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ORIGINAL PAPER

The Synthesis and Crystal Structure of New Bis(3-chlorophenyl)-[5-methyl-1-(4-methylphenyl)-1,2,3-triazol-4-yl]-methanol

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Abstract The title compound bis(3-chlorophenyl)-[5-methyl-1-(4-methylphenyl)-1,2,3-triazol-4-yl]-methanol **8** has been synthesized and established by H NMR, IR and MS spectra and X-ray diffraction crystallography. Compound **8**, $C_{23}H_{29}Cl_2N_3O$, Mr = 424.31, crystallizes in the monoclinic space group $P2_1/c$ with unit cell parameters $a = 14.5402(6)$ Å, $b = 12.5888(5)$ Å, $c = 11.6510(5)$ Å, $\alpha = 90°$, $\beta = 100.183°(2)$, $\gamma = 90°$, $V = 2099.05(15)$ Å^3, $D_x = 1.343$ mg m^{-3} and $Z = 4$. The final R was 0.0514. The molecular conformation and packing is stabilized by interactions of intermolecular O1–H1···N3′.

Keywords Crystal structure · Synthesis · 1H-1,2,3-triazole · H-bond · Methanol

Introduction

In recent years in various publications, certain compounds that 1-aryl-5-methyl-4-substituted-1,2,3-triazoles often exhibit broad spectrum biological actions [1, 2], antibacterial [3], antifungal [4], antiviral [5], anti-inflammatory and analgetic properties [6]. Some of 1,2,3-triazole derivatives had been reported to inhibit tumor proliferation, invasion and metastasis [7]. Therefore, it is worthwhile to investigate these properties of 1,2,3-triazole. As a great deal of interest has been focused on it, we synthesized a new title compound.

The route of syntheses of the title compound is in Scheme 1.

Experimental Section

All melting points were uncorrected and determined on an XT_4-100x microscopic melting point apparatus. IR spectra were obtained in KBr discs on a Nicolet NEXUS 670 FT-IR spectrometer. MS were performed on a HP-5988A spectrometer (EI at 70 eV). ^1H NMR spectroscopy ($CDCl_3$) was recorded on Varian Mercury plus-300 instrument with TMS as an internal standard.

Preparation of the Title Compound

5-Methyl-1-(4-methylphenyl)-1,2,3-triazol-4-carboxylic acid **3** was prepared following methods in the literature [8] Mp182–183 °C(Lit. Mp182–183 °C).

5-Methyl-1-(4-methylphenyl)-1,2,3-triazol-4-carboxylic acid ethyl ester **4** was prepared following methods in the literature [8] Mp130–132 °C(Lit. Mp130–132 °C).

1-Bromo-3-chlorobenzene **6** was prepared following methods in the literature [9].

3-Chlorophenylmagnesium bromide **7** was prepared following methods in the literature [10].

Preparation of bis(3-chlorophenyl)-[5-methyl-1-(4-methylphenyl)-1,2,3-triazol-4-yl]-methanol **8** was following method in the literature [10].

A mixture of 3-chlorophenylmagnesium bromide **7** (4.31 g, 0.02 mol) and 35.0 mL ether was dripped to a mixture of 5-methyl-1-(4-methylphenyl)-1,2,3-triazol-4-carboxylic acid ethyl ester **4** (0.5 g, 0.002 mol) and benzene 20.0 mL under stirring. After 3-chlorophenyl-

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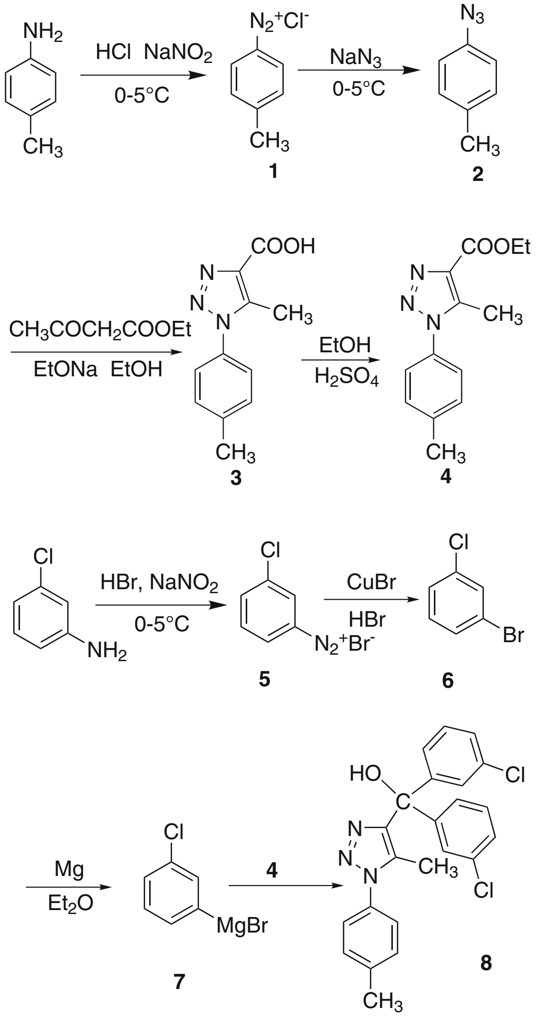

Scheme 1 The synthesis route of compound **8**

magnesium bromide was dripped, the mixture liquid was stirred for 1 h. The 5 mL 6 N HCl was poured into the reaction mixture and the thick and cloudy liquor was filtered and then the resulting solution was evaporated. The solid was purified by recrystallisated with EtOH to give white blocks of compound **8**, Yield 80% (0.85 g), Mp143–144 °C. ^{1}H NMR δ(ppm): 4.437 (b, OH), 1.789 (s, 3H, CH_3), 2.428 (s, 3H, CH_3), 7.186–7.401 (m, 12H, phenyl). MS M/z (%): 423.8 (M^+) 394 (7.2) 256 (6.7) 139 (45.5) 132 (44.2) 111 (31.7) 107 (84.2) 91 (100). IR(KBr) υ_{max}: 3376(w, OH), 2921(s), 1515(s), 1470(s), 1196(s), 1139(s), 1098(s), 1041(s), 876(s), 790(s), 751(s), 708(s).

The purified product was dissolved in ethyl acetate and petroleum ether solvent. The crystal was obtained after 20d by evaporation of the solvent.

Single crystals were selected and mounted on the tip of a glass fiber. Data were collected on a SMART APEX II CCD using graphite monochromatized MoKα radiation ($\lambda = 0.71073$ Å). The structure was determined by direct

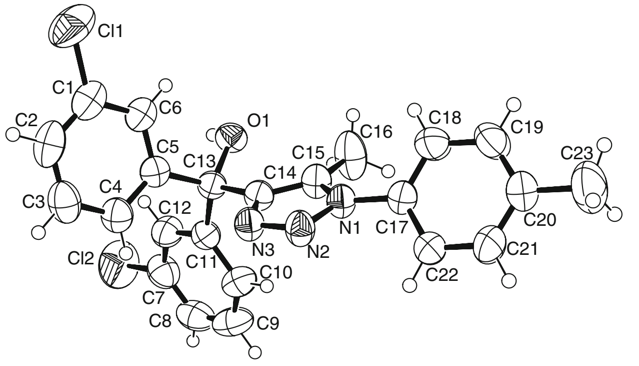

Fig. 1 ORTEP diagram of the compound **8** showing 50% thermal ellipsoids

Table 1 Crystal data and structure refinement details

Empirical formula	$C_{23}H_{29}Cl_2N_3O$
Formula weight	424.31
Deposit no.	619676
Temperature (K)	294(2)
Wavelength (Å)	0.71073
Reflns. for cell determination	25
2θ range for above	10°−20°
Crystal system	Monoclinic
Space group	$P2_1/c$
Cell dimensions	$a = 14.5402(6)$ Å
	$b = 12.5888(5)$ Å
	$c = 11.6510(5)$ Å
	$\alpha = 90$
	$\beta = 100.183(2)$
	$\gamma = 90°$
Volume (Å^3)	2099.05(2)
Z	4
Density(calculated), mg/m^3	1.343
Absorption coefficient (mm^{-1})	0.328
Diffractometer/scan	Smart Apex II
	CCD area detector $\omega/2\theta$
F(000)	880
θ range for data collection, deg	2.15–26
Index ranges	$-17 \le h \le 15$;
	$-15 \le k \le 14$;
	$-9 \le l \le 14$
Reflections collected	4107
Independent reflection	2348
Data/restrains/parameters	4107/0/266
Extinction Coeff.	0.0030(12)
Goodness-of-fit on F^2	0.939
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0514$, $wR_2 = 0.1420$
R indices	$R_1 = 0.1000$, $wR_2 = 0.1797$
Largest diff. peak and hole	0.195 and −0.292 e Å^{-3}

methods (SHELXS-97) and refined by full covariance matrix methods (SHELXL-97). The structure of the title compound is shown in Fig. 1. The crystal data and the refinement details are given in Table 1. The selected bond lengths are given in Table 2, selected bond angles are given in Table 3. The geometric calculations were performed using the program SHELX-97.

Table 2 Selected bond lengths (Å)

Atoms	Length	Atoms	Length
C14···N3	1.358(3)	C7···Cl-2	1.744(3)
C14···C15	1.372(3)	C8···C9	1.365(5)
C14···C13	1.512(3)	C9···C10	1.381(4)
N3···N2	1.313(3)	C10···C11	1.385(4)
N2···N1	1.353(3)	C11···C12	1.386(4)
O1···C13	1.431(3)	C11···C13	1.540(3)
C1···C2	1.378(4)	C15···N1	1.355(3)
C1···C6	1.380(4)	C15···C16	1.493(4)
C1···Cl-1	1.737(3)	N1···C17	1.440(3)
C2···C3	1.371(4)	C17···C22	1.364(4)
C3···C4	1.387(4)	C17···C18	1.370(4)
C4···C5	1.385(4)	C18···C19	1.379(4)
C5···C6	1.382(4)	C19···C20	1.373(4)
C5···C13	1.533(3)	C20···C21	1.358(4)
C7···C8	1.372(4)	C20···C23	1.502(4)
C7···C12	1.373(4)	C21···C22	1.380(4)

Table 3 Selected bond angles (°)

Atoms	Angle	Atoms	Angle
N3···C14··· C15	108.7(2)	C7···C12···C11	120.7(3)
N3···C14···C13	122.0(2)	O1···C13···C14	104.03(18)
C15···C14···C13	129.3(2)	O1···C13···C5	110.9(2)
N2···N3···C14	109.4(2)	C14···C13···C5	109.75(19)
N3···N2···N1	106.52(18)	O1···C13···C11	109.42(18)
C2···C1···C6	121.1(3)	C14···C13···C11	111.4(2)
C2···C1···Cl1	119.7(2)	C5···C13···C11	111.1(2)
C6···C1···Cl1	119.2(3)	N1···C15···C14	104.1(2)
C3···C2···C1	118.7(3)	N1···C15···C16	122.3(2)
C2···C3···C4	120.7(3)	C14···C15···C16	133.5(2)
C5···C4···C3	120.5(3)	N2···N1···C15	111.3(2)
C6···C5···C4	118.6(3)	N2···N1···C17	118.08(19)
C6···C5···C13	119.6(2)	C15···N1···C17	130.6(2)
C4···C5···C13	121.8(2)	C22···C17···C18	119.7(3)
C1···C6···C5	120.4(3)	C22···C17···N1	118.9(2)
C8···C7···C12	121.2(3)	C18···C17···N1	121.3(2)
C8···C7···Cl2	119.2(3)	C17···C18···C19	119.4(3)
C12···C7···Cl2	119.6(3)	C20···C19···C18	122.1(3)
C9···C8···C7	118.6(3)	C21···C20···C19	116.8(3)
C8···C9···C10	121.0(3)	C21···C20···C23	121.6(3)
C9···C10···C11	120.7(3)	C19···C20···C23	121.6(3)
C10···C11···C12	117.8(3)	C20···C21···C22	122.6(3)
C10···C11···C13	123.3(2)	C17···C22···C21	119.4(3)
C12···C11···C13	118.8(2)		

Results and Discussion

Title compound was obtained by the reaction of compound **4** and Grignard regent which was prepared with *m*-chlorobromobenzene from *m*-chloroaniline. The reaction of compound **4** and Grignard regent excessively was an addition reaction from ester function to hydroxyl group through intermediate of carbonyl group function. The main product of reaction was given by the addition reaction of carbonyl group and Grignard regent.

An ORTEP diagram of the compound **8** showing 50% thermal ellipsoids is show in Fig. 1. The X-ray structure analysis indicated that the compound **8** consisted of three phenyl rings and one triazole ring. The four aromatic rings do not share a common plane. The two m-chlorophenyl rings and a triazole ring are attached to the same carbon atom (C13) which owe to the sp^3 character. The force of steric repulsion is obvious between two *m*-chlorophenyl rings and a triazole ring. So the bond angles of O1–C13–C14 [104.03(18)°], O1–C13–C5 [110.9(2)°], O1–C13–C11 [109.42(18)°], C11–C13–C14 [111.4(2)°], C11–C13–C5 [111.1(2)°] and C14–C13–C5 [109.75(19)°] have different variety compared with the normal bond angles(109°28′).

The dihedral angles between the phenyl rings and triazole rings are 47.3–49.7° [N2–N1–C17–C22 47.3(3)°, C15–N1–C17–C22 −134.1(3)°, N2–N1–C17–C18 −128.8(3)°, C15–N1–C17–C18 49.7(4)°].

In the crystal structure, there is an intermolecular O1–H1···N3′ hydrogen bond involving the O–H atom and other molecular triazole ring 3 positions N. The molecular

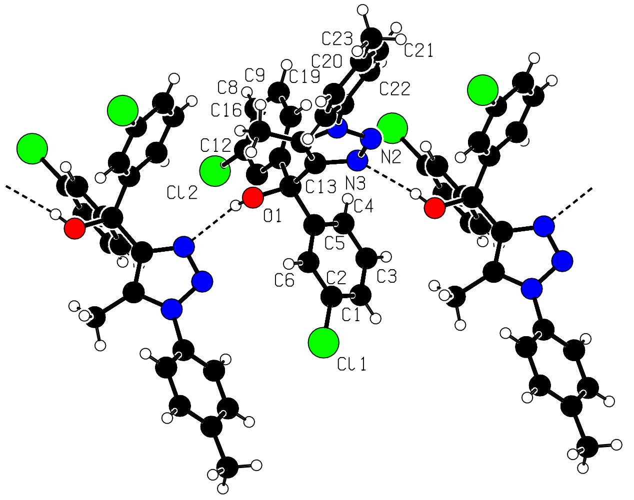

Fig. 2 The H-bond structure of the compound **8** (PWT drawing for the Platon)

conformation and packing is stabilized by interactions of intermolecular O1–H1···N3′. The bond length of Donor-H···Acceptor is 2.93Å (O–H 0.82; H···N3 2.20Å), the bond angle is 149°. The H-bond structure of the compound **8** is shown in Fig. 2.

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