Synthesis and Spectral Characterization of Hydrazone Schiff Bases Derived from 2,4-Dinitrophenylhydrazine. Crystal Structure of Salicylaldehyde-2,4-Dinitrophenylhydrazone

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Reactions of 2,4-dinitrophenylhydrazine with salicylaldehyde, pyridine-2-carbaldehyde and 2-aminobenzophenone in methanol result in the hydrazone Schiff base ligands salicylaldehyde-, pyridine-2-carbaldehyde-, and 2-aminobenzophenone-2,4-dinitrophenylhydrazone, respectively. Crystals of salicylaldehyde-2,4-dinitrophenylhydrazone are monoclinic, space group $P2_1/c$, $a = 13.820(3)$, $b = 4.3515(9)$, $c = 25.159(7)$ Å, $\beta = 123.01(2)^\circ$ with $Z = 4$. The molecular packing is mostly a zigzag or herring-bone pattern.

Key words: Hydrazone, Schiff Base, 2,4-Dintrophenylhydrazine, Salicylaldehyde, X-Ray Structure

Introduction

Hydrazones, $RR'C{=}N{-}NR''R'''$, are used as intermediates in synthesis [1], as functional groups in metal carbonyls [2], in organic compounds [3, 4] and in particular in hydrazone Schiff base ligands (Fig. 1) [5 – 8], which are among others employed in dinuclear catalysts [9]. Furthermore, hydrazones exhibit physiological activities in the treatment of several diseases such as tuberculosis. This activity is attributed to the formation of stable chelate complexes with transition metals which catalyze physiological processes [10 – 12]. They also act as herbicides, insecticides, nematocides, rodenticides, plant growth regulators, sterilants for houseflies, among other applications [10, 11, 13]. In analytical chemistry hydrazones find applications as multidentate ligands for transition metals in colorimetric or fluorimetric determinations [14, 15].

We report here the synthesis and characterization of hydrazone Schiff base compounds **1** – **3**.

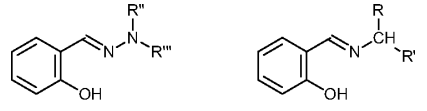

Fig. 1. Hydrazone (a) and Schiff base (b) based on salicylaldehyde.

Results and Discussion

Reaction of 2,4-dinitrophenylhydrazine with salicylaldehyde, pyridine-2-carbaldehyde and 2-aminobenzophenone readily yields the hydrazone Schiff base compounds **1** – **3** in high yield. IR and ^{1}H NMR spectral features agree with the formula assignments. The similar IR spectra of compounds **1** – **3** indicate the formation of the Schiff base product by the absence of the carbonyl group (1700 cm^{-1}) band and the appearance of a strong band in the region of 1610 – 1640 cm^{-1}, assignable to the ν(C=N)$_{\text{imine}}$ group [16]. The X-ray

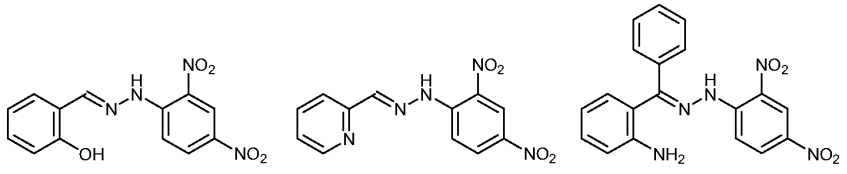

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Table 1. Hydrogen bonding interactions in **1**[a].

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (deg)
intramolecular:				
O5–H5···N3	0.94(3)	1.88(3)	2.688(3)	143(3)
N4–H4···O2	0.88(3)	1.96(3)	2.618(3)	130(2)
intermolecular:				
N4–H4···O2[3]	0.88(3)	2.58(3)	3.420(3)	158(2)

[a] D = Donor, A = acceptor. For found and refined atoms the estimated standard deviations are given in units of the last significant figure. Symmetry transformation: [3] $-x+1, -y+1, -z+1$.

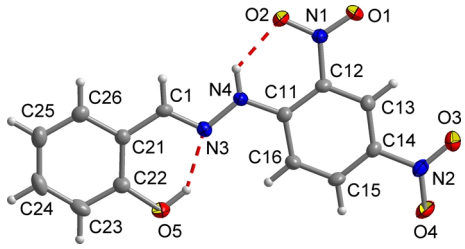

Fig. 2. Molecular structure of **1** with intramolecular hydrogen bonds (see Table 1). Displacement ellipsoids are drawn at the 50 % probability level.

structure of **1** (Fig. 2) shows the whole molecule to be almost planar. The two aryl ring planes form an angle of 3.5(1)°. The dihedral angle of the nitro groups to the bound aryl group (C11-C16) is only 5.0(3)° (O1–N1–O2) and 1.7(3)° (O3–N2–O4), respectively. The plane defined by the central C1=N3–N4 portion is tilted by 4.0(3)° and 2.6(3)° to the planes of the aryl groups (C11-C16 and C21-C26, respectively). Bond lengths are within the expected range. Intramolecular hydrogen bonds are observed between the salicyl-OH group and the imine nitrogen atom and between the hydrazone-NH and the *ortho* nitro group (Fig. 2 and Table 1).

The molecular packing in **1** appears as an in-plane arrangement of molecules when projected onto the *ac* plane (Fig. 3, top). However, it turns out to be a zigzag or herring-bone pattern when viewed along the *ac* diagonal (Fig. 3, bottom). There is a single classical intermolecular, albeit rather weak N–H···O hydrogen bond (Table 1, not shown in Fig. 3) [17, 18]. Adjacent molecules stacked on top of each other along the *b* axis exhibit some medium to weak π-π interactions between their exactly parallel (by symmetry) aryl planes. Centroid-centroid contacts are 4.35 Å, interplanar distances 3.34 and 3.31 Å, slip angles (angle between centroid-centroid vector and normal to plane) 50.2 and 49.6°, and vertical displacements (between ring centroids) 2.79 and 2.82 Å for the interactions

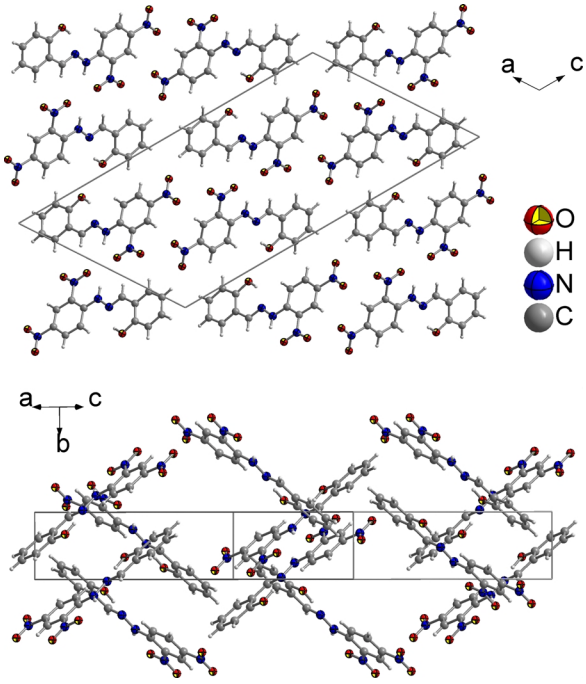

Fig. 3. Packing of the molecules in **1** projected onto the *ac* plane (top), and viewed along the *ac* diagonal perpendicular to the *b* axis (bottom).

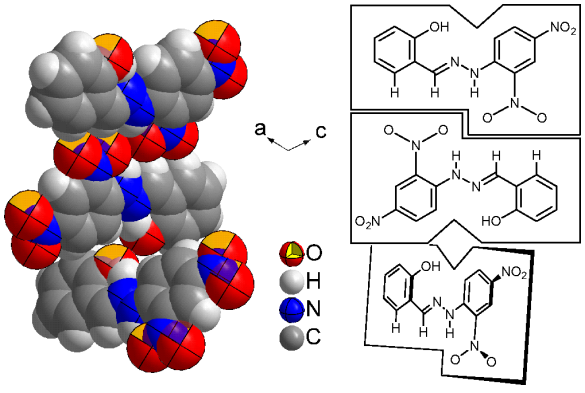

Fig. 4. Space-filling presentation of three adjacent molecules in the *ac* plane (*cf.* Fig. 3, top) and concomitant schematic formula drawing.

of ring C11-C16 and C21-C26, respectively, with their symmetry related counterparts with operation x, $1\pm y$, z [19 – 21]. The program PLATON, which was used for calculating the supramolecular interactions, did neither indicate the presence of strong intermolecular C–H···O hydrogen bonds [22, 23] nor the existence of C–H···π interactions [17, 20, 24, 25]. Instead, a space-filling presentation of adjacent molecules, shown in Fig. 4, suggests that the shape of the van der Waals

surface of the molecules may be the main contributing factor for their packing in the solid-state structure of **1**. Adjacent molecules along the *ac* diagonal, which lie in the same plane, can turn to each other with their *ortho*-nitro group facing the opposite salicyl aryl ring (Fig. 4, upper two molecules). The resulting (aryl-C)–H···O(nitro) contacts between 2.58 and 2.72 Å lie to the long end of "normal" C–H···O bonds [23]. Molecules along the *ac* diagonal, with their planes tilted to each other, assemble through the indentation which is present in the molecule between the salicyl-hydroxy group and the nitro-substituted aryl ring (Fig. 4, lower two molecules).

Experimental Section

All chemicals were reagent grade and used without further purification. Melting points were determined on an Electrothermal 9100 apparatus. FT-IR spectra were collected on a Mattson 1000 spectrophotometer using KBr pellets in the range of 4000 – 450 cm^{-1}. Elemental analyses (CHN) were performed using a Carlo ERBA model EA 1108 analyzer, ^{1}H NMR spectra were obtained on a Bruker spectrometer at 250 MHz in [D_6]DMSO.

*Salicylaldehyde-2,4-dinitrophenylhydrazone (**1**)*

This compound was prepared according to the method given in the literature [26]. Salicylaldehyde (0.122 g, 1.0 mmol) was added slowly to a clear solution of 2,4-dinitrophenylhdrazine (0.198 g, 1.0 mmol) and 1 mL of concentrated hydrochloric acid in 15 mL of methanol. After a few minutes an orange yellow precipitate was obtained which was filtered, washed with methanol and dried in air. Yield: 95 %, m. p. 255 °C. – IR (KBr): ν = 3456 (m, br, NH), 3270 (m, OH), 3101 (w), 2924 (m), 2854 (w), 1620 (vs, C=N), 1512 (s, NO_2), 1419 (m), 1334 (s, NO_2), 1273 (vs, C–O), 1142 (s), 833 (w), 764 (w), 578 (m) cm^{-1}. – ^{1}H NMR ([D_6]DMSO): δ = 11.7 (s, 1H, NH), 10.2 (s, 1H, OH), 8.1 (s, 1H, CH=N), 6.7 – 8.5 (m, 7H, aromatic CH). – $C_{13}H_{10}N_4O_5$ (302.3): calcd. C 51.65, H 3.30, N 18.54; found C 51.65, H 3.80, N 18.00.

*Pyridine-2-carbaldehyde-2,4-dinitrophenylhydrazone (**2**)*

This compound was prepared using the same procedure as for **1**, from 2,4-dinitro-phenylhydrazine (0.198 g, 1.0 mmol), 1 mL of concentrated hydrochloric acid, 15 mL of methanol and pyridine-2-carbaldehyde (0.177 g, 1.0 mmol). The mixture was brought to boil and after a few minutes a yellow solid precipitated, which was filtered, washed with methanol, and air dried. Yield: 90 %, m. p. 239 °C. – IR (KBr): ν = 3424 (s, br, NH), 3209 (vs), 2931 (w), 2862 (w), 1612 (m, C=N), 1566 (w), 1501 (m, NO_2), 1450 (vs), 1331 (s, NO_2), 1195 (m), 1119 (m), 1110 (m), 779 (w), 655 (w), 548 (w) cm^{-1}.

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

	1
Formula	$C_{13}H_{10}N_4O_5$
M_r	302.26
Cryst. size [mm^3]	$0.53 \times 0.14 \times 0.06$
Crystal system	monoclinic
Space group	$P2_1/c$
a [Å]	13.820(3)
b [Å]	4.3515(9)
c [Å]	25.159(7)
β [deg]	123.01(2)
V [$Å^3$]	1268.7 (4)
Z	4
D_{calcd} [g cm^{-3}]	1.582
μ(MoK_α) [cm^{-1}]	1.25
F(000) [e]	624
hkl range	±16, ±4, ±25
$[(\sin\theta)/\lambda]_{max}$ [$Å^{-1}$]	0.615
Refl. measured	8424
Refl. unique	2324
R_{int}	0.1048
Param. refined	205
$R(F)/wR(F^2)$[a] (all reflexions)	0.0835/0.1132
GoF (F^2)[a]	1.016
$\Delta\rho_{fin}$ (max/min) [e $Å^{-3}$]	0.255/–0.236

[a] $R(F) = [\Sigma(||F_o| - |F_c||)/\Sigma|F_o|]$; $wR(F^2) = [\Sigma[w(F_o{}^2 - F_c{}^2)^2/\Sigma[w(F_o^2)^2]]^{1/2}$. – Goodness-of-fit = $[\Sigma[w(F_o{}^2 - F_c{}^2)^2/(n-p)]^{1/2}$. – Weight. scheme w; a/b = 0.0317/0.1922 with $w = 1/[\sigma^2(F_o{}^2) + (aP)^2 + bP$ where $P = (\max(F_o{}^2 \text{ or } 0) + 2F_c{}^2)/3$.

– ^{1}H NMR ([D_6]DMSO): δ = 11.9 (s, 1H, NH), 8.1 (s, 1H, CH=N), 6.8 – 9 (m, 7H, aromatic CH). – $C_{12}H_9N_5O_4$ (287.2): calcd. C 50.17, H 3.13, N 24.40; found C 50.00, H 3.30, N 24.80.

*2-Aminobenzophenone-2,4-dinitrophenylhydrazone (**3**)*

To the clear solution of 2,4-dinitrophenylhdrazine (0.198 g, 1.0 mmol), 1 mL of concentrated hydrochloric acid and 15 mL of methanol was added 2-aminobenzophenone (0.197 g, 1.0 mmol). The mixture was heated at reflux for 1 h, and allowed to stand overnight. The product precipitated as a red powder, was separated by filtration, washed with methanol, and air dried. Yield: 61 %, m. p. 265 °C. – IR (KBr): ν = 3432 (br, N–H), 3370 (br, NH_2), 3324 (vs, NH_2), 3085 (w), 2923 (w), 2854 (w), 1635 (vs, C=N), 1511 (m, NO_2), 1411 (m), 1316 (vs, NO_2), 1280 (s), 1126 (w), 1056 (w), 979 (w), 833 (w), 701 (w), 632(w) cm^{-1}. – ^{1}H NMR ([D_6]DMSO): δ = 10.96 (s, 1H, NH), 6.69 (s, 2H, NH_2), 6.5 – 8.5 (m, 12H, aromatic CH). – $C_{19}H_{15}N_5O_4$ (377.4): calcd. C 60.47, H 4.01, N 18.56; found C 60.40, H 3.96, N 18.40.

X-Ray structure determination

Single crystal X-ray diffraction data for salicylaldehyde-2,4-dinitrophenylhydrazone (**1**) were collected at 293(2) K on a Bruker AXS Smart CCD diffractometer using graphite-

monochromated MoK_α radiation ($\lambda = 0.71073$ Å). The structure was solved by Direct Methods using SHELXS-97, and refined with full-matrix least-squares techniques on F^2 with SHELXL-97 [27]. The crystal data, data collection and refinement parameters are presented in Table 2. All non-hydrogen positions were found and refined with anisotropic temperature factors. Hydrogen atoms on oxygen (OH) and nitrogen (–NH–) were found and refined with $U_{eq}(H) = 1.5\ U_{eq}(O/N)$. Hydrogen atoms on C (phenyl and CH=N) were calculated with appropriate riding models (AFIX 43) and $U_{eq}(H) = 1.2\ U_{eq}(C)$. Graphics were drawn with DIAMOND [28]. Computations on the supramolecular interactions were carried out with PLATON for Windows [29].

CCDC 631452 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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