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ORIGINAL PAPER

Synthesis and Crystal Structure of (5-Methyl-3-phenyl-1*H*-pyrazol-1-yl)-[5-(*p*-tolylamino)-2*H*-1,2,3-triazol-4-yl]methanone

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Abstract (5-Methyl-3-phenyl-1*H*-pyrazol-1-yl)-[5-(*p*-tolylamino)-2*H*-1,2,3-triazol-4-yl]methanone was synthesized and characterized by ^{1}H NMR, MS and IR spectra data. The structure of title compound was identified by X-ray diffraction. Compound, $C_{20}H_{18}N_6O$, Mr = 358.40, crystallizes in the triclinic space group *P-1* with unit cell parameters $a = 10.303(6)$, $b = 12.489(7)$, $c = 15.305(9)$ Å, $\alpha = 108.489(12)$, $\beta = 101.920(11)$, $\gamma = 96.971(13)°$, $V = 1790.0(17)$ Å^3, $Z = 4$, $Dx = 1.330$ mg/cm^3. The final *R* was 0.0520.

Keywords Pyrazole · Crystal structure · Synthesis · 2*H*-1,2,3-Triazole · 1*H*-1,2,3-Triazole

Introduction

In recent years, 1,2,3-triazole derivatives have been found on a variety of biological activity and outstanding properties in many fields such as pharmacy [1, 2], pesticide [3], material [4], etc. The heterocyclic derivatives containing 1*H*-1,2,3-triazole and pyrazole nucleus had been developing, but they had been studied and reported a little in the literature till now. For this reason, we obtained (5-methyl-3-phenyl-1*H*-pyrazol-1-yl)-[5-(*p*-tolylamino)-2*H*-1,2,3-triazol-4-yl]methanone in reaction of 5-amino-1-*p*-tolyl-2*H*-1,2,3-triazole-4-carboxylic acid hydrazide and 1-phenyl-butane-1,3-dione. The route of synthesis is shown in Scheme 1.

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Experimental Section

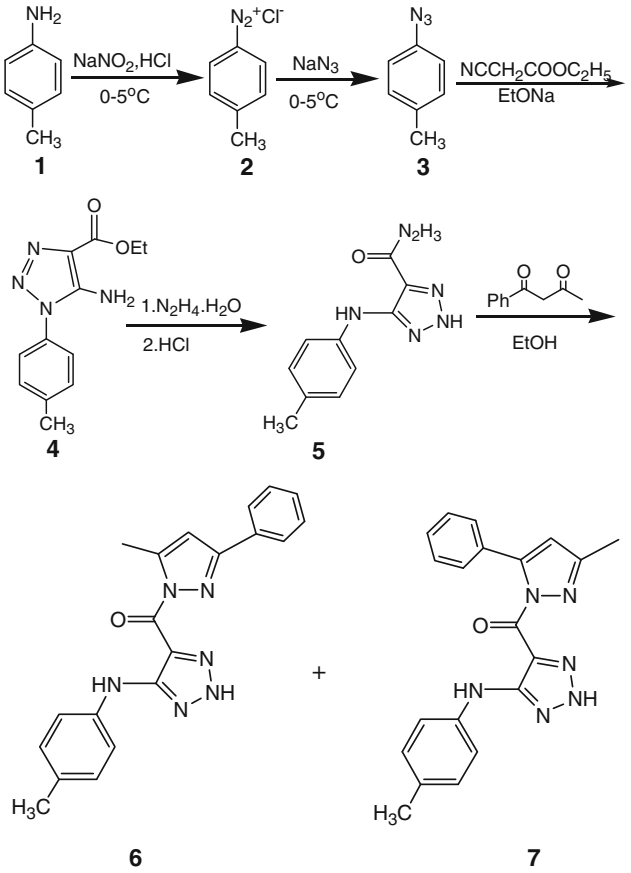
Melting points were determined on an XT4-100X microscopic melting point apparatus (uncorrected). IR spectra were obtained in KBr pellets on a Nicolet 170SX FT-IR spectrometer. The mass spectrum was performed on a HP-5988A spectrometer (EI at 70 eV). ^{1}H NMR spectroscopy was recorded at Varian Mercury Plus-300NMR instrument with TMS as an internal standard.

Preparation of Ethyl 5-Amino-1-*p*-tolyl-1*H*-1,2,3-triazol-4-carboxylate **4**

Preparation of ethyl 5-amino-1-*p*-tolyl-1*H*-1,2,3-triazol-4-carboxylate **4** was following method in the literature [5].

Synthesis of 5-(*p*-Tolylamino)-2*H*-1,2,3-triazol-4-carbohydrazide **5**

To add ethyl 5-amino-1-*p*-tolyl-1*H*-1,2,3-triazol-4-carboxylate **4** (0.003 mol) and hydrazine hydrate (0.012 mol) in a 100 mL flask, the mixture was heated at 80 °C for 1 h and refluxed in EtOH (25 mL) for 5 h. After it was cooled to room temperature and the solid was filtered. The filtrate was neutralized with diluted HCl, and the precipitated solid was filtered and dried. Compound **5**, 5-(*p*-tolylamino)-2*H*-1,2,3-triazol-4-carbohydrazide was given. Yield 35%, mp 199–200 °C, IR υ_{max}: 3388, 3356, 3325, 3304, 3118 (b, NH or NH_2), 3032, 2966(m, Ar-H), 2914(m, CH_3), 1641(s, C=O), 1599(C=N), 1549, 1514(s, Ar), 981(m, triazole ring)cm^{-1}; ^{1}HNMR(DMSO) δ_H: 2.241(s, 3H, CH_3),



Scheme 1 The synthesis route of title compound

7.091–7.118(d, 2H, $J = 8.1$ Hz, *p*-MeC_6H_4-H), 7.386–7.413(d, 2H, $J = 8.1$ Hz, *p*-MeC_6H_4-H)ppm; MS m/z: 232($M^{+\cdot}$, 100%), 233(M + 1,14), 217(1), 201(39), 188(1), 175(9), 173(16), 158(9), 146(28), 145(18), 133(9), 118(24), 106(11), 91(93), 77(26), 65(55), 51(19), 44(33), 39(24).

Synthesis of (5-Methyl-3-phenyl-1*H*-pyrazol-1-yl)-[5-(*p*-tolylamino)-2*H*-1,2,3-triazol-4-yl]methanone **6** and (3-Methyl-5-phenyl-1*H*-pyrazol-1-yl)-[5-(*p*-tolylamino)-2*H*-1,2,3-triazol-4-yl]methanone **7**

To add 5-*p*-tolylamino-2*H*-1,2,3-triazol-4-carboxylic acid hydrazide **5** (0.003 mol), 1-phenyl-butane-1,3-dione (0.003 mol) and EtOH (25 mL) in a 100 mL flask. The mixture was controlled at 80 °C till completely dissolved and refluxed for 4 h. It was cooled to room temperature and the solid was filtered, washed with a cool anhydrous ethanol and dried. The solid was separated by chromatographic column (silica gel, eluent for ethyl acetate:petroleum ether = 1:6). Compounds **6** and **7** were given.

(5-Methyl-3-phenyl-1*H*-pyrazol-1-yl)-[5-(*p*-tolylamino)-2*H*-1,2,3-triazol-4-yl]methanone **6**. Yield 39%, mp 170–171 °C, IR υ_{max}: 3437, 3348(b, NH), 3106(Ar–H), 2922(w, CH_3), 1661(s, C=O), 1607(C=N), 1570, 1510, 1448, 1408(s, Ar), 1261(m, C=N–N), 945(w, N=N–N)cm^{-1}; ^1H NMR($CDCl_3$) δ_H: 2.341(s, 3H, CH_3), 2.782(s, 3H, CH_3); 6.616(s, 1H, CH), 7.173–7.200(d, 2H, $J = 8.1$ Hz, *p*-MeC_6H_4-H), 7.636–7.663(d, 2H, $J = 8.1$ Hz, *p*-MeC_6H_4-H), 7.495–7.519(m, 3H, Ph-H), 7.825–7.851(d, 2H, Ph-H), 8.382(b, 1H, NH)ppm; MS m/z: 358($M^{+\cdot}$, 27%), 359(M + 1, 6), 330(7), 301(7), 212(4), 196(6), 184(6), 172(4), 159(100), 144(12), 128(17), 117(63), 107(12), 91(78), 77(47), 65(38), 57(30), 51(25), 43(27), 39(16).

(3-Methyl-5-phenyl-1*H*-pyrazol-1-yl)-[5-(*p*-tolylamino)-2*H*-1,2,3-triazol-4-yl)methanone **7**. Yield 34%, mp 179–180 °C, IR υ_{max}: 3359(b, triazole-NH), 3210, 3135 (b, N–H···O=C), 2919(w, CH_3), 1668(s, C=O), 1613(C=N), 1570, 1512, 1444, 1409(s, Ar), 1275(b, C=N–N), 973(m,

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

Compound	$C_{20}H_{18}N_6O$
CCDC deposit no.	635047
Color	Light yellow
Formula weight	358.40
Temperature, °C	21(294 K)
Crystal system	Triclinic
Space group	*P-1*
Unit-cell dimensions	$a = 10.303(6)$ Å; $b = 12.489(7)$ Å; $c = 15.305(9)$ Å; $\alpha = 108.489(12)°$; $\beta = 101.920(11)°$; $\gamma = 96.971(13)°$
Volume (Å^3)	1790.0(17)
Z	4
D_{calc}, g cm^{-3}	1.330
$F(000)$	752
Absorption coefficient, mm^{-1}	0.087
Diffractometer/scan	Enraf-Nonius CAD4, $\omega/2\theta$
Radiation/λ	$k\alpha$ (graphite monochromator)/ 0.71073 Å
θ_{min}, θ_{max} (°)	1.84–25.75
Reflections measured	3055
Independent/observed reflections	4648
Data/restraints/ parameters	6529/0/492
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.011
Shift/su_max	0.000
Final R indices	$R_1 = 0.0520$, $WR_2 = 0.1489$
R indices[$I > 2\sigma(I)$]	$R_1 = 0.0760$, $WR_2 = 0.1714$
Extinction coefficient	0.0067(13)
Largest diff. peak and hole	0.512 and −0.413 e Å^{-3}

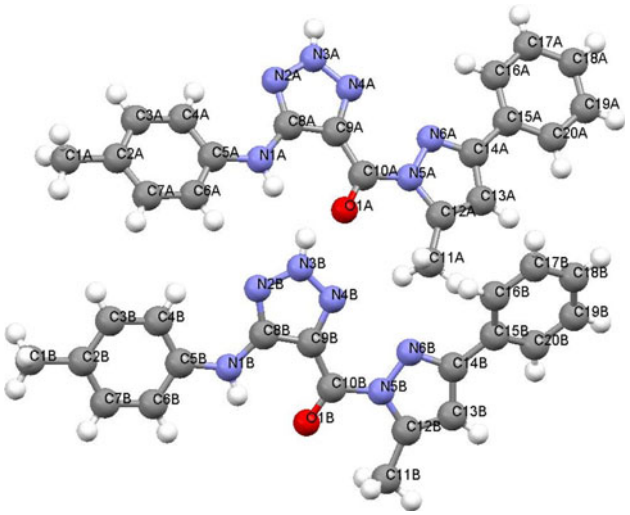


Fig. 1 Mercury view (CCDC, 2005) of the molecular structure for the title compound **6** showing the atom numbering scheme

N=N–N)cm^{-1}; ^{1}HNMR($CDCl_3$) δ_H: 2.305(s, 3H, CH_3), 2.444(s, 3H, CH_3), 6.324(s, 1H, CH), 7.114–7.142(d, 2H, $J = 8.4$ Hz, *p*-MeC_6H_4-H), 7.549–7.577(d, 2H, $J = 8.4$, *p*-MeC_6H_4-H), 7.475(s, 5H, Ph-H), 8.161(b, 1H, NH)ppm; MS m/z: 358(M ‡, 7.5%), 359(M + 1, 1), 330(1), 301(1), 246(2), 232(5), 219(3), 188(2), 158(52), 145(15), 117(26), 111(21), 97(31), 91(61), 77(43), 69(60), 65(32), 57(100), 51(25), 43(94), 39(22).

The purified product (5-methyl-3-phenyl-1*H*-pyrazol-1-yl)-[5-(*p*-tolylamino)-2*H*-1,2,3-triazol-4-yl]methanone **6** was dissolved in a mixture solvent of ethyl acetate and petroleum ether. Crystals were grown by especially slow evaporation of the solvent from this solution. The yellow needlelike crystals were produced in 2 weeks.

Crystal Structure Determinations and Refinement

Single crystals were selected and mounted on the tip of a glass fiber. Preliminary examination and data collection were performed with Mo Kα radiation ($\lambda = 0.71073$ Å) on a Bruker SMART CCD area detector 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). The crystal data, data collection and the refinement parameter for the structure are given in Table 1.

The structure of the title compound **6** is shown in Fig. 1. The H-bond of the title compound **6** is shown in Fig. 2. Selected bond lengths, angles and dihedral angles are given in Tables 2, 3, and 4. The geometric calculations were performed using the program SHELX-97.

Table 2 Selected bond lengths (Å) (of the molecule A)

Atoms	Length	Atoms	Length
N1–C5	1.400(3)	C9–C8	1.388(3)
N1–C8	1.371(3)	O1–C10	1.221(2)
N4–C9	1.370(3)	N5–C10	1.393(3)
N4–N3	1.319(3)	N5–N6	1.380(2)
N2–N3	1.325(3)	N6–C14	1.324(3)
N2–C8	1.354(3)	N5–C12	1.391(3)

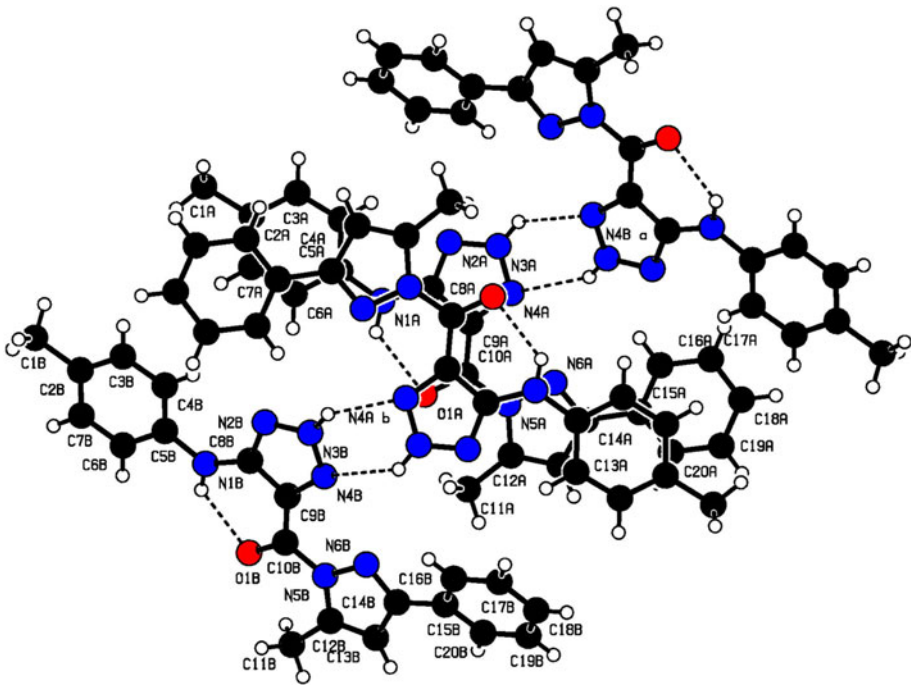


Fig. 2 The H-bond structure of the compound **6** (PWT drawing for the Platon)

Table 3 Selected bond angles (°) (of the molecule A)

Atoms	Angle	Atoms	Angle
C4–C5–N1	124.4(2)	N5–C12–C11	124.6(2)
C6–C5–N1	117.6(2)	N6–C14–C15	121.4(2)
N1–C8–C9	124.9(2)	N6–C14–C13	110.9(2)
N2–C8–C9	109.64(19)	C8–N1–C5	129.95(19)
N2–C8–N1	125.5(2)	N3–N2–C8	106.83(18)
N4–C9–C8	103.50(18)	N4–N3–N2	109.87(18)
N4–C9–C10	130.51(19)	N3–N4–C9	110.15(18)
N5–C10–C9	119.61(19)	C12–N5–C10	127.73(18)
O1–C10–C9	119.9(2)	N6–N5–C12	111.65(17)
O1–C10–N5	120.51(19)	N6–N5–C10	120.60(17)
C13–C12–N5	105.3(2)	C14–N6–N5	104.65(17)

Table 4 Selected dihedral angles (°) (of the molecule A)

Atoms	Angle	Atoms	Angle
C8–N1–C5–C6	−171.5(2)	N6–N5–C10–O1	178.71(19)
C8–N1–C5–C4	8.7(4)	C12–N5–C10–O1	0.2(3)
C5–N1–C8–N2	−0.4(4)	N6–N5–C10–C9	−1.2(3)
C5–N1–C8–C9	178.2(2)	C12–N5–C10–C9	−179.8(2)
N4–C9–C10–O1	176.3(2)	N6–C14–C15–C16	−0.6(3)
C8–C9–C10–O1	−3.9(3)	C13–C14–C15–C16	179.8(2)
N4–C9–C10–N5	−3.8(3)	N6–C14–C15–C20	178.9(2)
C8–C9–C10–N5	176.08(19)	C13–C14–C15–C20	−0.7(3)

Results and Discussion

The structure of the title compound **6** is shown in Fig. 1. In recent years, the synthesis and characteristics of 5-amino-1-(4-chlorophenyl)-1,2,3-triazol-4-yl and 5-methyl-1-(4-methylphenyl)-1,2,3-triazol-4-yl derivatives have been investigated [6–8]. These heterocyclic compounds contain 1,2,3-triazole ring, and they were a series stable compounds. In order to continue our studies, we now report the crystal structure of (5-methyl-3-phenyl-1*H*-pyrazol-1-yl)-[5-(*p*-tolylamino)-2*H*-1,2,3-triazol-4-yl]-methanone. 5-*p*-tolylamino-2*H*-1,2,3-triazol-4-carboxylic acid hydrazide **5** was one Dirmorth rearrangement [9–11] product by ethyl 5-amino-1-*p*-tolyl-1*H*-1,2,3-triazole-4-carboxylate and hydrazine hydrate.

Identified as a pyrazole compound showing ^{1}HNMR $\delta_{(\text{comp.}\mathbf{7},\text{CH})} = 6.324$ ppm and $\delta_{(\text{comp.}\mathbf{6},\ \text{CH})} = 6.616$ ppm, the chemical shift value is basic agreement with the value(6.44 ppm) reported for pyrazole ring [12]. The bond lengths is more agreement with [N1–N2 1.361(5) Å; N2–N3 1.295(5) Å] in 1,2,3-triazole ring [13]. The all plane of ring system are basically on the plane in title comp. **6** (in the molecule labeled with suffix A), because there is the conjugate of the л–л. It is shown in Table 4 selected dihedral angles.

In the crystal structure, there is an intra-molecular N1A–H···O1A (N1B–H···O1B) hydrogen bond involving the N–H atom and itself of molecular C=O [N1A–H 0.86 H···O1A 2.14 N1A–H···O1A 2.784(3) Å, N1A–H···O1A 131°; N1B–H 0.86 H···O1B 2.16 N1B–H···O1B 2.799(3) Å, N1B–H···O1B 131°] [14]. There is two intermolecular hydrogen bond (N3A–H···N4B; N3B–H···N4A) involving the N–H atom and other molecular triazole ring 4 positions N [N3A–H 0.86 H···N4B 2.54 N3A–H···N4B 3.156(3) Å, N3A–H···N4B 129°; N3B–H 0.86 H···N4A 2.30 N3B–H···N4A 3.046(3) Å, N3B–H···N4A 146°]. **A** view of H-bond structure for the title compound **6** is show in Fig. 2.

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References

1. Olessen PH, Sørensen AR, Ursø B, Kurtzhals P, Bowler AN, Ehrbar U, Hansen BF (2003) J Med Chem 46:3333
2. Cunha AC, Figueiredo JM, Tributino JLM, Miranda ALP, Castro HC, Zingali RB, Fraga CAM, Souza MCBV, Ferreirac VF, Barreiro EJ (2003) Bioorg Med Chem 11:2051
3. Stefan D European Patent Application EP 423566
4. Hoyen AH Jr Canadian Patent CA1258396 (CA 112:66622)
5. Dornow A, Helberg J (1960) Chem Ber 93:2001
6. Dong H-S, Quan B, Zhu D-W (2002) J Mol Struct 613:1
7. Zhang Z-Y, Dong H-S, Zhu Y (1996) Acta Chim Sin 54:1054
8. Dong H-S, Quan B (2000) J Mol Struct 553:31–36
9. Dirmoth O (1909) Ann 364,183:212
10. Labbe G (1990) Bull Soc Chim Belg 99:281
11. Labbe G, Essche GV, Delbeke P, Toppet S (1990) Bull Soc Chim Belg 99:833
12. Lokshin ASV, Vales M, Elguero J (2006) J Org Chem 71:6881
13. Olesen PH, Nielsen FE, Pedersen EB, Becher J (1984) J Heterocycl Chem 21:1603
14. Spek AL (2003) J Appl Cryst 36:7–13