

## Synthesis and X-Ray Structures of Hydrazones Derived from 2-(4-Nitrophenoxy)acetoaldehyde

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Two new hydrazones, (4-nitrophenoxy)acetic acid [1-(3,4-dihydroxyphenyl)methylidene]hydrazide (**1**) and (4-nitrophenoxy)acetic acid [1-(4-hydroxyphenyl)methylidene]hydrazide (**2**), derived from 2-(4-nitrophenoxy)acetoaldehyde have been prepared and determined by means of the infrared spectra, <sup>1</sup>H NMR and single crystal X-ray diffraction. Compound **1** crystallizes in the monoclinic space group P2<sub>1</sub>/n with a = 8.306(1) Å, b = 12.220(1) Å, c = 14.853(2) Å, β = 104.899(1)°, V = 1456.8(3) Å<sup>3</sup>, Z = 4. Compound **2** crystallizes in the monoclinic space group P2<sub>1</sub>/n with a = 8.356(3) Å, b = 12.392(3) Å, c = 14.595(3) Å, β = 105.598(2)°, V = 1455.6(7) Å<sup>3</sup>, Z = 4. Both molecules have similar bond lengths and angles pattern. The crystal structures of both compounds are stabilized by hydrogen bonds, as well as π···π interactions.

**Keywords:** Hydrazone, Schiff base, Synthesis, X-Ray structure, Hydrogen bonding.

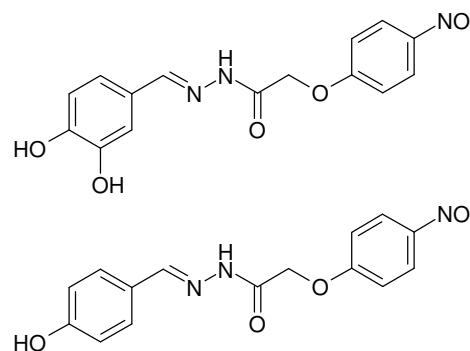
### INTRODUCTION

Hydrazones derived from hydrazides with various aldehydes have been attracted much attention for their structures<sup>1-3</sup>, coordination ability<sup>4-6</sup>, biological activities<sup>7-9</sup>, as well as promising properties for analytical applications<sup>10,11</sup>. Hydrazones 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 relating to their properties. Although there is a number of crystal structures of hydrazones. To the best of our knowledge the compounds described here are the first examples derived from 2-(4-nitrophenoxy)acetoaldehyde. In this paper, we report the synthesis and structures of two new hydrazones derived from 2-(4-nitrophenoxy)acetoaldehyde with 3,4-dihydroxybenzaldehyde and 4-hydroxybenzaldehyde (**Scheme-I**).

### EXPERIMENTAL

2-(4-Nitrophenoxy)acetoaldehyde, 3,4-dihydroxybenzaldehyde and 4-hydroxybenzaldehyde were obtained from Fluka. IR spectra of KBr discs were recorded with a Perkin Elmer 783 spectrometer. NMR spectra were recorded on a Varian XL gemini 300 spectrometer using tetramethylsilane as internal standard.

**Preparation of (4-nitrophenoxy)acetic acid [1-(3,4-dihydroxyphenyl)methylidene]hydrazide (**1**):** 2-(4-



**Scheme-I:** Hydrazones

Nitrophenoxy)acetoaldehyde (1 mmol, 0.21 g) and 3,4-dihydroxybenzaldehyde (1 mmol, 0.14 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. Yellow block-like single crystals of the compound were obtained by slow evaporation of the solution in air. Yield, 87 %. Elemental analysis for C<sub>15</sub>H<sub>13</sub>N<sub>3</sub>O<sub>6</sub>, calcd. (%): C 54.4, H 4.0, N 12.7; found (%): C 54.2, H 4.0, N 12.6. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>): δ (ppm) 4.65 (s, 2H), 6.82 (d, 1H), 7.23-7.36 (m, 4H), 8.11 (d, 2H), 8.57 (s, 1H), 11.06 (s, 1H), 12.31 (s, 1H), 12.53 (s, 1H).

**Preparation of (4-nitrophenoxy)acetic acid [1-(4-hydroxyphenyl)methylidene]hydrazide (**2**):** The same procedure as described for **1** was used for the preparation of

**2**, with 3,4-dihydroxybenzaldehyde replaced by 4-hydroxybenzaldehyde (1.0 mmol, 0.12 g). Yield, 79 %. Elemental analysis for  $C_{15}H_{13}N_3O_5$ , calcd. (%): C 57.1, H 4.2, N 13.3; found (%): C 56.9, H 4.1, N 13.4.  $^1H$  NMR (DMSO- $d_6$ ):  $\delta$  (ppm) 4.65 (s, 2H), 6.83 (d, 2H), 7.23 (d, 2H), 7.73 (d, 2H), 8.11 (d, 2H), 8.56 (s, 1H), 11.15 (s, 1H), 12.27 (s, 1H).

**X-ray diffraction:** Single crystal X-ray diffraction experiments were performed on a BRUKER SMART APEX CCD diffractometer using graphite monochromated  $MoK_{\alpha}$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 298(2) K. Crystals with dimensions  $0.18 \text{ mm} \times 0.18 \text{ mm} \times 0.17 \text{ mm}$  for **1** and  $0.30 \text{ mm} \times 0.27 \text{ mm} \times 0.23 \text{ mm}$  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.<sup>12</sup> 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  $\text{\AA}$ , O-H distances of 0.82  $\text{\AA}$ ) 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.

TABLE-1  
CRYSTAL DATA AND STRUCTURE  
REFINEMENT FOR THE COMPOUNDS

	<b>1</b>	<b>2</b>
Empirical formula	$C_{15}H_{13}N_3O_6$	$C_{15}H_{13}N_3O_5$
Formula weight	331.3	315.3
Temperature (K)	298(2)	298(2)
Wavelength ( $\text{\AA}$ )	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
Unit cell dimensions		
a ( $\text{\AA}$ )	8.306(1)	8.356(3)
b ( $\text{\AA}$ )	12.220(1)	12.392(3)
c ( $\text{\AA}$ )	14.853(2)	14.595(3)
$\beta$ ( $^\circ$ )	104.899(1)	105.598(2)
Volume ( $\text{\AA}^3$ )	1456.8(3)	1455.6(7)
Z	4	4
Calculated density ( $\text{Mg/m}^3$ )	1.510	1.439
Absorption coefficient ( $\text{mm}^{-1}$ )	0.119	0.110
$F_{(000)}$	688	656
Crystal size ( $\text{mm}^3$ )	$0.18 \times 0.18 \times 0.17$	$0.30 \times 0.27 \times 0.23$
$\theta$ range for data collection ( $^\circ$ )	2.8-27.0	2.5-24.5
$T_{min}$ and $T_{max}$	0.9788, 0.9800	0.9676, 0.9750
Index ranges	$-9 \leq h \leq 10$ ; $-14 \leq k \leq 13$ ; $-17 \leq l \leq 17$	$-6 \leq h \leq 10$ ; $-15 \leq k \leq 14$ ; $-18 \leq l \leq 15$
Reflections collected	10452	6737
Unique reflections	2697	3108
Observed reflections [ $I > 2\sigma(I)$ ]	2355	1485
Parameters	222	212
Restraints	1	1
$R_{int}$	0.0202	0.0468
Goodness-of-fit on $F^2$	1.156	0.996
Final R indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0385$ , $wR_2 = 0.1173$	$R_1 = 0.0589$ , $wR_2 = 0.1128$
R indices (all data)	$R_1 = 0.0471$ , $wR_2 = 0.1442$	$R_1 = 0.1366$ , $wR_2 = 0.1438$
Largest difference peak and hole ( $e \text{ \AA}^{-3}$ )	0.433, -0.284	0.148, -0.180

## RESULTS AND DISCUSSION

The molecular structures showing 30 % displacement ellipsoids with atomic-numbering schemes of the compounds **1** and **2** are shown in Figs. 1 and 2, respectively. Selected bond lengths and angles are listed in Table-2. Structures of the compounds reveal quasi-coplanarity of the whole molecular skeleton with localization of the double bonds in the central  $-C=N-NH-C(O)-$  which have E-configuration with respect to the double bonds of the hydrazone bridges. The dihedral angles between the two benzene rings are  $6.5(3)^\circ$  for **1** and  $6.2(3)^\circ$  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 dihedral angle of  $12.8(3)^\circ$  for **1** and  $10.0(3)^\circ$  for **2**. The bonds C7-N1 and C8-O3 in **1** and C7-N1 and C8-O2 in **2** have double bond character. All the bond lengths in the compounds are in agreement with the values found in analogues compounds<sup>1-3</sup>. Both crystals of the compounds are stabilized by hydrogen bonds (Table-3) and  $\pi \cdots \pi$  interactions (Table-4) acting among the aromatic rings (Figs. 3 and 4).

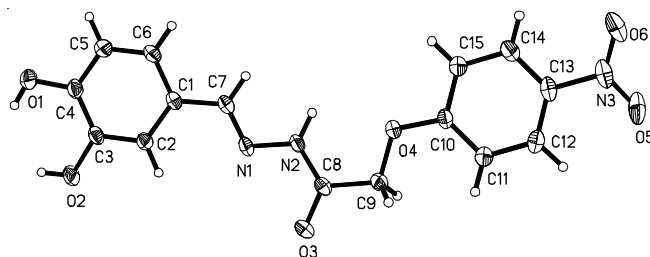


Fig. 1. Anisotropic ellipsoid representation of the compound **1** together with atom labeling scheme. The ellipsoids are drawn at 30 % probability level, hydrogen atoms are shown as spheres of arbitrary radii

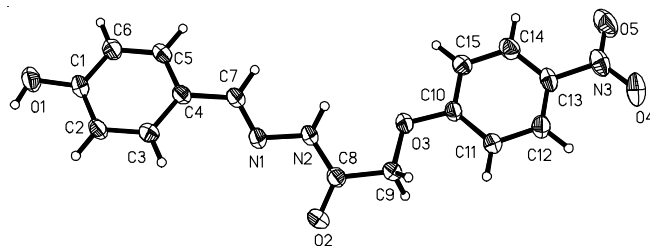


Fig. 2. Anisotropic ellipsoid representation of the compound **2** together with atom labeling scheme. The ellipsoids are drawn at 30 % probability level, hydrogen atoms are shown as spheres of arbitrary radii

In the IR spectra of the compounds, the OH stretching vibrations centered at  $3376 \text{ cm}^{-1}$  for **1** and  $3367 \text{ cm}^{-1}$  for **2**. Absorption due to O-H bending vibrations gave well-defined peaks at about  $1260 \text{ cm}^{-1}$ . The peaks at  $3178 \text{ cm}^{-1}$  for **1** and  $3163 \text{ cm}^{-1}$  for **2** could be attributed to N-H symmetric stretching. The aromatic C-H stretching vibrations are located at  $3030\text{-}3060 \text{ cm}^{-1}$ . The aliphatic C-H stretching vibrations are observed at  $2850\text{-}2990 \text{ cm}^{-1}$ . Both compounds exhibit stretching vibration frequencies of imino bonds at about  $1610 \text{ cm}^{-1}$ . Intensive bands originating from stretching vibrations of C=O groups are located at  $1650 \text{ cm}^{-1}$  for **1** and **2**. The C-O stretching vibration frequencies of hydroxy and methoxy groups substituted on benzene rings are in the region  $1240\text{-}1220 \text{ cm}^{-1}$ . The peaks at

TABLE-2  
SELECTED BOND LENGTHS (Å) AND BOND ANGLES (°) FOR THE COMPOUNDS

1					
N1-C7	1.267(2)	N1-N2	1.3891(18)	N2-C8	1.332(2)
N3-O6	1.221(3)	N3-O5	1.226(2)	N3-C13	1.455(2)
O1-C4	1.357(2)	O2-C3	1.365(2)	O3-C8	1.2306(19)
O4-C10	1.3659(18)	O4-C9	1.419(2)	C1-C7	1.454(2)
C8-C9	1.498(2)	—	—	—	—
C7-N1-N2	114.34(13)	C8-N2-N1	118.91(13)	O6-N3-O5	122.82(17)
O6-N3-C13	118.72(19)	O5-N3-C13	118.45(18)	C10-O4-C9	117.08(13)
C6-C1-C7	118.27(14)	C2-C1-C7	122.93(15)	O2-C3-C2	117.56(15)
O2-C3-C4	122.18(15)	O1-C4-C5	116.65(16)	O1-C4-C3	124.32(15)
N1-C7-C1	122.13(14)	O3-C8-N2	124.31(15)	O3-C8-C9	118.13(15)
N2-C8-C9	117.52(13)	O4-C9-C8	110.57(13)	O4-C10-C11	123.67(15)
O4-C10-C15	115.36(15)	C12-C13-N3	118.64(17)	C14-C13-N3	119.44(17)
2					
N1-C7	1.266(3)	N1-N2	1.385(3)	N2-C8	1.335(3)
N3-O5	1.221(3)	N3-O4	1.232(3)	N3-C13	1.453(3)
O1-C1	1.355(3)	O2-C8	1.217(3)	O3-C10	1.365(3)
O3-C9	1.420(3)	C4-C7	1.458(3)	C8-C9	1.497(4)
C7-N1-N2	115.3(2)	C8-N2-N1	119.0(2)	O5-N3-O4	122.5(3)
O5-N3-C13	118.8(3)	O4-N3-C13	118.7(3)	C10-O3-C9	117.9(2)
O1-C1-C6	116.9(3)	O1-C1-C2	123.3(2)	C3-C4-C7	123.2(2)
C5-C4-C7	118.7(2)	N1-C7-C4	121.9(3)	O2-C8-N2	124.8(3)
O2-C8-C9	119.0(3)	N2-C8-C9	116.1(2)	O3-C9-C8	110.6(2)
O3-C10-C15	115.4(2)	O3-C10-C11	123.5(2)	C12-C13-N3	119.0(3)
C14-C13-N3	119.5(3)	—	—	—	—

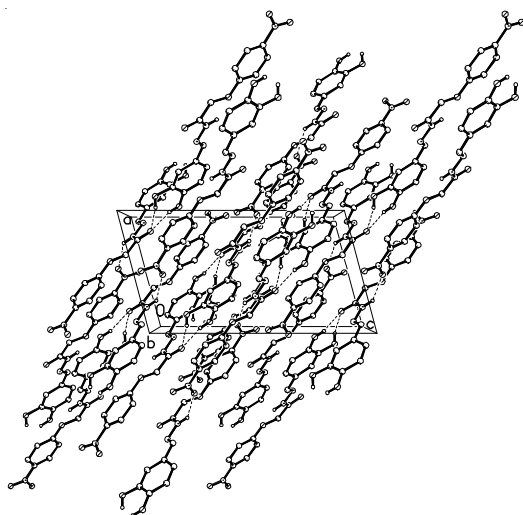


Fig. 3. Molecular packing diagram of 1 as seen along b direction. Hydrogen bonds are shown as dashed lines

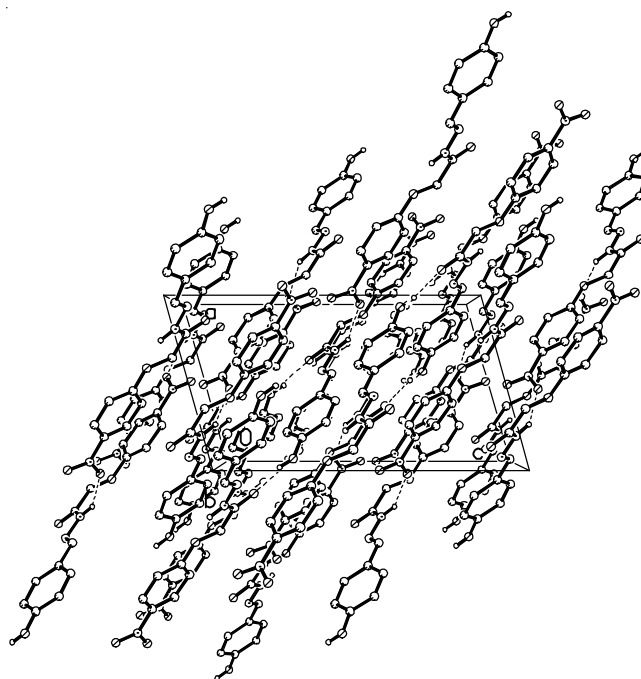


Fig. 4. Molecular packing diagram of 2 as seen along b direction. Hydrogen bonds are shown as dashed lines.

TABLE-3  
HYDROGEN BONDING INFORMATION

D-H...A	D-H (Å)	H...A (Å)	D...A (Å)	D-H...A (°)
1				
O1-H1...O3 <sup>i</sup>	0.82	2.07	2.865(2)	165
O1-H1...O2	0.82	2.49	2.889(2)	111
O1-H1...N1 <sup>i</sup>	0.82	2.63	3.127(2)	121
O2-H2...O3	0.82	1.89	2.693(2)	165
N2-H2B...O5 <sup>ii</sup>	0.90(1)	2.49(2)	3.251(2)	143(2)
N2-H2B...O2 <sup>iii</sup>	0.90(1)	2.58(2)	3.237(2)	130(2)
2				
O1-H1...O2 <sup>iv</sup>	0.82	1.95	2.755(3)	168
O1-H1...N1 <sup>iv</sup>	0.82	2.66	3.127(3)	118
N2-H2...O4 <sup>v</sup>	0.90(1)	2.48(2)	3.265(3)	147(2)

Symmetry codes: (i)  $3/2 - x, 1/2 + y, 3/2 - z$ ; (ii)  $-1/2 - x, 1/2 + y, 1/2 - z$ ; (iii)  $-1/2 + x, 1/2 - y, -1/2 + z$ ; (iv)  $-1/2 - x, 1/2 + y, 1/2 - z$ ; (v)  $3/2 - x, -1/2 + y, 1/2 - z$ .

TABLE-4  
 $\pi \cdots \pi$  INTERACTIONS (Å)

1			
Cg1...Cg2 <sup>iv</sup>	4.320(2)	Cg1...Cg2 <sup>v</sup>	4.024(2)
Cg1 and Cg2 are the centroids of the C1-C6 (benzene) and C9-C14 (benzene) rings, respectively.			
2			
Cg3...Cg3 <sup>vi</sup>	4.206(2)	—	—
Cg3 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)  $-x, 1 - y, -z$ .

775  $\text{cm}^{-1}$  are due to N-H out-of-plane bending. Symmetric and asymmetric stretching vibrations of N-O bonds of the nitro group usually give peaks in the region 1550-1500 and 1360-1290  $\text{cm}^{-1}$ . The first one was not clearly seen in the present spectra because of the presence of aromatic stretching absorptions, but the second one displayed as a sharp band at 1345  $\text{cm}^{-1}$ .

### Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, supplementary publication Nos. CCDC- 879965 (1) and 879966 (2). Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

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