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The Synthesis and Crystal Structure of Two New Hydrazone Compounds

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Abstract: Two new hydrazone compounds, 4-formylimidazole-4-hydroxybenzhydrazone dihydrate (**1**) and 2-nitrobenzaldehyde-2-furan formylhydrazone (**2**), were synthesized via the classical synthesis method. Their structure was determined via elemental analysis and X-ray single crystal diffraction analysis. Compound **1** crystallizes in triclinic, space group *P*-1 with a = 7.0321(14) Å, b = 7.3723(15) Å, c = 13.008(3) Å, α = 98.66(3)°, β = 101.69(3)°, γ = 92.25(3)°, V = 651.2(2) Å^3, Z = 2, Dc = 1.358 g·cm^{-3}, μ = 0.106 mm^{-1}, F(000) = 280, and final R_1 = 0.0564, wR_2 = 0.1420. Compound **2** crystallizes in monoclinic, space group $P2_1/c$ with a = 17.3618(9) Å, b = 9.1506(4) Å, c = 15.5801(7) Å, β = 104.532(5)°, V = 2396.05(19) Å^3, Z = 8, Dc = 1.437 g·cm^{-3}, μ = 0.111 mm^{-1}, F(000) = 1072, and final R_1 = 0.0633, wR_2 = 0.1649. Compound **1** forms a 2D-layered structure via the interactions of 1D chains and Compound **2** forms a 3D network structure via the interactions of 1D chains.

Keywords: hydrazone compound; crystal structure; characterization

1. Introduction

Hydrazone compounds (–NH–N=C–) and their complexes have been widely studied due to their facile synthesis and potential biological activities [1–5]. During recent years, many hydrazone compounds and their complexes have displayed novel structures and extensive applications in luminescent probes, antibacterial and antitumor agents, fluorescence markers, optical materials, and anticonvulsant agent [6–11]. In the past ten years, we have done some work in the synthesis, structural characterization, and properties of hydrazone compounds, which show novel structures and luminescent properties [12–16]. In this paper, two new hydrazone compounds have been synthesized via the classical synthesis method, and their crystal structures have also been determined by X-ray single crystal diffraction analysis. The schemes of the compounds are given in Figure 1.

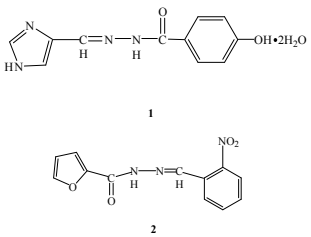


Figure 1. The scheme of the hydrazone compounds (**1** and **2**).

2. Results and Discussion

*Description of Compounds **1** and **2***

The molecular plots of Compounds **1** and **2** with the atomic labeling scheme are given in Figure 2. Compound **1** is of an almost coplanar configuration with a dihedral angle of 2.5° between Plane 1 (C9–N3–C10–N4–C11) and Plane 2 (C1–C2–C3–C4–C5–C6). The crystal structure analysis shows that Compound **1** contains two lattice water molecules. From the bond length data, it can be seen that the C8–N2 bond length of 1.2760(17) Å is shorter than that of C7–N1 (1.3464(16) Å), which indicates that the bond of C8–N2 is a double bond. Moreover, the C7–O2 bond length of 1.226(2) Å is shorter than that of C3–O1 (1.3537(16) Å), which indicates that the bond of C7–O2 is also double bond.

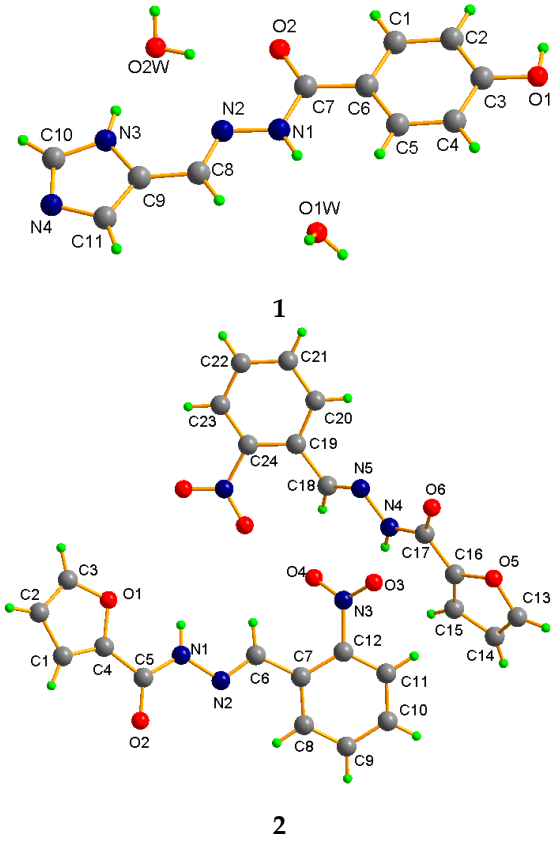


Figure 2. The molecular structure of Compounds **1** and **2.**

The dihedral angles between Plane 1 (C1–C2–C3–C4–O1) and Plane 2 (C7–C8–C9–C10–C11–C12) is 26.2°, and that of Plane 3 (C19–C20–C21–C22–C23–C24) and Plane 4 (C13–C14–C15–C16–O5) is 35.5° in Compound **2**. From the bond length data, it can be seen that the bond lengths of C6–N2 (1.267(4) Å) and C18–N5 (1.264(4) Å) are shorter than those of C5–N1 (1.337(4) Å) and C17–N4 (1.352(4) Å), which indicates that the bonds of C6–N2 and C18–N5 are double bonds. Moreover, the bond lengths of C5–O2 (1.234(4) Å) and C17–O6 (1.221(4) Å) are shorter than those of C3–O1 (1.361(4) Å), C4–O1 (1.358(4) Å), C13–O5 (1.360(4) Å), and C16–O5 (1.355(4) Å), which indicates that the bonds of C5–O2 and C17–O6 are also double bonds. The bond lengths and bond angles of two molecules in each asymmetric unit are different.

The bond lengths and bond angles in Compounds **1** and **2** are in accordance with the results in [17,18].

Bonds for **1**: C3–O1 1.3537(16) Å; C7–O2 1.2389(16) Å; C7–N1 1.3464(16) Å; C8–N2 1.2760(17) Å; C9–N3 1.3677(18) Å; C10–N4 1.311(2) Å; C10–N3 1.3376(18) Å; C11–N4 1.3692(18) Å; N1–N2 1.3786(14)

Å; C1–C2 1.3810(19) Å; C1–C6 1.3985(17) Å; C2–C3 1.376(2) Å; C3–C4 1.390(2) Å; C4–C5 1.3824(18) Å; C5–C6 1.384(2) Å; C6–C7 1.4869(16) Å; C9–C8 1.4441(16) Å; C9–C11 1.3675(18) Å.

Bonds for **2**: C4–O1 1.358(4) Å; C3–O1 1.361(4) Å; O2–C5 1.234(4) Å; N3–O3 1.218(4) Å; N3–O4 1.229(4) Å; C5–N1 1.337(4) Å; N1–N2 1.388(3) Å; C6–N2 1.267(4) Å; C12–N3 1.471(4) Å; C1–C4 1.328(4) Å; C1–C2 1.413(4) Å; C2–C3 1.330(5) Å; C4–C5 1.472(4) Å; C6–C7 1.460(4) Å; C7–C8 1.393(4) Å; C7–C12 1.402(4) Å; C9–C8 1.370(5) Å; C9–C10 1.373(5) Å; C10–C11 1.374(5) Å; C11–C12 1.374(5) Å. C16–O5 1.355(4) Å; C13–O5 1.360(4) Å; O6–C17 1.221(4) Å; N6–O7 1.187(5) Å; N6–O8 1.160(5) Å; C17–N4 1.352(4) Å; N4–N5 1.376(3) Å; C18–N5 1.264(4) Å; C24–N6 1.457(5) Å; C13–C14 1.304(6) Å; C14–C15 1.412(5) Å; C15–C16 1.323(5) Å; C16–C17 1.461(4) Å; C18–C19 1.475(4) Å; C19–C24 1.387(5) Å; C19–C20 1.388(5) Å; C20–C21 1.373(5) Å; C21–C22 1.364(6) Å; C22–C23 1.369(6) Å; C23–C24 1.378(5) Å.

Angles for **1**: C2–C1–C6 121.09(13)°; C3–C2–C1 120.34(12)°; O1–C3–C2 123.0(12)°; O1–C3–C4 117.66(14)°; C2–C3–C4 119.33(12)°; C3–C4–C5 120.15(14)°; C4–C5–C6 121.26(12)°; C5–C6–C1 117.83(12)°; C5–C6–C7 124.14(11)°; C1–C6–C7 118.03(12)°; O2–C7–N1 120.93(11)°; O2–C7–C6 121.83(11)°; N1–C7–C6 117.24(11)°; N2–C8–C9 119.40(12)°; C11–C9–N3 105.80(12)°; C11–C9–C8 129.66(13)°; N3–C9–C8 124.55(11)°; N4–C10–N3 111.96(14)°; C9–C11–N4 109.42(13)°; C7–N1–N2 117.51(11)°; C8–N2–N1 116.19(11)°; C9–N3–C10 107.19(12)°; C10–N4–C11 105.64(12)°.

Angles for **2**: C4–O1–C3 106.1(3)°; C5–N1–N2 120.0(3)°; C6–N2–N1 114.2(3)°; O3–N3–O4 124.6(3)°; O3–N3–C12 117.8(3)°; O4–N3–C12 117.5(3)°; C4–C1–C2 106.9(3)°; C3–C2–C1 106.3(3)°; C2–C3–O1 110.4(3)°; C1–C4–O1 110.3(3)°; C1–C4–C5 132.0(3)°; O1–C4–C5 117.7(3)°; O2–C5–N1 124.4(3)°; O2–C5–C4 120.3(3)°; N1–C5–C4 115.3(3)°; N2–C6–C7 120.5(3)°; C8–C7–C12 116.2(3)°; C8–C7–C6 121.0(3)°; C12–C7–C6 122.6(3)°; C9–C8–C7 121.7(3)°; C8–C9–C10 120.1(3)°; C9–C10–C11 120.6(3)°; C10–C11–C12 118.7(3)°; C11–C12–C7 122.6(3)°; C11–C12–N3 116.8(3)°; N3–C12–C7 120.6(3)°. C16–O5–C13 106.4(3)°; C17–N4–N5 119.0(2)°; C18–N5–N4 115.7(3)°; O8–N6–O7 119.2(5)°; O8–N6–C24 119.1(5)°; O7–N6–C24 121.0(4)°; C14–C13–O5 110.5(3)°; C13–C14–C15 106.5(4)°; C16–C15–C14 107.2(3)°; C15–C16–O5 109.3(3)°; C15–C16–C17 134.5(3)°; O5–C16–C17 116.1(3)°; O6–C17–N4 123.7(3)°; O6–C17–C16 121.7(3)°; N4–C17–C16 114.6(3)°; N5–C18–C19 118.7(3)°; C24–C19–C20 116.1(3)°; C24–C19–C18 125.0(3)°; C20–C19–C18 119.0(3)°; C21–C20–C19 122.0(4)°; C22–C21–C20 120.1(4)°; C21–C22–C23 120.0(4)°; C22–C23–C24 119.3(4)°; C23–C24–C19 122.5(4)°; C23–C24–N6 117.0(4)°; N6–C24–C19 120.5(3)°.

The molecules of both Compound **1** and Compound **2** form a 1D-chained structure via the intermolecular hydrogen bonds (N–H...O) (Figure 3). In addition, Compound **1** forms a two-dimensional layered structure via the interactions of 1D chains (Figure 4). Furthermore, Compound **2** forms a three-dimensional network structure via the interactions of 1D chains (Figure 4).

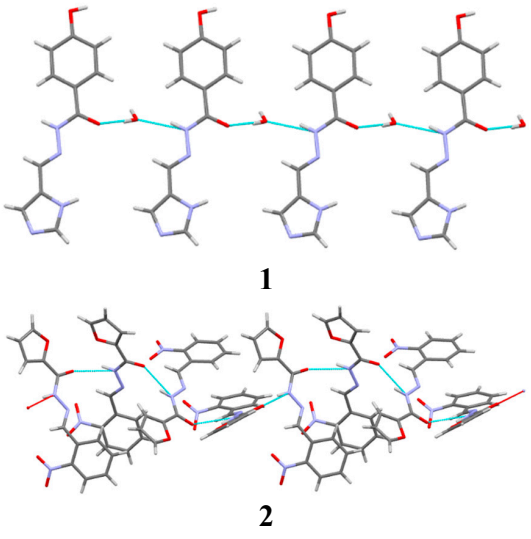
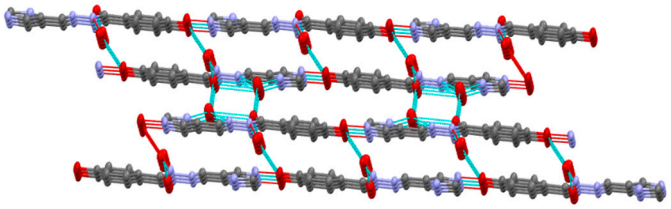


Figure 3. 1D-chained structure of Compounds **1** and **2** via hydrogen bonds.



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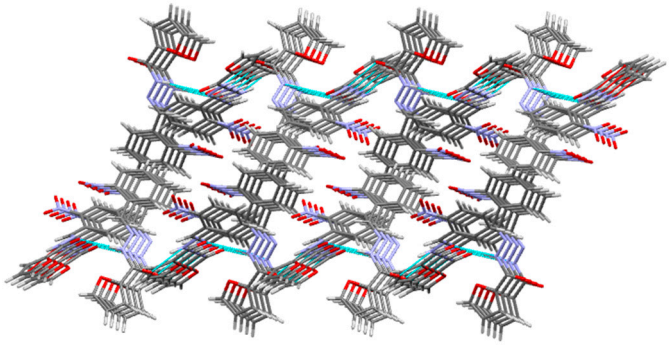

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Figure 4. 2D-layered structure of Compound **1** and 3D network structure of Compound **2.**

3. Experimental Section

3.1. Materials and Instrumentation

4-formylimidazole, 2-nitrobenzaldehyde, 4-hydroxybenzhydrazine, and 2-furan formylhydrazine were purchased from the Xiya Reagent Company. The analyses of C, H, and N were made on an Elementar Vario EL III elemental analyzer (Elementar, Hanau, Germany). IR spectra were recorded as KBr pellets with a Nicolet AVATAR 360 FTIR spectrometer (Nicolet Instrument Inc., Madison, WI, USA) in the 4000~400 cm^{-1} region. ^1H NMR spectra were recorded on a Bruker Avance-400 spectrometer (Bruker, Elisabethhof, Netherlands) with C_2D_6OS as the solvent. The X-ray single-crystal data collection for the hydrazone compounds **1** and **2** were performed on a Bruker Smart-1000 CCD diffractometer (Bruker, Billerica, MA, USA).

3.2. Preparation of Two Hydrazone Compounds

4-formylimidazole-4-hydroxybenzhydrazone dihydrate (1): 0.0961 g 4-formylimidazole (1.0 mmol) and 0.1522 g 4-hydroxybenzhydrazine (1.0 mmol) were dissolved in 10 mL of 95% CH3CH2OH. The mixture was refluxed for 5 h. Then, the solution was filtered. The colorless crystals of 4-formylimidazole-4-hydroxybenzhydrazone dihydrate were obtained from the above filtrate via slow evaporation at room temperature for 5 days. Elemental analysis calc. for $C_{11}H_{14}N_4O_4$: C, 49.58, H, 5.26, N, 21.03(%); Found: C, 49.32, H, 5.65, N, 21.43(%). IR: 3452 cm^{-1} (O–H and N–H), 1639 cm^{-1} (C=O), 1592 cm^{-1} (C=N). ^1H NMR (ppm): 14.22 (s, 1H, –OH), 12.81 (s, 1H, –NH–), 8.01 (s, 1H, –CH=N), 7.85 (d, 2H, Ar–H), 7.63 (s, 1H, imidazol–H), 7.45 (s, 1H, imidazol–H), 6.90 (d, 2H, Ar–H).

2-nitrobenzaldehyde-2-furan formylhydrazone (**2**): 0.1511 g 2-nitrobenzaldehyde (1.0 mmol) and 0.1261 g 2-furan formylhydrazine (1.0 mmol) were dissolved in 15 mL of 95% CH_3CH_2OH. The mixture was refluxed for 5 h. Then, the solution was filtered. The yellow crystals of 2-nitrobenzaldehyde-2-furan formylhydrazone were obtained from the above filtrate via slow evaporation at room temperature for 15 days. Elemental analysis calc. for $C_{12}H_9N_3O_4$: C, 55.55, H, 3.47, N, 16.20(%); Found: C, 55.32, H, 4.26, N, 15.81(%). IR: 1640 cm^{-1} (C=O), 1593 cm^{-1} (C=N). ^1H NMR (ppm): 12.23 (s, 1H, N–H), 8.87 (s, 1H, –CH=N), 8.10 (m, 2H, Ar–H), 7.94–8.02 (m, 1H, furan–H), 7.83 (t, 1H, Ar–H), 7.62–7.74 (m, 1H, Ar–H), 7.36 (s, 1H, furan–H), 6.73 (dd, 1H, furan–H).

3.3. Crystal Structure Determination

The important crystal data of Compound **1** and Compound **2** are listed in Table 1. Diffraction data of both Compound **1** and Compound **2** were collected at 293 (2) K on a Bruker Smart-1000 CCD diffractometer by using a ϕ~ω scan mode. The structures were solved via direct methods with SHELXL-97 program package [19] and refined with SHELXTL-97 [20].

Table 1. Crystal data for **1** and **2**.

Formula	$C_{11}H_{14}N_4O_4$	$C_{12}H_9N_3O_4$
Formula weight	266.26	259.22
Crystal system	triclinic	monoclinic
Space group	*P*-1	$P2_1/c$
a [Å]	7.0321(14)	17.3618(9)
b [Å]	7.3723(15)	9.1506(4)
c [Å]	13.008(3)	15.5801(7)
α [°]	98.66(3)	90.00
β [°]	101.69(3)	104.532(5)
γ [°]	92.25(3)	90.00
Z	2	8
F(000)	280	1072
Temperature [K]	293(2)	293(2)
V [Å^3]	651.2(2)	2396.05(19)
Calculated density [g· cm^{-3}]	1.358	1.437
Crystal size [mm^3]	0.21×0.20×0.19	0.21×0.20×0.19
μ [mm^{-1}]	0.106	0.111
S	1.046	1.028
Limiting indices	$-8 \leqslant h \leqslant 9$, $-9 \leqslant k \leqslant 9$, $-16 \leqslant l \leqslant 16$	$-20 \leqslant h \leqslant 14$, $-6 \leqslant k \leqslant 10$, $-15 \leqslant l \leqslant 18$
Reflections collected	6352	9815
Unique reflections	2949	4221
Parameters	172	344
Restraints	5	0
R_{int}	0.031	0.0477
R_1, wR_2 [all data]	0.0655, 0.1497	0.0970, 0.1925
R_1, wR_2 [I>2σ(I)]	0.0564, 0.1420	0.0633, 0.1649
Largest diff.peak and hole [e· Å^{-3}]	0.412, −0.302	0.422, −0.321

4. Conclusions

Two new hydrazone compounds, 4-formylimidazole-4-hydroxybenzhydrazone dihydrate (**1**) and 2-nitrobenzaldehyde-2-furan formylhydrazone (**2**), were synthesized via classical synthesis method. Their structures were determined via elemental analysis and X-ray single crystal diffraction analysis. The results show that Compound **1** forms two-dimensional layered structure via the interactions of 1D chains. And Compound **2** forms three-dimensional network structure via the interactions of 1D chains.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4352/6/5/57/s1. Figure S1: IR spectrum of compound 1; Figure S2: IR spectrum of compound 2; Figure S3: ^{1}HNMR spectrum of compound 1; Figure S4: ^{1}HNMR spectrum of compound 2. CCDC 1456984 (**1**) and 1469125 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk).

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Author Contributions: Wang Li-Hua synthesized Compound **1** and Compound **2**. Tai Xi-Shi designed the experiments and wrote the manuscript.

Conflicts of Interest: The author confirms that this article content has no conflict of interest.

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