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# The synthesis, molecular structure, FT-IR and XRD spectroscopic investigation of 4-[(2-{[(2-furylmethyl)imino]methyl}-4-methoxyphenoxy)methyl]benzonitrile: A comparative DFT study

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### ABSTRACT

4-[(2-{[(2-Furylmethyl)imino]methyl]-4-methoxyphenoxy)methyl]benzonitrile, a novel Schiff base compound, was prepared for the first time and its structural and vibrational properties were studied both experimentally and theoretically using FT-IR and XRD spectroscopic methods. FT-IR spectrum was recorded in the region of 4000–400 cm<sup>-1</sup>. The optimized geometric structures concerning to the minimum on the potential energy surface was investigated by Becke-3-Lee–Yang–Parr (B3LYP) hybrid density functional theory method together with 6-31(d) basis set. Vibrational wavenumbers were calculated using B3LYP/6-31G(d) level of theory. Comparison between the experimental and theoretical results indicates that density functional B3LYP method is able to provide satisfactory results for predicting vibrational wavenumbers and structural parameters of the prepared Schiff base compound. Furthermore, reliable vibrational assignments were made on the basis of total energy distribution (TED) calculated with scaled quantum mechanical (SQM) method.

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## 1. Introduction

Compounds with the structure XC=NY are known as Schiff bases, which are usually synthesized from the condensation of primary amines and active carbonyl groups. Some Schiff bases, are used as starting materials in the reactions of important drugs, such as antibiotics and antiallergic and antitumor substances [1–4]. Major advances have been made in these materials due to their interesting properties and potential in various applications, such as host guest chemistry, biochemical relevant studies of metal complexes, ion exchange, non-linear optics, electrical conductivity [5–8]. Synthesis of new Schiff bases and their metal complexes are still in the center of many recent investigations. 2-FuryImethylamine Schiff base derivatives are very useful biochemical materials having biological activities [9].

The B3LYP density functional model exhibits good performance on electron affinities, excellent performance on bond energies and reasonably good performance on vibrational frequencies and geometries of organic compounds [10–15]. A detailed quantum

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chemical investigation will aid in making assignments to the fundamental normal modes and clarifying the obtained experimental results for the investigated molecules.

In this study, first; 4-[(2-formyl-4-methoxyphenoxy)methyl]benzonitrile (I) was obtained by the reaction of 2-hydroxy-5-methoxy-benzaldehyde with 4-bromomethyl-benzonitrile. Later, 4-[(2-{[(2-furylmethyl)imino]methyl]-4-methoxyphenoxy)methyl]benzonitrile (II) was prepared by the condensation of compound (I) with 2-furylmethylamine in absolute ethanol (Scheme 1). Furthermore, X-ray crystallographic characterization, FT-IR vibrational wavenumbers and structural parameters were identified both experimentally and theoretically for compound (II) at B3LYP level of theory using 6-31G(d) basis set.

# 2. Experimental

### 2.1. Instrumentation

FT-IR spectrum (4000–400 cm<sup>-1</sup>) was recorded KBr pellet technique using Perkin–Elmer FT-IR 2000 spectrometer with single scan at a resolution of 4 cm<sup>-1</sup>. Crystallographic data were recorded on a Bruker Kappa APEXII CCD area detector diffractometer using Mo K $\alpha$  radiation (k = 0.71073 Å) at T = 100(2) K.

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Scheme 1. The structures of the new compounds (I and II).



Fig. 1. The optimized structure of compound II.

## 2.2. Synthesis of 4-[(2-formyl-4-methoxyphenoxy)methyl]benzonitrile (1)

2-Hydroxy-5-methoxy-benzaldehyde (0.388 g, 2.55 mmol), dissolved in 15 ml of DMF was added into 100 ml reaction flask equipped with a condenser and magnetic stir bar. Anhydrous NaOH (0.102 g, 2.55 mmol) was added to flask. After the mixture was stirred for 1 h and then 4-bromomethyl-benzonitrile (0.5 g, 2.55 mmol) was dissolved in 10 ml DMF and added into the reaction mixture. The resulting solution was heated for 6 days at 150 °C with continuous stirring, then the complete consumption of the starting material was observed by TLC (silica, eluent; CHCl<sub>3</sub>). After cooling, the product was poured into 250 ml cold water until the solution turned cloudy. The beige precipitate formed was isolated and recrystallized from ethanol. Yield 0.62 g, 73%, m.p. 110 °C.

# 2.3. Synthesis of 4-[(2-{[(2-furylmethyl)imino]methyl}-4-methoxy-phenoxy) methyl] benzonitrile (II)

The compound I (0.681 g, 2.55 mmol) was dissolved in 10 ml EtOH. 2-Furylmethylamine (0.171 g, 2.55 mmol) was added slowly dropwise to the reaction mixture. The resulting solution was stirred under reflux for 2 h and the reaction mixture was allowed to stand 2 h at room temperature. Yellow crystals formed and these were recrystallized from EtOH. Single crystals of compound II, suitable for X-ray analysis, were obtained by slow evaporation of ethanol at room temperature. Yield 0.40 g, 62%, m.p. 99 °C.

### 3. Calculations

For the calculations, compound II (Fig. 1) was first optimized at B3LYP/6-31G(d) level in the gas phase. The optimized geometric

structures concerning to the minimum on the potential energy surface were provided by solving self-consistent field (SCF) equation iteratively. Basic molecular structure was drawn considering the XRD data but no molecular restrictions were applied. For the vibrational calculations, the vibrational frequencies were calculated using the same method and the basis set under the keyword freq. No imaginary frequencies were observed, therefore; the optimized structure is not in the transition state for the investigated form. TED calculations, which show the relative contributions of the redundant internal coordinates to each normal vibrational mode of the molecule and thus make it possible to describe the character of each mode numerically, were carried out by the scaled quantum mechanical (SQM) program [16,17] using the output files created at the end of the wavenumber calculations. All the calculations were performed with Gaussian 03 program on a personal computer [18].

### 4. Results and discussion

### 4.1. Geometrical structures

The optimized geometric parameters (bond lengths, bond and dihedral angles) calculated by B3LYP/6-31G(d) are listed in Table 1. Obtained experimental XRD structure of compound II is given in Fig. 2. Some critical calculated/experimental geometric parameters are as following: R(10,12), R(11,16), R(16,19), R(29,30) and R(26,29) are found as 1.419/1.428 Å, 1.416/1.417 Å, 1.512/1.498 Å, 1.163/1.144 Å and 1.434/1.440 Å. A(6,10,12), A(3,11,16), A(2,31,33) and A(26,29,30) are found as 117.81/117.22°, 119.03/118.45°, 121.62/121.26° and 179.94/178.99°. D(4,3,11,16), D(3,11,16,17), D(6,10,12,13), D(31,33,34,36), D(33,34,37,38), D(19,20,22,26) and D(11,16,19,20) are found as 1.97/4.90°, 57.64/57.36°, 179.88/179.96°, 126.48/124.33°, 99.22/103.12°, 0.43/0.20° and 161.94/



Fig. 2. The structure obtained from XRD result.

176.14°. In general geometric parameters seem to an agreement with experimental findings. Possible differences could be due to the fact that while experimental findings were obtained at very low temperature and so the molecular rotations were restricted, the theoretical results were obtained for a single molecule in the gas phase without any intermolecular interactions.

## 4.2. FT-IR study

Compound II consists of 44 atoms, so it has 126 normal vibrational modes and it belongs to the point group  $C_1$  with only identity (E) symmetry operation. It is difficult to determine the vibrational assignments of compound II in the observed spectrum due to its low symmetry. According to the calculations, 24 normal vibrational modes of the title molecule are below the 200 cm<sup>-1</sup>. All the

Table 1

The magnitude of the optimized geometry parameters of compound II calculated by B3LYP method using 6-31G(d) basis set.

Coordinate <sup>a</sup>	Calc.	Exp.	Coordinate <sup>a</sup>	Calc.	Exp.	Coordinate <sup>a</sup>	Calc.	Exp.
R(1,2)	1.404	1.393	R(34,35)	1.098	0.970	A(19,21,25)	119.78	119.70
R(2,3)	1.409	1.397	R(34,36)	1.097	0.970	A(26,24,28)	119.80	120.10
R(3,4)	1.401	1.395	R(34,37)	1.497	1.482	A(26,22,27)	119.72	120.30
R(4,5)	1.391	1.376	R(37,38)	1.365	1.343	A(26,29,30)	179.94	178.99
R(5,6)	1.402	1.391	R(38,40)	1.082	0.930	A(2,31,32)	115.72	115.50
R(6,10)	1.367	1.372	R(38,39)	1.434	1.426	A(2,31,33)	121.62	121.26
R(10,12)	1.419	1.428	R(39,42)	1.081	0.930	A(32,31,33)	122.66	123.20
R(12,13)	1.092	0.960	R(39,41)	1.361	1.341	A(31,33,34)	119.78	119.48
R(12,14)	1.098	0.960	R(41,43)	1.079	0.930	A(33,34,37)	119.21	118.90
R(12,15)	1.098	0.960	R(41,44)	1.363	1.365	A(35,34,36)	105.87	107.00
R(1,7)	1.083	0.930	R(37,44)	1.374	1.377	A(34,37,44)	117.19	116.89
R(4,8)	1.084	0.930	A(6,10,12)	117.81	117.22	A(38,37,44)	109.35	109.79
R(5,9)	1.085	0.930	A(1,6,5)	119.27	120.01	A(37,44,41)	107.35	106.27
R(3,11)	1.373	1.369	A(6,1,2)	120.88	120.06	A(38,39,41)	105.95	106.31
R(11,16)	1.416	1.417	A(1,2,3)	119.32	119.38	A(37,38,39)	106.86	106.95
R(16,17)	1.102	0.970	A(2,3,4)	119.73	120.35	A(37,38,40)	125.97	126.50
R(16,18)	1.100	0.970	A(3,4,5)	120.18	119.57	A(38,39,42)	127.43	126.80
R(16,19)	1.512	1.498	A(4,5,6)	120.62	120.63	D(5,6,10,12)	179.86	174.46
R(19,20)	1.401	1.392	A(6,1,7)	122.26	120.00	D(4,3,11,16)	1.97	4.90
R(20,22)	1.390	1.379	A(6,5,9)	118.73	119.70	D(11,16,19,20)	161.94	176.14
R(22,27)	1.085	0.930	A(3,4,8)	120.90	120.20	D(3,11,16,17)	57.64	57.36
R(22,26)	1.405	1.398	A(3,11,16)	119.03	118.45	D(6,10,12,13)	179.88	179.96
R(26,29)	1.434	1.440	A(17,16,18)	107.26	108.40	D(1,2,31,32)	178.29	176.19
R(29,30)	1.163	1.144	A(11,16,19)	109.28	108.07	D(3,2,31,33)	178.07	177.77
R(24,26)	1.404	1.391	A(20,19,21)	119.14	119.13	D(2,31,33,34)	179.59	178.46
R(24,28)	1.085	0.930	A(19,20,22)	120.89	120.91	D(31,33,34,37)	3.70	1.80
R(21,24)	1.392	1.380	A(20,22,26)	119.75	119.35	D(31,33,34,36)	126.48	124.33
R(21,25)	1.083	0.930	A(19,21,24)	120.50	120.68	D(33,34,37,38)	99.22	103.12
R(19,21)	1.399	1.391	A(21,24,26)	120.14	119.75	D(38,39,41,44)	0.03	0.11
R(2,31)	1.474	1.475	A(22,26,24)	119.58	120.18	D(1,2,3,4)	0.04	1.10
R(31,32)	1.093	0.986	A(19,20,23)	119.83	119.50	D(19,20,22,26)	0.43	0.20

<sup>a</sup> Coordinate descriptions are carried out by the numbers in Fig. 1. R, A, and D characters represent bond length (Å), angle (°) and dihedral angle (°) type of coordinates, respectively.

Table 2	
Comparison of the experimental and calculated vibrational wavenumbers (cm <sup>-1</sup> ) of c	ompound II.

$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	Mode	$\text{TED}^{a} ( \geq 10\%)$	Exp. <sup>b</sup>	Scaled wave	Scaled waven.		B3LYP/6-31G(d)	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$			IR	$\overline{v^{\alpha}}$	$v^{\beta}$	$v^t$	I <sub>IR</sub>	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	V1	y 43-41 (89) + y 42-39 (10)	3146	3146	3153	3302	0.92	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Va	v 42-39 (51) + v 40-38 (45)	3108	3106	3113	3260	4.22	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	V <sub>7</sub>	v 27-22 (94)	3075	3069	3076	3221	5.50	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	V11	v 13-12 (91)	3023	3008	3015	3157	32.72	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	V13	v 15-12 (50) + v 14-12 (50)	2957	2940	2947	3086	41.29	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	V14	v 36-34 (72) + v 35-34 (28)	2928	2932	2939	3078	12.95	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	V16	v 18-16 (77) + v 17-16 (22)	2903	2890	2897	3034	29.54	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	V <sub>17</sub>	v 15-12 (46) + v 14-12 (45)	2864	2884	2891	3027	51.03	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	v <sub>18</sub>	v 17-16 (78) + v 18-16 (22)	2826	2855	2861	2996	34.19	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	V19	v 30-29 (89) + v 29-26 (11)	2224	2238	2241	2347	39.74	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	V20	v 33-31 (72)	1646	1653	1671	1728	86.03	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	V22	v 5-4 (19) + v 2-1 (15) + v 6-1 (11)	1611	1601	1612	1667	9.79	
	V24	v 6-5 (22) + v 3-2 (20) + v 4-3 (14) + v 6-1 (12)	1590	1572	1583	1637	3.48	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	v26 <sup>c</sup>	$\delta$ 27-22-20 (7) + $\delta$ 28-24-21 (7)	1510	1504	1507	1558	69.26	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	V28	δ 14-12-15 (40)	1496	1486	1493	1544	14.22	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	V32	$\delta$ 13-12-10 (15) + $\delta$ 13-12-14 (15)	1453	1458	1454	1504	17.41	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	52	$\delta$ 13-12-15 (13) + $\delta$ 14-12-10 (11)						
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		$\delta$ 15-12-10 (11) + $\delta$ 14-12-15 (10)						
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	V34	$v 2-1 (16) + \delta 6-5-9 (11) + v 5-4 (10)$	1421	1419	1420	1469	70.42	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	V36	$\delta$ 32-31-33 (31) + $\delta$ 32-31-2 (20)	1389	1393	1391	1439	59.40	
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	V <sub>38</sub> <sup>c</sup>	$v 24-21 (9) + \delta 18-16-11 (9) + \delta 18-16-19 (8)$	1375	1376	1379	1426	102.96	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		δ 17-16-11 (8) + δ 17-16-19 (7)						
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	V39	$\delta$ 35-34-33 (17) + $\delta$ 36-34-33 (15)	1319	1322	1326	1371	74.44	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	55	$\delta$ 35-34-37 (14) + $\delta$ 36-34-37 (11)						
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	V <sub>40</sub> <sup>c</sup>	v 3-2 (8) + v 5-4 (7)	1312	1305	1312	1357	42.03	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	V42	v 26-24 (18) + v 26-22 (17) + v 21-19 (15)	1299	1280	1294	1338	4.86	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		v 20-19 (11)						
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	V43	$v 2-1 (10) + \delta 5-4-8 (10)$	1277	1278	1281	1325	109.06	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	V45	v 11-3 (24) + v 4-3 (17) + v 10-6 (14)	1258	1253	1264	1307	89.01	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	V47	$v  11-3  (21) + \delta  2-1-7  (16) + v  10-6  (10)$	1217	1215	1218	1260	463.85	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	V49	v 19-16 (17) + v 29-26 (10)	1187	1192	1194	1235	10.81	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	V53	v 5-4 (10)	1161	1165	1168	1208	13.02	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	V54	v 29-26 (13) + v 19-16 (11)	1147	1160	1166	1206	24.69	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	V56	$v 44-41(29) + \delta 43-41-44(19) + v 41-39(14)$	1119	1140	1146	1185	18.06	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	V57	v 24-21 (10)	1111	1113	1115	1153	5.67	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	V59	v 44-41 (40) + v 41-39 (14) + v 39-38 (10)	1080	1074	1081	1118	4.25	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	V <sub>60</sub>	v 16-11 (45) + v 12-10 (25)	1049	1048	1057	1093	162.89	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	V <sub>62</sub>	$\delta$ 17-16-19 (12) + $\delta$ 18-16-19 (10)	1032	1016	1021	1056	1.39	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	V <sub>63</sub>	v39-38(30)+ $\delta$ 39-38-40(18)+ $\delta$ 40-38-37(10)	1015	1009	1011	1046	19.83	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	v <sub>64</sub> <sup>c</sup>	$v 21-19(9) + \delta 24-21-19(8) + \delta 26-22-20(8)$	991	1007	1004	1038	10.67	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		$\delta$ 26-24-21 (7) + $\delta$ 26-24-28 (7) + $\delta$ 23-20-19 (7)						
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		δ 22-20-19 (7) + v 26-22 (7) + v 26-24 (7)						
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	v <sub>66</sub>	v 31-2 (10) + v 12-10 (10)	973	966	968	1001	2.12	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	v <sub>69</sub>	$\tau$ 27-22-20-23 (42) + $\tau$ 29-26-22-27 (11)	934	929	938	970	0.16	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	v <sub>70</sub>	v 44-37 (12) + v 34-33 (11)	926	924	924	956	6.47	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	v <sub>71</sub>	$\tau$ 9-5-4-8 (34) + $\tau$ 10-6-5-9 (12) + $\tau$ 1-6-5-9 (10)	893	894	902	933	3.27	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	v <sub>72</sub>	δ 41-39-38 (21) + δ 44-41-39 (15) + v 44-37 (13)	884	884	888	918	27.98	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	V74	$\tau$ 10-6-1-7 (16) + $\tau$ 3-2-1-7 (10) + $\tau$ 31-2-1-7 (10)	865	865	868	898	4.24	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	v75 <sup>c</sup>	ν 4-3 (9) + ν 21-19 (8) + δ 19-16-11 (7)	850	842	844	873	6.60	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	v <sub>76</sub>	$\tau$ 42-39-38-40 (31) + $\tau$ 43-41-39-42 (17)	837	833	839	868	7.25	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	v <sub>78</sub> <sup>c</sup>	v 19-16 (7) + v 21-19 (7)	819	817	820	848	7.48	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	V79	$\tau$ 26-20-22-23 (14) + $\tau$ 29-26-22-27 (13)	805	805	811	839	42.20	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		τ 23-20-19-16 (10)						
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	v <sub>81</sub>	$\tau$ 8-4-3-11 (22) + $\tau$ 6-5-4-8 (18)	782	787	794	821	19.80	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		$\tau$ 10-6-5-9 (14) + $\tau$ 9-5-4-3 (13)						
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	v <sub>82</sub>	τ 40-38-37-44 (12)	757	772	772	798	37.13	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	v <sub>83</sub> <sup>c</sup>	v 29-26 (7)	712	727	726	751	34.86	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	v <sub>84</sub>	$\tau$ 43-41-39-38 (31) + $\tau$ 37-44-41-43 (18)	703	714	718	743	22.62	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		$\tau$ 44-41-39-42 (12) + $\tau$ 43-41-39-42 (10)						
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		$\tau$ 42-39-38-37 (10)						
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	v <sub>89</sub> <sup>c</sup>	$\delta$ 5-4-3 (9) + $\delta$ 6-5-4 (8) + $\delta$ 34-33-31 (8) $\delta$ 3-2-1 (7)	632	633	629	651	2.18	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	v <sub>91</sub>	δ 4-3-11 (11) + δ 10-6-1 (10)	603	593	595	615	7.47	
$ \begin{array}{cccccc} \nu_{94} & \tau & 30-26-29-24 & (12) + \tau & 30-26-29-22 & (12) \\ \nu_{98} & \nu & 37-34 & (12) \end{array} & \begin{array}{ccccccccccccccccccccccccccccccccccc$	v <sub>92</sub>	$\tau$ 1-6-5-9 (13) + $\tau$ 1-6-5-4 (11)	588	576	588	608	4.58	
v <sub>98</sub> v 37-34 (12) 466 458 468 484 5.77	v <sub>94</sub>	$\tau$ 30-26-29-24 (12) + $\tau$ 30-26-29-22 (12)	548	553	552	571	14.36	
	V <sub>98</sub>	v 37-34 (12)	466	458	468	484	5.77	

 $v^{\alpha}$ : Wavenumbers are scaled by SQM methodology,  $v^{\beta}$ : dual scaling factors were used, 0.955 above 1800 cm<sup>-1</sup>, 0.967 under 1800 cm<sup>-1</sup> [10],  $v^{t}$ : unscaled wavenumbers, IR: infrared,  $I_{IR}$ : infrared intensities, waven.: wavenumbers, Exp.: experimental.

<sup>a</sup> Our vibrational wavenumbers assignments on the basis of total energy distribution (TED) calculations.

<sup>b</sup> Our experimental IR wavenumbers, v,  $\delta$ ,  $\tau$ : Stretching, bending and torsion, respectively.

<sup>c</sup> TED  $\geq$  7.

experimental and theoretical vibrational modes obtained in this study are given in Table 2. The assignments of the vibrational modes

of the title molecule are provided by animation option of the Gauss-View package program for the B3LYP/6-31G(d) level of calculation.



Fig. 3. FT-IR spectrum of compound II.



Fig. 4. Plot of calculated vs. experimental wavenumbers of compound II.

Using the animation we identified vibrational motions of the studied molecule. For a heteroaromatic structure CH stretching vibrations are commonly appeared in the region of 3000–3200 cm<sup>-1</sup>. Experimental/theoretical (SQM methodology/with dual scaling factor) CH stretching modes were found as 3146/(3146/3153) cm<sup>-1</sup>, 3108/(3106/3113) cm<sup>-1</sup> and 3075/(3069/3076) cm<sup>-1</sup> (Fig. 3). CH<sub>3</sub> stretching modes were found as 3023/(3008/3015) cm<sup>-1</sup>, 2957/ (2940/2947) cm<sup>-1</sup> and 2864/(2884/2891) cm<sup>-1</sup>. CH<sub>2</sub> stretching modes were observed at 2928/(2932/2939) cm<sup>-1</sup>, 2903/(2890/ 2897) cm<sup>-1</sup> and 2826/(2855/2861) cm<sup>-1</sup>. C=N and C=N stretching vibrations were observed at 2224/(2238/2241) cm<sup>-1</sup> and 1646/ (1653/1671) cm<sup>-1</sup>, respectively. The carbon–carbon stretching modes of the phenyl group occur in the range of 1620–1320 cm<sup>-1</sup> [19]. In this study, the carbon-carbon stretching vibrations were observed at  $1611 \text{ cm}^{-1}$ ,  $1590 \text{ cm}^{-1}$ ,  $1421 \text{ cm}^{-1}$ ,  $1312 \text{ cm}^{-1}$ ,  $1299 \text{ cm}^{-1}$ ,  $1277 \text{ cm}^{-1}$  and  $1258 \text{ cm}^{-1}$ . The corresponding scaled theoretical values (SQM methodology/dual scaling) of these vibrations are 1601/1612  $cm^{-1},\ 1572/1583\ cm^{-1},\ 1419/1420\ cm^{-1},$  $1305/1312 \text{ cm}^{-1}$ ,  $1280/1294 \text{ cm}^{-1}$ ,  $1278/1281 \text{ cm}^{-1}$  and  $1253/1281 \text{ cm}^{-1}$  $1264 \text{ cm}^{-1}$ . We also made measurements in the frequency region of 1300–400  $\text{cm}^{-1}$ . These vibrations have revealed to be mixed type of vibrations as given in Table 2. In general, B3LYP/6-31G(d) level of calculation with the dual scaling factors [10] and SQM [16,17] methodology used in this study provided reasonable agreement with the experimental findings. The correlation values between the experimental and calculated vibrational wavenumbers are found to be 0.99983 ( $v^{\alpha}$ ) and 0.99985 ( $v^{\beta}$ ) and presented in Fig. 4. The results obtained in this study also indicate that B3LYP/6-31G(d) method is reliable and it is helpful for the understanding of vibrational spectrum and structural parameters of prepared Schiff base compound.

# 5. Conclusion

We prepared a novel Schiff base compound and conducted the experimental-theoretical structural and vibrational analysis of this compound for the first time. The structural parameters, IR wavenumbers and activities of vibrational bands were calculated with B3LYP methods and 6-31G(d) basis set. Calculated bond lengths are, in general, slightly bigger than experimental ones which are possibly due to the shortening of the bond lengths of the title molecule during the experimental measurements conducted at very low temperature. However, similar generalizations are not possible for bond-dihedral angles. In order to make a comparison with experimental wavenumbers, we calculated root mean square deviation (RMSD) based on the calculation. The following mean absolute error values were found for vibrational wavenumbers: 7.80 cm<sup>-1</sup> for SQM methodology and 7.63 cm<sup>-1</sup> for dual scaling factor. Any differences observed between the experimental and the calculated wavenumbers could be due to the fact that the calculations have been performed for single molecule in the gaseous state contrary to the experimental values recorded in the presence of intermolecular interactions. Henceforth, the assignments made at B3LYP/6-31G(d) level of theory with only reasonable deviations from the experimental values seem feasible.

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