Crystal structure of 5-methyl-2-phenyl-4-[1-(4-*p*-tolyl-thiazol-2-ylamino)-ethylidene]-2,4-dihydropyrazol-3-one, $C_{22}H_{20}N_4OS$

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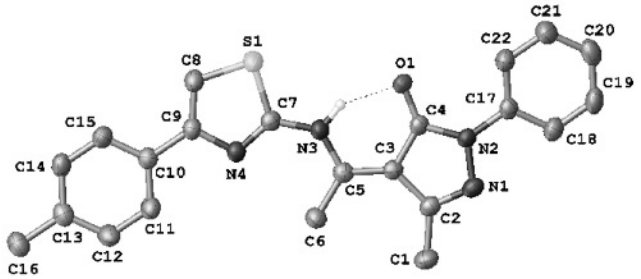

Abstract

$C_{22}H_{20}N_4OS$, monoclinic, $P2_1/c$ (no. 14), a = 18.2884(7) Å, b = 7.5829(3) Å, c = 14.8509(5) Å, β = 111.104(2)°, V = 1921.4 Å^3, Z = 4, $R_{gt}(F)$ = 0.0401, $wR_{ref}(F^2)$ = 0.1100, T = 173 K.

Table 1. Data collection and handling.

Crystal:	colourless blocks, size 0.10×0.20×0.32 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	1.89 cm^{-1}
Diffractometer, scan mode:	Nonius Kappa CCD, φ and ω
$2\theta_{max}$:	54.92°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	46980, 4398
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3400
$N(param)_{refined}$:	260
Programs:	COLLECT [15], SADABS [16], OLEX2 [17], SHELX [18]

Source of material

A solution of 4-acetyl-5-methyl-2-phenyl-2,4-dihydro-pyrazol-3-one (1.0 g, 4.62 mmol) in methanol (30 mL) was added to a solution of 4-*p*-tolyl-thiazol-2-ylamine (0.88 g, 4.62 mmol) in methanol (20 mL) under an inert atmosphere. The reaction mixture was refluxed for two hours. Completion of the reaction was monitored by *TLC* using hexane/ethyl acetate (9:1). The reaction was allowed to cool to room temperature and stirred overnight. A yellow precipitate formed which was filtered and washed with methanol (10 mL). The crude product, purified by crystallization from ethanol, gave yellow crystals. (1.4 g, 78% yield, **m.p.** = 483-485 K). Crystals suitable for X-ray diffraction were obtained by slow evaporation from a combination of dichloromethane and hexane at room temperature.

Experimental details

All non-hydrogen atoms were refined anisotropically. All hydrogen atoms, except H3, were placed in idealised positions and refined in riding models with U_{iso} assigned the values to be 1.2 or 1.5 times those of their parent atoms and the constraint distances of C–H ranging from 0.95 Å to 0.98 Å. The hydrogen H3 was located in the electron difference maps and refined freely.

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Discussion

The pyrazole ring is an important structural motif found in many biologically and pharmaceutically active compounds. Over the past few years, both pyrazoles and their derivatives have attracted much attention because they possess a wide spectrum of biological activities, such as antimicrobial [1], anti-inflammatory [2], antiviral [3], anticancer [4], insecticidal [5], herbicidal [6] and plant growth regulatory [7]. Many pyrazoles are currently being tested and clinically evaluated as potential new drugs [8, 9]. Also the aminothiazole ring system has a useful structural element in medicinal chemistry [10-14]. In this report we synthesized a Schiff base ligand by fusing the carbonyl group of the pyrazole ring and the primary amine (–NH_2) of the aminothiazole. The diffraction data reveals that the nitrogen atom of the aminothiazole exist in the amine form (N–H group at N3). Consequently, a double bond is present between C3 and C5 (see Figure). This implies that the title compound exists in keto-amine tautomeric form in the solid state.

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

Atom	Site	x	y	z	U_{iso}
H(3)	4*e*	0.627(1)	0.408(2)	0.198(1)	0.051(5)
H(1A)	4*e*	0.8218	0.4906	–0.0292	0.074
H(1B)	4*e*	0.7291	0.5229	–0.0709	0.074
H(1C)	4*e*	0.7631	0.3279	–0.0428	0.074
H(6A)	4*e*	0.6365	0.3438	–0.0604	0.060
H(6B)	4*e*	0.5524	0.3936	–0.0575	0.060
H(6C)	4*e*	0.5871	0.1997	–0.0277	0.060
H(8)	4*e*	0.3640	0.1764	0.1643	0.049
H(11)	4*e*	0.3987	0.1282	–0.1256	0.051
H(12)	4*e*	0.2986	0.0070	–0.2559	0.056
H(14)	4*e*	0.1636	–0.0352	–0.0949	0.053
H(15)	4*e*	0.2636	0.0822	0.0365	0.053
H(16A)	4*e*	0.1174	–0.1646	–0.2517	0.071
H(16B)	4*e*	0.1770	–0.1893	–0.3075	0.071
H(16C)	4*e*	0.1282	–0.0102	–0.3194	0.071
H(18)	4*e*	0.9563	0.6930	0.2354	0.058
H(19)	4*e*	1.0549	0.8143	0.3687	0.066
H(20)	4*e*	1.0428	0.8189	0.5192	0.064
H(21)	4*e*	0.9319	0.6999	0.5371	0.068
H(22)	4*e*	0.8329	0.5757	0.4058	0.059

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}
S(1)	4*e*	0.49319(2)	0.29791(6)	0.21983(3)	0.0369(2)	0.0584(3)	0.0322(2)	–0.0066(2)	0.0093(2)	0.0037(2)
O(1)	4*e*	0.71972(6)	0.5017(2)	0.27938(7)	0.0289(5)	0.0582(7)	0.0354(6)	–0.0013(5)	0.0145(4)	–0.0043(5)
N(1)	4*e*	0.83728(7)	0.5413(2)	0.13901(9)	0.0374(7)	0.0416(7)	0.0390(7)	0.0027(6)	0.0194(6)	0.0014(6)
N(2)	4*e*	0.82349(7)	0.5562(2)	0.22553(9)	0.0278(6)	0.0399(7)	0.0342(6)	0.0022(5)	0.0131(5)	–0.0003(5)
N(3)	4*e*	0.59821(7)	0.3714(2)	0.13733(9)	0.0281(6)	0.0454(8)	0.0328(7)	0.0001(6)	0.0084(5)	–0.0020(6)
N(4)	4*e*	0.47439(7)	0.2451(2)	0.04121(9)	0.0292(6)	0.0402(7)	0.0353(7)	0.0015(5)	0.0099(5)	0.0001(5)
C(1)	4*e*	0.7716(1)	0.4530(3)	–0.0257(1)	0.052(1)	0.062(1)	0.0407(9)	–0.0026(9)	0.0247(8)	–0.0005(8)
C(2)	4*e*	0.77302(9)	0.4798(2)	0.0745(1)	0.0366(8)	0.0359(8)	0.0379(8)	0.0042(6)	0.0162(7)	0.0028(6)
C(3)	4*e*	0.71319(8)	0.4507(2)	0.1147(1)	0.0309(7)	0.0334(8)	0.0327(7)	0.0052(6)	0.0112(6)	0.0026(6)
C(4)	4*e*	0.74900(8)	0.5036(2)	0.2149(1)	0.0272(7)	0.0347(8)	0.0365(8)	0.0043(6)	0.0116(6)	0.0005(6)
C(5)	4*e*	0.63795(8)	0.3837(2)	0.0758(1)	0.0341(7)	0.0302(7)	0.0333(7)	0.0059(6)	0.0103(6)	0.0039(6)
C(6)	4*e*	0.60028(9)	0.3252(2)	–0.0261(1)	0.0388(8)	0.0447(9)	0.0339(8)	–0.0020(7)	0.0100(7)	0.0002(7)
C(7)	4*e*	0.52436(8)	0.3035(2)	0.1219(1)	0.0305(7)	0.0361(8)	0.0350(8)	0.0048(6)	0.0102(6)	0.0034(6)
C(8)	4*e*	0.40630(9)	0.2086(2)	0.1448(1)	0.0333(8)	0.049(1)	0.0372(8)	–0.0028(7)	0.0102(6)	0.0058(7)
C(9)	4*e*	0.40623(8)	0.1901(2)	0.0537(1)	0.0296(7)	0.0332(8)	0.0381(8)	0.0018(6)	0.0100(6)	0.0038(6)
C(10)	4*e*	0.34196(8)	0.1176(2)	–0.0305(1)	0.0317(7)	0.0319(8)	0.0366(8)	0.0035(6)	0.0098(6)	0.0043(6)
C(11)	4*e*	0.3510(1)	0.0946(2)	–0.1186(1)	0.0380(8)	0.049(1)	0.0398(9)	–0.0073(7)	0.0124(7)	0.0047(7)
C(12)	4*e*	0.2910(1)	0.0229(2)	–0.1965(1)	0.049(1)	0.054(1)	0.0348(8)	–0.0084(8)	0.0135(7)	0.0035(8)
C(13)	4*e*	0.21983(9)	–0.0265(2)	–0.1898(1)	0.0389(8)	0.0321(8)	0.0406(8)	0.0011(7)	0.0064(7)	0.0036(7)
C(14)	4*e*	0.21150(9)	–0.0026(2)	–0.1017(1)	0.0310(8)	0.048(1)	0.051(1)	–0.0022(7)	0.0135(7)	–0.0057(8)
C(15)	4*e*	0.27117(9)	0.0678(2)	–0.0231(1)	0.0349(8)	0.054(1)	0.0448(9)	–0.0012(7)	0.0160(7)	–0.0058(8)
C(16)	4*e*	0.1550(1)	–0.1044(2)	–0.2745(1)	0.0458(9)	0.046(1)	0.0429(9)	–0.0054(8)	0.0061(7)	–0.0001(8)
C(17)	4*e*	0.88443(8)	0.6247(2)	0.3077(1)	0.0266(7)	0.0359(8)	0.0408(8)	0.0037(6)	0.0098(6)	–0.0015(7)
C(18)	4*e*	0.95095(9)	0.6945(3)	0.2967(1)	0.0349(8)	0.059(1)	0.052(1)	–0.0053(8)	0.0187(7)	–0.0046(8)
C(19)	4*e*	1.0095(1)	0.7663(3)	0.3761(1)	0.0309(8)	0.066(1)	0.066(1)	–0.0101(8)	0.0153(8)	–0.008(1)
C(20)	4*e*	1.0026(1)	0.7689(3)	0.4653(1)	0.0354(9)	0.059(1)	0.055(1)	–0.0020(8)	0.0040(8)	–0.0116(9)
C(21)	4*e*	0.9368(1)	0.6984(3)	0.4756(1)	0.044(1)	0.080(1)	0.043(1)	–0.010(1)	0.0118(8)	–0.0101(9)
C(22)	4*e*	0.8778(1)	0.6253(3)	0.3977(1)	0.0357(8)	0.068(1)	0.0439(9)	–0.0098(8)	0.0149(7)	–0.0060(9)

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