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Synthesis, Characterization and Mutagenic Evaluation of Novel Bromobenzaldehyde Derivatives of α-Benzilmonoxime Hydrazone

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Abstract: **Novel Bromobenzaldehyde derivatives of α- Benzil monoxime hydrazone are synthesized by condensation of *o*-, *m*-, and *p*-Bromobenzaldehyde with α- Benzil monoxime hydrazone in acidic condition at reflux temperature. The newly synthesized compounds were characterized by elemental analysis and spectral techniques including UV-Visible, Infra-red and H^1NMR spectroscopic studies. The newly synthesized compounds were theoretically evaluated for their Mutagenicity as per ICH guidelines.**

Key words: α- Benzil monoxime hydrazone, *o*-, *m*-, and *p*-Bromobenzaldehyde, Spectral studies, Mutagenicity, ICH guideline.

I. INTRODUCTION

Hydrazones are a class of organic compounds with the structure $R_1R_2C{=}NNH_2$ (Vogel AI *1956)*. They are related to ketones and aldehydes by the replacement of the oxygen with the NNH_2 functional group. They are formed usually by the action of hydrazine on ketones or aldehydes (Esmail and etal 2013). Hydrazone-based coupling methods are used in medical biotechnology to couple drugs to targeted antibodies, *e.g.* antibodies against a certain type of cancer cell. The hydrazone-based bond is stable at neutral pH (Raman N and etal *2006*).

Hydrazones are mainly used as a foaming agent in preparing polymer foams, but applications also include its uses as a precursor to polymerization catalysts, pharmaceuticals, and agrochemicals, as well as a long-term storable propellant for in-space spacecraft propulsion. Hydrazone shows wide range of pharmaceutical activities such as antibacterial, antimalerial, antifungal, antimicrobial and anticonvulsant agents(Dhadke and etal 1978)

II. LITERATURE SURVEY

Scanning of the literature reveals that the hydrazonyl derivative of α-Benzilmonoxime and its metal complexes have been studied and reported (Badekar R and etal 2017; Singh MS and etal 2001). However, literature review on condensation reactions of α-benzilmonoximehydrazone with bromobenzaldehyde derivative is not available. In view of this we wish to report condensation of bromobezaldehyde derivatives with α-benzilmonoximehydrazone compounds. As such the present work deals with the synthesis and characterization of the bromobenzaldehyde derivatives of α-Benzilmonoximehydrazone and their theoretical Mutagenic evaluation..

III. EXPERIMENTAL

A. Materials and methods:

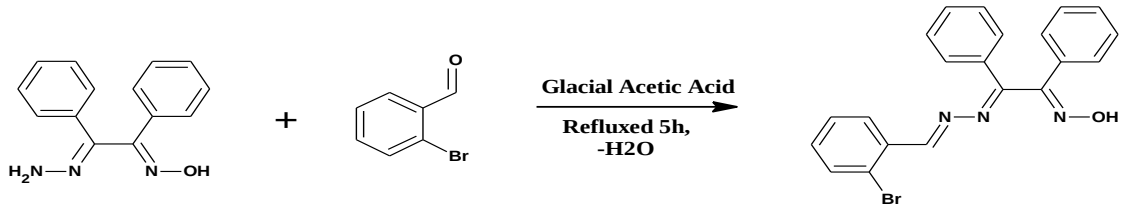
The analytical Grade (AR) chemicals were used in all the experiments. The melting points of newly prepared compounds were determined by Electrothermal melting point apparatus. FT-IR spectra were recorded using KBR pellets using Perkin - Elmer Infrared spectrophotometer. UV-visible spectra were recorded on JASCO 450 spectrophotometer using methanol/0.1N NaOH solvents. The proton magnetic resonance spectra were recorded on 'Brucker AV300 NMR Spectrometer' using TMS as internal standard. The Mutagenicity of novel compounds waw evaluated using Toxicity Estimation Software Tool (TEST).

B. Synthesis of Bromobenzaldehyde derivatives of α-Benzilmonoximehydrazide.

1) Synthesis of Novel α-Benzil monoximehydrazone-o-bromo benzaldehyde [HBMHoBB]

The title compound was prepared by mixing of methanolic solution of the α-Benzilmonoximehydrazone (0.10mol) and 2-bromobenzaldehyde (0.15mol). 2-3 drops of glacial acetic acid was added to the reaction mass. The resulting mixture was refluxed for 5h. After complete reflux the mixture was cooled to room temperature, a solid was separated which was dried at 110°C in hot air oven.

The Yellow colored solid is having melting point 205^0 C with 76.98% yield.

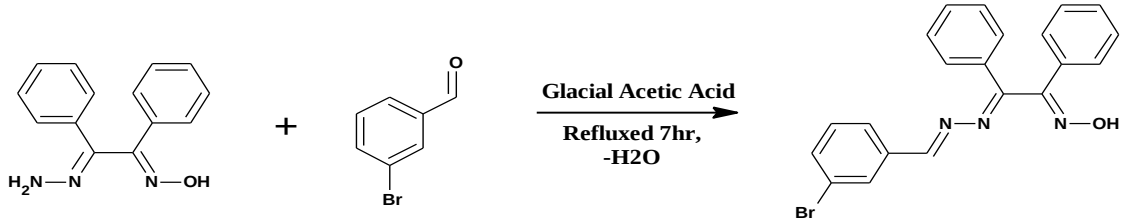


α-Benzilmonoximehydrazone **2- bromobenzaldehyde** **HBMHoBB**

2) Synthesis of Novel α-Benzil monoximehydrazone-m-bromo benzaldehyde [HBMHmBB]:

The title compound was prepared by mixing of methanolic solution of the α-Benzilmonoximehydrazone (0.100mol) and 3-bromobenzaldehyde (0.125mol) in presence of 2-3 drops of glacial acetic acid. The resulting mixture was refluxed for 7hrs. After complete refluxing the pH of solution was raised to 5 using 0.1N aqueous NaOH solution, reaction mass cooled to room temperature, solid separated, dried at 110°C in oven.

The Yellow colored solid is having melting point 209^0C with 81.12% yield.

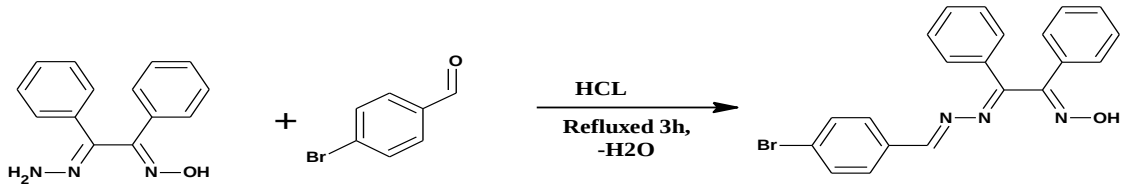


α-Benzilmonoximehydrazone **3- bromobenzaldehyde** **HBMHmBB**

3) Synthesis of Novel α-Benzil monoximehydrazone-p- bromo benzaldehyde [HBMHpBB]:

The title compound was prepared by mixing of Ethanolic solution of the α-Benzilmonoximehydrazone (0.100mol) and 4-bromobenzaldehyde (0.11mol), 2ml of Hydrochloric acid was added to the reaction mass. The resulting mixture was refluxed for 3hr. After complete reflux the pH of solution was adjusted to 5 using 0.1N aquoues NaOH solution, Reaction mass further cooled at room temperature, solid separated, dried at 110°C in oven.

The Yellow colored solid is having melting point 207^0 C with 72.68% yield



α-**Benzilmonoximehydrazone** **4- bromobenzaldehyde** **HBMHpBB**

IV. RESULTS AND DISCUSIONS

The Interaction of α-Benzilmonoximehydrazone with *o*-, *m*- and *p*-bromobenzaldehyde in 1:1 molar ratio in alcoholic solvent, led to preparation of α-Benzilmonoximehydrazone-*o*-bromobenzaldehyde, α-Benzilmonoximehydrazone-*m*-bromobenzaldehyde,α-Benzilmonoximehydrazone-*p*-bromobenzaldehyde derivatives respectively, an interesting organic moiety which can act as bidentate ligand.

The yellow crystalline solid melts at 205˚C-209^{0}C, insoluble in water, soluble in common organic solvents i.e. chloroform, acetone, DMF, DMSO, 1, 4-Dioxane, dilute alkali etc. and is partially soluble in alcohol. The ligand has one probable ionizable proton; and our studies also reveal that the ligand have monobasic in nature, which is supported by ligand-KOH titration curve (monobasic acid).

The resultant yellow coloured compound was characterized by elemental analysis, physico-chemical and spectral analysis such as FTIR, H^{1}NMR, UV-visible spectroscopy. The Theoretical Mutagencity of isolated compounds were evaluated using TEST software.

A. Physical and Analytical data of o-, m- and p-Bromobenzaldehyde derivatives of α-Benzilmonoximehydrazone:

The Physical data of *o,m,p*-Bromobenzaldehyde derivatives of α-Benzilmonoximehydrazone (Table-1) corresponds to the molecular formula $C_{21}H_{16}N_3OBr$, which corresponds to the molecular weight 406g/mol. The Purity of isolated compounds were checked by Gas chromatography and found to be more than 98% pure.

Table-1: Physical and Analytical data of *o*-, *m*- and *p*-bromobenzaldehyde derivatives of α-Benzilmonoximehydrazone.

Compound	**Color**	**% Yield**	**MP/DP in ^{o}C**	**% Element Content, Expected (Observed)**				
				C	**H**	**N**	**O**	**Br**
HBMHoBB	Yellow	76.98	205	62.08 (61.92)	3.97 (3.88)	10.94 (10.02	3.94 (3.85)	19.67 (19.00)
HBMHmBB	Yellow	81.12	209	62.08 (61.99)	3.97 (3.78)	10.94 (10.28)	3.94 (3.85)	19.67 (19.66)
HBMHpBB	Yellow	72.68	207	62.08 (62.00)	3.97 (3.92)	10.94 (10.61)	3.94 (3.96)	19.67 (19.59)

For the sake of convenience, novel compounds are labeled as HBMHoBB, HBMHmBB and HBMHpBB. The first H in the abbreviation of the compound assigned to the presence of one ionisable proton.

The IUPAC names of these newly synthesized compounds are

1) 2-[(2-bromobenzylidene)hydrazinylidene]-1,2-diphenylethanimine.
2) 2-[(3-bromobenzylidene)hydrazinylidene]-1,2-diphenylethanimine.
3) 2-[(4-bromobenzylidene)hydrazinylidene]-1,2-diphenylethanimine.

B. Electronic Spectrum Study of o,m,p-*Bromobenzaldehyde derivatives α-Benzilmonoximehydrazone:*

The UV spectroscopic investigations of bromobenzaldehyde derivatives of α-Benzilmonoximehydrazone were carried out in methanol solution in the range 200-400nm. The UV spectrum of 2-[(2-bromobenzylidene)hydrazinylidene]-1,2-diphenylethanimine exhibit two major bands at 339nm (ε = 12723dm3/mol/cm) and 249nm (ε = 20905dm3/mol/cm). These bands are due to π to π* transition of both oximino and Schiff base groups. The π to π* transition (more intense) is due to the nonbonding electrons present on the >C=N group in oximino or in the azomethine group.

The electronic absorption spectrum of 2-[(3-bromobenzylidene)hydrazinylidene]-1,2-diphenylethanimine in methanol, reveals two high intensity bands at 392nm (ε = 14385 dm^3 /mol/cm) and 243nm (ε = 7867 dm^3 /mol/cm) respectively. These may be due to $\pi \rightarrow \pi^*$ transitions possible from the azomethine and oximino environment in the molecule.

The electronic absorption spectrum of 2-[(4-bromobenzylidene)hydrazinylidene]-1,2-diphenylethanimine in methanolic solution shows three intense bands at, 391nm (ε = 10631 $dm^3cm^{-1}mol^{-1}$), 325nm (ε = 3998 $dm^3cm^{-1}mol^{-1}$), and at 244nm (ε = 5728$dm^3cm^{-1}mol^{-1}$). These bands can be attributed for the quantum mechanically allowed transitions of $\pi^* \leftarrow \pi$ origin from the oximino and azomethine environment of the compound.

Table-2: Electronic spectrum data of Bromobenzaldehyde derivatives of α-Benzilmonoximehydrazone

Compound	λnm	ε (dm^3/mol/cm)	Transition
HBMHoBB	339	12723	$\pi \rightarrow \pi^*$
	249	20905	$\pi \rightarrow \pi^*$
HBMHmBB	392	14385	$\pi \rightarrow \pi^*$
	324	3845	$\pi \rightarrow \pi^*$
	243	7867	$\pi \rightarrow \pi^*$
HBMHpBB	391	10631	$\pi \rightarrow \pi^*$
	325	3998	$\pi \rightarrow \pi^*$
	244	5728	$\pi \rightarrow \pi^*$

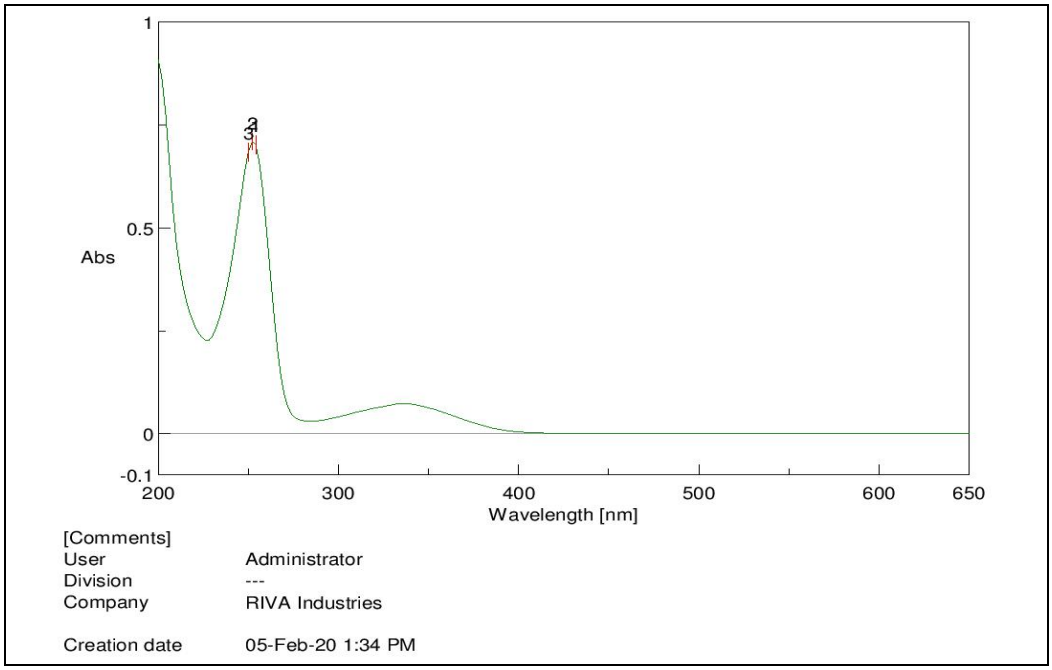


Figure-1: UV-Visible spectrum of 2-[(2-bromobenzylidene)hydrazinylidene]-1,2-diphenylethanimine in methanol

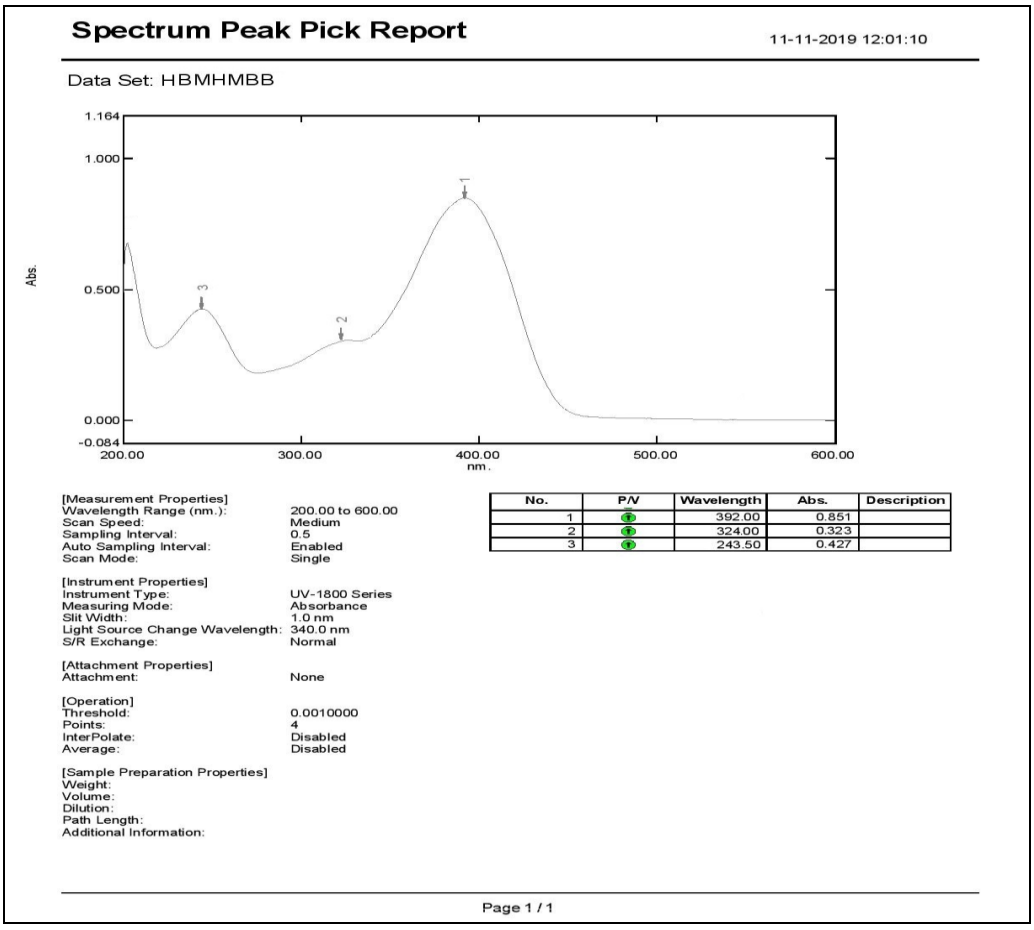


Figure-2: UV-Visible spectrum of 2-[(3-bromobenzylidene)hydrazinylidene]-1,2-diphenylethanimine in methanol

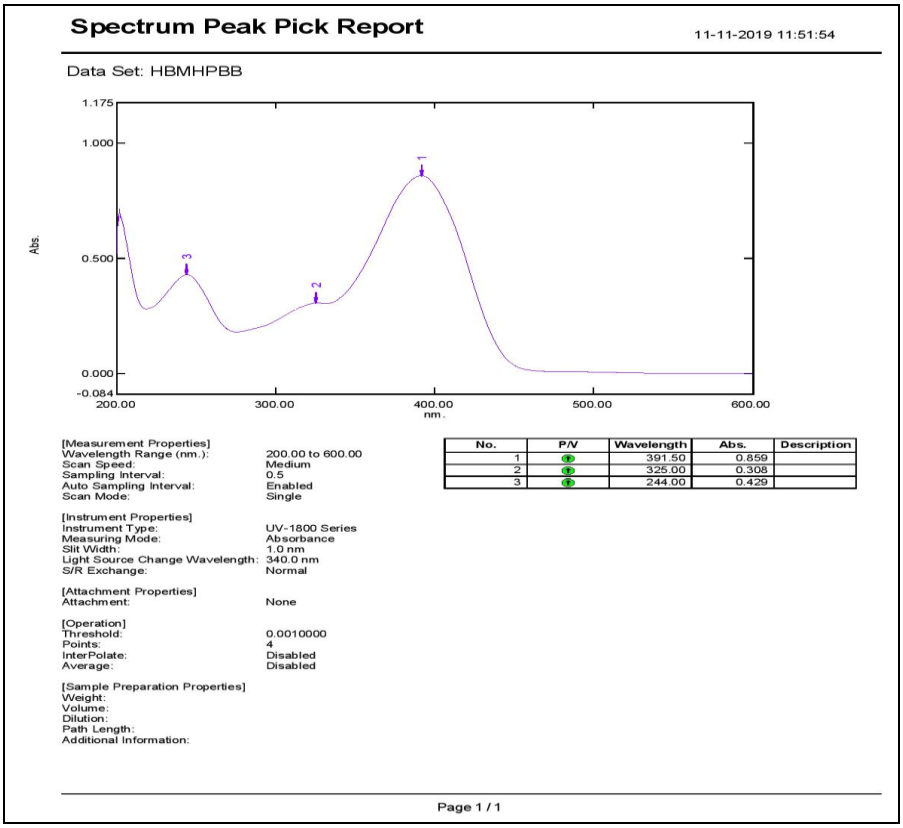


Figure-3: UV-Visible spectrum of 2-[(4-bromobenzylidene)hydrazinylidene]-1,2-diphenylethanimine in methanol

C. FT-IR spectrum studies of the o,m,p-Bromobenzaldehyde derivatives of α-Benzilmonoximehydrazone:

The FT-IR spectrum of 2-[(2-bromobenzylidene)hydrazinylidene]-1,2-diphenylethanimine shows a broad band at 3209cm^{-1} due to the presence of free –OH of the oximino in the synthesized compound and another band observed at 3082cm^{-1} in the FT-IR spectra of the HBMHoBB ligand is ascribed to aromatic stretching vibrations and the aliphatic C-H group band is merged into aromatic C-H stretching which are observed.

The very strong's absorption band at 1625cm^{-1} which is assigned as azomethine ν(>C=NN-) group. The band appear at 1569cm^{-1} could be due to the ν(>C=NO-) oximino stretches of the o-bromobenzaldehyde derived benzilmonoximehydrazide.

The FT-IR stretching frequencies of 2-[(3-bromobenzylidene)hydrazinylidene]-1,2-diphenylethanimine shows bands at 3229, 3154 and 3110cm^{-1} assignable to ν(-OH), Ar C=C and Ar C-H respectively. Free ligand α-Benzilmonoximehydrazone-m-bromobenzaldehyde show very strong vibrational band at 1605cm^{-1} region in the individual FT-IR spectrum which is representative of the azomethine group. Another strong vibration observed nearby above band at 1545cm^{-1}, which is assigned as oximino group of the Benzilmonoximehydrazone-m-bromobenzaldehyde.A medium band confirming to phenolic bromine was identified at 749cm^{-1} of ligand Benzilmonoximehydrazone-m-bromobenzaldehyde. Another two bands observed at the 1067 and 1154cm^{-1}, which may be assigned as νN-O and νN-N bands respectively.

The FT-IR spectra of 2-[(4-bromobenzylidene)hydrazinylidene]-1,2-diphenylethanimine in the range 4000-400cm^{-1} is recorded using KBr pellet on Shimadzu instrument. A medium broad band at 3239 cm^{-1} is observed due to the existence of Oximino -OH group. The weak peak seen at 3079cm^{-1} can possibly be attributed to the stretching vibrations of aromatic C-H bands. No absorption peak seen at about 3200cm^{-1} can be ascribed to -NH_2 group condensing and confirms that the ligand formation took place.The peak at 1614cm^{-1} is attributed mainly because of the >C=N- vibrational modes of stretching type of the azomethine function in α-Benzilmonoxime hydrazone-p-bromobenzaldehyde. The band seen at 1093 cm^{-1} is attributed to the =N-N= vibrations, same vibrations are reported at 1093 cm^{-1}.

Table-3: Characteristic peaks of *o,m,p*-Bromobenzaldehyde derivatives of α-Benzilmonoximehydrazone in FT-IR spectrum

Compound	**-OH**	**Ar C=C**	**Ar C-H**	**ν(>C=NN-)**	**ν(>C=NO-)**	**νN-O**	**νN-N**	**Ph-Br**
HBMHoBB	3209	3107	3082	1625	1569	1018	1095	769
HBMHpBB	3229	3154	3110	1605	1545	1067	1154	749
HBMHpBB	3239	3100	3079	1614	1556	1010	1093	793

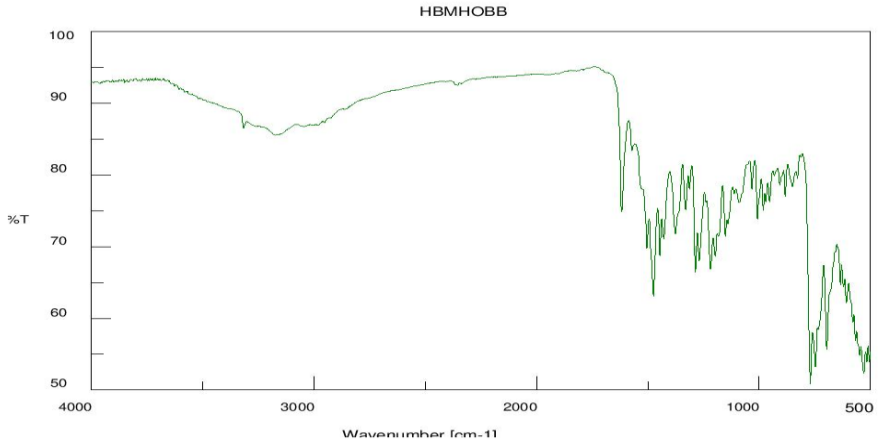


Figure-4 : FT-IR spectrum of 2-[(2-bromobenzylidene)hydrazinylidene]-1,2-diphenylethanimine

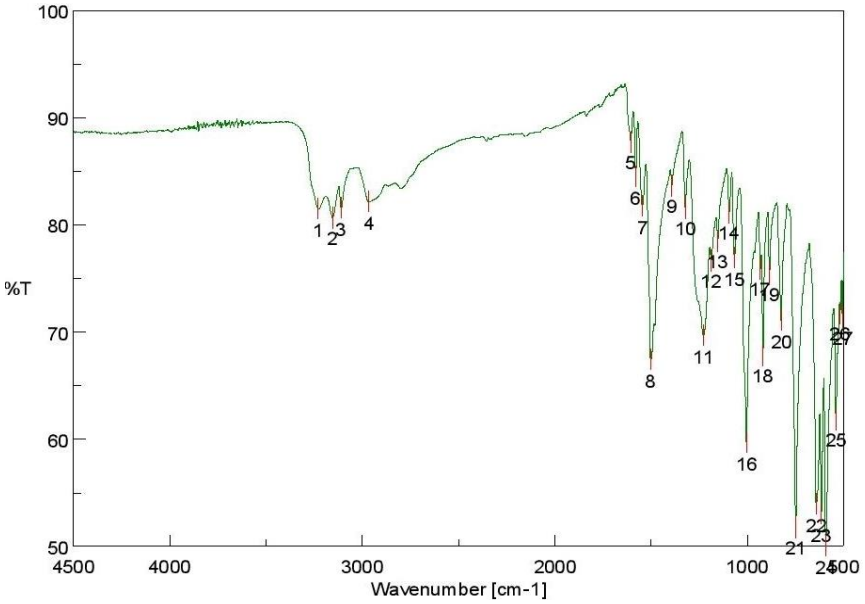


Figure-5 : FT-IR spectrum of 2-[(3-bromobenzylidene)hydrazinylidene]-1,2-diphenylethanimine

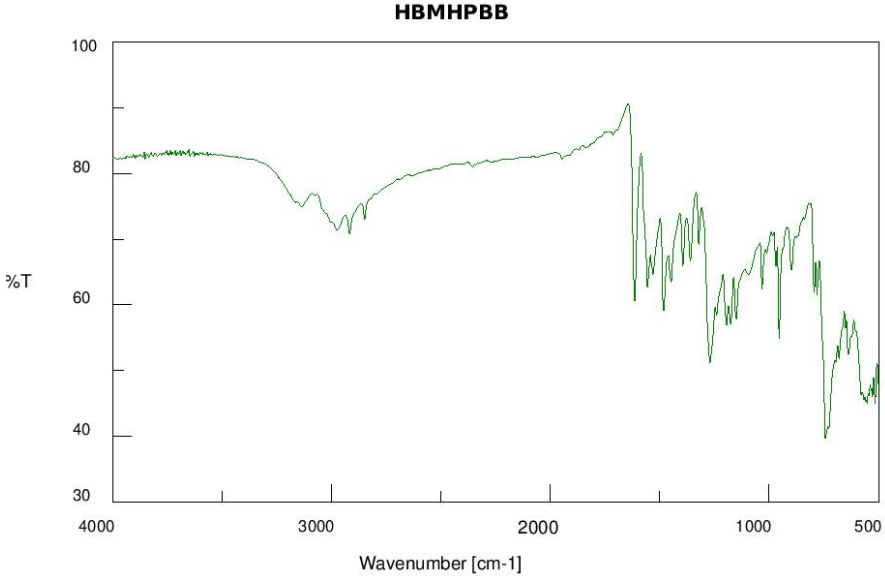


Figure-6 : FT-IR spectrum of 2-[(4-bromobenzylidene)hydrazinylidene]-1,2-diphenylethanimine

D. H^1NMR studies of o,m,p-Bromobenzaldehyde derivatives of α-Benzilmonoximehydrazone:

The H^1NMR spectrum of *o,m,p*-Bromobenzaldehyde derivatives of α-Benzilmonoximehydrazone in deuturated DMSO was recorded using tetramethylsilane as the internal standard.

In the H^1NMR spectrum of 2-[(2-bromobenzylidene)hydrazinylidene]-1,2-diphenylethanimine the oximino proton appears as a singlet at δ 10.17ppm and all the 14 aromatic protons appears as a multiplet in the range δ 7.5 to δ 7.9 ppm. In addition to this, aliphatic protons present as a bridge between azomethine (>C=NN-) groups appears at δ 8.7ppm.

In the H^1NMR spectrum of 2-[(3-bromobenzylidene)hydrazinylidene]-1,2-diphenylethanimine, the oximino proton appears as a singlet at δ 10.50ppm and all the 14 aromatic protons appears as a multiplet in the range δ 7.0 to δ 7.7 ppm. In addition to this, aliphatic protons present as a bridge between azomethine (>C=NN-) groups appears at δ 8.5ppm.

The oximino proton in 2-[(4-bromobenzylidene)hydrazinylidene]-1,2-diphenylethanimine appears as a singlet at δ 10.20ppm and all the 14 aromatic protons appears as a multiplet in the range δ 8.2 to δ 8.7 ppm. In addition to this, aliphatic protons present as a bridge between azomethine (>C=NN-) groups appears at δ 9.1ppm.

Table-4: Comparision of PMR spectrum of *o*-, *m*- and *p*-Bromobenzaldehyde derivative of α-Benzilmonoximehydrazone ligands

Compound	-OH(ppm)	-CH=(ppm)	Phenyl Rings(ppm)
HBMHoBB	10.17	8.7	7.5-7.9
HBMHmBB	10.50	8.50	7.0-7.7
HBMHpBB	10.20	9.10	8.20-8.70

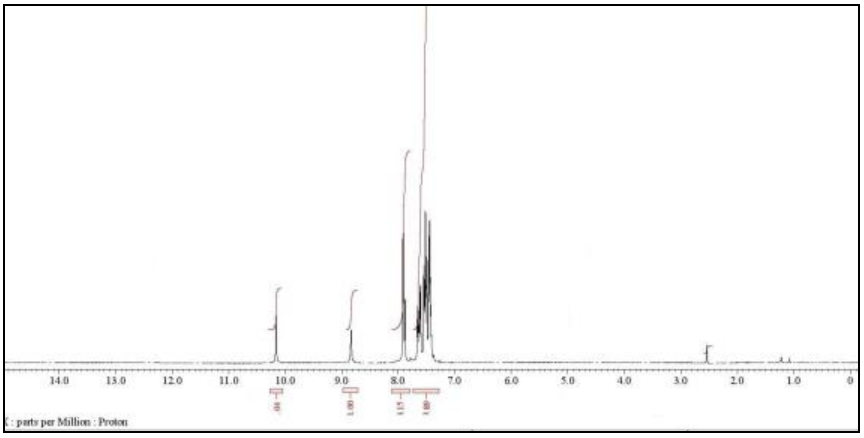


Figure-7 : H^1NMR spectrum of 2-[(2-bromobenzylidene)hydrazinylidene]-1,2-diphenylethanimine

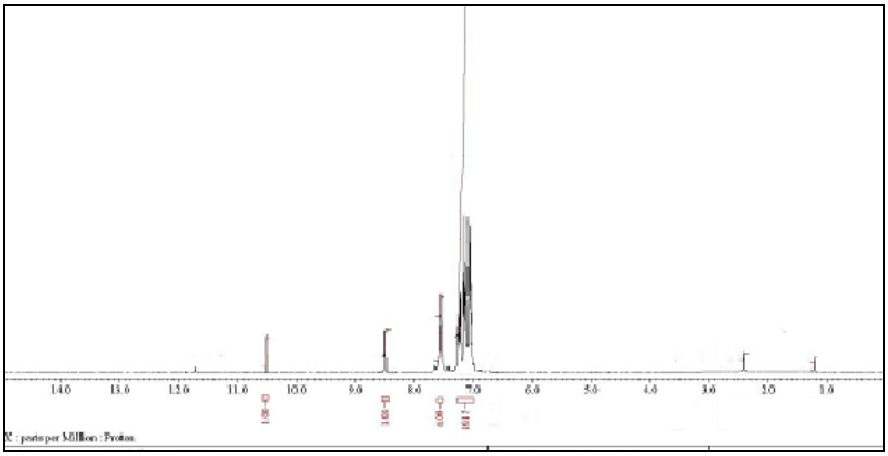


Figure-8: H^1NMR spectrum of 2-[(3-bromobenzylidene)hydrazinylidene]-1,2-diphenylethanimine

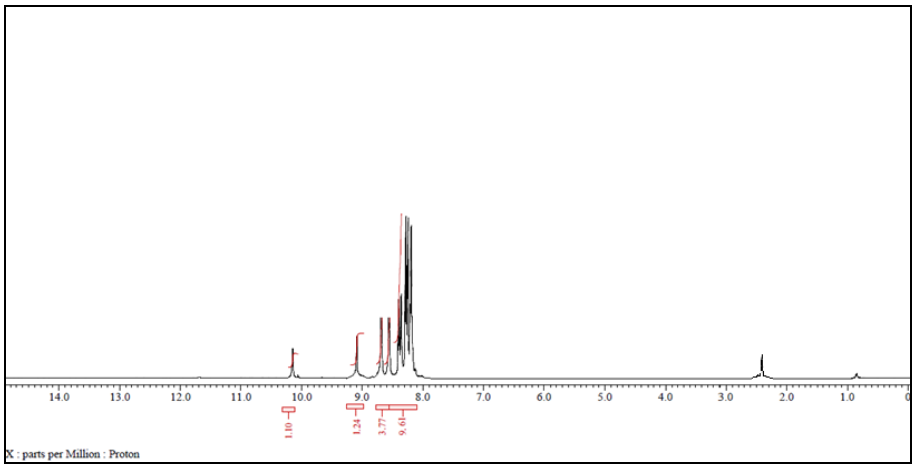
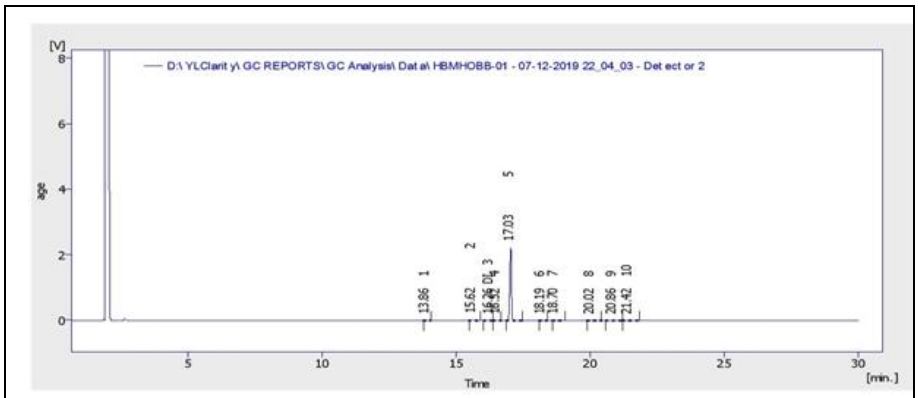


Figure-9:H^1NMR spectrum of 2-[(4-bromobenzylidene)hydrazinylidene]-1,2-diphenylethanimine

E. Gas chromatographic purity of o,m,p-Bromobenzaldehyde derivatives of α-Benzilmonoximehydrazone :

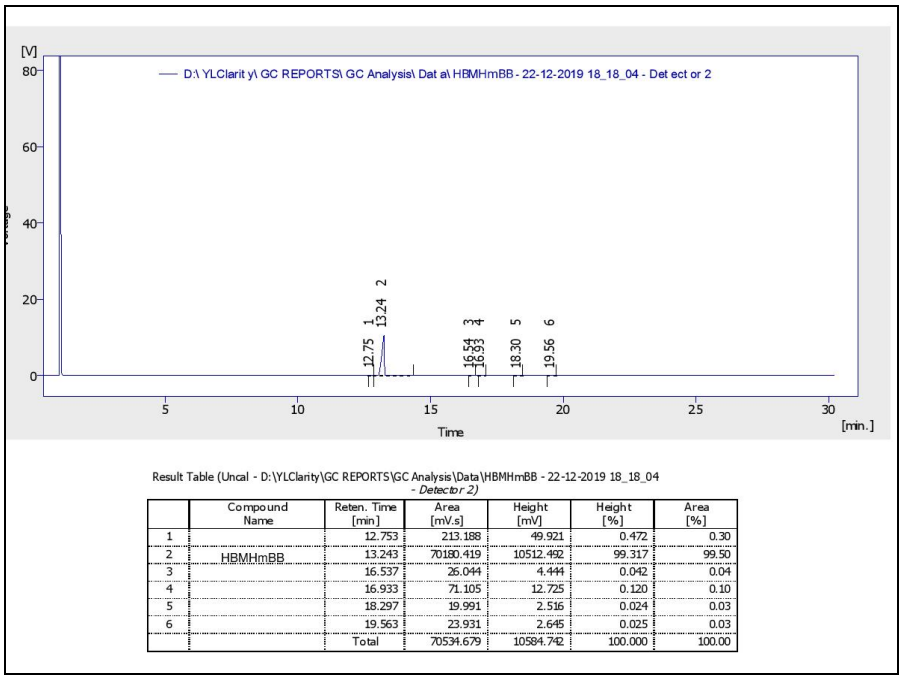
The purity of 2-[(2-bromobenzylidene)hydrazinylidene]-1,2-diphenylethanimine is checked by Gas chromatography technique shows purity-98.13%.The purity of 2-[(3-bromobenzylidene)hydrazinylidene]-1,2-diphenylethanimine is 99.31% and purity of 2-[(4-bromobenzylidene)hydrazinylidene]-1,2-diphenylethanimine is found to be 99.46%.



Result Table (Uncal - D:\YLClarity\GC REPORTS\GC Analysis\Data\HBMHOBB - 07-12-2019 22_04_03 - Detector 2)

	Compound Name	Reten. Time [min]	Area [mV.s]	Height [mV]	Height [%]	Area [%]
1		13.863	2.015	0.408	0.018	0.02
2	HBMOH	15.620	86.933	21.739	0.956	0.90
3	OBBA	16.263	44.374	8.968	0.394	0.46
4		16.520	3.248	0.463	0.020	0.03
5	HBMHOBB	17.033	9397.838	2231.702	98.132	97.69
6		18.190	5.218	0.795	0.035	0.05
7		18.697	29.653	5.201	0.229	0.31
8		20.017	14.266	1.313	0.058	0.15
9		20.857	15.657	1.556	0.068	0.16
10		21.423	20.510	2.034	0.089	0.21
		Total	9619.713	2274.180	100.000	100.00

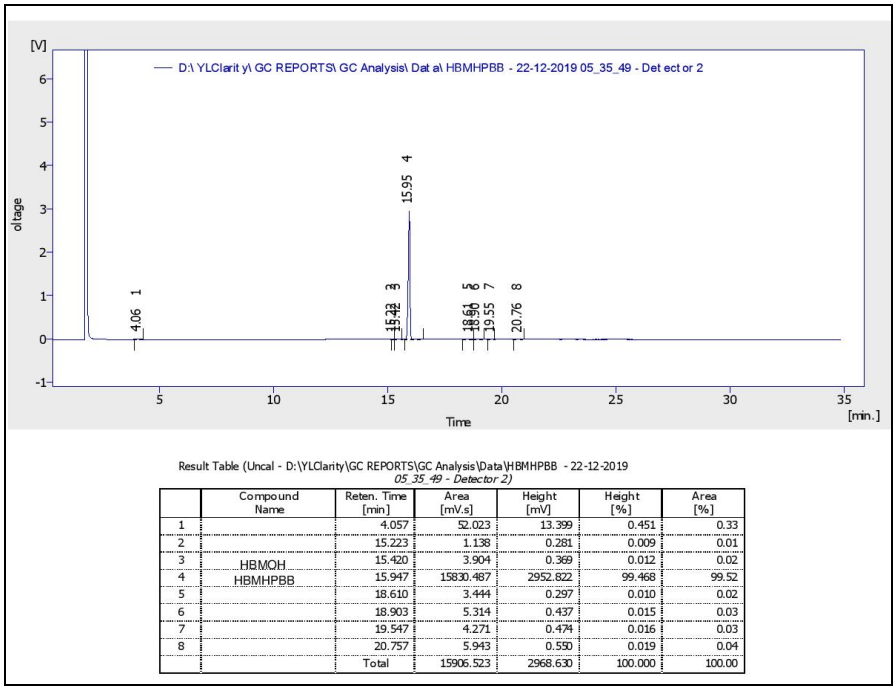
Figure-10: Gas Chromatographic purity of 2-[(2-bromobenzylidene)hydrazinylidene]-1,2-diphenylethanimine



Result Table (Uncal - D:\YLClarity\GC REPORTS\GC Analysis\Data\HBMHmBB - 22-12-2019 18_18_04 - *Detector 2)*

	Compound Name	Reten. Time [min]	Area [mV.s]	Height [mV]	Height [%]	Area [%]
1		12.753	213.188	49.921	0.472	0.30
2	HBMHmBB	13.243	70180.419	10512.492	99.317	99.50
3		16.537	26.044	4.444	0.042	0.04
4		16.933	71.105	12.725	0.120	0.10
5		18.297	19.991	2.516	0.024	0.03
6		19.563	23.931	2.645	0.025	0.03
		Total	70534.679	10584.742	100.000	100.00

Figure-11: Gas Chromatographic purity of 2-[(3-bromobenzylidene)hydrazinylidene]-1,2-diphenylethanimine



Result Table (Uncal - D:\YLClarity\GC REPORTS\GC Analysis\Data\HBMHPBB - 22-12-2019 05_35_49 - *Detector 2)*

	Compound Name	Reten. Time [min]	Area [mV.s]	Height [mV]	Height [%]	Area [%]
1		4.057	52.023	13.399	0.451	0.33
2		15.223	1.138	0.281	0.009	0.01
3	HBMOH	15.420	3.904	0.369	0.012	0.02
4	HBMHPBB	15.947	15830.487	2952.822	99.468	99.52
5		18.610	3.444	0.297	0.010	0.02
6		18.903	5.314	0.437	0.015	0.03
7		19.547	4.271	0.474	0.016	0.03
8		20.757	5.943	0.550	0.019	0.04
		Total	15906.523	2968.630	100.000	100.00

Figure-12 : Gas Chromatographic purity of 2-[(4-bromobenzylidene)hydrazinylidene]-1,2-diphenylethanimine

F. Mutagenic Evaluation of o,m,p-Bromobenzaldehyde derivatives of α-Benzilmonoximehydrazone:

The theoretical evaluation of Mutagenicity of isolated novel compounds is checked as per the International council of harmonization of technical requirements for pharmaceuticals for human use (ICH) ‘‘Assessment and control of DNA reactive (mutagenic) impurities in pharmaceuticals to limit potential carcinogens risk M7(R1)’’ by using Toxicity Estimation Software Tool version 4.2.1 (TEST software).

TEST software allows estimating toxicity values using several different advanced Quantitative structure, activity, relationship models (QSAR) methodologies. The Novel compounds were theoretically evaluated for Mutagenicity by Consensus method, FDA method, Nearest Neighbor method and Hierarchical clustering methods. The predicted statistical Mutagenicity value considering Concordance, Sensitivity, Specificity by Consensus method, FDA method, Nearest Neighbor method shows positive Mutagenicity whereas the value obtained by Hierarchical clustering method shows Negative Mutagencity.

Table-5: Mutagenicity result of *o*,*m*,*p*-Bromobenzaldehyde derivatives of α-Benzilmonoximehydrazone

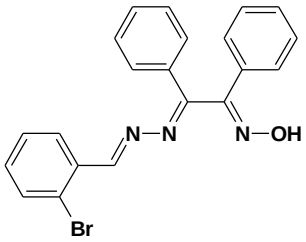
Sr.No.	**Compound**	**Method For Evaluation**	**Mutagenicity Value**	**Result**
1	2-[(2-bromobenzylidene)hydrazinylidene]-1,2-diphenylethanimine	Consensus method	0.63	Positive Mutagenicity
		FDA method	0.83	Positive Mutagenicity
		Nearest Neighbor method	1.00	Positive Mutagenicity
		Hierarchical clustering method	0.06	Negative Mutagenicity
2	2-[(3-bromobenzylidene)hydrazinylidene]-1,2-diphenylethanimine	Consensus method	0.51	Positive Mutagenicity
		FDA method	0.42	Negative Mutagenicity
		Nearest Neighbor method	1.00	Positive Mutagenicity
		Hierarchical clustering method	0.12	Negative Mutagenicity
3	2-[(4-bromobenzylidene)hydrazinylidene]-1,2-diphenylethanimine	Consensus method	0.56	Positive Mutagenicity
		FDA method	0.56	Positive Mutagenicity
		Nearest Neighbor method	1.00	Positive Mutagenicity
		Hierarchical clustering method	0.12	Negative Mutagenicity

CONCLUSION

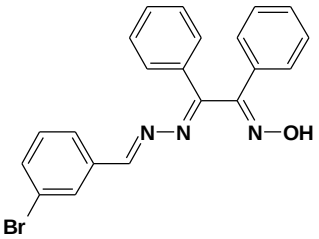
Based on various physicochemical results and spectral studies, the structure for Bromobenzaldehyde derivatives of α-benzilmonoximehydrazone is being proposed.

The Theoretical evaluation of all three novel compounds shows positive mutagenicity by Toxicity Estimation Software Tool, version 4.2.1 (TEST software). All synthesized novel compounds can act as good bidented ligands and can be further used for complex formation with metals. The pharmaceutical activities of these synthesized compounds such as antibacterial, antimalerial, antifungal, antimicrobial and anticonvulsant can be explored.

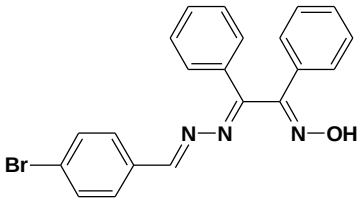
The following structures I, II and III are proposed on the basis of physiochemical results and spectral studies:



Structure I: 2-[(2-bromobenzylidene)hydrazinylidene]-1,2-diphenylethanimine



Structure II: 2-[(3-bromobenzylidene)hydrazinylidene]-1,2-diphenylethanimine



Structure III: 2-[(4-bromobenzylidene)hydrazinylidene]-1,2-diphenylethanimine

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