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Synthesis and Crystal Structure of Aromatic Hydrazone Compounds Containing Pyrazole

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Abstract Two novel aromatic hydrazone compounds containing pyrazole group were synthesized with 1-phenylpyrazole-4-carbaldehyde and benzene hydrazine (or *p*-tolylhydrazine hydrochloride) as the starting materials. As-synthesized aromatic hydrazone compounds were characterized by means of ¹H NMR, FT-IR, Ms and singlecrystal X-ray diffraction. Results shown that two aromatic hydrazone compounds crystallizes in the monoclinic system of space group *P21/n* for **A** and *Pc* for **B** respectively.

Keywords Aromatic hydrazone · Pyrazole · Synthesis · Crystal structure · Characterization

Introduction

As a kind of heterocyclic compounds which possessed special physiological and pharmacological activities, such as antibacterial, antispasmodic, diminish inflammation, regulating plant growth and antiplatelet agglomeration etc., pyrazole derivatives play an important role in

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medicine and pesticide, and have been widely used in biology, medicine and plant protectant [1–4]. Furthermore, the excellent photoelectric properties and carrier transmission capacity of pyrazole derivatives add to their wide use in photoelectric functional materials and organic lightemitting diodes (OLED) [5, 6]. On the other hand, due to the high ionization potential (6-7 eV), aromatic hydrazone compounds have been developed into a kind of important hole-transporting materials and have been widely used in organic photoconductors [7]. At the same time, with strong antibacterial and antiviral ability, aromatic hydrazone compounds have been widely used in biology, medicine, metallurgy, dye and metal ion recognition fields [8-11]. Therefore, research of pyrazole based on hydrazone compounds also appear more and more important and valuable.

Experiments

Physical Measurement and Materials

Mass spectra (MS) were determined with an Agilent 1100LC-MS mass spectrometer. Infrared (IR) spectra of as-obtained products within 400–4,000 cm⁻¹ were recorded with a Nicolet 170 SXFT-IR spectrometer (mixed with KBr and pressed into pellets). Nuclear magnetic resonance (¹H NMR) spectra in DMSO– d_6 solvent were recorded with an INOVA-400 spectrometer in the presence of tetramethylsilane as an internal standard. Intensity data were collected on Bruker Apex II CCD detector.

All chemicals and solvents are of commercial reagent grade and used without further purification. And 1-phenylpyrazole-4-carbaldehyde was prepared according to procedures available elsewhere [12].

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Item	Α	В
CCDC deposit no.	881887	872015
Empirical formula	C ₁₇ H ₁₅ ClN ₄	$C_{19}H_{20}N_4$
Formula weight	310.78	304.39
Temperature (K)	296(2)	296(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	P 21/n	Pc
a (Å)	11.9469(10)	13.354(5)
<i>b</i> (Å)	10.1199(8)	5.8568(19)
c (Å)	13.8481(11)	11.650(4)
α (°)	90	90
β (°)	114.2910(10)	113.512(6)
γ (°)	90	90
Ζ	4	2
Density(calculated) (g cm^{-1})	1.353	1.210
<i>F</i> (000)	648	324
Crystal size (mm ³)	$0.69 \times 0.58 \times 0.36$	$0.62 \times 0.45 \times 0.29$
θ range for data collection (°)	1.90–25.00	1.66–25.00
Limiting indices	$-13 \le h \le 14, -12 \le k \le 9, -14 \le l \le 16$	$-15 \le h \le 13, -5 \le k \le 6, -13 \le l \le 13$
Reflections collected/unique	$7515/2683 \ [R_{(int)} = 0.0193]$	$4033/2539 \ [R_{(int)} = 0.0240]$
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	2683/0/201	2539/2/212
Goodness-of-fit on F^2	1.069	1.058
Volume (Å ³)	1526.0(2)	835.5(5)
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0315, wR_2 = 0.0826$	$R_1 = 0.0341, wR_2 = 0.0893$
R indices (all data)	$R_1 = 0.0372, wR_2 = 0.0854$	$R_1 = 0.0390, wR_2 = 0.0929$
Largest diff. peak and hole (e $Å^{-3}$)	0.200 and -0.225	0.144 and -0.124

 Table 1 Crystallographic data and structural refinements of A and B



 $\mathbf{A} \ \mathsf{R}_1 = \mathsf{Cl}; \ \mathsf{R}_2 = \mathsf{H}; \quad \mathbf{B} \ \mathsf{R}_1 = \mathsf{CH}_3; \ \mathsf{R}_2 = \mathsf{CH}_3$

Fig. 1 The synthesis of aromatic hydrazone compounds

Synthesis of Aromatic Hydrazone Compounds

5 mmol 1-phenylpyrazole-4-carbaldehyde and 5 mmol benzene hydrazine or *p*-tolylhydrazine hydrochloride were completely dissolved in 35 mL methanol, heated to 80 °C, reflowed 2 h, cooled to room temperature and placed overnight. After suction filtered and dried, crude mixed products were obtained follow purified by recrystallizing in the mixed solvent of EtOH and CH₂Cl₂ (V_{EtOH} : $V_{\text{CH}_2\text{Cl}_2} = 1:3$). While

the single crystal specimens of A and B were acquired via slow evaporation of their ethanol solutions at room temperature.

5-Chloro-3-methyl-1-phenyl-4-((2phenylhydrazono)methyl)-1H-pyrazole (A)

Deep yellow solid 0.70 g, yield 45 %. APCI-MS (m/z, M⁺):311.1. ¹H NMR (DMSO- d_6) δ : 2.62(s, 3H, CH₃),

Table 2 Bond length (Å) and bond angle (°) for A

Table 3 Bond length (Å) and bond angle (°) for B

Bond	Lengths (Å)	Bond	Lengths (Å)
Cl(1)–C(10)	1.7097(15)	C(4)–C(5)	1.384(2)
N(1)-C(10)	1.3601(19)	C(5)–C(6)	1.387(2)
N(1)-N(2)	1.3720(17)	C(7)–C(8)	1.493(2)
N(1)-C(6)	1.4340(18)	C(8)–C(9)	1.421(2)
N(2)-C(8)	1.3317(19)	C(9)–C(10)	1.379(2)
N(3)-C(11)	1.2800(19)	C(9)–C(11)	1.455(2)
N(3)–N(4)	1.3626(17)	C(12)–C(17)	1.393(2)
N(4)-C(12)	1.3932(19)	C(12)–C(13)	1.396(2)
C(1)–C(2)	1.385(2)	C(13)–C(14)	1.382(2)
C(1)–C(6)	1.386(2)	C(14)–C(15)	1.381(3)
C(2)–C(3)	1.378(2)	C(15)-C(16)	1.387(2)
C(3)–C(4)	1.380(3)	C(16)–C(17)	1.385(2)
Bond	Angles (°)	Bond	Angles (°)
C(10)–N(1)–N(2)	110.03(12)	C(9)–C(8)–C(7)	127.93(14)
C(10)-N(1)-C(6)	130.27(12)	C(10)-C(9)-C(8)	103.61(13)
N(2)-N(1)-C(6)	119.62(12)	C(10)–C(9)–C(11)	127.43(13)
C(8)–N(2)–N(1)	105.77(12)	C(8)-C(9)-C(11)	128.74(13)
C(11)-N(3)-N(4)	118.35(13)	N(1)-C(10)-C(9)	108.94(12)
N(3)-N(4)-C(12)	119.04(13)	N(1)-C(10)-Cl(1)	122.50(11)
C(2)–C(1)–C(6)	119.30(15)	C(9)–C(10)–Cl(1)	128.46(12)
C(3)–C(2)–C(1)	120.46(16)	N(3)-C(11)-C(9)	120.05(14)
C(2)–C(3)–C(4)	119.93(15)	C(17)-C(12)-N(4)	122.00(14)
C(3)–C(4)–C(5)	120.42(16)	C(17)–C(12)–C(13)	119.28(14)
C(4)-C(5)-C(6)	119.37(16)	N(4)-C(12)-C(13)	118.73(14)
C(1)-C(6)-C(5)	120.50(14)	C(14)-C(13)-C(12)	119.97(16)
C(1)-C(6)-N(1)	120.53(14)	C(15)-C(14)-C(13)	121.04(16)
C(5)-C(6)-N(1)	118.93(14)	C(14)-C(15)-C(16)	118.92(15)
N(2)-C(8)-C(9)	111.64(13)	C(17)-C(16)-C(15)	120.96(16)
N(2)-C(8)-C(7)	120.42(13)	C(16)-C(17)-C(12)	119.83(15)

6.88(d, 1H, J = 6.5 Hz, Ar–H), 7.06(d, 2H, J = 7.9 Hz, Ar–H), 7.29(t, 2H, J = 7.8 Hz, Ar–H), 7.40(s, 1H, N–H), 7.49–7.57(m, 5H, Ar–H), 7.69(s, 1H, N=C–H). IR(KBr, cm⁻¹) *v*: 3,232(N–H), 1,601(C=N), 1505, 1477(C=C), 1,251(C–N).

3,5-Dimethyl-1-phenyl-4-((2-(p-tolyl)hydrazono)methyl)-1H-pyrazole (**B**)

Deep yellow solid 0.90 g, yield: 59 %. APCI-MS (m/z, M⁺): 305.1. ¹H NMR (DMSO- d_6) δ : 2.17(s, 3H, CH₃), 2.36(s, 3H, CH₃), 2.41(s, 3H, CH₃), 6.86(d, 2H, J = 8.1 Hz, Ar–H), 6.99(d, 2H, J = 8.0 Hz, Ar–H), 7.40(s, 1H, N–H), 7.47–7.50(m, 5H, Ar–H), 7.87(s, 1H, N=C–H). IR(KBr, cm⁻¹) v: 3,233(N–H), 1,599(C=N), 1503, 1427(C=C), 1,263(C–N).

Bond	Lengths (Å)	Bond	Lengths (Å)
N(1)-C(10)	1.358(3)	C(8)–C(7)	1.494(3)
N(1)-N(2)	1.378(2)	C(13)–C(19)	1.390(3)
N(1)–C(6)	1.427(2)	C(13)–C(14)	1.391(3)
C(10)–C(9)	1.379(3)	C(16)–C(18)	1.388(3)
C(10)–C(11)	1.496(3)	C(16)–C(15)	1.389(3)
N(2)–C(8)	1.329(2)	C(16)–C(17)	1.506(3)
C(9)–C(8)	1.415(3)	C(14)–C(15)	1.384(3)
C(9)–C(12)	1.452(3)	C(18)–C(19)	1.384(3)
N(3)–C(12)	1.281(2)	C(4)–C(3)	1.371(3)
N(3)–N(4)	1.365(2)	C(4)–C(5)	1.377(3)
C(6)–C(1)	1.378(3)	C(1)–C(2)	1.380(3)
C(6)–C(5)	1.379(3)	C(3)–C(2)	1.368(3)
N(4)-C(13)	1.391(3)		
Bond	Angles (°)	Bond	Angles (°)
C(10)–N(1)–N(2)	112.13(14)	C(9)–C(8)–C(7)	129.00(19)
C(10)-N(1)-C(6)	128.98(15)	N(3)-C(12)-C(9)	121.93(18)
N(2)-N(1)-C(6)	118.88(15)	C(19)-C(13)-N(4)	122.15(18)
N(1)–C(10)–C(9)	106.36(16)	C(19)-C(13)-C(14)	118.82(18)
N(1)-C(10)-C(11)	121.78(16)	N(4)-C(13)-C(14)	119.03(18)
C(9)-C(10)-C(11)	131.74(19)	C(18)-C(16)-C(15)	116.95(18)
C(8)–N(2)–N(1)	104.60(15)	C(18)-C(16)-C(17)	121.8(2)
C(10)-C(9)-C(8)	105.57(17)	C(15)-C(16)-C(17)	121.2(2)
C(10)-C(9)-C(12)	125.05(18)	C(15)-C(14)-C(13)	120.12(19)
C(8)–C(9)–C(12)	129.34(17)	C(19)-C(18)-C(16)	122.2(2)
C(12)-N(3)-N(4)	116.51(17)	C(3)–C(4)–C(5)	120.3(2)
C(1)-C(6)-C(5)	120.35(18)	C(4)-C(5)-C(6)	119.4(2)
C(1)-C(6)-N(1)	119.44(17)	C(18)-C(19)-C(13)	119.94(19)
C(5)-C(6)-N(1)	120.18(17)	C(6)–C(1)–C(2)	119.52(19)
N(3)-N(4)-C(13)	119.68(17)	C(14)-C(15)-C(16)	122.0(2)
N(2)-C(8)-C(9)	111.34(15)	C(2)–C(3)–C(4)	120.2(2)
N(2)-C(8)-C(7)	119.64(18)	C(3)-C(2)-C(1)	120.1(2)

Single Crystal X-ray Crystallography

Single-crystal X-ray diffraction measurements of compounds **A** and **B** were carried out on a Bruker Smart CCD X-ray single-crystal diffractometer. The reflection data were collected at 296(2) K in $\omega/2\theta$ scan mode with graphite monochromated Mo- $K\alpha$ radiation ($\lambda = 0.71073$ Å) as the excitation source. The reflections of single crystal **A** were measured in a 2θ range of $1.90^{\circ}-25.00^{\circ}$, and those of single crystal **B** were measured in a 2θ range of $1.66^{\circ}-25.00^{\circ}$; and 2,683 and 2,539 independent reflections were measured for **A** and **B**, respectively. SADABS multi-scan empirical absorption corrections were adopted for data processing. The crystal structure was solved by direct method and refined based on full-matrix least-squares on F^2 . The final least



Fig. 2 a The molecular structure of A. b Diagram showing the C-H \cdots π and π - π interactions between the adjacent molecules in A. c Diagram showing the 3D network of A

Table 4 The bond length (Å) and bond angle (°) for hydrogen bond of A

D–H…A	d(D–H)	<i>d</i> (H…A)	<i>d</i> (D…A)	∠(DHA)
	(Å)	(Å)	(Å)	(°)
N(4)-H(4)N(2)	0.86	2.34	3.1643(18)	159.8

square cycle of refinement for **A** gave $R_1 = 0.0315$ and $wR_2 = 0.0854$; and that for **B** gave $R_1 = 0.0341$ and $wR_2 = 0.0893$. The crystallographic data and structural refinements for **A** and **B** are listed in Table 1.

Results and Discussion

Synthesis

The synthetic route of aromatic hydrazone compounds is outlined in Fig. 1.

1-Phenylpyrazole-4-carbaldehyde was prepared according to literature method [12] and obtained by Vilsmeier reaction. The target compounds were obtained by condensed reaction of 1-phenylpyrazole-4-carbaldehyde with benzene hydrazine or *p*-tolylhydrazine hydrochloride. The reaction required no acid or base as catalyst and can be performed in CH₃OH with refluxing 2 h under 80 °C. Crude products can be purified by recrystallizing in the mixed solvent of EtOH and CH₂Cl₂ (V_{EtOH} : $V_{\text{CH}_2\text{Cl}_2}$ = 1:3). While the single crystal specimens of **A** and **B** was acquired via slow evaporation of their ethanol solutions at room temperature.

Crystallography and Characterization

The crystallographic data, selected bond lengths and bond angles for as-synthesized compounds A and B are listed in Tables 2 and 3, respectively. The molecular structure of A is shown in Fig. 2. In compound A, the N-C distances (1.4340(18) Å of N(1)–C(6), 1.3601(19) Å of N(1)–C(10), and 1.3932(19) Å of N(4)–C(12)) and the N=C distances (1.3317(19) Å of N(2)-C(8)) lie between those of typical double bond C=N (1.287 Å) and single bond C-N (1.471 Å) suggesting that intra-annular \prod conjugated systems as well as $p-\pi$ conjugated systems are occurred; the N=C distance [1.2800(19) Å of N(3)–C(11)] similar to typical double bond C=N (1.287 Å) that means there are few conjugate composition for N(3)-C(11); the N-N distances [1.378(2) Å of N(1)–N(2), 1.365(2) Å of N(3)–N(4)] lie between those of typical double bond N=N (1.20 Å) and single bond N–N (1.44 Å) and shows the nature of partial double bond. The Cl(1)–C(10) distance (1.7097(15) Å), is shorter than typical single bond Cl-C (1.77 Å) and indicates the formation of $p-\pi$ conjugated systems; and the distances of C(9)–C(11) (1.455(2) Å) and C(7)–C(8) (1.493(2) Å) are shorter than typical single bond C-C (1.54 Å), due to the formation of $\sigma - \pi$ conjugated systems. Dihedral angle between plane C(6)-C(1)-C(2)-C(3)-C(4)-C(5) and plane



Fig. 3 a The molecular structure of **B**. b Diagram showing the C-H $\cdots\pi$ interactions between the adjacent molecules in **B**. c Diagram showing the 3D architecture of **B**

C(10)-N(1)-N(2)-C(8)-C(9) is 47.9610(60)°, whereas that between plane C(10)-N(1)-N(2)-C(8)-C(9) and plane C(12)-C(17)-C(13)-C(14)-C(15)-C(16) is 2.0900(51)°. Findings indicate that the C–H $\cdots\pi$ (corresponding distances are 2.8422 and 2.9456 Å), hydrogen bonding (N(4)-H(4)…N(2): 2.34 Å, 159.8°, see Table 4) and π - π interactions (with the distance of 3.6329 Å) between the adjacent molecules, as illustrated in Fig. 2b. As a result, all the molecules are interconnected to give rise to a 3D network through weak interactions above-mentioned in clinker-built fashion (as shown in Fig. 2c). The bond lengths of compound **B** are similar to those of compound **A** (see Table 3). Corresponding distances of C–H··· π interactions are 3.1553, 2.9618, 3.0355 and 2.9860 Å, respectively. Dihedral angle between planes are 64.1870(66)° [between plane C(6)-C(5)-C(1)-C(2)-C(3)-C(4) and plane C(8)-N(2)-C(9)-C(10)-N(1)] and 14.7940(73)° [between plane C(8)-N(2)-C(9)-C(10)-N(1) and plane C(18)-C(19)-C(13)-C(14)-C(15)-C(16)]. 3D architecture is formed through C–H·· π interactions above-mentioned (see Fig. 3).

Conclusion

We synthesized 2 novel aromatic hydrazone compounds containing pyrazole group, using MS, ¹H NMR, IR and

single-crystal X-ray diffraction for their structure characterization and determination.

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