Quantum mechanical investigation of vibrational and electronic spectra of some 5-substituted isoquinolines

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Fourier Transform infrared (FTIR) and FT-Raman spectra of 5-bromoisoquinoline (5-BIQ), 5-aminoisoquinoline (5-AIQ) and 5-nitroisoquinoline (5-NIQ) have been recorded and analyzed. The geometric bond lengths and bond angles have been optimized. The equilibrium geometry, bonding features and harmonic vibrational frequencies have been investigated by *ab-initio* and density functional theory (DFT) methods. The assignments of the vibrational spectra have been carried out. The calculated HOMO and LUMO energies indicate that charge transfer occurs within the molecule. Stability of the molecule due to conjugative interactions arising from charge delocalization has been analyzed using extensive natural bond orbital (NBO) analysis. Electronic spectral properties have been computed in benzene medium for the three compounds and compared with the experimental values. Thermodynamic parameters such as zero point vibrational energy (ZPVE), thermal energy and specific heat capacity, entropy of 5-BIQ, 5-AIQ and 5-NIQ at 298 K in ground state have been calculated by HF and DFT methods.

Keywords: Vibrational spectra, Electronic spectra, 5-Substituted isoquinolines, DFT, *Ab initio*, FMO, NBO analysis, Thermodynamic properties

1 Introduction

Isoquinoline derivatives are biologically important nitrogen containing hetero cyclic aromatic compounds. They are used as solvents for the extraction of several medicinally useful natural products and also employed as a corrosion inhibitor. Quinoline and isoquinoline derivatives are used as effective and efficient anesthetics[1]. Its anesthetic activity is similar to those of procaine or cocaine when injected. In pharmaceutical synthesis 5-bromoisoquinoline is used as a synthetic intermediate. It is a starting material employed in metal-catalyzed aminomethylationand amination-reactions[2-4]. 5-Nitroisoquinoline derivatives are versatile heterocyclic building blocks. For example in 6-methyl 5-nitroisoquinoline the ortho substituted nitroisoarene motif present is amenable to the Leimgruber-Batchoindole synthesis. Alternatively, the nitro group can be reduced to an amino group and enable access to further functionalization[5,6]. It has been demonstrated that 5-aminoisoquinoline (5-AIQ) can reduce ischaemia/reperfusion injury of the heart, intestine and liver and 5-AIQ has also been shown to

provide beneficial effects in rodent models lung injury[6-9]. 5-AIQ possesses interesting photo physical properties and it enhanced the intensity of luminal-H_2O_2 chemiluminescence in the presence of horseradish peroxidase enzyme[10]. It may be pointed out that there are some computational and spectral studies[11,12] on quinoline derivatives in recent years. Arjunan *et al*[13]. analyzed the molecular structure and NMR of 4-bromoisoquinoline by DFT method. Literature survey reveals that neither the complete Raman and IR spectra nor the quantum mechanical calculations for 5-substituted isoquinoline derivatives have been reported so far. Therefore, the detailed theoretical and experimental investigation of the vibrational spectra of three 5-substituted isoquinolines has been undertaken. In the present study, it is planned to have experimental as well as theoretical investigation of vibrational characteristics and electronic spectral characteristics of 5-bromoisoquinoline, 5-amino-isoquinoline and 5-nitroisoquinoline and thermo-dynamic properties are computed for these molecules and discussed.

2 Experimental Details

The compounds under investigation namely, 5-BIQ, 5-AIQ and 5-NIQ were spectral grade samples purchased from M/S Aldrich Chemicals, USA and used as such without further purification. The FT-IR spectra of the compounds were recorded in Perkin-Elmer Spectrometer in the range 4000-100 cm^{-1} with KBr pellet technique. The spectral resolution is 0.1 cm^{-1}. The FT-Raman spectra of the compounds were also recorded in the BRUKER RFS 27 Standalone FT-Raman Spectrometer in the frequency range 50-4000 cm^{-1}. The Laser source is Nd:YAG laser source operating at 1064 nm line with 200 mW power. The spectra were recorded with scanning speed of 20 cm^{-1}. The frequencies of all sharp bands are accurate to ±1 cm^{-1}. UV-Vis. spectra were recorded on a Shimadzu UV-1650 model spectrophotometer. Absorbance was measured at the scanning rate of 0.2 nm/s and a slit width of 1 cm. The solvent benzene was used for the base line correction.

2.1 Computational Details

The molecular geometry optimization and vibrational frequency calculations were carried out at 5-substituted isoquinolines, with GAUSSIAN 09W software package, HF functional[14] combined with standard 6-311++G(d,p) basis set (large basis) and the density functional method used is B3LYP i.e. Becke's three-parameter hybrid functional with the Lee-Yang-Parr correlation functional method[15,16] combined with 6-311++G(d,p) basis set. The prediction of Raman intensities was carried out by the following procedure. The Raman activities (S-Ra) calculated by Gaussian 09 program converted to relative Raman intensities (I-Ra) using Eq. (1) derived from the intensity theory of Raman scattering[16, 17]. Scaled IR and Raman frequencies are reported for the investigated molecules.

$$I_i = \frac{[f(v_0 - v_i)^4 S_i]}{v_i[1 - \exp(-hcv_i / kT)]} \qquad \ldots(1)$$

In Eq.(1), v_0 is the exciting frequency (in cm^{-1}), v_i is the vibrating wave number of the ith normal mode h, c and k are the fundamental constants S_i is the Raman scattering activity of the normal mode v_i and f is a normalization factor for all peak intensities. Mulliken population analysis and Natural Bond Orbital (NBO) analysis have been carried out on the three hetero-cyclic aromatic molecules by HF and DFT methods. Thermodynamic parameters such as rotational constants, rotational temperature, vibrational temperature and

dipole moment have been computed for the title compounds by the two different methods. Scale factors have been included to get the accurate Zero-Point Vibration Energies (ZPVE) and the entropy, S vib(T) and the molar capacity at constant volume.

3 Results and Discussion

The Density Functional Theory (DFT) and *ab-initio* (HF and MP2) calculations have been performed by earlier researchers on the quinoline and its derivatives, namely quinaldine and quinaldic acid to investigate their possible role as corrosion inhibitors for mild steel in acidic medium[19,20]. In the present paper, the results obtained in *ab-initio* and DFT calculations on three 5-substituted isoquinolines have been reported.

3.1 Molecular Geometry

The molecular structures of 5-bromoisoquinoline, 5-aminoisoquinoline and 5-nitroisoquinoline along with the atom numbers as per IUPAC rule are shown in Fig. 1. The optimized structural parameters obtained by HF and B3LYP with 6-311++G(d,p) basis set are presented as supplementary data (Table S1). The calculated values are compared with available experimental results. The bond length values obtained in both HF and B3LYP/6-311++G(d,p) methods are similar and they are closer to experimental data. The comparative plots of bond lengths and bond angles obtained by two different methods for the three heterocyclic molecules are shown in Figs. 2 and 3, respectively. It is found that both HF and DFT levels of theory in general estimate almost same values of bond lengths and bond angles. The perfect and hexagonal structure of benzene in the three molecules is slightly distorted by the substitution of hetero atoms inside the heterocyclic ring and outside the benzene rings and is evident by the order of C-C bond length of ring as C5-C6>C9-C10>C7-C8 and C5-C10>C6-C7>C8-C9. It may be pointed out that C1-N2 is shorter than N2-C3 bond. This is because the benzene ring is closer to C1 and shortens the C1-N2 bond. The bond angles containing the bridged carbon atoms are less than the bond angles containing normal sp^2 hybridized carbon atoms. The calculated C-Br bond length in 5-BIQ obtained by HF/6-311++G (d, p) method is 1.902Å and by B3LYP method is 1.9198Å which are closer to the reported experimental values[21] of 1.867Å. The interesting observation is that the bond angles C6-C7-H15 in 5-BIQ and 5-AIQ obtained in HF method are 119.96 and 119.48, respectively while similar bond

(a) 5-Bromoisoquinoline
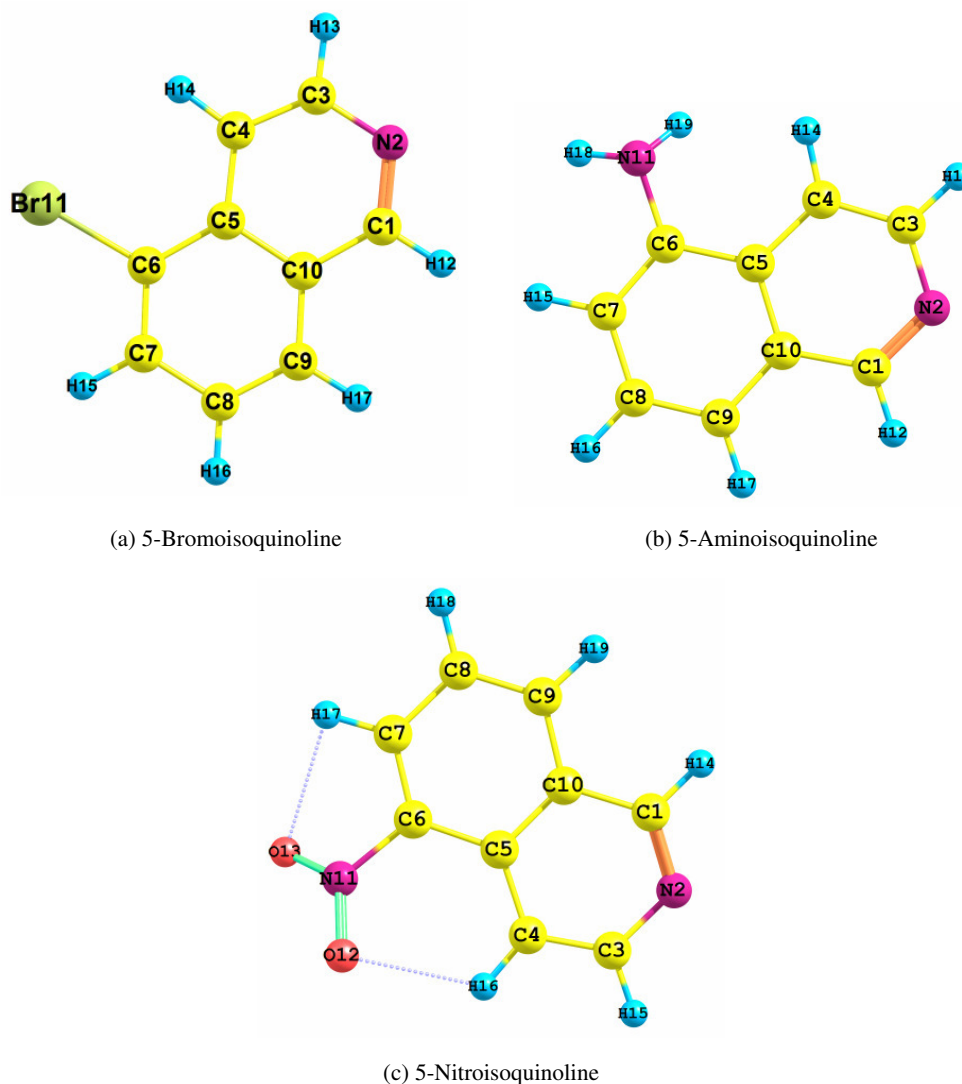
(b) 5-Aminoisoquinoline

(c) 5-Nitroisoquinoline

Fig. 1 — Optimized structures of 5-substituted isoquinolines

angle C6-C7-H17 in 5-NIQ obtained by the same method is 119.18 suggesting that there is intra molecular hydrogen bond between nitro group and hydrogen attached to C7 in 5-NIQ which is absent in other two molecules. The same trend in bond angles is observed in B3LYP/6-311++G(d,p) method. The consequence of hydrogen bond is that C7-H17 bond is compressed and it is slightly shorter in 5-NIQ than the corresponding C-H bond lengths (C7-H15) in the other two molecules [Table 1(a)].

3.2 Vibrational Spectra

5-Bromoisoquinoline consists of 17 atoms hence, undergoes 45 normal modes of vibrations are active both in Raman and infrared absorption and all the frequency modes are produced in A spices.5-AIQ and 5-NIQ molecules contain 19 atoms each and hence possess 51 modes of vibrations. The observed and theoretical frequencies using HF and DFT (B3LYP) with 6-311++G(d,p) basis set, infrared and Raman activities and vibrational assignments for the three molecules are presented in Tables 1-3.The recorded FT-IR spectra of the three compounds under investigation are shown in Fig. 4. Figure 5 shows the FT Raman spectra of the three compounds investigated in the present work. The detailed vibrational assignment of experimental wave number is based on normal mode analysis and comparison with theoretically calculated values using HF and B3LYP with 6-311++G (d,p) basis sets.
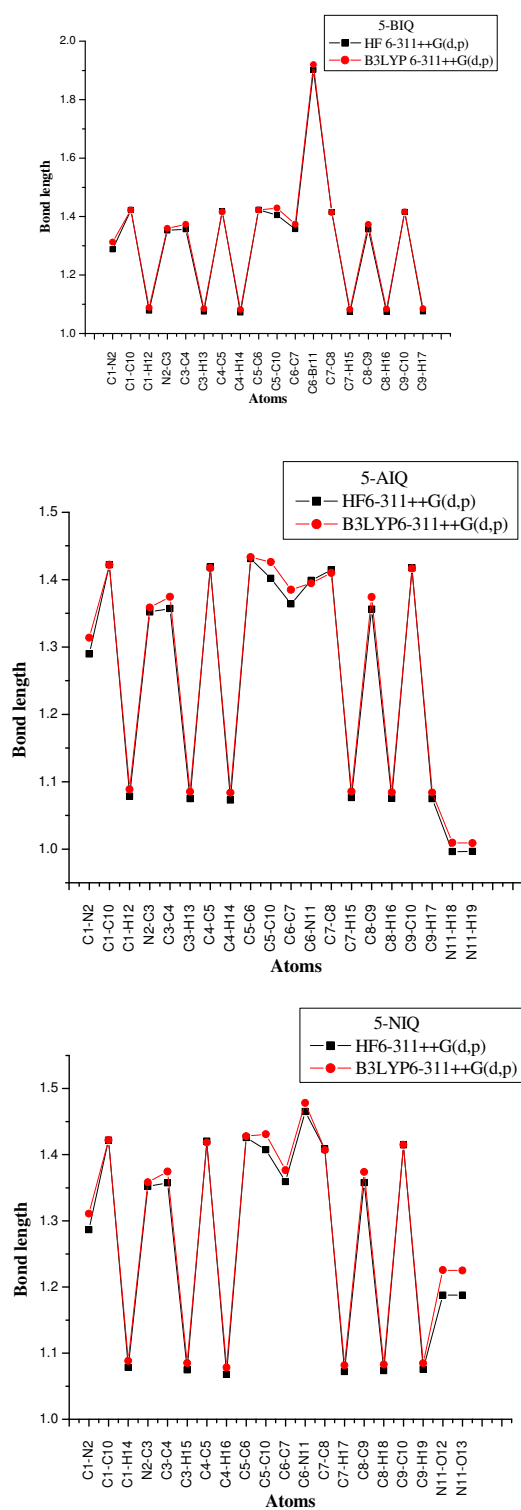
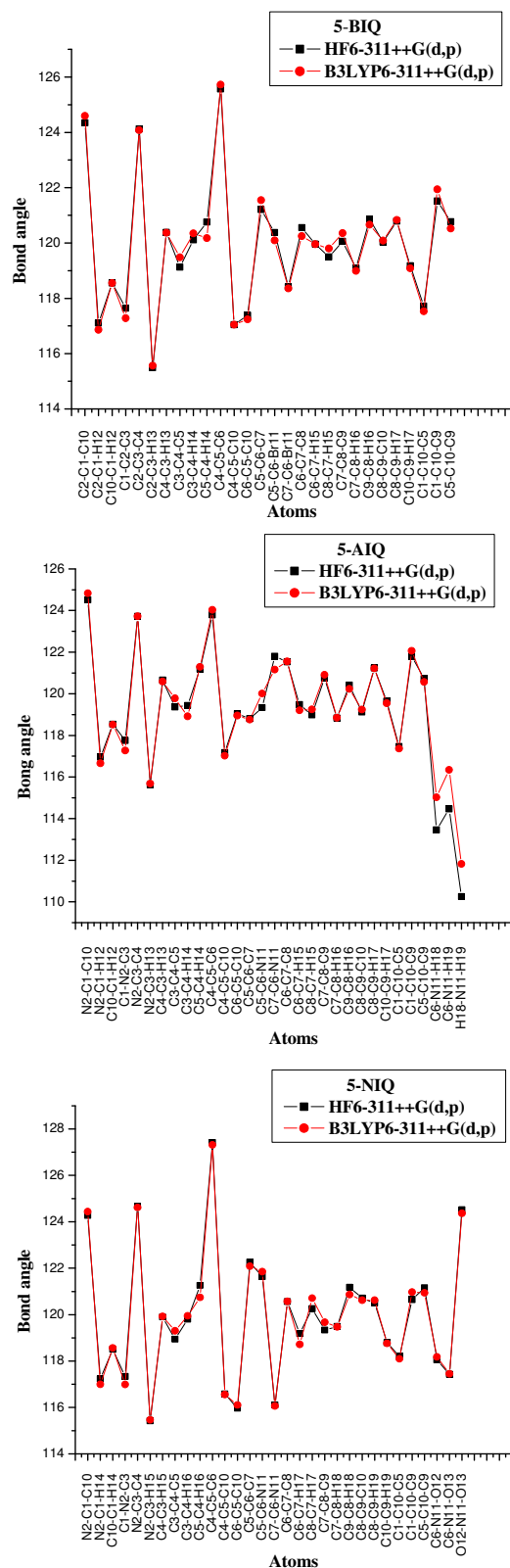Fig. 2 — Bond length of various bonds in 5-substituted isoquinolines

Fig. 3 — Bond angles of various angles in 5-substituted isoquinolines

Table 1 — Experimental and calculated frequencies, IR intensity(I-IR), Raman activity(S), Raman intensity(I-Ra) and vibrational assignment of 5-bromo isoquinoline using HF/6-311++G(d,p) and B3LYP/6-311++G(d,p) basis sets

S.NO	Experimental		HF/6-311++G(d,p)				B3LYP/6-311++G(d,p)				Scaled
	IR	Raman	Freq.	I-IR	S	I-Ra	Freq.	I-IR	S	I-Ra	Vibrational assignment
1		176	188	0.0375	2.3942	9.186	173	0.0269	2.9191	12.187	C-C-C in plane bending
2			198	0.0103	3.4961	12.640	198	0.0053	3.4991	12.690	C-C-N in plane bending
3		235	256	0.1663	0.1825	0.499	236	0.112	0.1317	0.394	C-C-C in plane bending
4			285	1.9882	0.1053	0.255	272	1.8563	0.0331	0.084	C-C-C out of plane bending
5		298	300	1.1129	5.4216	12.390	308	1.4028	3.869	8.583	C-C-C out of plane bending
6		412	432	0.564	1.4128	2.114	436	0.5439	1.6538	2.449	C-C-C out of plane bending
7	455		469	3.8178	2.6643	3.614	445	3.8613	1.3955	2.018	C-Br Stretching
8			487	2.0646	9.1239	11.825	506	1.0317	10.3071	12.736	C-Br Stretching
9		509	497	0.455	10.6929	13.495	510	3.6073	2.7748	3.399	C-Br Stretching
10			525	1.696	14.9871	17.706	535	1.0327	18.3519	21.158	Ring vibration
11	528	542	530	4.4337	8.2493	9.633	558	2.4088	0.4043	0.443	C-Br Stretching
12			570	3.2007	0.3242	0.345	564	0.3131	14.543	15.696	C-H out of plane bending
13	667	675	669	5.1766	0.7076	0.614	662	3.5062	0.8003	0.705	C-H out of plane bending
14			704	38.386	4.1355	3.359	711	34.6238	1.1621	0.932	Ring stretching
15	746		777	5.7722	3.3557	2.388	769	6.9923	0.831	0.599	C-H out of plane bending
16			777	7.8291	1.3468	0.957	796	2.8306	5.5372	3.812	C-H out of plane bending
17		795	799	3.9972	36.4357	24.959	828	2.4503	30.5894	19.939	C-H out of plane bending
18			874	24.052	1.1141	0.673	833	13.7559	0.9644	0.623	C-H out of plane bending
19			902	12.790	14.1159	8.160	864	70.2256	0.1506	0.093	C-H out of plane bending
20			906	77.557	1.5067	0.865	940	3.0295	0.3573	0.195	C-H out of plane bending
21	960		953	16.104	3.2092	1.714	962	1.2048	0.3261	0.172	C-H in plane bending
22			991	3.3497	0.54	0.272	963	16.6192	1.4313	0.752	C-H in plane bending
23			1002	10.518	18.9505	9.394	982	0.4657	2.4527	1.253	C-C-C out of plane bending
24			1011	0.6951	2.9638	1.451	1006	1.4565	0.4914	0.242	C-H in plane bending
25	1029	1030	1027	0.9287	6.2915	3.009	1023	4.0944	7.2769	3.499	C-H in plane bending
26	1056		1047	1.7357	1.2793	0.595	1069	6.0746	49.2131	22.161	C-H in plane bending
27			1090	5.2555	98.8263	43.202	1121	6.6887	5.4145	2.267	C=C Stretching
28			1122	25.0726	75.8879	31.748	1145	14.9352	2.7361	1.109	C=N Stretching
29	1130	1136	1128	14.7337	107.68	44.674	1185	18.198	57.9415	22.253	C=C Stretching
30	1195		1184	18.6711	1.4149	0.544	1222	9.5699	15.6767	5.737	C-H in plane bending
31			1242	2.676	37.9596	13.532	1271	18.4884	3.8033	1.306	C-H in plane bending
32	1253	1265	1260	23.9221	3.6091	1.257	1276	7.385	61.3694	20.934	C-H in plane bending
33			1302	7.109	37.238	12.295	1313	6.6442	30.3559	9.879	C-H in plane bending
34	1365		1388	10.1312	11.2246	3.331	1397	20.4411	16.7442	4.915	C-H in plane bending
35			1419	3.9526	42.9708	12.272	1415	2.4139	40.7382	11.701	C-H in plane bending
36			1434	11.9591	16.598	4.659	1447	3.5019	11.1397	3.079	C-H in plane bending
37	1477	1484	1473	32.3937	3.0013	0.804	1481	30.1882	3.9691	1.053	C-C-C stretching
38			1516	8.9099	88.3252	22.506	1526	10.9126	73.1419	18.406	C-C-C stretching
39	1570	1556	1558	44.3497	22.5196	5.464	1552	14.6603	16.5533	4.043	C-C-C stretching
40			2820	1.5652	42.644	2.831	2905	1.3846	34.9298	2.138	C-H Stretching
41			2830	0.3132	45.7737	3.010	2909	5.3563	95.3018	5.808	C-H Stretching
42			2836	15.0117	151.37	9.904	2914	1.4516	70.519	4.279	C-H Stretching
43			2836	0.0723	19.0626	1.246	2915	8.5158	94.1123	5.704	C-H Stretching
44			2843	11.3505	254.588	16.542	2925	9.2493	277.46	16.664	C-H Stretching
45	2854		2854	2.5892	179.64	11.542	2935	2.134	202.84	12.068	C-H Stretching

*For wave numbers less than 1700 cm⁻¹, scale factor of 0.903 and for frequencies greater than 1700 cm⁻¹, scale factor of 0.924 are used in the present calculation. (Ref. 39)

Table 2 — Experimental and calculated frequencies, IR intensity(I-IR), Raman activity(S), and Raman intensity(I-Ra) of 5-aminoisoquinoline using HF/6-311++G and B3LYP/6-311++G basis sets

S.No	Experimental		Freq*	HF/6-311++G(d,p)			Freq*	B3LYP/6-311++G(d,p)			Scaled Vibrational assignment
	IR	Raman		I-IR	S	I-Ra		I-IR	S	I-Ra	
1			226	10.042	1.125	3.163	211	46.414	1.942	6.436	NH2 Twisting
2			259	0.568	0.482	1.162	238	7.0775	0.8903	2.589	NH2 Twisting
3		263	274	49.044	1.671	3.779	241	61.645	0.405	1.157	C-N(H2) in plane bending
4		307	331	2.884	0.895	1.630	318	4.9539	0.5619	1.176	C-N(H2) in plane bending
5			404	121.826	2.145	3.091	361	72.2596	2.7035	4.895	C-C-C out of plane bending
6	459	461	458	0.804	1.931	2.389	460	8.2747	1.2317	1.676	C-C-C in plane bending
7	469		462	27.064	9.395	11.501	465	9.9401	8.3739	11.234	C-C-C out of plane bending
8	487	485	483	12.748	2.491	2.889	482	1.9574	5.3517	6.869	C-C-C in plane bending
9			496	2.713	9.181	10.302	518	9.1324	0.5065	0.596	C-C-C in plane bending
10	514	514	528	10.478	4.096	4.241	530	1.608	6.8186	7.798	C-N-C in plane bending
11			535	13.547	0.399	0.407	547	0.8452	3.6656	4.026	C-N-C in plane bending
12			576	2.245	26.175	24.295	589	1.0899	1.9689	1.970	C-N-C in plane bending
13		597	600	1.171	0.289	0.254	599	1.894	25.3418	24.820	NH2 wagging&twisting
14	648		684	3.550	0.259	0.191	675	35.268	17.6044	14.777	C-C-C in plane bending
15	728	734	721	36.156	7.453	5.126	680	7.7996	3.2424	2.695	C-C-C in plane bending
16	750		752	12.744	27.606	17.930	744	15.7889	27.5246	20.269	C-H out of plane bending
17			780	1.248	0.920	0.568	779	9.035	1.0989	0.760	C-H out of plane bending
18	794	799	787	10.125	1.205	0.734	798	2.2337	0.6426	0.430	C-H in plane bending
19			836	8.383	14.822	8.287	835	13.7853	0.5816	0.366	C-H in plane bending
20	866	886	871	23.993	1.757	0.926	859	49.048	4.8819	2.951	C-H out of plane bending
21			901	83.084	0.968	0.485	865	24.9398	6.7856	4.059	NH2 rocking
22	925		910	7.284	10.675	5.273	938	2.667	0.6022	0.321	C-H in plane bending
23	960		982	1.951	2.105	0.929	960	1.8916	0.4643	0.239	C-H in plane bending
24			993	1.083	3.771	1.636	984	0.8412	1.997	0.992	C-H in plane bending
25			1004	1.371	0.166	0.071	1004	1.2447	0.4965	0.239	C-N stretching
26		1022	1021	18.453	24.322	10.102	1012	2.2664	1.0921	0.520	C-H in plane bending
27			1024	1.169	6.498	2.686	1035	8.8925	2.6524	1.221	C-H in plane bending
28	1040	1041	1041	1.598	0.991	0.399	1068	6.6715	60.0972	26.414	C-H in plane bending
29	1096	1097	1085	1.378	82.721	31.232	1121	4.2088	5.0071	2.041	C-H in plane bending
30			1123	29.679	163.274	58.410	1162	16.3168	10.5599	4.074	C-C in plane bending
31	1171		1146	12.034	7.138	2.470	1168	12.4487	44.5258	17.038	C-N(H2) stretching
32	1198		1184	36.964	0.423	0.139	1213	30.4027	0.3823	0.138	C-N stretching
33	1226	1208	1231	6.375	2.980	0.916	1230	0.3528	8.6157	3.032	C-C stretching
34	1260		1251	15.637	58.774	17.600	1265	20.452	4.8694	1.637	C-C stretching
35	1295	1259	1255	13.957	6.730	2.003	1294	8.208	71.6876	23.240	C-C stretching
36		1300	1302	5.244	37.397	10.450	1314	7.3533	36.8457	11.648	C-N stretching
37	1381	1381	1390	27.054	19.357	4.826	1401	28.1084	29.4988	8.367	C-C stretching
38			1415	8.818	53.997	13.045	1414	10.2435	41.6252	11.620	C-C stretching
39	1447	1455	1442	3.487	7.765	1.813	1458	1.697	6.1282	1.622	C-C stretching
40	1494	1494	1472	39.121	2.882	0.648	1482	33.6985	6.3847	1.642	C=N stretching
41			1520	11.092	86.450	18.301†	1536	10.6039	79.2121	19.112	C-C out of plane bending
42	1581	1571	1562	21.537	15.575	3.135	1561	7.0331	12.9491	3.036	(C-C) skeletal vibration
43	1644	1643	1642	26.406	14.900	2.722	1630	24.6361	21.0795	4.564	C=C stretching vibration
44			2815	2.611	46.928	2.366	2902	2.5647	38.8319	2.110	C-H stretching vibration
45			2826	1.795	54.876	2.736	2907	4.7405	91.3274	4.936	C-H stretching vibration
46			2832	21.264	140.569	6.965	2912	1.3683	84.0432	4.519	C-H stretching vibration
47			2832	3.640	17.731	0.878	2913	20.4135	92.1111	4.948	C-H stretching vibration
48			2839	16.794	253.851	12.482	2923	13.6461	266.8495	14.191	C-H stretching vibration
49			2851	7.201	186.410	9.053	2933	5.4495	217.7858	11.475	C-H stretching vibration
50	3170	3172	3168	35.412	225.430	10.677	3185	27.9617	287.1222	14.362	NH2 symmetric stretching
51	3308	3310	3296	54.842	70.300	2.958	3312	44.1454	77.9218	3.472	NH2 asymmetric stretching

*For wave numbers less than 1700 cm⁻¹, scale factor of 0.903 and for frequencies greater than 1700 cm⁻¹ scale factor of 0.924 are used in the present calculation. (Ref. 39)

Table 3 — Experimental and calculated frequencies, IR intensity (I-IR), Raman activity (S), and Raman intensity (I-Ra) of 5-nitroisoquinoline using HF/6-311++G and B3LYP/6-311++G basis sets

S.No	Experimental		HF/6-311++G(d,p)				B3LYP/6-311++G(d,p)				Scaled Vibrational assignment
	IR	Raman	Freq*	I-IR	S	I-Ra	Freq*	I-IR	S	I-Ra	
1			51	1.105	4.106	55.891	-221	1.219	5.581	-21.326	NO$_2$ twisting
2			194	2.762	3.560	11.816	140	2.125	3.740	19.332	C-N Out-of-plane-bending
3		209	242	6.341	2.300	5.991	224	4.621	2.648	8.200	C-N Out-of-plane-bending
4			259	0.649	0.539	1.298	238	0.450	0.692	2.003	C-C-C Out-of-plane-bending
5			277	0.981	1.079	2.412	255	0.844	1.427	3.835	C-N Out-of-plane-bending
6			321	5.359	3.696	6.989	325	0.768	2.935	5.999	C-N in-plane-bending
7			384	1.585	1.898	2.909	370	0.300	2.057	3.621	C-NO$_2$ Out-of-plane bending
8		358	434	1.042	2.097	2.771	430	0.285	1.332	1.965	C-C-C Out-of-plane bending
9	469	448	472	0.561	4.656	5.546	464	0.728	4.543	6.112	C-C-C Out-of-plane bending
10	500	472	487	0.122	8.935	10.249	502	1.672	10.102	12.329	C-C-C Out-of-plane bending
11		505	511	4.176	4.349	4.696	523	11.008	2.146	2.493	C-C-C-in plane bending
12			526	1.821	19.784	20.600	533	1.031	14.229	16.150	C-C-C-in plane bending
13	542	545	534	9.760	1.523	1.558	564	0.595	12.055	12.735	C-C-C-in plane bending
14	587	589	585	22.837	2.237	2.033	592	3.026	3.183	3.166	C-in-plane bending
15	674	676	665	17.014	0.572	0.439	660	6.837	1.217	1.051	C-C Out-of-plane bending
16			699	41.020	1.535	1.102	703	31.675	1.633	1.298	C-C Out-of-plane bending
17	732	738	756	2.882	7.356	4.742	720	2.237	3.683	2.837	C-H Out-of-plane bending
18			772	57.661	3.314	2.075	772	11.855	2.216	1.553	C-H Out-of-plane bending
19			778	27.627	18.846	11.675	794	7.241	19.229	12.964	C-H Out-of-plane bending
20			779	8.739	13.381	8.270	802	5.419	14.715	9.780	C-H Out-of-plane bending
21	799	801	800	44.257	14.299	8.517	849	12.832	0.688	0.423	N-O$_2$ deformation
22	874	876	885	37.855	2.304	1.186	855	13.411	5.011	3.049	C-H in-plane bending
23			906	94.284	13.867	6.898	871	68.231	1.243	0.737	C-H in-plane bending
24	927		912	95.646	3.392	1.672	947	9.665	1.037	0.545	C-H in-plane bending
25		969	922	24.320	12.517	6.063	958	37.274	13.865	7.162	C-H in-plane bending
26			995	3.393	0.441	0.191	979	7.218	5.323	2.665	C-H in-plane bending
27			1004	12.765	5.143	2.193	993	0.891	1.648	0.808	C-H in-plane bending
28	1011	1012	1021	120.309	69.233	28.750	1015	11.300	1.944	0.922	C-H in-plane bending
29			1028	17.723	7.615	3.128	1027	102.909	70.051	32.629	C-H in-plane bending
30	1039	1041	1038	33.165	8.186	3.316	1044	175.438	63.594	28.935	C-N Stretching
31			1053	3.892	1.981	0.784	1077	1.011	67.646	29.330	C-H in-plane bending
32	1080	1083	1098	9.060	72.334	26.813	1128	8.083	7.111	2.870	C-N Stretching
33			1126	14.191	74.223	26.415	1155	7.744	5.104	1.988	C-NO$_2$ Stretching
34	1147	1150	1147	8.050	88.166	30.467	1184	8.615	64.889	24.275	C-C Stretching
35	1182	1184	1183	1.076	3.269	1.074	1226	2.132	11.640	4.121	N-O$_2$ Symmetric Stretching
36			1245	1.007	40.370	12.187	1287	1.809	15.534	5.080	N-O$_2$ Symmetric Stretching
37	1259	1269	1274	9.758	11.975	3.472	1294	7.198	75.438	24.457	N=O Stretching
38			1301	11.574	29.065	8.131	1313	4.050	26.514	8.384	N=O Stretching
39	1370	1377	1398	0.209	10.985	2.710	1402	0.688	19.446	5.504	C=C Out-of-plane bending
40	1421	1423	1430	3.658	38.462	9.113	1424	1.616	40.993	11.302	N-O$_2$ Asymmetric Stretching
41		1458	1438	20.613	6.417	1.504	1454	9.465	7.241	1.926	N-O$_2$ Asymmetric Stretching
42			1478	32.893	10.236	2.285	1488	24.639	7.769	1.984	(C=C) Skeletal Vibration
43	1515	1520	1519	14.690	105.272	22.314	1531	9.425	98.550	23.919	(C=C) Skeletal Vibration
44	1559	1561	1565	87.783	30.026	6.016	1562	32.721	19.326	4.522	C≡N Out-of-plane bending
45			1809	366.331	48.879	7.351	1898	255.280	38.572	5.896	C=C Out-of-plane bending
46			2823	0.984	40.973	2.049	2908	2.562	23.173	1.251	C-H Stretching Vibration
47			2831	3.907	63.792	3.162	2911	5.307	128.307	6.908	C-H Stretching Vibration
48			2838	8.859	161.800	7.962	2919	3.622	55.349	2.955	C-H Stretching Vibration
49			2841	4.960	40.406	1.982	2921	5.707	130.195	6.941	C-H Stretching Vibration
50			2847	2.106	184.584	9.002	2930	2.264	212.909	11.248	C-H Stretching Vibration
51	2854		2856	1.728	177.883	8.593	2937	0.844	200.378	10.509	C-H Stretching Vibration

*For wave numbers less than 1700 cm⁻¹, scale factor of 0.903 and for frequencies greater than 1700 cm⁻¹ scale factor of 0.924 are used in the present calculation (Ref. 39)
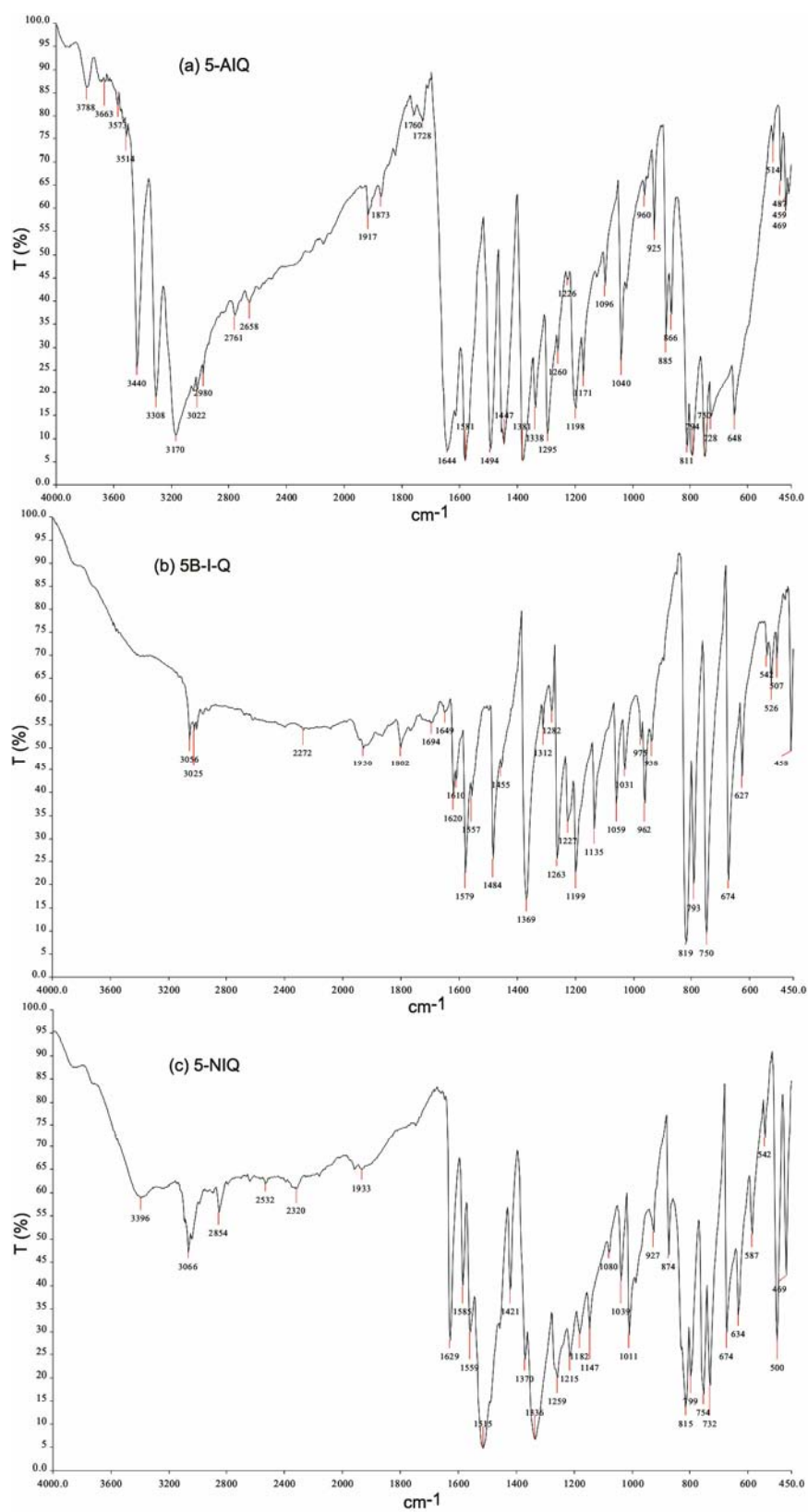
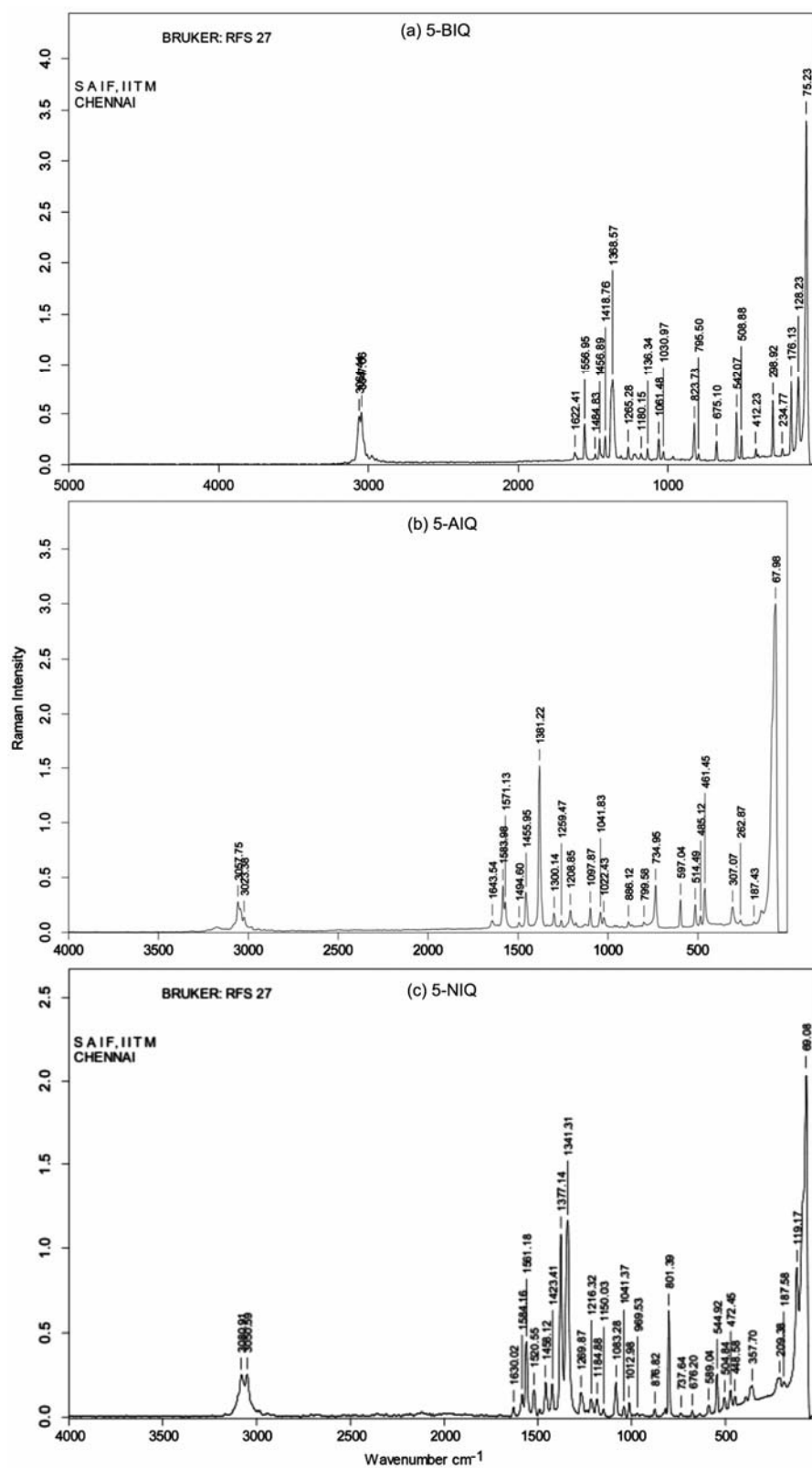Fig. 4 — Recorded FT-IR spectra of 5-substituted isoquinolines

Fig. 5 — Recorded FT-Raman spectra of 5-substituted isoquinolines

3.2.1 C-H Vibrations

Aromatic compounds commonly exhibit multiple weak bands in the region 3100-3000 cm^{-1} due to aromatic C-H stretching vibrations[22-24]. In the present study, the 5-BIQ is mono substituted aromatic system and it has six C-H adjacent moieties. In 5-BIQ molecule, the C−H vibrations are observed at 2854 cm^{-1} in FT-IR spectrum. The amino group in position 5 shifts these frequencies to higher frequencies while nitro group at position 5 has no significant effect. All bands are weak and of medium intensities in the expected region. The bands due to C-H in-plane bending vibrations[25] are observed in the region 1000-1300 cm^{-1}. In these compounds, the above vibrations are observed at 1029, 1056, 1195 and 1253 cm^{-1} in FTIR and 1012, 1022, 1030 and 1265cm^{-1} in FT-Raman. The theoretically calculated vibrations by HF and B3LYP/6-311++G (d,p) level method also show good agreement with experimentally recorded data.

The C−H out-of-plane bending vibrations[25,26] appeared within the region 900-675 cm^{-1}. The vibrations obtained at 732, 740,750 and 795 cm^{-1} in FT-IR and 795 cm^{-1} in FT-Raman spectrum are assigned to C−H out-of-plane bending for 5-BIQ. In 5-AIQ, the frequency is more and in 5-NIQ the vibrational frequency is less than those in 5-BIQ. The C−H out-of-plane bending vibrations also lie within the characteristic region.

3.2.2 Ring Vibrations

The ring stretching vibrations[27] are expected within the region 1620–1390 cm^{-1}. Generally, the C–C stretching vibrations in aromatic compounds form the strong bands. In present study, the bands are of different intensities and observed at 1570 and 1477 cm^{-1} in FT-IR and 1484 and 1516 cm^{-1} in FT-Raman in 5-BIQ, 1494 and 1447 cm^{-1} (IR) and 1494 and 1455 cm^{-1} in 5-AIQ; 1515 and 1559 cm^{-1} (IR) and 1520 and 1561 cm^{-1} (Raman) in 5-NIQ molecules. The theoretically calculated frequency values by HF and B3LYP/6-311++G (d,p) method show fairly satisfactory agreement with experimental data. The C-C-C out-of-plane vibrations are represented by 703 cm^{-1} and 404 cm^{-1} modes of benzene. The ring in-plane bending and out-of-plane bending modes are also in good agreement with experimental data. Only one infrared band at 412 cm^{-1} in Raman is assigned to C-C-C in-plane bending vibrations of 5-BIQ. The C-C in-plane-bending vibrations appeared as the combination vibrations with CH in-plane bending

vibrations. Theoretically calculated values at 662,761,608 and 692 cm^{-1} by HF and B3LYP/6-311++G(d,p) method and these values agree with experimental data. The bands assigned to C–C–C out-of-plane bending vibrations are observed at 458 cm^{-1} in FT-IR and 412 cm^{-1} in FT-Raman spectrum. The calculated values by HF and DFT methods for C-C-C out of plane bending vibrations are at 432, 434, 472, 485 and 487 cm^{-1}, respectively. Experimental frequencies match well with calculated frequencies. It may be pointed out that the C-C-C bending vibrations in the region of about 470 cm^{-1} are not affected by type of substituent present at 5-position.

3.2.3 C-Br Vibrations

The assignments of C-Br stretching and deformation vibrations have been made on the basis of the calculated PED and by comparison with similar molecules, p-bromophenol[28] and the halogen-substituted benzene derivatives[29]. In the present study, a strong band observed at 455 and 528 cm^{-1} in FT-IR and the bands observed at 542 and 509 cm^{-1} in FT-Raman spectrum are assigned to C-Br stretching. Theoretically calculated frequencies of C-Br stretching vibrations were fall in the region 587, 497 and 530 cm^{-1} by HF and B3LYP/6-311++G(d,p) methods.

3.2.4. C-NH$_2$ Vibrations

The absorption frequency at 263 and 307 cm^{-1} in IR spectrum of 5-AIQ is due to C-(NH$_2$)twisting[22,23] and the calculated values of 274 and 331 cm^{-1} by HF method are to these modes. The observed IR frequency at 1300 cm^{-1} is due to C-N stretching and the HF method of calculation yielded a value of 1302 cm^{-1} which is close to the observed frequency. The C-(NH$_2$) stretching is observed at 1171 cm^{-1} in both IR and Raman and in this case also HF method gives satisfactory value of 1146 cm^{-1}. It can be concluded that the HF method gives satisfactory values of the frequencies in both IR and Raman which are comparable to experimental values.

3.2.5 C-NO$_2$ Vibrations

The C-N stretching for nitroaromatic[22,23] is expected at about 870 cm^{-1}. The experimental frequencies of 791cm^{-1}(IR) and 801 cm^{-1} (Raman) in 5-NIQ are due to NO$_2$ deformation. The HF and B3LYP/6-311++G(d,p) methods gave the values as 800 cm^{-1} and 849 cm^{-1}, respectively. Thus, both the

methods give satisfactory frequencies comparable to experimental values in this case. The coupled pair of IR bands at 1182 cm^{-1} and 1269 cm^{-1} also indicates NO$_2$ group in 5-NIQ and HF method gives frequency values close to these values.

3.2.6 C=N Stretching

The C=N stretching vibrations[18-21] are observed in the range 1672-1566 cm^{-1}. Thus, the very weak bands occurring in IR at 1559 cm^{-1} and Raman spectra at 1561 cm^{-1} are assigned to the C=N stretching vibration for 5-NIQ molecule. Theoretically, the calculated frequencies of C=N stretching vibrations fall in the region 1565 and 1562 cm^{-1} by HF and B3LYP/6-311++G (d,p) method. In 5-AIQ, this vibration is observed at 1570 cm^{-1} and in 5-NIQ it is shifted to a lower frequency of 1494 cm^{-1}.

3.2.7 NH$_2$ Vibrations

5-Aminoisoquinoline contains amino group and the symmetric stretching frequency of this group is observed at 3170 cm^{-1} in infrared and at 3172 cm^{-1} in Raman which are in agreement with the calculated value of 3168 cm^{-1} by HF method. The asymmetric stretching frequency is 3308 cm^{-1} in IR and 3310 cm^{-1} in Raman in the recorded spectra. The computed frequency for this vibration by HF method is 3296 cm^{-1} which agrees with the observed value satisfactorily.

3.3 Frontier Molecular Orbitals (FMOs)

The highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) are called frontier molecular orbital's (FMOs). The FMOs play important trole in the optical and electric properties, as well as in quantum chemistry and UV-Visible spectra[30]. The HOMO represents the ability to donate an electron; LUMO as an electron acceptor represents the ability to obtain an electron. The energy gap between HOMO and LUMO determines the kinetic stability, chemical reactivity, and optical polarizability and chemical hardness-softness of a molecule[31, 32].In order to evaluate the energetic behaviour of the three isoquinoline derivatives, we carried out calculations in a non-polar benzene medium. The energies of important molecular orbitals of the three isoquinoline molecules, the highest occupied MOs (HOMO) the lowest unoccupied MOs (LUMO) were calculated using HF/6-311++G(d, p) and DFT methods. The energy values of HOMO and LUMO in a typical molecule

(5-BIQ) are −0.2650 and−0.1164 au, respectively. The 3D plots of the HOMO, LUMO orbitals computed for 5-BIQ molecule are shown in Fig. 6. The positive phase is red and the negative one is green. It is evident from Fig. 6 that while the HOMO is localized on almost the whole molecule, LUMO is localized on the pyridine ring. Both the HOMOs and the LUMOs are mostly π anti-bonding type orbitals. The energy separation between the HOMO and the LUMO in 5-BIQ is 0.1623 au. The energy gap of HOMO-LUMO explains the eventual charge transfer interaction within the molecule, which influences the biological activity. The wavelength of maximum absorption, excitation energies (eV), and oscillator strengths (*f*) of 5-BIQ, 5-AIQ and 5-NIQ in benzene are calculated by HF and B3LYP/6-311++G(d,p)
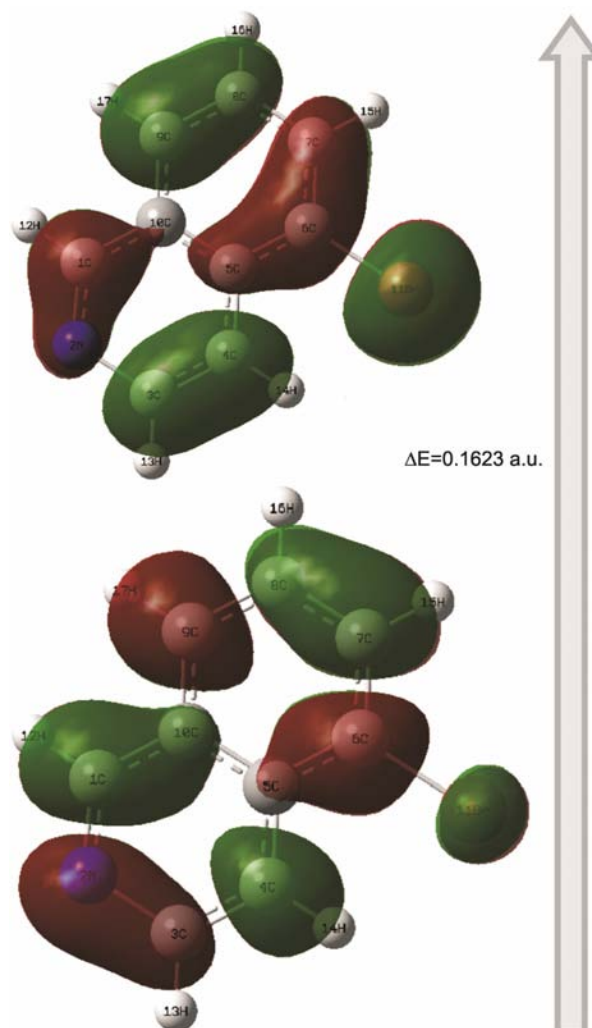

Fig. 6 — Molecular orbitals and energies for the HOMO and LUMO of 5-BIQ

Table 4 — Calculated absorption wavelength λ(nm), excitation energies E(eV) and oscillator strengths(f) along with the observed wave length of maximum absorption of 5-substituted isoquinolines in benzene

Compound	HF/6-311++G(d,p)			B3LYP/6-311++G(d,p)		
	λ(nm)	f	E(eV)	λ(nm)	f	E(eV)
5-BIQ	275.8(277)	0.1491	4.4949	319.5	0.0962	3.879
	262.1(272)	0.0555	4.7298	294.6	0.0582	4.208
	223.7(224)	0.0037	5.5418	285.7	0.0021	4.338
5-AIQ	279.7(333)	0.1305	4.432	339.8	0.093	3.648
	266.2(314)	0.0979	4.656	311.0	0.064	3.985
	219.0(284)	0.0195	5.660	288.4	0.003	4.298
5-NIQ	285.4(294)	0.1121	4.3438	377.5	0.0973	3.2836
	275.7(279)	0.0831	4.4958	345.9	0.0231	3.5841
	258.6(269)	0.0077	4.7936	326.0	0.0068	3.8025

The observed λ$_{max}$ values are given in parenthesis

methods and given in Table 4. The recorded UV-visible spectra of the three isoquinoline compounds in benzene are shown in Fig. 7. There are three absorption maxima in the recorded UV-visible spectra of these isoquinoline derivatives and they are also given in Table 5. Comparison of λ_{max} values of the three compounds obtained by the two different methods with experimental values shows that HF method is satisfactory in predicting the wave length of maximum absorption in these compounds.

3.4 Mulliken Population Analysis

Calculation of effective atomic charges plays an important role in the application of quantum chemical calculations to molecular systems. Our interest here is in the comparison of different methods to describe the electron distribution in the three 5-substituted isoquinolines and assess the sensitivity of calculated charges to changes in the choice of the method of computation and the influence of substituent at 5-position. Mulliken charges determine the electron population of each atom defined in the basic functions. The Mulliken charge calculated at different levels and at same basis set listed in Table 6. The distribution of electronic charges in the three molecules computed by the two different methods are illustrated by the plots shown in Fig. 8. Two methods give similar charge distribution in the three substituted isoquinoline molecules. Isoquinoline reacts as a base (pKa = 5.4) by protonation or as a nucleophile by quaternization through the electron lone pair on the ring nitrogen to form an aromatic isoquinolinium cation[33]. It can be seen from the data in Table 6 that the nitrogen atom in the heterocyclic ring is negatively charged in all the three molecules investigated. The charge distribution obtained by HF
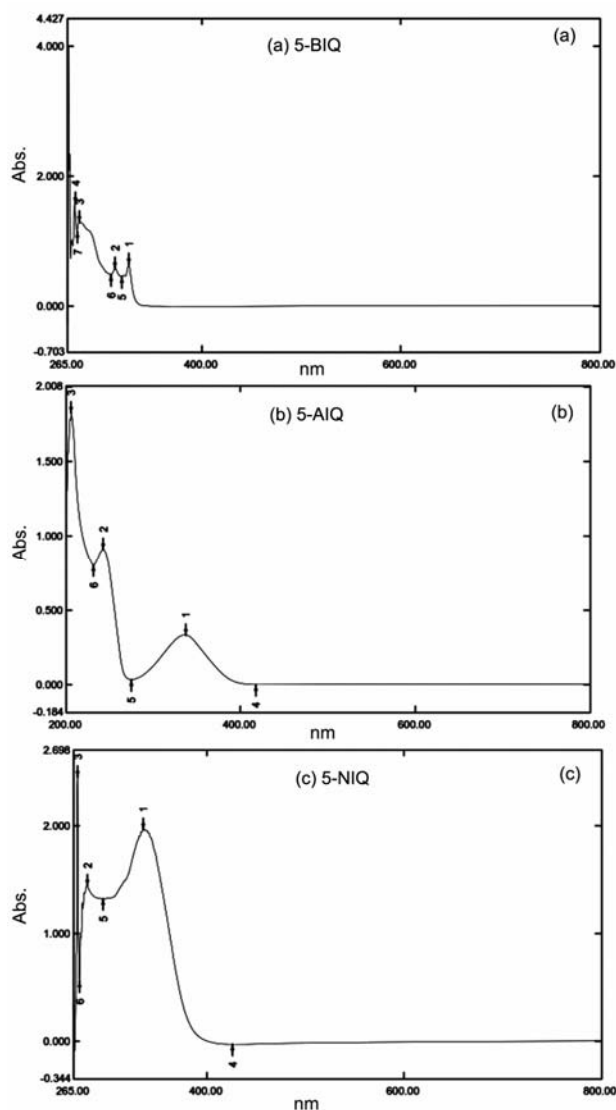

Fig. 7 — Recorded UV-Visible spectra of 5-substituted isoquinolines in benzene

Table 5 — Second order perturbation theory analysis of Fock Matrix in NBO basis calculated at B3LYP level using 6-311++G(d,p) basis set for 5-BIQ,5-AIQ and 5-NIQ

5-BIQ

Donor (i) Type	Acceptor (j) Type	E(2) kJ/mol.	E(j)-E(i) a.u	F(i,j) a.u.
σ C1 - N2	σ* C1 - C10	6.60	1.34	0.041
	σ*C3 - H13	4.47	1.23	0.032
	σ*C9 - C10	9.53	1.35	0.05
π C1 - N2	π* C3 - C4	48.82	0.31	0.054
	π*C5 - C10	8.36	0.32	0.059
σ C1 - C10	σ* C1 - N2	4.39	1.2	0.032
	σ* C1 - H12	2.09	1.1	0.021
	σ* C5 - C6	12.33	1.22	0.054
	σ* C5 - C10	14.38	1.24	0.059
	σ* C8 - C9	7.73	1.23	0.043
	σ* C9 - C10	12.87	1.23	0.055
σ C1 - H12	σ* N2 - C3	22.20	0.84	0.059
	σ*C5 - C10	18.56	1.07	0.062
σ N2 - C3	σ*C1 - H12	13.71	1.07	0.053
	σ*C4 - H14	9.70	1.09	0.045
σ C3 - C4	σ*C4 - C5	10.53	1.23	0.05
	σ*C4 – H14	3.59	1.12	0.028
	σ*C5 - C6	1.13	1.22	0.056
π C3 - C4	π* C1 - N2	37.83	0.26	0.043
	π*C5 - C10	74.99	0.28	0.067
σ C3 - H1	σ* C 1 - N 2	8.90	1.04	0.042
	σ*C4 - C5	14.55	1.06	0.054
σ C4 - C5	σ*C3 - C4	8.74	1.22	0.045
σ C4 - C5	σ* C3 – H13	7.32	1.11	0.039
	σ* C4 - H14	2.97	1.11	0.025
	σ* C5 - C6	15.09	1.21	0.059
	σ*C5 - C10	16.18	1.23	0.062
	σ* C6 - C7	10.45	1.21	0.049
	σ* C9 - C10	11.62	1.22	0.052
σ C4 - H14	σ* N2 - C3	18.22	0.83	0.054
	σ* C3 - C4	2.88	1.05	0.024
	σ* C4 - C5	2.80	1.05	0.024
	σ* C5 - C10	17.89	1.06	0.06
σC5 - C6	σ* C1 - C10	9.07	1.25	0.046
	σ* C3 - C4	7.11	1.25	0.041
	σ*C4 - C5	16.35	1.25	0.062
	σ* C5 - C10	16.47	1.26	0.063
	σ*C6 - C7	10.58	1.24	0.05
	σ* C7 - H15	8.49	1.13	0.043
σ C5 - C10	σ* C1 - C10	12.29	1.22	0.054
	σ*C1 - H12	6.73	1.09	0.038
	σ*C4 - C5	15.59	1.22	0.061
	σ* C4 - H14	8.44	1.11	0.043
	σ*C5 - C6	18.89	1.21	0.066
	σ*C6 -Br11	19.06	0.79	0.054
	σ* C9 - C10	14.38	1.22	0.058
	σ*C9 - H17	3.05	2.71	0.04
π C5 - C10	π* C1 - N2	87.15	0.26	0.069
	π*C3 - C4	61.78	0.27	0.061
	π*C6 - C7	73.36	0.25	0.061
	π*C8 - C9	72.69	0.27	0.064
σ C6 - C7	σ*C4 - C5	13.42	1.25	0.057

Contd —

Table 5 — Contd

Donor (i) Type	Acceptor (j) Type	E(2) kJ/mol.	E(j)-E(i) a.u	F(i,j) a.u.
σ C6 - C7	σ* C5 - C6	12.33	1.24	0.054
	σ* C7 - C8	9.41	1.25	0.047
	σ* C7 - H15	3.64	1.13	0.028
	σ* C8 - H16	7.48	1.14	0.04
π C6 - C7	π*C5 - C10	75.61	0.3	0.069
	π* C8 - C9	68.05	0.29	0.061
σ C6 -Br11	σ*C5 - C10	13.96	1.22	0.057
	σ* C7 - C8	10.07	1.21	0.048
σ C7 - C8	σ* C6 - C7	12.21	1.22	0.053
	σ* C6 -Br11	20.11	0.8	0.056
	σ* C7 - H15	2.93	1.11	0.025
	σ*C8 - C9	8.11	1.23	0.044
	σ* C8 - H16	2.51	1.12	0.023
	σ* C9 - H17	2.93	2.72	0.039
σ C7 - H15	σ*C5 - C6	16.85	1.05	0.058
	σ*C6 - C7	2.72	1.04	0.023
	σ*C8 - C9	14.55	1.06	0.054
σ C8 - C9	σ* C1 - C10	13.04	1.22	0.055
	σ* C7 - C8	8.07	1.22	0.043
	σ* C7 - H15	9.28	1.1	0.044
	σ* C8 - H16	2.88	1.11	0.025
	σ*C9 - C10	9.45	1.23	0.047
π C8 - C9	π*C5 - C10	72.86	0.28	0.065
	π* C6 - C7	88.83	0.26	0.066
	π* C9 - H17	15.34	2.28	0.088
σ C8 - H16	σ*C6 - C7	14.51	1.04	0.054
	σ* C9 - C10	14.05	1.06	0.053
σ C9 - C10	σ*C1 - N2	9.12	1.2	0.046
	σ*C1 - C10	11.70	1.22	0.052
σ C9 - C10	σ*C4 - C5	11.79	1.22	0.052
	σ*C5 - C10	15.72	1.23	0.061
	σ*C8 - C9	8.40	1.23	0.044
	σ* C8 - H1	8.95	1.11	0.044
σ C9 - H17	σ* C5 - C10	18.73	1.07	0.062
	σ* C7 - C8	14.42	1.05	0.054
n1N2	σ* C1 - C10	33.19	0.9	0.076
	σ*C1 - H12	10.07	0.77	0.039
	σ*C3 - C4	20.15	0.9	0.059
	σ* C3 - H1	4.43	0.79	0.026
n1 Br11	σ*C5 - C6	7.82	1.52	0.048
	σ*C6 - C7	7.03	1.52	0.045
n2 Br11	σ* C3 - C4	2.43	0.83	0.02
	σ*C4 - H14	5.02	0.72	0.026
	σ*C5 - C6	17.02	0.82	0.052
	σ* C6 - C7	15.89	0.82	0.05
Br11	π* C6 - C7	48.62	0.3	0.056
π* C1 - N2	π*C3 - C4	277.84	0.01	0.055
	π*C5 - C10	611.95	0.02	0.081
π*C6 - C7	π*C5 - C10	523.63	0.02	0.077
	π*C8 - C9	660.57	0.02	0.079

5-AIQ

Donor (i) Type	Acceptor (j) Type	E(2) kJ/mol.	E(j)-E(i) a.u	F(i,j) a.u.
σ C1-N2	σ*C1 - C10	6.69	1.35	0.042
	σ*C3 - H13	4.52	1.23	0.033
	σ* C9 - C10	9.54	1.35	0.05

Contd —

Table 5 — Contd

5-AIQ

Donor (i) Type	Acceptor (j) Type	E(2) kJ/mol.	E(j)-E(i) a.u	F(i,j) a.u.
π C1-N2	π*C3 - C4	48.49	0.31	0.054
	π*C5 - C10	46.86	0.33	0.059
σ C1 - C10	σ*C1 - N2	4.48	1.20	0.032
	σ*C1 - H12	2.10	1.10	0.021
	σ*C5 - C6	11.33	1.24	0.052
	σ*C5 - C10	14.09	1.24	0.058
	σ*C8 - C9	7.86	1.23	0.043
	σ*C9 - C10	12.80	1.24	0.055
σ C1 - H12	σ*N2 - C3	22.37	0.83	0.06
	σ*C5 - C10	18.65	1.07	0.062
	σ*N11 - H18	2.43	3.32	0.039
σ N2 - C3	σ*C1 - H12	13.72	1.07	0.053
	σ*C4 - H14	9.66	1.09	0.045
σ C3 - C4	σ*C4 - C5	10.62	1.23	0.05
	σ*C4 - H14	3.22	1.12	0.026
	σ*C5 - C6	12.42	1.24	0.055
π C3 - C4	π*C1 - N2	37.58	0.26	0.044
	π*C5 - C10	71.02	0.29	0.067
σ C3 - H13	σ*C1 - N2	8.95	1.04	0.042
	σ*C4 - C5	14.43	1.07	0.054
σ C4 - C5	σ*C3 - C4	8.66	1.22	0.045
	σ*C3 - H13	7.61	1.11	0.04
	σ*C4 - H14	2.97	1.11	0.025
	σ*C5 - C6	14.13	1.23	0.058
	σ*C5 - C10	14.09	1.23	0.062
	σ*C6 - C7	10.29	1.21	0.049
	σ*C9 - C10	11.79	1.23	0.053
σ C4 - H14	σ*N2 - C3	18.68	0.83	0.054
	σ*C3 - C4	2.39	1.05	0.022
	σ*C4 - C5	2.60	1.06	0.023
	σ*C5 - C10	17.85	1.07	0.06
σ C5 - C6	σ*C1 - C10	10.29	1.23	0.049
	σ*C3 - C4	7.36	1.23	0.042
	σ*C4 - C5	14.55	1.23	0.059
	σ*C5 - C10	15.81	1.24	0.061
	σ*C6 - C7	10.75	1.21	0.05
	σ*C6 - N11	3.18	1.05	0.025
	σ*C7 - H15	7.82	1.12	0.041
	σ*N11 - H18	2.89	3.49	0.044
σ C5 - C10	σ*C1 - C10	12.29	1.22	0.053
	σ*C1 - H12	7.07	1.08	0.038
	σ*C4 - C5	15.60	1.22	0.06
	σ*C4 - H14	8.74	1.11	0.043
	σ*C5 - C6	14.80	1.23	0.059
σ C5 - C10	σ*C6 - N11	14.55	1.04	0.054
	σ*C9 - C10	14.89	1.22	0.059
	σ*C9 - H17	8.20	1.13	0.042
π C5 - C10	π*C1 - N2	89.00	0.25	0.069
	π*C3 - C4	63.50	0.26	0.061
	π*C6 - C7	75.58	0.27	0.065
	π*C8 - C9	69.14	0.27	0.063
σ C6 - C7	σ*C4 - C5	72.82	1.23	0.055
	σ*C5 - C6	55.06	1.24	0.056
	σ*C6 - N11	12.42	1.05	0.024
	σ*C7 - C8	45.44	1.22	0.05
	σ*C7 - H15	14.34	1.12	0.027
	σ*C8 - H16	37.08	1.12	0.044
π C6 - C7	π*C5 - C10	72.82	0.29	0.066
	π*C8 - C9	80.18	0.28	0.066
	σ*N11 - H18	6.27	3.05	0.066
	σ*N11 - H19	3.52	3.46	0.052
σ C6 - N11	σ*C5 - C6	4.55	1.3	0.034
	σ*C5 - C10	9.03	1.3	0.048
	σ*C6 - C7	2.88	1.27	0.027
	π*C8 - C9	3.27	0.78	0.024
	σ*C9 - H17	7.11	1.2	0.04
	σ*N11 - H18	184.0	3.55	0.353
	σ*N11 - H19	124.5	3.96	0.307
σ C7 - C8	σ*C6 - C7	10.33	1.21	0.049
	σ*C6 - N11	17.27	1.05	0.059
σ C7 - C8	σ*C7 - H15	3.14	1.12	0.026
	σ*C8 - C9	8.41	1.23	0.044
	σ*C8 - H16	2.72	1.12	0.024
	σ*C9 - H17	9.32	1.14	0.045
σ C7 - H15	σ*C5 - C6	17.18	1.06	0.059
	σ*C6 - C7	2.72	1.04	0.023
	σ*C8 - C9	14.63	1.05	0.054
σ C8 - C9	σ*C1 - C10	13.13	1.22	0.055
	σ*C7 - C8	7.78	1.22	0.043
	σ*C7 - H15	9.58	1.12	0.045
	σ*C8 - H16	2.76	1.11	0.024
	σ*C9 - C10	9.78	1.23	0.048
	σ*C9 - H17	2.68	1.14	0.024
π C8 - C9	π*C5 - C10	71.40	0.29	0.065
	π*C6 - C7	75.95	0.27	0.064
σ C8 - H16	σ*C6 - C7	12.33	1.04	0.05
	σ*C9 - C10	13.97	1.06	0.053
σ C9 - C10	σ*C1 - N2	9.28	1.19	0.046
	σ*C1 - C10	11.54	1.22	0.052
	σ*C4 - C5	11.96	1.22	0.053
	σ*C5 - C10	15.88	1.24	0.061
	σ*C8 - C9	8.57	1.22	0.045
	σ*C8 - H16	8.95	1.11	0.044
	σ*C9 - H17	2.51	1.14	0.023
σ C9 - H17	σ*C5 - C10	18.23	1.07	0.061
	σ*C7 - C8	13.59	1.05	0.052
σ N11 - H18	σ*C5 - C6	7.11	1.18	0.04
	π*C6 - C7	7.98	0.66	0.034
	π*C8 - C9	2.26	0.66	0.018
	σ*C9 - H17	5.35	1.09	0.033
	σ*N11 - H18	26.10	3.43	0.131
	σ*N11 - H19	145.8	3.85	0.327
σ N11 - H19	π*C5 - C10	2.18	0.65	0.019
	σ*C6 - C7	4.48	1.14	0.031
	π*C6 - C7	7.74	0.64	0.033
	σ*C7 - C8	6.40	1.15	0.037
	π*C8 - C9	8.24	0.65	0.034
	σ*C8 - H16	2.22	1.04	0.021
	σ*C9 - H17	18.48	1.07	0.061
	σ*N11 - H18	232.9	3.41	0.39
	σ*N11 - H19	354.1	3.83	0.509

Table 5 — Contd

5-AIQ

Donor (i) Type	Acceptor (j) Type	E(2) kJ/mol.	E(j)-E(i) a.u	F(i,j) a.u.
n1N2	σ*C1 - C10	33.02	0.9	0.076
	σ*C1 - H12	10.08	0.77	0.039
	σ*C3 - C4	20.40	0.9	0.06
	σ*C3 - H13	4.44	0.79	0.026
n1N11	σ*C5 - C6	24.12	0.79	0.061
	σ*C6 - C7	21.12	0.76	0.056
	π*C6 - C7	30.48	0.26	0.042
	σ*C7 - C8	2.51	0.77	0.02
	σ*N11 - H19	9.37	3.45	0.08
π*C1 - N2	π*C3 - C4	301.9	0.01	0.055
	π*C5 - C10	435.1	0.03	0.081
π*C3 - C4	π*C5 - C10	613.3	0.02	0.077
π*C5 - C10	σ*N11 - H18	4.62	2.76	0.101
π*C6 - C7	π*C5 - C10	1009.8	0.01	0.079
π*C8 - C9	σ*N11 - H18	3.34	2.77	0.109
	σ*N11 - H19	5.27	3.18	0.146

5-NIQ

Donor (i) Type	Acceptor (j) Type	E(2) kJ/mol.	E(j)-E(i) a.u	F(i,j) a.u.
σ C1 - N2	σ* C1 - C10	6.53	1.34	0.041
	σ*C3 - H15	4.35	1.24	0.032
	σ*C9 - C10	9.58	1.34	0.05
π C1 - N2	π*C3 - C4	49.07	0.31	0.054
	π*C5 - C10	49.18	0.31	0.058
σ C1 - C10	σ*C1 - N2	4.31	1.21	0.032
	σ*C5 - C6	12.67	1.22	0.054
	σ*C5 - C10	14.72	1.24	0.059
	σ*C8 - C9	7.65	1.23	0.042
	σ*C9 - C10	12.91	1.23	0.055
σ C1 - H14	σ*N2 - C3	22.12	0.84	0.059
	σ*C5 - C10	19.14	1.06	0.062
σ N2 - C3	σ*C1 - H14	13.63	1.07	0.053
	σ*C4 - H16	9.24	1.1	0.044
σ C3 - C4	σ*C4 - C5	10.75	1.22	0.05
	σ*C4 - H16	3.55	1.13	0.028
	σ*C5 - C6	13.08	1.22	0.055
π C3 - C4	π*C1 - N2	37.87	0.26	0.043
	π*C5 - C10	80.13	0.28	0.069
σ C3 - H15	σ*C1 - N2	8.99	1.03	0.042
	σ*C4 - C5	14.88	1.06	0.055
σ C4 - C5	σ*C3 - C4	8.70	1.23	0.045
	σ*C3 - H15	7.15	1.12	0.039
	σ*C4 - H16	2.88	1.13	0.025
	σ*C5 - C6	13.13	1.21	0.055
	σ*C5 - C10	16.60	1.23	0.063
	σ*C6 - C7	10.87	1.2	0.05
	σ*C9 - C10	11.88	1.22	0.053
σ C4 - H16	σ*N2 - C3	18.31	0.83	0.054
	σ*C3 - C4	3.14	1.05	0.025
	σ*C4 - C5	2.51	1.05	0.023
	σ*C5 - C10	18.19	1.05	0.061
σ C5 - C6	σ*C1 - C10	9.58	1.24	0.048
	σ*C3 - C4	7.61	1.25	0.043
	σ*C4 - C5	14.42	1.24	0.058
	σ*C5 - C10	13.86	1.25	0.058

Table 5 — Contd

Donor (i) Type	Acceptor (j) Type	E(2) kJ/mol.	E(j)-E(i) a.u	F(i,j) a.u.
	σ*C6 - C7	15.02	1.23	0.059
	σ*C7 - H17	7.62	1.13	0.041
	π*N11 - O12	2.14	0.63	0.019
	σ*N11 - O13	6.78	1.01	0.037
σ C5 - C10	σ*C1 - C10	12.04	1.22	0.053
	σ*C1 - H14	6.50	1.1	0.037
	σ*C4 - C5	16.31	1.23	0.062
	σ*C4 - H16	8.08	1.13	0.042
	σ*C5 - C6	15.26	1.22	0.06
	σ*C6 - N11	15.82	0.94	0.054
	σ*C9 - C10	14.65	1.22	0.059
σ C5 - C10	σ*C9 - H19	8.07	1.11	0.042
π C5 - C10	π*C1 - N2	85.66	0.26	0.069
	π*C3 - C4	58.52	0.27	0.06
	π*C6 - C7	69.31	0.26	0.061
	π*C8 - C9	77.38	0.27	0.066
σ C6 - C7	σ*C4 - C5	12.42	1.24	0.054
	σ*C5 - C6	16.14	1.23	0.062
	σ*C7 - C8	7.53	1.24	0.042
	σ*C7 - H17	3.31	1.13	0.027
	σ*C8 - H18	8.03	1.13	0.042
	σ*N11 - O12	7.28	1.3	0.043
π C6 - C7	π*C5 - C10	83.52	0.29	0.071
	π*C8 - C9	62.29	0.28	0.059
	σ*N11 - O12	2.93	0.86	0.023
	π*N11 - O12	63.38	0.19	0.051
	σ*N11 - O13	5.77	0.57	0.026
σ C6 - N11	σ*C5 - C10	7.74	1.34	0.045
	σ*C7 - C8	5.53	1.33	0.037
σ C7 - C8	σ*C6 - C7	9.04	1.21	0.046
	σ*C6 - N11	17.10	0.95	0.057
	σ*C7 - H17	2.93	1.12	0.025
	σ*C8 - C9	8.08	1.23	0.044
	σ*C8 - H18	2.24	1.12	0.022
	σ*C9 - H19	9.38	1.12	0.045
σ C7 - H17	σ*C5 - C6	17.10	1.05	0.058
	σ*C6 - N11	4.14	0.77	0.025
σ C7 - H17	σ*C8 - C9	15.02	1.05	0.055
σ C8 - C9	σ*C1 - C10	12.84	1.23	0.055
	σ*C7 - C8	7.70	1.22	0.042
	σ*C7 - H17	2.08	1.12	0.043
	σ*C8 - H18	8.70	1.11	0.024
	σ*C9 - C10	8.99	1.23	0.046
	σ*C9 - H19	2.72	1.11	0.024
π C8 - C9	π*C5 - C10	69.10	0.28	0.063
	π*C6 - C7	95.68	0.26	0.07
σ C8 - H18	σ*C6 - C7	14.93	1.04	0.054
	σ*C9 - C10	13.80	1.05	0.053
σ C9 - C10	σ*C1 - N2	8.95	1.2	0.045
	σ*C1 - C10	11.66	1.22	0.052
	σ*C4 - C5	11.42	1.23	0.052
	σ*C5 - C10	15.01	1.23	0.06
	σ*C8 - C9	8.03	1.23	0.043
	σ*C8 - H18	8.78	1.11	0.043
	σ*C9 - H19	2.38	1.11	0.022

Table 5 — Contd

5-NIQ

Donor (i) Type	Acceptor (j) Type	E(2) kJ/mol.	E(j)-E(i) a.u	F(i,j) a.u.
σ C9 - H19	σ*C5 - C10	18.94	1.07	0.062
	*C7 - C8	14.42	1.05	0.054
σ N11 - O12	σ*C6 - C7	2.34	1.74	0.028
	σ*C6 - N11	4.60	1.48	0.037
π N11 - O12	π*C6 - C7	9.08	0.52	0.033
π N11 - O12	π*N11 - O12	14.33	0.43	0.04
σ N11 - O13	σ*C5 - C6	2.88	1.45	0.028
n1N2	σ*C1 - C10	33.28	0.9	0.076
n1N2	σ*C1 - H14	10.12	0.77	0.039
	σ*C3 - C4	19.82	0.9	0.059
	σ*C3 - H15	4.43	0.79	0.026
n1O12	σ*C4 - H16	3.14	1.22	0.027
	σ*C6 - N11	19.90	1.03	0.064
	σ*N11 - O13	8.03	1.08	0.041
n2O12	σ*C6 - N11	77.25	0.56	0.091
	σ*N11 - O13	120.56	0.6	0.119
n1O13	σ*C6 - N11	14.02	1.06	0.054
	σ*N11 - O12	8.36	1.4	0.048
n2O13	σ* C6 - N11	39.08	0.52	0.063
	σ*N11 - O12	44.77	0.85	0.086
	π*N11 - O12	5.23	0.19	0.016
n3 O13	π*N11 - O12	370.3	0.17	0.111
π*C1 - N2	π*C3 - C4	244.9	0.01	0.055
	π*C5 - C10	792.5	0.02	0.081
π*C6-C7	π*C5 - C10	780.16	0.02	0.078
	σ*N11 - O13	3.01	0.29	0.029
σ*C6 - N11	σ*C4 - C5	3.64	0.28	0.056
	σ*C5 - C10	4.73	0.29	0.062
	σ*C7 - C8	3.98	0.28	0.06
	σ*C7 - H17	5.82	0.17	0.057
	σ*N11 - O13	13.64	0.05	0.034
π*N11 - O12	π*C6 - C7	63.46	0.08	0.049
	π*N11 - O12	29.40	0.66	0.113

method is better than that given by B3LYP method. This is evident from the electron population at nitrogen in 5-AIQ and 5-NIQ molecules. Further, nitrogen atom is more negative in 5-AIQ than the other two because of electron release by the amino group. However, NO_2 group at 5-position in 5-NIQ withdraws electron and hence in this molecule the electron population at nitrogen is less. It can be seen that the bridged carbon atoms (C5, C10) are electron deficient and similar charge distribution is obtained at these positions by both the methods.

The halogen atom is electronegative and hence electron population is more at bromine in 5-BIQ. Both HF and DFT methods give the same result. With regard to the electron distribution on the non-bridged carbon atoms, the HF method shows that these carbon atoms are negatively charged. It has been found that isoquinoline undergoes nitration[34,35] at positions C5

and C9. In the present investigation, position 5-is occupied by a group and the electrophilic substitution can occur at position C9. The present results establish that C9 is richer in electron than other carbon atoms in all the three molecules. It is interesting to note that the electron population at C9 is greater in 5-NIQ than in both 5-BIQ and 5-AIQ. Both the methods give the same result. The possible reason may be that when electron withdrawing group like NO_2 group is present in the benzene ring the release of electron by the hetero atom (in this case N1) may be enhanced. The ring hydrogen atoms are positively charged in all the three heterocyclic molecules under investigation. The interesting point is that both HF and DFT methods suggest that in 5-NIQ molecule, the hydrogen atoms H16 and H17 are more electron deficient than the other ring carbon atoms in the three molecules. This is because these atoms are adjacent to electron withdrawing NO_2 group. Further, the oxygen of NO_2 group is negatively charged and the electron population is more at O12 and O13. These observations establish the formation of intramolecular hydrogen bond [Fig. 1(c)] in this molecule.

3.5 Natural Bond Orbital (NBO) Analysis

NBO analysis is an essential tool for studying intra- and intermolecular bonding and interaction among bonds, and also provides a convenient basis for investigating charge transfer or conjugative interaction in molecular systems. Some electron donor orbital, acceptor orbital and the interacting stabilization energy resulting from the second-order micro disturbance theory is reported[36,37]. The larger the $E(2)$ value, the more intensive is the interaction between electron donors and electron acceptors. NBO analysis has been performed extensively on the three molecules at the DFT/B3LYP/6-311++G(d,p) level and the results obtained are presented in Table 5. In the molecules under investigation, the hetero atom (nitrogen) can interact with the remaining part of the ring while the substituents can either release electron (-Br and-NH_2) or withdraw electron (−NO_2). These intramolecular interactions can be established in the NBO analysis. The most important interaction (n−σ*) energies, related to the resonance in these molecules, are electron donation from the LP(1)N2 atom of the electron donating groups to the anti-bonding acceptor σ^*(C-C) of the phenylring (LP1N2→σ^*(C1-C10 and C3-C4) which are in the range 20-30 kJ mol⁻¹. This larger energy shows the resonance interaction between

Table 6 — Mulliken atomic charges at different atoms of 5-BIQ, 5-AIQ and 5-NIQ molecules computed by HF/B3LYP/ methods with 6-311++G(d,p) basis sets

| | 5-Bromoisoquinoline | | | 5-Aminoisoquinoline | | | 5-Nitroisoquinoline | |
Atoms	HF	B3LYP	Atoms	HF	B3LYP	Atoms	HF	B3LYP
C1	-0.5830	-0.5953	C1	-0.5374	-0.5578	C1	-0.4652	-0.5144
N2	-0.0816	0.0009	N2	-0.0822	-0.0046	N2	-0.0727	0.0104
C3	-0.3401	-0.4478	C3	-0.5386	-0.5018	C3	-0.5601	-0.6109
C4	-0.3184	-0.0129	C4	0.0526	0.1138	C4	0.4846	0.5692
C5	1.2925	1.0538	C5	1.3569	1.4395	C5	2.1901	1.7911
C6	-0.2973	-0.3355	C6	-0.8589	-0.9229	C6	-1.5647	-1.3473
C7	-0.2560	-0.1677	C7	-0.3242	-0.2169	C7	-0.5014	-0.2543
C8	-0.3689	-0.2652	C8	-0.2594	-0.2194	C8	-0.3156	-0.2759
C9	-1.1618	-1.0358	C9	-1.2298	-1.1369	C9	-1.3886	-1.2078
C10	1.0779	0.9180	C10	1.1082	0.8531	C10	0.9131	0.7657
Br11	-0.2789	-0.1857	N11	-0.3841	-0.2569	N11	-0.0294	-0.1153
H12	0.2142	0.1823	H12	0.2140	0.1806	O12	-0.0792	-0.0288
H13	0.2354	0.1978	H13	0.2147	0.1810	O13	-0.0427	0.0031
H14	0.2124	0.1610	H14	0.2041	0.1290	H14	0.2195	0.1867
H15	0.2580	0.2062	H15	0.1723	0.1354	H15	0.2289	0.1961
H16	0.2102	0.1739	H16	0.2060	0.1662	H16	0.2880	0.2457
H17	0.1857	0.1519	H17	0.1652	0.1329	H17	0.2859	0.2476
			H18	0.2751	0.2511	H18	0.2260	0.1870
			H19	0.2454	0.2346	H19	0.1833	0.1520

the hetero atom and the remaining part of the aromatic ring.

The second significant interaction is between the substituent at position 5-and the aromatic ring. In 5-BIQ the interaction (n–π^*) energies, related to the resonance in the molecules, are electron donation from the LP(3)Br atom of the electron releasing bromine group to the anti-bonding acceptor π^*(C-C) of the phenyl ring (LP3Br11 →π^*(C6–C7) = 48.62 kJ/mol. In 5-AIQ molecule, the interaction (n–σ^*) as well as ((n–π^*) energies, indicate resonance in the molecules. It is evident from electron donation from the LP(1)N11 atom of the electron releasing amino group to the anti-bonding acceptor σ^*(C5-C6 and C6-C7) of the phenyl ring (LP3N11 →π^*(C6–C7) = 30.48 kJ/mol. The other significant interaction in this molecule is the interaction (π–π^*) energies which is related to the conjugation in the molecule, are electron donation from the donor π (C5-C10) to the anti-bonding acceptor π^*(C1-N2, C-C4, C6-C7 and C8-C9) of both the phenyl and hetero cyclic rings. The π^*(C1-N2) of the NBO conjugated with π^*(C3–C4) and π^*(C5-C10) resulting in an enormous stabilization of 301.92 and 435.18 kJ/mol, respectively. Similar large stabilization of about 1010 kJ/mol is observed in π^* (C6-C7) of the NBO conjugated with π^* (C5-C10).These results indicate the resonance interaction between amino substituent at 5-position and both the rings through the bridging (C5-C10) bond. The most

important interactions in the nitro substituent are (n–σ^*) energies, related to the resonance in 5-NIQ molecule are electron donation from the LP(2) O12 atom of the nitro group to the anti-bonding acceptor σ^*(C6-N11) and N11-O13 of the nitro group (LP2O12→σ^*(C6–N11))= 77.25 kJ/mol and (LP2O12→σ^* (N11-O13)) = 120.56 kJ/mol. These observations indicate that there in conjugative interactions within the substituent as well as between the −NO₂ group and the phenyl ring. Similarly, the interaction between O13 and N11-O12 is also strong as indicated by the high (n–π^*) interaction energy of (LP3O13→π^*(N11–O12)) = 370.35 kJ/mol. The intramolecular conjugative interaction in 5-NIQ molecule is established by the enormous (π– π^*) interaction energies from the donor π^* of C1-N2 to the $\pi^*$of the acceptors C3-C4, C5-C10 and N11-O13. Thus, the extensive NBO analysis in the three heterocyclic aromatic molecules suggests electronic transmission due to conjugative effect in the substituent as well as in the aromatic rings.

3.6 Thermodynamic Properties

The values of thermodynamic parameters, zero point vibrational energy (ZPVE), thermal energy, specific heat capacity, and entropy of 5-BIQ, 5-AIQ and 5-NIQ at 298 K in ground state are calculated by HF and DFT methods and the values obtained are listed in Table 7. The variation in zero point vibrational
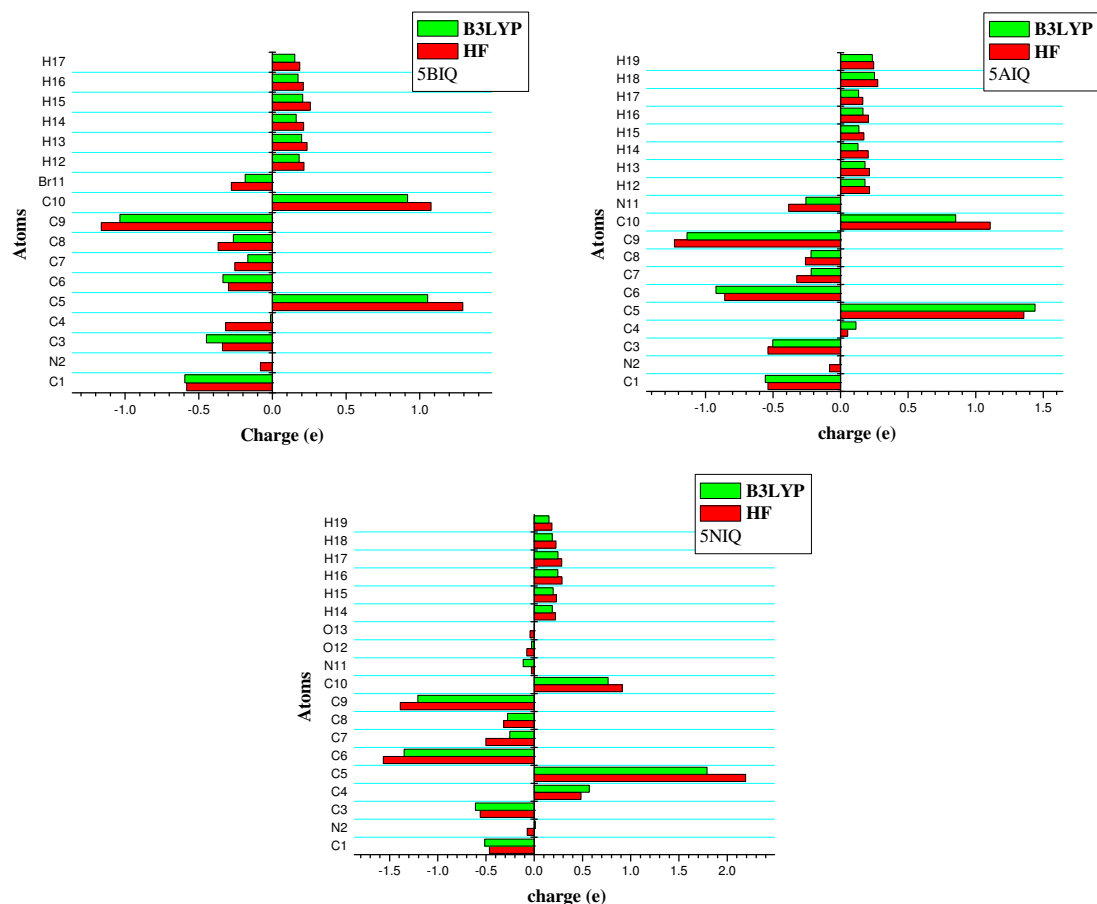
Fig. 8 — Atomic charge distribution in 5 substituted isoquinolines

Table 7 — Calculated thermodynamical parameters of 5-BIQ, 5-AIQ & 5-NIQ by HF and B3LYP methods with 6-311++G(d,p) basis sets at 298 K

Parameters	5-BIQ		5-AIQ		5-NIQ	
	HF	B3LYP	HF	B3LYP	HF	B3LYP
Zero point energy (kJ/mol)	338.16	318.85	407.67	384.4	371.56	350.2
Thermal energy(kJ/mol)						
Total	357.01	339.33	426.1	404.79	393.42	371.97
Translational	3.72	3.72	3.72	3.72	3.72	3.72
Rotational	3.72	3.72	3.71	3.72	3.72	3.72
Vibrational	349.61	331.93	418.6	397.3	385.98	364.6
Molar capacity at constant volume (J K^{-1} mol^{-1})						
Total	124.4	135.1	127.8	141.1	143.4	147.5
Translational	12.46	12.46	12.46	12.46	12.46	12.46
Rotational	12.46	12.46	12.46	12.46	12.46	12.46
Vibrational	99.5	110.2	102.9	116.2	118.5	122.6
Entropy (J K^{-1} mol^{-1})						
Total	383.3	372.7	347.9	359.6	382	376.1
Translational	175	175	170.6	170.6	172.9	172.9
Rotational	130.1	130.4	124.5	124.5	129.1	129.2
Vibrational	57.9	67.3	52.8	64.5	80.0	74.0
Dipole moment (Debye units)	2.375	2.249	3.697	3.397	4.383	4.027

energies (ZPVEs) seems to be significant. The computed ZPVE is much lower in the DFT/B3LYP method than that obtained in HF method. The values of ZPVE of the three compounds are in the order 5-AIQ > 5-NIQ > 5-BIQ. The calculated thermal energy also follows the same trend in these isoquinolines. The thermal energy of a given compound is also much lower in the DFT/B3LYP method than that obtained in HF method. However, the entropy values obtained by DFT method are greater than those calculated by HF method in all the three compounds. The entropy values obtained in both the methods follow the order 5-NIQ > 5-BIQ > 5-AIQ. Dipole moment reflects the molecular charge distribution and is given as a vector in three dimensions. Therefore, it can be used as descriptor to depict the charge movement across the molecule. Direction of the dipole moment vector in a molecule depends on the centers of positive and negative charges. Dipole moments are determined for neutral molecules. For charged systems, its value depends on the choice of origin and molecular orientation. As a result of HF and DFT (B3LYP) calculations, higher dipole moment was observed in B3LYP/6-311G++(d,p) method. It is found that in both the methods highest dipole moment value is obtained for 5-NIQ while the lowest value is for 5-BIQ among these three compounds. It may be pointed out these values are in the same order of group moments, which is $-NO_2$ >$-NH_2$>-Br as found in benzene derivatives[38].

4 Conclusions

In the present paper, we have performed the experimental and theoretical vibrational analysis of three biologically and industrially important heterocyclic aromatic molecules, namely, 5-bromo-isoquinoline, 5-aminoisoquinoline and 5-nitroiso-quinoline. The results obtained and the conclusions drawn are summarized below:

(a) The optimized molecular geometry, vibrational frequencies, infrared activities and Raman scattering activities of the molecules in the ground state have been calculated by *ab initio* HF and DFT (B3LYP) methods with 6–311++G (d, p) basis set. The vibrational frequencies have been calculated with scale factor and compared with the experimental frequencies obtained from recorded FT-IR and FT-Raman spectra.

(b) The observed and the calculated frequencies by HF method are found to being in good agreement.

(c) The wavelength of maximum absorption, excitation energies (eV), and oscillator strengths (*f*) of the investigated compounds in benzene are calculated by HF and B3LYP/6-311++G(d,p) methods. The recorded UV-visible spectra of the three isoquinoline derivatives are recorded in benzene and the observed wave lengths of maximum absorption agree with the computed values.

(d) The thermodynamic properties and total dipole moments of the compounds have been calculated in order to get insight into molecular structure of the compound. These computations are carried out with the main aim that the results will be of assistance in the quest of the experimental and theoretical evidence for the molecules under investigation in biological activity and coordination chemistry.

References

1. Kuroda Y, Ogawa, Nasu H, Jerashima M, Kasahara M, Kiyama Y, Wakita M, Fujiwara Y, Fujii N & Nakagawa J, *Biophys J*, 71 (1996) 1191.
2. Shen Qilong, Shekhar Shashank, Stambuli James P & Hartwig John F, *Angew Chem Int Ed*, 44 (2005) 1371.
3. Park Sae Hume, Park Yoonsu & Chan Sukbok, *Org Synth*, 91 (2014) 52.
4. Qilong Shen & Hartwig J F, *J Amer Chem Soc*, 128 (2006) 10028.
5. Andrew D, Batcho A D & Willy Leimgruber, *Org Synth*, 63 (1985) 214.
6. Adams D R, Bentley J M, Benwell K R, Bickerdike M J, Bodkin C D, Cliffe I A, Dourish C T, George A R, Kennett G A, Knight A R, Malcolm C S, Mansell H L, Anil Misra, Kathleen Quirk, Jonathan Roffey R A,Steven & Vickers P, *Bioorg Med Chem Lett*, 16 (2006) 677.
7. Cuzzocrea S, McDonald M C & Mazzon E, *Biochem Pharmacol*, 63 (2002) 293.
8. Mota-Filipe Sepodes B & McDonald M C, *Med Sci Monit*, 8 (2002) 444.
9. Wayman N S, McDonald M C & Thompson A C, *Eur J Pharmacol*, 430 (2001) 93.
10. Garcia Sanchez F, Navas Diaz A & Gonzalaz J A, *J Photochem Photobiol*, 105 (1997) 11.
11. Krishnakumar V, Prabavathi N & Muthunatesan S, *Spectrochim Acta A*, 69 (2008) 853.
12. Arjunan V, Mohan S, Ravindran P & Mythili C V, *Spectrochim Acta A*,72 (2009) 783.
13. Arjunan V, Thillai Govindaraja S & Jayaprakash A, *Spectrochim Acta A*, 107 (2013) 67.
14. Frisch J, Trucks G W, Schlegel H B, Scuseria G E, Robb M A, Cheeseman J R, Scalmani G, Barone V, Mennucci B, Petersson G A, Nakatsuji H, Caricato M, Li X, H Hratchian P, Izmaylov A F, Bloino J, Zheng G, Sonnenberg J L, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Vreven T, Montgomery A, Jr. Peralta J E, Ogliaro F, Bearpark M, Heyd

J J, Brothers E, Kudin K N, Staroverov V N, Keith T, Kobayashi R, Normand J, Raghavachari K, Rendell A, Burant J C, Iyengar S S, Tomasi J, Cossi M, Rega N, Millam J M, Klene M, Knox J E, Cross J B, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann R E, Yazyev O, Austin A J, Cammi R, Pomelli C J, Ochterski J W, Martin R L, Morokuma K, Zakrzewski V G, Voth G A, Salvador P, Dannenberg J J, Dapprich S, Daniels A D, Farkas O, Foresman J B, Ortiz J Cioslowski J & Fox D J, Gaussian 09 Program, Revision C.01, Wallingford CT, (2010).

15   Axel D & Becke, *J Chem Phys*, 98 (1993) 5648.
16   Rauhut G & Pulay P, *J Phys Chem*, 99 (1995) 3093.
17   Pulay P, Geza Fogarasi, Gabor Pongor, Boggs J E & Anna Vargha, *J Amer Chem Soc*, 105 (1983) 7037.
18   Fogarasi G, Zhou X, Taylor P W & Pulay P, *J Amer Chem Soc*, 114 (1992) 8191.
19   Keresztury G, Holly S, Varga J, Besenyei G, Wang A Y & Durig Y R, *Spectrochim Acta A*, 49 (1993) 2007.
20   Mwadham Kabanda E M, Taner Arslan, Murat Saracoglu, Fatma Kandemirli, Lutendo C Murulana, K, Ashish Singh K, Sudhish K, Shukla B, Hammouti B, Khaled K F, Quraishi M A, Obot, I B & Eddy N O, *Int J Electrochem Sci*, 7 (2012) 5643.
21   Udayakumara V, Periandy S & Ramalingam S, *Spectrochimica Acta A*, 79 (2011) 920.
22   Keresztury G, Raman Spectroscopy: *Theory in Handbook of Vibrational Spectroscopy*, Chalmers J M & Griffith P R, John wiley & Sons Ltd, (2002).
23   Silverstein R M, Bassler G C & Morrill T C, *Spectrometric Identification of Organic Compounds*, 5ᵗʰed.,Chichester, John Wiley, (1991).
24   Socrates G, *Infrared Raman Characteristic Group Frequencies – Tables and Charts*, third ed, Wiley, New York, (2001).

25   Krishnakumar V & John Xavier R, *Indian J Pure & Appl Phys*, 41 (2003) 597.
26   Jamroz M H, Dobrowolski J C & Robert, *J Mol Struct*, 787 (2006) 172.
27   Altun A, Golcuk K & Kumru M, *J Mol Struct Theochem*, 625 (2003) 17.
28   Zierkiewicz W, Danuta Michalska, Thérèse Zeegers-Huyskens, *J Phys Chem A*, 104(2000) 11685.
29   Varsanyi G, *Assignment for Vibrational spectra of seven hundred benzene derivatives*, vol-1, II ed, Adam Hilger, (1974).
30   Fleming I, *Frontier Orbitals and Organic Chemical Reactions*, John Wiley & Sons, London, UK, (1976).
31   Asiri A M, Karabacak M, Kurt M & Alamry K A, *Spectrochim Acta A*, 82 (2011) 444.
32   Liu J N, Chen Z R & Yuan S F, *J Zhejiang Univ Sci B*, 6 (2005) 584.
33   Ramón Alajarín & Carolina Burgos, Six-Membered Heterocycles-Quinoline and Isoquinoline, eds.Julio Alvarez-Builla, Juan Jose Vaquero & José Barluenga, Modern Heterocyclic Chemistry, Wiley-VCH Verlag& Co, Weinheim, Germany, (2011) 1588.
34   Dewar M J S & Maitlis P M, *J Chem Soc*, (1957) 2521.
35   Kathawala F G, Coppola G M & Schuster H F, (Eds), The Chemistry of Heterocyclic compounds: Isoquinolines, Part 3, John Wiley & Sons, Inc., New York, 38 (1995).
36   James C, AmalRaj A, Reghunathan R, Hubert Joe I & Jaya Kumar V S, *J Raman Spectroscopy*, 37 (2006) 1381.
37   Jun-Na Liu, Zhi-Rong Chen & Shen-Feng Yuan, *J Zhejiang Univ Sci*, 6 (2005) 584.
38   Tridib Tripathy & De B R, *J Phys Sci*, 12 (2008) 155.
39   Xavier R J & Gobinath E, *Spectrochemica Acta Part A*, 86 (2012) 242.