0.0844	0.172
H(273)	4*e*	−0.2197	−0.2527	0.0756	0.172
H(311)	4*e*	0.4373	−0.2845	0.4275	0.160
H(312)	4*e*	0.3598	−0.2085	0.4486	0.160
H(313)	4*e*	0.4297	−0.2619	0.4987	0.160
H(321)	4*e*	0.6760	−0.1644	0.4692	0.147
H(322)	4*e*	0.6379	−0.2512	0.4326	0.147
H(323)	4*e*	0.6210	−0.2433	0.5045	0.147

Table 3: Atomic displacement parameters (Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cl(1)	4*e*	−0.36313(9)	0.00994(8)	0.12764(6)	0.1053(7)	0.134(1)	0.223(1)	−0.0352(6)	0.0275(8)	0.0044(9)
Cl(2)	4*e*	0.83729(8)	0.16068(8)	0.33565(6)	0.0896(6)	0.1338(9)	0.169(1)	−0.0166(6)	0.0171(7)	0.0007(7)
S(1)	4*e*	0.31824(6)	0.11693(6)	0.16868(5)	0.0680(5)	0.0769(5)	0.1074(7)	0.0096(4)	0.0010(4)	−0.0006(5)
S(2)	4*e*	0.19997(6)	0.04430(6)	0.35827(5)	0.0715(5)	0.0861(6)	0.1123(8)	0.0070(4)	0.0082(5)	−0.0132(5)
O(11)	4*e*	0.1437(2)	0.1622(2)	0.0971(1)	0.075(1)	0.093(2)	0.088(2)	0.016(1)	−0.008(1)	−0.020(1)
O(12)	4*e*	0.5599(2)	0.3064(2)	0.2679(1)	0.125(2)	0.172(2)	0.085(2)	−0.070(2)	−0.024(2)	0.057(2)
O(13)	4*e*	0.5813(2)	0.3053(2)	0.3705(1)	0.136(2)	0.106(2)	0.088(2)	−0.034(2)	−0.018(2)	0.025(2)
O(21)	4*e*	0.3749(2)	−0.0171(2)	0.4205(1)	0.081(2)	0.136(2)	0.075(2)	0.028(1)	−0.007(1)	−0.041(2)
O(22)	4*e*	−0.0491(2)	−0.1365(2)	0.2382(1)	0.173(2)	0.197(3)	0.119(2)	−0.113(2)	−0.037(2)	0.068(2)
O(23)	4*e*	−0.0422(2)	−0.1205(2)	0.1375(2)	0.185(2)	0.118(2)	0.117(2)	−0.040(2)	−0.028(2)	0.029(2)
N(11)	4*e*	0.3052(2)	0.2300(2)	0.2589(1)	0.065(2)	0.079(2)	0.072(2)	0.000(1)	−0.009(1)	0.017(1)
N(12)	4*e*	0.1627(2)	0.2414(1)	0.1860(1)	0.065(2)	0.071(2)	0.065(2)	0.012(1)	−0.008(1)	−0.004(1)
N(21)	4*e*	0.1973(2)	−0.0569(2)	0.2606(1)	0.071(2)	0.079(2)	0.074(2)	−0.004(1)	−0.008(2)	0.011(2)
N(22)	4*e*	0.3454(2)	−0.0834(2)	0.3273(1)	0.059(1)	0.075(2)	0.063(2)	0.007(1)	−0.003(1)	−0.011(1)
C(1)	4*e*	0.2582(2)	0.2033(2)	0.2072(1)	0.053(2)	0.063(2)	0.074(2)	0.004(1)	−0.003(2)	0.012(2)
C(2)	4*e*	0.4144(2)	0.1166(2)	0.2275(2)	0.059(2)	0.093(2)	0.112(3)	0.006(2)	−0.006(2)	0.022(2)
C(3)	4*e*	0.3974(2)	0.1791(2)	0.2706(2)	0.059(2)	0.091(2)	0.082(2)	−0.010(2)	−0.008(2)	0.032(2)
C(4)	4*e*	0.4648(2)	0.1998(2)	0.3271(2)	0.069(2)	0.114(2)	0.087(2)	−0.011(2)	−0.016(2)	0.041(2)
C(5)	4*e*	0.5389(2)	0.2763(2)	0.3169(2)	0.092(2)	0.127(2)	0.102(2)	−0.020(2)	−0.021(2)	0.030(2)
C(6)	4*e*	0.6571(4)	0.3787(3)	0.3651(2)	0.132(5)	0.124(3)	0.135(4)	−0.030(4)	−0.033(4)	0.036(3)
C(7)	4*e*	0.7134(5)	0.3935(4)	0.4268(2)	0.132(7)	0.152(7)	0.128(4)	−0.035(6)	−0.032(5)	0.047(4)
C(8)	4*e*	0.1095(2)	0.2190(2)	0.1315(2)	0.065(2)	0.070(2)	0.074(2)	0.001(2)	0.001(2)	0.002(2)
C(9)	4*e*	0.0041(2)	0.2685(2)	0.1172(1)	0.064(2)	0.070(2)	0.072(2)	0.013(2)	−0.011(2)	−0.000(2)
C(10)	4*e*	0.0102(2)	0.3171(2)	0.0546(1)	0.078(2)	0.073(2)	0.078(2)	0.006(2)	−0.007(2)	0.008(2)
C(11)	4*e*	0.0902(2)	0.3945(2)	0.0597(2)	0.099(2)	0.109(3)	0.153(3)	−0.014(2)	−0.013(2)	0.044(2)
C(12)	4*e*	−0.0964(2)	0.3526(2)	0.0313(2)	0.094(2)	0.099(2)	0.114(3)	0.008(2)	−0.021(2)	0.026(2)
C(13)	4*e*	−0.0864(2)	0.2022(2)	0.1200(2)	0.062(2)	0.079(2)	0.065(2)	0.007(2)	−0.013(2)	0.006(2)
C(14)	4*e*	−0.0964(2)	0.1308(2)	0.0793(2)	0.070(2)	0.088(2)	0.072(2)	−0.002(2)	−0.008(2)	0.003(2)
C(15)	4*e*	−0.1811(2)	0.0708(2)	0.0818(2)	0.091(2)	0.083(2)	0.090(2)	0.003(2)	−0.017(2)	0.000(2)
C(16)	4*e*	−0.2558(2)	0.0853(2)	0.1257(2)	0.076(2)	0.087(2)	0.120(3)	−0.006(2)	0.002(2)	0.016(2)
C(17)	4*e*	−0.2478(2)	0.1554(2)	0.1663(2)	0.091(2)	0.098(3)	0.121(3)	0.007(2)	0.023(2)	0.002(2)
C(18)	4*e*	−0.1632(2)	0.2133(2)	0.1635(2)	0.081(2)	0.082(2)	0.095(2)	0.007(2)	0.009(2)	0.003(2)
C(21)	4*e*	0.2511(2)	−0.0386(2)	0.3121(1)	0.059(2)	0.066(2)	0.069(2)	−0.003(2)	0.007(2)	0.003(2)
C(22)	4*e*	0.1080(2)	−0.0012(2)	0.2558(2)	0.059(2)	0.078(2)	0.103(3)	−0.012(2)	−0.008(2)	0.027(2)
C(23)	4*e*	0.0989(2)	0.0557(2)	0.3030(2)	0.068(2)	0.087(2)	0.139(3)	0.005(2)	−0.007(2)	0.004(2)
C(24)	4*e*	0.0369(2)	−0.0083(2)	0.1985(2)	0.073(2)	0.108(2)	0.120(3)	−0.005(2)	−0.023(2)	0.038(2)
C(25)	4*e*	−0.0223(2)	−0.0958(2)	0.1952(2)	0.098(2)	0.126(3)	0.120(3)	−0.034(2)	−0.034(2)	0.038(3)
C(26)	4*e*	−0.0949(5)	−0.2060(3)	0.1284(3)	0.159(8)	0.130(4)	0.120(7)	−0.031(5)	−0.031(6)	0.031(4)
C(27)	4*e*	−0.1774(4)	−0.1987(3)	0.0771(2)	0.136(6)	0.152(5)	0.138(6)	−0.039(4)	−0.034(5)	0.036(4)
C(28)	4*e*	0.4040(2)	−0.0696(2)	0.3813(2)	0.060(2)	0.091(2)	0.065(2)	0.003(2)	0.004(2)	−0.013(2)
C(29)	4*e*	0.5087(2)	−0.1211(2)	0.3880(1)	0.067(2)	0.081(2)	0.056(2)	0.012(2)	−0.002(2)	−0.012(2)
C(30)	4*e*	0.5157(2)	−0.1674(2)	0.4522(2)	0.082(2)	0.099(2)	0.075(2)	0.012(2)	0.001(2)	−0.001(2)
C(31)	4*e*	0.4275(3)	−0.2370(2)	0.4572(2)	0.129(3)	0.153(4)	0.117(3)	−0.023(3)	0.001(2)	0.040(3)
C(32)	4*e*	0.6223(2)	−0.2105(2)	0.4659(2)	0.116(2)	0.143(3)	0.107(3)	0.034(2)	0.001(2)	0.028(2)
C(33)	4*e*	0.5959(2)	−0.0542(2)	0.3766(1)	0.060(2)	0.080(2)	0.052(2)	0.019(2)	−0.003(2)	−0.007(2)
C(34)	4*e*	0.6237(2)	0.0115(2)	0.4201(1)	0.067(2)	0.101(2)	0.060(2)	0.004(2)	0.000(2)	−0.019(2)
C(35)	4*e*	0.6982(2)	0.0765(2)	0.4079(2)	0.069(2)	0.099(2)	0.084(2)	0.012(2)	−0.010(2)	−0.024(2)
C(36)	4*e*	0.7461(2)	0.0763(2)	0.3519(2)	0.057(2)	0.095(2)	0.101(3)	0.010(2)	−0.002(2)	−0.004(2)
C(37)	4*e*	0.7231(2)	0.0106(2)	0.3079(2)	0.086(2)	0.104(2)	0.085(2)	0.016(2)	0.020(2)	−0.001(2)
C(38)	4*e*	0.6471(2)	−0.0540(2)	0.3209(2)	0.083(2)	0.087(2)	0.069(2)	0.018(2)	0.001(2)	−0.015(2)

Source of material

Ethyl 2-(2-aminothiazol-4-yl)acetate (1.86 g, 10 mmol), 4-dimethylaminopyridine (0.12 g, 1 mmol), triethylamine (1.31 g, 13 mmol) and chloroform (100 mL) were added to a 250 mL flask. The mixture was stirred and cooled to 273 K, and then 2-(4-chlorophenyl)-3-methylbutanoyl chloride (2.31 g, 15 mmol) was added dropwise within 30 min. The mixture was stirred at room temperature for 3 h and then 1% aqueous HCl was added

(5 mL). The organic layer was washed with water to a neutral pH and dried over Na_2SO_4. After being filtered and concentrated, the organic residue was purified by silica gel column chromatography, eluted with ethyl acetate-petroleum ether-formic acid (10:80:1, *v*/*v*/*v*), to give a white solid (yield 80%, 3.0 g). It was then recrystallized from ethyl acetate-petroleum ether (2:1, *v*/*v*) to give colourless blocks.

Experimental details

H atoms were included in calculated positions and refined using a riding model, with C–H distances, O–H distances, N–H distances constrained to 0.98 Å, 0.84 Å and 0.91 Å, respectively, and with $U_{iso}(H) = 1.2U_{eq}(C)$.

Discussion

Pyrethroids are one kind of effective synthetic pesticides and known as green pesticides because of their low toxicity and biodegradation [1]. 2-(4-Chlorophenyl)-3-methylbutanoyl chloride is one of the pharmacophore of Fenvalerate, which was known as an excellent pyrethroid insecticide [2]. At the same time, ethyl 2-(2-aminothiazol-4-yl)acetate is an important thiazole intermediate [3]. Thiazole compounds have being become noteworthy in recent years because of their high bioactivity and low toxicity, and widely used as insecticedes, fungicides, herbicides and plant growth regulators, for example Fosthiazate, Lythiazate, Lythidathion and Thiamethoxam [4, 5]. In our previous work, we had synthesized a number of *N*-(substituted-thiazole-2-yl)-chrysanthemumamide derivatives [6]. In this paper, the synthesis and single-crystal structure of 2-(4-chlorophenyl)-3-methyl-*N*-(4-ethyl thiazoleacetate-2-yl)butanamide are reported. The asymmetric unit contains two crystallographically independent molecules (see the figure). The angle between the thiazole ring and the benzene ring is 77.89(8)°, which is larger than the angle between the thiazole and benzene rings of the compound 2-(4-chlorophenyl)-3-methyl-*N*-(thiazol-2-yl)butanamide and 2-(4-chlorophenyl)-3-methyl-*N*-(5-methylthiazol-2-yl)butanamide [7, 8]. There are N—H···O interactions in the crystal structure, which lead to the formation of hydrogen-bonded chains.

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References

1. Ding, Z. H.; Liu, J. K.; Ding, J. K.; Gu, K.: Progress on the research of pyrethroids. Yunnan Chem. Technol. **28** (2001) 22–24.
2. Holmstead, R. L.; Fullmer, D. G.; Ruzo, L. O.: Pyrethroid photodecomposition: pydrin. J. Agric. Food Chem. **26** (1978) 954–959.
3. Forlani, L,; Medici, A.: Intermediates in the halogenation of some 2-aminothiazoles. J. Chem. Soc., Perk. Trans. 1 **10** (1978) 1169–1171.
4. Chen, C. J.; Song, B. A.: Research advances with thiazole insecticides. Chin. J. Pestic. **44** (2005) 53–55.
5. Sun, X. J.; Zhou, J. F.: Research progress on thiazole heterocyclic compounds with the bioactivity. J. Anhui Agri. Sci. **36** (2008) 14389–14393.
6. Zhao, J. H.; Zhou, Y.; Xu, X.-H.; Zhu, L.; Zhu, G. N.; Cheng, J. L.: Synthesis and biological activities of *N*-(substituted-thiazole-2-yl)-chrysanthemumamide. Chin. J. Org. Chem. **30** (2010) 719–725.
7. Zhao, J. H.; Cheng, J. L.; Huang, Y. K.; Zhu, G. N.: 2-(4-Chlorophenyl)-3-methyl-*N*-(thiazol-2-yl) butanamide. Acta Crystallogr. **E62** (2006) o4840.
8. Cheng, J. L.; Zhao, J. H.; Zhu, G. N.; Lin, F. C.: 2-(4-Chlorophenyl)-3-methyl-*N*-(5-methylthiazol-2-yl) butanamide[J]. Acta Crystallogr. **E65** (2009) o184.
9. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112–122.