Crystal structure of 5-methyl-4-[1-(5-methyl-4-phenyl-thiazol-2-ylamino)-ethylidene]-2-*p*-tolyl-2,4-dihydro-pyrazol-3-one, C₂₃H₂₂N₄OS

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Abstract

C₂₃H₂₂N₄OS, triclinic, *P* $\bar{1}$ (no. 2), *a* = 7.1726(9) Å, *b* = 11.138(2) Å, *c* = 13.861(2) Å, α = 102.719(6)°, β = 103.317(5)°, γ = 106.645(5)°, *V* = 982.6 Å³, *Z* = 2, *R*_{gt}(*F*) = 0.0320, *wR*_{ref}(*F*²) = 0.0892, *T* = 173 K.

Table 1. Data collection and handling.

Crystal:	yellow, block, size 0.11 x 0.24 x 0.48 mm
Wavelength:	Mo <i>K</i> _α radiation (0.71073 Å)
μ :	1.87 cm ⁻¹
Diffractometer, scan mode:	Bruker Smart ApexII CCD, φ and ω
$2\theta_{\max}$:	56.66°
<i>N</i> (<i>hkl</i>) _{measured} , <i>N</i> (<i>hkl</i>) _{unique} :	23645, 4827
Criterion for <i>I</i> _{obs} , <i>N</i> (<i>hkl</i>) _{gt} :	<i>I</i> _{obs} > 2 σ (<i>I</i> _{obs}), 4366
<i>N</i> (<i>param</i>) _{refined} :	266
Programs:	SADABS [18], OLEX2 [19], WinGX [20], SHELX [21]

Source of material

A solution of 4-acetyl-5-methyl-2-*p*-tolyl-2,4-dihydro-pyrazol-3-one (1.00 g, 4.3 mmol) in methanol (30 mL) was added to another solution of 5-methyl-4-phenyl-thiazol-2-ylamine (0.83 g, 4.3 mmol) in methanol (20 mL) under an inert atmosphere. The reaction mixture was refluxed for two hours. Completion of the reaction was monitored by thin layer chromatography (TLC) using hexane/ethyl acetate (7:3). The reaction was allowed to cool to room temperature and then stirred overnight. A yellow precipitate formed which was then filtered and washed with methanol (10 mL). The crude product was purified by crystallization from ethanol yielding brown crystals. (1.38 g, 79% yield). M.p. = 495–496 K. Crystals suitable for X-ray diffraction were obtained by slow evaporation of a solution of the title compound in a mixture of dichloromethane and hexane at room temperature.

Experimental details

All H atoms were positioned geometrically and allowed to ride on their respective parent atoms. All H atoms were refined isotropically. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements [18].

Discussion

Schiff base ligands have been employed in a diverse range of applications. These areas include biochemical mimics [1] and coordination chemistry [2, 3]. This family of ligands can coordinate to metals anywhere from a monodentate [4] to a multidentate [5] arrangement. More recently Schiff base metal complexes have been studied for use as antibacterial [6, 7], antifungal [8, 9], antitumor drugs [10, 11] as well as homogenous catalysts [12, 13]. We previously have reported the synthesis of the title compound and from solution NMR deduced that this Schiff base is present as the keto-imine tautomeric form [14]. In this report we demonstrate that this is also the dominant isomer in the solid phase. This phenomenon has been reported for derivatives of the same general family of molecules [15–17]. The diffraction data revealed an intramolecular hydrogen bond N3–H3A...O1 2.6445(13) Å (Fig.).

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(2)	2i	0.1324	−0.4114	0.0691	0.021
H(3)	2i	0.1437	−0.4062	−0.0969	0.023
H(5)	2i	0.2989	−0.0116	−0.0042	0.030
H(6)	2i	0.2888	−0.0138	0.1624	0.029
H(7A)	2i	0.0931	−0.2207	−0.2199	0.036
H(7B)	2i	0.2793	−0.2741	−0.2056	0.036
H(7C)	2i	0.3244	−0.1190	−0.1710	0.036
H(11A)	2i	0.0628	−0.5175	0.3290	0.029
H(11B)	2i	−0.0438	−0.4473	0.4017	0.029
H(11C)	2i	0.1942	−0.4253	0.4454	0.029
H(13A)	2i	0.2761	−0.1418	0.6382	0.032
H(13B)	2i	0.1138	−0.2707	0.5480	0.032
H(13C)	2i	0.0425	−0.1533	0.5953	0.032
H(17A)	2i	0.4495	0.3465	0.9324	0.031
H(17B)	2i	0.2112	0.2586	0.8958	0.031
H(17C)	2i	0.2808	0.4034	0.8844	0.031
H(19)	2i	0.6065	0.5304	0.8776	0.026
H(20)	2i	0.7669	0.7525	0.8972	0.029
H(21)	2i	0.7399	0.8278	0.7514	0.029
H(22)	2i	0.5450	0.6794	0.5852	0.026
H(23)	2i	0.3851	0.4571	0.5650	0.023
H(3A)	2i	0.2870	0.0491	0.4665	0.020

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Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
C(1)	2i	0.2107(2)	−0.2129(1)	0.13260(8)	0.0165(5)	0.0173(5)	0.0127(5)	0.0052(4)	0.0051(4)	0.0043(4)
C(2)	2i	0.1670(2)	−0.3297(1)	0.05470(8)	0.0211(5)	0.0158(5)	0.0158(5)	0.0067(4)	0.0059(4)	0.0047(4)
C(3)	2i	0.1741(2)	−0.3262(1)	−0.04431(9)	0.0225(5)	0.0190(5)	0.0146(5)	0.0077(4)	0.0059(4)	0.0025(4)
C(4)	2i	0.2247(2)	−0.2082(1)	−0.06805(8)	0.0198(5)	0.0227(6)	0.0138(5)	0.0058(4)	0.0058(4)	0.0058(4)
C(5)	2i	0.2658(2)	−0.0931(1)	0.01057(9)	0.0385(7)	0.0174(6)	0.0196(6)	0.0059(5)	0.0118(5)	0.0076(4)
C(6)	2i	0.2597(2)	−0.0938(1)	0.11012(9)	0.0380(7)	0.0152(5)	0.0179(5)	0.0059(5)	0.0113(5)	0.0039(4)
C(7)	2i	0.2309(2)	−0.2052(1)	−0.17556(9)	0.0284(6)	0.0262(6)	0.0153(5)	0.0058(5)	0.0084(4)	0.0069(4)
C(8)	2i	0.1366(2)	−0.3211(1)	0.34484(8)	0.0141(4)	0.0153(5)	0.0147(5)	0.0046(4)	0.0037(4)	0.0046(4)
C(9)	2i	0.1955(2)	−0.1822(1)	0.39771(8)	0.0158(5)	0.0152(5)	0.0139(5)	0.0049(4)	0.0046(4)	0.0058(4)
C(10)	2i	0.2419(2)	−0.1172(1)	0.32120(8)	0.0159(5)	0.0151(5)	0.0132(5)	0.0053(4)	0.0045(4)	0.0039(4)
C(11)	2i	0.0828(2)	−0.4379(1)	0.38359(9)	0.0235(5)	0.0156(5)	0.0179(5)	0.0052(4)	0.0061(4)	0.0064(4)
C(12)	2i	0.2049(2)	−0.1125(1)	0.49607(8)	0.0153(5)	0.0160(5)	0.0139(5)	0.0053(4)	0.0036(4)	0.0050(4)
C(13)	2i	0.1550(2)	−0.1749(1)	0.57630(9)	0.0309(6)	0.0191(6)	0.0156(5)	0.0078(5)	0.0101(4)	0.0070(4)
C(14)	2i	0.2911(2)	0.1191(1)	0.60720(8)	0.0162(5)	0.0179(5)	0.0124(5)	0.0068(4)	0.0046(4)	0.0043(4)
C(15)	2i	0.3861(2)	0.3270(1)	0.70363(8)	0.0156(5)	0.0179(5)	0.0141(5)	0.0073(4)	0.0036(4)	0.0030(4)
C(16)	2i	0.3247(2)	0.2681(1)	0.77383(8)	0.0164(5)	0.0189(5)	0.0141(5)	0.0075(4)	0.0037(4)	0.0025(4)
C(17)	2i	0.3158(2)	0.3240(1)	0.88094(9)	0.0219(5)	0.0261(6)	0.0142(5)	0.0098(4)	0.0067(4)	0.0033(4)
C(18)	2i	0.4789(2)	0.4699(1)	0.71918(9)	0.0178(5)	0.0175(5)	0.0177(5)	0.0085(4)	0.0065(4)	0.0038(4)
C(19)	2i	0.5939(2)	0.5600(1)	0.81800(9)	0.0247(6)	0.0206(6)	0.0176(5)	0.0099(4)	0.0039(4)	0.0043(4)
C(20)	2i	0.6897(2)	0.6925(1)	0.8297(1)	0.0274(6)	0.0183(6)	0.0225(6)	0.0087(5)	0.0036(5)	0.0002(4)
C(21)	2i	0.6732(2)	0.7375(1)	0.7432(1)	0.0259(6)	0.0168(6)	0.0300(6)	0.0094(5)	0.0100(5)	0.0057(5)
C(22)	2i	0.5582(2)	0.6491(1)	0.6445(1)	0.0261(6)	0.0223(6)	0.0235(6)	0.0122(5)	0.0112(5)	0.0095(5)
C(23)	2i	0.4625(2)	0.5167(1)	0.63259(9)	0.0208(5)	0.0205(6)	0.0175(5)	0.0087(4)	0.0068(4)	0.0043(4)
N(1)	2i	0.2012(1)	−0.21830(9)	0.23264(7)	0.0200(4)	0.0126(4)	0.0137(4)	0.0044(3)	0.0058(3)	0.0044(3)
N(2)	2i	0.1385(1)	−0.34206(9)	0.24842(7)	0.0180(4)	0.0130(4)	0.0161(4)	0.0044(3)	0.0052(3)	0.0056(3)
N(3)	2i	0.2628(1)	0.02012(9)	0.51817(7)	0.0207(4)	0.0166(5)	0.0120(4)	0.0060(3)	0.0062(3)	0.0043(3)
N(4)	2i	0.3627(1)	0.24127(9)	0.60835(7)	0.0179(4)	0.0171(5)	0.0138(4)	0.0068(3)	0.0050(3)	0.0035(3)
O(1)	2i	0.3058(1)	0.00358(8)	0.33180(6)	0.0249(4)	0.0130(4)	0.0155(4)	0.0045(3)	0.0072(3)	0.0043(3)
S(1)	2i	0.24113(4)	0.09854(3)	0.72046(2)	0.0197(1)	0.0183(1)	0.0129(1)	0.0067(1)	0.0062(1)	0.0048(1)

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