DOI: 10.32571/ijct.469000 **E-ISSN:2602-277X**

International Journal of Chemistry and Technology

http://dergipark.gov.tr/ijct

Research Article

Molecular structure of Zn (II) compound containing 8-hydroxyquinoline and 2-picoline ligands [I], theoretical HF and DFT studies [II]

Kani ARICI[1,*], Özkan GÜL[2]

ID on the last page

[1] *Department of Physics, Faculty of Sciences and Arts, Kilis 7 Aralık University, Kilis, Turkey*
[2] *Anatolian High School Tatvan / Bitlis, Turkey*

Received: 10 October 2018, Revised: 15 November 2018; Accepted: 16 November 2018

*Corresponding author e-mail: arici@kilis.edu.tr

Citation: Arici, K.; Gül, Ö. *Int. J. Chem. Technol.* **2018**, 2 (2), 141-152.

ABSTRACT

In this study, Zn (II) compound containing 8-hydroxyquinoline (L1:8-Hq) and 2-picoline (L2: 2P) ligands was prepared and its elemental analysis was recorded. Infrared spectra of the ligands and the compound were obtained. The structure of the prepared compound was determined approximately based on the spectroscopic and analytical results. The infrared vibration frequencies of the prepared compound were calculated theoretically employing the ab-initio Hartree-Fock (HF) and density functional theory (DFT) methods with 6-311G(dp) basis set. Finally, the vibrational frequency values of the compound obtained both experimentally and theoretically were compared in details. It was observed that all the experimental and theoretical results are in good agreement with the literature.

Keywords: 8-hydroxyquinoline, 2-picoline, HF, DFT.

8-hidroksikinolin ve 2-pikolin ligandları içeren Zn (II) bileşiğinin moleküler yapısı [I], teorik HF ve DFT çalışmaları [II]

ÖZ

Bu çalışmada, 8-hidroksikinolin (L1: 8-Hq) ve 2-pikolin (L2:2P) ligandlarını içeren Zn (II) bileşiği hazırlandı ve elemental analizi yapıldı. Ligandların ve bileşiklerin infrared spektrumları elde edildi. Hazırlanan bileşiğin yapısı yaklaşık olarak spektroskopik ve analitik sonuçlara dayanarak belirlendi. Hazırlanan bileşiğin titreşim frekansları teorik olarak 6-311G (dp) temel seti ile ab-initio Hartree-Fock (HF) ve yoğunluk fonksiyon teorisi (DFT) yöntemleri kullanılarak hesaplandı. Son olarak, bileşiğin deneysel ve teorik olarak elde edilen titreşim frekans değerleri detaylı olarak karşılaştırıldı. Tüm deneysel ve teorik sonuçların literatürle iyi bir uyum içinde olduğu gözlendi.

Anahtar Kelimeler: 8-hidroksikinolin, 2-pikolin, HF, DFT.

1. INTRODUCTION

8-hydroxyquinoline and its derivatives are known to have activities against bacteria, fungi and amoebic[1] and they also exhibit therapeutic properties.[2] When 8-Hq lose a proton, they acquire the ability to compound with transition metals.[3] Merrit and co-workers have investigated crystal structures of 8-Hq aqueous compounds.[4] Magee and co-workers have obtained infrared spectra of some bivalent and tervalent metal chelate compounds of 8-Hq and they have given some vibrational modes of 8-Hq.[5-7] Ohkaku and Nakamoto later Engelter and co-workers[8,9] have reported the infrared spectra of $M(8\text{-}Hq)_2(H_2O)_2$ [M = Mn, Co, Zn, Ni, Cu] compounds over the range 700-50 cm^{-1} and they have determined the metal-ligand vibrations. Yurdakul and Arıcı[10] have reported the IR spectra of the $M(8\text{-}HOq)_2X_2$ type complexes (where M=Zn, Co; X=CI, Br, I and 8-HOq=8-hydroxyquinoline) and they approximated the geometric structures of the compounds via ligand and metal vibration bands.

Picoline derivatives have hypolipidemic, antineoplastic and anti-inflammatory effects. They also show activity against glioblastoma and leukemia cells.[11] The Picoline derivatives prepared from aminopyridine derivatives have been shown to have cholesterol lowering properties, anticancer and anti-inflammatory agents.[12]

Numerous studies have been carried out on pyridines and metal compounds of the derivatives.

Mutton and Thornton[13] have reported the infrared spectra of $Zn(Py)_2X_2$ [X= CI, Br and I] compounds over the range 650-145 cm^{-1} and they have identified the metal-ligand and metal-halogen vibrations. Steffen and Palenik have determined the structure of the $Zn(Py)_2CI_2$ (Py: pyridine) compound as tetrahedral.[14] The crystal structure of $Cu(l)L_2$, (L = 2-methylpyridine or 2-picoline) have been determined by single-crystal X-ray diffraction methods.[15] Greenwood and Wade have prepared boron compounds with pyridine and piperidine.[16] Many authors have obtained transition metal compounds with mixed ligands and studied their properties. Shaker and co-workers[17] have obtained Fe(II), Co(II), Ni(II) and Cu(II) transition metal compounds with mixed 8-hydroxyquinoline and o-hydroxybenzylidene-1-phenyl-2,3-dimethyl-4-amino-3-pyrazolin-5-on ligands. They have used their infrared and UV-Vis spectroscopy to characterize the materials. In 2013, Kindel and co-workers[18] have prepared Mn (I), Co (II), Ni (II), Cu (II), Zn (I), Cd (II), and Hg (II) compounds with 2-picoline and 8-hydroxyquinoline ligands. Using elemental analysis and M-N and M-O vibrations, they have determined the structure of the compound.

In the literature, both experimental transition metal compounds and theoretical vibrational calculations of 8-hydroxyquinoline and 2-picoline ligands have been studied. However, there is no study of mixed ligands both experimentally and theoretically. The aim of this study, for the first time, is to provide description of the molecular structure and infrared vibrations spectra of the Zn (II) compound containing 8-hydroxyquinoline and 2-picoline ligands.

2. MATERIALS AND METHODS

2.1. Experimental details

All chemical substances were purchased from Sigma Aldrich Company and used without further purification. Firstly, 1 mmol $ZnCI_2$ was dissolved in 10 ml absolute ethanol. Secondly, 2 mmol of both 8-hydroxyquinoline and 2-picoline ligands were dissolved separately in 20 ml of absolute ethanol. Finally, $ZnCl_2$ solution was added the obtained solutions, and the mixture was stirred magnetically at room temperature for 24 hours. The precipitated complex was filtered, washed with ether and dried. The freshly prepared compound was analyzed by a Leco CHNS-932 for C, H and N and by a ICPS-OES analyzer for Zn (Table 1), but single crystal of the $ZnL^1_2 L^2_2$ compound could not be obtained.

Table 1. Analytical data for the compound prepared

Compound	(%C)		(%H)		(%N)		(%Zn)	
$ZnL^1_2 L^2_2$	**Calculation**	**Found**	**Calculation**	**Found**	**Calculation**	**Found**	**Calculation**	**Found**
	57.981	51.012	4.002	3.986	9.019	8.692	10.871	11.960

Infrared spectra of 8-Hq and 2P ligands and the compound ($ZnL^1_2L^2_2$) prepared were recorded between 4000-400 cm^{-1} and 700-30 cm^{-1} with ATR technical by Perkin Elmer Spectrum 400 FT-IR/FT-FIR spectrometer. In the free state, the infrared spectra of 8-Hq and 2P ligands at 4000-400 cm^{-1} are given in Figure 1 and 2, respectively. The infrared spectra of the prepared $ZnL^1_2L^2_2$ compound between 4000-400 cm^{-1} and 700-30 cm^{-1} are given in Figure 3 and 4, respectively. Also, the bands observed in the infrared spectrum of the 8-Hq ligand, 2P ligand and the prepared $ZnL^1_2L^2_2$ compound are given in Table 2.

2.2. Computational details

The infrared vibrations frequencies of the prepared $ZnL^1_2L^2_2$ compound were calculated quantum mechanically using the 6-311G(dp) basis set in HF and DFT methods. Therefore, the ligands and the compound were optimized using the same basis set at HF and DFT methods. Thus, our calculations make sure that there are not imaginary frequencies at the lowest energy state. In general, theoretical calculations show systematic deviations from experimental results. Therefore, all the calculated vibrational frequencies are scaled by 0.9024 for HF/6-311G(dp) and 0.9602 for DFT/6-311G(dp) basis sets[19] in order to determine the vibrational spectra of the molecule accurately. Molecular structures of $ZnL^1_2L^2_2$ compound was optimized at C_1 symmetry and was not restricted. All the calculations were performed by using Gauss View molecular visualization program[20] and GAUSSIAN09 program package on the personal computer.[21] The infrared vibration frequencies obtained from the calculations and the experimental data are given in Table 3.

3. Results and discussion

3.1. Molecular structure of $ZnL^1_2L^2_2$ compound

It is known from the literature that 8-Hq and 2P ligands in a free state are linked via the N and O-H groups to form complexes with metals.

When the infrared spectrum of the prepared $ZnL^1_2L^2_2$ compound is compared with the spectra of 8-Hq and 2P ligands in the range of 4000-400 cm^{-1}, it is observed that some bands are down or up, and some are missing or split (see Figures 1-4).

Table 2. The observed wavelengths of the 8-hydroxyquinoline ligand, the 2-Picoline ligand and the prepared ZnL$^1_2$ L$^2_2$ compound in the infrared spectrum

8-hydroxyquinoline(8-Hq)		**2-Picoline (2P)**		**ZnL$^1_2$L$^2_2$ compound**		**Assignment**
3046	m.	3050	w. br.	3051	w. sh.	υ(C-H)
------	------	3012	w. sh.	------	------	υ(C-H)
------	------	2967	w.	------	------	υ(C-H) in CH_3
1619	m. sh.	1590	m.	1603	m.	υ(C=N)
1576	m.	1569	m.	1577	s.	υ(C-C)
1499	s.	------	------	1498	s.	β(C-H)
1469	m.	1477	m.	1464	v.s.	β(C-H)
1433	m.	------	------	------	------	β(C-H)
------	------	1432	m.	1428	w.	Methyl As. Bending
1405	m.	------	------	------	------	β(O-H)
1375	s.	1377	w. sh.	1378	w. s.	β(C-H)
------	------	------	------	1316	w. s.	β(C-H)
1272	s.	1295	m.	1270	s.	υ(C-N)
1243	m.	------	------	------	------	υ(C-O)
------	------	1237	w.	1235	m.	υ(C- CH_3)
1201	s.	------	------	------	------	β(C-H)
1138	m.	1147	m.	1137	w.	β(C-H)
1091	m.	1099	w.	1107	w. s.	υ(C-C)
1054	m	1049	m.	1035	m.	Ring Breathing
971	m.	998	m.	972	v.w	γ(C-H)
893	m.	------	------	878	w. sh.	γ(C-H)
842	m. br.	------	------	------	------	--------
812	m.	806	v. w.	826	s.	γ(C-H)
------	------	------	------	790	s.	γ(C-H) + γ(C-C)
776	v.s.	750	v. s.	755	s.	γ(C-H) + γ(C-C) + γ(C-N)
738	v.s.	730	s.	734	v.s.	γ(C-H)
704	v. s.	------	------	------	------	γ(O-H)
633	m.	628	m.	646	m.	γ(C-C)
573	s.	------	------	589	s.	β(C-C-C)
542	m.	547	m.	553	w.	β(C-C-C)
480	m.	475	s.	484	s.	γ(C-C)
463	s.	------	------	------	------	-------
				398	br.	β ring
				364	br.	β(C-CH_3)
				283	w.	υ(Zn-N)
				246	m.	υ(Zn-O)
				216	br. w.	υ(Zn-N)
				187	br.	2P Butterfly
				148	w.	2P Rocking
				124	m. br.	2P Rocking
				102	s.	υ(Zn-2P)
				77	m. sh.	β(Z-Zn-N)

As.: asymmetric, Br.: broad, m.: medium, s.: strong, sh.: shoulder, v.: very, w.: weak, υ: stretch, β: in plane bending, γ: out of plane bending.

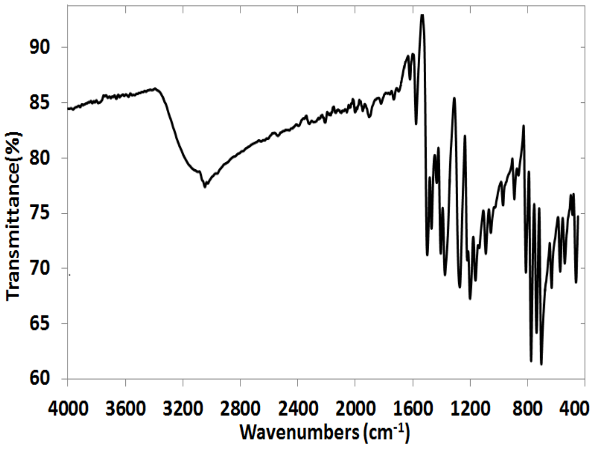

Figure 1. Infrared spectrum of 8-Hq ligand between 4000-400 cm^{-1}.

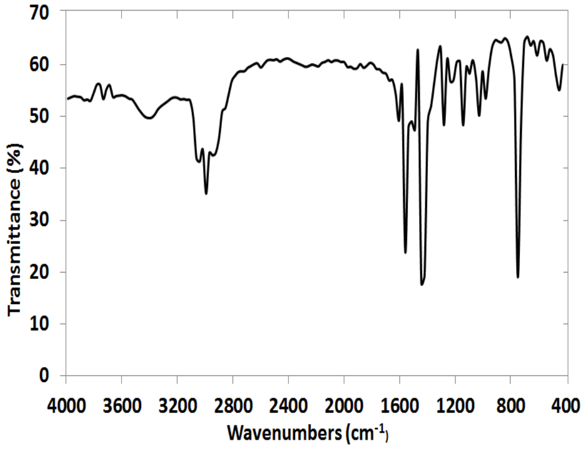

Figure 2.Infrared spectrum of 2P ligand between 4000-400 cm^{-1}.

As seen in Table 2, the C=N stretching band was observed at 1619 cm^{-1} with medium intensity for the 8-Hq ligand and at 1590 cm^{-1} with medium intensity for 2P ligand. We observed medium intensity band at 1603 cm^{-1} in the infrared spectra of the prepared $ZnL^1_2\ L^2_2$ compound. This C=N stretching vibration band was observed at a frequency of 17 cm^{-1} lower than the 8-Hq ligand and at a frequency of 29 cm^{-1} higher than 2P ligand.. In the literature, this C=N stretching vibration band is observed at 1630 cm^{-1},[22] at 1600 cm^{-1},[23] at 1625 cm^{-1}[24] for 8-Hq, at 1595 cm^{-1}[25] for picoline, 1600 cm^{-1}[26] for pyridine and at 1556 cm^{-1}[27] for 2-aminopicoline. The C-N stretching band was observed as intensity band at 1272 cm^{-1} in the free 8-Hq ligand and as strong intensity at 1295 cm^{-1} in the free 2P ligand. We observed the C-N band at 1270 cm^{-1} in the prepared $ZnL^1_2L^2_2$ compound. The C-N band appears to be shifted down compared to both ligands. All these shifts indicate that they are attached to the zinc atom via the nitrogen atoms in the ligands.

The C-O stretching band was observed at 1243 cm^{-1} with middle intensity in the 8-Hq ligand and at 1237 cm^{-1} with weak intensity in the 2P ligand. It is observed that this band shifted down at 1235 cm^{-1} in the prepared $ZnL^1_2L^2_2$ compound. The C-O stretching band was also observed at 1222 cm^{-1} by Khaled and co-workers.[28]

The O-H in-plane bending band is observed at 1405 cm^{-1} in the free 8-Hq ligand but does not appear in the spectrum of the $ZnL^1_2L^2_2$ compound. In the literature, the OH in-plane bending band has been observed at 1407 cm^{-1}[29], 1408 cm^{-1}[30] and 1380 cm^{-1}.[22] Similarly the O-H out-of-plane twist band is observed to have middle intensity at 704 cm^{-1} but does not appear in the spectrum of the $ZnL^1_2\ L^2_2$ compound. According to the results from the infrared spectra, it can be said that 8-Hq (L^1) ligand binds to both the N atom and the O atom of OH group and the 2P (L^2) ligand only binds to the metal from the nitrogen atom.

Metal ligand vibration bands can help determine the molecular structure around metal ions and generally, metal ligand vibrations are observed below 400 cm^{-1} in the infrared spectrum.

In this context, there are Zn-O, Zn-N_1 vibration bands for the L^1 ligand and Zn-N_2 vibration bands for the L^2 ligand below 400 cm^{-1} of the infrared spectrum of the $ZnL^1_2L^2_2$ compound. From Table 2 and 4, it is observed that the Zn-O vibration band formed by the zinc metal with oxygen of the 8-Hq ligand at 246 cm^{-1} shows middle intensity. This band was observed at 241 cm^{-1} in an anhydrous $Zn(8\text{-}Hq)_2$ compound by Engelter and co-workers[9] and also at 315 cm^{-1} in $Zn(8\text{-}Hq)_2Cl_2$ compound with middle intensity by Yurdakul and co-workers.[10] Ohkako and co-workers have observed the Zn-O band at 330-310 cm^{-1}[18] in the compounds of 8-Hq ligand with Ni, Cu and Zn.

The vibration of the Zn-N bond formed by the N atom of the 8-Hq ligand with Zn atom were observed at 193 cm^{-1} by Engelter and co-workers,[9] at 380 cm^{-1} by Mabrouk and co-workers[31] and at 276 cm^{-1} by Yurdakul and co-workers[10] with medium intensity. In this study, we observed moderate intensity of Zn-N stretch vibration band at 283 cm^{-1}.

We also observed that 2P ligand cause to Zn-N bond vibration with weak intensity at 216 cm^{-1}. This band was observed at 310 cm^{-1} by Ahmet-El-Toukhy,[32] at 288-256 cm^{-1} by Dimitra Kovala and co-workers[33] as in compounds made with pyridine and its derivatives at 213 cm^{-1} by Mutton and Thornton[13] and at 222-203 cm^{-1} by WLSteffen and co-workers observed.[34]

It can be said that all the experimental values discussed above are in accordance with the literature. According to Table 1, it can be said that $ZnL^1_2L^2_2$ compound has one Zn atom and two 8-Hq and 2P ligands. In Figure 3, it is shown that the absence of the expected O-H band at 3400-4000 cm^{-1} in the infrared

DOI: 10.32571/ijct.469000 **E-ISSN:2602-277X**

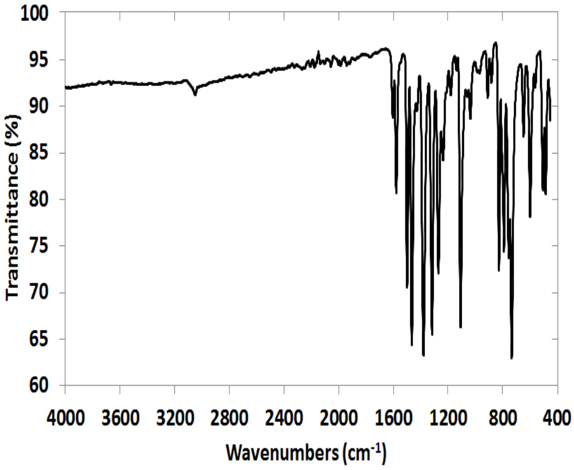

Figure 3. Infrared spectrum of $ZnL^1_2\,L^2_2$ compound between 4000-400 cm^{-1}.

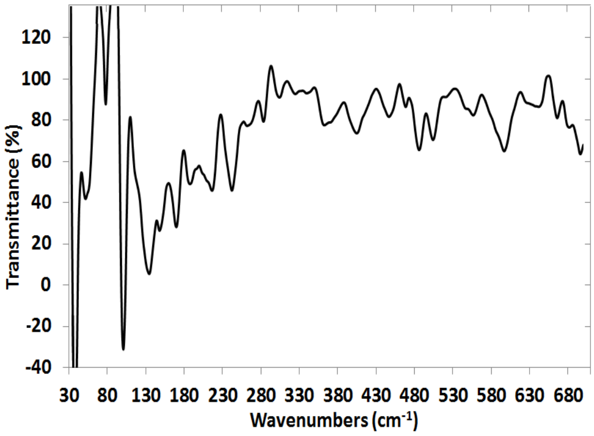

Figure 4. Infrared spectrum of $ZnL^1_2\,L^2_2$ compound between 700-30 cm^{-1}.

spectrum suggests that there is no water in the prepare $ZnL^1_2L^2_2$ compound. According to the Jan Teller theorem, the splitting of bands around 730 cm^{-1} and 750 cm^{-1} in the infrared spectrum of the $ZnL^1_2L^2_2$ compound indicates that the molecular geometry is slightly distorted.

According to the results obtained from the spectrum and elemental analysis, it can be deduced that $ZnL^1_2L^2_2$ compound is in deteriorated octahedral structure. The molecular structure of the considered $ZnL^1_2L^2_2$ compound is given in Figure 5.

3.2. Theoretical HF and DFT calculations of the considered $ZnL^1_2L^2_2$ compound and fundamental vibrational assignments

As is known, it is difficult to make theoretical calculations of large compounds containing metals and to assignment their infrared vibration bands.

The theoretically calculated number of vibrations is considerably greater than observed experimentally. This means that the compound is large and the calculations are done in gas phase. The compound does not have exactly symmetry because it has a distorted octahedral structure. Thus all vibrations are active in both infrared spectroscopy and Raman spectroscopy.

Molecular symmetry was not considered in calculations. All the frequencies are assigned in terms of fundamental, overtone and combination bands. As shown in Figure 5, the compound has 63 atoms and 183 fundamental vibrations.

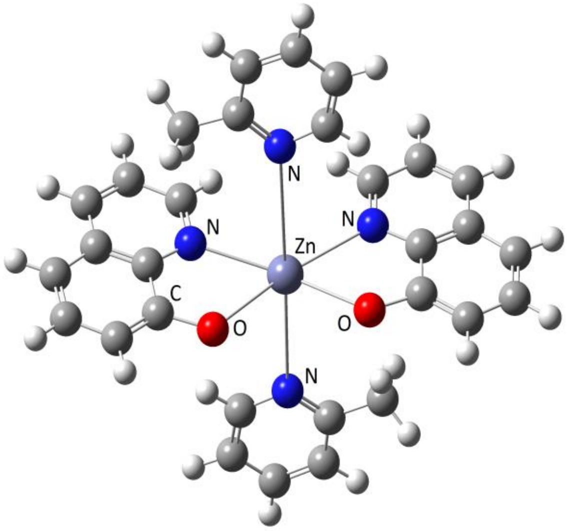

Figure 5. Molecular the structure of the considered $ZnL^1_2L^2_2$ compound.

3.2.1. C-H vibrations

Usually, the bands observed in the infrared spectrum between 3000 and 3250 cm^{-1} are C-H stretching vibration bands[35] and they are pure. The weak band observed at 3051 cm^{-1} in the spectrum is assigned to C-H vibration band which shows good correlation with computed wave number at 3022.16 cm^{-1} by HF and at 3058.51 cm^{-1} by B3LYP methods (see Table 3).

Other the C-H stretching bands which are not visible in the infrared spectrum of the compound was calculated at (3008.20 cm^{-1} - 3087.90 cm^{-1}) at HF and (3048.82 cm^{-1} - 3121.68 cm^{-1}) at DFT as the theoretical.

In-plane and out-of-plane C-H bending vibrations are observed at 1000-1300 cm^{-1} and 950-800 cm^{-1}, respectively.[36-38] We observed very strong bands at 1498 cm^{-1} and 1316 cm^{-1} in the infrared spectra of the $ZnL^1_2L^2_2$ compound and they are determined as β(C-H) + υ(C=C) and β(C-H) + υ(C-C) in Table 3. These bands arise from the coupling between the in-plane C-H bending and ring C-C stretching vibrations.

DOI: 10.32571/ijct.469000 **E-ISSN:2602-277X**

Table 3. The infrared vibration frequencies of $ZnL^{1}_{2}L^{2}_{2}$ compound obtained from the calculations and the experimental data, approximately assignment

	HF/6-311G(dp)			**DFT/B3LYP/6-311G(dp)**			**Exp. IR**	**Approximately Assignment**
No:	**IR in.**	**(cm^{-1})**	**Scaled^{a}**	**IR in.**	**(cm^{-1})**	**Scaled^{b}**	**(cm^{-1})**	
1	0.021	5.04	4.57	0.023	6.50	6.28	-----	Molecule Torsion
2	0.519	18.08	16.42	0.183	19.74	19.08	-----	Molecule Butterfly
3	0.311	22.81	20.72	0.000	23.60	22.81	-----	Molecule Torsion
4	0.002	25.26	22.94	1.083	27.45	26.54	-----	Molecule Torsion
5	1.127	28.54	25.92	0.418	33.12	32.02	-----	Molecule Torsion
6	0.581	32.37	29.40	0.547	33.58	32.46	-----	Molecule Butterfly
7	0.069	56.46	51.29	0.616	55.44	53.60	-----	Molecular Fluctuation
8	0.009	57.23	51.99	0.002	60.54	58.53	-----	8Hq Fluctuation
9	9.422	61.81	56.15	0.288	69.28	66.98	-----	υ(Zn-2P)
10	0.477	67.35	61.18	3.214	74.47	72.00	-----	2P Fluctuation
11	1.207	75.41	68.50	0.005	77.71	75.13	-----	Skeleton Vibration
12	0.015	77.05	69.99	0.248	80.96	78.28	77 m.	β(N-Zn-N)
13	0.460	97.24	88.34	0.342	97.99	94.74	-----	Methyl Torsion
14	17.818	100.59	91.38	17.102	113.70	109.93	102 s.	υ(Zn-2P)
15	0.912	114.90	104.38	0.247	121.62	117.59	-----	2P Waking
16	1.544	119.12	108.22	0.704	125.74	121.57	124 br.	2P Rocking
17	0.027	133.45	121.23	0.010	140.35	135.70	-----	Methyl Torsion
18	2.365	134.97	122.62	6.069	142.32	137.60	-----	Skeleton Vibration
19	0.028	149.37	135.70	5.543	145.30	140.49	-----	Molecular Vibration
20	7.819	151.21	137.37	5.393	157.27	152.06	148 w.	2P Rocking
21	15.845	161.91	147.09	0.750	161.53	156.18	-----	Fluctuation
22	0.049	186.09	169.06	0.029	182.92	176.86	-----	Fluctuation
23	67.198	201.08	182.68	17.460	192.08	185.72	-----	8-Hq Butterfly
24	0.007	207.40	188.42	0.160	192.81	186.42	187 br.	2P Butterfly
25	24.878	211.66	192.29	66.814	202.66	195.95	-----	8-Hq Butterfly
26	1.717	233.01	211.68	1.075	210.73	203.75	-----	2P Butterfly
27	7.339	234.98	213.47	5.690	221.57	214.23	-----	υ(Zn-N) with 2P
28	0.532	241.50	219.40	0.362	221.90	214.55	216 w.	υ(Zn-N) with 2P
29	118.316	288.44	262.04	110.555	268.67	259.77	246 m.	υ(Zn-O) with 8Hq
30	0.113	302.31	274.64	0.232	277.62	268.43	-----	υ(Zn-O) with 8Hq
31	13.540	307.72	279.56	17.366	282.72	273.36	283 w.	υ(Zn-N) with 8Hq
32	4.326	396.88	360.56	5.568	373.31	360.95	-------	υ(Zn-N) with 8Hq
33	11.147	408.71	371.31	0.088	382.76	370.09	364 br.	β(C-CH_3)
34	0.048	409.69	372.20	11.329	386.26	373.47	-----	β(C-CH_3)
35	16.843	418.91	380.57	17.945	395.16	382.08	-----	β ring
36	3.003	471.15	428.03	0.017	432.58	418.26	402 br.	γ(C-C)
37	30.748	475.38	431.88	42.649	437.96	423.46	-----	γ(C-C)
38	0.071	493.29	448.15	0.049	453.08	438.08	-----	γ(C-C)
39	3.101	494.71	449.44	5.161	455.17	440.10	-----	γ(C-C)
40	0.000	520.14	472.54	0.000	476.97	461.18	-----	γ(C-C)
41	0.382	524.58	476.58	0.059	481.75	465.80	-----	γ(C-C)
42	7.326	527.94	479.63	4.643	483.23	467.23	-----	γ(C-C)
43	1.592	529.60	481.14	1.405	492.60	476.29	-----	β(C-C-C)
44	1.307	533.40	484.59	1.362	494.02	477.66	477 s.	β(C-C-C)
45	1.907	536.42	487.33	0.163	497.41	480.94	-----	γ(C-C)
46	76.958	546.77	496.74	61.944	508.44	491.61	-----	β(C-C-C)
47	1.238	550.74	500.34	0.055	513.09	496.10	-----	β(C-C-C)
48	1.540	592.23	538.04	0.580	558.02	539.54	-----	β(C-C-C)
49	0.602	593.44	539.14	0.127	558.53	540.04	-----	β(C-C-C)
50	1.255	611.88	555.89	0.170	571.59	552.67	553 w.	β(C-C-C)
51	0.987	615.04	558.76	0.941	573.99	554.99	-----	β(C-C-C)
52	14.898	659.14	598.82	0.087	603.56	583.58	589 s.	β(C-C-C)
53	6.616	662.41	601.79	0.372	603.60	583.62	-----	β(C-C-C)
54	0.002	664.12	603.35	7.108	617.39	596.95	-----	γ(C-C) + γ(C-N)
55	0.410	664.43	603.63	2.728	621.60	601.02	-----	γ(C-C) + γ(C-N)
56	6.747	691.36	628.10	6.297	649.45	627.95	-----	β(C-C-C)
57	4.653	697.96	634.09	3.270	655.01	633.32	-----	β(C-C-C)
58	0.264	725.68	659.28	0.045	663.33	641.37	-----	γ(C-C)

Table 3. Continuation

59	33.493	731.46	664.53	16.010	669.93	647.75	646 m.	γ(C-C)
60	99.429	792.47	719.95	60.926	739.12	714.65	-----	β(C-C-C)
61	3.712	797.87	724.86	0.655	743.53	718.52	-----	β(C-C-C)
62	30.557	809.06	735.03	1.164	746.94	722.21	-----	γ(C=C) + γ(C-N)
63	44.465	813.16	738.75	63.609	747.50	722.75	-----	γ(C=C) + γ(C-N)
64	0.488	824.23	748.81	26.790	749.07	724.27	-----	γ(C-H) + γ(C=N)
65	98.686	824.63	749.17	40.647	752.76	727.84	734 v.s.	γ(C-H) + γ(C=N)
66	22.443	848.13	770.52	8.254	770.48	744.97	755 s.	γ(C-H) + γ(C=C)
67	34.820	849.12	771.42	26.449	772.71	772.71	-----	γ(C-H) + γ(C=C)
68	40.723	863.63	784.60	0.207	794.19	767.90	-----	β(C-C-C) + β(N=C-C)
69	19.221	865.69	786.47	96.071	799.62	773.15	-----	β(C-C-C) + β(N=C-C)
70	0.706	868.41	788.95	20.530	812.68	785.78	-----	β(C-C-C) + β(N=C-C)
71	0.188	871.94	792.15	12.501	814.41	787.45	-----	β(C-C-C) + β(N=C-C)
72	1.275	878.60	798.20	4.091	817.58	790.51	790 v.s.	γ(C-H) + γ(C=C)
73	85.925	881.86	801.16	0.883	818.93	791.82	-----	γ(C-H) + γ(C=C)
74	0.3177	915.20	831.45	0.023	828.99	801.55	-----	γ(C=C) + γ(C=N)
75	63.144	916.43	832.57	31.821	831.24	803.72	-----	γ(C=C) + γ(C=N)
76	0.079	956.19	868.69	0.282	869.20	840.42	826 s.	γ(C-H)
77	23.414	956.75	869.20	15.622	869.54	840.75	-----	γ(C-H)
78	0.156	978.56	889.02	0.619	896.07	866.41	-----	γ(C-H)
79	0.489	981.15	891.37	0.230	896.16	866.49	-----	γ(C-H)
80	0.382	981.70	891.87	0.350	916.80	886.45	878 w.	γ(C-H) + γ(C=C)
81	0.236	987.32	896.98	0.002	919.46	889.02	-----	β(C-C-C)
82	0.151	1055.66	959.06	0.010	922.81	892.26	-----	γ(C-H) + γ(C=C)
83	0.337	1070.28	972.34	0.216	934.97	904.02	909 w.	γ(C-H) + γ(C=C)
84	4.072	1073.83	975.57	0.104	974.62	942.36	-----	γ(C-H)
85	3.897	1078.96	980.23	0.023	975.26	942.97	-----	β(C-N-C)
86	18.928	1085.98	986.61	0.200	975.29	943.00	-----	β(C-N-C)
87	0.013	1089.62	989.91	4.912	979.65	947.22	-----	γ(C-H)
88	0.640	1089.67	989.96	0.004	994.16	961.25	-----	Methyl Wagging
89	3.613	1091.53	991.65	1.035	994.82	961.89	962 w.	Methyl Wagging
90	0.000	1096.24	995.93	3.185	1002.34	969.16	-----	γ(C=C)
91	7.748	1097.82	997.36	0.460	1013.57	980.02	-----	β(C-C-C) + β(C-N=C)
92	12.078	1099.92	999.27	0.045	1014.78	981.19	-----	β(C-C-C) + β(C-N=C)
93	2.515	1102.09	1001.24	3.037	1015.47	981.85	-----	γ(C-H)
94	0.001	1115.54	1013.46	8.509	1028.31	994.27	-----	Methyl Rocking
95	0.297	1116.22	1014.08	6.980	1035.13	1000.86	-----	Methyl Rocking
96	0.017	1125.73	1022.72	0.039	1058.86	1023.81	-----	γ(C-H)
97	0.318	1129.41	1026.06	6.619	1066.30	1031.00	1029 m.	Ring Breathing
98	0.060	1151.65	1046.27	13.383	1068.78	1033.40	-----	γ(C-H)
99	13.851	1153.43	1047.89	8.954	1075.16	1039.57	-----	Ring Breathing
100	2.180	1155.21	1049.50	9.732	1082.74	1046.90	-----	γ(C-H)
101	15.184	1158.24	1052.26	2.133	1084.14	1048.25	-----	Ring Breathing
102	7.410	1167.15	1060.35	15.787	1085.28	1049.35	-----	Ring Breathing
103	20.340	1169.70	1062.67	0.358	1090.08	1053.99	-----	β(C-C-C)
104	7.454	1175.63	1068.05	79.428	1132.13	1094.65	-----	γ(C-H)
105	1.570	1179.53	1071.60	9.766	1132.90	1095.40	-----	υ(C-C)
106	18.227	1181.49	1073.38	7.907	1133.49	1095.97	-----	β(C-H)
107	3.852	1186.01	1077.49	5.288	1136.05	1098.44	1107w.v	υ(C-C)
108	133.510	1214.41	1103.29	1.572	1158.22	1119.88	-----	β(C-C-C) + β(C-N=C)
109	1.053	1215.59	1104.36	0.056	1158.95	1120.58	1129 w.	β(C-H)
110	25.387	1217.18	1105.80	5.631	1179.91	1140.85	-----	β(C-C-C) + β(C-N=C)
111	5.179	1221.04	1109.31	6.609	1180.21	1141.14	-----	β(C-H)
112	0.514	1277.16	1160.29	16.879	1193.84	1154.32	-----	β(C-H) + υ(C-C)
113	8.087	1277.89	1160.96	6.561	1194.39	1154.85	-----	β(C-H) + υ(C-C)
114	27.263	1283.09	1165.68	6.306	1239.36	1198.33	-----	υ(C-C)
115	6.504	1284.07	1166.57	0.028	1239.85	1198.81	-----	υ(C-C)
116	0.670	1299.38	1180.48	59.906	1247.53	1206.23	1179 w.	β(C-H)
117	1.026	1299.70	1180.77	13.474	1256.32	1214.73	-----	β(C-H)
118	96.965	1341.67	1218.90	0.512	1262.37	1220.58	-----	β(C-H) + υ(C-C)
119	6.241	1351.10	1227.47	2.533	1263.34	1221.52	-----	β(C-H) + υ(C-C)
120	0.696	1354.26	1230.34	0.404	1277.81	1235.51	1235 m.	υ(C-CH$_3$)
121	0.744	1355.53	1231.49	0.702	1279.16	1236.81	-----	υ(C-CH$_3$)
122	0.323	1387.63	1260.66	16.917	1315.22	1271.68	1270 s.	υ(C-N)

Table 3. Continuation

123	10.075	1388.83	1261.75	2.134	1316.88	1273.29	-------	β(C-H)
124	20.748	1438.31	1306.70	19.705	1330.92	1286.86	-----	υ(C-N)
125	55.965	1453.34	1320.35	30.829	1346.04	1301.48	-----	υ(C-C) + υ(C-N)
126	60.476	1455.02	1321.88	77.155	1361.79	1316.71	1316 v.s.	β(C-H) + υ(C-C)
127	169.307	1459.20	1325.68	29.566	1367.61	1322.34	-----	υ(C-C)
128	153.805	1470.33	1335.79	5.524	1385.11	1339.26	-----	β(C-H)
129	7.494	1475.33	1340.33	138.363	1386.02	1340.14	-----	β(C-H)
130	187.148	1529.95	1389.95	1.396	1415.17	1368.32	-----	β(C-H)
131	0.434	1538.89	1398.08	82.227	1417.87	1370.93	-----	υ(C-C)
132	97.124	1542.13	1401.02	62.649	1425.33	1378.15	1378 v.s.	Methyl Umbrella (Sy. Bend.)
133	0.723	1553.55	1411.40	1.196	1430.57	1383.21	-----	Methyl Umbrella (Sy. Bend.)
134	41.235	1575.05	1430.93	15.828	1456.75	1408.53	-----	β(C-H)
135	2.653	1575.89	1431.69	40.227	1458.34	1410.06	-----	β(C-H)
136	14.165	1580.00	1435.43	3.352	1460.22	1411.18	-----	β(C-H)
137	18.213	1581.58	1436.86	7.627	1462.63	1414.21	-----	υ(C-N)
138	207.078	1592.14	1446.45	70.558	1464.96	1416.46	-----	υ(C-C)
139	0.042	1600.20	1453.78	0.175	1479.60	1430.62	1428 w.	υ(C=C)
140	822.243	1611.49	1464.03	641.313	1495.02	1445.53	-----	υ(C=C)
141	25.405	1616.19	1468.30	119.797	1498.73	1449.12	-----	Methyl As. Bending
142	112.106	1617.36	1469.37	34.534	1500.60	1450.93	-----	Methyl As. Bending
143	22.221	1633.17	1483.73	27.651	1514.21	1464.08	-----	Methyl As. Bending
144	27.500	1648.89	1498.01	46.694	1514.99	1464.84	1464 v.s.	Methyl As. Bending
145	183.769	1651.51	1500.39	17.476	1522.72	1472.31	-----	β(C-H) + υ(C-C)
146	9.989	1653.13	1501.86	62.992	1533.36	1482.60	-----	β(C-H) + υ(C=C)
147	21.062	1655.80	1504.29	8.173	1534.04	1483.26	1498 v.s.	β(C-H) + υ(C=C)
148	47.513	1759.16	1598.19	129.412	1601.91	1549.85	-----	υ(C=C)
149	316.464	1762.22	1600.95	2.240	1606.68	1553.49	-----	υ(C=C)
150	39.101	1764.43	1602.98	10.913	1610.59	1557.27	-----	υ(C=C)
151	6.580	1765.73	1604.16	124.586	1612.63	1559.25	-----	υ(C=N)
152	3.925	1765.93	1604.34	7.359	1613.40	1559.99	-----	υ(C=C)
153	29.491	1771.36	1609.28	11.075	1616.60	1563.09	-----	υ(C=N) + υ(C=C)
154	56.764	1796.02	1631.68	198.690	1633.99	1579.90	1577 s.	υ(C=C)
155	80.605	1796.32	1631.95	9.183	1638.89	1584.64	-----	υ(C=N) + υ(C=C)
156	26.565	1799.38	1634.73	33.845	1645.23	1590.77	-----	υ(C=C)
157	68.328	1802.88	1637.91	53.597	1648.29	1593.73	1603 m.	υ(C=N)
158	17.523	3188.44	2896.69	45.255	3038.71	2938.12	-----	Sy. υ(C-H) in methyl
159	38.174	3192.08	2900.00	12.039	3045.17	2944.37	-----	Sy. υ(C-H) in methyl
160	28.154	3256.57	2958.59	53.597	3100.30	2997.67	-----	As. υ(C-H) in methyl
161	16.636	3257.51	2959.44	45.255	3108.85	3005.95	-----	As. υ(C-H) in methyl
162	10.418	3269.24	2970.10	12.039	3117.97	3014.76	-----	As. υ(C-H) in methyl
163	0.327	3278.05	2978.10	9.858	3123.14	3019.76	-----	As. υ(C-H) in methyl
164	25.934	3311.18	3008.20	24.884	3153.16	3048.79	-----	υ(C-H)
165	8.110	3311.22	3008.24	8.458	3153.20	3048.82	-----	υ(C-H)
166	10.193	3325.55	3021.26	3.933	3162.93	3058.23	-----	υ(C-H)
167	0.713	3326.54	3022.16	1.743	3163.22	3058.51	3051 w.	υ(C-H)
168	0.278	3327.69	3023.20	6.166	3168.06	3063.19	-----	υ(C-H)
169	7.278	3329.27	3024.64	3.854	3170.18	3065.24	-----	υ(C-H)
170	1.415	3336.60	3031.30	34.854	3175.14	3070.04	-----	υ(C-H)
171	4.742	3337.40	3032.02	12.387	3178.34	3073.13	-----	υ(C-H)
172	117.183	3338.80	3033.29	43.484	3178.35	3073.14	-----	υ(C-H)
173	41.553	3346.98	3040.73	6.957	3180.78	3075.49	-----	υ(C-H)
174	16.881	3347.07	3040.81	13.836	3184.13	3078.73	-----	υ(C-H)
175	3.917	3349.62	3043.12	15.133	3186.16	3080.69	-----	υ(C-H)
176	21.744	3349.75	3043.24	16.629	3186.29	3080.82	-----	υ(C-H)
177	10.785	3350.31	3043.75	17.070	3186.73	3081.24	-----	υ(C-H)
178	12.693	3358.39	3051.09	17.843	3191.18	3085.55	-----	υ(C-H)
179	1.223	3358.58	3051.26	0.063	3194.33	3088.59	-----	υ(C-H)
180	22.350	3359.01	3051.66	10.002	3196.20	3090.40	-----	υ(C-H)
181	6.442	3370.25	3061.87	15.309	3200.34	3094.40	-----	υ(C-H)
182	30.576	3374.43	3065.66	22.335	3201.28	3095.31	-----	υ(C-H)
183	2.451	3398.91	3087.90	5.260	3228.55	3121.68	-----	υ(C-H)

As.: asymmetric, a: 0.9024, b: 0.9602 Br.: broad, m.: medium, s.: strong, sh.: shoulder, Sy.: symmetric, v.: very, w.: weak, υ: stretch, β: in plane bending, γ: out of plane bending.

DOI: 10.32571/ijct.469000 **E-ISSN:2602-277X**

This indicates that during this normal mode the total dipole moment changes substantially, and this is consistent with the large IR intensity of this mode. These in-plane C-H bending vibrations were observed at 1510 cm^{-1} for p-Fluorophenol-OH, at 1508 cm^{-1} for *p*-Fluorophenol-OD,[39] p-chloro and p-bromophenol, respectively.[40] As seen in Table 3, we observed a very intense in-plane (C-H) bending band at 1316 cm^{-1}. This band was observed weakly at 1310 cm^{-1} in the p-Fluorophenol-OH molecule by Zierkiewicz and Michalska.[39] Also, the bands observed at 1179 and 1129 cm^{-1} in the infrared spectrum of the compound were assigned as C-H in-plane bending vibrations. These observed C-H in-plane bending vibrations were calculated as 1180.48 and 1104.36 cm^{-1} via HF method, 1206.23 and 1120.58 cm^{-1} via DFT method, respectively. However, the C-H in plane bending vibrations not visible in the spectrum are theoretically calculated and given in Table 3.

The C-H out-of-plane bending vibrations are observed at 878, 826, 790, 755 and 734 cm^{-1}. While the 826 cm^{-1} band was assigned as pure, the other bands were assigned in combination with the γ(C=C) and γ(C=N) bands. These bands were calculated as 891.87, 798.20, 770.52 and 749.17cm^{-1} via HF, 886.45, 840.42, 790.51, 744.97 and 727.84 cm^{-1} via DFT methods respectively.

According to the literature, the in-plane and out-of-plane bending vibrational frequencies have been found to be well within their characteristic regions.

3.2.2. Ring vibrations

The C=N stretching band generally seems between 1645 and 1575 cm^{-1}.[41] This band has been observed at 1630 cm^{-1}[22] at 1600 cm^{-1}[23], at 1625 cm^{-1}[24] for 8-hydroxyquinoline, at 1595 cm^{-1}[25] for picoline, at 1600 cm^{-1}[26] for pyridine in the literature. In the spectrum of the compound we have indicated the medium intensity band at 1603 cm^{-1} as the C=N stretching vibration which calculated as 1637.91 cm^{-1} by HF and 1593.73 cm^{-1} by DFT methods. The other three C=N stretching vibrations not visible in the spectrum are calculated and given in Table 3. The C–N stretching usually lies in the region 1400–1200 cm^{-1}.[42] The C-N stretching vibration is assigned at 1270 cm^{-1} with very strong intensity. This band is calculated as 1260.66 cm^{-1} by HF and 1271.68 cm^{-1} by DFT methods. As mentioned above, we assigned the band γ (C-H) + γ (C =N), which appears to be very strong at 734 cm^{-1}.

Arjuna and co-workers have observed the C=C ring stretching vibration for the 7-bromo-5-chloro-8-hydroxyquinoline and 5-aminoquinoline molecules in the range 1611 to 1412 cm^{-1}.[43,44] The C=C stretching vibrations are assigned at 1577, 1498 and 1428 cm^{-1} with strong, very strong and weak intensity, respectively. These bands are calculated as 1631.68, 1504.29 and 1453 cm^{-1} by HF and 1579.90, 1483.26 and 1430.62 cm^{-1} by DFT method, respectively. The stretching vibrations bands for C-C bond are assigned at 1316 cm^{-1} with very strong and at 1107 cm^{-1} with weak intensity. The experimentally observed bands are found to be at 1321.88 and 1077.49 cm^{-1} via HF method and 1316.71 and 1098.44 cm^{-1} via DFT method, respectively. These theoretically calculated values are in agreement with both the intensity and the spectrum of the bands. This result is also consistent with the literature.[45] We assigned the band γ(C = C) as a combination of γ (C-H) which appears to be weak at 878, very strong at 790, strong at 755 cm^{-1} and medium at 646 cm^{-1}. In addition, the band we have observed with medium intensity at 646 and broad at 402 cm^{-1} are determined as the pure out-of-plane C-C vibration.

In the spectrum, we labeled the bands that were strong at 598, weak at 553, and strong at 477 cm^{-1} as β(C-C-C) in-plane angle bending. These bands are calculated at 598.82, 555.89 and 484.59 cm^{-1} by HF and 583.58, 552.62 and 477.66 cm^{-1} by DFT method, respectively. This result is in consistent with the literature.[44]

We observed a medium intensity band at 1029 cm^{-1} and assigned the band as ring breathing. This band is calculated at 1026.06 cm^{-1} by HF and 1031.00 cm^{-1} by DFT method and it is in consistent with the literature.[46]

3.2.3. Methyl group vibrations

The CH_3 methyl group is known to have nine types of vibrations. These are one symmetric stretch, two asymmetric stretches, one symmetrical bending, two asymmetric bendings, two rocks and one torsion vibration. Symmetrical and asymmetric vibrations in the methyl group are observed in the range of 3000-2900 cm^{-1}. Symmetrical and asymmetric bending vibrations are observed in the range of 1465-1370 cm^{-1} and rocking vibrations are observed in the range of 1040-990 cm^{-1}.[25] Symmetrical and asymmetric stretching vibrations frequencies are not observed in the infrared spectra but asymmetric bending modes at methyl CH_3 are assigned at 1464 cm^{-1} to be very strong. The experimentally observed band is found at 1504.29 cm^{-1} via HF and 1483.26 cm^{-1} via DFT method. The methyl symmetric bending vibration is obtained at 1378 cm^{-1} with very strong intensity. We calculated this band at 1401.02 cm^{-1} with HF and at 1378.15 cm^{-1} with DFT method. In this study, we could not observe the methyl rocking and methyl torsion vibrations, but we observed the methyl wagging vibration at 962 cm^{-1} with weak intensity. We also observed the stretching vibration between the methyl groups and the ring as a broad band at 364 cm^{-1}. It is calculated as 371 cm^{-1}, 370.09 cm^{-1} with HF and DFT methods, respectively. These values are given in Table 3. It can be said that the assignments made for methyl are in good agreement with the literature.

DOI: 10.32571/ijct.469000 **E-ISSN:2602-277X**

3.2.4. Zn-N, Zn-O and other vibrations

As mentioned above, these vibration bands are assigned in more detail in Table 3. The Zn-N stretching band between the zinc atom and the nitrogen atom in 8-Hq was calculated at 279.56 cm^{-1} with HF method and 273.36 cm^{-1} with DFT method. Also, the band between the zinc atom and the nitrogen atom in 2P was calculated at 219.40 cm^{-1} with HF method and 214.55 cm^{-1} with DFT method. Zn-O bands between 8-hq ligand and zinc were calculated as 274.64 cm^{-1} and 262.04 cm^{-1} with HF and 259.77 cm^{-1} and 268.43 cm^{-1} with DFT methods.

We observed a broad band at 364 cm^{-1} and assigned the band as $\beta(C\text{-}CH_3)$. This broad band observed at 187 cm^{-1} was assigned as a butterfly of the 2P ligand. The weak band observed at 148 cm^{-1} and broad band at 124 cm^{-1} were assigned as a rocking of the 2P ligand. In addition, the bands observed at 102 cm^{-1} and 77 cm^{-1} in the spectrum were assigned as $\upsilon(Zn\text{-}2P)$ and $\beta(N\text{-}Zn\text{-}N)$ vibrations, respectively. Table 3 shows that these observed bands are in good agreement with the calculations.

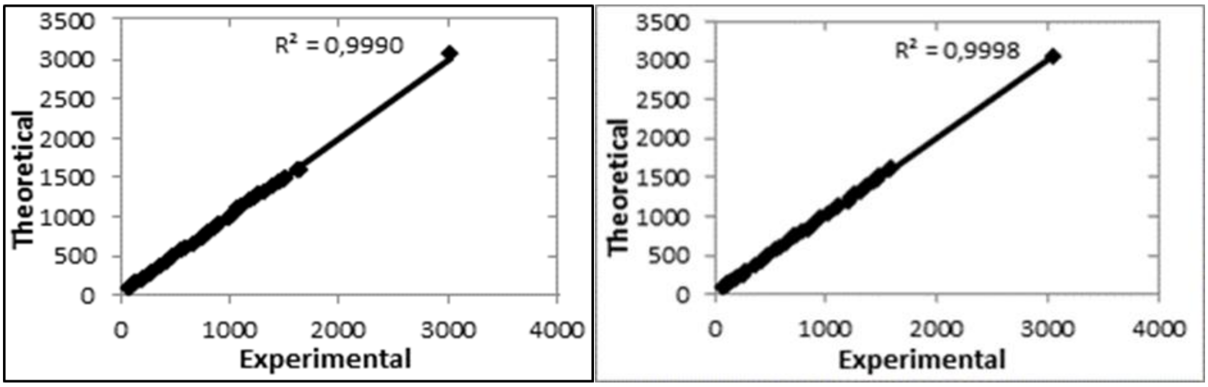

Figure 6. Correlation graphs of theoretical and experimental vibration frequencies.

Correlation diagrams for comparison of the experimental and theoretical infrared vibration frequencies of the prepared $ZnL^1_2L^2_2$ compound are shown in Figure 6.

As can be seen from Figure 6, the experimental vibration frequencies are in better agreement with the scaled vibration frequencies and are found to have a better correlation for DFT/B3LYP/6-311G(dp) than and HF/6-311G(dp).

4. CONCLUSIONS

The structure of the prepared $ZnL^1_2L^2_2$ compound was determined with the help of analyzing C, H, N and Zn via observed infrared spectra. The geometry of $ZnL^1_2L^2_2$ compound were optimized using the HF and DFT/B3LYP methods with 6-311G(dp) basis set. Then, using this optimized data, the vibration frequencies of the compound were calculated and compared with the experimental values one by one. It has been shown that the results are in perfect agreement and these results are supported by correlation graphics.

ACKNOWLEDGEMENTS

In this study, we used the Gaussian09 program which was obtained from the BAP project number 2010/02/08 supported by Kilis 7 Aralık University.

Conflict of interest

We declare that there is no a conflict of interest with any person, institute, company, etc.

REFERENCES

1. Bambury, R. E.; Wolff, M. E. *Burger's Medicinal Chemistry, Part II, John Wiley*, (New York), 1979, p 41.

2. Buchmann, G.; Proffit, E.; *Arzneimittelforsch*, **1960**, 10, 181.

3. Hamada, Y.; Sano, T.; Fijujita, M.; Fujii, Y.; Nishio, Y.; Shibata, K. *Jpn. J. Appl. Phys.* **1993**, 32, L512.

DOI: 10.32571/ijct.469000 **E-ISSN:2602-277X**

4. Merritt, L. L. *Anal. Chem*. **1953**, 25, 718-721.

5. Magee, R. J.; Gordon, L. *Talanta* **1963**, 10 (8), 851-859.

6. Magee, R. J.; Gordon, L. *Talanta* **1963**, 10 (9), 961-966.

7. Magee, R. J.; Gordon, L. *Talanta* **1963**, 10 (9), 967-970.

8. Ohkaku, N.; Nakamoto, K. *Inorg. Chem*. **1971**, 10 (4), 798-805.

9. Engelter, C.; Jackson, G. E.; Knight, C. L.; Thornton, D. A. *J. Mol. Struct*. **1989**, 213, 133-144.

10. Yurdakul, Ş.; Arıcı, K. *J. Mol. Struct*. **2004**, 691 (1-3), 45-49.

11. Das, M. K.; Maiti, P. K.; Roy, S.; Mittakanti, M.; Morse, K. W.; Hall, I. H. *Arch. Pharm-Weinheim*. **1992**, 325 (5), 267-272.

12. Saravanan, S. P.; Sankar, A.; Parimala, K. *IJSRM*, **2017**, 7 (3), 74-82.

13. Mutton, A. T.; Thornton, D. A. *Spectrosc. Lett*. **1977**, 10 (1), 57-65.

14. Steffen, W. L.; Palenik, G. J. *Acta Cryst*. **1976**, B32, 298-302.

15. Healy, P. C.; Pakawatchai, C.; White, A. H. *J. Chem. Soc. Dalton Trans*. **1983**, 9, 1917-1927.

16. Greenwood, N. N.; Wade, K. *J. Chem. Soc.* **1960**, 1130-1141.

17. Shayma, A. S., Farina, Y.; Salleh, A. A. *Euro. J. Sci.* Res. **2009**, 33 (4), 702-709.

18. Kindeel, A.S.; I.; Dawood, I. J.; Aziz, M. R. *Baghdad Sci. J.* **2013**, 10, 396-403.

19. Irikura, K. K.; Johnson, R. D.; Kacker, R. N. *J. Phys. Chem*. **2005**, A 109 (37), 8430-8437.

20. Frisch, A.; Nielsen, A. B.; Holder, A. J. *Gauss 09 View User Manual (Pittsburg: Gaussian Inc.)* 2009.

21. Frisch, M.J et al, GAUSSIAN 09: Revision C.02 (Pittsburg, PA: Gaussian Inc.) 2009.

22. Ramakrishnan, L.; Soundararajan, S. *Indian. Acad*. *Sci*. **1977**, 86A, 59-64.

23. Krishnakumar, V.; Ramasamy, R. *Spectrochım. Acta* 2005, 61 (4), 673-683.

24. EI-Asmy, A.A.; EI-Sonbati, A.Z., Ba-Issa, A.A. *Transit. Metal Chem*. **1990**, 15, 222-225.

25. Arenas, J.F.; Tocon, I.L.; Otero, J.C.; Marcos, J.I. *J. Mol. Struct.* **1997**, 410-411, 443-446.

26. Greenwood, N.N.; Wade, K. *J. Chem. Soc.* **1960**, 1130 1141.

27. Sujin, P.J.; Mohan, S.; *Spectrochım. Acta* **2006**. 64 (1), 240-25.

28. Bahgat, K.; Ragheb, A. G. *Cent. Eur. J. Chem.* **2007**, 5 (1), 201-220.

29. Srivastava, SL.; *Rohitashava*, M.P. *Spectrochım. Acta* **1984**, 40 (7), 681-685.

30. Arıcı, K.; Yurdakul, M.; Yurdakul, S. *Spectrochım. Acta* **2005**, 61 (1-2), 37-43.

31. Mabrouk, H.E.; EI-Asmy, A.A.; Mounir, M. *Transit. Metal Chem*. **1993**, 18 (6), 573-575.

32. El Toukhy, A. *Qatar Univ. Sci. Bull.* **1990**, 10, 83-97.

33. Kovala-Demertzi, D.; Yadav, P. N.; Wiecek, J.; Skoulika, S.; Varadinova, T.; Demertzis, M .A. *J. Inorg. Bıochem.* 2**006**, 100 (9), 1558–1567.

34. Steffen, W. L.; Palenik, G. J. *Inorg. Chem*. **1977**, 16 (5), 1119-1127.

35. Sharma, A.; Gupta, V.P.; Virdi, A. *IJPAP*, **2004**, 42, 251-257.

36. Krishnakumar, V.; Prabavathi, N. *Spectrochim. Acta* **2008**, 71 (2), 449-457.

37. Altun, A.; Golcuk, K.; Kumru, M. *J. Mol. Struct. THEOCHEM*. **2003**, 637 (1-3), 155-169.

38. Singh, S. J.; Pandey, S. M. *Indian J. Pure Ap. Phy.* **1974**, 12, 300-304.

39. Zierkiewicz, W.; Michalska, D. *J. Phys. Chem. A.* **2003**, 107, 4547-4554.

40. Zierkiewic, W.; Michalska, D.; Zeegers-Huyskens, T. *J. Phys. Chem. A.* **2000**, 104 (50), 11685-11692.

41. Gunasekaran, S.; Natarajan, R.K.; Syamala, D.; Rathikha, R. *Indian J. Pure Ap. Phy*. **2006**, 44 (04), 315-319.

DOI: 10.32571/ijct.469000 **E-ISSN:2602-277X**

42. Prabhaharan, M.; Prabakaran, A.R.; Srinivasan, S.; Gunasekaran, S. *Spectrochim. Acta* **2015**, 138, 711-722.

43. Arjunan, V.; Mohan, S.; Ravindran, P.; Mythili, C. V. *Spectrochim. Acta* **2009**, 72 (4), 783-788.

44. Arjunan, V.; Mohan, S.; Balamourougane, P.S.; Ravindran, P. *Spectrochim. Acta* **2009**, 74, 1215-1229.

45. Srivastava, A.; Singh, V. B. *Indian Pure Appl. Phys.* **2007**, 45, 714-720.

46. Varsányi G. *Vibrational spectra of benzene derivatives*, Academic Press New York and, London, 1969, P. 215.

ORCID

ID 0000-0001-7947-0766 (K. Arıcı)

ID 0000-0001-7204-7957 (Ö. Gül)