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SYNTHESIS, CRYSTAL STRUCTURE ANALYSIS, SPECTRAL INVESTIGATION, DFT COMPUTATION ON BENZALDEHYDE, 2-HYDR OXY,-[(2-HYDROXYPHENYL) METHYLENE]HYDRAZONE-A POTENTIAL BOIACTIVE AGENT

Namitha R[1]*, Ampily J S[1], Swathi Vinod[1]

[1]Department of Chemistry, RSM SNDP Yogam Arts and Science College. Koyilandy, Kozhikode. 673305, Kerala. India

***Corresponding author e-mail:namithasajish@gmail.com**

***Abstract*—** Benzaldehyde, 2-hydr oxy,-[(2-hydroxyphenyl) methylene]hydrazone was synthesized and its structural parameters were compared experimentally and theoretically. It was theoretically investigated using B3LYP/6-31G(d,p) level by using density functional theory. The second order hyperpolarisability and thus nonlinear optical properties of the compound was calculated using *ab initio* and density functional theory (DFT) by *insilico* method. Results obtained were compared with that of the urea. Corrosion inhibition properties of the compound were analysed theoretically. Antioxidant property of the compound was screened using DPPH assay. An antimicrobial study of the compound was conducted using well diffusion method. The antibacterial and antifungal activities were analyzed by comparing the zone of inhibition in mm.

***Keywords*—** B3LYP/6-31G(d,p), energy gap, Nonlinear optical, corrosion inhibition, Antioxidant, Antimicrobial.

1. INTRODUCTION

An open chain compound or acyclic compound is a compound with a linear structure than a cyclic one. There are many such compounds synthesized and investigated in various laboratories in the world. Many sophisticated instruments are utilized for this purpose. Azines are organic molecules which contain C=N-N=C as the functional unit. They are well known for their chemical and biological properties .Azines have been widely investigated using crystal analysis and computation considering their importance in non linear optics [1]. Azines, namely, 2,3-diazabuta-1,3-dienes, are an important class of that display diverse reactivity and are useful for many applications, such as the synthesis of N-heterocycles and functional polymers[2,3]. Metal-promoted transformations of azines have led to new synthetic applications[4]. Azine formation has also proven beneficial in studying metal meditated N_2 activation[5]. Recently, azines have generated much interest in the construction of covalent organic frameworks (COFs) having photo catalytic activity[6] or serving as chemo sensing detectors. Because of their unique electronic structure and stereochemical versatility[7], azine units give also rise to remarkable chromophoric properties[8] and are interesting as nonlinear optical materials[9].Applications as ferroelectric liquid crystals were also described[10].The biological activity of azine derivatives holds promise for pharmacological applications[11].

Organic molecules like azines exhibit extended pi conjugation show enhanced second order NLO properties. They show lower dielectric constants, ultra fast response time and enhanced NLO responses. They can be used to manipulate electric fields especially photonic signals[12]. Another important property exhibited by organic compounds containing electronegative functional groups and pi bonds in their structure is corrosion inhibition. The extent to which the compound can inhibit corrosion is based on its ability to get on the metal surface which consist of replacement of water molecules at the corroding interface [13,14].Apart from all these, they show wide biological properties and can be used in pharmaceuticals and medicinal field.

Considering the above all properties of azines, have synthesised **Benzaldehyde, 2-hydroxy-, [(2-hydroxyphenyl)methylene] hydrazone,** investigated the corrosion inhibition property of the synthesized diazine by considering theoretical calculations. Compared bond angle and

bond length using theoretical and experimental data. Using theoretical data, non linear optical properties of the compound were analyzed and its applications were studied considering its polarizability and hyperpolarisability [15].Considering the electronegative groups in the structure of compound, its antioxidant property were investigated using DPPH assay. Many compounds can be applied in industries as antioxidants if they possess electronegative groups in their structure [16].Antibacterial and antifungal properties of the compound were also studied. Antimicrobial study was also carried out.

EXPERIMENTAL

Chemicals used are of Analar grade purchased from Aldrich, Alfa Aesar, Merck, Loba, SRL and Sd-Fine (India) and used directly without further purification. Visualization on TLC was done by iodine and eluted with petroleum ether and ethyl acetate. X-ray diffraction (XRD) studies were conducted .Bond angle. Bond length details were collected and analysed.

The DFT employing the closed-shell Becke-Lee–Yang–Parr hybrid exchange-correlation three parameter functional (B3LYP) was adopted. All the calculations were performed using Gaussian 03program (G03W) package. The 6-31G (d, p) basis set augmented by d polarization functions on heavy atoms and p polarization functions on hydrogen atoms as well as diffuse functions for both hydrogen and heavy atoms were used.

Invitro antibacterial, antifungal activity were studied by the agar well diffusion method[17] is used to determine the growth inhibition. Antioxidant activity was determined by DPPH radical scavenging activity.

Synthesis of Benzaldehyde, 2-hydr oxy,-[(2-hydroxyphenyl) methylene]hydrazone

1 g of Salicylaldehyde and 0.5mlof hydrazine hydrate was refluxed for 12.5 hours in 20 ml of ethanol and completion of reaction was monitored with TLC. Excess solvent was evaporated, dried at room temperature and recrystallized from alcohol. Experimental investigation of the structural details of the compound was carried out by X-ray diffraction analysis. Theoretical investigations on the structural parameters and properties of the hydrazone were carried out using Gaussian03 package[18].In computational procedure, energy minima is obtained by using B3LYP hybrid exchange- correlation functional[19] and the 6-31G(d,p) basis set. Route section used for geometry optimization is #B3LYP/6-31G(d,p) opt and the optimized geometry is used for further studies. At the optimized geometry, no imaginary frequency modes were obtained, so true minimum on the potential surface was found and the optimized geometry can be viewed by Chemcraft visualization program. Structural parameters of the hydrazone were obtained from the theoretical data.

Corrosion inhibition properties of the hydrazone were studied by calculating LUMO-HOMO energy gap, charge distribution ,electron affinity,(EA),ionization potential(IP),dipole moment(μ), hardness(η), softness(*S*), absolute electronegativity(χ),fractions of electrons transferred(ΔN) and back donation[20].The energies of HOMO and LUMO are related to the IP and EA respectively in framework of koopman's theorem. $IP=-E_{HOMO.}$ $EA=-E_{LUMO.}$ The χ and η are obtained by $\chi=(IP+EA)/2$, $\eta=(IP-EA)/2$

Electrophilicity index and back donation is given by $W=\mu^2/2\eta$, $\Delta E_{Backdonation}=\eta/4$

Interaction of electromagnetic radiation in some molecules shows NLO effect and it shows some alterations in phase frequency and amplitude from the incident field. The NLO property of the material can be theoretically calculated using mean polarizability (α_0),total static dipole moment(μ) and first order hyperpolarisability(β_0) with respect to x,y,z components. $\alpha_0=1/3(\alpha_{xx}+\alpha_{yy}+\alpha_{zz})$, $\beta_0=(\beta_x^2+\beta_y^2+\beta_z^2)^{1/2}$

$\beta_x^2=(\beta_{xxx}+\beta_{xyy}+\beta_{xzz})^2$,$\beta_y^2=(\beta_{yyy}+\beta_{yxx}+\beta_{yzz})^2$,$\beta_z^2=(\beta_{zzz}+\beta_{zxx}+\beta_{zyy})^2$.

By calculating using these equations sufficient details about the properties can be obtained [21]. Biological properties of the compound including its antioxidant activity and antimicrobial activity were studied. Antioxidant activity of the compound was analyzed using DPPH assay considering Ascorbic acid as the reference standard[22].The stock solution was prepared by dissolving ascorbic acid in distilled water(1 mg/1000µl).Solution of DPPH in methanol 60µM was prepared freshly before UV measurements.3.9 ml of this solution was mixed with 25,50,100 and 200 µg of samples. Control sample was prepared in same volume without any extract and radical scavenging can be calculated using the formula

% inhibition=(Absorbance of control at 0minute–Absorbance of test)/Absorbance of control at 15 minutes×100

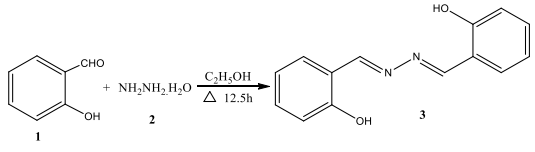
Antifungal and antibacterial studies were conducted using well diffusion method. Each bacterial strain was suspended in nutrient broth; each fungal strain was suspended in potato dextrose broth and incubated at 37°C. Nutrient Agar (NA) plates were seeded with 8 h broth culture of different bacteria. A 16 h broth culture of *Candida albicans, Aspergillus flavus* and *Fusarium sp* was used to seed potato dextrose agar (PDA) plates. In each of these plates, wells were cut out using sterile cork borer. Using sterilized dropping pipettes, different concentrations (25, 50, 75 and 100%) of samples were carefully added into the wells and allowed to diffuse at room temperature for 2 h. The plates were then incubated at 37°C for 18–24 h. Gentamycin (10 µg) and Clotrimazole (10 µg) were used as positive controls and the respective solvents as negative control. The antimicrobial activity was evaluated by measuring the diameter of inhibition zone.

RESULTS AND DISCUSSION

During the past several years, one of the active areas of organic chemistry is the study of systems containing two conjugated double bonds. Hence we felt that it would be worthwhile to explore the synthesis of Salicylaldehyde azine **from easily available starting materials.**

Synthesis of Benzaldehyde, 2-hydroxy-, [(2-hydroxyphenyl)methylene]hydrazone:-

It is obtained by refluxing salicylaldehyde with hydrazine hydrate. Accordingly Salicylaldehyde 1g (8.1967mmol) and hydrazine hydrate 0.5mL (8.1967mmol) were refluxed for 12.5 hours in 20 mL of ethanol. Completion of the reaction was monitored with TLC. After the completion of reaction the excess solvent was evaporated and the product obtained was dried at room temperature and recrystallized from alcohol. The physical properties of the synthesized compound benzaldehyde,2-hydroxy-,[(2-hydroxyphenyl)methylene] was studied and found that the compound obtained was yellow crystals having melting point at 115˚C.The reaction scheme as follows.



Scheme 1

IR (cm^{-1}) spectrum of **Benzaldehyde, 2-hydroxy-, [(2-hydroxyphenyl)methylene]hydrazone 3** showed absorption peak at 3396.79 cm^{-1}, 3371 cm^{-1}, are due to the presence of N-H stretching. Broad and weak band above 3000 cm^{-1}indicates OH stretching. A band at 1463 cm^{-1}, is due to the C-H bending. A band of medium intensity obtained at 1396 cm^{-1}, is due to OH bending. A medium band obtained at 1028 cm^{-1}, is due to C-N stretching .Overtones can be visualized indicating presence of aromatic groups.

To study the structural properties of the compound X-ray diffraction analysis was carried out. Bond angle, bond length and other structural details were obtained and were compared with the theoretical data. The geometry was optimized to minimum energy level and to obtain stable configuration.

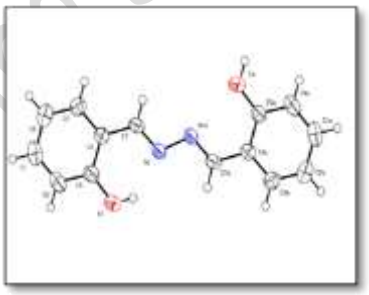


Figure 1. An ORTEP view of 3

E_{LUMO}	-1.5897	Absolute electronegativity χ	3.5921
E_{HOMO}	-5.5944	Hardness ?	2.002
ΔE	4.005	Softness S	0 .4995
EA	1.5897	Electrophilicity index *W*	1.2106
IP	5.5944	ΔE back donation	0.5005

Table 1.Crystal data and structure refinement of 3

From the x-ray diffraction studies the physical parameters and structural parameters like formula weight, temperature, wavelength, unit cell dimensions, volume, absorption coefficient and

crystal size are obtained.

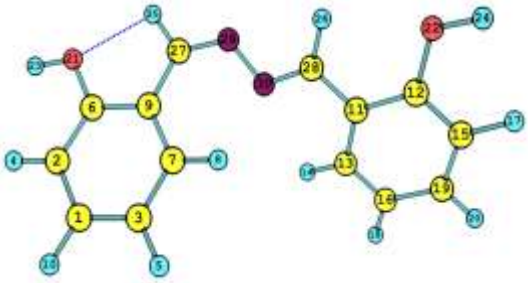


Figure 3. Optimized geometry of 3.

By comparing the data obtained from computational studies and with that from x-ray diffraction studies(Table 2), it is found that the values are comparable and approximately equal. Since the experimental and theoretical investigation lead to similar results, either of the two methods can be adopted for the investigation of compounds. Corrosion inhibition studies of the hydrazone was analysed using theoretical calculations.

Table 3.optimised geometrical parameters of 3

Empirical formula	C14 H12 N2 O2					
Formula weight	240.24					
Temperature	296(2) K					
Wavelength	0.71073 A					
Unit cell dimensions	a/A° = 8.53	α = 90°.	b/A° = 6.31	β = 107.89°.	c/A° = 11.84	γ = 90°.
Volume	605.92(16) A^3					
Absorption coefficient	0.090 mm^{-1}					
Crystal size	0.30 x 0.20 x 0.20 mm					

From the tabulated data, it can be concluded that Benzaldehyde,2-hydroxy-,[(2-hydroxyphenyl) methylene]hydrazone can be used as a good corrosion inhibitor. Here higher HOMO energy end lower LUMO energy indicates that it can easily offer electrons to unoccupied 'd'orbital and can easily accept electrons from metal surface respectively. It is experimentally proven LUMO-HOMO energy gap of thiosemicarbazide is 8.981 and shows high % of inhibition efficiency. Thus this hydrazone shows ΔE value of 4.005 indicates that it is a very good corrosion inhibitor. Bulk metals are chemically softest metals and the compounds with high **S** value are good inhibitors. Electrophilicity is the measure of maximal electron flow between donor and acceptor. Here the value is high and thus it acts as a good inhibitor. This compound shows high value of dipole moment and it indicates there is greater adsorption between chemical compound and metal surface. An electronic back donation process occurs governing the interaction between the metal surface and inhibitor molecule according to simple charge transfer model for donation and back donation of charges. From the above all data, it is obvious that the compound is a good corrosion inhibitor.

DPPH radical scavenging activity

The analysis was conducted at 515 nm and found that optical density of the sample decreases as the concentration increases. The percentage of inhibition increased about three fold when the concentration increased eight fold. A very small amount of the sample is required for high percentage of inhibition. Ascorbic acid shows high percentage of inhibition while sample require more concentration but still in micro quantities. Percentage of inhibition of sample was found 15.42% even by taking 200µg of sample and the property can be increased by taking changing concentration. Ascorbic acid shows 79.61% of inhibition by considering 25 µg of sample. Comparing the percentage of inhibition of standard and sample, it is found that the diazine compound is not a very good antioxidant but still shows antioxidant property to a certain extent.

Antimicrobial screening

In vitro screening of the synthesized compound was analysed using well diffusion method. The activity of the compound against gram positive bacterial strains *Staphylococcus aureus, Bacillus cereus, Micrococcus luteus* and gram negative bacterial strains *Escherichia coli, Pseudomonas aeruginosa* were analysed. Values expressed as are Mean ± SD (n= 3).From the data, the antibacterial property of compound can be analysed and shows good inhibition and inhibition increases as the concentration increases. Thus in future it may be used as a good antibacterial agent. Antifungal activity of the hydrazone was analyzed against fungus *Candida albicans,* The compound shows activity against the fungus *Candida albicans.*.Its antifungal properties increases as the concentration increases and can be used as a useful antifungal compound.

Non linear optical calculations

First hyperpolarisability is a measure of the nonlinear optical activity of any molecular system and is associated with intramolecular charge transfer resulting from electron transfer in a conjugated system from electron donor to electron

acceptor groups within a molecule. Then we studied the nonlinear optical properties of the synthesised compound. The dipole moment, polarizability and hyperpolarisability of the synthesized compounds were calculated. The results obtained from the calculations were tabulated and the values were compared with that of urea ($0.11x10^{-30}$esu)[23] , since it is one of the molecules used in the study of the NLO properties of the molecules. And the values obtained for urea was used as the threshold value for the compounds. Gaussian outputs are reported in atomic units, so the calculated values were converted to esu [α (1au= $0.1482x10^{-24}$ esu) β (1au=$8.639x10^{-33}$esu)].

μ_{total}	α_{total} esu	β_{total} esu
2.2016	-12.9982 X 10^{-24}	0.4703 X 10^{-30}

β_x^2	β_y^2	β_z^2
623.8705	666.564	1672.884

It was found that Benzaldehyde, 2-hydr oxy,-[(2-hydroxyphenyl) methylene]hydrazone **3** possess hyperpolarisibility approximately **4** times greater than that of urea.

CONCLUSION

Benzaldehyde, 2-hydroxy,-[(2-hydroxyphenyl) methylene]hydrazone was synthesized and its structural parameters were compared experimentally and theoretically. The second order hyperpolarisability and thus nonlinear optical properties of the compound was calculated using *ab initio* and density functional theory (DFT). Results obtained were compared with that of the urea. Corrosion inhibition properties of the compound were analysed theoretically. An antimicrobial and antioxidant property of the compound was analysed. The compound showed good antimicrobial character. Non linear optical property was analysed from its second order hyperpolarisability and compared with that of standard urea. The compound exhibits high nonlinear optical character thus can be used as an OLED material in future.

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Table 2. Comparison of theoretical & experimental values of bond length, bond angle of atom labelling according to the figure 3.

Atom No.	Theoret.Value	Exptal value	Angle between	Theoret. value	Exptal value
C1-C6	1.393	1.362	C_6-C_1-H_1	120.4	119.7
C1-C2	1.395	1.385	C_2-C_1-H_1	120.5	119.7
C1-H1	1.086	0.93	C_3-C_2-C_1	119.8	119.46
C2-C3	1.392	1.375	C_3-C_2-H_2	119.9	120.3
C2-H2	1.085	0.93	C_1-C_2-H_2	120.3	120.3
C3-C4	1.409	1.404	C_2-C_3-C_4	121.6	121.18
C3-H3	1.081	0.93	C_2-C_3-H_3	120.1	119.4
C4-C5	1.418	1.404	C_4-C_3-H_3	118.2	119.4
C4-C7	1.468	1.453	C_3-C_4-C_5	117.4	118.54
C5-O1	1.367	1.349	C_3-C_4-C_7	124.9	119.69
C5-C6	1.396	1.391	C_5-C_4-C_7	117.7	121.77
C6-H6	1.088	0.93	O_1-C_5-C_6	121.2	118.81
C7-N1	1.292	1.278	O_1-C_5-C_4	117.8	121.74
C7-H7	1.087	0.93	C_6-C_5-C_4	121	119.44
N1-N1	1.381	1.398	C_1-C_6-C_5	120.1	120.79
			C_1-C_6-H_6	120.4	119.6
			C_5-C_6-H_6	119.5	119.6
			C_6-C_1-C_2	120	120.58
			N_1-C_7-C_4	113.2	121.14
			C_4-C_7-H_7	114.7	119.4

Table 4 Antioxidant activity of compound 3

Sample	Concn (µg)	OD at 515nm	% of Inhibition
Control at zero minute	-	1.059	
Control at 15 minute	-	1.05	
Benzaldehyde, 2-hydroxy-, [(2-hydroxyphenyl)methylene]hydrazone	25	1.008	4.85
	50	0.969	8.57
	100	0.925	12.76
	200	0.897	15.42
Standard	-	1.059	-
Control at zero minute			
Control at 15 minute	-	1.05	-
Ascorbic acid (standard)	3	0.906	14.57
	6.25	0.761	28.38
	12.5	0.564	47.14
	25	0.223	79.61

Table 5. Antimicrobial activity of the compound 3

Concentration %	Zone of inhibition(mm)					
	S. a	*B. c*	*M. l*	*E. c*	*P. a*	*C.a*
25	-	10.0 ± 0.0	11.5 ±0.71	-	10.0 ± 0.0	10.5 ± 0.71
50	10.0 ± 0.0	10.0 ± 0.0	12.5 ±0.71	-	10.0 ± 0.0	11.0 ± 0.0
75	11.0 ± 0.0	10.5 ±0.71	13.5 ±0.71	10.0 ± 0.0	10.5 ±0.71	11.5 ± 0.71
100	12.5 ±0.71	13.0 ± 0.0	17.5 ±0.71	11.0 ±1.41	11.0 ± 0.0	11.5 ± 0.71