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ORIGINAL PAPER

Synthesis and Crystal Structure of New *N,N′*-Bis[1-(4-methoxyphenyl)-5-methyl-1*H*-1,2,3-triazole-4-carbonyl]hydrazide

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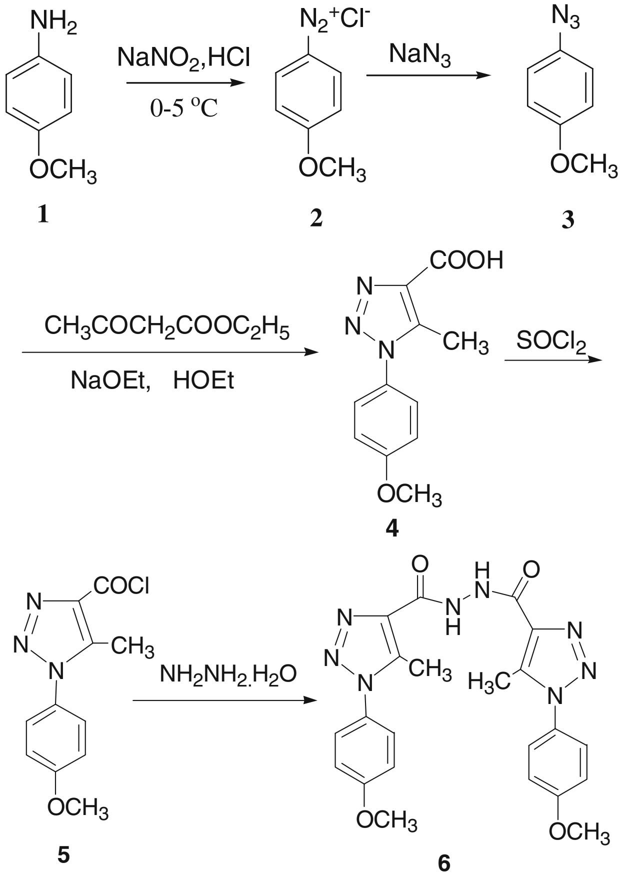
Abstract The *N,N′*-bis[1-(4-methoxyphenyl)-5-methyl-1*H*-1,2,3-triazole-4-carbonyl]hydrazide **6** was synthesized from aryl triazole acids and its structure is established by MS, IR, and ^{1}H NMR spectral data. Compound **6**, $C_{22}H_{22}N_8O_4$, Mr = 462.48, crystallizes in the monoclinic space group P2(1)/c with unit cell parameters a = 15.3451(8), b = 8.6486(4), c = 16.8502(9) Å, $\alpha = 90.00$, $\beta = 95.731(2)$, $\gamma = 90.00°$, V = 2225.1(2) Å^3, Z = 4, and Dx = 1.381 mg m^{-3}. The final R was 0.0450. The four aromatic rings are close to linear because of N···H–N hydrogen bonds.

Keywords Crystal structure · 1,2,3-triazole · *N,N′*-Bis(1-aryl-5-methyl-1*H*-1,2,3-triazole-4-carbonyl)hydrazide · Hydrogen bond · Crystal data

Introduction

In recent years, certain compounds having 1,2,3-triazole nucleus have been reported as antibacterial [1], antifungal [2], antiviral [3], anti-inflammatory, and analgesic [4]. Recently, some new 1,2,3-triazole derivatives have been synthesized to inhibit tumor proliferation, invasion and metastasis [5] and as anti-HIV agents [6, 7]. For this reason, the heterocyclic derivatives containing two 1,2,3-triazoles nuclei are very interesting. The route of syntheses is in Scheme 1.



Scheme 1 The synthesis route of title compound

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Experimental

All melting points were determined on a Sapphire DSC (Differential Scanning Calorimeter) which is made by Perkin Elmer (USA). IR spectra were obtained in KBr discs on a Shimadzu IR-435 spectrometer. MS were performed on a HP-5988A spectrometer (EI at 70 eV). ^{1}H NMR spectroscopy ($CDCl_3$) was recorded on a Varian Mercury plus-300 instrument with TMS as an internal standard.

5-Methyl-1-(4-methoxyphenyl)-1,2,3-triazol-4-carboxylic acid **4** was prepared by following methods in the literature [8].

Preparation of 1-(4-Methoxyphenyl)-5-methyl-1,2,3-triazol-4-carbonyl chloride **5**

In a 150 mL round bottomed flask was placed a mixture of **4** (20 mmol) and $SOCl_2$ (20 mL) and the mixture was refluxed gently for 5–8 h. After excessive $SOCl_2$ was distilled from the mixture, remaining $SOCl_2$ was removed, which was washed by absolute benzene (20 mL × 2). The resulting solid was purified by recrystallization from Et_2O. The 1-(4-methoxyphenyl)-5-methyl-1,2,3-triazol-4-carbonyl chloride **5** was obtained.

N,*N*′-Bis(1-(4-methoxyphenyl)-5-methyl-1*H*-1,2,3-triazole-4-carbonyl)hydrazide **6** was Prepared From **5** as Follows

A solution of 10 mmol (85% hydrazine hydrate) in 10 mL of 20% NaOH was added drip to 1-(4-methoxyphenyl)-5-methyl-1,2,3-triazol-4-carbonyl chloride **5** and it was cooled with ice-water. Then, the solution of **5** (about 0.02 mol) and hydrazine hydrate was refluxed for 5 h with stirring. The reaction mixture was cooled and the resulting solid was purified by recrystallization from DMF to give white blocks of compound **6** yield 30.5%, m.p. 282.6 °C. ^{1}HNMR: 10.459 (s, 2H, –NHNH–), 7.526-7.556 (d, 4H, *J* = 8.7 Hz, Ar-2,6), 7.136–7.165 (d, 4H, *J* = 8.7 Hz, Ar-3,5), 3.842 (s, 6H, Ar–OCH_3), 2.507 (s, 6H, TRZ–CH_3). MS m/z: 514 (M^+, FAB). IR: 3343, 3074, 2935, 2836, 1705, 1679, 1639, 1579, 1552, 1516, 1461, 1372, 1350, 1302, 1254, 1174, 1148, 1125, 1034, 1018, 1001, 981, 828, 771, 699, 646, 611, 530, 433.

The purified product was dissolved in DMSO. Crystals were obtained after 60 days by evaporation of the solvent.

A single crystal was selected and mounted on the tip of a glass fiber. Preliminary examination and data collection were performed with MoKα radiation (λ = 0.71073 Å) on a D8 Smart APEX II computer controlled APEX II detector diffractometer operating in the $\omega/2\theta$ scanning mode. The structure was determined by direct methods (SHELXS-97) and refined by full covariance matrix methods (SHELXL-97).

Table 1 Crystal data and summary of data collection and structure refinement

Compound no.	6
CCDC deposition number	616414
Empirical formula	$C_{22}H_{22}N_8O_4$
Color/shape	Colorless/block
Formula weight	462.48
Temperature (K)	294(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Cell dimensions	
a (Å)	15.3451(8)
b (Å)	8.6486(4)
c (Å)	16.8502(9)
α (°)	90
β (°)	95.731(2)
γ (°)	90
Volume (Å^3)	2225.1(2)
Z	4
D_{calc} (g cm^{-3})	1.381
Absorption coefficient (mm^{-1})	0.100
Diffractometer/scan	Smart apex II CCD area detector $\omega/2\theta$
F(000)	968
θ range for data collection (°)	2.43～28.79
Index ranges	$-19 \le h \le 19$ $-11 \le k \le 11$ $-22 \le l \le 15$
Reflections collected	5251
Independent reflection	3784
Data/restrains/parameters	3015/0/312
Extinction coefficient	0.0030(12)
Goodness-of-fit on F^2	0.527
Final R indices [I > 2σ(*I*)]	
R indices	$R_1 = 0.0450$, $wR_2 = 0.1304$ $R_1 = 0.1000$, $wR_2 = 0.1797$
Largest different peak and hole	0.225 and −0.173 eÅ^{-3}

The crystal data and the refinement details are given in Table 1.

The structure of the compound **6** is shown in Fig. 1. 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.

Results and Discussion

The new *N*,*N*′-bis(1-(4-methoxyphenyl)-5-methyl-1*H*-1,2,3-triazole-4-carbonyl)hydrazide **6** has been synthesized

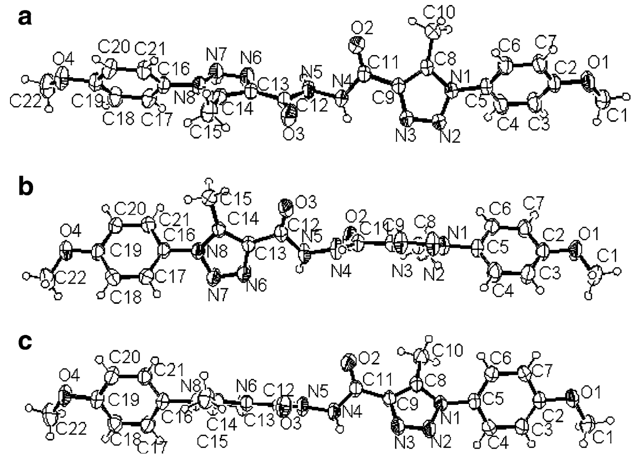


Fig. 1 ORTEP drawing of the compound **6** is showing the atom numbering scheme

from 1-(4-methoxyphenyl)-5-methyl-1,2,3-triazol-4-carboxylic acid **4**. The structure of this compound was characterized with ^{1}HNMR, IR, and MS spectroscopy. IR absorption peaks of **6** at 3373, 3074 cm^{-1} are assigned to its NH and 1679, 1705 cm^{-1} is assigned to its –CO– group. The chemical shift of the triazole ring methyl group show in the range δ2.507 ppm in compound **6**. The chemical shift of the triazole ring Me-proton is in agreement with the values reported for triazole (typical chemical shift of the triazole ring Me-proton is at about δ2.45 ppm in the NMR spectra) by Ykman [9] and (typical chemical shift of the triazole ring Me-proton is at about δ2.26–2.62 ppm in the NMR spectra) (Dong [10]). The crystal structure of **6** agrees with the structure (Fig. 1). The 1,2,3-triazole ring system is planar. The bond lengths N1–N2 1.359(2) Å, N2–N3 1.302(2) Å, N7–N8 1.363(7) Å, N6–N7 1.307(2) Å are in agreement with the values reported for triazole, N1–N2 1.361(5) Å, N2–N3 1.295(5) Å, but the bond lengths of N4–N5 is 1.381(2) Å.

The dihedral angles between 4-methoxyphenyl rings and 1,2,3-triazole rings are 50.1–56.1°[N2–N1–C5–C4—53.0(3), C8–N1–C5–C4—125.0(2), C8–N1–C5–C6—56.1(3), N2–N1–C5–C6—125.9(2)°, C14–N8–C16–C17—127.2(2), N7–N8–C16–C17—50.1(3), C14–N8–C16–C21—55.4(3), N7–N8–C16–C21—127.3(2), C15–N1–C17–C22—134.1(3)°], the 4-methoxyphenyl ring and 1,2,3-triazole ring system is not planar [also see Fig. 1b, c].

The dihedral angles between N4–C11–C9–N3 is −13.0(3)°, bond angles N4–C11–C9 113.73(16); N5–N4–H4 120.3; N4–N5–H5 119.5; N5–N4–H4 120.3; N3–C9–C11 122.87(16); C11–N4–H4 120.3° in ring A, all atom are close to a plane in the A ring system. And so is in ring B, all atoms are close to a plane in the B ring system. The intramolecular hydrogen bond is in the A and B ring system. The bond length of Donor-H···Acceptor is 2.41 Å, the bond angle is 106° [N(4)–H(4)···N(3)], and 2.32 Å, 108° [N(5)–H(5)···N(6)].The structure of the compound **6** is shown in Scheme 2 and Fig. 1.

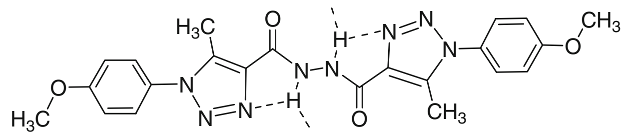
Table 2 Selected bond lengths (Å)

Atoms	Length
O1–C1	1.429(3)
N8–C14	1.354(2)
N8–N7	1.363(2)
N8–C16	1.433(2)
N1–C8	1.357(2)
N1–N2	1.359(2)
N1–C5	1.438(2)
N6–N7	1.302(2)
N6–C13	1.361(3)
O3–C12	1.217(2)
N5–C12	1.348(2)
N5–N4	1.381(2)
C21–C20	1.377(3)
C21–C16	1.391(3)
C2–C7	1.383(3)
C2–C3	1.387(3)
C16–C17	1.378(3)
O4–C19	1.364(2)
O4–C22	1.418(3)
C11–O22	1.215(2)
C11–N4	1.355(2)
C11–C9	1.479(2)
N2–N3	1.307(2)
C12–C13	1.476(2)
C14–C13	1.380(2)
C14–C15	1.483(3)
N3–C9	1.358(2)
C20–C19	1.389(3)
C17–C18	1.388(3)
C19–C18	1.381(3)
C8–C9	1.377(2)
C8–C10	1.485(3)
C5–C4	1.380(3)
C5–C6	1.385(3)
C6–C7	1.382(2)
C3–C4	1.385(3)

The X-ray structure analysis indicated that the compound **6** consisted of two phenyl rings and two triazole ring. The four aromatic rings are approximately linear because the intramolecular hydrogen bond is in the A and B ring system. The most noticeable change is that the signals of imino protons appeared in δ10.459 ppm (1-(4-ethoxyphenyl)-5-methyl-1,2,3-triazol-4-carbonylhydrazine 4.450–4.720 [broad peak, 3H, –NHNH$_2$]) [8].

Table 3 Selected bond angles (°)

Atoms	Angle
C2–O1–C1	117.29(16)
C14–N8–N7	111.15(14)
C14–N8–C16	130.92(15)
N7–N8–C16	117.89(14)
C8–N1–N2	111.54(14)
C8–N1–C5	129.84(15)
N2–N1–C5	118.59(15)
N7–N6–C13	108.91(15)
C12–N5–N4	120.97(17)
C20–C21–C16	119.48(18)
O1–C2–C7	116.36(17)
O1–C2–C3	123.75(18)
C7–C2–C3	119.88(17)
C17–C16–C21	120.61(16)
C17–C16–N8	118.80(16)
C21–C16–N8	120.53(16)
C19–O4–C22	117.74(17)
O2–C11–N4	123.20(17)
O2–C11–C9	123.06(17)
N4–C11–C9	113.73(16)
N3–N2–N1	106.78(14)
O3–C12–N5	124.31(17)
O3–C12–C13	122.91(17)
N5–C12–C13	112.78(17)
N8–C14–C13	103.42(15)
N8–C14–C15	124.17(15)
C13–C14–C15	132.40(16)
N2–N3–C9	108.96(15)
C21–C20–C19	120.32(18)
C16–C17–C18	119.52(18)
O4–C19–C18	124.95(18)
O4–C19–C20	115.24(17)
C18–C19–C20	119.80(17)
N6–C13–C14	109.33(15)
N6–C13–C12	121.32(16)
C14–C13–C12	129.29(17)
C11–N4–N5	119.30(16)
N1–C8–C9	103.09(15)
N1–C8–C10	123.81(16)
C9–C8–C10	132.94(17)
N3–C9–C8	109.61(15)
N3–C9–C11	122.87(16)
C8–C9–C11	127.47(17)
C4–C5–C6	120.75(16)
C4–C5–N1	118.28(16)
C6–C5–N1	120.96(17)
N6–N7–N8	107.19(15)
C19–C18–C17	120.24(18)
C7–C6–C5	119.28(18)
C6–C7–C2	120.42(17)
C4–C3–C2	119.87(19)
C5–C4–C3	119.67(18)



Scheme 2 The hydrogen bonds of title compound

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