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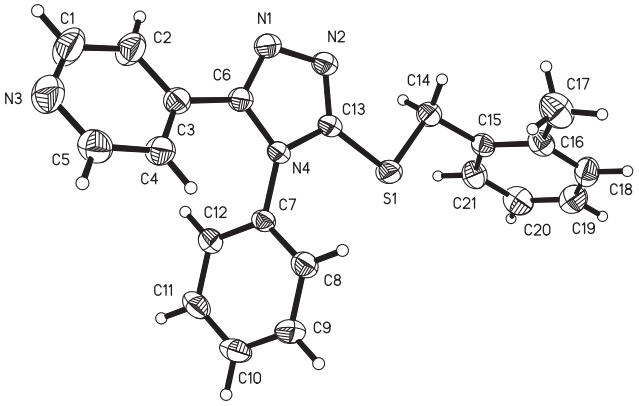
Crystal structure of 4-(5-((2-methylbenzyl)thio)-4-phenyl-4*H*-1,2,4-triazol-3-yl)pyridine, $C_{21}H_{18}N_4S$



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Abstract

$C_{21}H_{18}N_4S$, monoclinic, $P2_1/c$ (no. 14), $a = 18.264(2)$ Å, $b = 11.6302(14)$ Å, $c = 8.9289(10)$ Å, $\beta = 101.683(7)°$, $V = 1857.3(4)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0435$, $wR_{ref}(F^2) = 0.1122$, $T = 296(2)$ K.

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The 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.

Source of material

The educts were synthesized according the reference [1]. A mixture of isonicotinyl hydrazine (1.37 g, 10 mmol) with isothiocyanatobenzene (1.35 g, 10 mmol) was refluxed for 5 h

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Table 1: Data collection and handling.

Crystal:	Colourless block
	Size 0.24 × 0.08 × 0.06 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	1.9 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$2\theta_{max}$, completeness:	50°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	14076, 3280, 0.044
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2102
$N(param)_{refined}$:	239
Programs:	SHELX [10], Bruker programs [11]

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

Atom	x	y	z	U_{iso}*/U_{eq}
S1	0.15954(3)	0.46243(6)	0.38932(6)	0.0620(2)
N4	0.30011(9)	0.53615(14)	0.51205(17)	0.0425(4)
N1	0.33240(10)	0.63250(16)	0.3235(2)	0.0545(5)
C13	0.24242(11)	0.53408(18)	0.3865(2)	0.0446(5)
N2	0.25987(10)	0.59125(16)	0.27279(19)	0.0531(5)
C15	0.03129(12)	0.44105(19)	0.1841(2)	0.0479(6)
C6	0.35486(11)	0.59902(18)	0.4650(2)	0.0444(5)
C7	0.29539(10)	0.49897(17)	0.6637(2)	0.0398(5)
C12	0.30048(11)	0.57938(19)	0.7777(2)	0.0495(6)
H12A	0.3073	0.6567	0.7575	0.059*
C8	0.28474(12)	0.38432(19)	0.6908(2)	0.0532(6)
H8A	0.2821	0.3305	0.6129	0.064*
C11	0.29542(13)	0.5440(2)	0.9225(2)	0.0613(7)
H11A	0.2999	0.5974	1.0014	0.074*
C14	0.10398(12)	0.5074(2)	0.2071(2)	0.0566(6)
H14A	0.0944	0.5894	0.2077	0.068*
H14B	0.1301	0.4906	0.1253	0.068*
C16	0.02076(13)	0.3386(2)	0.1035(2)	0.0560(6)
C10	0.28374(12)	0.4297(2)	0.9507(3)	0.0626(7)
H10A	0.2797	0.4063	1.0483	0.075*
C3	0.43006(12)	0.6209(2)	0.5546(2)	0.0507(6)
C4	0.46676(12)	0.5475(2)	0.6678(3)	0.0572(6)
H4A	0.4430	0.4823	0.6947	0.069*
C18	−0.04972(15)	0.2851(2)	0.0860(3)	0.0680(7)
H18A	−0.0585	0.2168	0.0312	0.082*
C9	0.27801(13)	0.3506(2)	0.8357(3)	0.0629(7)
H9A	0.2695	0.2737	0.8552	0.076*
C20	−0.09421(15)	0.4310(3)	0.2289(3)	0.0766(8)

Table 2 (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
H20A	−0.1322	0.4618	0.2720	0.092*
N3	0.57732(12)	0.6633(2)	0.7079(3)	0.0866(7)
C5	0.53906(14)	0.5731(3)	0.7397(3)	0.0715(7)
H5A	0.5626	0.5234	0.8160	0.086*
C21	−0.02689(14)	0.4852(2)	0.2464(3)	0.0641(7)
H21A	−0.0196	0.5535	0.3014	0.077*
C2	0.46943(14)	0.7160(2)	0.5206(3)	0.0749(8)
H2A	0.4473	0.7679	0.4458	0.090*
C19	−0.10505(15)	0.3316(3)	0.1479(3)	0.0730(8)
H19A	−0.1511	0.2947	0.1346	0.088*
C17	0.08107(15)	0.2853(3)	0.0367(3)	0.0895(9)
H17A	0.0631	0.2149	−0.0139	0.134*
H17B	0.1235	0.2694	0.1167	0.134*
H17C	0.0955	0.3373	−0.0358	0.134*
C1	0.54141(16)	0.7324(3)	0.5986(4)	0.0939(9)
H1A	0.5669	0.7964	0.5732	0.113*

in ethanol. After cooling down to room temperature, the products were obtained and recrystallized from methanol to give a yield of 95%. A mixture of compound 3 (10 mmol) in aqueous NaOH solution (5 mL, 2 N) was refluxed for 4 h. After cooling down to room temperature, HCl aqueous solution (4 N) was added to afford a large amount of precipitate. The solid was filtered, dried and recrystallized from methanol to give 4-phenyl-5-(pyridin-4-yl)-4*H*-1,2,4-triazole-3-thiol, yield 88%. A CEM designed 10 mL pressure-rated vial was charged with DMF (5 mL), 4 (0.25 g, 1 mmol), 2-methyl-1-(chloromethyl)benzene (1.1 mmol), and NaOH (0.05 g, 1.2 mmol). The mixture was irradiated in a CEM Discover Synthesizer (150 w, 90 °C, 200 psi, 15 min). The mixture was cooled to room temperature. It was poured into cold ice (40 mL) and the formed precipitate was filtered. The crude solid was recrystallized from EtOH to give the title compound as colourless crystal, yield 86%; m.p. 173–174°; **^{1}H NMR** ($CDCl_3$, 400 MHz), δ: 2.35(s, 3H, Me), 4.50(s, 2H, SCH2), 7.10–7.17 (m, 4H, ArH and Py), 7.29–7.59 (m, 7H, ArH), 8.57(d, J = 5.8Hz, 2H, Py). **MS (ESI)**, m/z: 359 $(M+1)^+$. **Elemental anal.** (%), calculated: C, 70.36; H, 5.06; N, 15.63; found: C, 70.15; H, 4.99; N, 15.76.

Experimental details

The H atoms were positioned geometrically and refined using a riding model aliphatic C—H = 0.97(2) Å, $U_{iso}(H) = 1.2U_{eq}(C)$.

Discussion

Heterocycles have received important attentions because of their diversity bioactivities [2, 3], such as 1,2,4-triazole. The 1,2,4-triazoles are often possessed excellent biological activities, such as herbicidal activity [4, 5], antifungal activity [6, 7]. Generally, the average bond lengths and bond angles of ring systems (phenyl, pyridine and triazole) are in the normal ranges [8, 9]. The C6N1 bond [1.307(2)Å] is longer than the general CN double bond length of 1.27 Å. The bond angle of C13—S1—C14 is 100.39(10). The torsion angle of the thioether group C(13)—S(1)—C(14)—C(15) is 86.1(2). The plane of the triazole ring makes dihedral angles of 27.7, 13.4 and 112.7° to the three other rings.

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