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**CRYSTAL STRUCTURES OF NEW 4-HYDROXY-*N'*-(3,5-DIIODO-2-HYDROXYBENZYLIDENE)BENZOHYDRAZIDE METHANOL AND 4-HYDROXY-*N'*-(2-METHOXYNAPHTH-1-yl-METHYLENE)BENZOHYDRAZIDE DIMETHANOL SOLVATE**

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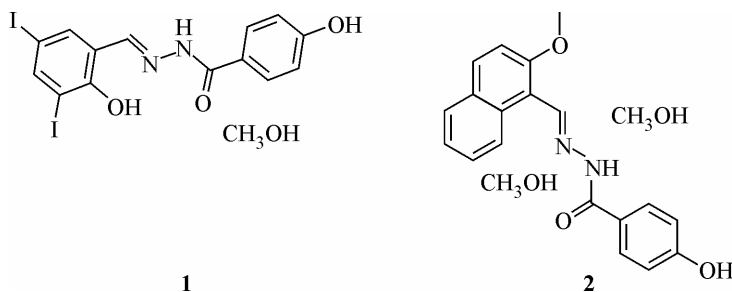
*Department of Chemistry, Huainan Normal College, Huainan 232001, P. R. China**Received July, 10, 2009*

Two new hydrazone compounds  $C_{14}H_{10}I_2N_2O_3 \cdot CH_3OH$  (**1**) and  $C_{19}H_{16}N_2O_3 \cdot 2CH_3OH$  (**2**) are synthesized by the condensation reactions of the equimolar quantities of 4-hydroxybenzohydrazide with 3,5-diiodo-2-hydroxybenzaldehyde and 2-methoxynaphth-1-yl-methylene respectively in methanol solutions. Compound **1** consists of a hydrazone molecule and a methanol molecule of crystallization, and compound **2** consists of a hydrazone molecule and two methanol molecules of crystallization. Both compounds are characterized by elemental analysis, IR spectra, and single crystal X-ray diffraction. As expected, each hydrazone molecule adopts an *E* configuration about the C=N double bond. In the crystal structures of both compounds, the hydrazone and methanol molecules are linked through intermolecular N—H···O and O—H···O hydrogen bonds, forming layers along the *bc* direction.

**Keywords:** hydrazone, crystal structure, hydrogen bonding.

**INTRODUCTION**

Hydrazone compounds are a kind of versatile ligands [1–3], which are usually synthesized by the condensation of hydrazides with compounds bearing carbonyl groups. The compounds are very important in medicinal and pharmaceutical fields. Many of them show antibacterial, antifungal, and antitumor activities [4–7]. However, the compounds derived from the reactions of 4-hydroxybenzohydrazide with 3,5-diiodo-2-hydroxybenzaldehyde and 2-methoxy-1-naphthaldehyde respectively have never been reported so far. In this paper, we report the synthesis and crystal structures of two new hydrazone compounds: 4-hydroxy-*N'*-(3,5-diiodo-2-hydroxybenzylidene)benzohydrazide methanol solvate **1** and 4-hydroxy-*N'*-(2-methoxynaphth-1-yl-methylene)benzohydrazide dimethanol solvate **2**.

**EXPERIMENTAL**

**Materials and methods.** All starting materials and organic solvents for the synthesis were of analytical grade as purchased commercially and purified by standard methods prior to use. Infrared spec-

\* E-mail: huainanweiyijun@163.com

tra were recorded on a Nicolet 55XC Fourier transform spectrophotometer using KBr pellets (4000–400 cm<sup>-1</sup>). Elemental analyses were carried out on a Perkin-Elmer model 240 analyzer.

**Synthesis of 1.** A solution of 3,5-diiodo-2-hydroxybenzaldehyde (37.4 mg, 0.1 mmol) in MeOH (10 cm<sup>3</sup>) was added dropwise into a solution of 4-hydroxybenzohydrazide (15.2 mg, 0.1 mmol) in MeOH (10 cm<sup>3</sup>) with stirring. The resulting colorless solution was further stirred for about 30 min and then filtered. The filtrate was left to stand for three days under ambient conditions, and colorless block crystals of the compound were obtained. Yield, 97 %. IR (KBr pellets): 3443 (m), 3232 (m), 3043 (m), 1630 (s), 1597 (s), 1472 (w), 1320 (s), 1280 (m), 1191 (w), 823 (m), 725 (m), 534 (w) cm<sup>-1</sup>. Anal. Calcd. (%) for C<sub>15</sub>H<sub>14</sub>I<sub>2</sub>N<sub>2</sub>O<sub>4</sub>: C, 33.4; H, 2.6; N, 5.2. Found (%): C, 33.2; H, 2.6; N, 5.4.

**Synthesis of 2.** A solution of 2-methoxy-1-naphthaldehyde (18.6 mg, 0.1 mmol) in MeOH (10 cm<sup>3</sup>) was added dropwise into a solution of 4-hydroxybenzohydrazide (15.2 mg, 0.1 mmol) in MeOH (10 cm<sup>3</sup>) with stirring. The resulting colorless solution was further stirred for about 30 min and then filtered. The filtrate was left to stand for a week under ambient conditions, and colorless block crystals of the compound were obtained. Yield, 95 %. IR (KBr pellets): 3435 (m), 3220 (m), 3045 (m), 1633 (s), 1596 (s), 1471 (w), 1321 (s), 1278 (m), 1189 (w), 817 (m), 723 (m), 537 (w) cm<sup>-1</sup>. Anal. Calcd. (%) for C<sub>21</sub>H<sub>24</sub>N<sub>2</sub>O<sub>5</sub>: C, 65.6; H, 6.3; N, 7.3. Found (%): C, 65.2; H, 6.5; N, 7.6.

**X-ray crystallography.** X-ray diffraction data were collected on a Bruker SMART 1000 CCD area detector diffractometer, using graphite monochromic MoK<sub>α</sub> radiation (λ = 0.71073 Å). The crystals were covered with Vaseline to avoid efflorescence when exposed in air. The crystal data, data collection, and refinement parameters for the compounds are presented in Table 1. The structures were

Table 1

Crystal data for the compounds

	1	2
CCDC	738595	738596
Chemical formula	C <sub>15</sub> H <sub>14</sub> I <sub>2</sub> N <sub>2</sub> O <sub>4</sub>	C <sub>21</sub> H <sub>24</sub> N <sub>2</sub> O <sub>5</sub>
Fw	540.1	384.4
T, K	298(2)	298(2)
Crystal shape/color	block/colorless	block/colorless
Crystal size, mm <sup>3</sup>	0.23 × 0.20 × 0.20	0.30 × 0.27 × 0.27
Crystal system	Monoclinic	Monoclinic
Space group	P2 <sub>1</sub> /n	P2 <sub>1</sub> /c
a, b, c, Å	7.886(1), 19.584(1), 11.933(1)	7.600(1), 22.775(2), 11.443(1)
β, deg.	104.696(1)	100.275(2)
V, Å <sup>3</sup>	1782.6(3)	1948.9(4)
Z	4	4
D <sub>c</sub> , g/cm <sup>3</sup>	2.012	1.310
μ(MoK <sub>α</sub> ), cm <sup>-1</sup>	3.548	0.094
F(000)	1024	816
θ range, deg.	2.05/27.00	1.79/27.00
Index ranges (h, k, l)	-10/9, -24/23, -11/15	-9/9, -26/28, -14/14
Independ. refl.	3862 (R <sub>int</sub> = 0.0292)	4232 (R <sub>int</sub> = 0.0388)
Observed refl. [I ≥ 2σ(I)]	3353	2157
T(min)/T(max)	0.496/0.537	0.972/0.975
Data/restraints/parameters	3862/2/217	4232/2/264
GOOF on F <sup>2</sup>	1.027	1.043
R <sub>1</sub> , wR <sub>2</sub> [I ≥ 2σ(I)] <sup>a</sup>	0.0315, 0.0777	0.0557, 0.1400
R <sub>1</sub> , wR <sub>2</sub> (all data) <sup>a</sup>	0.0373, 0.0812	0.1159, 0.1739
Large diff. peak and hole, e/Å <sup>3</sup>	1.147 and -1.272	0.181 and -0.198
(Δ/σ) <sub>max</sub>	0.000	0.000

<sup>a</sup> R<sub>1</sub> = Σ||F<sub>0</sub>| - |F<sub>c</sub>||/Σ|F<sub>0</sub>|, wR<sub>2</sub> = [Σw(F<sub>0</sub><sup>2</sup> - F<sub>c</sub><sup>2</sup>)<sup>2</sup>/Σw(F<sub>0</sub><sup>2</sup>)<sup>2</sup>]<sup>1/2</sup>.

solved by direct methods using the SHELXS-97 program [ 8 ]. Refinements were made by the full-matrix least-squares on  $F^2$  using SHELXL-97 [ 9 ]. Nonhydrogen atoms were refined with anisotropic displacement parameters. In **1**, the H(1) atom attached to O(1) and the H(2) atom attached to N(2) and in **2**, the H(5) atom attached to O(5) and the H(2) atom attached to N(2) were located in difference Fourier maps and refined isotropically with O—H and N—H distances restrained to 0.85(1) and 0.90(1) Å respectively. All other hydrogen atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms. CIF files containing complete information on the studied structures were deposited with CCDC, deposition numbers 738595 and 738596, and are freely available upon request from the following web site: [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

## RESULTS AND DISCUSSION

The crystals of both compounds are not very stable in air at room temperature; they are easily air slaked. Both compounds were synthesized in good yields (over 90 %). The IR spectra of the compounds confirm the formation of the Schiff base functional groups —C=N—, as well as the lack of the —C=O groups from the starting aldehydes.

**Structure description of the compounds.** X-ray single crystal structural analyses indicate that the asymmetric unit of **1** consists of a hydrazone molecule and a methanol molecule of crystallization (Fig. 1, *a*), and that of **2** consists of a hydrazone molecule and two methanol molecules of crystallization (Fig. 1, *b*). The hydrazone molecule in **1** is nearly coplanar with a mean deviation from the plane of 0.049(2) Å, and with the dihedral angle between the two phenyl rings of 3.2(3)°. However, the hydrazone molecule in **2** is twisted with a mean deviation from the plane of 0.246(2) Å, and with the dihedral angle between the phenyl and naphthyl rings of 15.1(2)°. The bond lengths and angles (Table 2) in the compounds are comparable to each other, and also comparable to those observed in other similar hydrazone compounds [ 10–13 ]. The bond lengths of C(7)=N(1) in **1** and C(11)=N(1) in **2** conform to the values for double bonds. The bond lengths of C(8)—N(2) in **1** and C(12)—N(2) in **2** are intermediate between the C—N single bonds and the C=N double bonds because of the conjugation effects in the molecules. As expected, the molecules adopt *E* configurations about the C=N double bonds. In **1**, the C(1)—C(7)—N(1)—N(2), C(7)—N(1)—N(2)—C(8), N(1)—N(2)—C(8)—C(9), and N(1)—N(2)—C(8)—O(2) torsion angles are 1.0(3), 2.8(4), 2.7(4), and 3.4(4)° respectively. In **2**, the C(1)—C(11)—N(1)—N(2), C(11)—N(1)—N(2)—C(12), N(1)—N(2)—C(12)—C(13), and N(1)—N(2)—C(12)—O(2) torsion angles are 1.7(3), 5.4(3), 2.1(3), and 1.5(3)° respectively. An intramolecu-

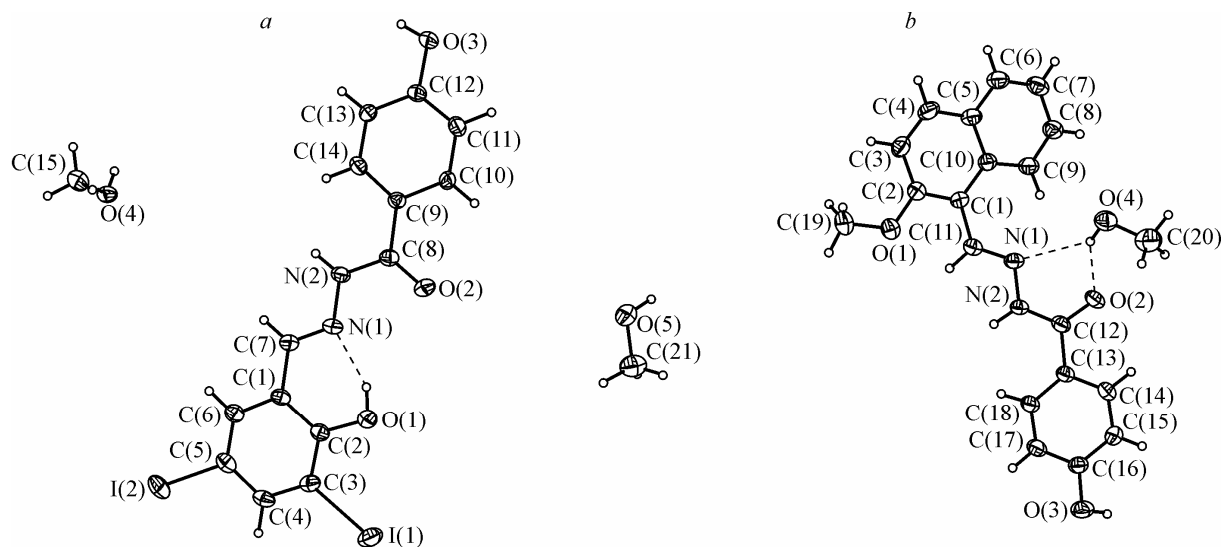


Fig. 1. Molecular structure of **1** (*a*) and **2** (*b*) with 30 % probability thermal ellipsoids. The H atoms are shown as small spheres of arbitrary radii and the intramolecular O—H...N hydrogen bond as a dashed line

Table 2

Selected bond lengths ( $\text{\AA}$ ) and angles (deg.) for the compounds

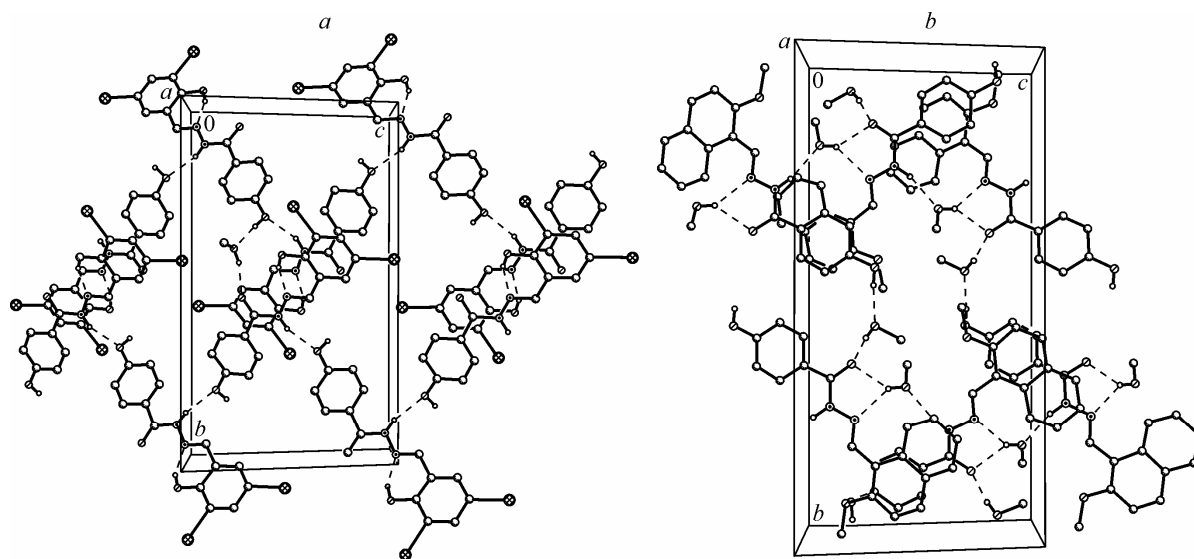
1				2			
N(1)—C(7)	1.278(4)	C(7)—N(1)—N(2)	119.0(3)	N(1)—C(11)	1.285(3)	C(11)—N(1)—N(2)	114.9(2)
N(2)—C(8)	1.364(4)	N(1)—C(7)—C(1)	119.5(3)	N(2)—C(12)	1.340(3)	O(2)—C(12)—N(2)	121.2(2)
O(2)—C(8)	1.221(4)	O(2)—C(8)—C(9)	122.0(3)	O(2)—C(12)	1.241(2)	N(2)—C(12)—C(13)	117.9(2)
N(1)—N(2)	1.363(4)	N(1)—N(2)—C(8)	117.7(3)	N(1)—N(2)	1.386(2)	C(12)—N(2)—N(1)	119.3(2)
O(1)—C(2)	1.342(4)	O(2)—C(8)—N(2)	121.7(3)	O(1)—C(2)	1.361(3)	O(2)—C(12)—C(13)	120.8(2)
		N(2)—C(8)—C(9)	116.3(3)				

Table 3

Distances ( $d$ ,  $\text{\AA}$ ) and angles (deg.) involving hydrogen bonding of the compounds

$D-H \cdots A$	$d(D-H)$	$d(H \cdots A)$	$d(D \cdots A)$	Angle( $D-H \cdots A$ )
<b>1</b>				
O(1)—H(1) $\cdots$ N(1)	0.85(4)	1.80(3)	2.566(4)	149(5)
N(2)—H(2) $\cdots$ O(3) <sup>#1</sup>	0.90(4)	2.17(2)	3.029(4)	161(5)
O(4)—H(4) $\cdots$ O(2) <sup>#2</sup>	0.82	1.92	2.715(3)	163
O(3)—H(3) $\cdots$ O(4) <sup>#3</sup>	0.82	1.83	2.645(4)	174
<b>2</b>				
O(3)—H(3) $\cdots$ O(5) <sup>#4</sup>	0.82	1.86	2.675(3)	171
O(4)—H(4) $\cdots$ O(2)	0.82	2.16	2.858(2)	143
O(4)—H(4) $\cdots$ N(1)	0.82	2.44	3.137(3)	144
N(2)—H(2) $\cdots$ O(4) <sup>#5</sup>	0.90(1)	2.06(1)	2.944(3)	164(2)
O(5)—H(5) $\cdots$ O(2) <sup>#6</sup>	0.84(1)	1.90(1)	2.737(3)	170(3)

Symmetry transformations used to generate the equivalent atoms: #1:  $1/2+x, 3/2-y, 1/2+z$ ; #2:  $1/2-x, -1/2+y, 1/2-z$ ; #3:  $-1+x, y, -1+z$ ; #4:  $x, -1+y, z$ ; #5:  $x, 1/2-y, 1/2+z$ ; #6:  $1-x, 1-y, 1-z$ .

Fig. 2. Molecular packing of **1** (a) and **2** (b). Intermolecular hydrogen bonds are shown as dashed lines

lar O(1)—H(1)···N(1) hydrogen bond in **1** and two intermolecular O(4)—H(4)···N(1) and O(4)—H(4)···O(2) hydrogen bonds in **2** (Table 3) are observed in the molecular structures. The methanol molecules are linked to the hydrazone molecules through O—H···O, O—H···N and N—H···O hydrogen bonds (Table 3).

In the crystal structures of both compounds, the hydrazone molecules and the methanol molecules are linked through intermolecular O—H···O and N—H···O hydrogen bonds, forming three-dimensional networks (Fig. 2).

### CONCLUSIONS

Two new hydrazone compounds have been synthesized according to the standard procedure with high yields, and their structures were characterized by X-ray crystallography. The methanol molecules easily reside in the crystal structures of the compounds, forming hydrogen bonds.

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