

# “Structural and Analytical Studies of *o*-, and *p*-substituted nitrobenzaldehyde derivatives of Benzilmonoximethiocarbohydrazide”

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## Abstract

Reaction between *o*-, and *p*-substituted nitrobenzaldehyde and Benzilmonoximethiocarbohydrazide are *N*'-[(*Z*)-(2-nitrophenyl)methylidene]-*N*'''-[(1*E*,2*E*)-2-(hydroxyimino)-1,2-diphenylethylidene]carbonohydrazide(HBMT*o*NA), and *N*'-[(*Z*)-(4-nitrophenyl)methylidene]-*N*'''-[(1*E*,2*E*)-2-(hydroxyimino)-1,2-diphenyl-ethylidene] carbonohydrazide(HBMT*p*NA). The synthesized compounds have been characterized on the basis of various physico - chemical techniques

## 1. Introduction:

Schiff bases are formed when any primary amine reacts with an aldehyde or a ketone. Structurally, a Schiff base and they are also known as azomethine or imine) is a nitrogen analogue of an aldehyde or ketone in which the carbonyl group (CO) has been replaced by an amino group. Schiff base compounds are synthesized easily and almost form complexes with all transition metal ions. Many Schiff base derived compounds reports on their applications in anti-bacterial<sup>1-2</sup>, anti-oxidant<sup>3</sup>, anti-malarial<sup>4</sup>, anti-viral<sup>5</sup>, anti-cancer<sup>6-7</sup>, anti-fungal<sup>8-9</sup>, anti-inflammatory<sup>10</sup> activities and also used as catalyst in several reactions such as polymerization reaction, reduction of thionyl chloride, oxidation of organic compounds, reduction reaction of ketones, aldol reaction, Henry reaction, epoxidation of alkenes, hydrosilylation of ketones, synthesis of bis(indolyl) methanes and Diels Alder reaction. In many biochemical reactions Schiff bases plays an important role.

The Schiff bases derived benzilmonoxime and its derivatives are reported many researchers<sup>11-12</sup>. Benzilmonoximehydrazone<sup>13-16</sup> and benzilmonoximethiocarbohydrazide and its various metal complexes are reported earlier. In view of these we wish to the present study deals with the preparation of new Schiff bases derived from *o*-, and *p*-substituted nitro-benzaldehyde and benzilmonoximethiocarbohydrazide. IUPAC name and abbreviated of the prepared compounds are *N*'-[(*Z*)-(2-nitrophenyl)methylidene]-*N*'''-[(1*E*,2*E*)-2-(hydroxyimino)-1,2-diphenylethylidene]carbonohydrazide(HBMT*o*NA), and *N*'-[(*Z*)-(4-nitrophenyl)methylidene]-*N*'''-[(1*E*,2*E*)-2-(hydroxyimino)-1,2-diphenyl-ethylidene] carbonohydrazide(HBMT*p*NA). The solid compounds have been synthesized and studied by elemental analyses and various spectroscopic techniques.

## 2. Experimental:

### Materials and instruments

All chemicals were used by AR grade and were used without further purification. Melting points were determined in an Electrothermal 9200. <sup>1</sup>H-NMR spectra in CDCl<sub>3</sub> were recorded on Bruker AV300 NMR spectrometers using TMS as internal standard. The FT-IR spectra were recorded in the range 400–4000 cm<sup>-1</sup> by KBr pellet using a ‘Perkin- Elmer spectrum 100’ model FT-IR spectrophotometer. The UV–Vis spectra in methanol were recorded with a JASCO V-650 Spectrophotometer.

### *General method for synthesis of o-, and p-substituted nitrobenzaldehyde derivatives of Benzilmonoximethiocarbohydrazide:*

Benzilmonoximethiocarbohydrazide were prepared by reported method<sup>18</sup>. A mixture of 0.10mol of nitrobenzaldehydes (o-, and p-substituted) in 50mL ethanol was added to alcoholic solution of 0.15 mol of benzilmonoximethiocarbohydrazide and 2ml of conc. HCl. This mixture was refluxed 8h and then allowed to cool. The precipitated compounds was collected and purified by crystallization method using methanol (yield: 80-83%).

## 3. Results and Discussions:

Characterization of the prepared compounds are done by using analytical data obtained from UV-VISIBLE, FT(IR), <sup>1</sup>H NMR spectroscopy and elemental analysis etc. The molecular weight of proposed compounds is 480g mol<sup>-1</sup> determined by Rast method<sup>19</sup>; they are melts at 210-215<sup>0</sup>C. They are yellowish brown crystalline solids, soluble in common organic solvents such as, methanol, chloroform, acetone, DMF, DMSO, dioxane, dilute alkali etc. partially soluble in ethanol. Structural studies of the synthesized compounds of FTIR, PMR, UV-VISIBLE spectroscopy and elemental analysis etc. the prepared compounds are monobasic in nature by compounds-KOH titration curve.

### UV-Visible Spectroscopy:

The UV- spectra of the prepared compounds in the ultra-violet region show high intensity band at around 360-370nm ( $\epsilon = 20945-21500 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ), 274-289nm ( $\epsilon = 13195-13218 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) and at 218-226 ( $\epsilon = 12222-12300 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ). These are due to the  $\pi \rightarrow \pi^*$  (allowed) transitions of azomethine environment in the all molecules. In many isonitrosoketones<sup>20-21</sup>, a bands occurs at similar positions and intensity, are reported as the ( $\pi \rightarrow \pi^*$ ) transitions in the present compounds<sup>17-18</sup>.

**Table-1:** UV-Visible spectra of the o-, and p-substituted nitro-benzaldehyde derivatives  $\alpha$ -Benzilmonoximethiocarbohydrazide

Compounds	$\lambda$ (nm)	$\epsilon$ (dm <sup>3</sup> mol <sup>-1</sup> cm <sup>-1</sup> )
HBMT <sub>o</sub> NA	365	21500
	281	13218
	226	12300
	360	20999

HBMTpNA	274	13200
	218	12222

### <sup>1</sup>H NMR:

<sup>1</sup>H NMR spectra of the synthesized compounds was recorded in CDCl<sub>3</sub> solvent and important bands summarized in **Table-2**. The singlet at observed at δ11.50-11.59ppm (s, 1H) region indicated oximino proton in the prepared compounds and since it is expected to be rather acidic and therefore the weakest shielded proton in the molecules. The singlet observed at δ10.07-10.10ppm ascribed to proton of the secondary amine (>C=N-NH-). A singlet observed at region δ8.57-8.68ppm (s, 1H) assigned to either the NH -SH moiety, such an assignment is favored by the thione- thiol tautomerism<sup>17</sup> possible in the proposed compounds. A singlet at δ4.97-5.00 ppm ascribed to the methine group in the all prepared compounds. The multiplets in the region δ 7.60 - 8.44ppm were ascribed to the aromatic ring protons in synthesized compounds.

**Table-2:** <sup>1</sup>H NMR data of *o*-, and *p*-substituted nitro-benzaldehyde derivatives α-Benzilmonoximethiocarbohydrazide in ppm

Compounds	-OH	>C=N-NH-	-SH	-CH=	Phenyl rings
HBMT <sub>o</sub> NA	11.50	10.07	8.68	4.99	7.60-8.44
HBMT <sub>p</sub> NA	11.59	10.10	8.57	5.00	7.60-8.44

### FTIR Spectra:

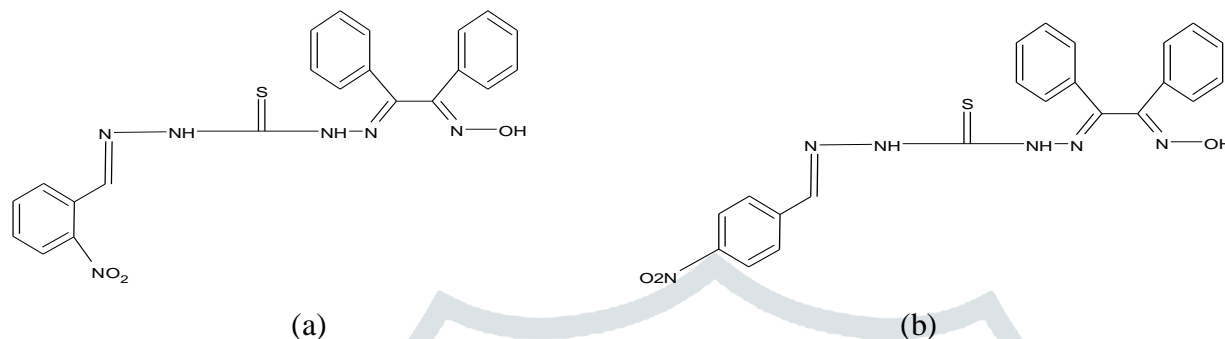
A significant feature of the FT(IR) spectra of the *o*-, and *p*-substituted nitro-benzaldehyde derivatives α-Benzilmonoximethiocarbohydrazide is the absence of band between 3300 - 3350cm<sup>-1</sup> due to the -NH<sub>2</sub> vibration reported<sup>17</sup> at 3300cm<sup>-1</sup> in α-Benzilmonoximethiocarbohydrazide indicating a successful replacement of the amino group by the azomethine group during Schiff base formation. The spectra show a band at 3218-3226cm<sup>-1</sup> due to the presence of -OH of the oximino in the synthesized compounds. Also another band observed at 3011-3023cm<sup>-1</sup> in the FT(IR) spectra of the all compounds are ascribed to aromatic C-H stretching vibrations and the aliphatic C-H group band is merged into aromatic C-H stretching which are observed in synthesized compounds. Rest of the bands observed in title compounds are almost at the same frequencies in comparisons with bands of benzilmonoximethiocarbohydrazide (**Table-3**).

**Table-3:** FT(IR) spectra of the *o*-, and *p*-substituted nitro-benzaldehyde derivatives α-Benzilmonoximethiocarbohydrazide in cm<sup>-1</sup>

Compounds	-OH	v(C-S-H)	v(C=NO)	v(C=NN)	v(N-H)	v(N-O)	v(N-N)	v(Ph-Br)
HBMT <sub>o</sub> NA	3226	2345	1611	1699	1590	1002	1070	725
HBMT <sub>p</sub> NA	3222	2356	1609	1692	1587	1003	1069	755

#### 4. Conclusion:

The title compounds are soluble in most of the common organic solvents and they have high melting point, indicating strongly bonded all functional groups and other molecules. The synthesized compounds are monobasic in nature concluded on the basis of the compounds-KOH titration curve method. On the basis of the spectroscopic methods tentatively assigned the structures of the proposed compounds as follow;



**Figure-1:** (a)  $N'$ -[(Z)-(2-nitrophenyl)methylidene]- $N''$ -[(1E,2E)-2-(hydroxyimino)-1,2-diphenylethylidene]carbonohydrazide (HBMTToNA), (b)  $N'$ -[(Z)-(4-nitrophenyl)methylidene]- $N''$ -[(1E,2E)-2-(hydroxyimino)-1,2-diphenylethylidene]carbonohydrazide (HBMTpNA)

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