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ORIGINAL PAPER

Synthesis, Characterization, and Crystal Structures of 3-bromo-*N*′-(2-methoxybenzylidene)benzohydrazide and *N*′-(2-methoxybenzylidene)-3,4-methylenedioxybenzohydrazide

Hai-Yun Zhu

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Abstract Two new hydrazone compounds, 3-bromo-*N*′-(2-methoxybenzylidene)benzohydrazide (**1**) and *N*′-(2-methoxybenzylidene)-3,4-methylenedioxybenzohydrazide (**2**), have been synthesized and characterized by elemental analysis, IR, and single crystal X-ray diffractions. Compound (**1**) crystallizes in the triclinic space group $P1$ with unit cell dimensions $a = 8.4088(5)$ Å, $b = 8.5398(5)$ Å, $c = 10.6572(6)$ Å, $\alpha = 90.356(3)°$, $\beta = 102.868(3)°$, $\gamma = 97.987(3)°$, $V = 738.28(7)$ Å^3, $Z = 2$, $R_1 = 0.0406$, and $wR_2 = 0.0804$. Compound (**2**) crystallizes in the tetragonal space group $P4_1$ with unit cell dimensions $a = b = 9.792(4)$ Å, $c = 15.788(6)$ Å, $V = 1513.8(10)$ Å^3, $Z = 4$, $R_1 = 0.0415$, and $wR_2 = 0.0818$. The molecules of both compounds display *E* configurations with respect to the C=N double bonds. In the crystal structure of (**1**), molecules are linked through N–H···O hydrogen bonds, forming chains running along the *b* axis. In the crystal structure of (**2**), molecules are linked through N–H···O hydrogen bonds, forming chains running along the *c* axis.

Keywords Hydrazone · Synthesis · Hydrogen bonds · X-ray crystallography

Introduction

Considerable attention has been focused on the hydrazones for their excellent biological properties, such as antimicrobial, anticonvulsant, analgesic, antiinflammatory, antiplatelet, antitubercular, anticancer and antitumor activities [1–4]. Hydrazones possessing an azomethine –NHN=CH– group constitute an important class of compounds for new drug development. Many researchers have therefore synthesized these compounds as target structures and evaluated their biological activities [5–8]. In this paper, the author reports the syntheses, characterization, and crystal structures of two new hydrazone compounds 3-bromo-*N*′-(2-methoxybenzylidene)benzohydrazide (**1**) and *N*′-(2-methoxybenzylidene)-3,4-methylenedioxybenzohydrazide (**2**) (Scheme 1).

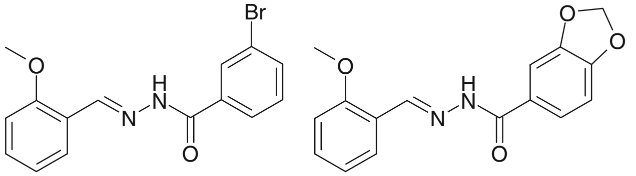
Experimental

All chemicals with AR grade were commercially available and used without further purification. C, H, and N elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. The IR spectra were measured with a FT-IR 170-SX (Nicolet) spectrophotometer using KBr discs in the range 4000–400 cm^{-1}.

Synthesis of 3-Bromo-*N*′-(2-methoxybenzylidene)benzohydrazide (**1**)

2-Methoxybenzaldehyde (135 mg, 1.0 mmol) and 3-bromobenzohydrazide (215 mg, 1.0 mmol) were mixed and stirred in methanol (100 mL) for 1 h at ambient temperature to give a colourless solution. The solution was left to slow evaporation of the methanol for a week, yielding colourless block-shaped single crystals. The crystals were filtered out and washed with methanol. Yiled: 261 mg (78%). Anal. Calcd. (%) for $C_{15}H_{13}BrN_2O_2$: C, 54.1; H, 3.9; N, 8.4. Found (%): C, 53.8; H, 4.0; N, 8.5. IR data (KBr, cm^{-1}): 3272 (m), 1643 (s), 1639 (s), 1486 (s), 1413

H.-Y. Zhu (✉)
Department of Chemistry and Chemical Engineering,
Baoji University of Arts and Sciences, Baoji 721013,
People's Republic of China
e-mail: zhuzhuhaiyun@126.com



Scheme 1 The hydrazone compounds

(m), 1351 (m), 1294 (m), 1266 (s), 1240 (s), 1182 (w), 1160 (w), 1110 (m), 1015 (m), 898 (w), 860 (w), 823 (w), 746 (m), 698 (w), 657 (w), 579 (w), 536 (w), 460 (w).

Synthesis of *N*′-(2-Methoxybenzylidene)-3,4-methylenedioxybenzohydrazide (**2**)

2-Methoxybenzaldehyde (135 mg, 1.0 mmol) and 3,4-(methylenedioxy)benzohydrazide (180 mg, 1.0 mmol) were mixed and stirred in methanol (100 mL) for 1 h at ambient temperature to give a colourless solution. The solution was left to slow evaporation of the methanol for 5 days, yielding colourless block-shaped single crystals. The crystals were filtered out and washed with methanol. Yiled: 220 mg (74%). Anal. Calcd. (%) for $C_{16}H_{14}N_2O_4$: C, 64.4; H, 4.7; N, 9.4. Found (%): C, 64.2; H, 4.7; N, 9.5. IR data (KBr, cm^{-1}): 3211 (m), 1648 (s), 1602 (s), 1540 (m), 1504 (m), 1456 (m), 1417 (w), 1350 (m), 1283 (m), 1245 (s), 1177 (m), 1110 (w), 1063 (w), 1024 (m), 953 (w), 912 (w), 845 (m), 827 (w), 760 (w), 683 (m), 617 (w), 525 (w), 460 (w).

X-Ray Crystallography

X-ray diffraction intensities were collected using a Bruker Apex II CCD area detector equipped with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 298(2) K. Absorption corrections were applied by SADABS program [9]. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares methods using the SHELXTL package [10]. All non-hydrogen atoms were refined anisotropically. The amino H atom in compound (**2**) was located in a difference Fourier map and refined

Table 1 Crystal data, data collection and structure refinement for the compounds

Compound	(**1**)	(**2**)
Molecular formula	$C_{15}H_{13}BrN_2O_2$	$C_{16}H_{14}N_2O_4$
Molecular weight	333.2	298.3
Crystal system	Triclinic	Tetragonal
Space group	$P1$	$P4_1$
Temperature (K)	298(2)	298 (2)
a (Å)	8.4088(5)	9.792(4)
b (Å)	8.5398(5)	9.792(4)
c (Å)	10.6572(6)	15.788(6)
α (°)	90.356(3)	
β (°)	102.868(3)	
γ (°)	97.987(3)	
V ($Å^3$)	738.28(7)	1513.8(10)
Z	2	4
D_{calc} (g cm^{-3})	1.499	1.309
Crystal dimensions (mm)	0.20 × 0.20 × 0.18	0.17 × 0.15 × 0.15
Absorption coefficient (mm^{-1})	2.786	0.096
Radiation λ	Mo Kα(0.71073 Å)	Mo Kα(0.71073 Å)
T_{min}/T_{max}	0.606/0.634	0.984/0.986
Reflections measured	4456	4757
Range/indices (h, k, l)	−10, 10; −10, 10; −13, 12	−12, 8; −12, 6; −19, 19
θ limit (°)	1.96–26.99	2.45–27.00
Total no. of unique data	3768 [$R_{int} = 0.0295$]	1706 [$R_{int} = 0.0296$]
No. of observed data, $I > 2\sigma(I)$	2248	1211
No. of variables	364	217
No. of restraints	3	2
Goodness of fit on F^2	0.977	1.003
R_1, wR_2 [$I \geq 2\sigma(I)$]^a	0.0406, 0.0804	0.0415, 0.0818
R_1, wR_2 (all data)^a	0.0914, 0.0992	0.0672, 0.0928

[a] $R_1 = \sum||Fo|—|Fc||/\sum|Fo|$, $wR_2 = [\sum w(Fo^2-Fc^2)^2/\sum w(Fo^2)^2]^{1/2}$

Table 2 Selected bond lengths (Å) and bond angles (°) for the compounds

(**1**)			
Distances (Å)			
C8–N2	1.265(7)	N1–N2	1.391(7)
C7–N1	1.339(8)	C7–O1	1.238(7)
C23–N4	1.267(8)	N3–N4	1.384(6)
C22–N3	1.347(8)	C22–O3	1.224(7)
Angles (°)			
C3–C7–N1	117.2(5)	C3–C7–O1	120.3(6)
N1–C7–O1	122.5(6)	C7–N1–N2	118.1(5)
N1–N2–C8	115.6(5)	N2–C8–C9	119.8(6)
C16–C22–O3	121.4(6)	C16–C22–N3	116.3(6)
O3–C22–N3	122.3(6)	C22–N3–N4	118.4(5)
N3–N4–C23	116.9(5)	N4–C23–C24	118.3(6)
(**2**)			
Distances (Å)			
C8–N1	1.278(4)	N1–N2	1.386(3)
N2–C9	1.349(4)	C9–O2	1.231(3)
Angles (°)			
C1–C8–N1	120.8(3)	C8–N1–N2	115.2(2)
N1–N2–C9	118.8(2)	N2–C9–C10	116.0(3)
N2–C9–O2	122.3(6)	O2–C9–C10	121.7(3)

Table 3 Distances (Å) and angles (°) involving hydrogen bonding of the compounds

D–H···A	d (D–H, Å)	d (H···A, Å)	d (D···A, Å)	Angle (D–H···A,°)
(**1**)				
N3–H3···O1^{i}	0.86	2.15	2.910(6)	148
N1–H1···O3	0.86	2.20	2.952(7)	146
(**2**)				
N2–H2···O2^{ii}	0.897(10)	2.131(17)	2.941(3)	150(3)

Symmetry codes i x, 1 + *y*, *z*; *ii* 1 −*y*, *x*, 1/4 + *z*

isotropically, with N–H distance restrained to 0.90(1) Å, and with U_{iso}(H) values fixed at 0.08 Å^2. The remaining H atoms were placed in idealized positions and constrained to ride on their parent atoms. The details of the crystallographic data are summarized in Table 1. Selected bond lengths and angles are summarized in Table 2. Hydrogen bonding interactions are listed in Table 3.

Results and Discussion

The compounds were readily synthesized by the reaction of equimolar quantities of 2-methoxybenzaldehyde with 3-bromobenzohydrazide and 3,4-(methylenedioxy)benzohydrazide, respectively, in methanol. The element analyses are in good agreement with the formulae proposed for the compounds. The single crystals of both compounds are stable in air for at least 3 months, soluble in methanol, ethanol, acetonitrile, chloroform, and dichloromethane, insoluble in water.

Structure Description of the Compounds

Figures 1 and 2 give perspective views of the compounds (**1**) and (**2**), respectively. The structures of the two compounds are very similar. The asymmetric unit of the compound (**1**) consists of two hydrazone molecules connected to each other by a N–H···O hydrogen bond. All the bond lengths and angles in the two compounds are comparable to each other, and also comparable to those observed in other hydrazone compounds [11–22]. The bond lengths of C8=N2 and C23=N4 in (**1**) and C8=N1 in (**2**) confirm them as double bonds. The bond lengths of C7–N1 and C22–N3 in (**1**) and C9–N2 in (**2**) are relatively short, suggesting some degree of delocalization in the

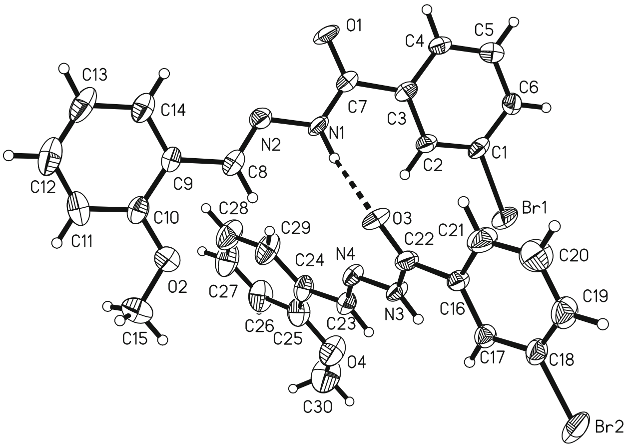


Fig. 1 Molecular structure of (**1**) at 30% probability displacement. N–H···O hydrogen bond is shown as a *dashed line*

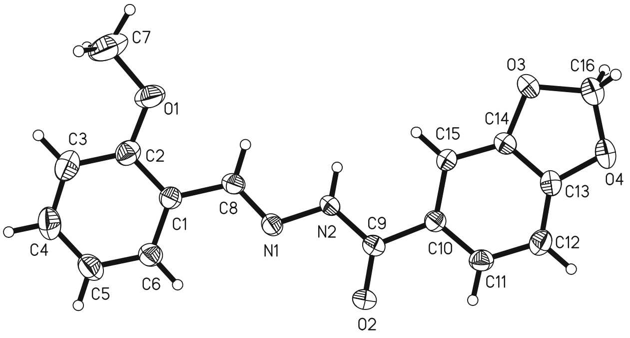


Fig. 2 Molecular structure of (**2**) at 30% probability displacement

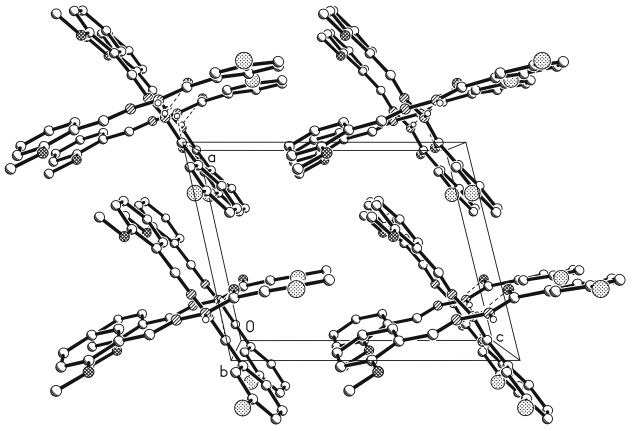


Fig. 3 Molecular packing of (**1**), viewed along the *b* axis. Hydrogen bonds are shown as *dashed lines*

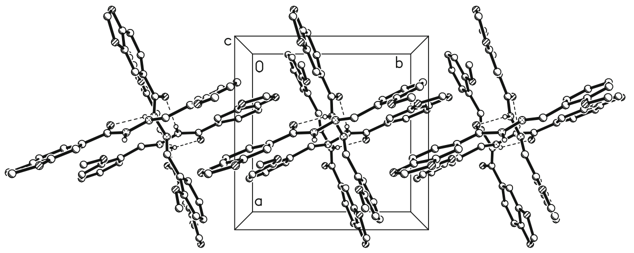


Fig. 4 Molecular packing of (**2**), viewed along the *c* axis. Hydrogen bonds are shown as *dashed lines*

acetohydrazide systems. In (**1**), the dihedral angle between the C1–C6 and C9–C14 benzene rings is 1.2(5)°, and that between the C16–C21 and C24–C29 benzene rings is 22.9(5)°. In (**2**), the dihedral angle between the C1–C6 and C10–C15 benzene rings is 6.5(3)°.

In the crystal structure of (**1**), molecules are linked through N–H···O hydrogen bonds, forming chains running along the *b* axis (Fig. 3). In the crystal structure of (**2**), molecules are linked through N–H···O hydrogen bonds, forming chains running along the *c* axis (Fig. 4). In both structures, there are also short π-electron ring—π-electron ring interactions with *Cg*–*Cg* distances<6.0 Å and $\beta < 60.0°$ that are specified in Table 4 [23].

IR Spectra

The middle and sharp bands at 3272 cm^{-1} for (**1**) and 3211 cm^{-1} for (**2**) are assigned to ν(N–H). The strong bands at 1643 cm^{-1} for (**1**) and 1648 cm^{-1} for (**2**) are due to ν(C=O). The characteristic C=N stretching vibrations of Schiff bases are at 1637 cm^{-1} for (**1**) and 1639 cm^{-1} for (**2**), respectively.

Table 4 π–π interactions

Cg	Distance between ring centroids (Å)	Dihedral angle (°)	Perpendicular distance of *Cg*(I) on *Cg*(J) (Å)	Perpendicular distance of *Cg*(J) on *Cg*(I) (Å)
(**1**)				
$Cg1\cdots Cg2^{\#1}$	3.734	1.23	3.494	3.517
$Cg1\cdots Cg4^{\#2}$	4.979	70.38	0.535	4.685
$Cg2\cdots Cg3^{\#3}$	4.995	58.11	1.362	4.748
$Cg3\cdots Cg1^{\#4}$	5.951	59.34	0.512	4.123
$Cg3\cdots Cg4^{\#2}$	4.362	22.88	3.929	2.894
$Cg4\cdots Cg2^{\#1}$	5.748	69.19	0.522	5.211
(**2**)				
$Cg5\cdots Cg6^{\#5}$	4.577	7.79	3.406	3.446
$Cg5\cdots Cg6^{\#6}$	5.822	83.19	1.059	5.052
$Cg6\cdots Cg6^{\#7}$	5.903	89.33	0.080	3.923
$Cg6\cdots Cg7^{\#1}$	3.698	6.51	3.384	3.489
$Cg7\cdots Cg5^{\#8}$	4.747	89.42	1.292	4.200

*Cg*1, *Cg*2, *Cg*3, and *Cg*4 are the centroids of the C1–C2–C3–C4–C5–C6, C9–C10–C11–C12–C13–C14, C16–C17–C18–C19–C20–C21, and C24–C25–C26–C27–C28–C29 rings in (**1**), respectively. *Cg*5, *Cg*6, and *Cg*7 are the centroids of the O3–C14–C13–O4–C16, C1–C2–C3–C4–C5–C6, and C10–C11–C12–C13–C14–C15 rings in (**2**), respectively. *Symmetry codes* #1 $-1+x, y, z$; #2 $x, y, 1+z$; #3 $x, -1+y, -1+z$; #4 $1+x, 1+y, z$; #5 $1+x, y, z$; #6 $1-y, 1+x, 1/4+z$; #7 $y, -x, -1/4+z$; #8, $y, 2-x, -1/4+z$

Conclusions

In the above study, two new hydrazone compounds have been prepared, and their structures were confirmed by elemental analysis, IR spectra, and single crystal determination.

Supplementary Material

CCDC—782447 for (**1**) and 782448 for (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at http://www.ccdc.cam.ac.uk/const/retrieving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336033 or e-mail: data_request@ccdc.cam.ac.uk.

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