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Vibrational Spectroscopic Studies of Schiff base compounds derived from 4-Amino Antipyrine by Quantum chemical investigations

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Abstract

In this study 4-N-[Salicyledene]amino antipyrine (SAAPy), 4-N-[Benzalidene] aminoantipyrine (BAAPy),4-N-[(þ-Dimethylamino)benzalidene] amino antipyrine (þ-DABAAPy) schiff base of 4-Amino Antipyrine has been subjected to experimental and theoretical study by using Semi-empirical AM1, PM3, MNDO and ZINDO1 quantum chemical methods. The normal mode frequencies of vibration were analyzed. The theoretically obtained results were found to be consistent with the experimental data reported. A good correlation has been observed between experimental and calculated values of vibration modes.

Keywords: Semi-empirical methods, AM1, PM3, MNDO, ZINDO1, vibration modes, correlation coefficient.

Introduction

Schiff's bases are an important class of organic compounds. Schiff bases form a class of compounds with azomethine (-C=N-) group which can be obtained by condensation of primary amine and carbonyl compounds by elimination of water molecule[1-5]. In this present work three Schiff base are reported which were derived from 4-amino pyrine and Salicylaldehyde, Benzaldehyde and þ-Dimethylaminobenzaldehyde. In this respect, we report here the vibration modes of 4-N-[Salicyledene] aminoantipyrine (SAAPy),4-N-[Benzalidene]aminoantipyrine(BAAPy),4-N-[(þ-Dimethylamino)benzalidene] amino antipyrine (þ-DABAAPy) schiff base by using AM1, PM3, MNDO and ZINDO1 computational Semi-empirical methods and compare with experimental data[6-7].

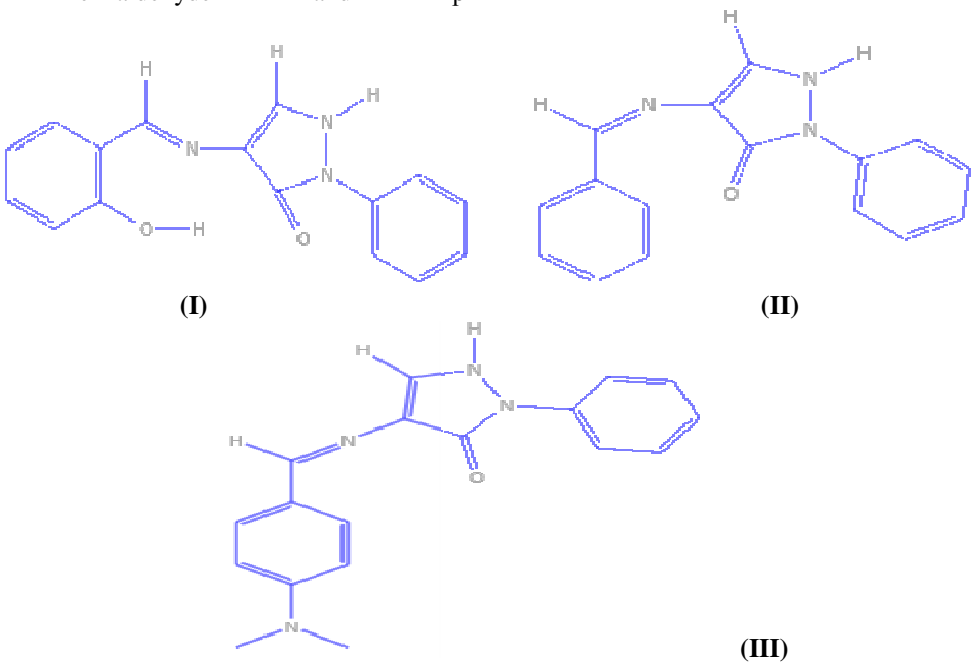

Figure-1
Molecular structure of 4-N-[Salicyledene]amino antipyrine (SAAPy)(C-1), 4-N-[Benzalidene]aminoantipyrine (BAAPy)(C-2) , 4-N-[(þ-Dimethylamino)benzalidene] amino antipyrine (þ-DABAAPy)(C-3) schiff base of 4-Amino Antipyrine (I, II and III, respectively)

Material and Methods

All the chemicals used were of AR grade and were used with further purification where ever required. C , H , N analysis of the compound under the studies were carried out on CHNS-O Elemental Vario EL III Carlo Erba 1108 and Melting Point of the compound are noted by usual method in chemistry research laboratory which are listed in table 1. The FTIR spectra of the compounds were recorded on a Perkin Elmer Infrared Spectrophotometer in the range of 4000 to 400 cm^{-1}.

Computational details: Intel based Pentium core-2 Duo machine with configuration Intel (R) core^{TM} 2 Duo CPU, T_{5450} @ 1.66 GHZ, 2 GB RAM , 250 GB HDD was used to run all the calculations. Semi-empirical AM1, PM3, MNDO and ZINDO1 quantum chemical calculations were carried out by the computer software HYPERCHEM 8.0 version and calculated parameters such as normal modes frequencies of vibration[8-9].

Results and Discussion

The experimental and calculated IR fundamental vibration modes for the 4-N-[Salicyledene]amino antipyrine (SAAPy), 4-N-[Benzalidene] aminoantipyrine (BAAPy),4-N-[(þ-Dimethylamino) benzalidene] amino antipyrine (þ-DABAAPy) Schiff based on AM1, PM3, MNDO and ZINDO1 Semi-empirical methods are presented in Table 2, 3 and 4 respectively and molecular structure of these compounds are presented in figure-1[10-11]. The correlation coefficients obtained for 4-N-[Salicyledene]amino antipyrine (SAAPy) are 0.999945, 0.999972, 0.999888 and 0.999941 by using AM1, PM3, MNDO and ZINDO1 Semi-empirical methods respectively[16-18]. It is evident that PM3 Semiempirical method gives the more satisfactory correlation (CC = 0.999972) between experimental and calculated vibration modes. In the case of 4-N-[Benzalidene] aminoantipyrine (BAAPy) Schiff base compound, the correlation coefficients obtained 0.999883, 0.999948, 0.999893 and 0.999815 by using AM1, PM3, MNDO and ZINDO1 Semi-empirical methods respectively. It is evident that PM3 Semiempirical method gives the more satisfactory correlation (CC = 0.999948) between experimental and calculated vibration modes[12]. In the case of 4-N-[(þ-Dimethylamino)benzalidene] amino antipyrine (þ-DABAAPy) Schiff base compound, the correlation coefficients obtained 0.999072, 0.999643, 0.999935 and 0.999514 by using AM1, PM3, MNDO and ZINDO1 Semi-empirical methods respectively[19-20]. It is evident that MNDO Semiempirical method gives the more satisfactory correlation (CC = 0.999935) between experimental and calculated vibration modes. Graphical correlations between experimental and calculated fundamental vibrational modes are presented in figures-2, 3 and 4 for the title Schiff base compounds, respectively. The experimental IR spectra for title Schiff base compounds are given in figure-5, 6 and 7 respectively[13].

Table-1
Analytical data for Schiff base compounds

CODE	Melting Point (^{0}C)	Elemental Analysis		
		C (In %)	H (In %)	N (In %)
C-1	185-190	63.51	5.15	12.77
C-2	158-162	76.34	7.04	17.44
C-3	198-202	67.22	6.46	16.48

Conclusion

Semi-empirical AM1, PM3, MNDO and ZINDO1 calculations have been carried out on the vibration mode frequencies. PM3 Semi-empirical method can be considered as the most appropriate quantum chemical method to facilitate the vibrational frequencies identification of such compounds, since the IR frequencies simulated by this method best linearity between the calculated and experimental frequencies data (CC = 0.999972, 0.999948 respectively) used in 4-N-[Salicyledene]amino antipyrine (SAAPy), 4-N-[Benzalidene] aminoantipyrine (BAAPy) Schiff base compounds. But MNDO Semi-empirical method gives most satisfactory correlation (0.999935) in the case of 4-N-[(þ-Dimethylamino)benzalidene] amino antipyrine (þ-DABAAPy) compound[14]. Thus, Quantum chemical Semiempirical calculation can be successfully used for the prediction of vibration modes of making more active ligands and other molecules.

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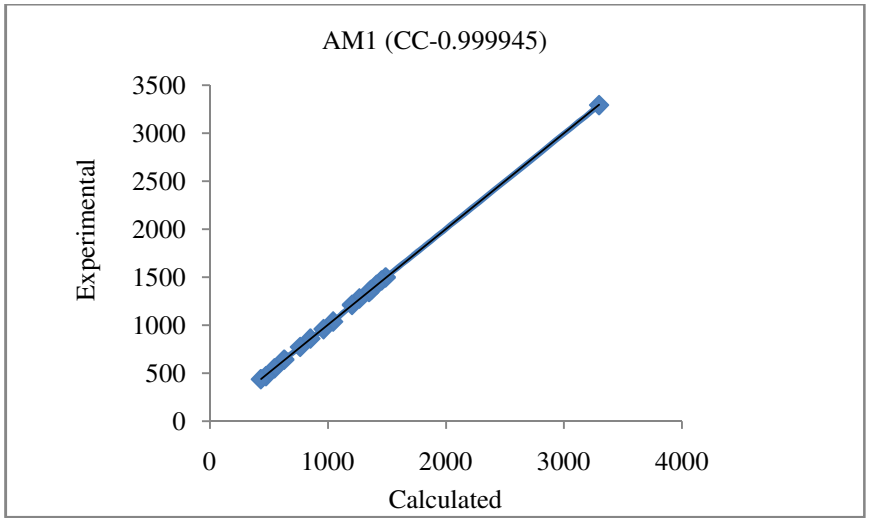
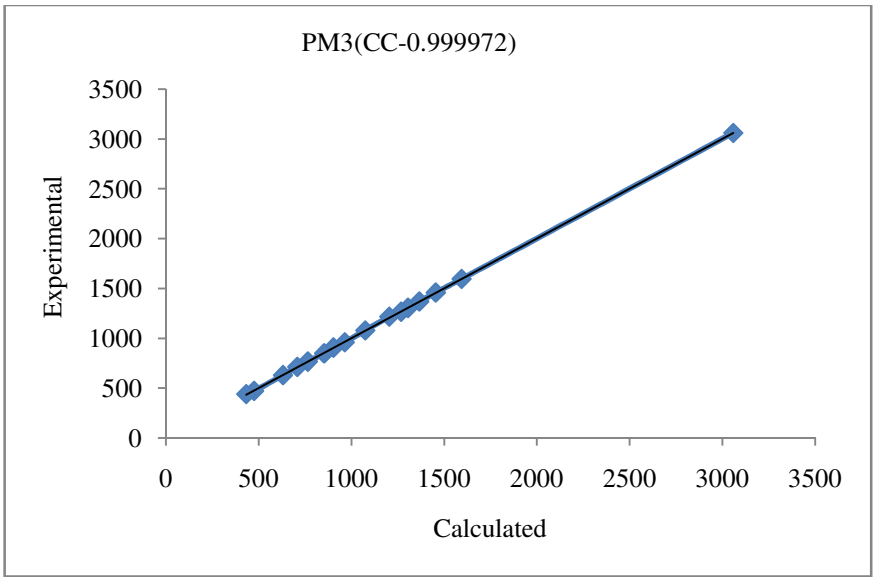
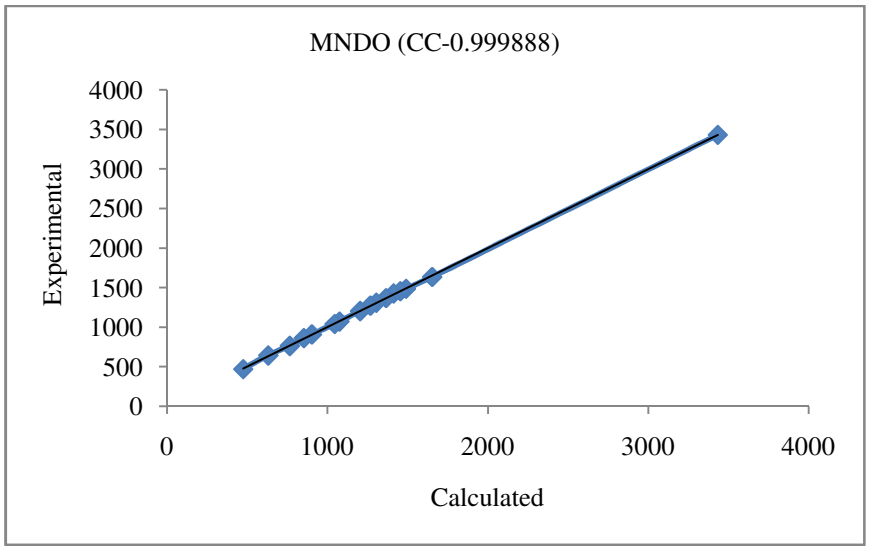

AM1 (CC-0.999945)
Experimental
Calculated
0
500
1000
1500
2000
2500
3000
3500
4000


PM3(CC-0.999972)
Experimental
Calculated
0
500
1000
1500
2000
2500
3000
3500


MNDO (CC-0.999888)
Experimental
Calculated
0
500
1000
1500
2000
2500
3000
3500
4000

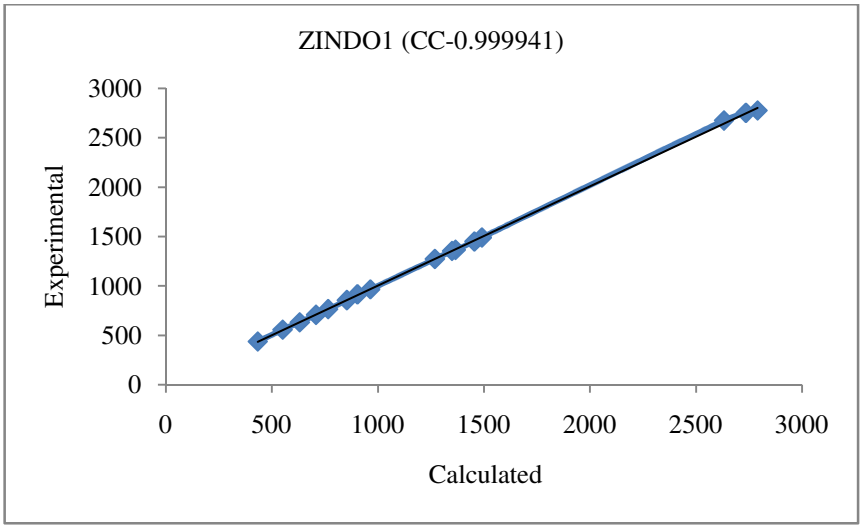
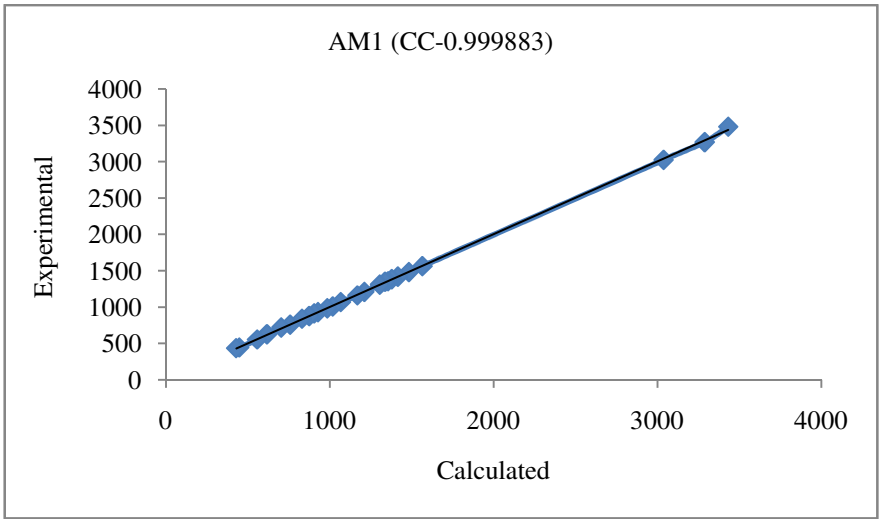
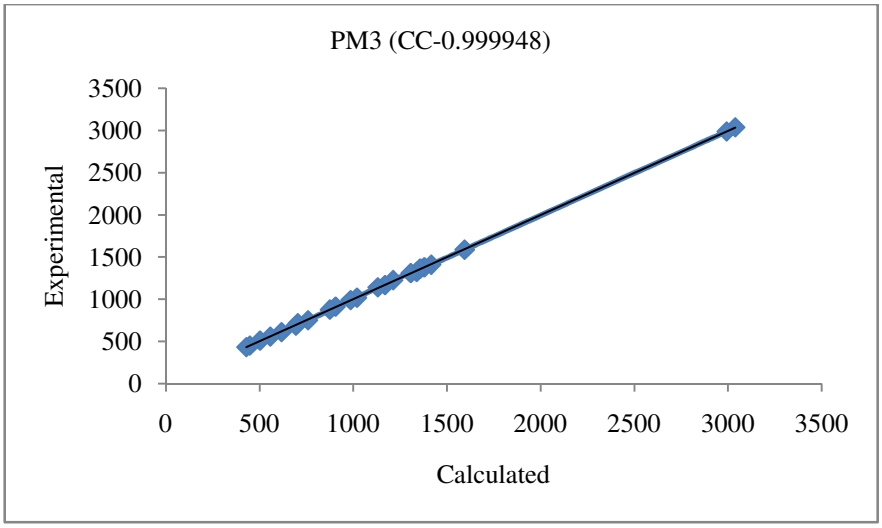
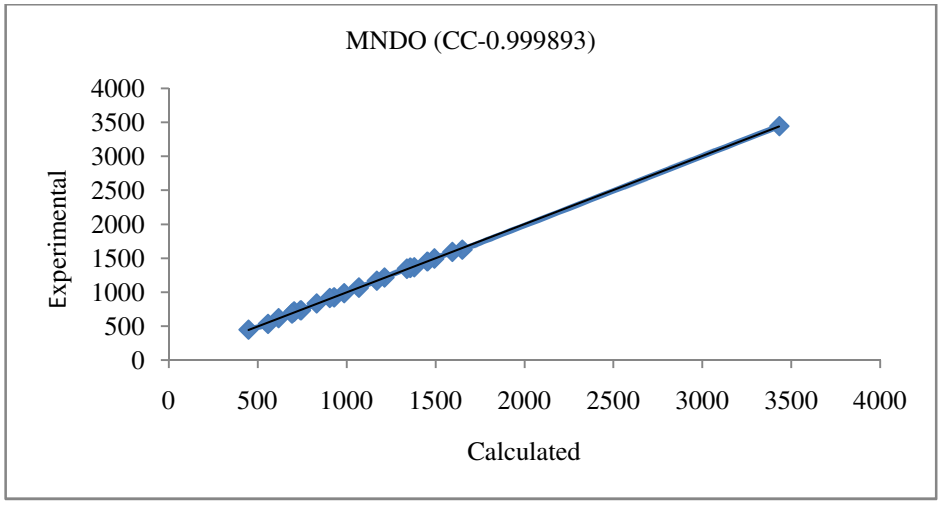


Figure-2
Graphical correlation between experimental and calculated fundamental vibration modes obtained by AM1, PM3, MNDO and ZINDO1 Semi-empirical methods for 4-N-[Salicyledene]amino antipyrine (SAAPy) (CC-Correlation coefficient)







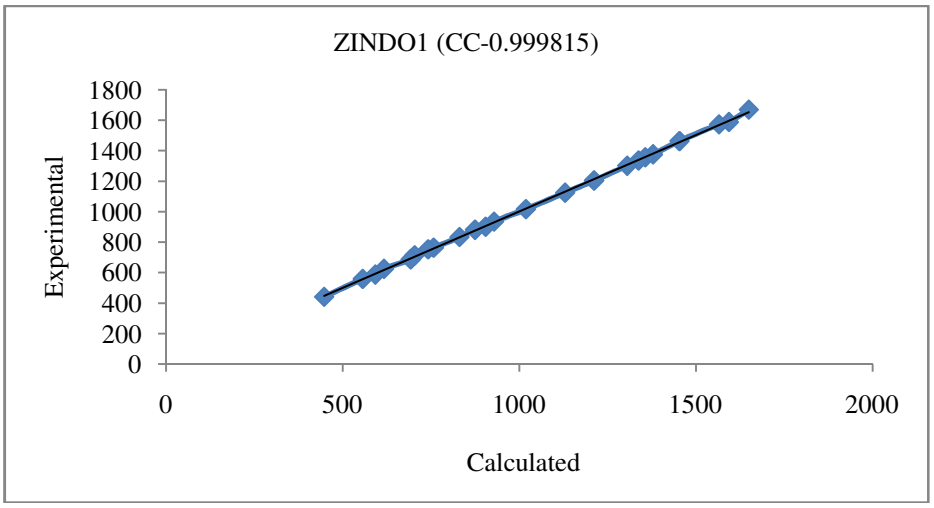
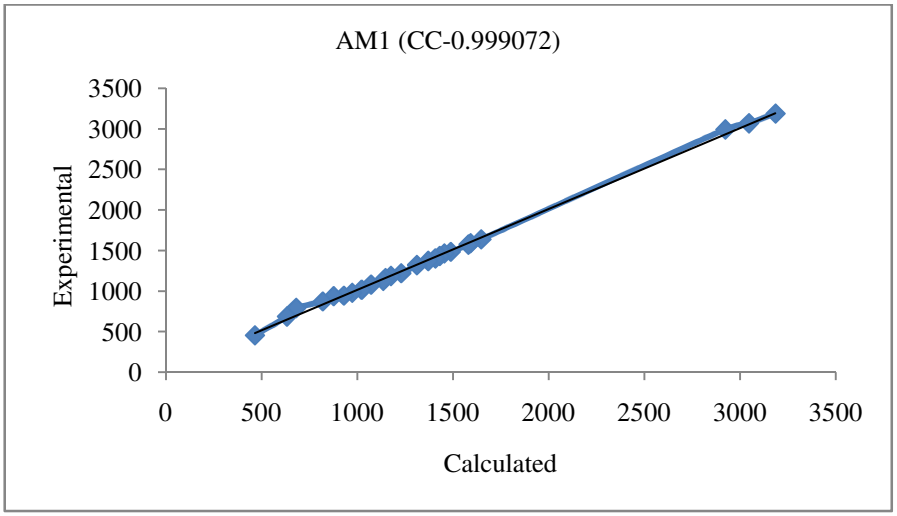


Figure-3
Graphical correlation between experimental and calculated fundamental vibration modes obtained by AM1, PM3, MNDO and ZINDO1 Semi-empirical methods for 4-N-[Benzalidene]amino antipyrine (BAAPy)(CC-Correlation coefficient)



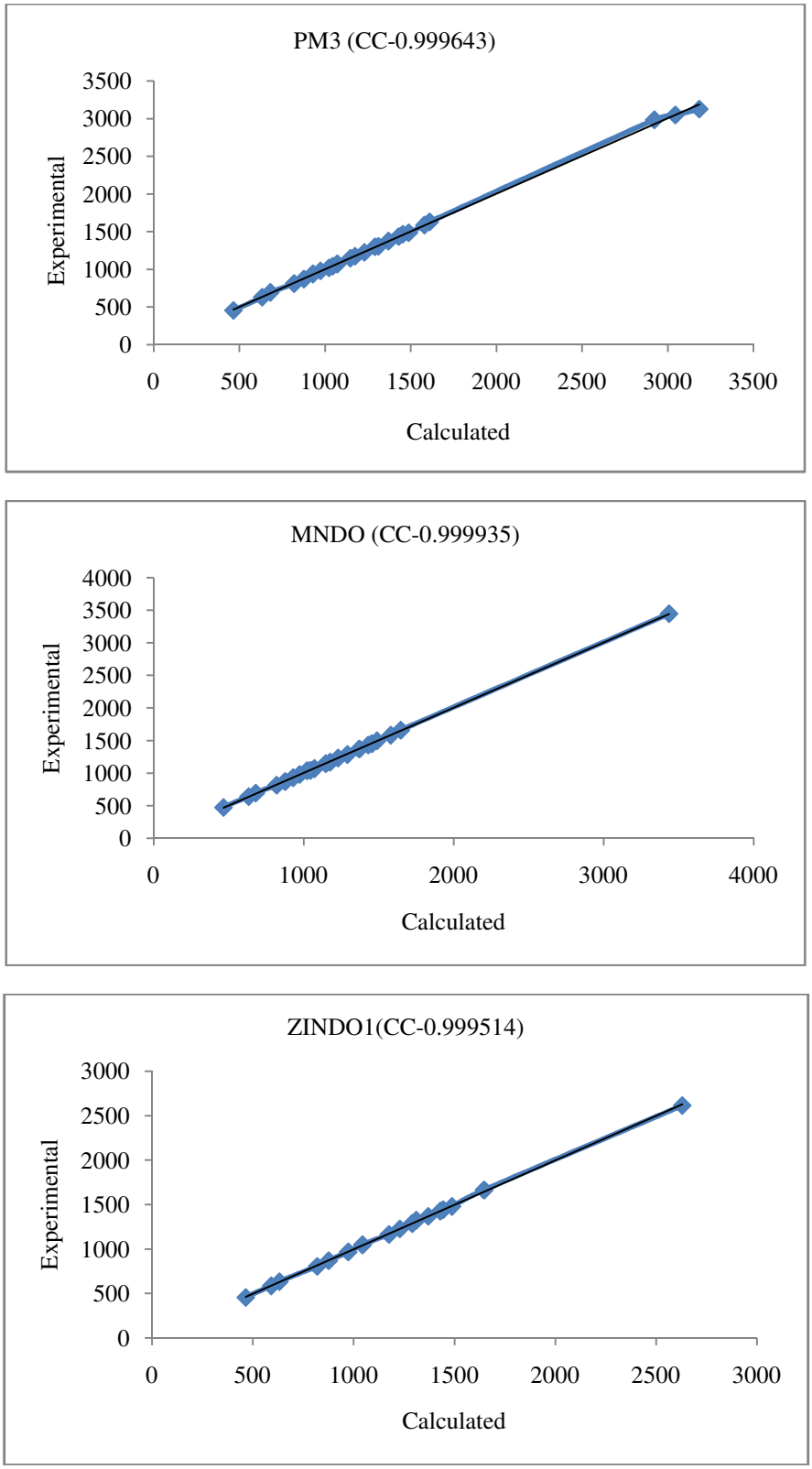


Figure-4
Graphical correlation between experimental and calculated fundamental vibration modes obtained by AM1, PM3, MNDO and ZINDO1 Semi-empirical methods for 4-N-[(þ-Dimethylamino)benzalidene]aminoantipyrene (þ-DABAAPy) (CC-Correlation coefficient)

Table-2
Normal Mode Frequency of Vibration (cm^{-1}) for 4-N-[Salicyledene]amino antipyrine (SAAPy)

Experimental Group Frequency (cm^{-1})	AM1 Computed Group Frequency (cm^{-1})	PM3 Computed Group Frequency (cm^{-1})	MNDO Computed Group Frequency (cm^{-1})	ZINDO1 Computed Group Frequency (cm^{-1})	Assignment
3434	-	-	3429	-	υ_{as} (N-H) in NH_2
3296	3291	-	-	-	υ_s (N-CH_3)
3241	-	-	-	-	υ_s (N-CH_3)
3059	-	3058	-	-	υ(C-H)
3017	-	-	-	-	υ(C-H)
2868	-	-	-	-	υ(=C-H) Aldehyde
2632	-	-	-	2673	υ_{as} (C-NH_2)
1653	-	-	1634	-	υ(C=O)
1594	-	1594	-	-	(NH_2) Sci
1490	1498	-	1485	1489	υ(C=C)
1455	1465	1457	1454	1449	υ(C=C)
1413	1423	-	1425	-	υ_{as}(C-CH_3)
1366	1368	1368	1367	-	υ(N-C)
1349	1345	-	-	1353	υ(C-N)
1305	-	1304	1309	-	υ(C-C)
1268	1278	1265	1272	1272	υ(C-H)
1204	1212	1215	1203	-	δ (C-H)
1139	-	-	-	-	δ (C=O)
1075	-	1078	1071	-	δ (C-H)
1045	1038	-	1040	-	(NH_2) Twi
964	959	959	-	965	δ (C-H)
934	-	-	-	-	δ (C-H)
903	-	905	907	914	δ (C-H)
853	861	847	862	856	δ (C-H)
765	774	765	763	765	δ (C-H)
753	-	-	-	-	δ (C-H)
708	-	711	-	708	υ(N-N)
631	642	629	642	632	δ (CCC)
550	553	-	-	557	δ (CCC)
475	470	470	470	-	δ (CCC)
433	438	439	-	438	τ (NH_2)

Table-3
Normal Mode Frequency of Vibration (cm^{-1}) for 4-N-[Benzalidene]amino antipyrine (BAAPy)

Experimental Group Frequency (cm^{-1})	AM1 Computed Group Frequency (cm^{-1})	PM3 Computed Group Frequency (cm^{-1})	MNDO Computed Group Frequency (cm^{-1})	ZINDO1 Computed Group Frequency (cm^{-1})	Assignment
3432	3480	-	3443	-	υ_{as} (N-H) in NH_2
3289	3268	-	-	-	υ_s (N-CH_3)
3038	3025	3035	-	-	υ_s (C-H)
2992	-	2986	-	-	υ(C-H)
1650	-	-	1627	1668	υ(C=O)
1594	-	1586	1594	1587	υ(NH_2) Sci
1566	1562	-	-	1572	υ(NH_2) Sci
1493	-	-	1496	-	υ(C=C)
1483	1480	-	-	-	υ(C=C)
1454	-	-	1452	1462	υ(C=C)
1416	1417	1408	-	-	υ_{as} (C-CH_3)
1379	1383	1378	1368	1375	υ(C-C)
1357	1353	1363	1361	1355	υ(C-C)
1338	1346	1322	1347	1334	υ(C-N)
1306	1307	1308	-	1300	υ(C-C)
1212	1207	-	1217	1203	δ (C-H)
1169	1159	1166	1169	-	δ (C-H)
1130	-	1140	-	1123	δ (C-H)
1068	1067	-	1068	-	δ (C-H)
1019	1007	1017	-	1015	δ (C-H)
985	982	988	985	-	δ (C-N)
929	928	-	925	933	δ (C-H)
905	912	911	915	900	δ (C-H)
875	876	876	-	880	δ (C-H)
831	839	-	835	832	(CCC) rb
758	756	750	-	751	δ (C-H)
742	-	-	734	-	δ (C-H)
704	717	714	716	712	δ (N-N)
693	-	685	687	686	ω (NH_2)
617	625	610	619	623	δ (CCC)
593	-	-	-	586	δ (CCC)
557	552	557	533	557	δ (CCC)
503	-	509	-	-	δ (CNN)
448	443	450	450	440	δ (CCN)
429	434	432	-	-	τ (NH_2)

Table-4
Normal Mode Frequency of Vibration (cm^{-1}) for 4-N-[(þ-Dimethylamino)benzalidene]aminoantipyrene(þ-DABAAPy)

Experimental Group Frequency (cm^{-1})	AM1 Computed Group Frequency (cm^{-1})	PM3 Computed Group Frequency (cm^{-1})	MNDO Computed Group Frequency (cm^{-1})	ZINDO1 Computed Group Frequency (cm^{-1})	Assignment
3435	-	-	3444	-	υ_{as} (N-H) in NH_2
3184	3185	3124	-	-	υ_s (N-CH_3)
3045	3066	3047	-	-	υ_s (C-H)
2922	2990	2982	-	-	υ(C-H)
2863	-	-	-	-	υ_{as}(C-H) in CH_3
2804	-	-	-	-	(=C-H) Aldehyde
2630	-	-	-	2614	υ_s (C-H) in CH_3
1647	1637	1628	1659	1664	υ(C=O)
1610	-	-	-	-	υ(C=O)
1591	1590	1586	1582	-	(NH_2) Sci
1488	1483	1483	1495	1480	υ(C=C)
1454	1463	-	1450	-	υ(C=C)
1444	-	-	1444	1444	υ(C=C)
1430	1432	1434	1431	1427	υ_{as}(C-CH_3)
1407	1402	-	-	-	υ_s(C-CH_3)
1370	1370	1373	1369	1369	υ(N-C)
1311	1319	1305	-	1325	υ(C-C)
1291	-	1297	1285	1288	υ(C-N)
1229	1219	1224	1232	1227	δ (C-H)
1175	1185	1173	1168	1165	δ (C-H)
1147	1158	1146	1145	-	δ (C-H)
1135	1127	-	-	-	δ (C-H)
1071	-	1070	1068	-	δ (C-H)
1044	-	1041	1038	1048	(NH_2) Twi
1022	1016	1018	-	-	δ (C-N)
1002	-	-	-	-	(CCC) Tri
973	978	978	980	968	δ (C-H)
929	936	938	929	-	δ (C-H)
876	872	870	870	869	δ (C-H)
819	-	809	814	805	(CCC) rb
680	686	693	693	-	δ (CCC)
632	-	628	639	635	δ (CCC)
591	-	-	-	587	δ (CCC)
465	455	454	474	457	δ (CCC)

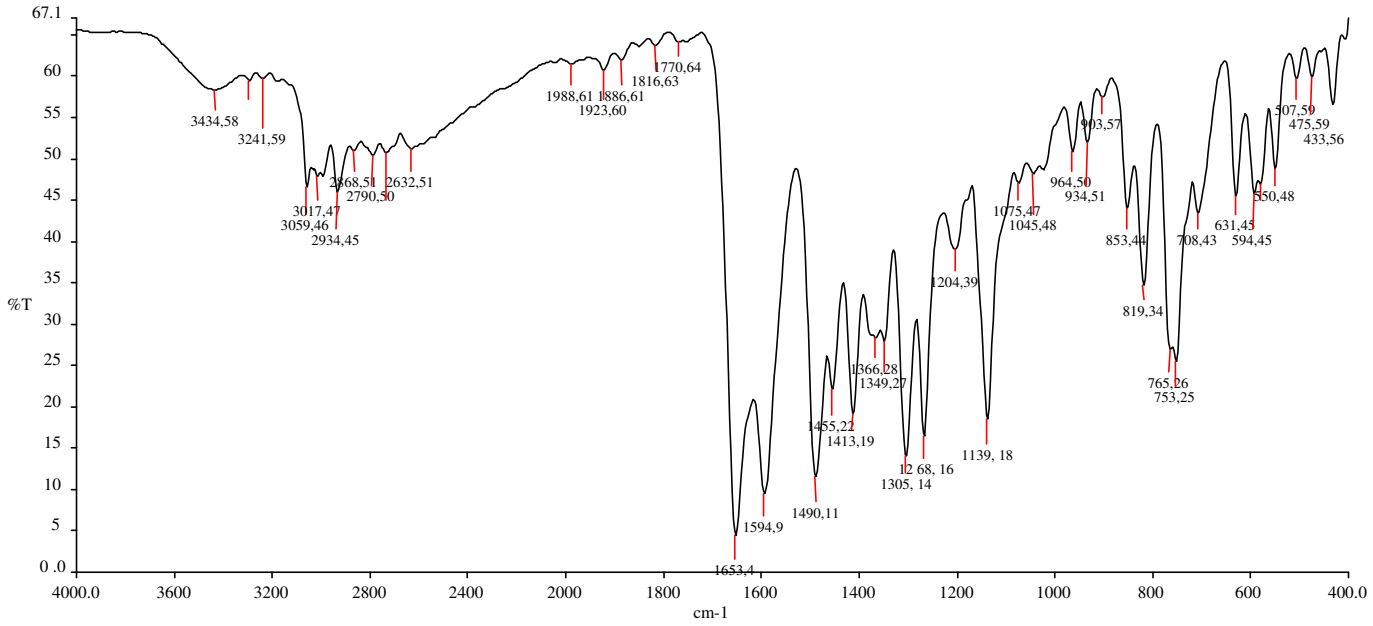


Figure-5
Experimental spectra of 4-N-[Salicyledene]amino antipyrine (SAAPy)

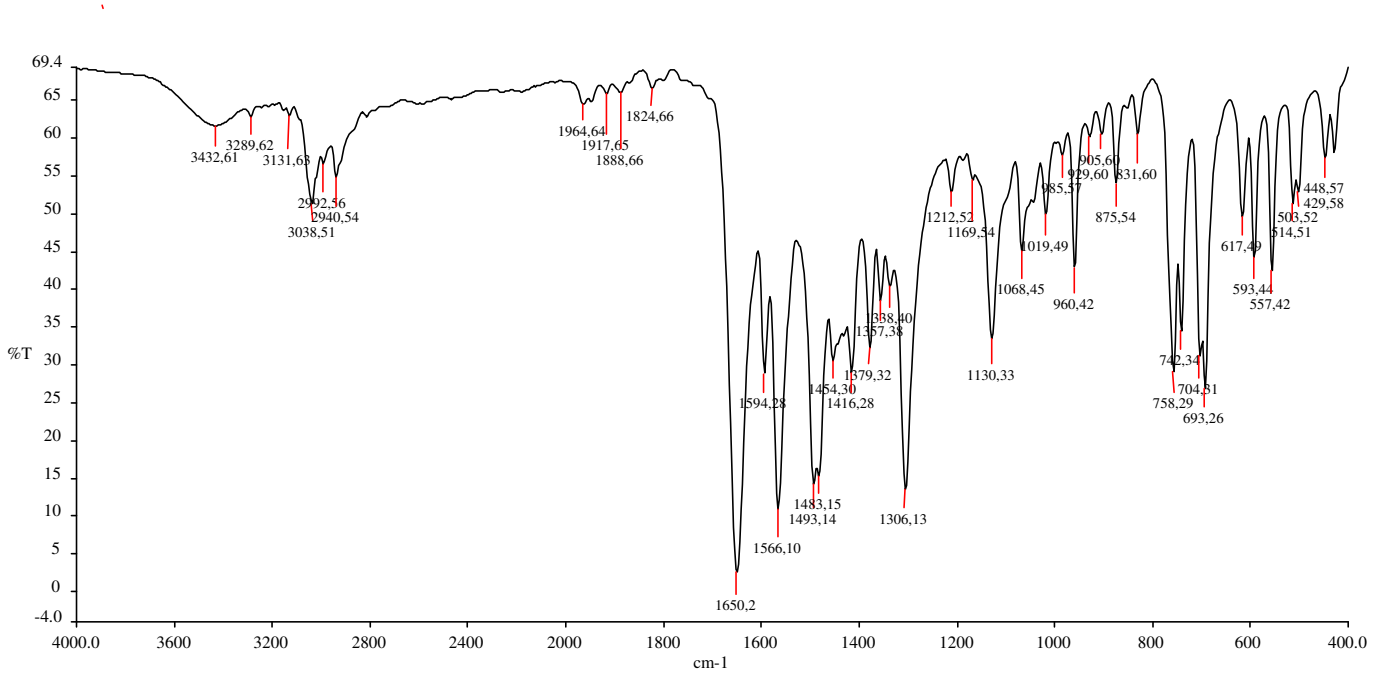


Figure-6
Experimental spectra of 4-N-[Benzalidene]amino antipyrine(BAAPy)

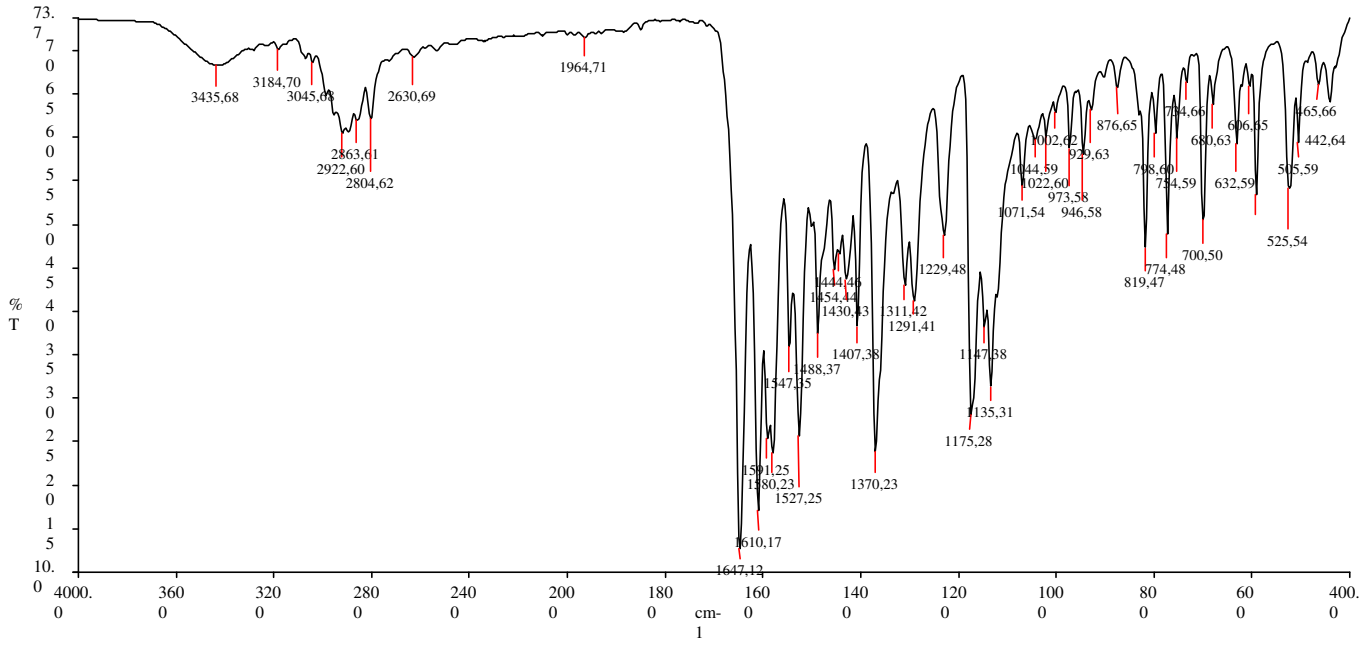


Figure-7
Experimental spectra of 4-N-[(þ-Dimethylamino)benzalidene]aminoantipyrene (þ-DABAAPy)

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