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The syntheses and crystal structure of novel 5-methyl-3-substituted-1,2,4-triazolo[3,4-b]benzothiazoles

Heng-Shan Dong[a,*], Bin Quan[b], Er-Feng Chai[b], Xue-Rong Mao[b]

[a]*National Laboratory of Applied Organic Chemistry, Institute of Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, Gansu 730000, People's Republic of China*

[b]*Department of Chemistry, Guansu Education College, Lanzhou, Gansu 730000, People's Republic of China*

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Abstract

Novel 5-methyl-3-substituted-1,2,4-triazolo[3,4-b]benzothiazoles were synthesized from *o*-methylaniline to **5** with various aromatic carbonic acids. The yielded product **6a**–**e** were confirmed by Elemental Analyses, NMR, MS, IR spectra and **6e** was investigated with X-ray crystallography. Compound **6e**, $C_{24}H_{16}N_4S$, Mr = 392.69, crystallized in the triclinic space group $P\bar{1}$ with unit cell parameters $a = 9.713(3)$ Å, $b = 14.645(4)$ Å, $c = 15.641(3)$ Å, $\alpha = 113.17(2)°$, $\beta = 90.11(2)°$, $\gamma = 109.29(2)°$, $V = 1908.1(7)$ Å^3, $Z = 4$, $D_m = 1.366$ Mgm^{-3}.

Keywords: Tricyclazole derivative; Synthesis; 1,2,4-Triazolo[3,4-b]benzothiazole; Crystal structure

1. Introduction

Tricyclazole is one of the benzothiazole derivatives, which are well known for developing this synthesis of many compounds with this ring system beading diverse biological activities such as application as potent antibacterials [1,2] and fungicides for the control of *Piricularia oryzae* in the prevention of rice blast [3]. The crystal structure of this heterocyclic system was not found in literature up to now. In recent years, fused heterocycles have been found to possess many unique properties in synthesis and pharmacology. In particular, *s*-triazolo[3,4-b]benzothiazole derivatives are of interest because of their broad spectra of biological activities. The structure, which is established, should be yearned for studying relation between definite structure and properties in these fields. It should be referenced that studies of analogous compounds are promoted. We have reported the crystalline structure of 2-(3-bromoanilino)-5-[5-amino-1-(4-chlorophenyl)-1,2,3-triazol-4-yl]-1,3,4-thiodiazole and their derivatives [4–7]. We have obtained the crystalline structure of a new compound 3-[5-methyl-1-(4-methylphenyl)-1,2,3-triazol-4-yl]-6-(4-methylphenyl)-*s*-triazolo[3,4-b]-1,3,4-thiadiazole. Therefore, it was planned to investigate a system, which combines these three biologic components in a ring to give a compact system for screening their biologic activities. Recently, we have synthesized several novel 5-methyl-3-substituted-1,2,4-triazolo[3,4-b]benzothiazoles from *o*-methylaniline to **5** with various aromatic carbonic acids. The yielded products **6a**–**e** were investigated with Elemental Analyses, NMR, MS, IR techniques and **6e** was investigated with X-ray crystallography. Compound **6e**, $C_{24}H_{16}N_4S$, Mr = 392.69, crystallized in the triclinic space group $P\bar{1}$ with unit cell parameters $a = 9.713(3)$ Å, $b = 14.645(4)$ Å, $c = 15.641(3)$ Å,

* Corresponding author. Tel.: +86-931-891-582.

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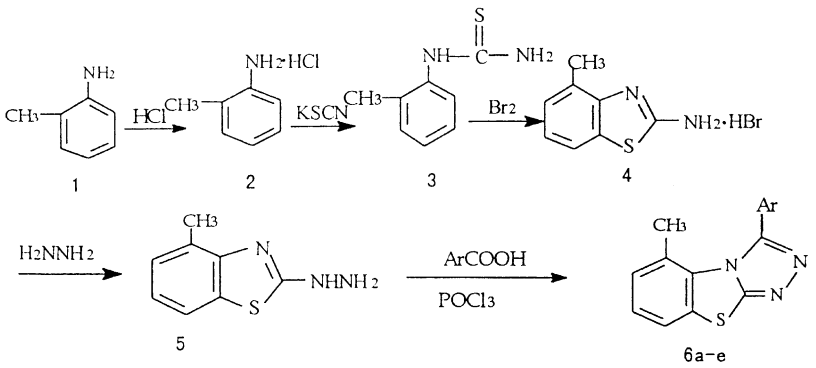


Scheme 1.

$\alpha = 113.17(2)°$, $\beta = 90.11(2)°$, $\gamma = 109.29(2)°$, $V = 1908.1(7)$ Å^3, $Z = 4$, $D_m = 1.366$ Mgm^{-3}.

The synthesis pathway of compound **6** is shown in Scheme 1 (the syntheses route of compounds **6a–e**).

2. Results and discussion

The structure of the title compound is shown in Fig. 1. The unit cell parameters of the title compound is shown in Fig. 2. In recent years the synthesis and characteristics of *s*-triazolo[3,4-b]1,3,4-thiadiazoles [8,9] and 7*H*-*s*-triazolo[3,4-b]-1,3,4-thiadiazine derivatives [10] have been investigated. These heterocyclic compounds contain 1,2,4-triazole and benzothiazole rings condensed through a C–N bond. The substituted groups at the 3 positions cannot conjugate with the heterocyclic nucleus giving it new characteristics in a continuation of our earlier studies [4]. We report the syntheses of several novel 5-methyl-3-substituted-1,2,4-triazolo[3,4-b]benzothiazoles **6a–e** show in Table 1.

The spectral data of **6a–e** presented in Tables 2–4. IR absorption peaks of **5** at 3167, 3203 cm^{-1} are assigned to its $NHNH_2$ group. When **5** is converted **6**, the $NHNH_2$ perk disappears but a new peak characteristic of $\nu_{C=N}$ appears at 1588–1626 cm^{-1}. Like the allied system [4]. The ν_{C-S-C} absorption peaks of compound **6a–e** are in the region of 693–702 cm^{-1}.

In ^{1}H NMR spectra, compared **5** and **6a–e**, we found that after cyclization the evident change is that the signals of $-NHNH_2$ protons are at δ 3.11 ppm. The chemical shifts of the aromatic methyl group show in the range of δ 2.36–2.52 ppm. The chemical shifts of the triazole methyl group show in the range δ 2.33–2.75 ppm, and the chemical shift of the aromatic ring methyl group on the 1,2,4-triazolo[3,4-b]benzothiazole ring in compound **6e** occurs at higher frequency than the other compounds.

Single crystals were selected and were mounted on

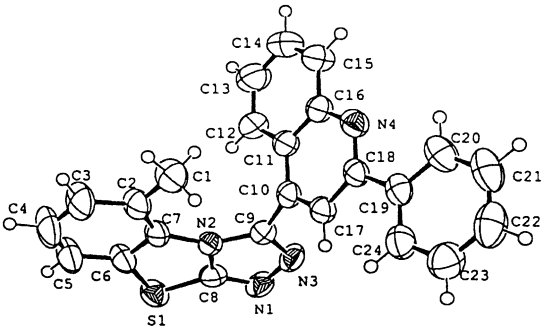


Fig. 1. ORTEP drawing of the title compound showing the atom numbering scheme.

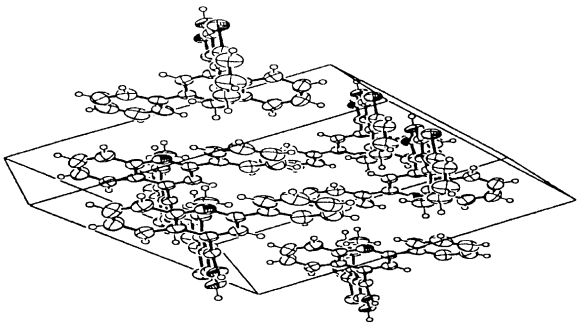


Fig. 2. The unit cell parameters of the title compound.

Table 1
Structures, yields and melting points of the compounds **6a–e** (Ar = **6a** 5-methyl-1-(4-chlorophenyl)-1,2,3-triazol-4-yl; **6b** 5-methyl-1-(4-methylphenyl)-1,2,3-triazol-4-yl; **6c** 5-methyl-1-(2-methylphenyl)-1,2,3-triazol-4-yl; **6d** 2,4-dichlorophoxymethylene; **6e** 2-phenylquinoline-4-yl)

Compound	Yield (%)	Mp (°C)	Formula	Found (required) (%)		
				C	H	N
6a	42	252–253	$C_{18}H_{13}ClN_6S$	56.68(56.77)	3.40(3.44)	22.27(22.07)
6b	60	220–221	$C_{19}H_{16}N_6S$	63.27(63.31)	4.42(4.47)	23.43(23.32)
6c	67	143–144	$C_{19}H_{16}N_6S$	63.23(63.31)	4.46(4.47)	23.45(23.32)
6d	57	125–126	$C_{16}H_{11}Cl_2N_3OS$	52.68(52.76)	3.10(3.04)	11.62(11.54)
6e	45	228–229	$C_{24}H_{16}N_4S$	73.39(73.45)	4.08(4.11)	14.38(14.28)

the tip of a glass fiber. Preliminary examination and data collection were performed with Mo Kα radiation ($\lambda = 0.71073$ Å) on an Enraf–Nonius CAD4 computer controlled kappa axis diffractometer operating in the $\omega/2\theta$ scanning mode using the crystal. The structure was determined by direct methods (SHELXS-86) and refined by full covariance matrix methods (SHELXL-93). The crystal data and the refinement detail gives in Table 5.

The structure of the title compound is shown in Fig. 1. The fractional coordinates and mean temperature factors with estimated standard deviations for non-hydrogen atoms are listed in Table 6 and selected bond lengths are given in Table 7, selected bond angles are given in Table 8. The geometric calculations were performed using the program SHELXS-86.

The central ring system in the present compound is already determined. The bond lengths indicate a degree of delocalization around the ring system with the three C=N bonds ranging from 1.294(4) to 1.306(4) Å and the N–N bond lengths ranging 1.392(4) Å. The benzothiazole ring system is planar. The bond lengths N2–C8 1.373(4) Å, N2–C7 1.422(4) Å, S1–C6 1.756(4) Å, S1–C8 1.719(3) Å are not in agreement with the values reported for benzothiazole by Fehlmann [11] (the bond lengths N2–C8 1.297 Å, N2–C7 1.381 Å, S1–C6 1.739 Å, S1–C8 1.763 Å). The bond lengths N2–C8 1.297 Å [11] and N2–C8 1.373(4) Å are between the bond lengths of C=N and C–N. The structure of the title

Table 2
IR spectral data for compounds **6a–e**

Compound	IR(cm^{-1}) (KBr disc)
6a	3067, 3014, 2919, 2851, 1679, 1551, 1498, 1426, 1369, 1258, 980, 861, 823, 723.5
6b	3067, 2969, 2922, 2864, 1650, 1558, 1518, 1483, 1383, 971, 862, 798, 722.4
6c	3077, 2968, 2930, 2864, 1612, 1501, 1481, 1407, 1382, 1259, 971, 861, 807, 722.1
6d	3191, 2918, 1615, 1556, 1480, 1454, 1362, 1291, 1231, 1122, 984, 860, 815, 720.9
6e	3057, 2974, 2917, 1600, 1548, 1481, 1445, 1355, 1240, 956.9, 824, 762, 721.1

Table 3
^{1}H NMR spectral data for compounds **6a–e** (Bti: benzothiazole; Tazo: 1,2,3-triazol)

Compound	^{1}H NMR ($CDCl_3$ – *d*), δ (ppm), *J* (Hz)
6a	7.14–7.72 (m, 3H, Bti-H), 7.14–7.47 (q or 2d, 4H, $J = 8.5$, *p*-ClC_6H_4–), 2.45 (s,3H, Bti-CH_3), 2.75 (s,3H,Tazo-CH_3)
6b	7.13–7.60 (m, 3H, Bti-H), 7.42 (s, 4H, 4-$CH_3C_6H_4$), 2.49 (s, 6H, Bti-CH_3, Tazo-CH_3), 2.10 (s, 3H, 4-$CH_3C_6H_4$)
6c	7.15–7.63 (m, 7H, Bti-H, 2-$CH_3C_6H_4$), 2.33 (s, 3H, Tazo-CH_3), 2.33 (s, 3H, Bti-CH_3), 2.14 (s, 3H, 2-$CH_3C_6H_4$)
6d	6.93–7.60 (m, 6H, –$C_6H_3Cl_2$, Bti-4H), 4.97 (s,2H, –OCH_2–), 2.58 (s, 3H, Bti-CH_3)
6e	8.35–8.33 (d,1H, $J = 8.3$, 8′-H), 8.25–8.26 (m, 1H, $J = 1.5$, Bti-8H),8.23 (s, 1H, 5′-H), 8.22 (s, 1H, 7′-H), 7.79–7.83 (m, 1H, $J = 8.2$, $J = 1.52$, Bti-7H), 7.48–7.58 (m, 5H, Ph-H), 7.31 (s, 1H, 3′-H), 7.26–7.27 (d, 1H, $J = 1.48$, Bti-6H), 6.99–7.01 (d, 1H, $J = 7.63$, 6′-H), 1.51 (s, 3H, Bti-5CH_3)

Table 4
MS spectral data for compounds **6a–e**

No	M^+	*m/z* (%)
6a	381(25)	353(6), 326(5), 320(8), 300(1), 292(9), 285(2), 229(4), 285(2), 229(4), 194(6), 191(29), 181(11), 175(15), 163(20), 154(23), 153(32), 152(62), 149(34), 146(10), 139(5), 136(23), 128(15), 123(10), 121(22), 119(6), 113(33), 111(100), 109(19), 102(16), 101(11), 92(13), 91(7), 77(23), 75(59), 51(13)
6b	360(22)	345(54), 332(17), 331(22), 318(22), 317(100), 303(9), 290(10), 289(14), 274(2), 263(4), 247(2), 214(2), 200(7), 197(4), 190(2), 184(3), 171(5), 170(29), 169(49), 163(22), 162(16), 156(19), 155(11), 143(31), 136(18), 132(34), 128(13), 122(11), 121(14), 119(9), 102(10), 91(75), 77(19), 65(50)
6c	360(17)	345(49), 332(12), 331(16), 318(22), 317(100), 303(8), 290(8), 289(13), 276(2), 274(2), 263(3), 256(2), 247(2), 214(2), 200(7), 197(4), 190(1), 184(2), 171(4), 170(25), 169(48), 163(23), 162(21), 156(15), 143(27), 136(18), 132(22), 128(15), 121(17), 117(13), 109(10), 102(12), 91(80), 89(23), 77(25), 65(77)
6d	363(4)	328(1), 240(17), 239(6), 238(47), 223(1), 203(15), 202(100), 184(2), 177(27), 173(8), 163(9), 161(26), 150(12), 148(8), 136(8), 133(7), 121(7), 117(13), 109(8), 103(3), 92(5), 77(6), 65(5)
6e	392(70)	378(27), 377(100), 364(10), 359(1), 334(1), 317(2), 315(24), 289(3), 256(2), 231(17), 230(73), 229(98), 204(9), 203(10), 196(16), 189(1), 176(6), 175(5), 162(53), 161(55), 151(14), 147(9), 136(15), 135(27), 126(5), 122(7), 121(12), 118(24), 110(12), 109(12), 92(17), 91(13), 77(20, 65(12)

Table 5
Crystal data and summary of data collection and structure refinement

Compound	$C_{24}H_{16}N_4S$
Color/Shape	Colorless/rhombic pillared
Formula weight	392.47
Temperature (°C)	20 (293 K)
Crystal system	Triclinic
Space group	$P\bar{1}$
Cell constants	
a (Å)	9.713(3)
b (Å)	14.645(4)
c (Å)	15.641(8)
α (°)	113.17(2)
β (°)	90.11(2)
γ (°)	109.29(2)
Volume (Å^3)	1908.1(7)
Formula units/units cell	4
D_{calc} (g cm^{-3})	1.366
F(000)	816
Absorption coefficient (mμ^{-1})	0.188
Diffractometer/scan Enraf–Nonius CAD4	$\omega/2?$
Radiation, graphite monochromator Mo Kα	0.71073
Reflections for cell measurement and θ range (°)	25, 0 ~ 25
Index ranges	$0 \le h \le 11$; $-17 \le k \le 16$; $-18 \le l \le 18$
Standard reflections	7149
Reflections measured	6714
Reflection observed [$1 > 2\sigma(I)$]	4237 ($R_{int} = 0.0322$)
Maximum value of θ (°)	25.02
Computing	Data collection CAD4 Cell refinement CAD4 Data reduction PCSDP Structure solution SHELXS-86
Structure refinement	SHELXL-93
Data/restrains/parameters	6649/0/523
Goodness-of-fit on F^2	1.134
Final *R* indices	$R_1 = 0.0514$, $wR_2 = 0.1364$
Largest diff. peak and hole	0.369 and −0.391 eÅ^{-3}

compound is shown in Scheme 2 (the structure of 5-methyl-3-(2-phenylquinoline-4-yl)-1,2,4-triazolo [3,4-b]benzothiazole **6e**).

3. Experimental

Melting points were determined on a Kofler melting point apparatus and are uncorrected. The mass spectrum was performed on a HP-5988A

Table 6
The fractional coordinates and mean temperature factors with estimated standard deviations for non-hydrogen atoms

	X	Y	Z	U
S1	0.31523(10)	0.60184(7)	0.95148(7)	0.0647(3)
N1	0.5804(3)	0.5688(2)	0.9294(2)	0.0616(7)
N2	0.3749(3)	0.4377(2)	0.8413(2)	0.0462(6)
N3	0.6140(3)	0.4810(2)	0.8721(2)	0.0609(7)
N4	0.5497(3)	0.1107(2)	0.6564(2)	0.0552(7)
C1	0.1623(4)	0.2240(3)	0.6770(3)	0.0734(11)
C2	0.1218(4)	0.3130(3)	0.7449(3)	0.0610(9)
C3	−0.0241(4)	0.3061(4)	0.7380(3)	0.0830(12)
C4	−0.0689(5)	0.3864(4)	0.7954(4)	0.0954(15)
C5	0.0269(4)	0.4779(4)	0.8634(3)	0.0834(12)
C6	0.1737(4)	0.4871(3)	0.8719(3)	0.0609(9)
C7	0.2203(3)	0.4060(3)	0.8157(2)	0.0518(7)
C8	0.4389(3)	0.5398(2)	0.9094(2)	0.0539(8)
C9	0.4931(3)	0.4034(2)	0.8212(2)	0.0486(7)
C10	0.4974(3)	0.2982(2)	0.7604(2)	0.0490(7)
C11	0.4486(3)	0.2124(2)	0.7881(2)	0.0512(7)
C12	0.3757(4)	0.2149(3)	0.8660(3)	0.0604(8)
C13	0.3333(5)	0.1294(3)	0.8880(3)	0.0780(11)
C14	0.3634(5)	0.0381(3)	0.8331(3)	0.0836(12)
C15	0.4341(4)	0.0332(3)	0.7581(3)	0.0708(10)
C16	0.4785(3)	0.1197(3)	0.7324(2)	0.0540(8)
C17	0.5662(3)	0.2869(3)	0.6829(2)	0.0506(7)
C18	0.5912(3)	0.1911(2)	0.6315(2)	0.0483(7)
C19	0.6750(3)	0.1808(3)	0.5511(2)	0.0537(8)
C20	0.7266(4)	0.0974(3)	0.5146(3)	0.0697(10)
C21	0.8168(5)	0.0927(4)	0.4463(3)	0.0855(13)
C22	0.8540(5)	0.1685(4)	0.4115(3)	0.0875(13)
C23	0.7991(5)	0.2492(4)	0.4444(3)	0.0813(11)
C24	0.7105(4)	0.2552(3)	0.5133(3)	0.0666(9)

spectrometer (EI at 70 eV). IR spectra were obtained in KBr discs using a Nicolet 170SX FT-IR spectrometer. ^{1}H NMR spectroscopy were recorded at room temperature at 400.13 MHz on a Bruker AM 400 instrument. Elemental Analyses were carried out on a Yanaco CHN Corder MT-3 analyzer.

Phosphorus oxychloride was redistilled (bp 105 °C).

5-Methyl-1-(4-methylphenyl)-1,2,3-triazol-4-carboxylic acid, 5-Methyl-1-(2-methylphenyl)-1,2,3-triazol-4-carboxylic acid and 5-Methyl-1-(4-cholophenyl)-1,2,3-triazol-4-carboxylic acid were prepared by the literature [9].

3.1. The preparation of the o-tolylthiourea **3**

A mixture of *o*-toluidine (25.4 g, 0.24 mol) and chlorobenzene (130 ml) was heated. After *o*-toluidine was dissolved, concentrated hydrochloride (21 ml, 0.25 mol) was dripped and a white precipitate was obtained. Powdered potassium thiocyanate (26 g, 0.26 mol) was poured rapidly into the mixture and refluxed for 16 h and then allowed to cool. The solid was crushed, collected, and washed with water. The *o*-tolylthiourea was recrystallized from aqueous alcohol, yielded 30.4 g (78.3%), mp 155–156 °C (Lit. mp 155–156 °C [12]).

3.2. The preparation of the 2-amino-4-methylbenzothiazole ***4***

A solution of bromine (6.8 ml, 0.17 mol) in chloroform (50 ml) was poured into a mixture of the dry powdered *o*-tolylthiourea (20 g, 0.13 mol) and chloroform (60 ml) which was heated to boil contained in a 3-necked flask. Heat was evolved and the mixture rapidly gave a clear solution which was kept below 30 °C by external cooling. When the initial reaction had subsided the flask was fitted with a stirrer and condenser carrying a calcium chloride tube and the mixture refluxed until evolution of hydrogen bromide ceased (ca. 24 h), the hydrobromide of the 2-amino-4-methylbenzothiazole crystallizing out meanwhile. The mixture was set aside overnight. The cold mixture was filtered and the insoluble residue suspended in water and treated with sodium sulfite until traces of free bromine had been removed. The mixture was again filtered. The precipitate was collected, washed with water, and dried (average yield, 22.5 g, 76.2%) mp 253–254 °C (Lit. 254 °C [12]), ^{1}H NMR (DMSO-d_6) $\delta = 14.27$ (s,1H), 11.52 (s, 2H), 7.25–7.37 (m, 3H), 2.67 (s, 3H).

3.3. 2-Hydrazino-4-methylbenzothiazole ***5***

2-Amino-4-methylbenzothiazole (20 g, 0.82 mol) and hydrazine hydrate 85% (0.11 mol) in 50 ml of glycol refluxed (110–120 °C) while stirring for 4 h. The color of the reaction mixture changed to green, and gave a homogeneous solution. A white solid was precipitated at the end of the reflux period. The mixture was cooled and the product was filtered, washed with water, air-dried and recrystallized from ethanol to give white needles of **5**. It gave 11 g (75.3%), mp 169–170 °C.

Table 7
Selected bond lengths (Å)

S1C8	1.719(3)	N4C16	1.360(4)	C10C17	1.365(4)	C18C19	1.483(5)
S1C6	1.756(4)	C1C2	1.495(5)	C10C11	1.424(4)	C19C24	1.384(5)
N1C8	1.294(4)	C2C3	1.388(5)	C11C12	1.405(5)	C19C20	1.388(5)
N1N3	1.392(4)	C2C7	1.394(5)	C11C16	1.420(5)	C20C21	1.379(6)
N2C8	1.373(4)	C3C4	1.373(6)	C12C13	1.362(5)	C21C22	1.367(6)
N2C9	1.389(4)	C4C5	1.357(6)	C13C14	1.402(6)	C22C23	1.373(6)
N2C7	1.422(4)	C5C6	1.388(5)	C14C15	1.350(6)	C23C24	1.374(5)
N3C9	1.306(4)	C6C7	1.387(5)	C15C16	1.412(5)		
N4C18	1.324(4)	C9C10	1.473(4)	C17C18	1.418(4)		

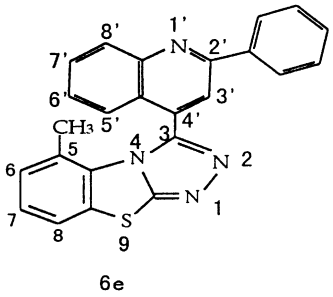
Table 8
Selected bond angles (°)

C8S1C6	88.7(2)	C5C6C7	121.9(3)	C17C10C9	119.3(3)	N4C18C17	121.8(3)
C8N1N3	105.1(3)	C5C6S1	123.4(3)	C11C10C9	120.7(3)	N4C18C19	117.4(3)
C8N2C9	103.4(2)	C7C6S1	114.6(2)	C12C11C10	124.3(3)	C17C18C19	120.6(3)
C8N2C7	113.7(3)	C6C7C2	121.1(3)	C12C11C16	119.3(3)	C24C19C20	117.9(3)
C9N2C7	142.9(3)	C6C7N2	109.1(3)	C10C11C16	116.4(3)	C24C19C18	122.0(3)
C9N3N1	109.6(3)	C2C7N2	129.8(3)	C13C12C11	120.6(4)	C20C19C18	119.9(3)
C18N4C16	118.8(3)	N1C8N2	112.9(3)	C12C13C14	120.0(4)	C21C20C19	120.5(4)
C3C2C7	115.7(3)	N1C8S1	133.3(3)	C15C14C13	121.0(4)	C22C21C20	120.7(4)
C3C2C1	119.1(3)	N2C8S1	113.8(2)	C14C15C16	120.7(4)	C21C22C23	119.3(4)
C7C2C1	125.3(3)	N3C9N2	108.9(3)	N4C16C15	118.3(3)	C22C23C24	120.3(4)
C4C3C2	122.5(4)	N3C9C10	120.2(3)	N4C16C11	123.3(3)	C23C24C19	121.1(4)
C5C4C3	122.1(4)	N2C9C10	130.7(3)	C15C16C11	118.4(3)		
C4C5C6	116.7(4)	C17C10C11	119.5(3)	C10C17C18	120.1(3)		

^{1}H NMR ($CDCl_3$) $\delta = 6.93–7.57$ (m, 3H), 4.96 (broad, 3H), 2.58 (s, 3H).

3.4. Novel 5-methyl-3-substituted-1,2,4-triazolo[3,4-b]benzothiazoles **6a–e**

A mixture of 2-hydrazino-4-methylbenzothiazole **5** (1 mmol), various aromatic carbonic acids (1 mmol) and $POCl_3$ (5 ml) was heated under reflux for 12 h. A portion of $POCl_3$ was distilled out and the remaining reaction mixture poured into ice-water. The solution was basifyed by adding potassium hydroxide solution, the deposited solid was filtered off and recrystallized from ethanol to give the title 5-methyl-3-substituted-1,2,4-triazolo[3,4-b]benzothiazoles **6a–e**. The solid was separated by chromatographic column (silica gel, eluant ethyl acetate/petroleum ether 1:1). The results are given in Table 1.



6e

Scheme 2.

The purified product was dissolved in ethyl acetate/petroleum ether/ethanol solution. The crystal was obtained after 7 days by evaporation of the solution.

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