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TECHNOLOGY****SYNTHESIS, CHARACTERIZATION AND CHROMOGENIC PROPERTIES OF 4-
HYDROXY-(2-HYDROXYBENZYLIDENE) BENZOHYDRAZIDE****Hesham H. A. Rassem*, Abdurahman H.Nour**

* Faculty of chemical and Natural Resources Engineering, University Malaysia Pahang (UMP), Malaysia.
Faculty of chemical and Natural Resources Engineering, University Malaysia Pahang (UMP), Malaysia

ABSTRACT

In this work, hydrazine and hydrazide compounds were subjected to condensation reaction with ketone and different aldehyde derivatives affording the corresponding expected hydrazone, 4-hydroxy-(2-hydroxybenzylidene)benzohydrazide(L1) is synthesized and characterized. The chemical structures were found to be consistent with both analytical and spectroscopic data (CHN, FTIR, UV/Vis, TGA, ¹H NMR and ¹³C NMR). The chromogenic property of the ligand was carried out in different solvents including methanol, ethanol, acetone, acetonitrile, dimethylsulphoxide, and tetrahydrofuran.

KEYWORDS: Acetonitrile; Dimethylsulfoxide; Ethano; 4-hydroxybenzoylhydrazine; Tetrahydrofuran; Methanol; Hydrochloric acid..

INTRODUCTION

Hydrazones are organic compounds of formula $R_1C=N-NR_2$ where R_1 and R_2 represent H, aliphatic and aromatic group. They are usually formed by the condensation reaction between hydrazine and ketones or aldehydes. The oxygen atoms in aldehydes and ketones are replaced with the $N-NR_2$ functional group. Hydrazones are practically insoluble in hot and cold water but some are partially soluble in cold ethyl alcohol and ether. They possess a free amino group and can condense with another molecule of the carbonyl component to form hydrazone derivative or azine (Fieser and Fieser, 1956). The hydrazone unit offers a number of attractive features: a degree of rigidity, a conjugate π -system and a deprotonation (Beveset *al.*, 2009).

Hydrazone ligands and their complexes with different transition metal ions have been thoroughly investigated due to their biological activity. The arylhydrazones contain in their structure the $(-CO-NH-N=C<$ group) that imparts on these chelating agents fungicidal. This paper reports the synthesis, characterization and chromogenic properties of 4-hydroxy-(2-hydroxybenzylidene)benzohydrazide.

EXPERIMENTAL**Chemicals and solvents**

In the preparation of 4-hydroxy-(2-hydroxybenzylidene)benzohydrazide, the chemicals and solvents considered were of analytical grade, and were used without further purification. Table 1 List of the chemicals and solvents.

Table 1: Chemicals and solvents used in the study

Chemical name	Formula	Purity%	Symbol	Source
4-Hydroxybenzhydrazide	C ₇ H ₈ N ₂ O ₂	96	HB	MERCK
2-Hydroxybenzaldehyde	C ₇ H ₆ O ₂	98	S1	FLUKA
Methanol	CH ₃ OH	99.8	MeOH	QR&C
Ethanol	CH ₃ CH ₂ OH	99.7	EtOH	QR&C
Acetonitrile	C ₂ H ₃ NO	99.5	MeCN	QR&C
Acetone	C ₃ H ₆ O	99.5	—	QR&C
Tetrahydrofuran	C ₄ H ₈ O	99.8	THF	SYSTER M
Dimethylsulphoxide	(CH ₃) ₂ SO	99.9	DMSO	QR&C
Lead acetate	C ₄ H ₆ O ₄ Pb	99.5	—	MERCK

Instrumentation

Elemental (CHN) analysis of the prepared of 4-hydroxy-(2-hydroxybenzylidene)benzohydrazide analysis were carried out using Perkin – Elmer Series II, 2400 elemental analysis. The infrared spectra (IR) was recorded by using KBr system on a Perkin - Elmer 2000 FT-IR spectroscopy unit within region of 400 – 4000 cm⁻¹. The ¹H NMR spectra and ¹³C NMR spectra were recorded using a Bruker 300 MHz spectrometer. Thermogravimetric analysis (TGA) were carried out using a Perkin – Elmer Thermogravimetric analyzer TGA 7 under nitrogen gas from 0-1000 C°. A scanning rate of 20 C° min and 5.0 – 10.0 mg of the samples was used. A Perkin- Elmer lambda 35 (dual beam) spectrophotometer was used to obtain UV spectra for all over the 600-200 nm range with a quartz cell of 1.0 cm path length.

Synthesis of 4-hydroxy-(2-hydroxybenzylidene)benzohydrazide.

A solution of 2-hydroxybenzaldehyde (S1) (0.122 gm, 1 mmol) in methanol (10 mL) was added dropwise to a methanol solution (10 mL) of 4-hydroxybenzhydrazide (0.152 gm, 1 mmol, HB) and the mixture was refluxed for 2 h. The resulting solution was condensed on a steam bath to 5 mL and left to cool to room temperature. Yellow crystals suitable for X-ray diffraction were separated out, filtered off, and then washed with 5 mL of cooled methanol and dried in air (yield 85%). Figure 1 shows the schematic diagram of the reaction.

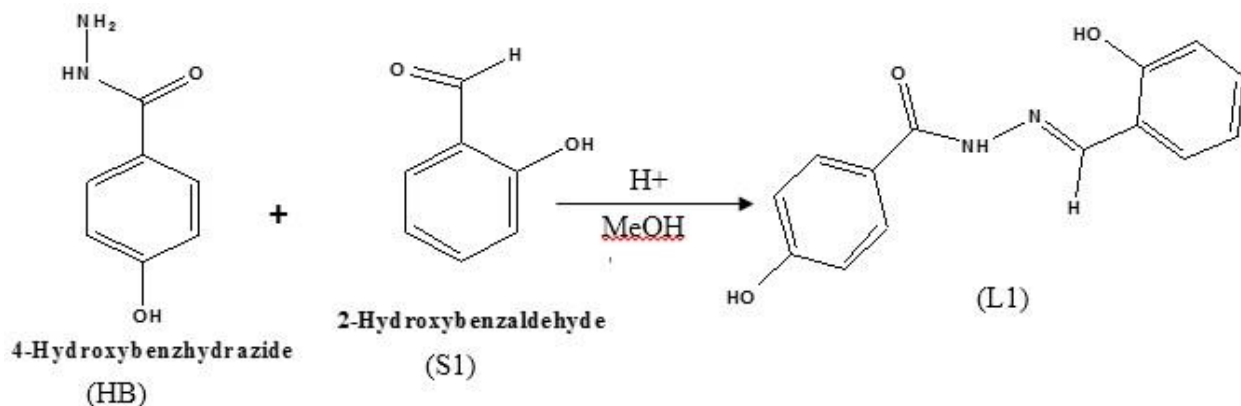


Figure.1 Synthesis of 4-hydroxy-(2-hydroxybenzylidene) benzohydrazide,L1

RESULTS AND DISCUSSION

Elemental analysis (CHN)

Results obtained from the microanalysis of the elements of carbon, hydrogen and nitrogen are comparable with those calculated from the suggested formula. The CHN analysis for the studied ligand are depicted in Table 2.

Table 2: The elemental analysis (CHN) of the synthesized ligand

Compound/ Complex	%					
	C		H		N	
	Calculated	Found	Calculated	Found	Calculated	Found
L1	65.62	65.48	4.72	4.26	10.93	10.84

FT-IR analysis

The FTIR data of the ligand (L1) is given in Table 3 and shown Figure 2. The result showed that the O-H functional groups in L1 were assigned at 3444 cm⁻¹, (Kemp, 1996). The azomethine stretching at vibration for the ligand is observed at 1522 cm⁻¹ (Stamatouiet al., 2008). Moreover, a strong bond at the frequency range of 1431 cm⁻¹ can be assigned to the C=C stretching (Yeap et al., 2003).

Table 3: The FT-IR spectral data for L1

Absorption band	Vibration assignment (ν) (cm ⁻¹)					
	O-H	C-H	C=O	C=C	C=N	C-O
L1	3444	3017	1607	1494	1559	1050

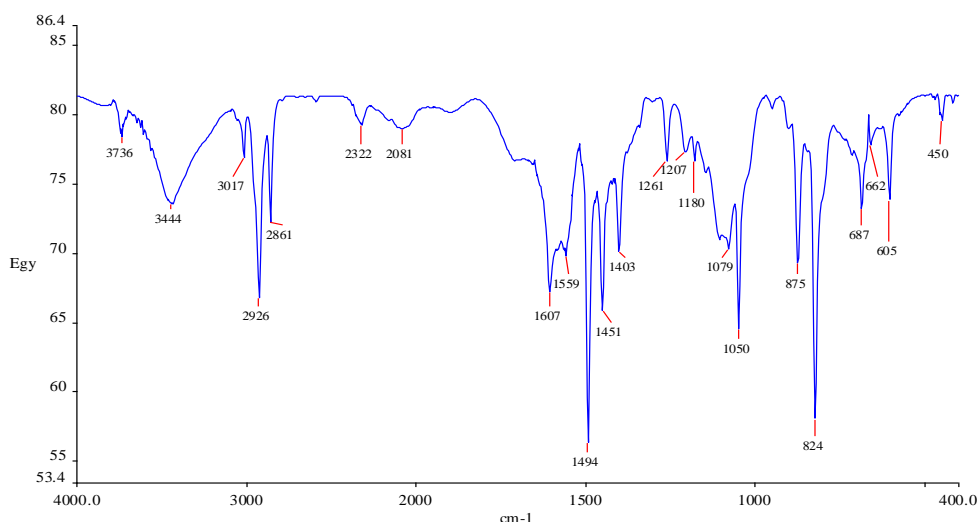


Figure 2 FT-IR spectrum of ligand (L1)

NMR spectroscopy analysis**¹H NMR analysis**

The ¹H NMR spectra of the studied ligand compound (L1) was measured in dimethyl sulfoxide solutions (DMSO-*d*₆). The solvent was chosen for the following reasons: firstly, insufficient solubility of the studied compound in solvents such as chloroform or acetone. Secondly, electron-conducting properties of DMSO minimize the possibility of the formation of hydrogen-bonded association between the active groups of the substituent of the compounds studied (Quelletteet al., 1965; Tumkeviciuset al., 2005).

The spectrum of L1 (Figure 3) shows nine groups of resonance (6.91, 6.93, 7.31, 7.52, 7.86, 8.61, 10.21, 11.45 and 11.94 ppm). The signal at 3.45 ppm is due to solvent peak (DMSO-*d*₆). Additionally, the N-H proton in L1 (Hm) is observed at 11.94 ppm. The spectrum also displayed the O-H protons of the phenolic groups and azomethine

protons (H-C=N), which appear at 10.21, 11.45 ppm and 8.61 ppm, as singlets, respectively. The data for the L1 spectrum is summarized in the condensed format as :

Hd : δ 6.91 ppm (2H, d, $^3J_{HH} = 5.2$ Hz), He δ 6.93 ppm (2H, t, $^3J_{HH} = 4.3$ Hz), Ha δ 7.31 ppm (1H, t, $^3J_{HH} = 2.5$ Hz), Hb δ 7.52 ppm (1H, d, $^3J_{HH} = 3.7$ Hz), Hc δ 7.86 ppm (2H, d, $^3J_{HH} = 5.1$ Hz), Hf δ 8.61 ppm (1H, s), Hg δ 10.21 ppm (1H, s), Hh δ 11.45 ppm (1H, s) and Hm δ 11.94 ppm (1H, s).

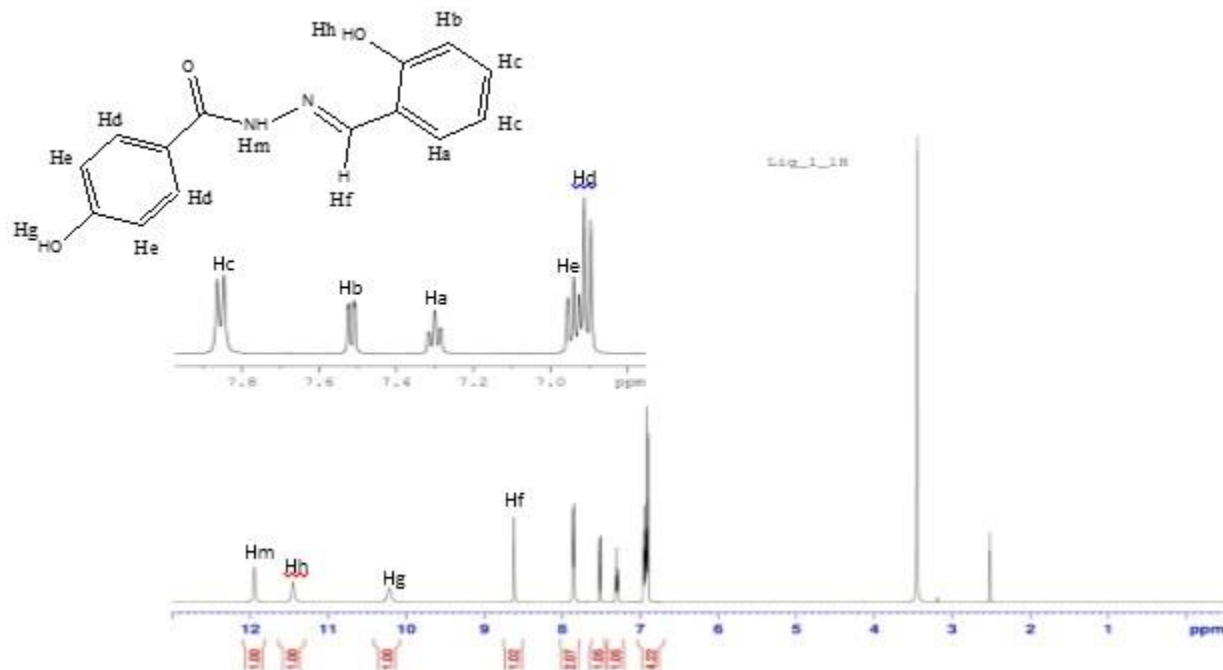


Figure 3 the ^1H NMR spectrum of the ligand L1 in DMSO- d_6

^{13}C NMR analysis

The ^{13}C NMR spectrum for L1, gives rise to eleven signals (115.1, 116.4, 118.7, 119.2, 123.2, 129.7, 131.1, 147.7, 157.4, 160.9 and 162.5 ppm). The signal at 39.6 ppm is due to solvent peak (DMSO- d_6). The figure 4 shows the ^{13}C NMR spectra of ligand (L1).

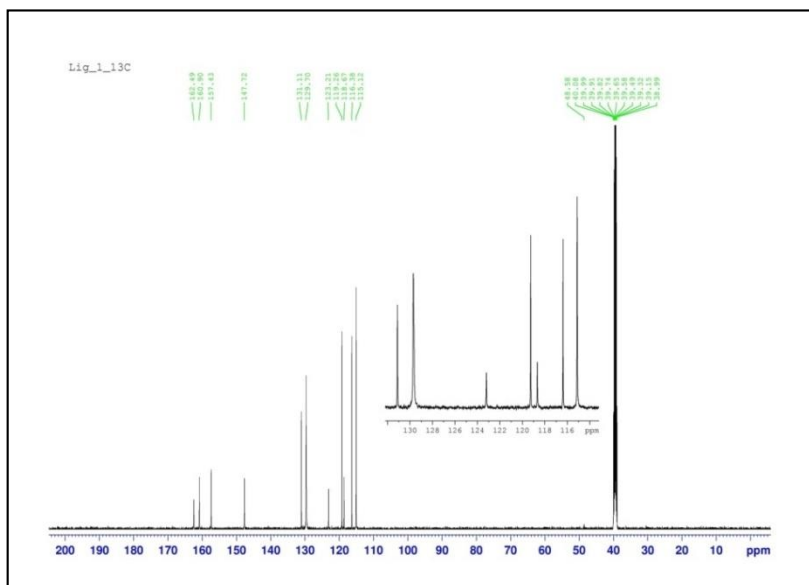


Figure 4 The ^{13}C NMR spectra of ligand (L1).

Thermal analysis

Thermogravimetric analysis (TGA) of the ligand (L1) show that the free ligand exhibited high thermal stabilities. Tables 4 present the TGA data of this ligand (L1). The decomposition of this ligand began around 200 °C and took place in two steps for L1. The figure 5 showed the thermogravimetric analysis of ligand (L1).

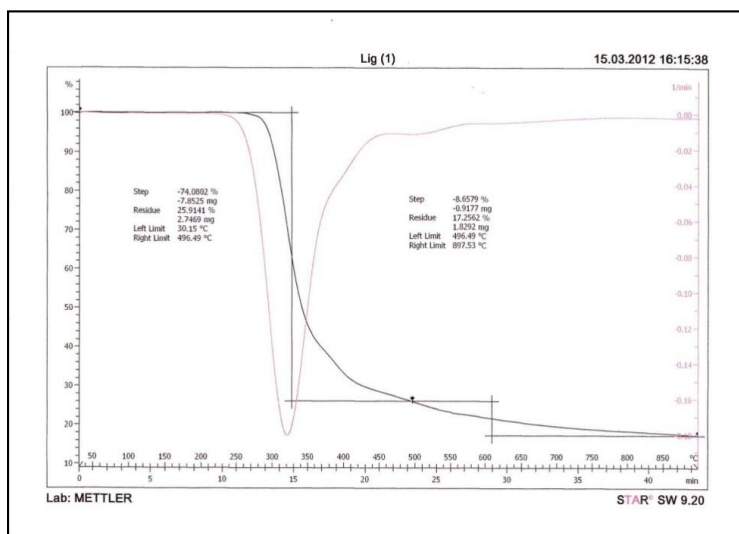


Figure 5 The thermogravimetric analysis of ligand (L1).

Table 4 Thermal data for the decomposition processes of ligand L1

Compounds	M. wt	Temperature °C	Wt. Loss %	Residue %
L1	256.26	30.15 – 496.49	74.08	25.91
		496.49 – 897.53	8.56	17.25

Heating rate; 20°C/min in the range from 0 – 1000°C, under nitrogen atmosphere

Chromogenic properties of the ligand (L1).

Solvent effects on the absorption spectra for the ligand (L1).

The effect of solvent on the chromogenic properties of the ligand was investigated. The absorption spectra of ligand (L1) were recorded in various solvents at a concentration of 1×10^{-5} M for ligand (Figure 6). Their corresponding wavelength (λ_{\max}) and their absorption are given in Table 5. The main absorption band is located in the visible region within a range from 200 - 600 nm, which could be assigned to $\pi-\pi^*$ transition in the large conjugated system. Figure 5 show the UV-Vis spectra of ligand (L1).

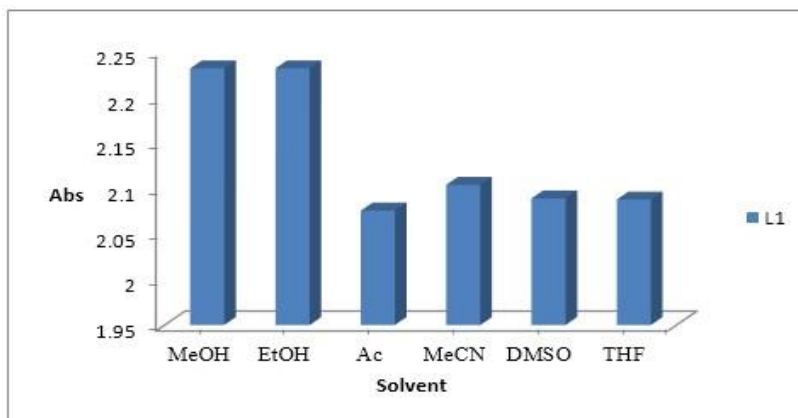


Figure 6 Show the UV-Vis spectra of ligand (L1)

Table 5: The λ_{max} for ligand in different solvent

Comp	MeOH		EtOH		Acetone		MeCN		DMSO		THF	
	λ_{max} (nm)	Abs.	λ_{max} (nm)	Abs.	λ_{max} (nm)	Abs.	λ_{max} (nm)	Abs.	λ_{max} (nm)	Abs.	λ_{max} (nm)	Abs.
L1	354	2.2310	354	2.2310	354	2.0753	352	2.1034	352	2.0886	351	2.0874

CONCLUSIONS

The hydrazone ligand, (L1) was synthesized. Their structure were characterized and confirmed by using CHN, FTIR, ^1H NMR, ^{13}C NMR, TGA and UV-Vis spectroscopy.

The synthesized ligand is insoluble in water, but soluble in other common organic solvents studied, such as acetone, acetonitrile, tetrahydrofuran and dimethylsulfoxide. The chromogenic properties of the ligand was carried out in different solvents including methanol, ethanol, acetone, acetonitrile, dimethylsulphoxide, and tetrahydrofuran. Methanol was the best solvent with ligand (L1) for the chromogenic properties.

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