Synthesis Structural Study and Spectroscopic Characterization of Azo Compound Derived from Mercaptothiadiazole and Methoxybenzaldehyde

Ghalib A. Atiya, Nada J. Khadm, Abd-Karim Fadhil Ali, Waseela Abdul Redha Abdul Razaq, Abdulqadier Hussian Neamal and Ibtsiam Khalil Alwan
Department of Chemistry, College of Education for Pure Sciences, University of Diyala, 32001 Baqubah, Diyala, Iraq
Nada.Jaffar.Khadm@uodiyala.edu.iq

Keywords: Azoaldehyde , O-Vanillin , IR, Gussian, Vibration, Bending.

Abstract: The vibrational and electronic properties of 2-hydroxy-5-((5-mercapto-1,3,4-thiadiazol-2-yl)diazenyl)-3-methoxy benzaldehyde were theoretically studied in the present paper by carrying out quantum chemical calculations. Vibrational wavenumbers and their respective assignments were computed at the Hartree-Fock and DFT/B3LYP levels with the 6-311++G(d,p) basis set using Gaussian03 software. The theoretical IR and Raman spectra were calculated and compared with the experimental IR spectrum, which showed good agreement. The vibrational assignments were made by PEG analysis to ensure proper characterization of the modes. Theoretical IR and Raman intensities have also been calculated to provide further spectroscopic insight. Frontier molecular orbitals have been estimated to obtain an in-depth analysis of the electronic structure. (FMOs) were analyzed. The HOMO and LUMO energies have been computed thereby giving HOMO–LUMO energy which, in turn, gives insight into the reactivity and stability of the molecule. Also, Mulliken charges and Molecular Electrostatic Potential (MEP) analysis were computed for charge transfer character and electrostatic interaction within the molecule, respectively. This study is also supplemented by Natural Bond Orbital (NBO) analysis of charges to investigate intramolecular and intermolecular charge delocalization effects on their mean stabilization interactions in the system. Thus, it can parse from the electronic and vibrational features that it can be useful in spectroscopic applications further in molecular design. The paper would, therefore, reveal the power that computational chemistry brings in the prediction and interpretation of vibrational and electronic properties that would go a long way to unravel compounds structurally similar to the heterocyclic compound.

1 INTRODUCTION

Azo compounds comprise a vital group of organic compounds characterized by their containing the azo functional grouping (-N=N-), - that is, the double bonding of two nitrogen atoms bonded to some organic groupings (R-N=N-R'). Powerful coloration and abundantly varied chemical properties account for their wide use in the manufacture of dyes, chemical indicators, and pharmaceuticals [1], [2]. The most popular synthetic dyes for coloring textiles, plastics, and inks are the azo dyes on account of their bright colors and stability. Among them are methyl orange, acid red, and direct blue [3], [4]. Among other azo compounds are sulfa drugs, an important class of drugs because of its antibacterial activity [5]-[11]. the five-membered heterocyclic compound called thiadia zole contains two nitrogen and one sulfur atoms. It emanates from the union of a benzene ring and a heterocyclic group of sulfur atoms and nitrogen atoms. In medicinal chemistry, the thiadiazole and its derivatives are interesting because they usually present many other biological activities, including antimicrobial, antifungal, anti-inflammatory, and antitumor properties [12], [13]. Different thiadiazole derivatives, like 1,3,4-thiadiazole, have been studied for possible use in the field of drug development and are also used to synthesize agrochemicals, which include herbicides and pesticides [14]-[16]. Nonlinear chemical phenomena occur as a result of the interaction of applied electromagnetic radiation with different molecular species and new responses to electromagnetics are generated. In these systems, the induced molecular polarization does not scale linearly with the intensity of the incident field, leading to modifications at wavenumber, phase, and other related properties. Efficient organic molecules

can control photonic signals, which therefore play a role dynamically in optical communications, optical computing, and dynamic image processing. Phenyl substitution can enhance molecular hyperpolarizability-an effect said to be not obvious in most cases. Most of the organic molecules are comprised of conjugated π electrons have large molecular first hyperpolarizabilities and are large values of molecular first studied by using vibrational spectroscopy [17]-[19]. The IR spectrum is currently simulated by some ab initio quantum mechanical method, and these are the simulations that will help perform normal coordinate analysis. There is no place for contemporary vibrational spectroscopy without such simulations; these are necessary tools. The wavenumbers and hyperpolarizability of the title compound are the subjects of theoretical calculations in the present work, which are also compared with experimental results.

2 EXPERIMENTAL

2.1 Chemicals

All chemicals were supplied by Fluka, Merck, and Aldrich Chemicals Co. and used as received.

2.2 The Techniques

FTIR spectra were recorded using KBr pellets on a Nexus 400 Shimadzu FT-IR Spectrometer with a spectral resolution of 16 cm^{-1}.

2.3 Synthesis of (E)-2-Hydroxy-5-((5-Mercapto-1,3,4-Thiadiazol-2-yl) Diazenyl)-3- Methoxy Benzaldehyde

Compound 2-amino-5-marcapto-1,3,4-thiadiazole (0.44 g, 0.0017 mol) was dissolved by heating and stirring in 8 mL of 85% phosphoric acid. The solution was cooled to 0 ºC in an ice bath, and then concentrated nitric acid 4 mL and a solution of sodium nitrite (0.10 g, 0.0017mol) in water 2 mL The mixture was stirred and allowed to stand at below 5oC for 10 minutes. Thereafter, a solution of o-vanillin (0.15g, 0.0017mol) in water (0.5mL) was added dropwise with stirring. The brown solid was filtered, washed with several portions of water, and then taken up in 30 mL of 10% hydroxyl soduim solution. The solution was filtered, and the crude product precipitated during neutralization with 10% hydrochloricacid [20], then filtered and washed with water several times, and recrystallized from ethanol to give 78% yield, m.p = 60-62oC.

Computational details were carried out with the Gaussian program G09 using the HF/6-31G* and B3LYP/6-31G* basis sets for predicting the molecular structure and wave numbers. The molecular geometry was fully optimized using Berny's optimization algorithm including redundant internal coordinates. Harmonic vibrational wavenumbers were calculated using the analytic second derivatives to confirm the convergence to the minimum on the potential surface. Also, the wave number is associated with known systematic errors due to the negligence of electron correlation. The W values computed at the Hartree-Fock and DFT level contain a scaling factor value of Hartree-Fock level 0.8929; therefore, the scaling factor value is taken as the counterpart for HF/6-31G*. The Parameters corresponding to optimized geometry imaginary wave number on the calculated (Fig. 1).

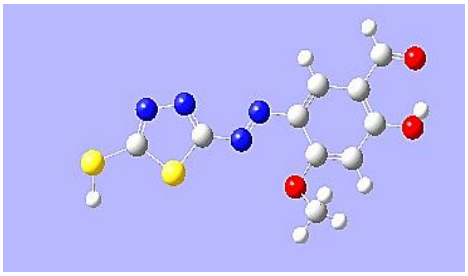

Figure 1: Optimization of 2-hydroxy-5-((5-mercapto-1,3,4-thiadiazol-2- yl)diazenyl)-3- Methoxy benzaldehyde.

3 RESULTS AND DISCUSSION

The broad band seen in the spectrum at 3450 cm-1 is of very high frequency, indicating a strong stretching vibration of the hydroxyl (-OH) group. The absorption intensity (324.66) is high, meaning this mode is clearly visible in the infrared spectrum. The aromatic compound, this vibration is associated with aromatic ring stretching. The absorption intensity (20.76) is much lower than the previous one, meaning the IR absorption is weaker. Raman activity (85.38) is medium (see Table 1, mode 1). It was experimentally measured at 3355 cm^{-1}. This frequency corresponds to the stretching vibration of the thiol (-SH) group. The absorption intensity (10.57) is relatively low. Raman activity (183.50) is high, meaning this group may appear more prominently in the Raman spectrum. It was

experimentally measured at 2882 cm^{-1} (see Table 1, mode 7).

The range from 420-575 cm^{-1} includes eight fundamental vibration modes, all of which are structural. It is noted that the methyl group is observed at 497 cm^{-1} is weak. The 1600-1800 cm^{-1} region exhibits a strong absorption band centered at 1666 cm^{-1}, which corresponds to multiple C-H bending vibrations appearing at 1501 cm^{-1} (see Table 2, mode 16). Additionally, a C=O stretching vibration is observed, attributed to an acetate 1666 cm^{-1} (see Table 2, mode 13), which corresponds to the C-H vibration, is weak due to a polarization of 9.3°. and has merged under the previously mentioned strong band. The frequency 1672 cm^{-1} corresponds to the out-of-plane C-H vibrational motion. The frequency 1677 cm^{-1} is attributed to the hydrazine group functional group at the same spectral region (see Table 2, mode 15). The absorption band at 1708 cm^{-1} is attributed to the skeletal vibrational modes of the aromatic ring and appears as an envelope-shaped band in the infrared (IR) spectrum. This feature may result from conjugation effects or electronic interactions within the aromatic system, leading to slight shifts or broadening in the absorption profile (Fig, 2).

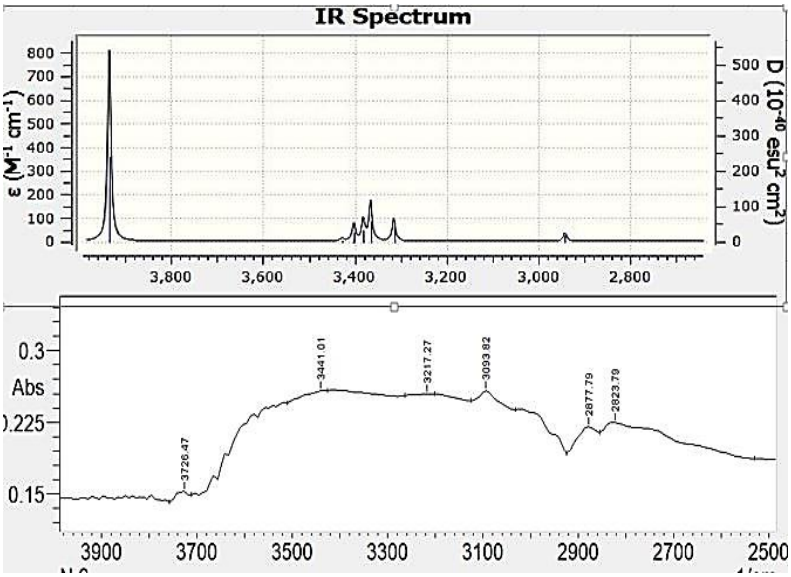

Figure 2: IR and predicted spectra a) and b) for the region 2700 cm^{-1} to 4000 cm^{-1} respectively.

Table 1: Calculated vibrational wave numbers, measured band positions and assignments of hydroxy and aromatic ring using (HF/6-31G*-B3LYP/6-31G*).

Mode	Predicted frequency υ cm^{-1}	Intensity	Raman activity	Frequency υ cm^{-1}	IR intensity	Raman activity	Found υ cm^{-1}	Assignments
1	3934.32	324.66	234.66	3831	57.83	147.93		υO-H
2	3428.01	3.58	75.76	3828	56.97	145.39	3401b	υO-H
3	3405.18	0.425	61.499	3358	11.25	152.57		
4	3402.55	20.76	85.38	3353	17.19	198.99	3093w	υph*[22]
5	3381.37	26.31	37.71	3346	20.88	112.94	3024w	υph
6	3365.65	49.19	112.87	3340	21.01	60.75		
7	2942.14	10.57	183.50	2880	45.01	69.52	2823	υS-H*[21]

υ refer to stretching vibration, υph* refer to aromatic C-H stretching, υS-H* refer to S-H bond stretching

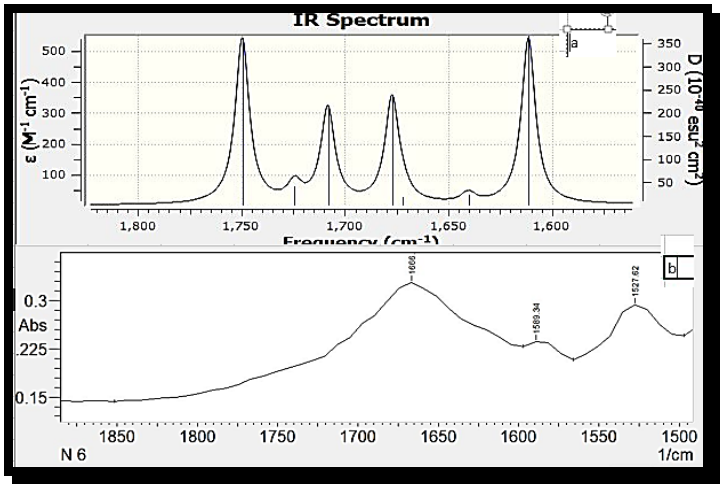

Figure 3: IR and predicted spectra a) and b) for the region 1800 cm^{-1} to 1500 cm^{-1} respectively.

Table 2: Calculated vibrational wave numbers, band positions and assignments of carbonyl and aromatic ring (HF/6-31G*-B3LYP/6-31G*).

	Predicted frequency, υ cm^{-1}	Intensity	Raman activity	υ cm^{-1}	Intensity	Raman	υ cm^{-1}	Assignments
9	1749.77	155.59	5.73	1705.71	72.99	7.88		
10	1724.65	17.68	51.38	1765.98	66.90	2.15		
11	1708.74	89.63	135.22	1700.88	23.55	8.21	1527m	υc=c[25]
12	1677.33	98.63	98.29	1695.44	77.99	10.70		
13	1672.88	7.15	44.77	1665.88	45.99	19.79	1666s	υC=O[26]
14	1640.45	9.37	18,81	1635.06	67.88	2.17		
15	1611.14	156.72	30.06	1607.67	34.87	67.90	1598s	υN=N[27]
16	1501.99	80.53	0.27	1494.77	45.88	18.30	1450s	υc=c

Methylen Group Vibrations: Symmetrical and asymmetrical bending vibrations of C-H bonds in a methylen group are discussed The asymmetrical deformations are expected in the range of 1400–1463 cm^{-1} with calculated values at 1463 and 1422 cm^{-1} (see Table 3, mode 17 and 18). Symmetric deformations are expected around 1391 ±25 cm^{-1} [21]. HF (Hartree-Fock) calculations predict the δasCH2 mode at 1463 cm^{-1}. Observed IR bands at 1572, 1473, and 1440 cm^{-1} are assigned to deformation bands of the methylen group (see Table 3) [22]. Primary Aromatic Amines: These are chemical compounds that contain an amino group (-NH_2) directly attached to an aromatic ring (such as benzene). Primary aromatic amines are significant in organic chemistry and are used in the synthesis of various organic compounds, including dyes and pharmaceuticals [23], [24]. Infrared (IR) spectroscopy is an analytical technique used to study chemical interactions and molecular structures by measuring the absorption of infrared radiation Each chemical bond in a molecule has a characteristic vibrational frequency that can be measured using IR spectroscopy. Carbon-Nitrogen Stretching Vibration (C-N Stretch): Primary aromatic amines absorb IR at 1260 ± 60 cm^{-1} in the carbon-nitrogen bond within the aromatic ring (Fig. 3). It is assigned to the stretching vibration of the C-N bond. (C-N stretch). Experimental and Theoretical Results: In experimental observations, absorption peaks were noted at wavenumbers 1277, and 1205 cm^{-1} (see Table 3, mode 23 and 25). Theoretical calculations, such as quantum chemical computations, predicted absorption peaks at about 1297, 1296, and 1299 cm^{-1} [26]. Significance of These Findings: Such results can be very imperative in identifying the presence of aromatic amines as chemical samples

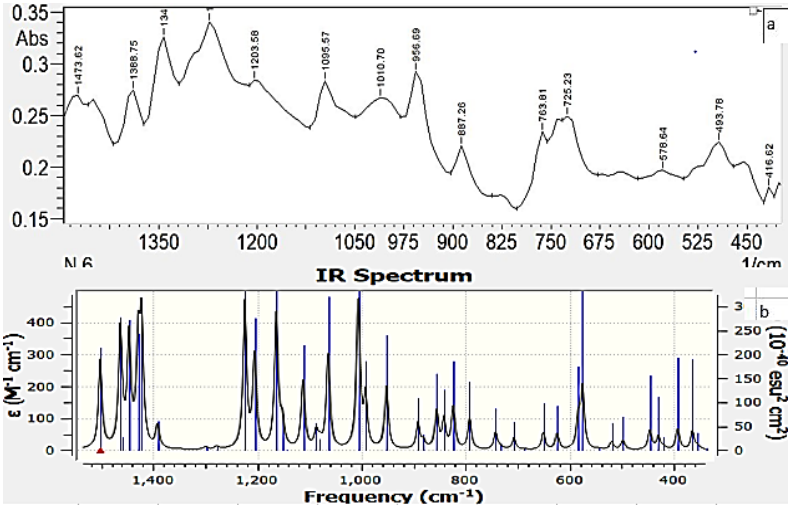

Figure 4: IR and predicted spectra a) and b) for the region 400 cm^{-1} to 1400 cm^{-1} respectively.

Table 3: Calculated vibrational waves numbers and measured bands positions and assignments of carbonyl and aromatic ring using (HF/6-31G*-B3LYP/6-31G*).

Mode	υ cm^{-1}	Intensity	Raman activity	υ cm^{-1}	Intensity	Raman activity	υ cm^{-1}	Assignments
17	1463.42	87.007	3.3	1455	84.03	14.7	1473m	υ-C-C-H [31]
18	1459	2.28	19.48	1450	72.60	3.92	1440m	υC-C -H
19	1428	20.98	11.97	1424	6.03	38.88		υC-O [32]
20	1422	2.83	53.40	1405	30.55	66.19		
21	1391	83.14	99.39	1371	14.26	81.99	1388s	υC-O-H [33]
22	1298	132.88	50.48	1270	16.63	66.99	1342s	υC-O [341]
23	1277	87.77	396.388	1260	21.90	99.8		
24	1223	101.17	16.55	1218	16.63	82.88		Pph
25	1205	13.89	12.87	1205	14.63	89.90		Pph
26	1163	80.007	101.14	1150	72.88	15.99	1095w	
27	1151	156.78	98.28	1164	3.88	55.90		
28	1142	155.98	89.77	1130	85.77	88.90		
29	1111	69.89	51.99	1105	12.90	90.88		
30	1078	80.53	89.28	1060	55.27	0.78		
31	1079	22..005	69.52	1056	16.88	19.30		
32	1063	133.88	183.77	1078	15.98	14.88		
33	1006	57.08	120.61	1010	30.81	19.45	1010s	pph
34	992	26.55	53.16	982	14.16	16.70		
35	951	34.31	54.93	978	14.76	11.81	956m	pph
36	891	121.82	16.55	887	15.78	1.98		
37	880	22.05	396.38	874	67.99	30.90	887s	pph
38	855	61.36	18.99	840	16.97	89.89		
39	841	85.45	53.16	824	21.33	76.90		
40	823	46.99	46.77	876	76.90	65.09		
41	792	34.31	55.90	706	09.99	98.90	763m	pph
42	742	28.9	2.8	734	0.45	0.87		

In turn, the above information may find general applicability in pharmaceutical analysis and characterization of chemical materials. Bending vibrational band of the hydroxyl group (C-OH), normally in the 1220-1440 cm^{-1} region, is characterized by composite bands of different appearances, arising from diversity. This is assigned based on the band appearing at 1370 cm^{-1}, and thus the C–O–H bending modes in this region are highly sensitive to changes in the chemical environment mainly through the variations in the hydrogen bonding and neighboring groups [27]. The presence of the band at 1370 cm^{-1} can be associated with bending vibrations of the hydroxyl group and sometimes could change its intensity or position due to interaction between molecules, which could include tautomeric equilibria common in azo-phenolic systems [28], [29]. If one were looking at an IR spectrum of a compound, though also useful to check the region 3200-3600 cm^{-1}, where generally the stretching vibrations of an O–H group appear, such information further confirms the hydroxyl group in this compound. The stretching vibration of C–S generally may vary between 600-750 cm^{-1} depending on molecular structure and chemical environment. The intensity of the band at 727 cm^{-1} suggests that the bond has moderate dipole, making the absorption band neither too strong nor too weak. In-plane bending vibrations of C-H bonds are usually seen above 1000 cm^{-1}. They appear in the IR spectrum at 1111, 1162, and 1219 cm-1 in this case (Fig. 4 and Table 3, mode 24, 26, 29). The such-calculated frequencies are 1113, 1171, and 1209 cm^{-1} respectively. Out-of-Plane Deformations CH Modes: Generally, out-of-plane deformations of C-H bonds, CH, are observed within the region 1000-700 cm Typically of the out-of-plane deformations, those with a higher wavenumber such as those at lower wavenumbers are always of weak intensity than the low wavenumber ones. The IR spectrum shows these CH modes at 956, 900, 887, and 858 cm^{-1} (see Table 3, mode 35 - 38) [30]. Theoretically, these modes are calculated to be around 895 ± 60 cm^{-1}) [31]-[34].

4 CONCLUSIONS

This study presents a comprehensive analysis of the vibrational properties and geometry of 2-hydroxy-5-((5-mercapto-1,3,4-thiadiazol-2-yl)diazenyl)-3-Methoxy benzaldehyde -. The investigation employed both theoretical and experimental methodologies to provide a thorough understanding of the compound's IR spectrum. It was a quantum mechanical description of the geometry and vibrational wave numbers. Within the laser Raman spectral wavenumbers, calculated values kept relatively close to the experimental values, thereby confirming the accuracy of the theoretical model. Although minor discrepancies came up between the theoretical and experimental results, those discrepancies are usually attributed to the intrinsic anharmonicity of molecular vibrations and the well-known property of overestimation of the force constants at the equilibrium geometry by quantum mechanical methods.

It can be a very important hyperpolarizability value of the compound for applications in nonlinear optics and as a potential ligand for the synthesis of biologically active metal complexes [35], [36], [37]. This fact really gives us only that 2-hydroxy-5-((5-mercapto-1,3,4-thiadiazol-2-yl) diazenyl)-3-Methoxy benzaldehyde is an easy shortcut to future works tabling the nonlinear optical properties. To sum up, the present study merges theoretical and experimental analyses in the explanation of vibrational and geometric properties of the titled compound. The observed agreement between these two methodologies further compounds the promises of the compound in the prospects for more explorations in the field of nonlinear optics.

REFERENCES

[1] V.M. Dembitsky, T.A. Gloriozova and V.V. Poroikov, "Pharmacological and predicted activities of natural azo compounds," Natural Products and Bioprospecting, vol. 7, pp. 151-169, 2017.

[2] A.Z. El-Sonbati, G.G. Mohamed, A.A. El-Bindary, W.M.I. Hassan and A.K. Elkholy, "Geometrical structure, molecular docking, potentiometric and thermodynamic studies of 3-aminophenol azodye and its metal complexes," Journal of Molecular Liquids, vol. 209, pp. 625-634, 2015.

[3] A.A. El-Bindary, M.A. Hussein and R.A. El-Boz, "Molecular docking, theoretical calculations and potentiometric studies of some azo phenols," Journal of Molecular Liquids, vol. 211, pp. 256-267, 2015.

[4] E.M. Zayed, A.M. Hindy and G.G. Mohamed, "Molecular structure, molecular docking, thermal, spectroscopic and biological activity studies of bis Schiff base ligand and its metal complexes," Applied Organometallic Chemistry, vol. 32, no. 1, p. e3952, 2018.

[5] H.A. Hasan, W.M. Alwan, R.M. Ahmed and E.I. Yousif, "Synthesis and characterization of some mixed-ligand complexes containing azo dye and 1,10-phenanthroline with (CoII, ZnII, CdII and HgII ions)," Ibn Al-Haitham Journal for Pure & Applied Sciences, vol. 28, no. 3, pp. 187-203, 2015.

[6] T.R. Arun and N. Raman, "Antimicrobial efficacy of phenanthrenequinone based Schiff base complexes incorporating methionine amino acid: Structural elucidation and in vitro bio assay," Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, vol. 127, pp. 292-302, 2014.

[7] J. Bell, J.J. Plumb, C.A. Buckley and D.C. Stuckey, "Treatment and decolorization of dyes in an anaerobic baffled reactor," Journal of Environmental Engineering, vol. 126, no. 11, pp. 1026-1032, 2000.

[8] K.T. Chung, "Azo dyes and human health: A review," Journal of Environmental Science and Health, Part C, vol. 34, no. 4, pp. 233-261, 2016.

[9] S. Benkhaya, S. M'rabet and A. El Harfi, "Classifications, properties, recent synthesis and applications of azo dyes," Heliyon, vol. 6, no. 1, 2020.

[10] A.A. Ismail and S.M. Lateef, "Synthesis of novel complexes of VO(II), Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Pt(IV) derived from Schiff's base of pyridoxal and 2-amino-4-nitrophenol and study of their biological activities," Ibn Al-Haitham Journal for Pure and Applied Sciences, vol. 36, no. 2, pp. 259-275, 2023.

[11] B.K. Mohammed and E.I. Yousif, "Synthesis, structural characterisation and biological activity of new metal complexes derived from semicarbazone ligand," Revis Bionatur, vol. 8, no. 2, p. 14, 2023.

[12] A. Tupys, J. Kalembkiewicz, Y. Ostapiuk, V. Matiichuk, O. Tymoshuk, E. Woźnicka and Ł. Byczyński, "Synthesis, structural characterization and thermal studies of a novel reagent 1-[(5-benzyl-1,3-thiazol-2-yl) diazenyl] naphthalene-2-ol," Journal of Thermal Analysis and Calorimetry, vol. 127, pp. 2233-2242, 2017.

[13] A. Penchev, D. Simov and N. Gadjev, "Diazotization of 2-amino-6-methoxybenzothiazole at elevated temperature," Dyes and Pigments, vol. 16, no. 1, pp. 77-81, 1991.

[14] G.B. Bagihalli, P.G. Avaji, S.A. Patil and P.S. Badami, "Synthesis, spectral characterization, in vitro antibacterial, antifungal and cytotoxic activities of Co(II), Ni(II) and Cu(II) complexes with 1,2,4-triazole Schiff bases," European Journal of Medicinal Chemistry, vol. 43, no. 12, pp. 2639-2649, 2008.

[15] M.J. Al-Jeboori, A.T. Numan and D.J. Ahmed, "Synthesis and Characterisation of Novel Cobalt(II), Copper(II) and Mercury(II) Complexes of Poly Vinyl Urethanised Oxime," Ibn Al-Haitham Journal for Pure and Applied Sciences, vol. 21, no. 2, pp. 89-101, 2017.

[16] S.A. Hussain and M.J. Al-Jeboori, "New metal complexes derived from Mannich-base ligand; Synthesis, spectral characterisation and biological activity," Journal of Global Pharma Technology, vol. 11, no. 2, pp. 548-560, 2019.

[17] E. Ramachandran, V. Gandin, R. Bertani, P. Sgarbossa, K. Natarajan, N.S. Bhuvanesh, A. Venzo, A. Zoleo, A. Glisenti, A. Dolmella and A. Albinati, "Synthesis, characterization and cytotoxic activity of novel copper(II) complexes with aroylhydrazone derivatives of 2-oxo-1,2-dihydrobenzo[h]quinoline-3-carbaldehyde," Journal of Inorganic Biochemistry, vol. 182, pp. 18-28, 2018.

[18] A.B.P. Lever, Inorganic Electronic Spectroscopy, 2nd ed., 1984.

[19] R. Ramesh and S. Maheswaran, "Synthesis, spectra, dioxygen affinity and antifungal activity of Ru(III) Schiff base complexes," Journal of Inorganic Biochemistry, vol. 96, pp. 457-462, 2003.

[20] N. Aggarwal, R. Kumar, P. Dureja and D.S. Rawat, "Schiff bases as potential fungicides and nitrification inhibitors," Journal of Agricultural and Food Chemistry, vol. 57, no. 18, pp. 8520-8525, 2009.

[21] B.K. Al-Rubaye, M.J. Al-Jeboori and H. Potgieter, "Metal Complexes of Multidentate N2S2 Heterocyclic Schiff-base Ligands; Formation, Structural Characterisation and Biological Activity," Journal of Physics: Conference Series, vol. 1879, no. 2, p. 022074, 2021.

[22] C. Liu, W. Zhang and G. Cai, "Synthesis, crystal structures and catalytic activities of two copper coordination compounds bearing an N,N'-dibenzylethylenediamine ligand," Crystals, vol. 10, no. 6, p. 528, 2020.

[23] A.C. Olivieri, R.B. Wilson, I.C. Paul and D.Y. Curtin, "Carbon-13 NMR and x-ray structure determination of 1-(arylazo)-2-naphthols. Intramolecular proton transfer between nitrogen and oxygen atoms in the solid state," Journal of the American Chemical Society, vol. 111, no. 15, pp. 5525-5532, 1989.

[24] M.J. Al-Jeboori, E.I. Abdulkarim and S. Attia, "Synthesis and Characterization of Novel Ligand Type N2O2 and its Complexes with Cu(II), Co(II), Ni(II), Zn(II), and Cd(II) ions," Ibn Al-Haitham Journal for Pure and Applied Sciences, vol. 18, no. 2, pp. 51-67, 2015.

[25] H.J. Abaas and M.J. Al-Jeboori, "New dimeric complexes with semicarbazone Mannich-based ligand; formation, structural investigation and biological activity," Rev. Bionatura, vol. 8, no. 2, p. 15, 2023.

[26] J. Conradie, M.M. Conradie, Z. Mtshali, D. van der Westhuizen, K.M. Tawfiq, M.J. Al-Jeboori, S.J. Coles, C. Wilson and J.H. Potgieter, "Synthesis, characterisation and electrochemistry of eight Fe coordination compounds containing substituted 2-(1-(4-R-phenyl-1H-1,2,3-triazol-4-yl)pyridine ligands, R = CH3, OCH3, COOH, F, Cl, CN, H and CF3," Inorg. Chim. Acta, vol. 484, pp. 375-385, 2019.

[27] P.M. Tolstoy, J. Guo, B. Koeppe, N.S. Golubev, G.S. Denisov, S.N. Smirnov and H.H. Limbach, "Geometries and tautomerism of OHN hydrogen bonds in aprotic solution probed by H/D isotope effects on 13C NMR chemical shifts," The Journal of Physical Chemistry A, vol. 114, no. 40, pp. 10775-10782, 2010.

[28] L. Guasch, W. Yapamudiyansel, M.L. Peach, J.A. Kelley, J.J. Barchi Jr. and M.C. Nicklaus, "Experimental and chemoinformatics study of tautomerism in a database of commercially available screening samples," Journal of Chemical Information and Modeling, vol. 56, no. 11, pp. 2149-2161, 2016.

[29] L. Racane, Z. Mihalić, H. Cerić, J. Popović and V. Tralić-Kulenović, "Synthesis, structure and tautomerism of two benzothiazolyl azo derivatives of 2-naphthol: A crystallographic, NMR and computational study," Dyes and Pigments, vol. 96, no. 3, pp. 672-678, 2013.

[30] H. Kocaokutgen and E. Erdem, "Synthesis and spectral characterization of metal complexes of 1-(2-hydroxy-4-methylphenylazo)-2-naphthol," Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry, vol. 34, no. 10, pp. 1843-1853, 2004.

[31] K.Y. Law, I.W. Tarnawskyj and P.T. Lubberts, "Azo pigments and their intermediates: Effect of substitution on the diazotization and coupling reactions of o-hydroxyanilines," Dyes and Pigments, vol. 23, no. 4, pp. 243-254, 1993.

[32] A.J. Jarad, M.A. Dahi, T.H. Al-Noor, M.M. El Ajaily, S.R. Al-Ayash and A. Abdou, "Synthesis, spectral studies, DFT, biological evaluation, molecular docking and dyeing performance of 1-(4-((2-amino-5-methoxy) diazenyl) phenyl) ethanone complexes with some metallic ions," Journal of Molecular Structure, vol. 1287, p. 135703, 2023.

[33] E.J. Baron and S.M. Finegold, Diagnostic Microbiology, 8th ed., London: Mosby Company, 1990, pp. 53-62.

[34] S.A. Hussein and E.I. Yousif, "New mannich base (2R)-4-methyl-2-((S)(phenylamino)(p-tolyl)methyl)cyclohexan-1-one; synthesis and spectral characterisation," Journal of Physics: Conference Series, vol. 1, p. 012019, 1999.

[35] R.V. Singh, R. Dwivedi and S.C. Joshi, "Synthetic, magnetic, spectral, antimicrobial and antifertility studies of dioxomolybdenum(VI) unsymmetrical imine complexes having a N∩N donor system," Transition Metal Chemistry, vol. 29, no. 1, pp. 70-74, 2004.

[36] H.M. Salh and T.H. Al-Noor, "Preparation, structural characterization and biological activities of curcumin-metal(II)-L-3,4-dihydroxyphenylalanin (L-dopa) complexes," Ibn Al-Haitham Journal for Pure and Applied Sciences, vol. 36, no. 1, 2023.

[37] A.S.A.K.A. Rahman, N.J. Hussien, K.T. Abdullah, S.F.M. Yusof and E.I. Yousif, "Synthesis, characterization and antibacterial activity of some transition metal complexes of a new dioxime ligand," AIP Conference Proceedings, vol. 2593, p. 060001, 2023.