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ORIGINAL PAPER

Synthesis and Crystal Structure of 3-Methyl-4-phenyl-5-(2-pyridyl)-1,2,4-triazole

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Abstract The title compound, 3-methyl-4-phenyl-5-(2-pyridyl)-1,2,4-triazole was synthesized by reaction of diphenylphosphazoanilide with *N*-acetyl-*N*′-(2-pyridoyl) hydrazine. Crystals suitable for X-ray analysis were obtained from a mixed solution of water and ethanol in a one-to-one volume ratio. The crystal is orthorhombic, space group $P2_12_12_1$ with crystallographic parameters: $a = 19.414(4)$ Å, $b = 17.172(3)$ Å, $c = 7.4850(15)$ Å, $\beta = 90.00°$, $\mu = 0.079\ \mathrm{mm}^{-1}$, $V = 2495.3(8)$ Å^3, $Z = 8$, $\mathrm{Dc} = 1.258\ \mathrm{g/cm}^3$, $F(000) = 992$, $T = 295(2)$ K. The X-ray results showed that in the crystal structure of the title compound, the 1,2,4-triazole, pyridine and benzene rings are not coplanar.

Keywords 1,2,4-Triazole · Pyridine · Benzene ring · $\pi \cdots \pi$ Interaction

Introduction

The coordination chemistry of substituted 1,2,4-triazoles has gained considerable attention in recent years [1–6]. This arises, in part, because they can form complexes with transition-metal ions, and some of them exhibit spin crossover behavior, which can be used potentially in molecular-based memory devices, displays and optical switches [7–11].

1,2,4-triazoles with pyridine substituents are compounds that have been known for many years and are widely used in coordination chemistry. The first synthesized representative of this group of compounds was 3,5-di(4-pyridyl)-1,2,4-triazole, obtained by the deamination of 4-amino-3,5-di(4-pyridyl)-1,2,4-triazole [12]. A series of complexes have been synthesized by the use of pyridyl-1,2,4-triazoles. For example, the complexes $[\mathrm{Ni}^{\mathrm{II}}_2(\mathrm{NH_2dpt})_2\mathrm{Cl}_2(\mathrm{H_2O})_2]\mathrm{Cl}_2\cdot 4\mathrm{H_2O}$ [13], $[\mathrm{Cu}^{\mathrm{II}}(\mathrm{NH_2dpt})_2(\mathrm{H_2O})](\mathrm{HSO_4})_2$ [14], $[\mathrm{Ag}^{\mathrm{I}}(\mathrm{mpdpt})(\mathrm{pph_3})_2]\mathrm{ClO_4}$ [15], and $[\mathrm{Cu}^{\mathrm{II}}(\mathrm{emppt})_2](\mathrm{ClO_4})_2$ [16] have been described in the literature. In order to synthesize and examine the novel complexes of transition-metal ions with pyridyl-1,2,4-triazoles, the title compound was synthesized by reaction of diphenylphosphazoanilide with *N*-acetyl-*N*′-(2-pyridoyl)hydrazine in *N*,*N*-dimethylaniline at 463–473 K as shown in Scheme 1. The objective product was characterized by ^{1}HNMR, IR and MS, and its crystal structure was determined by X-ray analysis.

Experimental

Materials and Physical Measurements

The *N*-acetyl-*N*′-(2-pyridoyl)hydrazine and diphenylphosphazoanilide were synthesized according to literature methods [17, 18]. All other solvents and reagents were of analytical grade and were used without further purification. IR spectra in the range 4,000–400 cm^{-1} were obtained from samples in the form of KBr pellets using a Nicolet

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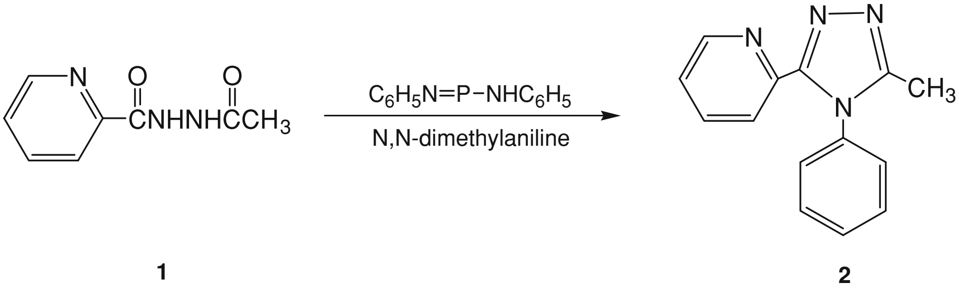

Scheme 1 Synthesis of compound 2

550 infrared spectrometer. MS spectra were recorded with a VG ZAB-HS mass spectrometer. Proton NMR spectra were obtained at 500 MHz on Bruker spectrometer in $CDCl_3$. Melting points were determined by using a RY-1 melting point apparatus.

Synthesis of 3-Methyl-4-phenyl-5-(2-pyridyl)-1,2,4-triazole (**2**)

To a solution of diphenylphosphazoanilide (8.6 g, 40 mmol) in anhydrous *N*,*N*-dimethylaniline (40 mL) under stirring was added *N*-acetyl-*N*′-(2-pyridoyl)hydrazine (7.2 g, 40 mmol). The mixture was heated under reflux at 463–473 K for 3 h, and the solvent was removed under reduced pressure. The residue was then added to a mixture of water (20 mL) and concentrated hydrochloric acid (10 mL) and was hydrolyzed under reflux for 1 h. The mixture was filtered, and K_2CO_3 was added to the filtrate until the pH reached 8–9. The solid substance separated out, and the crude product was recrystallized from acetone. White crystals (4.7 g, 20 mmol) were obtained. Yield: 50%. M.pt: 104–106 °C. MS, m/z: 237.1 $[M + H]^+$; 236.1 $[M]^+$; 235.1 $[M-H]^+$. IR (KBr, cm^{-1}): 3,048; 1,591; 1,498; 1,444; 1,380. ^1H NMR ($CDCl_3$, 500 MHz; δ): 2.37 (s, 3H, $-CH_3$); 7.18–7.49 (m, 5H, $-C_6H_5$); 7.50–8.30 (m, 4H, $-C_5H_4N$).

The colorless single crystal of compound **2** was grown from a mixed solution of water and ethanol in a one-to-one volume ratio by slow evaporation at room temperature.

X-Ray Crystallography

A single crystal of the title compound with dimensions 0.30 × 0.25 × 0.20 mm was chosen for X-ray diffraction study. The data were collected on a Enraf-Nonius CAD-4 diffractometer equipped with graphite-monochromatic Mo-Kα radiation ($\lambda = 0.71073$ Å) by using an ω scan mode at 295(2) K. In the range of $1.58° < \theta < 26.54°$, a total of 3,081 reflections were collected, of which 2,879 were independent ($R_{\text{int}} = 0.0251$) and 1,150 were observed with $I > 2\sigma(I)$.

The structure was solved by direct methods with SHELXS-97 [19]. Non-hydrogen atoms were refined by full-matrix least-squares techniques on F^2 with anisotropic thermal parameters, using SHELXL-97 [20]. All H atoms were located in a difference Fourier map and allowed to ride on their parent atoms at distances of 0.93 Å (C–H aromatic) and 0.96 Å (C–H methyl), with U_{iso}(H) values of 1.2–1.5 times U_{eq} of the parent atoms. The final full-matrix least-squares refinement gave $R = 0.0699$, $wR = 0.1961$ for 1,150 reflections with $I > 2\sigma(I)$; the weighting scheme, $w = 1/[\sigma^2(F_O^2) + (0.1480P)^2]$, where $P = (F_O^2 + 2F_C^2)/3$. The maximum and minimum difference peaks and holes are 0.256 and −0.268 e Å^{-3}, respectively. $S = 0.986$ and $(\Delta/\sigma)_{\max} = 0.000$. The crystal data and refinement details are listed in Table 1. The selected bond lengths and bond angles are listed in Table 2.

Results and Discussion

The title compound crystallized in the orthorhombic system, space group $P2_12_12_1$ with unit cell parameters: $a = 19.414(4)$ Å, $b = 17.172(3)$ Å, $c = 7.4850(15)$ Å, $\beta = 90.00°$, $\mu = 0.079$ mm^{-1}, $V = 2495.3(8)$ Å^3, $Z = 8$, Dc = 1.258 g/cm^3, $F(000) = 992$, $T = 295(2)$ *K*. The molecular structure of compound **2** is shown in Fig. 1 and a perspective view of the crystal packing in the unit cell is shown in Fig. 2.

There are three aromatic rings in the structure of compound **2**, namely 1,2,4-triazole, pyridine and benzene. None are coplanar. The dihedral angle between the 1,2,4-triazole and pyridine rings is 16.56°, and that between the 1,2,4-triazole and benzene rings is 80.05°.

In the five-membered triazole ring, the interatomic distances of N(2)–C(6) (1.303(8) Å) and N(3)–C(7) (1.316(9) Å) are shorter than typical carbon–nitrogen single bonds (1.336–1.416 Å) [21], suggesting that they have substantial double bond character. There is a little difference between the bond lengths of N(2)–C(6) and N(3)–C(7) due to the asymmetry of the 1,2,4-triazole ring, which is in accordance with the fact that the three substituents of triazole are different. The bond lengths of N(4)–C(6) (1.374(8) Å), N(4)–C(7) (1.354(8) Å) and N(2)–N(3) (1.399(9) Å) correspond to the typical carbon–nitrogen

Table 1 Crystallographic data and structure refinement details

CCDC deposit number	701445
Empirical formula	$C_{14}H_{12}N_4$
Formula weight	236.28
Temperature (K)	295 (2)
Wavelength (Å)	0.71073
Crystal size (mm)	0.30 × 0.25 × 0.20
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a (Å)	19.414 (4)
b (Å)	17.172 (3)
c (Å)	7.4850 (15)
α (°)	90.00
β (°)	90.00
γ (°)	90.00
V (Å^3)	2495.3 (8)
Z	8
D_{ca} (g cm^{-3})	1.258
F (000)	992
Absorption coeff. (mm^{-1})	0.079
θ range (°)	1.58–26.54
Index ranges	$0 \leq h \leq 23$; $0 \leq k \leq 20$; $-8 \leq l \leq 0$
Reflections collected	3,081
Independent reflections	2,879 [$R_{int} = 0.0251$]
Observed reflections	1,150
Data/restraints/parameters	2,879/0/326
Goodness-of-fit on F^2	0.986
R, wR indices [$I > 2\sigma(I)$]	0.0699, 0.1961
R, wR indices (all data)	0.2161, 0.2730
Largest diff. peak and hole (e Å^{-3})	0.256, −0.268

Table 2 Selected bond lengths (Å) and angles (°)

Bond lengths			
N(1)–C(1)	1.334(9)	C(3)–C(4)	1.393(13)
N(1)–C(5)	1.336(8)	C(4)–C(5)	1.367(10)
N(2)–C(6)	1.303(8)	C(5)–C(6)	1.497(10)
N(2)–N(3)	1.399(9)	C(7)–C(8)	1.485(10)
N(3)–C(7)	1.316(9)	C(9)–C(14)	1.367(12)
N(4)–C(7)	1.354(8)	C(9)–C(10)	1.433(12)
N(4)–C(6)	1.374(8)	C(10)–C(11)	1.388(11)
N(4)–C(9)	1.439(8)	C(11)–C(12)	1.390(16)
C(1)–C(2)	1.356(10)	C(12)–C(13)	1.418(17)
C(2)–C(3)	1.401(11)	C(13)–C(14)	1.370(12)
Bond angles			
C(1)–N(1)–C(5)	115.7(7)	N(2)–C(6)–C(5)	122.7(7)
C(6)–N(2)–N(3)	105.9(6)	N(4)–C(6)–C(5)	125.8(6)
C(7)–N(3)–N(2)	107.5(6)	N(3)–C(7)–N(4)	110.5(7)
C(7)–N(4)–C(6)	104.3(5)	N(3)–C(7)–C(8)	125.2(7)
C(7)–N(4)–C(9)	124.5(6)	N(4)–C(7)–C(8)	124.1(6)
C(6)–N(4)–C(9)	131.0(6)	C(14)–C(9)–C(10)	122.9(7)
N(1)–C(1)–C(2)	126.7(8)	C(14)–C(9)–N(4)	120.2(9)
C(1)–C(2)–C(3)	116.8(9)	C(10)–C(9)–N(4)	116.9(8)
C(4)–C(3)–C(2)	117.6(9)	C(11)–C(10)–C(9)	116.2(9)
C(5)–C(4)–C(3)	120.0(8)	C(10)–C(11)–C(12)	121.1(10)
N(1)–C(5)–C(4)	123.0(7)	C(11)–C(12)–C(13)	120.9(7)
N(1)–C(5)–C(6)	118.1(6)	C(14)–C(13)–C(12)	118.7(11)
C(4)–C(5)–C(6)	118.6(7)	C(9)–C(14)–C(13)	120.3(11)
N(2)–C(6)–N(4)	111.5(7)		

single bonds (1.336–1.416 Å) and nitrogen–nitrogen single bonds (1.366–1.454 Å) [21], respectively.

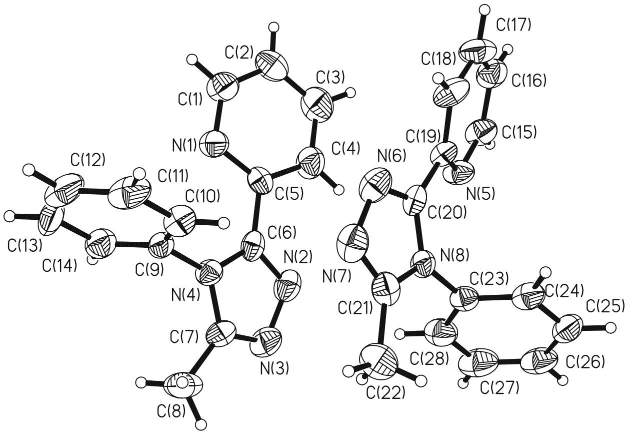

Fig. 1 The two symmetry-independent molecular structures of 3-methyl-4-phenyl-5-(2-pyridyl)-1,2,4-triazole; 50% probability *ellipsoids* are shown

$\pi\cdots\pi$ Interactions are important noncovalent intermolecular forces. There are two different patterns of the stacked arrangements in general aromatic systems for $\pi\cdots\pi$ interactions: offset face-to-face and edge-to-face packing. The distance between aromatic ring centroids with the range of 3.2–3.8 Å is the valid value of $\pi\cdots\pi$ interactions in the offset face-to-face stacking. Likewise, that between hydrogen atom and aromatic ring centriod with the range of 2.0–3.5 Å is the valid value of $\pi\cdots\pi$ interactions in the edge-to-face stacking [22]. In the crystal, molecules of compound **2** are stabilized by weak offset face-to-face $\pi\cdots\pi$ interactions and edge-to-face $\pi\cdots\pi$ interactions. The distance between ring centroids of Cg1 [Cg1 is the five-membered triazole ring (N2, N3, C7, N4, C6) with symmetry code: x, y, z] and Cg2 [Cg2 is the five-membered triazole ring (N6, N7, C21, N8, C20) with symmetry code: x, y, $-1 + z$] is 3.646 Å. The perpendicular distance between Cg1 and Cg2 is 3.606 Å, and the angle between the ring-centroid vector and the perpendicular vector of two-five-membered triazole planes is about 8.5°. The bond lengths of H18A$\cdots$Cg3 [Cg3 is the six-membered pyridine ring (N1, C1, C2, C3, C4, C5) with symmetry code: x, y,

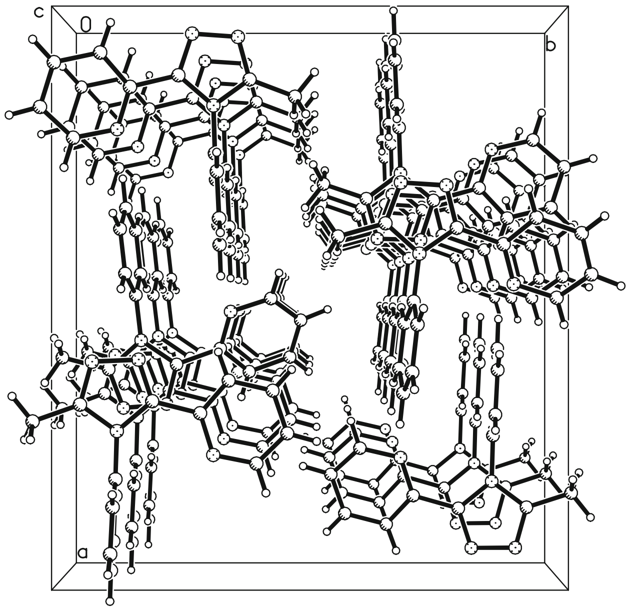

Fig. 2 Packing of the molecules viewed along the *c* axis

$1 + z$], H3B···Cg4 [Cg4 is the six-membered pyridine ring (N5, C15, C16, C17, C18, C19) with symmetry code: x, y, z], H25B···Cg5 [Cg5 is the six-membered benzene ring (C9, C10, C11, C12, C13, C14) with symmetry code: $-1/2 + x$, $1/2 - y$, $1 - z$] and H13A···Cg6 [Cg6 is the six-membered benzene ring (C23, C24, C25, C26, C27, C28) with symmetry code: $1/2 + x$, $1/2 - y$, $-z$] correspond to 2.946, 3.117, 3.358 and 3.320 Å, respectively.

Supplementary Material

CCDC-701445 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

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