Original Research Article

Synthesis of mono and bis-substituted compounds 1-(2-hydroxybenzylidene)carbonohydrazide and 1,5-bis(2-hydroxybenzaldehyde)carbohydrazone : Study spectroscopy and X-ray diffraction

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Abstract

The unsymmetricmonocarbonohydrazide Schiff base (H_5L^1) (**1**) and the symmetric dicarbonohydrazone (H_4L^2) (**2**) were preparedfrom a monocondensation reaction between carbonohydrazide and 2-hydroxybenzaldehyde, respectively, in 1/1 and 1/2 ratio. The compounds were characterized by elemental analysis, ^{1}H and ^{13}C NMR and FTIR spectroscopy. The NMR and FTIR data analysis revealed that compounds (**1**) and (**2**) are in the amide form in the solid state as well as in DMSO solution. The molecular structure of each Schiff base compound has been elucidated by single crystal X-ray diffraction analysis. Compound H_5L^1 (**1**) crystallizes in the monoclinic system in $P2_1/c$ space groupwith cell parameters: a = 17.0790(2) Å, b = 11.07410(10) Å, c = 10.56110(10) Å, β= 106.5730(10) °,V = 1914.49(3) Å^3 , Z = 4, R_1 = 0.0432, wR_2 = 0.1275 .The compound H_4L^2 (**2**) crystallizes in the orthorhombic system in$C222_1$ space group with cell parameters; a = 4.5494 (1) Å, b = 12.2213 (2) Å, c = 27.4001 (6) Å,V = 1523.43 (5) Å^3 , Z = 4, R_1= 0.039 , wR_2= 0.125 .Both compounds exhibit inter and intramolecular hydrogen bonds which consolidate the structures into three-dimensional networks.

Keywords: carbonohydrazide, 2-hydroxysbenzaldehyde, NMR, FTIR, crystal, and SCXRD

1. INTRODUCTION

Carbonohydrazide is symmetrical two-armed molecule bearing two highly reactive hydrazide units [1,2]. They are widely used to synthesize organic compounds with applications in various fields [3,4]. With ketones, less reactive than aldehydes, carbonohydrazides can perform monocondensation or di-condensation reactions to yield monocarbonohydrazide or dicarbonohydrazone Schiff bases[5]. However, the monocondensation of carbonohydrazide with aldehyde provides a mixture of dicarbonohydrazone and monocarbonohydrazide compounds due to the high reactivity of aldehydes. Thus, many chemists are looking for an easy, reproducible synthetic method to isolate monocarbonohydrazide derivatives of aldehydes in high yields. The only result observed in the literature is the compound 1-(2'-hydroxy-3'-methoxybenzylidene)carbonohydrazide [6] whose structure is confirmed by infrared spectroscopic techniques, NMR, and elemental analyses.“Many of these carbohydrazide derivatives are used as precursors in the preparation of heterocyclic compounds with interesting biological properties” [7]. Some of them have made it possible to develop drugs with a broad spectrum of activity such as antimicrobial [8], anticonvulsant [9], antidepressant [10], antioxidant [11], analgesic [12], antifungal [13], antiplatelet [14], antituberculosis [15], anti-HIV [16], inflammatory [17], antidiabetic [18], anticancer [19], and antimalarial [20]. “Due to the presence of several donor atoms in these derivatives and the possibility for these molecules to appear in different conformations, they can be used in coordination chemistry. Coordination compounds with various structures and properties are reported in the literature” [21,22]. “It has been reported in the literature that dicarbonohydrazone with their *cis-enol* conformations or *cis-enol* and *trans* association lead to square or rectangular grid polynuclear complexes, respectively, with interesting physical properties” [23]. In these coordination compounds, the dicarbonohydrazoneact as μ_2-O [24,25] and/or μ_2-N–N bridged pentadentate or hexadentate ligand[37-40]. Depending on their tridentate or tetradentate behavior, monocarbonohydrazideyield,generally,mononuclear or dinuclear complexes with transition metal ions [21]. Recently, derivative complexes with remarkable magnetic [27], luminescent [28] or catalytic [29] properties have been synthesized and studied. In this article, we report the synthesis and characterization of one monosubstituted (H_5L^1) and one di-substituted (H_4L^2) Schiff bases derived from carbonohydrazide.

2. METHODOLOGY

2.1 Materials and instruments

2-Hyroxybenzaldehyde, carbonohydrazide, and solvent from Sigma-Aldrich were analytical grade and were used directly without further purification. Elemental analyzes of C, H and N were recorded on a VxRio EL instrument.Infrared spectra were obtained on a Perkin Elmer Spectrum Two FTIR spectrometer in the 4000-400 cm^{-1}region.NMR spectra were recorded in DMSO-d$_6$ solution with a Bruker 250 MHz spectrometer at room temperature using TMS as internal reference. UV-Vis spectra were recorded in a DMF solution with a concentration of 10 $^{-3}$ M at 25 °C on a Perkin Elmer Lambda 365 UV–Vis spectrophotometer.

2.2 Synthesis of the 1-(2-hydroxybenzylidene)carbonohydrazide ligand (1)

3 g (33.3 mmol) of carbonohydrazide are dissolved in a 250 mL two-neckedflask containing 30 mL of methanol and 10 mL of distilled water. A methanol solution containing 4.0702 g (33.3 mmol) of 2-hydroxybenzaldehyde is added dropwise using a separatory funnel. After the total addition of the solution, the mixture is maintained at reflux for six hours. A clear yellow solution is obtained which gives a precipitate after cooling at 4°C overnight. This precipitate is filtered off and washed with cold methanol (2 x 10 mL) and then with diethyl ether (2 x 10 mL) before being dried under vacuum. The purity of the productis checked by thin layer chromatography (TLC) using gel plates ofsilica, the eluent being a methanol/dichloromethane mixture with a ratio of 9/1 (V/V).

2.3 Synthesis of the ligand 1,5-Bis(2-hydroxybenzaldehyde)carbohydrazone monohydrate (2)

1 g (11.1 mmol) of carbonohydrazide was suspended in 10 mL of methanol. 2.710 g (22.2mmol) of 2-hydroxybenzaldehyde previously dissolved in 10 mL of methanol were added. After adding a few drops of glacial acetic acid, the mixture was heated under reflux for two hours. The white precipitate formed, was recovered by filtration, and washed with 5 mL of methanol before being dried in the open air.

Table 1. Physical characteristics, yield and analytical data of the compounds.

Compound	Colour	M.p. (°C)	Yield (%)	Found (Calc) %		
				C	H	N
$C_8H_{10}N_4O_2$ (**1**)	Yellow	187	86.3	49.43 (49.48)	5.14 (5.19)	28.83 (28.63)
$C_{15}H_{16}N_4O_4$ (**2**)	White	218	93.4	56.93 (56.96)	5.08 (5.10)	17.68 (17.71)

Table 2. Main FT-IR and UV-visible spectral data of the compounds.

Compound	ν(O-H)	ν(N-H)	ν(C=O)	ν(C=N)	ν(C-O)	ν(N-N)	λ (nm)
$C_8H_{10}N_4O_2$ (**1**)	3280	3233	1676	1632	1272	1068	240, 285, 322
$C_{15}H_{16}N_4O_4$ (**2**)	3260	3184	1686	1620	1270	1073	257, 290, 316

Table 3. ^{1}H and ^{13}C NMR data of the compounds in dmso-d$_6$ solvent.

Compound	δ_H (ppm)	δ_C (ppm)
$C_8H_{10}N_4O_2$ (**1**)	4.14 (s, 2H, N**H**$_2$); 6.85-7.92 (m , 4H, **H**–Ph) ; 8.21 (s, 1H, –(C=O)–N**H**–NH$_2$); 8.44 (S, 2H, N=C–**H**); 10.41 (s, 1H, –O–**H**$_{phenol}$); 10.87 (s, 1H, –(C=O)–N**H**–(C=N)–)	156.13 (**C**=N); 151.99 (**C**$_{Ar}$–OH); 140.1 (**C**=N); 130.61 (**C**$_{Ar}$); 129.91 (**C**$_{Ar}$); 127.86 (C$_{ispo}$), 119.13 (**C**$_{Ar}$); 115.97 (**C**$_{Ar}$)
$C_{15}H_{16}N_4O_4$ (**2**)	6.90-7.27 (m, 8H, **H**–Ph); 7.71 (s, 2H, N**H**); 8.45 (s, 2H, N=C–**H**); 10.89 (s, 4H, –O–**H**$_{phenol}$).	156.57 (**C**=O); 151.44 (**C**$_{Ar}$–OH); 146.1 (**C**=N); 130.39 (**C**$_{Ar}$); 128.05 (**C**$_{Ar}$)**;** 119.90 (**C**$_{Ar}$); 118.85 (C$_{ispo}$); 116.13 (**C**$_{Ar}$).

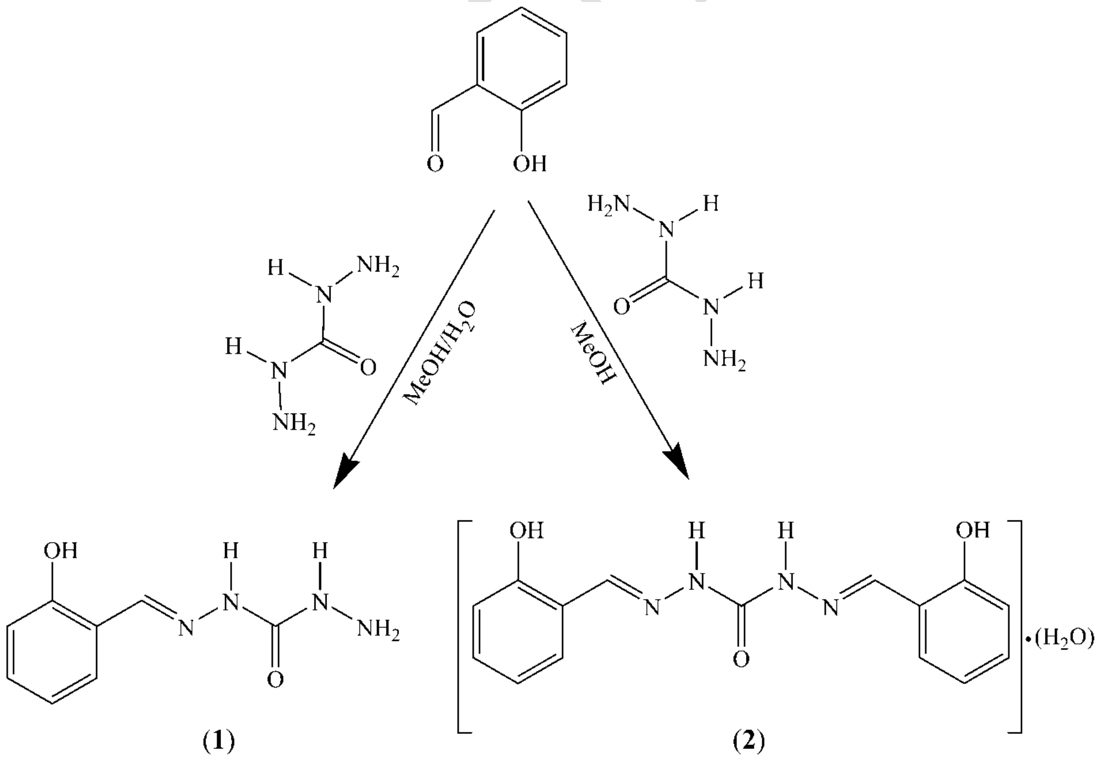
2.4 Crystal Structure Determination

Crystals suitable for single-crystal X-ray diffraction, of the reported compound, was grown by slow evaporation of MeOH solution of the compound. Details of the crystal structure solution and refinement are given in Table 4. Diffraction data were collected using a XtaLAB AFC12(RINC): Kappa single diffractometer with graphite monochromatized MoKα radiation (l =0.71073 Å). All data were corrected for Lorentz and polarization effects. The structure was solved and refined using the Bruker *SHELXTL* Software Package [30]. “All the structures were refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters for all non-hydrogen atoms”[31]. H atoms of the NH group was located in the Fourier difference maps and refined without restraints. Molecular graphics were generated using *ORTEP-3*[32].

3. RESULTS AND DISCUSSION

3.1 General study

The compounds H_5L^1 (**1**) wasobtained after the condensation reaction between carbonohydrazide and 2-hydroxybenzaldehyde in 1/1 in MeOH/H_2O (1/1) solution while the ligand H_4L^2 (**2**) was obtained after the condensation reaction between carbonohydrazide and 2-hydroxybenzaldehyde in 1/2in MeOH solution (Figure 1). The two compounds **1** and **2** were characterized by elementalanalyses, FTIR, ^{1}H and ^{13}C NMR spectroscopies Tables 1-3). The data of the elementary analyzes of the two compounds **1** and **2** confirm their formations with the chemical formulas$C_8H_{10}N_4O_2$ (**1**)and $C_{15}H_{14}N_4O_3{\cdot}H_2O$(**2**), respectively. The FTIR spectrum of the compound **1** shows bands at 3280 cm^{-1} and 3233 cm^{-1} attributable respectively to the phenolic ν(OH) andthe hydrazide ν(NH) vibrations [33].The bands pointed at 3352 cm^{-1} and 1606 cm^{-1} are,respectively, characteristic of the ν(NH_2) and □(NH_2) vibrations of the –NH_2 group. Their appearance proves the monocondensation reaction [6]. The ν(C=O) carbonyl vibration band appears at 1676 cm $^{-1}$ while the ν(C=N) band of the imine function is pointed at 1632 cm^{-1} [48].Between 1544 and 1460 cm^{-1}, bands corresponding to the ν(C=C) vibrations of the aromatic rings are pointed. A band at 1272 cm^{-1} corresponding to the vibration of the C_{Ar}–O–bond is also observed on the FTIR spectrum.



(1)

(2)

Figure 1. Synthesis diagram of compounds (1) and (2)

The vibration band of the N–N hydrazine bond appears at 1068 cm^{-1} . The absence of the ν(NH_2) and □(NH_2) vibration bands of the NH_2 group on the IR spectrum of the compound **2** expected respectively at *ca.*3300 cm^{-1} and 1600 cm^{-1} confirms the 1/2 ratio condensation reaction between carbonohydrazide and 2-hydroxybenzaldehyde. The ν(NH) vibration bands of the hydrazide function, ν(C=O) carbonyl and ν(C=N)imine of the ligand**2** are located respectively at 3184 cm^{-1} , 1686 cm^{-1} and 1620 cm^{-1}. The band attributable to ν(C_{Ar}–O–) vibration is observed at 1270 cm^{-1} and the band due to –N–N– bond of the hydrazine moietyis pointed at 1073 cm^{-1}. In the ^{1}HNMR spectrum of compound **1**, the presence of the signal due to –N**H**$_2$ at 4.14 ppm is indicative of the monocondensation reaction.The signal at 10.41 ppm is due to the single phenolic proton.In addition, the two –N**H** protons are observed at 7.44 ppm and 10.87 ppm.No signal due to an alcoholic proton is observed.These observations indicate that the compound remained in its keto form in DMSO solution. The signal of the azomethine proton in pointed at8.44 ppm and those corresponding to the protons of the aromatic rings are pointed between 6.85-7.92 ppm. Indeed, when the ^{13}C NMR spectrum of compound **1** is examined, the signals of the carbon atoms of the **C**=O, **C**$_{Ar}$–O and **C**=N functions appear respectively at 156.13 ppm, 151.99 ppm and 140.1 ppm. The signals between 115.97-130.61 ppm correspond to the carbon atoms of the aromatic ring. No signal attributable to a carbon atom carrying an alcohol function –N=C(OH)–N– was observed.This confirms that only the ketone form is present in solution of**1**. As in the case of compound **1**, compound **2** in solution may exhibit *Z*/*E* isomerism around the two imine bonds and the presence of the –HN–C(=O) motifcan induce keto tautomerism .Several conformers can coexist in solution.^{1}H and ^{13}CNMR of compound **2** at room temperature give information on tautomerism.In the ^{1}H spectrum, the singlet signal at 10.89 ppm is due to the –O**H** proton of the phenolic function while the signal at 7.71 ppm represents two –N**H** protons of the N–**H**N–C(=O) moiety. The absence of signal attributable to the –N**H**$_2$ group expected around 4.14 ppm is indicative of the success of the 1/2 ratio condensation reaction.In the ^{1}H NMR spectrum, no signal attributable to the enol proton –HN–C(O**H**)=N– is observed.This observation demonstrates clearly that compound **2** is only present in its keto form in solution. The ^{1}HNMR spectrum also contains a singlet signal at 8.45 ppm representing the azomethine proton and a multiplet representing eight aromatic protons in the range 6.90-7.27 ppm. On the ^{13}CNMR spectrum, the single signal observed at 156.57 ppm was attributed to **C**=O and two signals at 151.44 ppm and 146.1 ppm are, respectively,attributed to the carbon atoms **C**$_{Ar}$ -OH and**C**=N. Aromatic carbon atom signals are located between 116.13-130.39 ppm. No signal attributable to the enol carbon atom –HN–**C**(–OH)=N– is observed in the^{13}CNMR spectrum of compound **2**confirming that compound **2** is only present in its keto form in solution. The UV-visible spectra of the two compounds were recorded in DMSO solution. In the UV-vis spectra of the two compounds **1** and **2**, the characteristic transition bands of the aromatic ring π→π* and n→π* of the chromophore C=N are observed in the range 240-290 nm and 316-322 nm, respectively.

Table4. Crystallographic data and refinement parameters for compounds 1 and 2

	1	**2**
Chemical formula	$2(C_8H_{10}N_4O_2)$	$C_{15}H_{14}N_4O_3 \cdot H_2O$
M (g/mol)	388.38	318.33
Temperature (K)	295	298
Crystal system	monoclinic	Orthorhombic
Space group	$P2_1/c$	$C222_1$
a (Å)	17.0790(2)	4.5494 (1)
b (Å)	11.07410(10)	12.2213 (2)
c (Å)	10.56110(10)	27.4001 (6)
α (°)	90	90
β (°)	106.5730(10)	90

γ (°)	90	90
V (Å^3)	1914.49(3)	1523.43 (5)
Z	4	4
Radiation type	Cu Kα	Mo Kα
ρ_{calc} (g/cm^3)	1.347	1.388
μ(mm^{-1})	0.867	0.10
Crystal size (mm)	0.32 × 0.26 × 0.08	0.30 × 0.28 × 0.08
F(000)	816.0	672
θ_{max} ; θ_{min} (°)	71.0 ; 4,8	32.2 ; 3.3
h, k, l	$-20 \le h \le 20$, $-13 \le k \le 13$, $-12 \le l \le 12$	$-6 \le h \le 6$, $-18 \le k \le 18$, $-40 \le l \le 41$
No. of measured reflections	33758	48700
Independent reflections	3684	2627
Observed reflections [$I > 2\sigma(I)$]	3439	2086
R_{int}	0.0292	0.047
R_1, wR_2 ($\mathbf{I} \ge 2\sigma(\mathbf{I})$)	R_1 = 0.0432, wR_2 = 0.1275	R_1= 0.039, wR_2= 0.125
Data/parameters/restraints	3684/257/0	2627/107/0
GOF	1.112	1.08
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.16/-0.15	0.14 , −0.29

3.2 Description of the crystal structure of the compound 1

The monocarbonohydrazide compound **1**crystallizes in the monoclinic system with the space group $P2_1/c$. Selected bond lengths and bond angles are listed in Table 5. Figure 1 shows the ORTEP view of the compound **1**. The asymmetric unit of the crystal structure of compound **1**consists of two molecules of the ligand. In the structure each molecule adopts an *E* configuration with respect to the C=N bond of the azomethine functions [C7=N1 or C15=N5]. In each molecule, the oxygen atom of the carbonyl function and the nitrogen atom of the azomethine are in *syn* conformation with respect to the corresponding C–N bond [O2 and N1/C8 –N2 ; O4 and N5/C16–N6] with torsion angle values of -3.7(4)°[N1–N2–C8–O2] and 4.04(4) ° [N5–N6–C16–O4]. The carbonyl oxygen and the amino nitrogen atom in each molecule are also in *cis* conformation with respect to the C–N bond [O2 and N4/C8–N3 and O4 and N8/C16–N7] with torsion angle values of 3.9(4)°[N4–N3–C8–O2] and -2.9(4)° [N8–N7–C16–O4]. The nitrogen atom of the azomethine group C=**N** is in *trans* position with the hydrazine nitrogen atom (**N**H–NH$_2$) within each molecule with respect to the C–N bond [N1 and N3/C8–N2 and N5 and N7/C16–N6] with torsion angle values of 177.2(2)° [N1–N2–C8–N3] and -175.7(2)° [N5–N6–C16–N7]. The bond lengths C8–O2and C16–O4 of 1.197 (3) Å characteristic of a double bond character, show that the two molecules of compound **1** are in the keto form in the solid state [35].This tautomeric form is confirmed by bond distances N2–C8 [1.359 (3) Å], N1–N2 [1.360 (3) Å], N6–C16 [1.355 (3) Å], N5–N6 [1.363 (3) Å] which indicate that they are single bonds [36] and by the bonds C7–N1 [1.287 (3) Å] and C15–N5 [1.292 (3) Å] which are double bonds [37]. In each molecule of compound (**1**), intramolecular hydrogen bonds of the type O–H···N [O1–H1···N1 and O3–H3···N5] which are established between the phenolic oxygen atoms as donor and the azomethine nitrogen atoms as acceptor resulting in *S*(6) rings. The different molecules in the crystal are connected by intermolecular hydrogen bonds of type N–H⋯O [N2–H2⋯O1^{i} : i = −x, y+1/2, −z+3/2; N8–H8*A*⋯O4^{ii}, N4–H4*B* ⋯O2^{ii} ii = x, −y+1/2, z−1/2; and N6–H6⋯O3^{iii} : iii = −x+1, y+1/2, −z+1/2; N8–H8*B*⋯O2^{v} : v = x+1, −y+1/2, z−1/2]; N–H⋯N [N8–H8*A*⋯N5^{ii}] and C–H⋯N [C11–H11⋯N7^{iv}: iv = −x+1, y−1/2, −z+1/2] (Table6). All of these intramolecular and intermolecular hydrogen bonds ensure the stability of the structure and its development in a three-dimensional network (Figure 2).

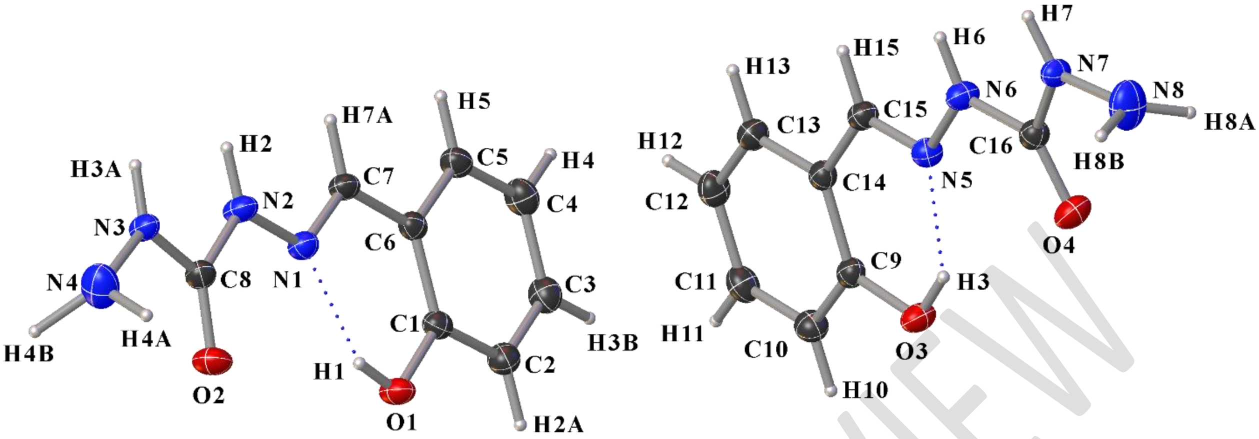


Figure 2.ORTEP view of compound 1

Table 5. Selected bond distances [Å] and angles [deg] for compound 1

1			
O3—C9	1.361 (3)	O1—C1	1.363 (3)
O4—C16	1.197 (3)	O2—C8	1.195 (3)
N7—C16	1.339 (3)	N3—C8	1.338 (3)
N7—N8	1.441 (4)	N3—N4	1.442 (4)
N5—C15	1.292 (3)	N1—C7	1.287 (3)
N5—N6	1.363 (3)	N1—N2	1.360 (3)
N6—C16	1.355 (3)	N2—C8	1.359 (3)
C15—N5—N6—C16	−175.7 (2)	N5—N6—C16—N7	−175.7 (2)
O3—C9—C10—C11	179.8 (2)	N4—N3—C8—O2	3.9 (4)
N8—N7—C16—O4	−2.9 (4)	N4—N3—C8—N2	−177.1 (2)
N5—N6—C16—O4	4.0 (4)	N1—N2—C8—O2	−3.7 (4)

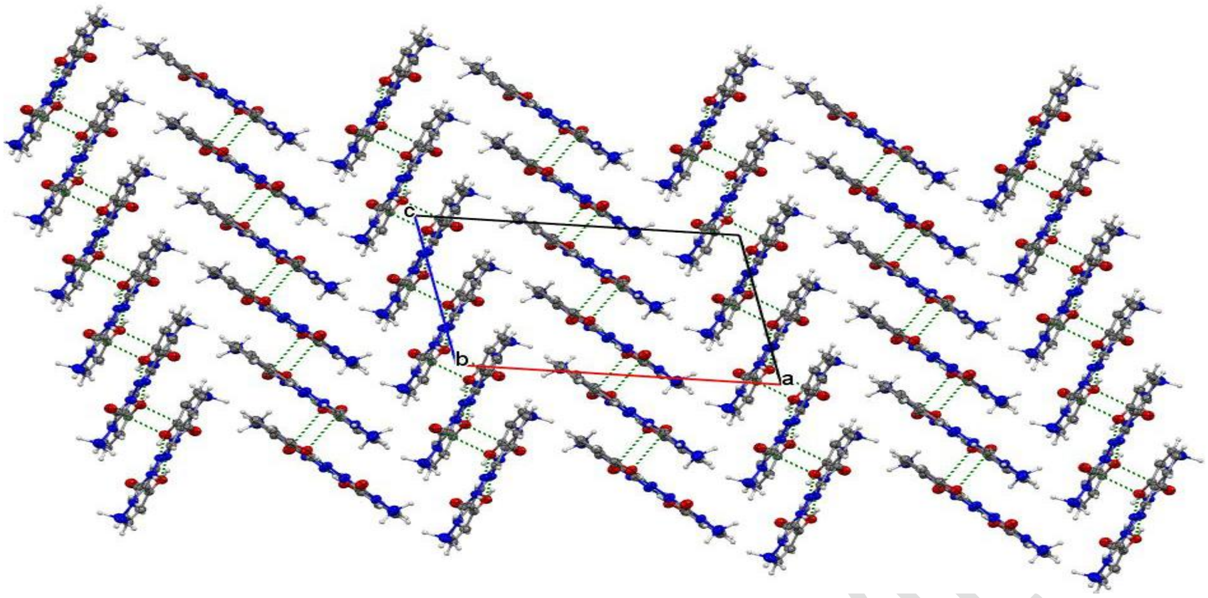


Figure 3: View of the Packing diagram of compound 1 along the b axis

Table 6. Hydrogen-bond geometry (Å, °) for compound 1

D–H···*A*	*D*–H	H···*A*	*D*···*A*	*D*–H···*A*
O1–H1···N1	0.82	1.88	2.592 (3)	144
N2–H2···O1^{i}	0.86	2.17	3.021 (3)	168
N4–H4*B*···O2^{ii}	1.15 (5)	2.54 (5)	3.656 (4)	163 (3)
O3–H3···N5	0.82	1.85	2.573 (3)	146
N6–H6···O3^{iii}	0.86	2.07	2.925 (3)	176
C11–H11···N7^{iv}	0.93	2.55	3.435 (4)	160
N8–H8*A*···O4^{ii}	1.27 (5)	2.58 (5)	3.507 (4)	128 (3)
N8–H8*A*···N5^{ii}	1.27 (5)	2.68 (5)	3.923 (4)	166 (3)
N8–H8*B*···O2^{v}	1.14 (5)	2.53 (5)	3.587 (4)	154 (3)

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

3.3 Description of the crystal structure of the compound 2

The compound **2** crystallizes in an orthorhombic system with *C*222$_1$ space group. The crystal structure is shown in Figure 4. The selected bond lengths and bond angles are listed in Table 7. The asymmetric unit contains one symmetrical carbohydrazoneligand molecule and one water molecule linked by a hydrogen bond of the type O_{water}–H···$O_{carbonyl}$ [O3–H3*A* ···O2].The crystal structure reveals that the Schiff base compound **2**adopts the keto form, as shown by the bond length C1–O1 [1.234 (2) Å] which has a double bond character [52]. Moreover, the bond lengths N1–N2 [1.3686 (17) Å] and C2–N2 [1.281 (2) Å] have single bond and double bond character, respectively, (Table 7) [34, 36].The oxygen atom O1 and the azomethine nitrogen atom N2 adopt a *cis* configuration with respect to the C1–O1 bond with a torsion angle 0.28° [N2–N1–C1–O1]. The mean plane of the carbonohydrazide moiety C=N–N–C(O)–N–N=C is twisted with respect to each mean plane of the phenyl rings with an angle value of 3.41(1)°. The value of the dihedral angle between the mean planes of the phenyl rings is 4.63(1)°.The torsion angle C2–N2–N1–C1 and the torsion angle defined by the related symmetry atoms (177.67(2)°) show that the central part of the molecule is almost linear. The molecule adopts an

E,*E* configuration with respect to the bond C2–N2 and the bond defined by the related symmetry atoms. The crystal structure of compound **2** is stabilized by intramolecular O_{phenol}–H···$N_{carbohydrazide}$ [O2–H2···N2] hydrogen bond resultingin*S*(6) rings and O_{water}–H···$O_{carbonyl}$ [O3–H3*A*···O1]. The different molecules in the crystal are connected by intermolecular hydrogen bonds of type O_{water}–H···$N_{hydrazinyl}$ [O3–H3*B*···N1^{i}: i = *x*−1/2, *y*−1/2, *z*]; O_{water}–H···$O_{phenolioc}$ [O3–H3*B* ···O2^{ii} :ii = *x*−1, *y*, z]and $N_{hydrazinyl}$–H···O_{water}[N–H···O^{iii}: iii = *x*+1/2, *y*+1/2, *z*] (Table 8,Figure 5).

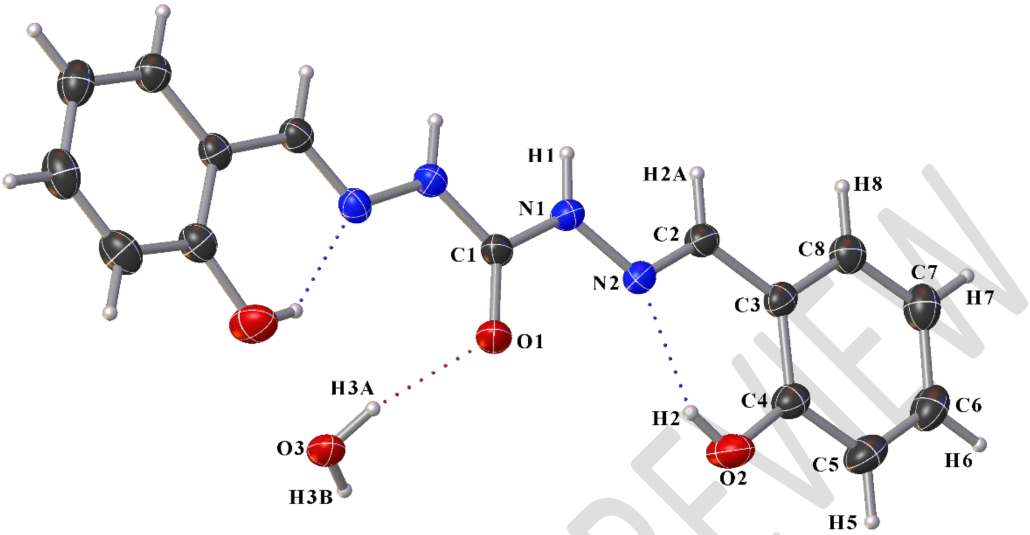


Figure 4. ORTEP view of compound 2

Table 7. Selected bond distances [Å] and angles [deg] for compound 2

2			
O1–C1	1.234 (2)	C3–C4	1.401 (2)
C3–C8	1.394 (2)	O2–C4	1.352 (2)
N2–C2	1.281 (2)	C6–C7	1.385 (3)
N1–C1	1.3549 (16)	C6–C5	1.363 (3)
C4–C5	1.395 (2)	N1–N2	1.3686 (17)
C8–C7	1.378 (3)	C2–C3	1.453 (2)
C1–N1–N2	119.27 (13)	C8–C3–C4	118.12 (15)
C2–N2–N1	116.34 (13)	O2–C4–C3	122.60 (15)
O1–C1–N1^{i}	123.62 (8)	O2–C4–C5	117.70 (17)
O1–C1–N1	123.62 (8)	C5–C4–C3	119.70 (18)
N1^{i}–C1–N1	112.77 (17)	C7–C8–C3	121.67 (17)
N2–C2–C3	121.86 (14)	C5–C6–C7	120.49 (18)
C4–C3–C2	122.68 (16)	C8–C7–C6	119.22 (19)
C8–C3–C2	119.19 (14)	C6–C5–C4	120.78 (19)

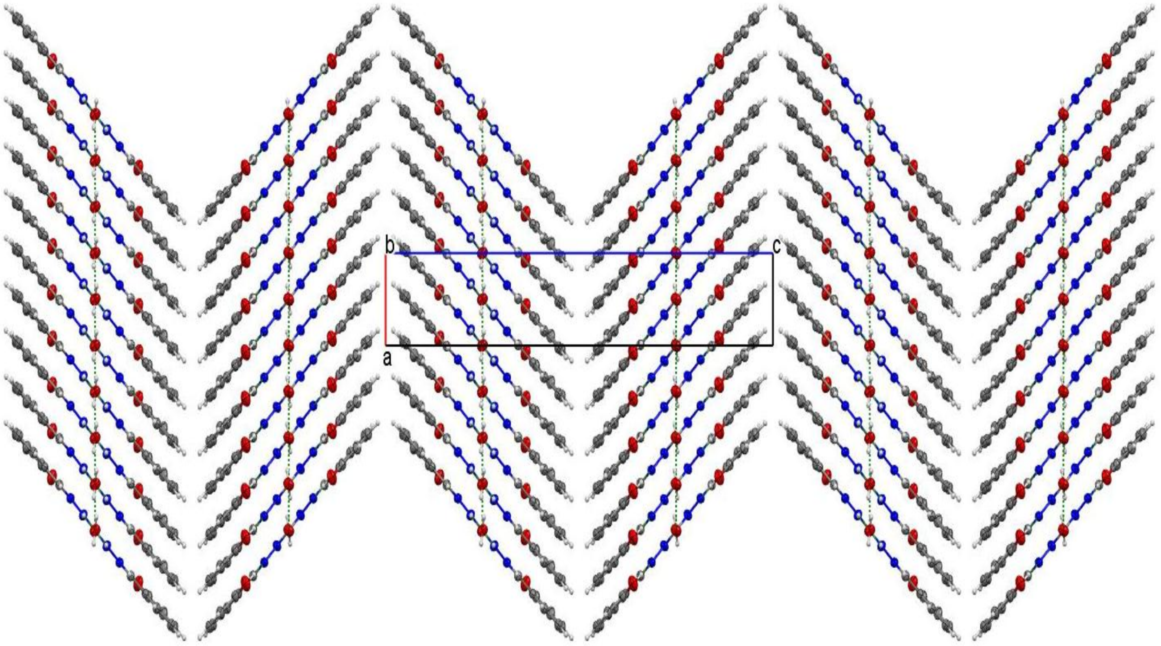


Fig. 5. View of the Packing diagram of compound 2 along the b axis

Table 8. Hydrogen-bond geometry (Å, °) for compound 2

D–H⋯*A*	*D*–H	H⋯*A*	*D*⋯*A*	*D*–H⋯*A*
O3–H3*A*⋯O1	0.85	1.90	2.7385 (11)	168
O3–H3*B*⋯N1^{i}	0.85	2.39	2.8358 (19)	113
O3–H3*B*⋯O2^{ii}	0.85	2.53	3.1716 (16)	133
N1–H1⋯O3^{iii}	0.86	2.05	2.8358 (19)	152
O2–H2⋯N2	0.82	1.95	2.6695 (17)	145

Symmetry codes: (i) *x*−1/2, *y*−1/2, *z*; (ii) *x*−1, *y*, *z*; (iii) *x*+1/2, *y*+1/2, *z*.

4. CONCLUSION

Monosubstituted 1-(2-hydroxybenzylidene)carbonohydrazide**1** and disubstituted carbohydrazide derivatives 1,5-bis(2-hydroxybenzaldehyde)carbohydrazone **2** were prepared by 1/1 ratio condensation and 1/2 ratio condensation reactions, respectively, between carbonohydrazide and 2-hydroxybenzaldehyde. The structures of the two compounds **1** and **2** were confirmed by elementary analyzes and FT-IR, ^{1}H and ^{13}C NMRspectroscopic techniques.The molecular structures of two the molecules **1** and **2**have been determined by of X-ray diffraction.

5. SUPPORTING INFORMATION

CCDC-2254010 and 2254011contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via https://www.ccdc.cam.ac.uk/structures/, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

Reference

1. Tandon, SS., Dul, M.-C., Lee, JL., Dawe, LN., Anwar, MU., Thompson, LK. Complexes of ditopic carbo- and thio-carbohydrazone ligands–mononuclear, 1D chain, dinuclear and tetranuclear examples. Dalton Transactions.2011;40(14):3466–3475.

Available https://doi.org/10.1039/C0DT01487G

2. Bacchi, A, Carcelli, M, Pelagatti, P, Pelizzi, C, Pelizzi, G, Zani, F. Antimicrobial, and mutagenic activity of some carbono- and thiocarbonohydrazone ligands and their copper(II), iron(II) and zinc(II) complexes. Journal of Inorganic Biochemistry. 1999;75(2):123–133.
Available https://doi.org/10.1016/S0162-0134(99)00045-8

3. Palomo, V, Perez, DI, Roca, C, Anderson, C, Rodríguez-Muela, N, Perez, C, Molares-Garcia, JA, Reyes, JA, Campillo, NE, Perez-Castillo, AM, Rubin, LL, Timchenko, L, Gil, C, Martinez, A. Subtly Modulating Glycogen Synthase Kinase 3 β: Allosteric Inhibitor Development and Their Potential for the Treatment of Chronic Diseases. Journal of Medicinal Chemistry. 2017;60(12):4983–5001.
Available https://doi.org/10.1021/acs.jmedchem.7b00395

4. Heo, DN, Alioglu, MA, Wu, Y, Ozbolat, V, Ayan, B, Dey, M, Kang, Y, Ozbolat, I. T. 3D Bioprinting of Carbohydrazide-Modified Gelatin into Microparticle- Suspended Oxidized Alginate for the Fabrication of Complex-Shaped Tissue Constructs. ACS Applied Materials Interfaces. 2020;12(18):20295–20306.
Available https://doi.org/10.1021/acsami.0c05096

5. Seck, TM, Faye, FD, Gaye, AA, Thiam, IE, Diouf, O, Gaye, M, Retailleau, P. Synthesis of mono and bis-substituted asymmetrical compounds, (1-(pyridin-2-yl)ethylidene)carbonohydrazide and 1-(2’-hydroxybenzylidene)-5-(1’-pyridylethylidene)carbonohydrazone: Structural characterization and antioxidant activity study. European Journal of Chemistry. 2020;11(4):285–290.
Available https://dx.doi.org/10.5155/eurjchem.11.4.285-290.2023

6. Fall, N, Faye, F D, Gaye, A A, Diouf, O, Gaye, M. Synthesis of mono and bis- substituted asymmetrical compounds, 1-(2’-hydroxy-3’- methoxybenzylidene)carbonohydrazide and 1(2’-hydroxy-3’-methoxybenzylidene)-5-(1’pyridylmethylene)carbonohydrazide: Structural characterization and antioxidant activity study. Journal of Applied Chemistry. 2020;13(12):22–30.
Available https://doi:10.9790/5736-1312022230

7. Moussa, Z, Al-Mamary, M, Al-Juhani, S, Ahmed, SA. Preparation and biological assessment of some aromatic hydrazones derived from hydrazides of phenolic acids and aromatic aldehydes. Heliyon. 2020;6(9):e05019.
Available https://doi.org/10.1016/j.heliyon.2020.e05019

8. Katariya, KD, Shah, SR, Reddy, D. Anticancer, antimicrobial activities of quinoline based hydrazone analogues: Synthesis, characterization, and molecular docking. Bioorganic Chemistry. 2020;94:103406.
Available https://doi.org/10.1016/j.bioorg.2019.103406

11. Demurtas, M, Baldisserotto, A, Lampronti, I, Moi, D, Balboni, G, Pacifico, S, Vertuani, S, Manfredini, S, Onnis, V. Indole derivatives as multifunctional drugs: Synthesis and evaluation of antioxidant, photoprotective and antiproliferative activity of indole hydrazones. Bioorganic Chemistry. 2019;85:568–576.
Available https://doi.org/10.1016/j.bioorg.2019.02.007

12. Taher, AT, Sarg, MTM, Ali, NRE-S, Elnagdi, NH (2019). Design, synthesis, modeling studies and biological screening of novel pyrazole derivatives as potential analgesic and anti-inflammatory agents. Bioorganic Chemistry. 2019;89:103023.
Available https://doi.org/10.1016/j.bioorg.2019.103023

13. Dascalu, A-E, Ghinet, A, Lipka, E, Furman, C, Rigo, B, Fayeulle, A, Billamboz, M. Design, synthesis and evaluation of hydrazine and acyl hydrazone derivatives of 5-pyrrolidin-2-one as antifungal agents. Bioorganic Medicinal Chemistry Letters. 2020;30(13):127220.
Available https://doi.org/10.1016/j.bmcl.2020.127220

14. Jordão, AK, Ferreira, VF, Lima, ES, Souza, MCBVde, Carlos, ECL, Castro, HC, Geraldo, RB, Rodrigues, CR, Almeida, MCB, Cunha, AC. (2009). Synthesis, antiplatelet and in silico evaluations of novel *N*-substituted-phenylamino-5-methyl- 1*H*-1,2,3-triazole-4-carbohydrazides. Bioorganic Medicinal Chemistry. 2009;17(10):3713–3719.
Available https://doi.org/10.1016/j.bmc.2009.03.053

15. Rawat, P, Singh, RN, Niranjan, P, Ranjan, A, Holguín, NRF. (2017). Evaluation of antituberculosis activity and DFT study on dipyrromethane-derived hydrazone derivatives. Journal of Molecular Structure. 2017;1149:539–548.
Available https://doi.org/10.1016/j.molstruc.2017.08.008

16. Vicini, P, Incerti, M, Colla, PL, Loddo, R. (2009). Anti-HIV evaluation of benzo[d]isothiazole hydrazones. European Journal of Medicinal Chemistry. 2009; 44(4): 1801–1807.
Available https://doi.org/10.1016/j.ejmech.2008.05.030

17. Sondhi, SM, Dinodia, M, Kumar, A. Synthesis, anti-inflammatory and analgesic activity evaluation of some amidine and hydrazone derivatives. Bioorganic Medicinal Chemistry. 2006;14(13):4657–4663.
Available https://doi.org/10.1016/j.bmc.2006.02.014

18. Karrouchi, K, Fettach, S, Jotani, MM, Sagaama, A, Radi, S, Ghabbour, HA, Mabkhot, YN, Himmi, B, Faouzi, MEA, Issaoui, N. Synthesis, crystal structure, hirshfeld surface analysis, DFT calculations, anti-diabetic activity and molecular docking studies of (*E*)-N'-(5-bromo-2-hydroxybenzylidene) isonicotinohydrazide. Journal of Molecular Structure. 2020;1221:128800.
Available https://doi.org/10.1016/j.molstruc.2020.128800

19. Narayanan, S, Gupta, P, Nazim, U, Ali, M, Karadkhelkar, N, Ahmad, M, Chen, Z-S. Anti-cancer effect of Indanone-based thiazolyl hydrazone derivative on colon cancer cell lines. The International Journal of Biochemistry Cell Biology.2019;110:21–28.
Available https://doi.org/10.1016/j.biocel.2019.02.004

20. Camacho, J, Barazarte, A, Gamboa, N, Rodrigues, J, Rojas, R, Vaisberg, A, Gilman, R, Charris, J. Synthesis, and biological evaluation of benzimidazole-5- carbohydrazide derivatives as antimalarial, cytotoxic and antitubercular agents. Bioorganic Medicinal Chemistry. 2011;19(6):2023–2029.
Available https://doi.org/10.1016/j.bmc.2011.01.050

21. Anwar, MU, Thompson, LK, Dawe, LN, Habib, F, Murugesu, M. Predictable self-assembled [2 × 2] $Ln(III)_4$ square grids (Ln = Dy,Tb)-SMM behaviour in a new lanthanide cluster motif. ChemicalCommunications. 2012;48(38):4576–4578.
Available https://doi.org/10.1039/C2CC17546K

22. Anwar, MU, Dawe, LN, Tandon, SS, Bunge, SD, Thompson, LK. Polynuclear lanthanide (Ln) complexes of a tri-functional hydrazone ligand–mononuclear (Dy), dinuclear (Yb, Tm), tetranuclear (Gd), and hexanuclear (Gd, Dy, Tb) examples. Dalton Transactions. 2013;42(21):7781–7794.
Available https://doi.org/10.1039/C3DT32732A

23. Li, J, Zhang, L, Xu, G-C, Yu, W-X, Jia, D-Z. A carbohydrazone based tetranuclear Co(II) complex: Self-assembly and magnetic property. Inorganic Chemistry Communications. 2014;45:40–43.
Available https://doi.org/10.1016/j.inoche.2014.03.042

24. Moustapha-Sow, M, Diouf, O, Gaye, M, Salam-Sall, A, Castro, G, Pérez-Lourido, P, Valencia, L, Caneschi, A, Sorace, L. Sheets of Tetranuclear Ni(II) [2 × 2] Square Grids Structure with Infinite Orthogonal Two-Dimensional Water–Chlorine Chains. Crystal Growth Design. 2013;13(10):4172–4176.
Available https://doi.org/10.1021/cg400885f

25. Fall, N, Traore, B, Ndiaye-Gueye, M, Diouf, O, Thiam, IE, Coles, S, Orton, J, Gaye, M. Synthesis, Spectroscopic Characterization, and X-ray Structure of the Co-crystal Copper(II) Complex of the Dissymmetrical 1-(2 hydroxy-3-methoxybenzylidene)-5-(pyridin-2 ylmethylene) Carbnohydrazide Ligand. Science Journal of Chemistry. 2023;11(1):18.
Available https://doi.org/10.11648/j.sjc.20231101.13

26. Lakma, A, Pradhan, RN, Hossain, SM, Leusen, Jvan, Kögerler, P, Singh, AK. (2019). Synthesis, structure and magnetic properties of Ni(II) and Cu(II), [2 × 2] grid complexes of pyrimidine-based symmetric ditopic ligands. Inorganica Chimica Acta. 2019;486: 88–94.
Available https://doi.org/10.1016/j.ica.2018.10.019

27. Sato, H., Miya, L., Mitsumoto, K., Matsumoto, T., Shiga, T., Newton, G. N., Oshio, H. (2013). Multiredox Active [3 × 3] Copper Grids. Inorganic Chemistry. 2013;52(17): 9714–9716.
Available https://doi.org/10.1021/ic401445u

28. Pethe, GB, Yaul, AR, Aswar, AS. Synthetic, characterization, and catalytic studies of some coordination compounds derived from unsymmetrical quadridentate Schiff base ligand. Russian Journal of General Chemistry. 2011;81(11):2304–2309.
Available https://doi.org/10.1134/S1070363211110144

29. Singh, AK, Pandey, OP, Sengupta, SK. Synthesis, spectral and antimicrobial activity of Zn(II) complexes with Schiff bases derived from 2-hydrazino-5-[substituted phenyl]-1,3,4-thiadiazole and benzaldehyde/2-hydroxyacetophenone/indoline-2,3-dione. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy. 2013;113: 393–399.
Available https://doi.org/10.1016/j.saa.2013.04.045

30. Sheldrick, G. M. (2015). SHELXT – Integrated space-group and crystal-structure determination. Acta Crystallographica Section A, 71 (1), 3–8.
Available https://doi.org/10.1107/S2053273314026370

31. Sheldrick, G. M. (2015). Crystal structure refinement with SHELXL. Acta Crystallographica Section C, 71 (1), 3–8.
Available https://doi.org/10.1107/S2053229614024218

32. Farrugia, L. J. (2012). WinGX and ORTEP for Windows: an update. Journal of Applied Crystallography, 45 (4), 849–854.
Available https://doi.org/10.1107/S0021889812029111

33. Tamboura, FB, Diouf, O, Barry, AH, Gaye, M, Sall, AS. Dinuclear lanthanide(III) complexes with large-bite Schiff bases derived from 2,6-diformyl-4-chlorophenol and hydrazides: Synthesis, structural characterization, and spectroscopic studies. Polyhedron. 2012;43(1):97–103.
Available https://doi.org/10.1016/j.poly.2012.06.025

34. Bikas, R, Anarjan, PM, Ng, SW, Tiekink, ERT. (2012). 2-[((*E*)-2-2-[(*E*)-2-Hydroxybenzylidene]hydrazinecarbonylhydrazinylidene)methyl]phenol. Acta Crystallographica Section E. 2012;68(1):o193.
Available https://doi.org/10.1107/S1600536811053268

35. Datta, R, Vittalacharya, R, Gudennavar, BSBS. Synthesis, characterization, and crystal structure of *N*'-[(*E*)-furan-2-ylmethylidene]furan-2-carbohydrazide. European Journal of Chemistry. 2014;5(3):394–396.
Available https://doi.org/10.5155/eurjchem.5.3.394-396.1043

36. Sylla-Gueye, R, Thiam, IE, Orton, J, Coles, S, Gaye, M. Crystal structure of *N*'- [4-(dimethylamino)benzylidene]furan-2-carbohydrazide monohydrate. Acta Crystallographica Section E. 2020;76(5):660–663.

Available https://doi.org/10.1107/S205698902000465X

37. Gueye, MN, Dieng, M, Thiam, IE, Lo, D, Barry, AH, Gaye, M, Retailleau, P. (2017). Lanthanide(III) complexes with tridentate Schiff base ligand, antioxidant activity and X-ray crystal structures of the Nd(III) and Sm(III) complexes. South African journal of chemistry. 2017;70:8–15.
Available http://dx.doi.org/10.17159/0379-4350/2017/v70a2