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Theoretical Vibrational Mode Analysis of Schiff Bases using Semi Empirical Methods-I

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Two new Schiff bases *viz.*, 2N-[(3,4,5-trimethoxybenzalidene)aminopyridine] and 2N-[(4-methoxybenzalidene)aminopyridine] were synthesized by condensation of 3,4,5-trimethoxybenzaldehyde or 4-methoxybenzaldehyde with 2-amino pyridine in separate procedures. Their IR spectra was obtained experimentally by KBr method and was analyzed for significant peaks. Semi empirical methods AM1, PM3, MNDO, ZINDO methods were used to compare the experimentally obtained IR spectra with the computer simulated IR spectra using transmittance *vs.* frequency plots given by four methods. Apart from the comparison of the significant part of the spectra, the statistical correlation was also calculated for the theoretical spectra and methods; to establish use of these methods as alternative and supportive tool in analytical chemistry and to establish purity of the synthesized compounds.

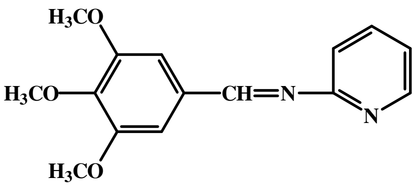
Key Words: Vibrational mode, 2N-[(3,4,5-Trimethoxybenzalidene)aminopyridine], 2N-[(4-Methoxybenzalidene)aminopyridine], AM1, PM3, MNDO, ZINDO, Comparison and correlation.

INTRODUCTION

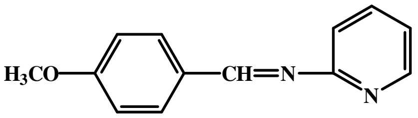
Schiff bases are obtained by condensation reaction of carbonyl compounds and amino compounds. They have been studied as early as 19th century[1] and still are studied as they serve as potent ligands for ligation with transition metals, lanthanides and actinides. Their analysis through IR spectra when compared to theoretical spectra can serve as an analytical tool for accurate structural elucidation. In this present paper the two novel synthesized Schiff bases are studied by semi empirical methods for analysis of their normal modes and comparison is done with experimentally obtained IR to study the correlation between the two.

Semi empirical methods like AM1, PM3, MNDO, ZINDO are one of the foundation of quantum chemical approach to obtain wave function solution. Various parameters can be obtained from these methods like heat of formation, electron population, *etc*.

Vibrational frequencies are an effective aid for structure elucidation of organic molecule and recently their use with semi empirical package has gained popularity for purpose of close analysis of their structure. More recently such efforts have been made by various workers as an effective tool for vibrational analysis of drug molecules, biological compounds and natural products[2-7]. This effort, describes the vibrational spectral investigations aided by semi empirical methods to elucidate correlation between observed and computer simulated IR frequencies and analyze their normal modes for two synthesized Schiff bases *viz.*, 2N-[(3,4,5-trimethoxybenzalidene)aminopyridine] (2-TBAPy) and 2N-[(4-methoxybenzalidene)aminopyridine] (2-MBAPy) (Fig. 1).



2N-[(3,4,5-Trimethoxybenzalidene)aminopyridine]



2N-[(4-Methoxybenzalidene)aminopyridine]

Fig. 1.

EXPERIMENTAL

Schiff bases are prepared by preparing solutions of corresponding aromatic aldehydes 3,4,5-trimethoxybenzaldehyde or 4-methoxybenzaldehyde in ethanol, respectively and refluxing it with solution of 2-amino pyridine in equimolar quantities in round bottom flask for 6 h. The IR spectra of these Schiff

TABLE-1
VIBRATIONAL ANALYSIS OF SCHIFF BASES *viz*., 2N-[(3,4,5-TRIMETHOXYBENZALIDENE)AMINOPYRIDINE]
AND 2N-[(4-METHOXYBENZALIDENE)AMINOPYRIDINE]

IR frequency (cm^{-1})	Semi empirically computer simulated frequencies (cm^{-1})				
	AM1	PM3	MNDO	ZINDO	Assignment
2N-[(3,4,5-Trimethoxybenzalidene)aminopyridine]					
522	520.40	514.43	511.36	539.98	–
615	603.81	588.70	605.35	588.19	–
625	638.25	638.91	635.80	635.21	–
673	686.67	664.30	681.15	650.77	Out-of-plane for benzene
729	734.90	700.20	729.12	718.14	Out-of-plane ring deformation for 2-pyridine
768	–	786.30	781.31	801.34	–
844	828.25	828.23	850.46	896.14	–
911	–	902.13	924.00	924.83	C-N-C bending
990	978.66	982.70	978.00	978.08	C-N-C bending
1037	1014.32	1031.24	1054.40	1091.94	–
1126	1138.63	1123.29	1134.44	1123.32	–
1176	1167.90	1170.00	1186.67	1154.17	–
1235	1249.94	1211.70	1224.84	1212.89	C-O-C stretching mode
1334	1339.14	1318.25	1347.65	1343.60	Ring stretching
1389	1360.31	1394.00	1375.95	1386.00	Ring stretching
1420	1434.31	–	–	–	–
1465	1461.51	–	1481.77	–	Ring bending and deformation
1506	1522.13	1511.99	–	1543.48	C=N stretching
1594	1614.80	1580.97	–	1606.87	C=N stretching
1620	1632.60	1643.23	1635.97	1635.00	–
Statistical correlation	0.99923	0.98679	0.99896	0.997539	–
2N-[(4-Methoxybenzalidene)aminopyridine]					
536	538.05	531.34	562.09	527.97	–
580	596.84	566.16	570.00	610.71	–
646	–	640.51	641.77	–	Out-of-plane ring deformation for 1,4-disubstituted benzene
718	735.42	702.67	722.22	–	Out-of-plane ring deformation for 1,4-disubstituted benzene
824	82723	833.75	849.79	885.48	Out-of-plane ring deformation for 1,4-disubstituted benzene
869	867.44	862.00	912.66	929.90	–
988	986.21	977.50	989.49	–	C-N-C bending
1025	1018.69	1029.75	1016.35	1056.57	–
1071	–	–	1064.23	–	–
1089	–	–	1081.35	1088.62	–
1165	1169.01	1164.44	1178.67	1178.25	Ring bending of benzene
1247	1251.18	1237.00	1262.28	1254.22	–
1288	1285.63	1295.00	1282.21	1289.88	–
1322	1326.48	1342.00	1300.00	1324.00	–
1385	1383.83	1380.00	1391.93	1391.98	Ring stretching, bending and deformation of benzene
1435	1441.78	1456.90	1437.83	–	Ring stretching, bending and deformation of benzene
1460	1462.83	–	–	1463.90	Ring stretching, bending and deformation of benzene
1512	1535.96	1523.80	1522.00	1542.48	Azomethine stretching
1596	1577.08	–	1622.53	1634.17	Azomethine stretching
3021	3057.00	3035.76	–	–	Aromatic C-H stretching
3213	3212.00	–	–	–	Aromatic C-H stretching
Statistical correlation	0.9997	0.99986	0.99914	0.99910	–

bases was obtained through Shimadzu 8201 PC in the range 4000-400 cm^{-1} from CDRI Lucknow, with the sample in KBr matrix. The structure of synthesized Schiff bases were drawn on Hyperchem version 8.0 and semi empirical calculations using different methods *viz.*, AM1, PM3, MNDO, ZINDO were carried through Hyperchem 8.0 version on Pentium dual core processor through which statistical correlation was also obtained[8,9].

RESULTS AND DISCUSSION

IR spectra were compared to the semi empirically obtained frequencies through four different methods namely AM1, PM3, MNDO, ZINDO and their statistical correlation was obtained[10-12]. For 2-TBAPy Schiff base the frequencies obtained at 781-740 cm^{-1} belong to pyridine system and the other at 1275-1200 cm^{-1} is due to C-O-C stretching mode of aryl alkyl ether. The C=N stretching frequency appears at 1594 and 1506 cm^{-1}, ring stretching at 1389 and 1334 cm^{-1}. Ring bending of benzene is clearly distinguished at 1235 and 1226 cm^{-1} along with ring bending and deformation at 1465 cm^{-1}(s). Another characteristics frequency appears at 990 cm^{-1} for C-N-C bending. Out of plane deformation apears at 768 and 729 cm^{-1}. Out-of-palne vibration for substituted benzene appears[13] around 673 cm^{-1}. These obtained frequencies from spectra were compared with semi empirically calculated frquencies and their statistical correlation was also calculated. The two set of values showed fairly good correlation in range of 0.999 to 0.986 signifying purity of synthesis and also indicating the alternative use of semi empirical methods to carry out vibrational anaysis as a tool for structural elucidation (Table-1). These four methods *viz.*, AM1, PM3, MNDO and ZINDO were also used to generate plots between calculated frquencies and their transmittance. A close look at the IR graph and computer simulated graph for significant frquencies suggest fiar resemblance between the two. Similarly for Schiff base 2-MBAPy comparative analysis was performed using IR spectra. For this Schiff base the characteristics peaks were obtained around 800 cm^{-1} which is typical to 1,4-disubstituted benzene ring and at 1900 cm^{-1} which is peculiar to aromatic aldehyde system. The azomethine stretching for the Schiff base appears at 1596 and 1512 cm^{-1} while ring stretching appears around 1385 cm^{-1}. The bending and deformation mode of benzene appears around 1460 cm^{-1}. The C-N-C bending appears at 988 cm^{-1} while out-of-plane ring deformation appears around 768 cm^{-1}. The theoretically calculated frequencies and their intensitites by different methods were used to obtain[14-16].

Common peaks featuring inthe IR spectra are corresponding to aromatic C-H stretching bands occuring between 3100 and 3000 cm^{-1} and out-of-plane bending of ring hydrogen atoms which is strongly coupled to adjacent hydrogen atoms; these appear as intense bands around 900 cm^{-1}. Another significant outcome of the comparison of theoretical obtained values and calculated ones could be that of normal modes. As the figures suggest these molecules are non-linear and formula 3N-6 for non-linear molecules for 2-TBAPy predicts 102 normal modes for 36 atoms which are obtained in same number through AM1, PM3, MNDO and ZINDO methods. Likewise for 2-MBAPy the molecular formula suggests presence of 28 atoms which corresponds to 78 normal modes which are obtained through semi empirical methods also.

Conclusion

A close look at the data obtained experimentally and those obtained through semi empirical methods is suggestive of fact that semi empirical methods not only serve as an alternate and supportive tool for vibrational analysis and also are less time consuming. Out of the various methods AM1 is found to have maximum potentials as it consumes least time for performing vibrational analysis and their statistical correlation between observed and computed frequencies for both of the Schiff bases are in order of 0.999 (Table-1).

These semi empirical methods are also helpful in predicting stability of Schiff bases as these correspnds to -81023.94 kcal/mol of total energy for 2-TBAPy and -59051.07 kcal/mol of total energy for 2-MBAPy through AM1 calculations along with 58.17 and 78.85 kcal/mol heats of formation, respectively. The methods confirmed the Cs point group to both of the Schiff bases as proposed by the structure of the molecules in addition to the normal mode analysis.

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