Crystal structure of (2*Z*,5*Z*)-3-allyl-5-(4-(methylthio)benzylidene)-2-(*p*-tolylimino)thiazolidin-4-one, $C_{21}H_{20}N_2OS_2$

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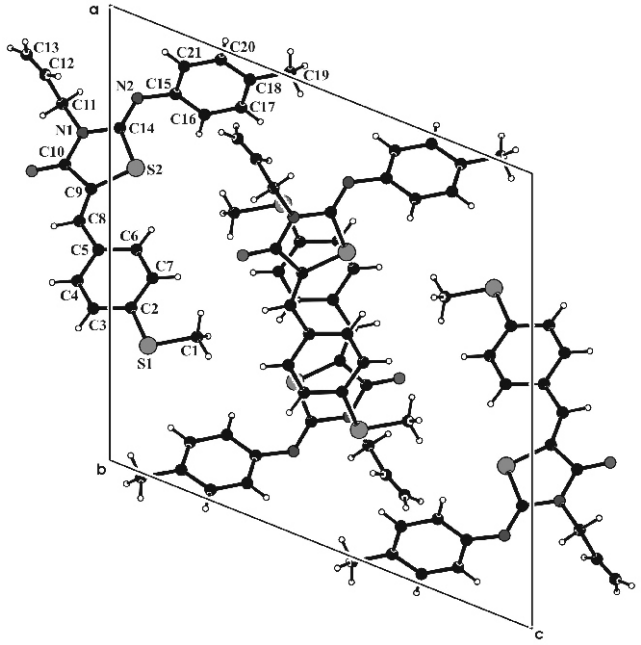

Abstract

$C_{21}H_{20}N_2OS_2$, monoclinic, $P12_1/c1$ (no. 14), a = 16.196(3) Å, b = 8.256(1) Å, c = 16.173(3) Å, β = 111.75(1)°, V = 2008.7 Å^3, Z = 4, $R_{gt}(F)$ = 0.084, $wR_{ref}(F^2)$ = 0.204, T = 298 K.

Source of material

To a solution of 3-allyl-2-(*p*-tolylimino)thiazolidin-4-one (3 mmol) and base supported ionic liquid-like phase (SILLP) (0.5 g) in ethanol (20 mL), 4-methylthiobenzaldehyde (3 mmol) was added and the mixture was heated at reflux for 3 h. SILLP was separated by filtration. Then the solution was concentrated in vacuum and kept at –15 ºC over 2 h. The residue was filtered off and recrystallized from methanol to give 3-allyl-5-(4-(methylthio)benzylidene)-2-(*p*-tolylimino)thiazolidin-4-one as a yellow solid in 87 % yield (m.p. = 138-140 °C). Elemental analysis — found: C, 66.13 %; H, 5.35 %; N, 7.47 %; calculated for $C_{21}H_{20}N_2OS_2$: C, 66.28 %; H, 5.30 %; N, 7.36 %. Melting points were measured on a Electrothermal 9100 instrument and are uncorrected. Elemental analyses were made by a Carlo-Erba EA1110CNNO-S analyzer.

Experimental details

All hydrogen atoms were refined in isotropic approximation in a riding model with U_{iso}(H) = 1.2 U_{eq}(C). The structure was checked with PLATON [1] and no solvent accesible void was found. The residual densities are 0.32 e Å^{-3} (highest peak at 1.24 Å from C13) and –0.21 e Å^{-3} (deepest hole at 0.61 Å from H12).

Discussion

Thiazolidinone moiety is an important structure element in medicinal chemistry [2-6] and substituted thiazolidinones show a broad spectrum of biological activities [7-11]. In particular, 5-arylidene-4-thiazolidinones have been synthesized and employed as new agents with SHP-2 inhibitory action [12], as potential antifungal and antibacterial drugs [13], as PTP1B and LMW-PTP inhibitors [14], anti-inflammatory agent [15] and antimicrobial drugs [16]. Therefore, facile preparation of various 5-arylidene thiazolidinones is highly desirable. In continuation of our ongoing interests in the development of benign methods targeted at the synthesis of biologically important heterocycles [17-19], we used base supported ionic liquid-like phase (SILLP) [20] as an efficient and recyclable solid phase catalyst in the synthesis of the title compound. The X-ray diffractometric analysis of the title product was carried out on the single crystal prepared in peteroleum ether/EtOAc (4:1).

The packing in the title crystal structure can be described as a succession of parallel layers. The conjugation between C=O and the amide nitrogen is evident from the value of the bond length d(Nl—C10) = 1.362(5) Å. The thiazole ring is planar as indicated by torsion angles ∠C9–C10–N1–C14 = –3.4(5)°, ∠N1–C10–C9–S2 = 0.4(4)°, ∠C10–C9–S2–C14 = 1.8(3)° and ∠N1–C14–S2–C9 = –36(3)°. In addition, the torsion angles ∠S2–C14–N2–C15 = 0.8(6)°, ∠O1–C10–N1–C11 = 1.2(6)°, ∠N2–C14–N1–C11 = 1.8(6)°, ∠C5–C8–C9–S2 = –1.0(7)° and ∠N1–C10–C9–S2 = 0.4(4)° revealed that the thiazole ring is coplanar with O1, N2, C5, C8, C11 and C15. The distances d(C14—N1) = 1.394(5) Å, d(C14—S2) = 1.773(4) Å, d(C9—S2) = 1.756(4) Å, d(C10—C9) = 1.49(5) Å, d(C10—N1) = 1.362(5) Å agree with the literature reports [21-25]. The bond length d(C14—N2) = 1.259(5) Å and the angles ∠N2–C14–S2 = 128.2(3)° and ∠N2–C14–N1 = 121.8(4)° confirm the imine nature of the N2–C14 bond. The distance d(C8—C9) = 1.331(5) Å and the angles ∠C8–C9–S2 = 129.7(3)° and ∠C8–C9–C10 = 120.5(3)° are consistant with double bond features of C8–C9. This analysis also unambiguously confirmed the *Z* configuration at the chiral axis and this is quite evident from the spatial orientation of aryl groups attached to C14–N2 and C8–C9 double bonds.

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Table 1. Data collection and handling.

Crystal:	yellow block, size 0.10 × 0.15 × 0.25 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	2.77 cm^{-1}
Diffractometer, scan mode:	STOE IPDS II, rotation method
$2\theta_{max}$:	58.44°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	14550, 5409
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2443
$N(param)_{refined}$:	236
Programs:	PLATON [1], SHELXS-97, SHELXL-97 [26], ORTEP-3 [27], WinGX [28]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(8)	4*e*	0.5347	0.1653	0.6326	0.067
H(4)	4*e*	0.6603	0.3066	0.6373	0.074
H(20)	4*e*	–0.0228	0.2670	0.2263	0.137
H(21)	4*e*	0.0550	0.1936	0.3701	0.116
H(19A)	4*e*	–0.0376	0.0873	0.0387	0.166
H(19B)	4*e*	0.0286	0.2312	0.0490	0.166
H(19C)	4*e*	–0.0562	0.2565	0.0723	0.166
H(7)	4*e*	0.5379	0.4356	0.3394	0.067
H(12)	4*e*	0.2022	0.0826	0.6233	0.179
H(11A)	4*e*	0.2168	–0.1928	0.5715	0.090
H(11B)	4*e*	0.3016	–0.1831	0.6590	0.090
H(17)	4*e*	0.1245	–0.0228	0.1440	0.093
H(3)	4*e*	0.7380	0.4591	0.5752	0.074
H(6)	4*e*	0.4575	0.2827	0.4021	0.065
H(1A)	4*e*	0.5970	0.6492	0.2848	0.103
H(1B)	4*e*	0.6415	0.4908	0.2676	0.103
H(1C)	4*e*	0.6855	0.6596	0.2668	0.103
H(13A)	4*e*	0.1816	–0.0841	0.7360	0.347
H(13B)	4*e*	0.1552	0.0984	0.7011	0.347
H(16)	4*e*	0.2045	–0.0969	0.2885	0.087

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(8)	4*e*	0.5015(3)	0.1844(5)	0.5728(2)	0.064(3)	0.051(2)	0.046(2)	0.006(2)	0.016(2)	–0.002(2)
O(1)	4*e*	0.4336(2)	0.0024(4)	0.6855(2)	0.090(2)	0.080(2)	0.051(2)	–0.006(2)	0.022(2)	0.007(2)
C(4)	4*e*	0.6345(3)	0.3329(5)	0.5772(3)	0.057(3)	0.067(3)	0.053(2)	–0.001(2)	0.010(2)	0.004(2)
C(20)	4*e*	0.0231(4)	0.1922(8)	0.2381(4)	0.107(5)	0.124(5)	0.099(4)	0.053(4)	0.025(4)	–0.006(4)
C(21)	4*e*	0.0698(4)	0.1486(7)	0.3248(3)	0.097(4)	0.108(4)	0.083(3)	0.036(4)	0.032(3)	–0.008(3)
C(14)	4*e*	0.2613(3)	0.0196(5)	0.4767(3)	0.058(3)	0.050(2)	0.061(2)	–0.001(2)	0.029(2)	–0.005(2)
C(19)	4*e*	–0.0107(5)	0.181(1)	0.0734(4)	0.140(6)	0.155(7)	0.083(4)	0.049(5)	–0.002(4)	0.005(4)
C(2)	4*e*	0.6464(3)	0.4620(5)	0.4500(2)	0.054(3)	0.049(2)	0.059(2)	0.001(2)	0.022(2)	–0.007(2)
C(15)	4*e*	0.1377(3)	0.0400(5)	0.3450(3)	0.049(2)	0.063(3)	0.071(3)	–0.010(2)	0.023(2)	–0.005(2)
C(10)	4*e*	0.3897(3)	0.0277(5)	0.6070(3)	0.069(3)	0.049(2)	0.054(2)	0.002(2)	0.027(2)	–0.004(2)
C(7)	4*e*	0.5626(3)	0.4096(5)	0.3996(3)	0.057(2)	0.059(2)	0.052(2)	–0.002(2)	0.018(2)	–0.005(2)
N(2)	4*e*	0.1804(3)	–0.0118(5)	0.4347(2)	0.059(2)	0.074(2)	0.075(2)	–0.011(2)	0.027(2)	0.003(2)
S(1)	4*e*	0.71491(8)	0.5788(2)	0.40992(8)	0.0665(8)	0.0682(7)	0.0751(7)	–0.0120(6)	0.0342(6)	–0.0071(5)
C(12)	4*e*	0.2100(6)	–0.0154(8)	0.6536(6)	0.24(1)	0.092(5)	0.214(8)	–0.008(5)	0.195(8)	0.005(5)
C(11)	4*e*	0.2585(3)	–0.1188(6)	0.6128(3)	0.093(4)	0.064(3)	0.078(3)	–0.012(3)	0.046(3)	0.003(2)
C(18)	4*e*	0.0412(3)	0.1304(7)	0.1684(3)	0.070(3)	0.088(4)	0.082(3)	0.016(3)	0.012(3)	–0.006(3)
C(17)	4*e*	0.1098(3)	0.0219(6)	0.1895(3)	0.065(3)	0.099(4)	0.069(3)	–0.003(3)	0.026(2)	–0.014(3)
N(1)	4*e*	0.3049(2)	–0.0266(4)	0.5652(2)	0.065(2)	0.054(2)	0.060(2)	–0.005(2)	0.032(2)	0.002(2)
C(9)	4*e*	0.4203(3)	0.1205(5)	0.5447(2)	0.051(2)	0.050(2)	0.048(2)	0.000(2)	0.019(2)	–0.003(2)
C(3)	4*e*	0.6815(3)	0.4229(5)	0.5400(3)	0.047(2)	0.066(3)	0.065(2)	–0.009(2)	0.013(2)	–0.005(2)
C(6)	4*e*	0.5141(3)	0.3182(5)	0.4376(2)	0.051(2)	0.058(2)	0.051(2)	–0.007(2)	0.017(2)	–0.004(2)
C(1)	4*e*	0.6526(4)	0.5967(7)	0.2939(3)	0.104(4)	0.093(4)	0.070(3)	–0.022(3)	0.042(3)	–0.008(3)
S(2)	4*e*	0.33514(7)	0.1281(1)	0.43900(6)	0.0544(6)	0.0555(6)	0.0481(5)	–0.0062(5)	0.0194(4)	–0.0009(4)
C(5)	4*e*	0.5480(3)	0.2780(4)	0.5280(2)	0.050(2)	0.048(2)	0.050(2)	0.000(2)	0.014(2)	–0.004(2)
C(13)	4*e*	0.182(1)	–0.000(2)	0.6978(8)	0.46(2)	0.26(1)	0.30(1)	0.23(2)	0.32(2)	0.18(1)
C(16)	4*e*	0.1580(3)	–0.0232(6)	0.2765(3)	0.053(3)	0.085(3)	0.081(3)	0.012(2)	0.025(2)	–0.004(3)

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