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

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Two new Schiff bases *viz.*, 2N-[(4-chlorobenzalidene)aminopyridine] and 2N-[(4-hydroxybenzalidene)aminopyridine] were synthesized using 4-chlorobenzaldehyde, 4-hydroxybenzaldehyde and 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 used here. 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 the use of these methods as alternative and supportive tool in analytical chemistry as well as to establish purity of the synthesized compound.

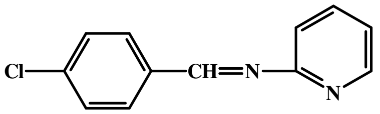
Key Words: Vibrational mode, 2N-[(4-chlorobenzalidene)aminopyridine], 2N-[(4-hydroxybenzalidene)aminopyridine], AM1, PM3, MNDO, ZINDO, Comparison and correlation.

INTRODUCTION

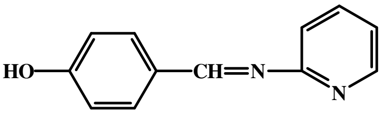
Semi empirical methods are based on quantum chemical methods of wave function solutions. Methods like AM1, PM3, MNDO, ZINDO are very helpful in predicting various parameters like heat of formation, electron population, *etc*. These methods are now extensively been used as an aid and alternative tool for analysis of IR spectra or vibrational frequencies to draw conclusions regarding structure of organic molecules like drugs, biological compounds and various natural products[1-6].

The present work deals with comparison of vibrational frequencies obtained exprimentally and those predicted by semi empirical methods for two novel synthesized Schiff bases which are derived by condensation of primary amine and carbonyl compounds. They have been studied as early as 19th century[7] but their comparative study using experimental traditional methods is a recent step.

In this present work, the comparison between experimentally obtained IR frequencies and semi-empirically computer simulated frequencies is done and apart from it their correlation is also established. Also a part of vibrational frequencies are used to construct prdicted spectra to confirm its structural resemblance with the theoretically obtained spectra thus to that these semi empirical methods like AM1, PM3, MNDO, ZINDO can be used as an alternative and supportive tool for structural elucidation of organic molecules like Schiff bases. The Schiff bases synthesized for this purpose are 2N-[(4-chlorobenzalidene)aminopyridine] (2-CBAPy) and 2N-[4-hydroxybenzalidene)aminopyridine] (2-HBAPy) for which structures are given in Fig. 1.



2N-[(4-chlorobenzalidene)aminopyridine] (2-CBAPy)



2N-[(4-hydroxybenzalidene)aminopyridine] (2-HBAPy)

Fig. 1.

EXPERIMENTAL

Schiff bases are prepared by preparing solutions of aromatic aldehydes 4-chlorobenzaldehyde and 4-hydroxybenzaldehyde in ethanol and refluxing it with solution of 2-amino pyridine in equimolar quantities in round bottom flask for 6 h. The IR spectra of these complexes 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 *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

The infrared spectra of these Schiff bases were compared to the semi empirically computer simulated spectra through AM1, PM3, MNDO, ZINDO methods as well as their statistical correlation was also calculated[10-12].

In the IR spectra of both complexes the azomethine peak appears at 1599 cm^{-1} and a typical peak of 1,4-disubstituted benzene ring appears at 800 cm^{-1}. The aromatic aldehyde apears in conjugation system imparts its peak at 1600 cm^{-1}. For 2-CBAPy the ring stretching frequency appears at 1351 cm^{-1} while it appears at 1384 cm^{-1} for 2-HBAPy. The ring bending of benzene for 2-CBAPy appears at 1118 cm^{-1} for 2-CBAPy while at 1250 cm^{-1} for 2-HBAPy. For pyridine ring bending for both ligands appears around 960 cm^{-1}. For Schiff bases the frequencies obtained at 781-740 cm^{-1} belong to 2 pyridine system and the other at 1275-1200 cm^{-1} is peculiar to C-O-C stretching mode of aryl alkyl ether. The C=N stretching frequency appears at 1593 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}. Another characteristic frequency appears at 990 cm^{-1} for C-N-C bending. Out-of-plane deformation appears at 768 and 729 cm^{-1}. Out-of-plane bending for substituted benzene appears[13] around 673 cm^{-1}. These frequencies were compared with semi empirically computer simulated frequencies and thier statistical correlation was also calculated. The two set of values showed fairly good correlation in range of 0.9998 to 0.9996 for 2-CBAPy and 0.9998-0.9554 for 2-HBAPy; signifying purity of synthesis and also indicating the alternative use of semi empirical methods to carry out vibrational analysis as a tool for structural elucidation (Table-1). These four methods *viz.*, AM1, PM3, MNDO and ZINDO were also used to generate plots (in part) between calculated frequencies and their intensities as transmittance. A close look

TABLE-1
VIBRATIONAL ANALYSIS OF SCHIFF BASES *viz.*, 2N-[(4-CHLOROBENZALIDENE)AMINOPYRIDINE] AND 2N-[(4-HYDROXYBENZALIDENE)AMINOPYRIDINE]

IR frequency (cm^{-1})	Semi empirically computer simulated frequencies (cm^{-1})				
	AM1	PM3	MNDO	ZINDO	Assignment
			2N-[(4-Chlorobenzalidene)aminopyridine]		
550	546.70	525.70	548.48	499.16	–
620	665.00	637.87	628.48	612.83	–
671	675.32	669.41	668.14	657.24	–
720	735.47	708.66	721.60	–	Out-of-plane for benzene
770	782.76	785.59	759.53	–	Out-of-plane ring deformation for 2-pyridine
820	826.58	858.30	850.40	810.52	–
910	923.10	918.36	918.00	929.47	C-N-C bending
980	982.12	980.30	941.31	979.42	C-N-C bending
1011	1019.63	1011.59	1019.12	1058.99	–
1083	1099.95	1105.43	1086.80	1060.00	Ring bending of benzene
1118	1119.08	1119.12	1168.49	1130.40	–
1200	1240.42	1207.22	1208.00	1197.84	C-O-C stretching mode
1300	1308.54	1325.23	1334.65	1287.19	Ring stretching
1351	1357.34	1349.20	1357.42	1342.28	–
1380	–	–	1383.81	1377.38	Pyridine ring bending
1471	1471.53	1397.30	1454.00	1477.50	–
1530	1559.19	–	1540.83	1541.83	Azomethine bending
1596	1614.18	1600.54	1594.42	1589.80	–
Statistical correlation	0.99972	0.99981	0.99965	0.999731	
			2N-[(4-Hydroxybenzalidene)aminopyridine]		
518	506.12	514.00	517.00	521.00	–
605	–	638.00	634.00	610.70	–
680	678.05	671.20	678.80	664.90	–
736	687.60	702.00	722.00	–	–
769	735.70	785.00	–	–	Out-of-plane for benzene
833	827.40	831.70	843.00	857.10	Out-of-plane ring deformation for 2-pyridine
888	894.40	887.50	896.50	885.80	1,4-disubstituted benzene system bending
995	987.00	974.90	956.50	979.70	–
1000	1003.90	1003.60	1006.90	–	C-N-C bending
1154	1120.00	1164.40	1169.70	1179.10	C-N-C bending
1250	1240.00	–	1265.00	1255.50	Ring bending of benzene
1282	1285.80	1290.00	1294.90	1287.20	–
1351	1374.60	1358.70	1340.70	1339.50	C-O-C stretching mode
1384	1405.00	1387.00	1366.30	1387.30	Ring stretching
1440	1449.00	1477.00	1434.20	1469.10	–
1508	1533.00	1526.90	1517.00	1502.70	Pyridine ring bending
1596	1574.00	1568.20	1563.30	1542.40	–
1610	1630.00	1639.00	1621.00	–	Azomethine bending
Statistical correlation	0.99986	0.96703	0.955548	0.96393	–

of the infrared spectra and semi empirically generated graph for significant frequencies suggest fair resemblance between the two.

Theoretical calculations for normal modes suggest 68 normal modes for 2-CBAPy and 69 normal modes for 2-HBAPy as per 3N-6; where n = 24 for 2-CBAPy and N = 25 for 2-HBAPy. The same number of normal modes are also obtained from semi empirical methods thus revealing its efficiency to be used as an supportive tool for structural elucidation of organic molecules.

Conclusion

From the semi empirically methods stability of organic molecules are predicted through their total energy and heats of formation. Thus these calculations can be also be carried out before synthesis to check their stability before hand. The total energy -56391.3 kcal/mol for 2-CBAPy and -55503.4 kcal/mol of 2-HBAPy confirms its stability which is reassured by heats of formation values for the Schiff bases 100.8 kcal/mol for 2-CBAPy and 63.47 kcal/mol for 2-HBAPy, respectively.

The point group for both ligands was found to be Cs. A close look at the data regarding vibrational frequencies obtained experimentally and those obtained through semi empirically 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.

With the help of these methods plots of absorbance *vs.* frequency can also be generated as a substitute for the experimentally obtained IR spectra so as to complete the vibrational analysis. Out of these four methods used; AM1 was found to be least time consuming and its statistical correlation was also in order of 0.999 thus reconfirming its utility as an alternative tool in vibrational analysis of organic molecules[14-16].

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