



STUDIES ON SOME NOVEL HYDRAZONE DERIVATIVES

Nilesh B. Jadhav

Jaipur National University-Jaipur, Rajasthan, and cDepartment of Chemistry, The Institute of Science, 15, Madam Cama Road, Mumbai; India.

Rama S. Lokhande

Jaipur National University-Jaipur, Rajasthan, and cDepartment of Chemistry, The Institute of Science, 15, Madam Cama Road, Mumbai; India.

Raju M. Patil

Jaipur National University-Jaipur, Rajasthan, and cDepartment of Chemistry, The Institute of Science, 15, Madam Cama Road, Mumbai; India.

ABSTRACT

The different hydrazone derivatives are obtained by condensation of 2-hydroxy benzohydrazide with various aldehydes such as anisaldehyde, benzaldehyde, p-nitro- benzaldehyde, α -naphthaldehyde and p-methylbenzaldehyde. The hydrazone derivatives have been characterized by elemental analysis, UV, IR, $^1\text{H-NMR}$ spectral studies. The physicochemical analysis data is in support of the structures of the compounds. The present hydrazone derivatives can acts as chelating ligands with metal ions.

KEYWORDS :Synthesis; Characteristics; Aldehydes; Hydrazone derivative.

INTRODUCTION

There is growing interest in the study of hydrazones because of their physiological activity, coordinative capability and its applications^{1,2} in analytical chemistry. The ligand containing oxygen and nitrogen donor atoms acts as excellent coordination property. First, they can show various coordination modes³ and hence the resulting metal complexes possess large structural diversities. Second, nitrogen and oxygen containing ligands as well as their metal complexes show biological activity. The presence of functional group, near the site of coordination in the hydrazone ligands, gives a five or six membered chelate ring on reaction with metal ion, which shows structural variations⁴ depending upon the type of substituent present on aromatic ring. Thus, the purpose of this study is to synthesis and structural elucidation of novel hydrazone derivatives.

EXPERIMENTAL

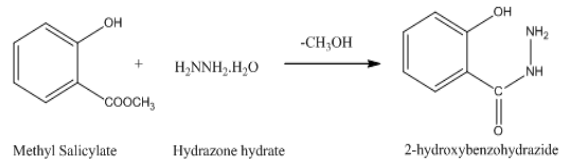
All chemicals and reagents used were of the analytical grade (AR). Solvent like ethanol and methanol whenever used were distilled and purified according to standard procedures⁵. The 2-hydroxyl benzoyl hydrazide was prepared by the method reported in the Vogel. The hydrazine hydrate and methyl salicylate were obtained from HIMEDIA while aldehydes such as anisaldehyde, benzaldehyde, p-nitrobenzaldehyde, α -naphthaldehyde and p-methylbenzaldehyde were obtained from THOMAS BAKER. The Pyrex glass wares were used all the time and calibrated according to Vogel standard procedures.

All the weighing was done on Citizen Model CY 220 analytical balance after performing its proper calibration procedures. The EQUIP-TRONICS digital pH meter of model EQ-614A equipped with magnetic stirrer was used for pH determination. The pH meter calibration was done by buffer solutions of pH 4.0, 7.0 and 9.2 which were prepared by dissolving the appropriate buffer capsules obtained from Merck in 100 mL of double distilled water. The electronic absorption spectra were recorded on Shimadzu UV/VIS - 160A spectrophotometer. IR spectra of all the ligands were recorded in KBr on a Perkin Elmer precisely spectrum 100 FTIR spectrometer in the region 4000 – 400 cm^{-1} . The $^1\text{H-NMR}$ spectra of complexes in DMSO were recorded on a Bruker 300MHz Spectrometer with TMS as an internal standard.

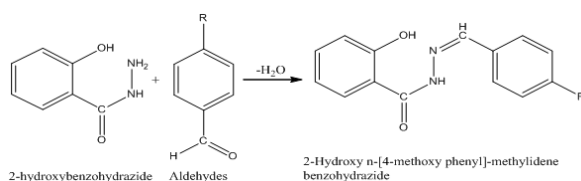
SYNTHESIS**STEP-I: Preparation of 2-hydroxyl benzoyl hydrazide**

Methyl salicylate (2.6 mL, 10 mmol) and hydrazine hydrate 80% (2.4 mL, 20 mmol) were placed in a 250 mL round bottom flask. This mixture was reflux in ethanol for 3 hrs on heating mantle. The

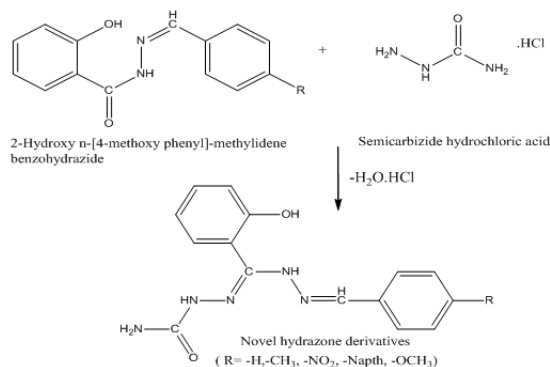
resulting reaction mixture was allowed to cool to room temperature. The separated product was filtered, washed with ethanol and purified by recrystallisation from ethanol, dried and weighed, yield 83.20%.

**STEP-II: Synthesis of hydrazones with various aldehydes**

The 2-hydroxy benzohydrazide (0.01 M) was taken in 250 mL round bottom flask and dissolved in ethanol and clear solution obtained using heating plate with magnetic stirrer. A solution of substituted aromatic aldehyde (0.01M) in ethanol was added slowly to this stirred solution. This reaction mixture in round bottom flask fitted with water condenser was reflux on heating mantle for 3 hrs then cooled and filtered. The product obtained was purified by recrystallisation in ethanol, dried under vacuum. The yield of the product was 78.50%.

**STEP-III: Scheme for the preparation of novel hydrazone derivatives**

The salicyloyl hydrazone derivative (0.01 M) in ethanol was taken in 250 mL round bottom flask then added semicarbazide (0.01M). This mixture was heated on hot plate with magnetic stirrer up to clear solution. This reaction mixture in round bottom flask fitted with water condenser was reflux on heating mantle for 3 hrs then cooled and filtered. The separated product was filtered washed with ethanol and purified by recrystallisation in ethanol, dried and weighed, yield 76.24%.



Scheme for preparation of hydrazone derivatives

RESULT AND DISCUSSION

All the compounds are non-hygroscopic stable solids, insoluble in water and shows varying solubility in common organic solvent. The elemental analysis data presented in Table-1 which is good agreement with the molecular formula of the compounds.

ELECTRONIC ABSORPTION SPECTRA

The UV-spectra of all the compounds in DMF was recorded. The results of the electronic spectral data show that the band observed in the range 250-270 nm are assigned to the $n \rightarrow \pi^*$ transition of the electron of the unshared electron pair on hetero atoms present in the compounds. The band observed in the range 184-220 nm assigned to $\pi \rightarrow \pi^*$ transition of aromatic chromophore of the compounds.

INFRARED SPECTRA

The FTIR spectra of the ligands were recorded in KBr over the range 4000-400 cm⁻¹. A broad band observed around 3250 cm⁻¹ due to O-H stretching mode. The band at 3020 cm⁻¹ assigned to C-H mode. The peak around 2830 cm⁻¹ can be assigned to C-H mode. The intense absorption at 1625 cm⁻¹ is due to C=O amide moiety and peak at around 1600 cm⁻¹ is for C=N. The shoulder near 1430 cm⁻¹ assigned to Ar-H.

Table 1: Physical and analytical data of hydrazone derivatives

Comp	Substituent	Molecular formula (Formula wt.)	Yield %	Decomposition Temperature in °C	Color	% Elemental analysis found (calculated)			
						C	H	N	O
L1	-OCH ₃	C ₁₂ H ₁₁ N ₃ O ₃ (327.34)	76	196	White shiny	58.73 (58.70)	5.24 (5.23)	21.39 (21.41)	14.64 (14.66)
L2	-H	C ₁₂ H ₁₂ N ₃ O ₂ (297.31)	73	202	White shiny	60.58 (60.59)	5.11 (5.10)	23.57 (23.55)	10.74 (10.76)
L3	-NO ₂	C ₁₂ H ₁₀ N ₃ O ₄ (342.31)	80	211	Light yellow	52.63 (52.63)	4.11 (4.12)	24.58 (24.55)	18.68 (18.70)
L4	-Ph	C ₁₂ H ₁₁ N ₃ O ₂ (347.37)	79	205	White shiny	65.70 (65.69)	4.94 (4.94)	20.13 (20.16)	9.23 (9.21)
L5	-CH ₃	C ₁₂ H ₁₁ N ₃ O ₂ (311.35)	74	208	White shiny	61.70 (61.72)	5.51 (5.50)	22.52 (22.50)	10.27 (10.28)

¹H-NMR SPECTRA

The ¹H-NMR spectra in DMSO were recorded on a Bruker 300MHz spectrometer and the data presented in Table-2. The signal at 6.5349-7.8980 ppm is assigned to aromatic protons. In the ¹H-NMR spectra, signal due to -NH proton observed at 11.9201-11.9804 ppm, whereas broad signals due to -OH proton observed at 10.1222-10.3292 ppm. A signal at 8.4272-8.7843 ppm is assigned to -CH=N- proton.

Table 2: ¹H-NMR spectral data of the compounds (δ in ppm)

Inference	L1	L2	L3	L4	L5
-NH	11.9201	11.9607	11.9403	11.9402	11.9804
-OH	10.1222	10.2662	10.2826	10.3292	10.2612
-CH=N-	8.5260	8.7843	8.7525	8.6446	8.4272
Aromatic	6.9239-6.9455	6.5685-7.9606	6.9424-7.4663	6.5349-8.4116	6.9391-7.8980
-OCH ₃	3.772	-	-	-	-
-CH ₃	-	-	-	-	2.4996

REFERENCES

- R. M. Patil and N. V. Thakkar, Synth. React. Inorg. Met. Org. Chem., 30(6), 1159, 2000.
- R. Tada, Naimish Chavda and Manish K. Shah, J. Chem. Pharm. Res., 3(2), 290, 2011.
- J. B. Biswal, S. S. Garje and B. L. Jadhav, Main Group Metal Chemistry, 32(6), 297, 2009.
- M. E. Mhadaye and R. M. Patil, Indian Journal of Research, 5(4), 63, 2016.
- Furnis BS, Hannaford AJ, Smith PWG and Tatchell AR. Vogel Textbook of Practical Organic Chemistry 5th Ed. ELBS Longman London, 1989.
- M. E. Mhadaye and R. M. Patil, Global Journal for Research Analysis, 4(8), 374, 2015.
- M. Emayavaramban, K. Kumar, P. Mani, B. Prabhakaran and A. Muthuvel, International Journal of Advanced Chemistry, 2(1), 20, 2014.
- J. B. Biswal, and S. S. Garje, Main Group Metal Chemistry, 30(2), 75, 2007.