THE INTERNATIONAL JOURNAL OF
SCIENCE & TECHNOLEDGE

Theoretical IR Spectral and Computational Study of Some Schiff Base Compounds

Dr. Kishor Arora
Professor, Department of Chemistry, Government Autonomous Post Graduate College, Datia, India
Anu Parmar
Ph.D. Scholar, Jiwaji University, Gwalior, India

Abstract:
Schiff base compounds were obtained using 2-nitrobenzaldehyde, Vaniline, ρ- Chlorobenzaldehyde and 4-amino antipyrine. The synthesized compounds were analytically studied through spectral studies, melting points along with semi empirical AM1, PM3, MNDO and ZINDO1 methods. A good correlation has been observed between experimental and calculated (by semi-empirical AM1, PM3, MNDO and ZINDO1) values for vibration modes.

Keywords: *Semi-empirical methods AM1, PM3, MNDO, ZINDO1, Vibration modes, correlation.*

1. Introduction

Schiff bases are typically formed by the condensation of a primary amine and an aldehyde/ketone. The resultant compound, $R_1R_2C=NR_3$, is called a Schiff base (named after Hugo Schiff), where R_1 is an aryl group, R_2 is a hydrogen atom and R_3 is either an alkyl or aryl group. However, usually compounds where R_3 is an alkyl or aryl group and R_2 is an alkyl or aromatic group are also regarded as Schiff bases. Schiff bases that contain aryl substituent are substantially more stable and more readily synthesized, while those which contain alkyl substituent are relatively unstable[1-3]. Schiff bases of aliphatic aldehydes are relatively unstable and readily polymerizable while those of aromatic aldehydes having effective conjugation are more stable. In general, aldehydes react faster than ketones in condensation reactions, leading to the formation of Schiff bases as the reaction centre of aldehyde are sterically less hindered than that of ketone. Furthermore, the extra carbon of ketone donates electron density to the azomethine carbon and thus makes the ketone less electrophilic compared to aldehyde[4-5].

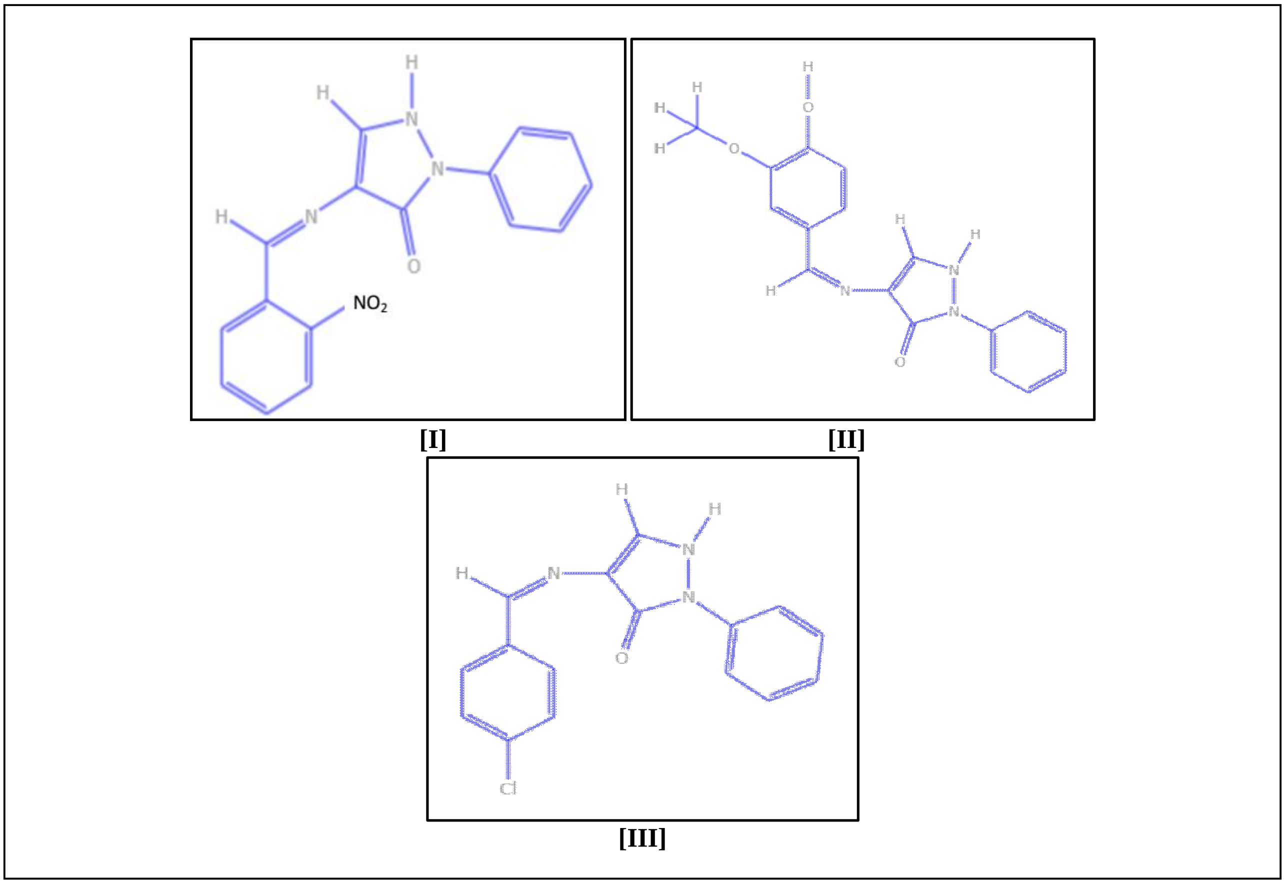
In this respect, we report here computed parameters viz. Total Energy (TE), Electronic Energy (EE), Core-core Interaction (CCI), Heat of Formation (HF), Highest Occupied Molecular Orbital (HOMO), Lowest Unoccupied Molecular Orbital (LUMO), Energy gap (EG), Dipole Moment (DM), Zero Point Energy (ZPE) and normal mode frequency of vibration for -N-[(2-Nitro)benzalidene]aminoantipyrine(2NBAAPy),4-N-[(4Hydroxy-3-methoxy)benzalidene]aminoantipyrine(4MBAAPy),4-N-[(þ-chloro) benzalidene] aminoantipyrine (þ-CBAAPy) schiff base of 4-Amino Antipyrine

1.1. Experiment

All the chemicals used were of AR grade and were used with further purification where ever required. Melting Point of the compounds are noted by usual method in chemistry research laboratory. The FTIR spectra of the compounds were recorded on a Perkin Elmer Infrared Spectrophotometer in the range of 4000 to 400 cm^{-1}.

1.2. Synthesis of Compounds

A mixture of 4-Amino Antipyrine (1M mol) in absolute ethanol(30ml) was slowly added to a solution of 2-nitrobenzaldehyde,Vaniline,ρ- Chlorobenzaldehyde(1.1M mol) in absolute ethanol(20 ml).The stirred reaction miture was refluxed for 12 hours. After cooling a precipitate was formed which was collected by filtration than washed with cold ethanol and recrystallized from it[6-7]. Molecular structure of the compounds are given in figure-1.



[I] [II] [III]

Figure 1: Molecular structure of 4-N-[(2-Nitro)benzalidene]aminoantipyrine(2NBAAPy),4-N-[(4Hydroxy-3-methoxy)benzalidene]aminoantipyrine(4MBAAPy),4-N-[(þ-chloro) benzalidene] aminoantipyrine (þ-CBAAPy) schiff base of 4-Amino Antipyrine (I, II & III, respectively)

1.3. 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[8-9] and calculated parameters such as Total Energy (TE), Electronic Energy (EE), Core-core Interaction (CCI), Heat of Formation (HF), Highest Occupied Molecular Orbital (HOMO), Lowest Unoccupied Molecular Orbital (LUMO), Energy gap between Highest Occupied Molecular Orbital and Lowest Unoccupied Molecular Orbital(EG), Dipole Moment (DM), Zero Point Energy (ZPE) and normal mode frequency of vibration[10-11].

2. Results and Discussion

The complexes are obtained in dry crystalline state and are quite stable for a long period of time. The melting point of these complexes was examined on melting point apparatus of our laboratory. The analytical results are discussed in Table-1.

IR Spectral studies:- The FTIR spectra of the compounds were recorded on a Perkin Elmer Infrared Spectrophotometer in the range of 4000 to 400 cm^{-1}[12-13]. The results obtained are given in Figure 2, 3 & 4 and discussed the peak in detail in Table 2, 3 & 4.

The AM1, PM3, MNDO, ZINDO1 semi-empirical methods with the help of computer software HYPERCHEM 8.0 version was used to calculate the normal modes frequency of vibration and to draw theoretically simulated spectra of these Schiff base compounds and the results obtained are given in Figure 5, 7 & 9.

A good matching between experimental and calculated vibration frequencies were observed in by all the four semi empirical method viz. AM1,PM3,MNDO,ZINDO1 (Correlation coefficient more than 0.999). Any discrepancy noted between the calculated and experimental frequency is due to the fact that the calculation have been done by taking all the number of electron present in the compounds Contrary to the experimental value recorded by the balanced electrons only[14-15].

Semi empirical studies:- With the help of AM1,PM3,MNDO and ZINDO1 semi-empirical methods parameters such as Total Energy (TE), Electronic Energy (EE), Core-core Interaction (CCI), Heat of Formation (HF), Highest Occupied Molecular Orbital (HOMO), Lowest Unoccupied Molecular Orbital (LUMO), Energy gap between Highest Occupied Molecular Orbital and Lowest Unoccupied Molecular Orbital(EG), Dipole Moment (DM), Zero Point Energy (ZPE) are obtained[16-17] and given in Table 5,6,7 respectively.

In computational method (AM1, PM3, MNDO) all values of heat of formation is positive which shows that the compounds are stable. The dipole moment (In Debye) is another important electronic parameter that results from non uniform distribution of charges on the various atoms in the molecule Heat of formation, Zero point energy and Dipole moment are very important parameters for chemical reactivity and biological activities of the studied compounds.

3. Conclusions

Semi-empirical AM1, PM3, MNDO and ZINDO1 calculations have been carried out on the vibration mode of frequencies. AM1 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 = 0.999957, 0.999899 respectively) used in 4-N-[(2-Nitro)benzalidene] aminoantipyrine,4-N-[(4Hydroxy-3-methoxy)benzalidene] amino anti- pyrine Schiff base compounds. But MNDO Semi-empirical method gives most satisfactory correlation (0.999944) in the case of 4-N-[(þ-chloro)benzalidene] aminoantipyrine compound. The correlation for the above compounds are discussed in figure 6, 8 &10. Thus Quantum chemical Semi-empirical calculation can be successfully used for the prediction of vibration modes for compounds.

CODE	Melting Point (^{o}c)	Elemental Analysis		
		C (In %)	H (In %)	N (In %)
C-1	180-182	63.51	5.15	12.77
C-2	177-180	65.23	6.09	13.84
C-3	166-170	67.14	6.01	15.20

Table 1: Analytical data for Schiff base compounds

S. No.	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
1.	3431	3437	3390	3431	-	υ_{as} (N-H) in NH_2
2.	3041	3080	3044	-	-	υ (C-H)
3.	2939	-	2983	-	-	υ (C-H)
4.	2864	-	-	-	-	υ(=C-H) Aldehyde
5.	1649	1657	-	1627	1681	υ(C=O)
6.	1591	-	1586	1585	-	(NH_2) Sci
7.	1568	1570	1560	-	-	NO_2 Grp. (Aromatic)
8.	1487	1484	-	1496	1481	υ (C=C)
9.	1453	-	-	1451	1448	υ (C=C)
10.	1430	-	-	-	1428	υ_{as} (C-CH_3)
11.	1385	1393	1381	1372	1396	υ (N-C)
12.	1356	1363	-	1356	1359	υ(C-C)
13.	1304	1310	1307	-	1303	υ(C-C)
14.	1170	1179	1168	1169	1164	δ (C-H)
15.	1131	-	1142	-	1127	δ (C-H)
16.	1071	1078	-	1068	1078	δ (C-H)
17.	1042	-	1032	1038	-	(NH_2) Twi
18.	1022	-	1019	1029	-	δ (C-N)
19.	972	-	970	982	969	δ (C-H)
20.	855	851	860	852	861	δ (C-H)
21.	826	828	823	-	-	(CCC) rb
22.	770	-	776	-	-	δ (C-H)
23.	746	749	747	-	-	δ (C-H)
24.	699	-	702	694	-	υ (N-N)
25.	662	668	669	671	663	ω (NH_2)
26.	620	617	615	621	621	δ (CCC)
27.	563	-	576	567	-	δ (CCC)
28.	457	450	-	-	-	δ (CCC)

Table 2: Experimental and Computed (AM1, PM3, MNDO, ZINDO1) Group frequencies of vibration (cm^{-1}) for 4-N-[(2-Nitro) benzalidene]aminoantipyrine (2NBAAPy)[C-1]

S. No.	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
1.	3113	3163	3079	-	-	υ (C-H)
2.	2993	-	2983	-	-	υ (C-H)
3.	2942	-	2960	-	-	υ_{as}(C-H) in CH_3
4.	2834	-	2877	-	-	(=C-H) Aldehyde
5.	1628	1636	1644	1634	1621	υ(C=O)
6.	1603	-	-	-	-	υ(C=C)
7.	1580	1572	1585	1585	-	(NH_2) Sci
8.	1497	-	-	-	-	υ(C=C)
9.	1486	-	1487	1480	1481	υ (C=C)
10.	1454	1456	-	1450	1454	υ (C=C)
11.	1435	-	-	1422	1434	υ_{as}(C-CH_3)
12.	1378	1380	1375	1368	1373	υ(N-C)
13.	1347	-	1342	1347	1341	υ(C-N)
14.	1258	1252	1258	-	-	υ (C-H)
15.	1215	-	1227	1215	1214	δ (C-H)
16.	1149	1142	1154	1158	1146	δ (C-H)
17.	1132	-	1134	-	-	δ (C-H)
18.	1071	1080	1074	1068	-	δ (C-H)
19.	1038	-	1031	1038	1028	(NH_2) Twi
20.	971	-	976	978	973	δ (C-H)
21.	922	925	915	926	916	δ (C-H)
22.	834	-	-	839	841	(CCC) rb
23.	815	813	-	-	-	(CCC) rb
24.	750	743	755	-	-	δ (C-H)
25.	724	-	722	716	723	δ (C-H)
26.	701	709	-	700	-	υ(N-N)
27.	636	630	-	637	644	δ (CCC)
28.	627	-	629	624	626	δ (CCC)
29.	554	558	-	543	-	δ (CCC)
30.	449	443	442	449	454	δ (CCN)

Table 3: Experimental and Computed (AM1, PM3, MNDO, ZINDO1) Group frequencies of vibration (cm^{-1}) for 4-N-[(4 Hydroxy-3-methoxy)benzalidene]aminoantipyrine (HMBAAPy) [C-2]

S.No.	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
1.	3433	-	3390	3443	-	υ_{as} (N-CH_3)
2.	3059	3078	3059	-	-	υ_{s} (C-H)
3.	3024	-	-	-	-	υ_{s} (C-H)
4.	2940	-	2990	-	-	υ (C-H)
5.	1650	1639	-	1628	1614	υ (C=O)
6.	1593	-	1594	1595	-	(NH_2) Sci
7.	1484	1481	-	-	-	υ(C=C)
8.	1455	-	-	1452	1446	υ(C=C)
9.	1430	-	-	-	-	υ_{as} (C-CH_3)
10.	1402	-	-	-	1403	υ_{s} (C-CH_3)
11.	1362	1361	1367	1369	1367	υ (N-C)
12.	1301	1301	1303	-	-	-CH_2Cl
13.	1214	-	1208	1217	1222	δ (C-H)
14.	1166	1158	1166	1168	1171	δ (C-H)

15.	1133	-	1131	-	-	δ (C-H)
16.	1098	-	1092	-	1095	δ (C=O)
17.	1043	-	1040	1041	1042	(NH_2) Twi
18.	1021	-	1017	-	-	δ (C-N)
19.	965	-	965	971	969	δ (C-H)
20.	947	948	936	-	-	δ (C-H)
21.	904	900	906	902	914	δ (C-H)
22.	833	-	842	835	-	(CCC)rb
23.	828	-	-	-	827	(CCC)rb
24.	749	756	753	-	-	δ (C-H)
25.	717	-	-	724	709	ʋ(N-N)
26.	698	-	-	-	-	δ (CCC)
27.	655	-	659	-	646	ω (NH_2)
28.	624	636	629	623	631	δ (CCC)
29.	591	-	-	585	597	δ (CCC)
30.	517	510	-	517	-	δ (CCC)
31.	502	-	508	-	-	δ (CNN)
32.	464	-	470	467	-	δ (CCC)
33.	408	400	-	-	418	(CH_3) Twi

Table 4: Experimental and Computed (AM1, PM3, MNDO, ZINDO1) Group frequencies of vibration (cm^{-1}) for 4-N-[(þ-chloro)benzalidene]aminoantipyrine (þ-CBAAPy) [C-3]

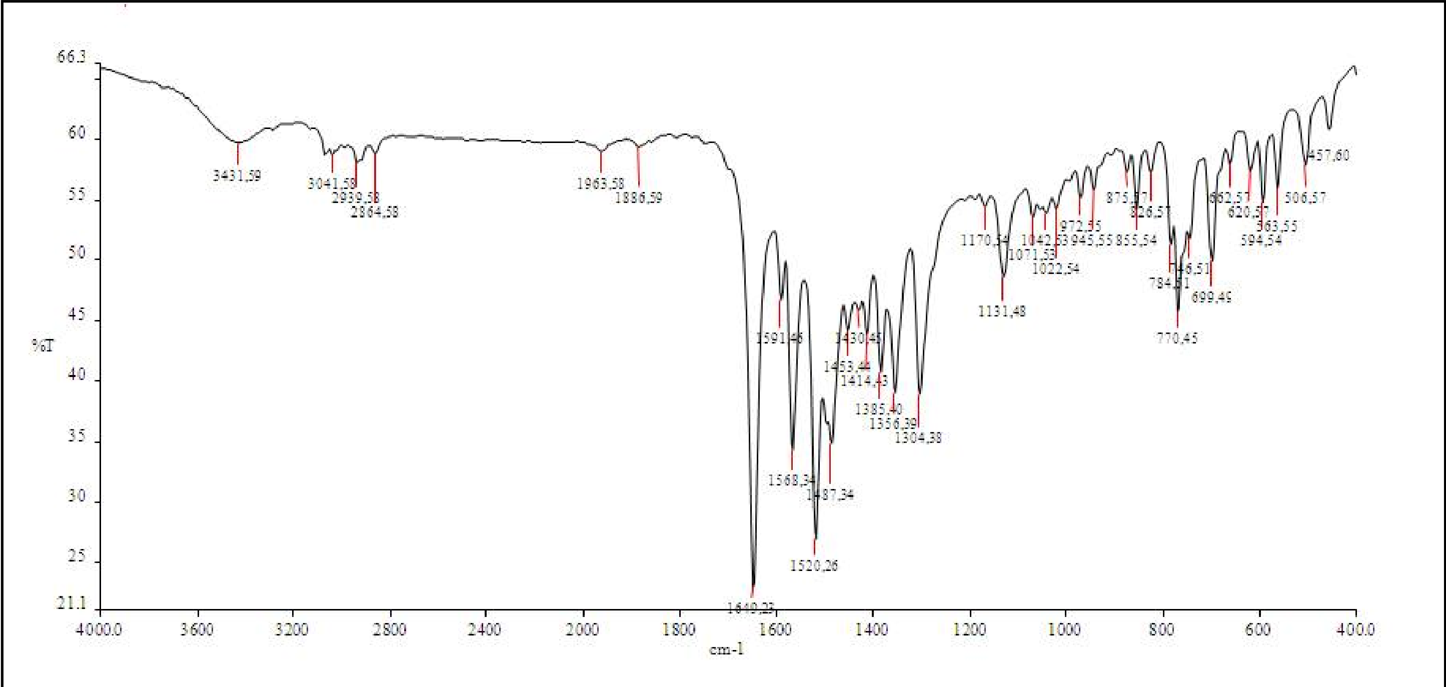


Figure 2: Experimental spectra of 4-N-[(2-Nitro)benzalidene]aminoantipyrine (2NBAAPy)[C-1]

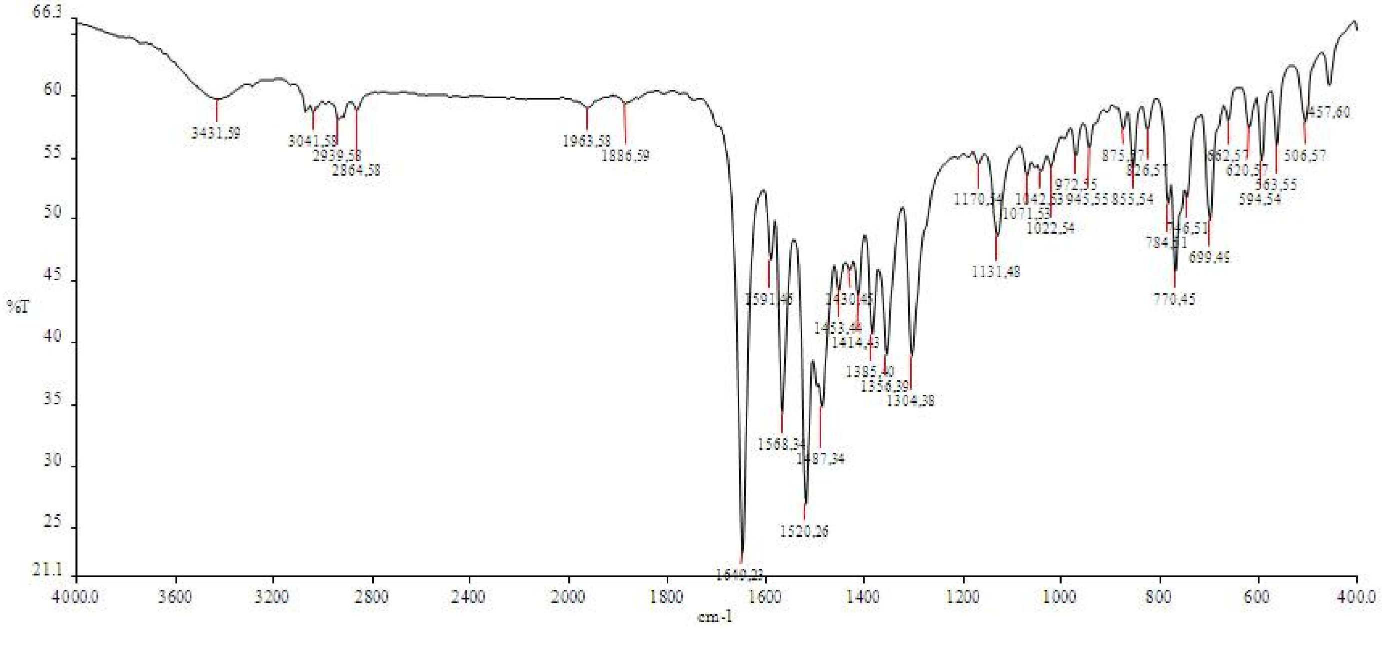


Figure 3: Experimental spectra of 4-N-[(2-Nitro)benzalidene]aminoantipyrine(2NBAAPy)[C-2]

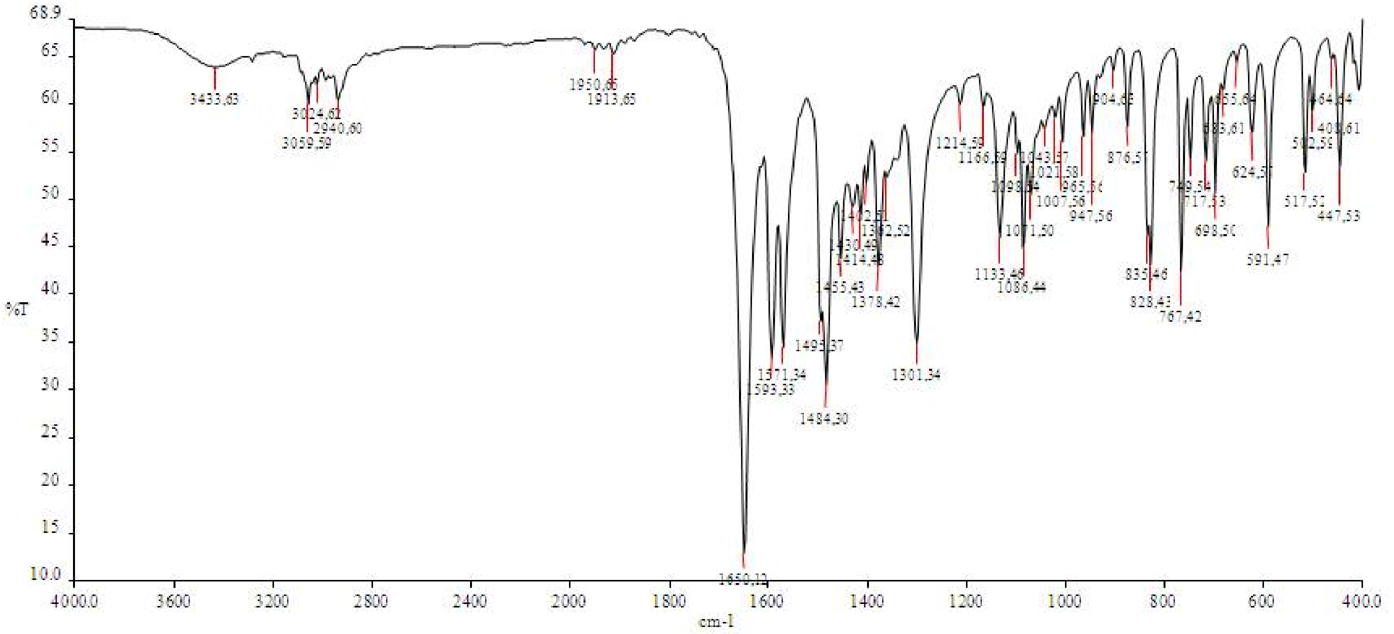


Figure 4: Experimental spectra of 4-N-[(þ-chloro)benzalidene]aminoantipyrine(þCBAAPy)[C-3]

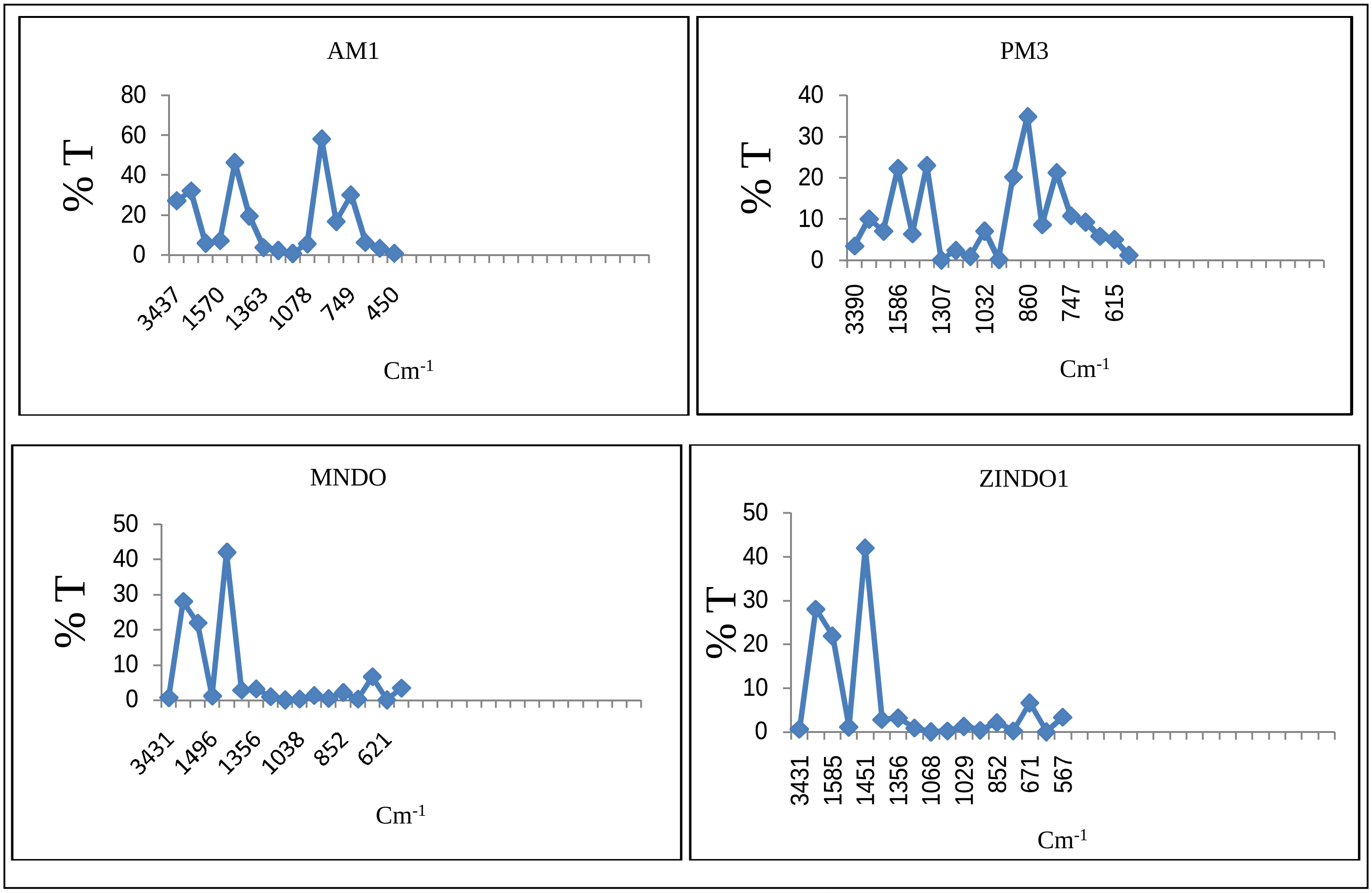
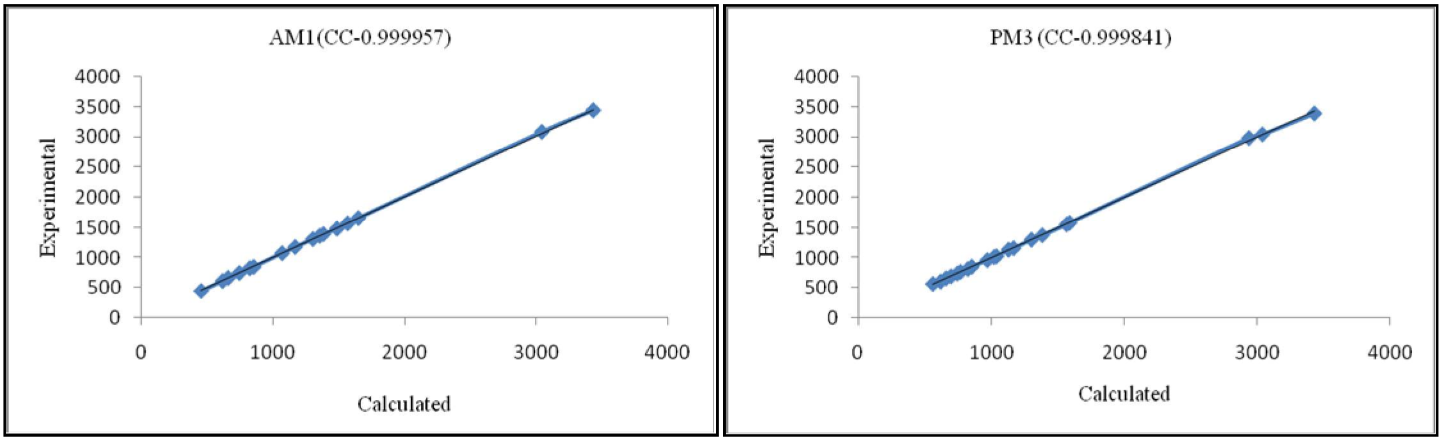


Figure 5: Theoretically AM1, PM3, MNDO & ZINDO1Simulated spectra for 4-N-[(2-Nitro)benzalidene]aminoantipyrine (2NBAAPy)[C-1]



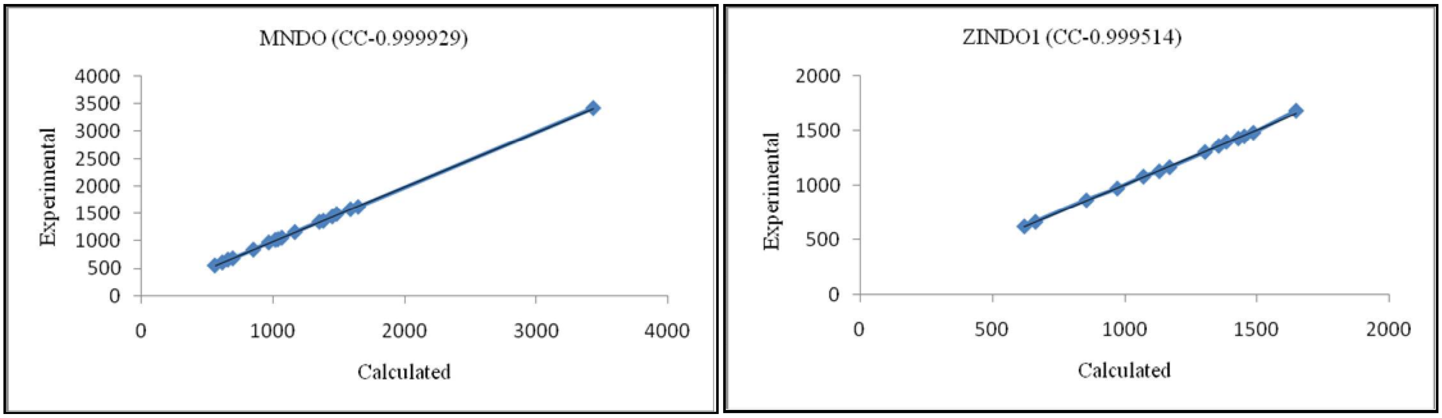


Figure 6: Graphical correlation between experimental and calculated fundamental vibration modes obtained by AM1, PM3, MNDO and ZINDO1 Semi-empirical methods for 4-N-[(2-Nitro)benzalidene]aminoantipyrine (2NBAAPy) [C-1](CC-Correlation coefficient).

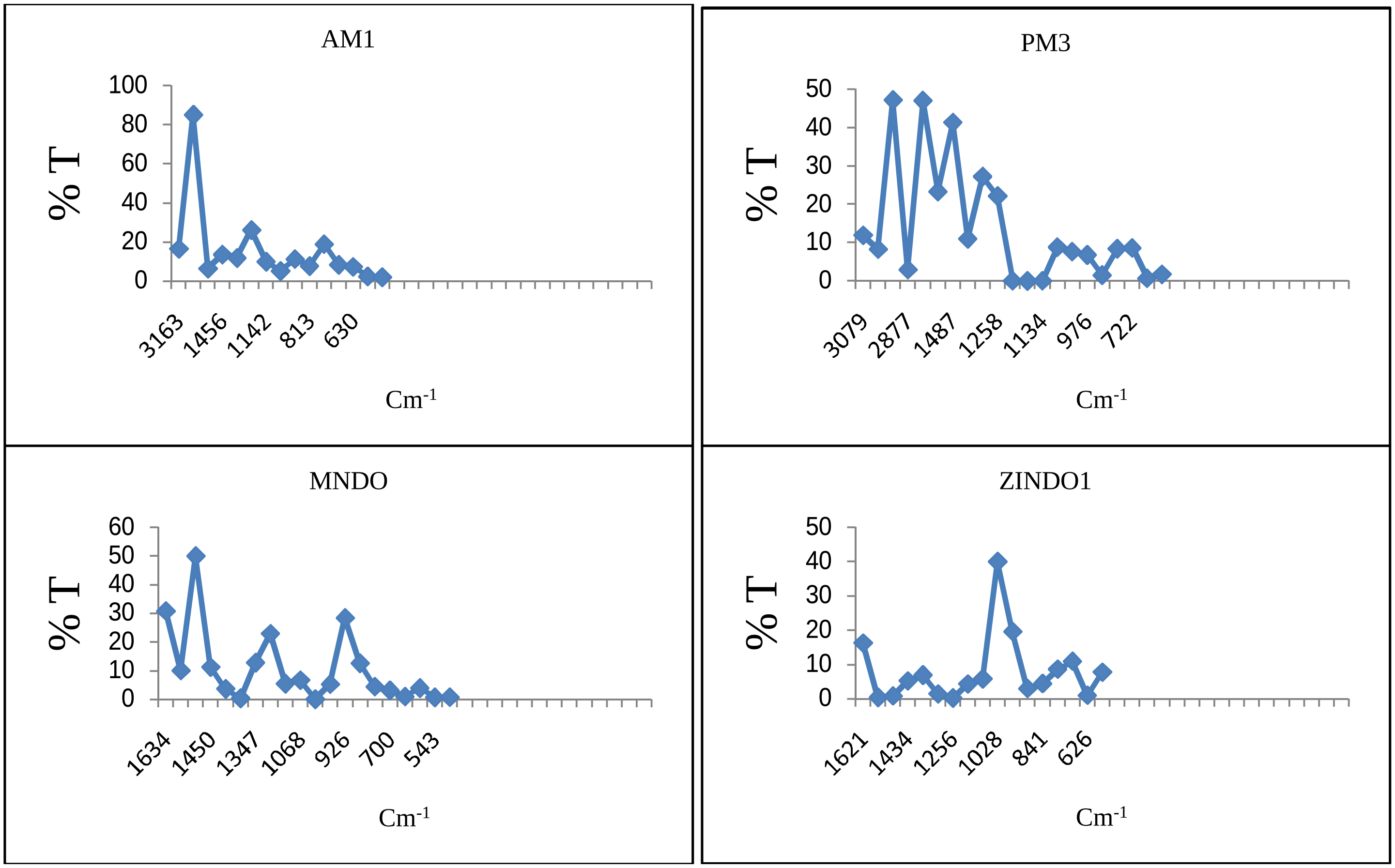


Figure 7: Theoretically AM1,PM3, MNDO & ZINDO1Simulated spectra for 4-N-[(4 Hydroxy-3 methoxy)benzalidene]aminoantipyrine (HMBAAPy) [C-2]

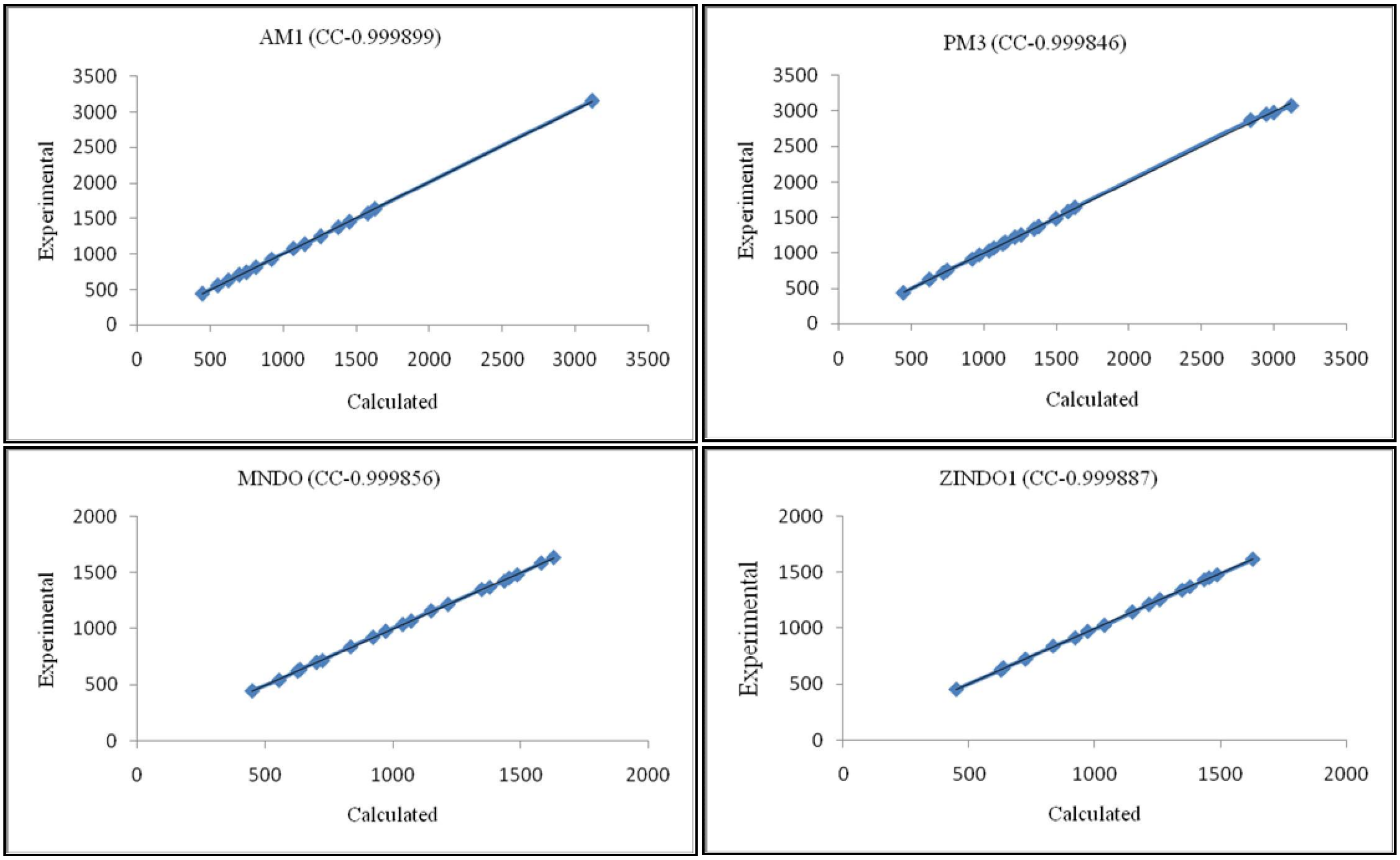


Figure 8: Graphical correlation between experimental and calculated fundamental vibration modes obtained by AM1, PM3, MNDO and ZINDO1 Semi-empirical methods for 4-N-[(4 Hydroxy-3-methoxy)benzalidene]aminoantipyrine (HMBAAPy) [C-2] (CC-Correlation coefficient)

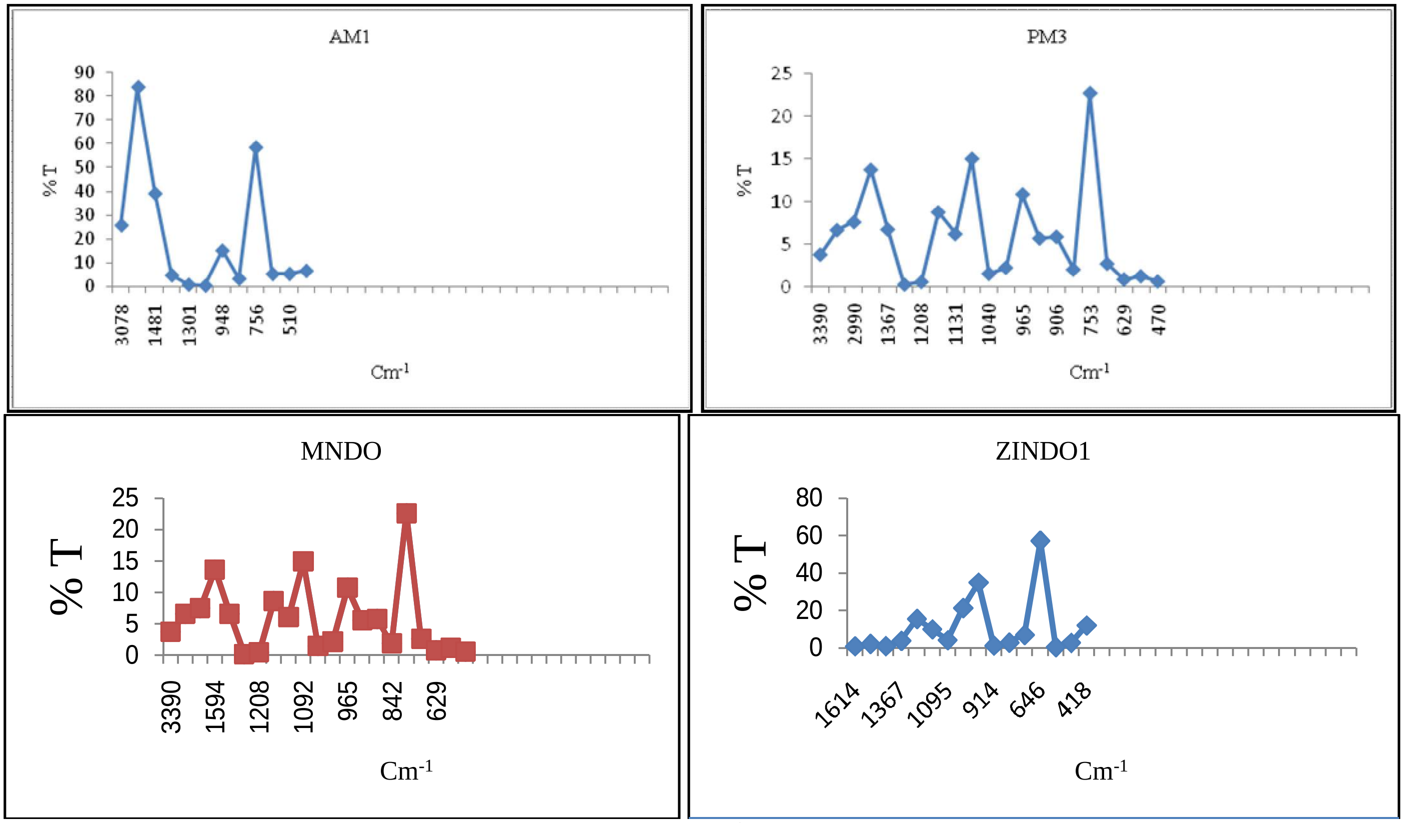


Figure 9: Theoretically AM1,PM3, MNDO & ZINDO1Simulated spectra for 4-N-[(þ-chloro)benzalidene]aminoantipyrine (þ-CBAAPy)[C-3]

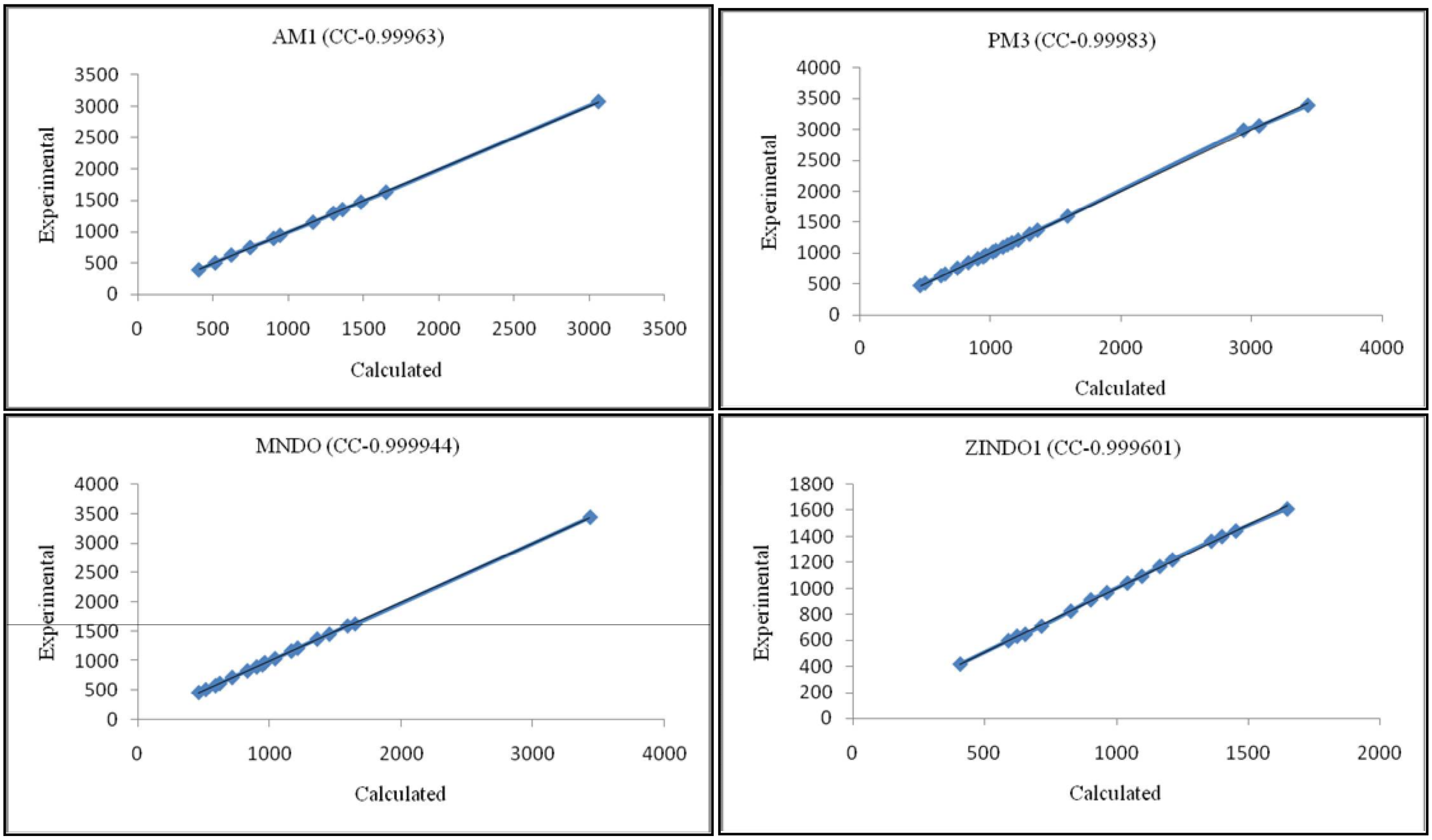


Figure 10: Graphical correlation between experimental and calculated fundamental vibration modes obtained by AM1, PM3, MNDO and ZINDO1 Semi-empirical methods for 4-N-[(þ-chloro)benzalidene]aminoantipyrine (þ-CBAAPy) [C-3] (CC-Correlation coefficient)

	AM1	**PM3**	**MNDO**	**ZINDO1**
TE(K.cal./Mol)	-92798.1	-83848.1	-93025.0	-130048.9
EE(K.cal/Mol)	-610285.0	-596695.3	-613624.9	-718916.3
CCI(K.cal/Mol)	517486.9	512847.1	520599.8	588867.3
HF(K.cal/Mol)	93.349	64.516	51.766	-8144.79
HOMO(eV)	-0.039	-0.148	-0.239	-5.477
LUMO(eV)	0.269	0.076	0.126	4.421
EG (eV)	0.23	-0.072	-0.113	-1.056
DM(Debye)	4.618	3.890	3.535	6.427
ZPE (K.cal/Mol)	183.28	175.92	189.07	249.78

Table 5: Computed parameters for 4-N-[(4 Hydroxy-3-methoxy)benzalidene]aminoantipyrine (HMBAAPy)

	AM1	**PM3**	**MNDO**	**ZINDO1**
TE(K.cal./Mol)	-91279.3	-83201.9	-91574.2	-127766.3
EE(K.cal/Mol)	-596886.6	-585032.2	-606355.4	-713323.9
CCI(K.cal/Mol)	505607.3	501830.2	514781.1	585557.5
HF(K.cal/Mol)	103.30	52.524	-5.392	-8331.51
HOMO(eV)	-0.259	-0.311	-0.274	-5.759
LUMO(eV)	0.284	0.096	0.181	4.432
EG (eV)	0.025	-0.215	-0.093	-1.327
DM(Debye)	5.842	5.805	5.725	7.808
ZPE(K.cal/Mol)	182.21	177.41	196.14	259.91

Table 6: Computed parameters for 4-N-[(4 Hydroxy-3-methoxy)benzalidene]aminoantipyrine (HMBAAPy)

	AM1	PM3	MNDO	ZINDO1
TE(K.cal./Mol)	81285.3	-73215.6	-80957.9	-11.425.6
EE(K.cal/Mol)	-504031.3	-492024	-505504.5	-605084.1
CCI(K.cal/Mol)	422746.0	418808.6	424546.5	494658.4
HF(K.cal/Mol)	109.55	75.696	73.536	-7428.79
HOMO(eV)	-0.124	-0.147	-0.224	-6.215
LUMO(eV)	0.255	0.065	0.079	5.326
EG (eV)	0.131	-0.082	-0.145	-0.889
DM(Debye)	3.881	3.700	2.831	5.232
ZPE(K.cal/Mol)	161.40	154.26	165.21	217.24

Table 7: Computed parameters for 4-N-[(þ-chloro)benzalidene]aminoantipyrine (þ-CBAAPy)

4. References

i. Dhar D N & Taploo C L.(1982).Schiff bases and their applications.J Sci. Ind. Res., 41,501–506.

ii. Arulmurugan S, Kavitha P H & Venkatraman R P.(2010).Biological activities of Schiff base and its complexes: a review.Rasayan J Chem.,3(3),385–410.

iii. Przybylski P, Huczyński A, Pyta K, Brzezinski B & Bartl F.(2009). Biological properties of Schiff bases and azo derivatives of phenols. Curr Org Chem.,13,124–148.

iv. Guo Z, Xing R, Liu S, Zhong Z, Ji X & Wang L.(2007).Antifungal properties of Schiff bases of chitosan, N-substituted chitosan and quaternized chitosan. Carbohydra Res,342(10),1329–1332.

v. Haddad R, Yousif E & Ahmed A.(2013). Synthesis and characterization of transition metal complexes of 4-amino-5-pyridyl-4H-1,2,4-triazole-3-thiol.Springer plus, 2,510-518.

vi. Arora K & Agrawal D.D.(2004).Synthesis and characterization of Lanthanide (III) Perchlorate complexes of some Schiff base ligands. Asian J. Chem., 16, 489.

vii. Hodnett, E.M. & Dunn, W.J. (1970). Synthesis of Novel Azo Schiff Base Bis[5,(4-methoxyphenylazo)-2-hydroxy-3-methoxy benzaldehyde]-1,2-Phenylenediamine.Journal of Medicinal Chemistry, 13, 768-770.

viii. HyperChem^{TM} Professional Release 8.0 for Window Molecular Modeling System.(2002).Dealer: Copyright ©

ix. Stewart J. J. P., Lipkowinz, K. B. & Boyal, D. B.(1990).Reviews in Computational Chemistry, V.C.H. 1- 45.

x. Arora K & Nathani V.(2013). QSAR studies of some pyrazolones as Antimicrobial agent.Int. J Pharm. Bio Sci., 4(1),657 – 671.

xi. Arora K & Nathani V.(2012).Anti-Microbial and QSAR Studies of Some Pyrazolone Compounds. Research Journal of Pharmaceutical, Biological and Chemical Sciences, 03,1423-1437.

xii. Marianne L. McKelvy, Thomas R. Britt & Bradley L. Davis.(1998).Infrared Spectroscopy. Anal. Chem.,70, 119-177.

xiii. P. Gans, Chapman & Hall.(1975).Vibrating Molecules: an Introduction to the Interpretation of Infrared and Raman Spectra. London.

xiv. Arora K, Kumar D., Burman K,Agnihotri S & Singh S.(2011). Theoretical studies of 2-nitrobenzaldehyde and furan-2-carbaldehyde Schiff base of 2-amino pyridine.J. Saudi Chem. Soc.,15, 161.

xv. Kumar D., Agrawal M. C. & Rajeev Singh.(2006).Theoretical Study of Pyridine-2-Amidoxime by Semi-empirical Methods, Oriental J. Chem., 22(1), 67.

xvi. Singh Rajeev, Kumar D., Singh Bhoop, Singh V.K. & Sharma Ranjana.(2013).Molecular structure, vibrational spectroscopic and HOMO, LUMO studies of S-2-picolyl-β-N-(2-acetylpyrrole) dithiocarbazate Schiff base by Quantum Chemical investigations. Res. J. Chem. Sci., 3(2),79-84.

xvii. Arora K.(2008).QSAR studies of some pharmacological Schiff base compounds. Asian Journal of chemistry, 28(8),5941-5946.