DE GRUYTER Heterocycl. Commun. 2014; 20(4): 201–206

Xin He, Bin Li, Lang Chen, Xuan Shen and Dun-Ru Zhu*

# Synthesis and crystal structural characterization of two new 3,5-disubstituted 4-amino-1,2,4-triazoles

**Abstract:** Two new asymmetrical 3-(*p*-R-phenyl)-4-amino-5-(2-pyridyl)-1,2,4-triazoles (**3a**, R = $CH_3$ and **3b**, R = $OCH_3$) were synthesized with a yield of 58% and 69%, respectively. The compounds **3a** and **3b** were characterized with FT-IR, $^1H$ NMR, ESI-MS spectra, and elemental analysis. Additionally, their molecular and crystal structures were determined by single crystal X-ray analysis.

**Keywords:** 4-amino-1,2,4-triazole; crystal structure; hydrazine; synthesis.

DOI 10.1515/hc-2014-0079
Received May 6, 2014; accepted May 27, 2014; previously published online July 3, 2014

## Introduction

During the past five decades, substituted 1,2,4-triazoles have aroused wide interest because of their anti-inflammatory, antitumor, fungicide, and herbicide properties [1]. Substituted 1,2,4-triazoles and their derivatives are also useful ligands in coordination chemistry due to their rich and versatile coordination modes [2–4]. In addition, some iron(II) complexes containing substituted 1,2,4-triazoles possess fascinating spin crossover properties which can be applied as molecular-based electronics, displays, and switching materials [5–10].

Recently, a series of symmetrical and asymmetrical 3,5-disubstituted 1,2,4-triazoles have been successfully prepared by our group [11–18] and others [3, 8]. However, the asymmetrical 3,5-disubstituted 4-amino-1,2,4-triazoles remain largely unexplored. As a continuation of our investigation on substituted 4-amino-1,2,4-triazoles [19, 20], in this article, we present synthesis of two new asymmetrical 3,5-disubstituted 4-amino-1,2,4-triazoles, namely 3-(*p*-R-phenyl)-4-amino-5-(2-pyridyl)-1,2,4-triazoles **3a** (R = $CH_3$) and **3b** (R = $OCH_3$) (Scheme 1). Compounds **3a** and **3b** were characterized by FT-IR, $^1H$ NMR, ESI-MS spectra, elemental analysis, and single crystal X-ray diffraction. For the purpose of comparison, a known homologous compound, **3c** (R = Cl), is also discussed [21].

## Results and discussion

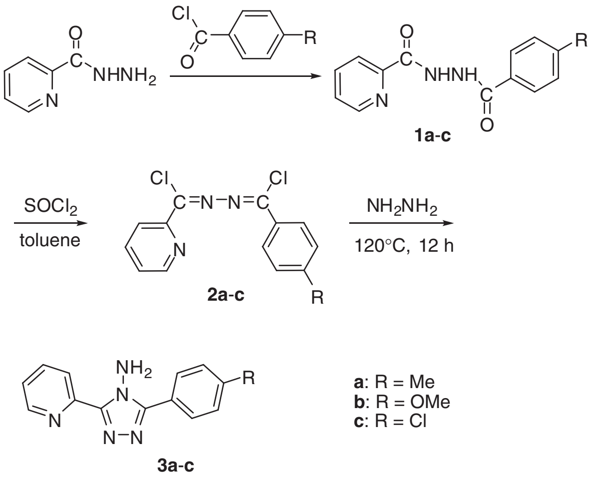
Synthesis of 3,4,5-trisubstituted 1,2,4-triazoles has recently been reviewed [22]. In general, there are three types of methods reported for the preparation of 3,4,5-trisubstituted 1,2,4-triazoles [23]. One of these methods was chosen for the synthesis of our target compounds – 3,5-disubstituted 4-amino-1,2,4-triazoles **3a**–**c**. Compounds **3a**,**b** are new and synthesis of **3c** has been previously published [21].

*N*-(*p*-R-phenylcarbonyl)-*N′*-(2-pyridylcarbonyl)hydrazines **1a**–**c** were obtained in a yield of 81%, 79%, and 82%, respectively, by stirring pyridine-2-carbonylhydrazine with the corresponding benzoyl chloride in anhydrous pyridine at ambient temperature [24]. Then, 1,4-dichloro-1-(2-pyridyl)-4-(*p*-R-phenyl)-2,3-diaza-1,3-butadienes **2a**–**c** were obtained by stirring **1** with thionyl chloride in dried toluene with the respective yield of 68%, 69%, and 72% [25]. Finally, the cyclization reaction of **2a,b** with anhydrous hydrazine conducted at 120°C for 12 h produced **3a**,**b** with a yield of 58% and 69%, respectively. Synthesis of the known compound **3c** in a 47% yield has previously been reported [21].

New compounds **3a**,**b** were characterized by FT-IR, $^1H$ NMR, ESI-MS, and elemental analysis. The molecular structures of **3a,b** were also confirmed by X-ray crystallography (Table 1). Single crystals of **3a** and **3b** suitable

---

***Corresponding author: Dun-Ru Zhu,** College of Chemistry and Chemical Engineering, State Key Laboratory of Materials-oriented Chemical Engineering, Nanjing Tech University, Nanjing 210009, P.R. China, e-mail: zhudr@njtech.edu.cn
**Xin He, Bin Li, Lang Chen and Xuan Shen:** College of Chemistry and Chemical Engineering, State Key Laboratory of Materials-oriented Chemical Engineering, Nanjing Tech University, Nanjing 210009, P.R. China



**Scheme 1** Synthesis of 3,5-disubstituted 4-amino-1,2,4-triazoles **3a–c**.

**Table 2** Selected bond lengths (Å) and angles (°) for **3a,b**.

| **3a** | | **3b** | |
|---|---|---|---|
| N1-C5 | 1.338(2) | N1-C5 | 1.332(4) |
| N2-N3 | 1.372(2) | N2-N3 | 1.365(4) |
| N4-N5 | 1.419(2) | N4-N5 | 1.407(4) |
| C11-C14 | 1.508(3) | O1-C11 | 1.361(4) |
| N1-C1 | 1.338(2) | N1-C1 | 1.324(4) |
| C6-N2-N3 | 108.2(1) | C6-N2-N3 | 107.9(2) |
| C6-C5-N1 | 118.6(2) | C6-C5-N1 | 118.8(2) |
| C7-N4-C6 | 106.2(1) | C7-N4-C6 | 105.5(3) |
| N5-N4-C7 | 124.8(2) | N5-N4-C7 | 124.3(2) |
| C10-C11-C14 | 121.7(2) | C11-O1-C14 | 118.4(3) |

for X-ray diffraction study were obtained upon slow concentration of ethanol solution at ambient temperature. The crystal structure of **3c** has been previously published

**Table 1** Crystallographic data for **3a–c.**

| **Compound** | **3a** | **3b** | **3c [21]** |
|---|---|---|---|
| Empirical formula | $C_{14}H_{13}N_5$ | $C_{14}H_{13}N_5O$ | $C_{13}H_{10}N_5Cl$ |
| Formula weight | 251.29 | 267.29 | 271.71 |
| Crystal system | Triclinic | Triclinic | Monoclinic |
| Space group | $P\bar{1}$ | $P\bar{1}$ | $C2/c$ |
| $a$ (Å) | 6.2709(10) | 6.183(10) | 28.68(7) |
| $b$ (Å) | 7.0252(12) | 7.245(12) | 6.041(16) |
| $c$ (Å) | 14.572(2) | 14.77(2) | 14.68(4) |
| $\alpha$ (°) | 86.277(2) | 76.816(17) | 90.00 |
| $\beta$ (°) | 84.922(2) | 85.501(18) | 103.90(3) |
| $\gamma$ (°) | 72.728(2) | 73.507(18) | 90.00 |
| $V$ (Å$^3$) | 610.09(17) | 617.7(17) | 2470(11) |
| $Z$ | 2 | 2 | 8 |
| $D_c$ (g·cm$^{-3}$) | 1.368 | 1.437 | 1.462 |
| $\mu$ (mm$^{-1}$) | 0.088 | 0.097 | 0.302 |
| $F$(000) | 264 | 280 | 1120 |
| Crystal size (mm) | 0.24 × 0.16 × 0.10 | 0.14 × 0.10 × 0.06 | 0.16 × 0.12 × 0.10 |
| $\theta$ Range | 1.40–25.00 | 1.42–25.00 | 1.46–25.00 |
| Reflections collected | 4295 | 4277 | 8203 |
| Independent reflections | 2125 [$R_{int}$ = 0.0174] | 2128 [$R_{int}$ = 0.0184] | 2175 [$R_{int}$ = 0.0757] |
| Reflections observed [$I>2\sigma(I)$] | 1607 | 1817 | 1436 |
| Data/restraints/parameters | 2125/3/180 | 2128/4/188 | 2175/3/178 |
| Goodness-of-fit on $F^2$ | 1.067 | 1.095 | 1.071 |
| $R/wR$ [$I>2\sigma(I)$] | 0.0449/0.1234 | 0.0594/0.1852 | 0.0682/0.1834 |
| $R/wR$ (all data) | 0.0624/0.1324 | 0.0675/0.1897 | 0.1027/0.1985 |
| Max., Min. $\Delta\rho$ (e·Å$^{-3}$) | 0.227, -0.221 | 0.397, -0.377 | 0.801, -0.280 |

Note: data of **3c** are given for comparison.

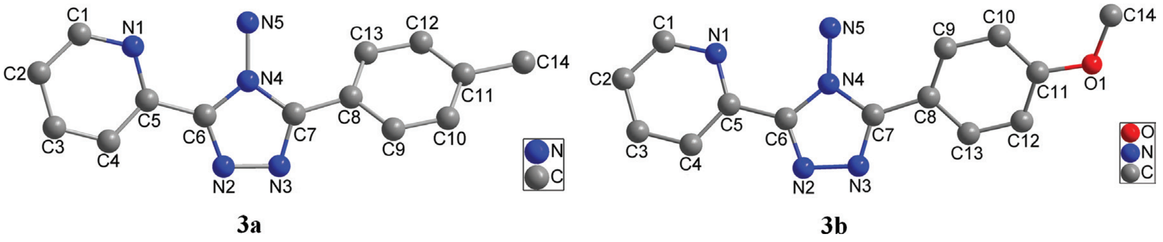


**Figure 1** Views of **3a** and **3b** showing the atom-numbering scheme. Hydrogen atoms are omitted for clarity.

**Table 3** The interplanar angles (°) for **3a**,**b**.

| Compound | Py/Trz | $CH_3$-Ph/Trz | $CH_3O$-Ph/Trz |
|---|---|---|---|
| **3a** | 2.0(1) | 30.2(1) | |
| **3b** | 7.1(1) | | 30.9(1) |

[21]. The crystal structures of **3a**,**b** with an atom-labeling scheme are shown in Figure 1, and selected bond lengths and bond angles are listed in Table 2. The X-ray crystallography analysis indicates that both **3a** and **3b** crystallize in the triclinic space group $P\bar{1}$, which is different from the

**Table 4** The hydrogen bonds, C-H···π and π···π interactions (Å, °) in **3a**,**b**.

| Compound | D-H···A | d(D-H)/Å | d(H···A)/Å | d(D···A)/Å | ∠D-H···A/° |
|---|---|---|---|---|---|
| **3a** | C1$^{v}$-H1A$^{v}$···N5 | 0.93 | 2.70 | 3.420(2) | 135 |
| | C4-H4A···N2$^{i}$ | 0.93 | 2.82 | 3.394(2) | 121 |
| | N5-H5A···N1 | 0.89 | 2.15 | 2.908(2) | 142 |
| | N5-H5B···N2$^{ii}$ | 0.88 | 2.41 | 3.106(2) | 137 |
| | C14-H14C···π (C8-C13)$^{iii}$ | 0.96 | 2.98 | 3.656(2) | 128 |
| | π···π interaction | | cent···cent (Å) | | Dihedral angle (°) |
| | π (Py) ···π (Trz)$^{iv}$ | | 3.687(2) | | 1.9 |
| **3b** | C1$^{viii}$-H1A$^{viii}$···N5 | 0.93 | 2.76 | 3.378(6) | 124 |
| | C2$^{vi}$-H2A$^{vi}$···O1 | 0.93 | 2.62 | 3.533(6) | 168 |
| | N5-H5B···N1 | 0.85 | 2.27 | 2.902(5) | 131 |
| | C14-H14A···π (C8-C13)$^{vii}$ | 0.96 | 3.29 | 3.927(5) | 126 |

Symmetry codes: (i) -*x*, 1-*y*, 2-*z*; (ii) 1+*x*, *y*, *z*; (iii) 2-*x*, -*y*, 1-*z*; (iv) 1-*x*, -*y*, 2-*z*; (v) 2-*x*, -*y*, 2-*z*; (vi) *x*, *y*-1, 1+*z*; (vii) 2-*x*, -1-*y*, 2-*z*; (viii) 2-*x*, -*y*, 1-*z*.

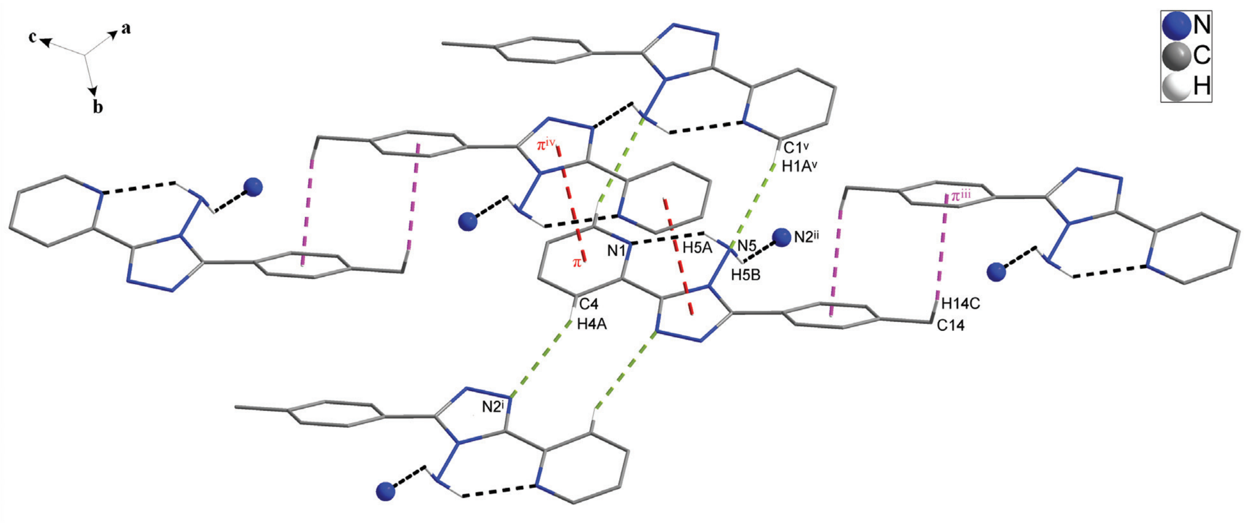


**Figure 2** View of the crystal packing for **3a** showing hydrogen bonds, C-H···π and π···π interactions.

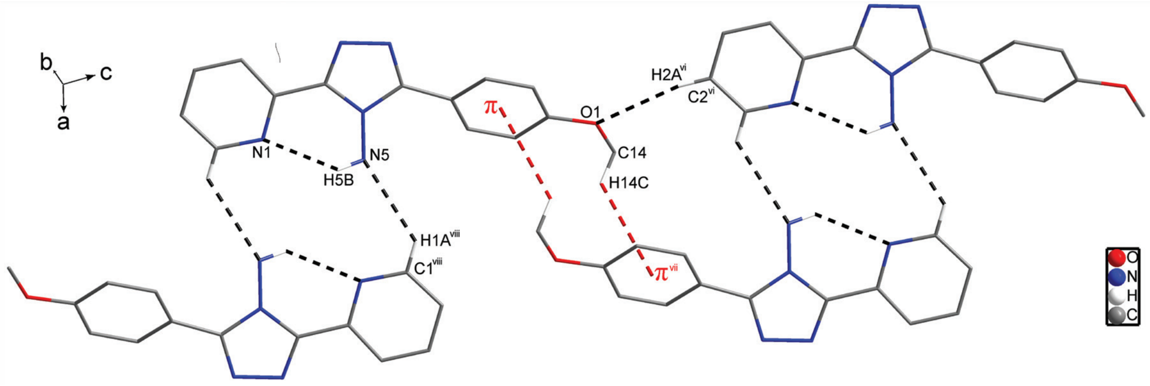


**Figure 3** View of the crystal packing for **3b** showing hydrogen bonds and C-H···π interactions.

homologous compound **3c** (*C*2/c). The central 1,2,4-triazole in **3a** is oriented at interplanar angles of 2.0(1)° and 30.2(1)° with respect to the pyridyl ring and the *p*-methylphenyl ring, respectively. Similarly, the central 1,2,4-triazole ring in **3b** is oriented at interplanar angles of 7.1(1)° and 30.9(1)° with respect to the pyridyl ring and the *p*-methoxyphenyl ring, respectively (Table 3). In addition, the N atom of the pyridyl group is oriented towards the amino group on the N4 position in both **3a** and **3b**. This feature is similar to that of the related substituted 4-amino-1,2,4-triazoles compounds [19, 20]. The bond lengths and bond angles of **3a** and **3b** are similar and in normal ranges [23, 26, 27]. The hydrogen bonds, a C-H$\cdots\pi$ interaction and a non-bonding $\pi\cdots\pi$ interaction in these compounds are given in Table 4. These interactions stabilize the crystal packing of **3a** and **3b**. The crystal packing diagrams of **3a** and **3b** are shown in Figures 2 and 3, respectively.

# Experimental

Melting points were determined on an X-4 digital microscope melting-point apparatus (Beijing) and are uncorrected. FT-IR spectra were recorded on a Nicolet 380 FT-IR instrument using KBr disks. $^1$H NMR spectra were measured on a Bruker AM 500 MHz spectrometer at ambient temperature in DMSO-$d_6$ for **1** and **2** but in $CDCl_3$ for **3**. Electrospray ionization mass spectra (ESI-MS) were recorded on an LCQ ADVANTAGE MAX mass spectrometer. The spray voltage, the capillary voltage, and the capillary temperature were 4 kV, 40 V, and 260°C, respectively. Elemental analyses were carried out with a Thermo Finnigan Flash 1112A elemental analyzer. All chemicals were of analytical grade and used as received. Toluene was freshly distilled from Na/benzophenone, whereas pyridine was distilled over NaOH. Pyridine-2-carbonylhydrazine was prepared according to a previously reported method [23].

## Preparation of *N*-(*p*-R-phenylcarbonyl)-*N′*-(2-pyridylcarbonyl)hydrazines 1a–c

A suspension of the corresponding *p*-substituted benzoyl chloride (48 mmol) in anhydrous pyridine (10 mL) was added dropwise to a stirred solution of pyridine-2-carbonylhydrazine (5.49 g, 40 mmol) in dichloromethane (80 mL) at 0°C. The mixture was stirred for 8 h at ambient temperature and then poured into 80 mL of ice water. The resultant precipitate was filtered, dried *in vacuo*, and crystallized from anhydrous ethanol to give **1a**–**c** as a white solid.

***N*-(*p*-Methylphenylcarbonyl)-*N′*-(2-pyridylcarbonyl)hydrazine (1a)** Yield 81%; mp 182–184°C; IR: 3189, 3010, 2922, 1674, 1633, 1607, 1500, 1280, 1114, 836, 743 cm$^{-1}$; $^1$H NMR: δ 2.44 (3H, s, $CH_3$), 7.13 (2H, d, *J* = 8 Hz, ArH), 7.54 (1H, dd, $J_1$ = 5 Hz, $J_2$ = 2 Hz, PyH), 8.01–8.05 (3H, m, PyH, ArH), 8.20 (1H, d, *J* = 8 Hz, PyH), 8.63 (1H, d, *J* = 5 Hz, PyH), 10.48 (1H, s, NH), 10.51 (1H, s, NH). Anal. Calcd for $C_{14}H_{13}N_3O_2$: C, 65.87; H, 5.13; N, 16.46. Found: C, 65.73; H, 5.31; N, 16.67.

***N*-(*p*-Methoxyphenylcarbonyl)-*N′*-(2-pyridylcarbonyl)hydrazine (1b)** Yield 79%; mp 154–156°C (lit. mp 153–155°C [22]); IR: 3285, 3021, 2964, 1703, 1642, 1610, 1566, 1508, 1488, 1303, 1260, 1026, 998 cm$^{-1}$; $^1$H NMR: δ 3.88 (3H, s, $CH_3$), 7.19 (2H, d, *J* = 8 Hz, ArH), 7.65 (1H, dd, $J_1$ = 5 Hz, $J_2$ = 2 Hz, PyH), 8.05–8.09 (3H, m, PyH, ArH), 8.25 (1H, d, *J* = 8 Hz, PyH), 8.80 (1H, d, *J* = 5 Hz, PyH), 10.51 (1H, s, NH), 10.53 (1H, s, NH). Anal. Calcd for $C_{14}H_{13}N_3O_3$: C, 61.99; H, 4.83; N, 15.49. Found: C, 61.82; H, 4.71; N, 15.77.

***N*-(*p*-Chlorophenylcarbonyl)-*N′*-(2-pyridylcarbonyl)hydrazine (1c)** Yield 82%; mp 179–181°C; IR: 3177, 3007, 1688, 1642, 1597, 1570, 1513, 1488, 1334, 1092, 1016, 844 cm$^{-1}$; $^1$H NMR: δ 7.62 (2H, d, *J* = 8 Hz, ArH), 7.68 (1H, dd, $J_1$ = 5 Hz, $J_2$ = 2 Hz, PyH), 7.94 (2H, d, *J* = 8 Hz, ArH), 8.05 (2H, m, PyH), 8.72 (1H, d, *J* = 5 Hz, PyH), 10.63 (1H, s, NH), 10.67 (1H, s, NH). Anal. Calcd for $C_{13}H_{10}N_3O_2Cl$: C, 56.64; H, 3.66; N, 15.24. Found: C, 56.42; H, 3.54; N, 15.39.

## Preparation of 1,4-dichloro-1-(2-pyridyl)-4-(*p*-R-phenyl)-2,3-diaza-1,3-butadienes 2a–c

A solution of thionyl chloride (5 mL) in anhydrous toluene (10 mL) was added dropwise to a stirred solution of **1** (16 mmol) in anhydrous toluene (50 mL). The mixture was heated under reflux for 8 h at 120°C and then the solvent was removed under reduced pressure. The residue was crystallized from ethanol to give **2** as colorless crystals.

**1,4-Dichloro-1-(2-pyridyl)-4-(*p*-methylphenyl)-2,3-diaza-1,3-butadiene (2a)** Yield 68%; mp 156–158°C; IR: 3054, 2993, 1613, 1588, 1556, 1494, 1458, 1443, 1247, 1183, 1079, 824, 743, 728 cm$^{-1}$; $^1$H NMR: δ 2.45 (3H, s, $CH_3$), 7.32–7.34 (2H, d, *J* = 8 Hz, ArH), 7.47 (1H, dd, $J_1$ = 5 Hz, $J_2$ = 2 Hz, PyH), 7.85 (1H, m, PyH), 8.09 (2H, d, *J* = 7 Hz, ArH), 8.32 (1H, d, *J* = 8 Hz, PyH), 8.72 (1H, d, *J* = 5 Hz, PyH). Anal. Calcd for $C_{14}H_{11}N_3Cl_2$: C, 57.55; H, 3.79; N, 14.38. Found: C, 57.31; H, 3.43; N, 14.49.

**1,4-Dichloro-1-(2-pyridyl)-4-(*p*-methoxyphenyl)-2,3-diaza-1,3-butadiene (2b)** Yield 69%; mp 152–154°C; IR: 3052, 2978, 1615, 1585, 1498, 1458, 1443, 1268, 1176, 1085, 1019, 832, 790, 741 cm$^{-1}$; $^1$H NMR: δ 3.85 (3H, s, $CH_3$), 7.02 (2H, d, *J* = 8 Hz, ArH), 7.45 (1H, dd, $J_1$ = 5 Hz, $J_2$ = 2 Hz, PyH), 7.83 (1H, m, PyH), 8.14 (2H, d, *J* = 8 Hz, ArH), 8.31 (1H, d, *J* = 8 Hz, PyH), 8.61 (1H, d, *J* = 5 Hz, PyH). Anal. Calcd for $C_{14}H_{11}N_3Cl_2O$: C, 54.57; H, 3.60; N, 13.64. Found: C, 54.36; H, 3.45; N, 13.41.

**1,4-Dichloro-1-(2-pyridyl)-4-(*p*-chlorophenyl)-2,3-diaza-1,3-butadiene (2c)** Yield 72%; mp 146–148°C; IR: 1605, 1586, 1553, 1479, 1463, 1442, 1275, 1151, 1090, 835, 794, 731 cm$^{-1}$; $^1$H NMR: δ 7.45 (1H, dd, $J_1$ = 5 Hz, $J_2$ = 2 Hz, PyH), 7.50 (2H, d, *J* = 8 Hz, ArH), 7.92 (1H, m, PyH), 8.16 (2H, d, *J* = 8 Hz, ArH), 8.32 (1H, d, *J* = 8 Hz, PyH), 8.82 (1H, d, *J* = 5 Hz, PyH). Anal. Calcd for $C_{13}H_8N_3Cl_3$: C, 49.95; H, 2.58; N, 13.44. Found: C, 49.66; H, 2.32; N, 13.68.

## Preparation of 3-(*p*-R-phenyl)-4-amino-5-(2-pyridyl)-1,2,4-triazoles 3a–c

A mixture of **2** (2 mmol) and anhydrous hydrazine (2 mL) was sealed in a 25 mL Teflon-lined stainless steel reactor and heated for 12 h at 120°C and then cooled to ambient temperature. The precipitate was filtered, washed with deionized water, and crystallized from anhydrous ethanol to give **3** as colorless crystals.

**3-(*p*-Methylphenyl)-4-amino-5-(2-pyridyl)-1,2,4-triazole (3a)** Yield 58%; mp 205–207°C; IR: 3345, 3272, 3193, 1640, 1591, 1472, 1422, 1284, 1151, 1034, 993, 961, 818, 786, 728, 696, 583 cm$^{-1}$; $^1$H NMR: δ 2.42 (3H, s, CH$_3$), 6.45 (2H, br, NH$_2$), 7.30 (2H, d, $J = 9$ Hz, ArH), 7.36 (1H, dd, $J_1 = 5$ Hz, $J_2 = 2$ Hz, PyH), 7.85 (1H, m, PyH), 8.08 (2H, d, $J = 9$ Hz, ArH), 8.36 (1H, d, $J = 7$ Hz, PyH), 8.62 (1H, d, $J = 5$ Hz, PyH); ESI-MS: *m/z* 252.25 (M+H)$^+$. Anal. Calcd for $C_{14}H_{13}N_5$: C, 66.92; H, 5.21; N, 27.87. Found: C, 66.76; H, 5.05; N, 27.99.

**3-(*p*-Methoxyphenyl)-4-amino-5-(2-pyridyl)-1,2,4-triazole (3b)** Yield 69%; mp 194–195°C; IR: 3342, 3278, 3157, 2993, 2833, 1611, 1582, 1488, 1441, 1247, 1188, 1035, 972, 840, 737, 696, 594 cm$^{-1}$; $^1$H NMR: δ 3.86 (3H, s, CH$_3$), 6.44 (2H, br, NH$_2$), 6.99 (2H, d, $J = 9$ Hz, ArH), 7.35 (1H, dd, $J_1 = 5$ Hz, $J_2 = 2$ Hz, PyH), 7.84 (1H, m, PyH), 8.14 (2H, d, $J = 9$ Hz, ArH), 8.32 (1H, d, $J = 7$ Hz, PyH), 8.61 (1H, d, $J = 5$ Hz, PyH); ESI-MS: *m/z* 268.3 (M+H)$^+$. Anal. Calcd for $C_{14}H_{13}N_5O$: C, 62.91; H, 4.90; N, 26.20. Found: C, 62.74; H, 4.78; N, 26.31.

**3-(*p*-Chlorophenyl)-4-amino-5-(2-pyridyl)-1,2,4-triazole (3c)** See reference [21].

**Single-crystal X-ray diffraction analysis of 3a and 3b** The single crystals of **3a** and **3b** were selected for lattice parameter determination and collection of intensity data at 296 K on a Bruker SMART CCD diffractometer with a detector distance of 5 cm and frame exposure time of 10 s using a graphite-monochromated Mo-$K_\alpha$ ($\lambda = 0.71073$ Å) radiation. The structures were solved by direct methods and refined on $F^2$ by full-matrix least squares procedures using SHELXTL software [28]. All non-hydrogen atoms were anisotropically refined. The H atoms were placed on calculated positions (C-H 0.96 Å) and assigned isotropic thermal parameters riding on their parent atoms; the H atoms of -NH$_2$ were located from difference Fourier maps and refined isotropically. Details on crystal data of **3a** and **3b** are summarized in Table 1.

CCDC 983076 (**3a**) and 983077 (**3b**) contain the supplementary crystallographic data for this article. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Acknowledgments:** This work was funded by the National Natural Science Foundation of China (nos. 20771059, 21171093).

## References

[1] Potts, K. T. The chemistry of 1,2,4-triazoles. *Chem. Rev.* **1961**, *61*, 87–127.

[2] Haasnoot, J. G. Mononuclear, oligonuclear and polynuclear metal coordination compounds with 1,2,4-triazole derivatives as ligands. *Coord. Chem. Rev.* **2000**, *200–202*, 131–185.

[3] Klingele, M. H.; Brooker, S. The coordination chemistry of 4-substituted 3,5-di(2-pyridyl) -4*H*-1,2,4-triazoles and related ligands. *Coord. Chem. Rev.* **2003**, *241*, 119–132.

[4] Beckmann, U.; Brooker, S. Cobalt(II) complexes of pyridazine or triazole containing ligands: spin-state control. *Coord. Chem. Rev.* **2003**, *245*, 17–29.

[5] Kahn, O.; Martinez, C. J. Spin-transition polymers: from molecular materials toward memory devices. *Science* **1998**, *279*, 44–48.

[6] Zhu, D.; Xu, Y.; Yu, Z.; Guo, Z.; Sang, H.; Liu, T.; You, X. A novel bis(*trans*-thiocyanate)iron(II) spin-transition molecular material with bidentate triaryltriazole ligands and its bis(*cis*-thiocyanate)iron(II) high-spin isomer. *Chem. Mater.* **2002**, *14*, 838–843.

[7] van Koningsbruggen, P. J. Special classes of iron(II) azole spin crossover compounds. *Top. Curr. Chem.* **2004**, *233*, 123–149.

[8] Kitchen, J. A.; Brooker, S. Spin crossover in iron(II) complexes of 3,5-di(2-pyridyl)-1,2,4-triazoles and 3,5-di(2-pyridyl)-1,2,4-triazolates. *Coord. Chem. Rev.* **2008**, *252*, 2072–2092.

[9] Malcolm, A. H. Structure: function relationships in molecular spin-crossover complexes. *Chem. Soc. Rev.* **2011**, *40*, 4119–4142.

[10] Shen, G. P.; Qi, L.; Wang, L.; Xu, Y.; Jiang, J. J.; Zhu, D.; Liu, X. Q.; You, X. Spin-crossover in a *trans*-[FeL$_2$(NCS)$_2$] family (L = triaryltriazole): remote substituent effects on spin transition modes and temperature. *J. Chem. Soc. Dalton. Trans.* **2013**, *42*, 10144–10152.

[11] Zhu, D. R.; Song, Y.; Xu, Y.; Zhang, Y.; Raj, S. S. S.; Fun, H. K.; You, X. Z. Syntheses, crystal structures and properties of the novel Co(II) and Ni(II) complexes with 4-(*p*-methylphenyl)-3,5-bis(pyridin-2-yl)-1,2,4-triazole. *Polyhedron* **2000**, *19*, 2019–2025.

[12] Zhu, D. R.; Xu, Y.; Zhang, Y.; Wang, T. W.; You, X. Z. 4-Phenyl-3,5-bis(2-pyridyl)-4H-1,2,4-triazole. *Acta Crystallogr.* **2000**, *C56*, 895–896.

[13] Zhu, D.; Xu, Y.; Mei, Y.; Shi, Y.; Tu, C.; You, X. Crystal and molecular structure of a novel complex [Mn(MOBPT)(H$_2$O)$_2$(NCS)$_2$] (MOBPT = 4-(*p*-methoxyphenyl)-3,5-bis(pyridin-2-yl)-1,2,4-triazole). *J. Mol. Struct.* **2001**, *559*, 119–125.

[14] Zhou, J.; Yang, J.; Qi, L.; Shen, X.; Zhu, D.; Xu, Y.; Song, Y. Synthesis, crystal structure and magnetic property of the novel dinuclear nickel(II) complex with 4-(*p*-methoxyphenyl)-3,5-bis(pyridine-2-yl)-1,2,4-triazole. *Transition Met. Chem.* **2007**, *32*, 711–715.

[15] Yang, J.; Bao, W. W.; Ren, X. M.; Xu, Y.; Shen, X.; Zhu, D. R. Synthesis, crystal structure, and magnetism of a dinuclear nickel(II) complex [Ni$_2$(MOBPT)$_2$(N$_3$)$_4$]·2H$_2$O. *J. Coord. Chem.* **2009**, *62*, 1809–1816.

[16] Chen, L.; Cheng, H. M.; Jiang, J. J.; Shen, X.; Zhu, D. R. Synthesis, crystal structure and thermal stability of [CuL$_2$(ClO$_4$)$_2$] (L = 3-(*p*-bromophenyl)-4-(*p*-methylphenyl)-5-(2-pyridyl)-1,2,4-triazole). *Chinese J. Inorg. Chem.* **2012**, *28*, 381–385.

[17] Lu, W.; Zhu, D. R.; Xu, Y.; Cheng, H. M.; Zhao, J.; Shen, X. Syntheses and crystal structures of two novel Cu(II) and Co(II) complexes with 3-methyl-4-(*p*-bromophenyl) -5-(2-pyridyl)-1,2,4-triazole. *Struct. Chem.* **2010**, *21*, 237–244.

[18] Zhao, J.; Cheng, H. M.; Shen, G. P.; Xu, Y.; Zhu, D. R. Syntheses, crystal structures, and spectral properties of Mn(II) and Co(II) complexes with 3-(*p*-chlorophenyl)-4-(*p*-methylphenyl)-5-(2-pyridyl)-1,2,4-triazole. *J. Coord. Chem.* **2011**, *64*, 942–951.

[19] Shen, G. P.; Jiang, J. J.; Sun, F.; Shen, X.; Zhu, D. R.; Liu, X. Q. Syntheses, crystal structures, and spectral characterization of

two novel quinolyl substituted triazoles. *J. Heterocycl. Chem*. **2013**, *50*, 1152–1156.

[20] Gong, J.; He, X.; Chen, L.; Shen, X.; Zhu, D. Syntheses, crystal structures, and spectral characterization of an asymmetrically substituted 1,2,4-triazole and its iron(II) complex. *J. Coord. Chem*. **2013**, *66*, 2875–2884.

[21] Wang, L.; Jiang, J. J.; Chen, L.; Shen, X.; Zhu, D. R. Coexistence of two distinct axial ligands and their thermo-induced substitution in *trans*-$[FeL_2(NCS)_2][FeL_2(CH_3OH)_2](NCS)_2$ (L = 4-amino-3-(*p*-chlorophenyl)-5-(2-pyridy1)-1,2,4-triazole). *Inorg. Chem. Commun*. **2013**, *28*, 104–108.

[22] Moulin, A.; Bibian, M.; Blayo, A. L.; Habnouni, S. E.; Martinez, J.; Fehrentz, J. A. Synthesis of 3,4,5-trisubstituted-1,2,4-triazoles. *Chem. Rev.* **2010**, *110*, 1809–1827.

[23] Zhao, J.; Shen, G. P.; Zhang, Y.; Shen X.; Zhu, D. R. Syntheses, crystal structures, and spectral characterization of three new asymmetrical substituted triaryltriazoles. *J. Heterocycl. Chem*. **2012**, *49*, 1114–1119.

[24] Hua, G.; Li, Y.; Fuller, A. L.; Slawin, A. M. Z.; Woollins, J. D. Facile synthesis and structure of novel 2,5-disubstituted 1,3,4-selenadiazoles. *Eur. J. Org. Chem*. **2009**, *10*, 1612–1618.

[25] Gautun, O. R.; Carisen, P. H. Synthesis of bis($\alpha$-alkylaminobenzylidene)hydrazines and their transformation into 4-alky-4H-1,2,4-triazoles. *Acta Chem. Scand*. **1991**, *45*, 609–615.

[26] Jiang, J. J.; Shen, G. P.; He, X.; Shen, X.; Zhu, D. R. One-pot synthesis of a 3,4,5-triaryltriazole from the subsitituted 1,3,4-oxadiazole: crystal structures characterization. *J. Heterocycl. Chem.*, **2014**, http://dx.doi.org/10.1002/jhet.1894.

[27] Cheng, H. M.; Zhu, D. R.; Lu, W.; Xu, R. H.; Shen, X. Synthesis and crystal structure characterization of 3,5-bis(2-quinolyl)-1,2,4-triazole. *J. Heterocycl. Chem*. **2010**, *47*, 210–213.

[28] Sheldrick, G. M. A short history of SHELX. *Acta Crystallogr*. **2008**, *A64*, 112–122.