Journal of Structural Chemistry. Vol. 54, No. 6, pp. 1151-1156, 2013

CRYSTAL STRUCTURES OF AROYLHYDRAZONES DERIVED FROM 5-METHOXYSALICYLALDEHYDE

Q.-S. Zong[1,2] and J.-Y. Wu[1]

UDC 548.737:541.12:543.422

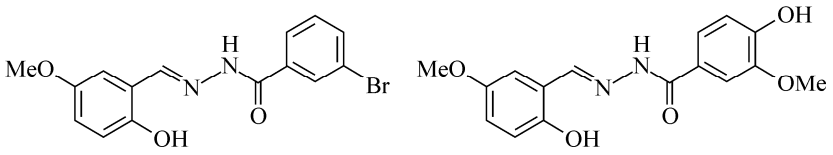
Two new aroylhydrazones 3-bromo-N′-(2-hydroxy-5-methoxybenzylidene)benzohydrazide (**1**) and 4-hydroxy-3-methoxy-N′-(2-hydroxy-5-methoxybenzylidene)benzohydrazide (**2**), derived from 5-methoxysalicylaldehyde, are prepared and determined by means of infrared and ^{1}H NMR spectroscopy and single crystal X-ray diffraction. Compound **1** crystallizes in the monoclinic space group $P2_1/n$ with a = 5.9406(7) Å, b = 31.833(3) Å, c = 7.6460(8) Å, β = 94.522(4)°, V = 1441.4(3) Å^3, Z = 4. Compound **2** crystallizes in the monoclinic space group $P2_1/c$ with a = 14.3471(9) Å, b = 11.3893(7) Å, c = 9.6853(6) Å, β = 94.063(2)°, V = 1578.6(2) Å^3, Z = 4. Both molecules have very similar bond lengths and angles. The crystal structures of both compounds are stabilized by N–H···O and O–H···O hydrogen bonds as well as π···π interactions.

DOI: 10.1134/S002247661306022X

Keywords: aroylhydrazone, Schiff base, synthesis, X-ray structure, hydrogen bonding.

Aroylhydrazones derived from salicylaldehyde and various benzohydrazides have attracted much attention for their structures [1-3], coordination ability [4-6], biological activities [7-9] as well as promising properties for analytical applications [10, 11]. Aroylhydrazones containing the typical –C(O)–NH–N=CH– functional groups are also regarded as Schiff base compounds. The detailed investigation of the structures of such compounds may supply important information about their properties. Although there is a number of crystal structures of aroylhydrazones, to the best of our knowledge, the compounds described here are the first examples derived from 5-methoxysalicylaldehyde. In this paper, we report the synthesis and structures of two new aroylhydrazones derived from 5-methoxysalicylaldehyde with 3-bromobenzohydrazide and 4-hydroxy-3-methoxybenzohydrazide (Scheme 1).

Experimental. Materials and methods. 5-Methoxysalicylaldehyde, 3-bromobenzohydrazide, and 4-hydroxy-3-methoxybenzohydrazide were obtained from Fluka. IR spectra of KBr discs were recorded with a Perkin Elmer 783



Scheme 1. Aroylhydrazones

[1]College of Biology and Chemical Engineering, Jiaxing University, Jiaxing Zhejiang, P. R. China; zongqianshou@163.com. [2]School of Pharmaceutical Sciences, Zhejiang University, Hangzhou Zhejiang, P. R. China. The text was submitted by the authors in English. *Zhurnal Strukturnoi Khimii*, Vol. 54, No. 6, pp. 1121-1126, November-December, 2013. Original article submitted May 19, 2012.

spectrometer. NMR spectra were recorded on a Varian XL gemini 300 spectrometer using tetramethylsilane as the internal standard. The electronic spectrum was recorded in a Cary 5000 spectrophotometer in the region 250-800 nm using DMF as a solvent (10^{-4} M).

Preparation of 3-bromo-N′-(2-hydroxy-5-methoxybenzylidene)benzohydrazide (1). 5-Methoxysalicylaldehyde (1.0 mmol, 0.15 g) and 3-bromobenzohydrazide (1.0 mmol, 0.22 g) were mixed and stirred in absolute ethanol (30 ml). The reaction mixture was refluxed for 1 h on a water bath, then cooled to room temperature. Colorless block-like single crystals of the compound were obtained by slow evaporation of the solution in air. Yield, 83%. Elemental analysis for $C_{15}H_{13}BrN_2O_3$, calculated: C 51.6%, H 3.8%, N 8.0%; found: C 51.4%, H 3.7%, N 8.1%. ^{1}H NMR (DMSO-d^6): δ (ppm) 3.85 (s, 3H), 6.90 (m, 2H), 7.30–8.01 (m, 4H), 8.27 (s, 1H), 8.81 (s, 1H), 11.23 (s, 1H), 12.17 (s, 1H).

Preparation of *N*′-(2-hydroxy-5-methoxybenzylidene)-4-hydroxy-3-methoxybenzohydrazide (2). The same procedure as described for **1** was used for the preparation of **2**, with 3-bromobenzohydrazide replaced by 4-hydroxy-3-methoxybenzohydrazide (1.0 mmol, 0.18 g). Yield, 72%. Elemental analysis for $C_{16}H_{16}N_2O_5$, calculated: C 60.8%, H 5.1%, N 8.9%; found: C 60.6%, H 5.1%, N 8.8%. ^{1}H NMR (DMSO-d^6): δ (ppm) 3.85 (d, 6H), 6.90 (m, 2H), 7.20-7.59 (m, 4H), 8.81 (s, 1H), 11.15 (s, 1H), 12.22 (s, 1H), 12.53 (s, 1H).

TABLE 1. Crystal Data and Structure Refinement for the Compounds

	1	**2**
Empirical formula	$C_{15}H_{13}BrN_2O_3$	$C_{16}H_{16}N_2O_5$
Formula weight	349.2	316.3
Temperature, K	298(2)	298(2)
Wavelength, Å	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
Unit cell dimensions a, b, c, Å; β, deg	5.9406(7), 31.833(3), 7.6460(8); 94.522(4)	14.3471(9), 11.3893(7), 9.6853(6); 94.063(2)
Volume, Å^3	1441.4(3)	1578.6(2)
Z	4	4
Calculated density, mg/m^3	1.609	1.331
Absorption coefficient, mm^{-1}	2.863	0.100
F(000)	704	664
Crystal size, mm	0.17×0.15×0.15	0.21×0.18×0.18
θ range for data collection, deg	2.5-28.3	2.8-28.5
T_{min} and T_{max}	0.6418 and 0.6733	0.9793 and 0.9822
Index ranges	$-7 \le h \le 7$; $-38 \le k \le 36$; $-8 \le l \le 9$	$-17 \le h \le 17$; $-13 \le k \le 13$; $-11 \le l \le 11$
Reflections collected	10442	16471
Unique reflections	2498	2920
Observed reflections [$I > 2\sigma(I)$]	2062	2312
Parameters	195	215
Restraints	1	1
R_{int}	0.0588	0.0252
$GOOF$ on F^2	1.118	1.048
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0671$, $wR_2 = 0.1845$	$R_1 = 0.0391$, $wR_2 = 0.0996$
R indices (all data)	$R_1 = 0.0818$, $wR_2 = 0.2075$	$R_1 = 0.0536$, $wR_2 = 0.1082$
Largest difference peak and hole, e/Å^{-3})	0.939, –0.762	0.171, –0.131

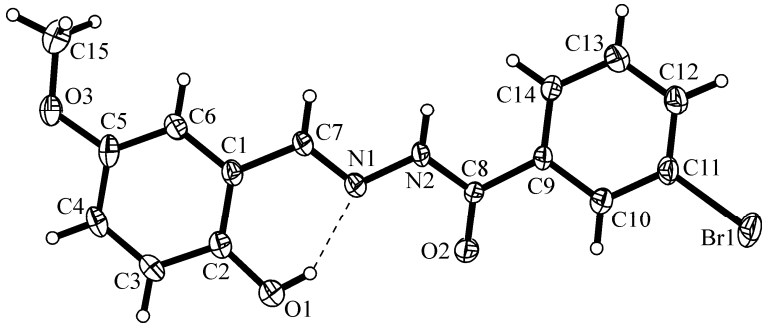


Fig. 1. Anisotropic ellipsoid representation of compound **1** together with the atom labeling scheme. The ellipsoids are drawn at the 30% probability level; hydrogen atoms are shown as spheres of arbitrary radii.

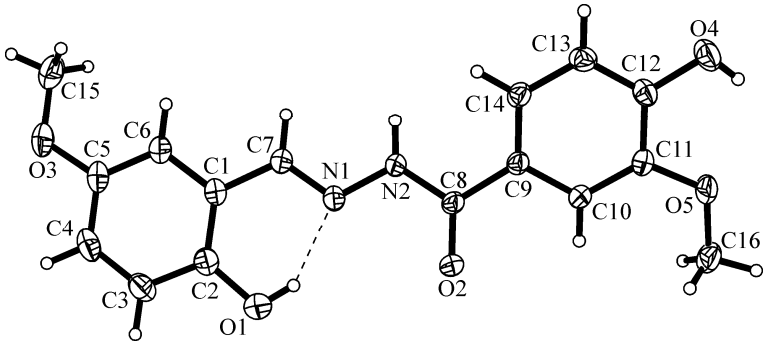


Fig. 2. Anisotropic ellipsoid representation of compound **2** together with the atom labeling scheme. The ellipsoids are drawn at the 30% probability level; hydrogen atoms are shown as spheres of arbitrary radii.

X-ray diffraction. Single crystal X-ray diffraction experiments were performed on a Bruker SMART APEX CCD diffractometer using graphite monochromated MoK_α radiation ($\lambda = 0.71073$ Å) at 298(2) K. Crystals with the dimensions of 0.17×0.15×0.15 mm for **1** and 0.21×0.18×0.18 mm for **2** were used. The structures were solved by direct methods with the program SHELXS-97 and refined by full matrix least squares on F^2 with SHELXL-97 [12]. All non-hydrogen atoms were refined anisotropically. The amino hydrogen atoms were located from difference Fourier maps. The remaining hydrogen atoms were placed geometrically in idealized positions (C–H distances of 0.93-0.96 Å, O–H distances of 0.82 Å) and refined as rigid groups with their U_{iso}'s as 1.2 or 1.5 times U_{eq} of the appropriate carrier atoms. The crystallographic data are listed in Table 1.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, supplementary publication Nos. CCDC — 879963 (**1**) and 879964 (**2**). Copies of the data may be obtained free of charge on application to CSD, 12 Union Road, Cambridge CB2 1EZ, UK (fax: 1441223/336033, e-mail: deposit@ccdc.cam.ac.uk).

Results and discussion. Crystal structures of the compounds. The molecular structures showing 30% displacement ellipsoids with atomic numbering schemes of compounds **1** and **2** are shown in Figs. 1 and 2 respectively. Selected bond lengths and angles are listed in Table 2. The structures of the compounds reveal quasi-coplanarity of the whole molecular skeleton with double bonds located in the central –C=N–NH–C(O)– group. They have *E*-configuration with respect to the double bonds of hydrazone bridges. The dihedral angles between the two benzene rings are 6.7(3)° for **1** and 22.0(3)° for **2**. In each molecule of the compounds, the C1–C6 benzene ring is nearly coplanar with the plane defined by the C7–N1–N2 moiety, with the dihedral angles being 8.1(3)° for **1** and 1.5(3)° for **2**. This planarity is assisted by the formation of an intramolecular O–H···N hydrogen bond (Table 3), which makes an *S*(6) ring motif [13]. The C7–N1 and C8–O2 bonds in the compounds have a double bond character, whereas the C8–N2 bonds are typical of single bonds. All the bond lengths in the compounds are in agreement with the values found in analogous compounds [1-3].

TABLE 2. Selected Bond Lengths (Å) and Bond Angles (deg) for the Compounds

			1		
Br1–C11	1.894(6)	N1–C7	1.280(7)	N1–N2	1.383(6)
N2–C8	1.342(7)	O1–C2	1.343(8)	O2–C8	1.226(7)
O3–C5	1.371(8)	O3–C15	1.421(10)	C8–C9	1.492(8)
C7–N1–N2	116.5(5)	C8–N2–N1	118.3(5)	C5–O3–C15	118.3(5)
C6–C1–C7	118.7(5)	C2–C1–C7	121.8(5)	O1–C2–C3	118.2(6)
O1–C2–C1	123.7(5)	C6–C5–O3	125.5(7)	O3–C5–C4	115.0(6)
N1–C7–C1	119.3(5)	O2–C8–N2	122.4(5)	O2–C8–C9	121.8(5)
N2–C8–C9	115.7(5)	C14–C9–C10	119.7(5)	C14–C9–C8	123.7(5)
C10–C9–C8	116.5(5)	C12–C11–Br1	120.4(5)	C10–C11–Br1	118.1(5)
			2		
N1–C7	1.282(2)	N1–N2	1.379(2)	N2–C8	1.351(2)
O1–C2	1.355(2)	O2–C8	1.232(2)	O3–C5	1.377(2)
O3–C15	1.412(2)	O4–C12	1.359(2)	O5–C11	1.364(2)
O5–C16	1.416(2)	C1–C7	1.450(2)	C8–C9	1.485(2)
C7–N1–N2	116.9(1)	C8–N2–N1	118.6(1)	C5–O3–C15	118.2(1)
C11–O5–C16	118.2(1)	C2–C1–C7	122.1(1)	C6–C1–C7	118.6(1)
O1–C2–C3	118.2(2)	O1–C2–C1	122.8(1)	C6–C5–O3	124.3(2)
O3–C5–C4	115.8(1)	N1–C7–C1	120.3(1)	O2–C8–N2	121.6(1)
O2–C8–C9	122.6(1)	N2–C8–C9	115.8(1)	C14–C9–C8	122.5(1)
C10–C9–C8	118.2(1)	O5–C11–C10	126.0(1)	O5–C11–C12	114.0(1)
O4–C12–C13	118.9(1)	O4–C12–C11	121.5(1)		

TABLE 3. Hydrogen Bonding Information

D–H···*A*	*D*–H, Å	H···*A*, Å	*D*···*A*, Å	*D*–H···*A*, Å
		1		
N2–H2···O2[i]	0.900(10)	2.03(4)	2.877(6)	157(8)
O1–H1···N1	0.82	1.91	2.619(6)	144
		2		
O1–H1···N1	0.82	1.90	2.6143(17)	145
O4–H4···O3[ii]	0.82	2.11	2.7984(16)	142
O4–H4···O5	0.82	2.23	2.6678(16)	114
N2–H2···O2[iii]	0.902(9)	1.897(10)	2.7952(15)	174(2)

Symmetry codes: [i] –1/2+*x*, 1/2–*y*, –1/2+*z*; [ii] –1+*x*, 1/2–*y*, –1/2+*z*; [iii] *x*, 1/2–*y*, 1/2+*z*.

In the crystal packing of compound **1**, the molecules are linked through intermolecular N–H···O hydrogen bonds to form chains running along the *c* axis (Fig. 3). In the crystal packing of compound **2**, the molecules are linked through intermolecular O–H···O hydrogen bonds to form chains running along the *a* axis. The adjacent two chains are further connected through N–H···O hydrogen bonds to form a twin chain (Fig. 4). In both compounds, the infinite chains are subjected to π···π interactions (Table 4) acting between the aromatic rings.

IR spectra. In the IR spectra of the compounds, the OH stretching vibrations are centered at 3387 cm^{-1} for **1** and 3365 cm^{-1} for **2**. The peaks at 3172 cm^{-1} for **1** and 3156 cm^{-1} for **2** could be attributed to N–H symmetric stretching. The aromatic C–H stretching vibrations are located at 3030-3060 cm^{-1}. The aliphatic C–H stretching vibrations are observed at 2860-2980 cm^{-1}. Both compounds exhibit stretching vibration frequencies of imino bonds at about 1610 cm^{-1}. Intense bands

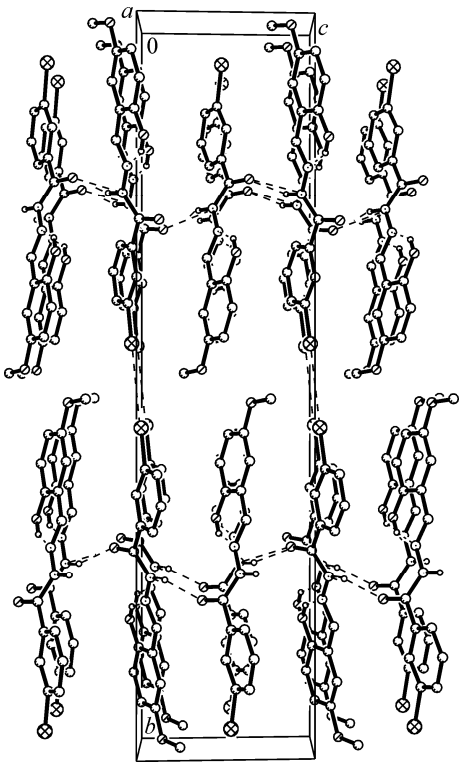


Fig. 3. Molecular packing diagram of **1** as seen along the *a* direction. Hydrogen bonds are shown as dashed lines.

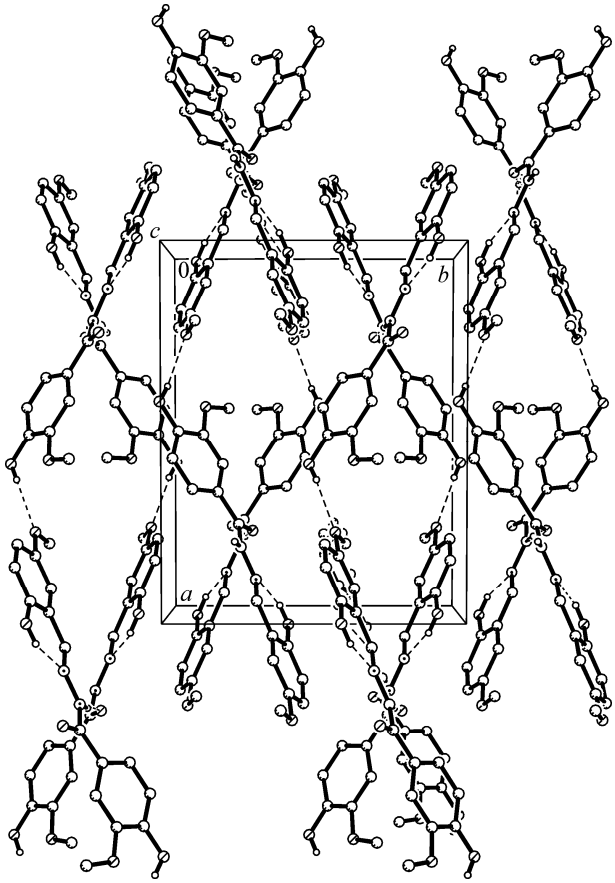


Fig. 4. Molecular packing diagram of **2** as seen along the *c* direction. Hydrogen bonds are shown as dashed lines.

TABLE 4. π···π Interactions (Å)

1		**2**	
*Cg*1···*Cg*2^{iv}	4.320(2)	*Cg*3···*Cg*3^{vi}	4.206(2)
*Cg*1···*Cg*2^{v}	4.024(2)		
*Cg*1 and *Cg*2 are the centroids of the C1–C6 (benzene) and C9–C14 (benzene) rings, respectively.		*Cg*3 is the centroid of the C1–C6 (benzene) ring.	

Symmetry codes: $^{iv}1/2+x$, $1/2-y$, $-1/2+z$; $^{v}1/2+x$, $1/2-y$, $1/2+z$; $^{vi}-x$, $1-y$, $-z$.

originating from the stretching vibrations of C=O groups are located at 1649 cm^{-1} for **1** and 1647 cm^{-1} for **2**. The C–O stretching vibration frequencies of hydroxy and methoxy groups substituted on benzene rings are in the region 1220-1230 cm^{-1}. The peaks at about 780 cm^{-1} are due to N–H out-of-plane bending.

Electronic spectra. In the electronic spectra of the compounds, two strong bands in the region 250-280 nm were observed with ε_{max} values of 7500-8200 respectively. These two bands may be due to $\pi \rightarrow \pi^*$ absorption of the substituted benzene rings and the azomethine bonds. Weak and broad bands in the region 270-280 nm with ε_{max} values of 23 (**1**) and 25 (**2**) were also observed. This absorption is assigned to the $n \rightarrow \pi^*$ transition of the carbonyl groups [14].

We thank the Natural Science Foundation of China (No. 21302063), the Excellent Yong Teachers Program (No. 00511024) and China Postdoctoral Science Foundation (No. 2011M500989) for the financial support.

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