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"Synthesis and Vibration mode study of Schiff base compounds of 4-Dimethyl-aminoantipyrine"

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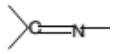
Abstract: *In this study 2,3-Dimethyl-4-[(þ-dimethoxy(amino)benzalidene]aminoantipyrine , 2,3-Dimethyl-4-[Glutaralidene]aminoantipyrine, 2,3-Dimethyl-4-[Furfuralidene]aminoantipyrine Schiff base compounds of 4-Dimethyl-aminoantipyrine were synthesized and stabilized their molecular structure by analytical methods such as melting point and elemental analysis. These Schiff base compounds has been subject to semi-empirical study by AM1, PM3, MNDO and ZINDO1 quantum chemical methods and find out some important parameters along with Vibration mode of frequency. A good correlation has been observed between different quantum chemical methods.*

Keywords*: Semi-empirical, AM1, PM3 , MNDO , ZINDO1, Vibration mode Frequency.*

I. Introduction

The condensation of primary amines with carbonyl compounds was first reported by Schiff and the condensation products are often referred to as Schiff bases[1]. Various studies have shown that group  has considerable biological importance. Schiff bases and their coordination compounds have gained importance recently because of their application as models in biological, biochemical, analytical, antimicrobial system, anticancer, antibacterial and antifungal activities[2-4]. The four main approaches for calculating molecular properties are Semi-empirical, ab-initio, density functional theory (DFT) and molecular mechanics (MM) methods. These quantum chemical methods can provide informations regarding vibration modes and other 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(EG), Dipole Moment (DM), Zero Point Energy (ZPE).

In this respect we reported here the synthesis and vibration modes with other parameters for Schiff base compounds 2,3-Dimethyl-4-[(þ-dimethoxy(amino)benzalidene]amino antipyrine (DMDMBAAPy) [C-1] , 2,3-Dimethyl-4-[Glutaralidene]amino antipyrine (DMGAAPy) [C-2] , 2,3-Dimethyl-4-[Furfuralidene]aminoanti pyrine (DMFAAPy)[C-3] of 4-Dimethylamino- antipyrine.

II. Experimental

2.1 Materials and Methods

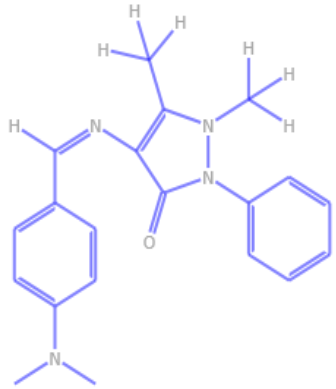
All the chemicals used were of AR grade and were used with further purification where ever required. C , H , N analysis of the compound under the studies were carried out on CHNS-O Elemental Vario EL III Carlo Erba 1108 and Melting Point of the compound are noted by usual method in chemistry research 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} at SAIF Panjab university, Chandigarh.

Table 1: Analytical data for Schiff base compounds

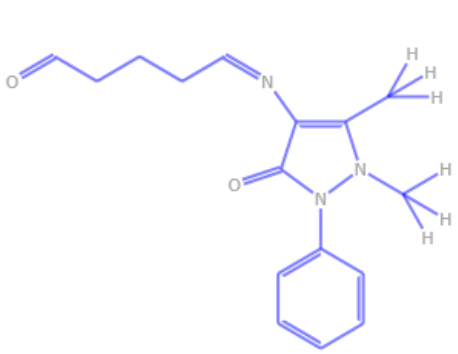
CODE	Melting Point (^oc)	Elemental Analysis C (In %)	H (In %)	N (In %)
C-1	78-80	68.27	7.64	13.46
C-2	70-72	65.75	7.66	16.65
C-3	65-70	63	7.08	7.48

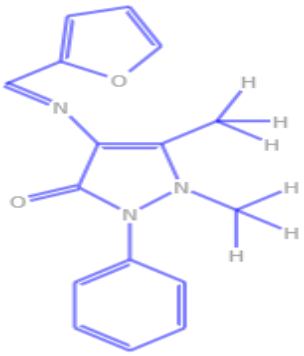
2.2 Synthesis of the Compounds:-

A mixture of 4-Dimethylaminoantipyrine (1M mol) in absolute ethanol(30ml) was slowly added to a solution of þ-Dimetylaminobenzaldehyde, Glutaraldehyde and Furfuraldehyde (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[5-7].Molecular structure of the compounds are given in Fig.1.



[I]





[II] [III]

Fig.1: Molecular structure of 2,3-Dimethyl-4-[(þ-dimethoxy(amino)benzalidene]amino antipyrine (DMDMBAAPy) [C-1] , 2,3-Dimethyl-4-[Glutaralidene]amino antipyrine (DMGAAPy) [C-2] , 2,3-Dimethyl-4-[Furfuralidene]aminoantipyrine (DMFAAPy)[C-3]

III. Computational Detail

Intel based Pentium core-2 Duo machine with configuration Intel (R) core ™ 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 frequency of Vibration modes and other parameters[8-10] 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(EG), Dipole Moment (DM), Zero Point Energy (ZPE).

IV. Results And Discussion

The experimental and calculated IR fundamental vibration modes for the 2,3-Dimethyl-4-[(þ-dimethoxy(amino)benzalidene]aminoantipyrine,2,3-Dimethyl-4-[Glutarali- dene]aminoantipyrine and 2,3-Dimethyl-4-[Furfuralidene]aminoantipyrine Schiff base compounds by semi-empirical methods AM1, PM3,MNDO and ZINDO1 are given in Table-2, 3 & 4 respectively[11-12]. The experimental results for synthesized Schiff base compounds are discussed in figure 2, 3 & 4. In case of 2,3-Dimethyl-4-[(þ-dimethoxy(amino)benzalidene] aminoantipyrine the correlation co-efficient are 0.999923, 0.999975,0.999972 and 0.999851 respectively. It is evident that PM3 method give most satisfactory result of correlation coefficient (CC) between experimental and calculated vibration frequencies. In case of compound 2,3-Dimethyl-4-[Glutaralidene] aminoantipyrine the correlation coefficient obtained for AM1, PM3, MNDO and ZINDO1 are 0.999933, 0.999959, 0.999941 and 0.99975 respectively. It is evident that PM3 method give most satisfactory result of correlation coefficient (CC) between experimental and calculated vibration frequencies.In case of compound 2,3-Dimethyl-4-[Furfuralidene]aminoantipyrine the correlation coefficient obtained for AM1, PM3, MNDO and ZINDO1 are 0.999835, 0.999927, 0.999887 and 0.999923 respectively. It is evident that PM3 method give most satisfactory result of correlation coefficient (CC) between experimental and calculated vibration frequencies. Graphical correlations between experimental and calculated fundamental vibrational modes are presented in Figure-5, 6 & 7 for the above Schiff base compounds, respectively[13-15].

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(EG), Dipole Moment (DM) and Zero Point Energy (ZPE) for above Schiff base compounds are given in Table-5, 6 and 7 respectively.

V. Conclusions

AM1, PM3, MNDO and ZINDO1 semi-empirical methods tested in the presented study on Schiff base compounds. 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 (respectively) used in 2,3-Dimethyl-4-[(þ-dimethoxy(amino)benzalidene]aminoantipyrine,2,3-Dimethyl-4-[Glutaralidene]aminoanti-pyrine and 2,3-Dimethyl-4-[Furfuralidene]aminoantipyrine Schiff base compounds. Thus, Quantum chemical Semiempirical calculation can be successfully used for the prediction of vibration modes of making more active ligands and other molecules. HOMO-LUMO, Energy gap, molecular hardness, Ionization energy, electron affinity and total energy are very important physical parameters for chemical reactivity and biological activities of the studied compounds.

Table 2: Experimental and Theoretically simulated vibration Modes (AM1, PM3, MNDO, ZINDO1) Group frequencies (cm^{-1}) for 2,3-Dimethyl-4-[(þ-dimethoxy(amino) benzalidene] aminoantipyrine (DMDMBAAPy) [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.	3427	-	-	3420	-	υ_{as} (N-H) in NH_2
2.	3321	-	-	3311	-	υ_{s} (N- CH_3)
3.	3056	3099	3056	-	-	υ (C-H)
4.	3023	3015	3024	-	-	υ (C-H)
5.	2969	2991	-	-	-	υ (C-H)
6.	2863	-	-	-	-	υ_{as} (C-H) in CH_3
7.	2780	-	-	-	2763	υ_{s} (C-H) in CH_3
8.	1626	1636	1619	1627	-	υ(C=O)
9.	1495	-	1498	1492	1480	υ(C=C)
10.	1451	1447	1446	-	1447	υ(C=C)
11.	1413	1414	-	1423	-	υ_{as}(C-CH_3)
12.	1314	1308	1319	1326	1327	υ (C-C)
13.	1221	1220	1221	1227	-	δ (C-H)
14.	1130	1132	1132	1125	1127	δ (C-H)
15.	1098	1095	1093	-	1095	δ (C=O)
16.	1036	1049	1035	1034	1055	(NH_2) Twi
17.	953	954	-	-	966	δ (C-H)
18.	910	-	918	910	-	δ (C-H)
19.	815	806	-	822	-	(CCC) rb
20.	753	749	-	744	743	δ (C-H)
21.	697	692	698	699	-	δ (CCC)
22.	675	671	673	679	674	δ (C=O)
23.	637	630	637	634	646	δ (CCC)
24.	502	-	-	-	-	δ (CNN)
25.	445	436	-	450	-	δ (CCN)

Table 3: Comparative study of Experimental and Computed (AM1, PM3, MNDO, ZINDO1) Group frequencies (cm^{-1}) for 2,3-Dimethyl-4-[Glutaralidene]aminoantipyrine (DMGAAPy) [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.	3411	-	-	3412	-	υ_{as} (N-H) in NH_2
2.	3057	3101	3054	-	-	υ (C-H)
3.	3024	-	3026	-	-	υ (C-H)
4.	2969	-	-	-	-	υ (C-H)
5.	2863	-	-	-	2898	υ (=C-H) Aldehyde
6.	2825	-	-	-	-	υ_{as} (C-H) in CH_3
7.	2779	-	-	-	-	υ_{s} (C-H) in CH_3

8.	1626	1625	-	1615	1615	υ(C=O)
9.	1498	-	-	1496	-	υ(C=C)
10.	1486	1484	-	-	-	υ(C=C)
11.	1449	1455	-	-	1440	υ(C=C)
12.	1410	1410	-	1418	1425	υ_{as}(C-CH_3)
13.	1342	-	1338	1333	1341	υ (C-N)
14.	1313	1324	1309	1316	1326	υ (C-C)
15.	1221	-	1228	1201	1206	δ (C-H)
16.	1172	1178	1177	1172	1134	δ (C-H)
17.	1037	1039	1031	1040	-	(NH_2) Twi
18.	954	959	948	961	961	δ (C-H)
19.	910	-	-	916	915	δ (C-H)
20.	816	816	819	814	809	(CCC) rb
21.	754	743	-	-	767	δ (C-H)
22.	697	696	693	694	-	δ (CCC)
23.	675	667	688	671	662	δ (C=O)
24.	636	632	641	637	641	δ (CCC)
25.	503	509	-	-	-	δ (CNN)
26.	449	443	442	457	451	δ (CCN)

Table 4: Comparative study of Experimental and Computed (AM1, PM3, MNDO, ZINDO1) Group frequencies (cm^{-1}) for 2,3-Dimethyl-4-[Furfuralidene]aminoantipyrine (DMFAAPy) [C-3]

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.	3430	-	-	3439	-	υ_{as} (N-H) in NH_2
2.	3057	3097	3060	-	-	υ (C-H)
3.	3023	-	3029	-	-	υ (C-H)
4.	2969	-	-	-	-	υ (C-H)
5.	2863	-	2899	-	-	υ (=C-H) Aldehyde
6.	2825	-	-	-	-	υ_{as} (C-H) in CH_3
7.	2778	-	-	-	2758	υ_s (C-H) in CH_3
8.	1626	1628	-	1606	-	υ(C=O)
9.	1498	1498	1496	-	-	υ(C=C)
10.	1485	-	-	1488	-	υ(C=C)
11.	1471	-	-	1476	-	υ(C=C)
12.	1449	1438	-	-	1451	υ(C=C)
13.	1411	-	-	1426	-	υ_{as}(C-CH_3)
14.	1342	-	1347	1350	1354	υ (C-N)
15.	1312	1316	1305	-	1319	υ (C-C)
16.	1221	-	1235	1208	1219	δ (C-H)
17.	1172	-	1166	1169	-	δ (C-H)
18.	1130	1134	1133	1131	1130	δ (C-H)
19.	1097	1089	-	-	1098	δ (C-H)
20.	1037	1034	1048	1039	1048	(NH_2) Twi
21.	909	-	-	901	906	δ (C-H)
22.	816	809	-	837	817	(CCC) rb
23.	771	-	776	-	787	δ (C-H)
24.	754	751	745	755	-	δ (C-H)
25.	697	-	697	-	-	δ (CCC)
26.	675	674	675	675	-	δ (C=O)
27.	636	643	635	636	633	δ (CCC)
28.	503	-	502	-	-	δ (CNN)
29.	449	-	-	-	457	δ (CCN)

Where:-

υ- stretching; υ_{as}- Asymmetric stretching; υ_s- Symmetric stretching; δ- In-plane and Out-of-plane bending; ω- Wagging; τ- Torsion; Sci- Scissoring; rb- Ring breathing; Tri- Trigonal; Twi- Twisting.

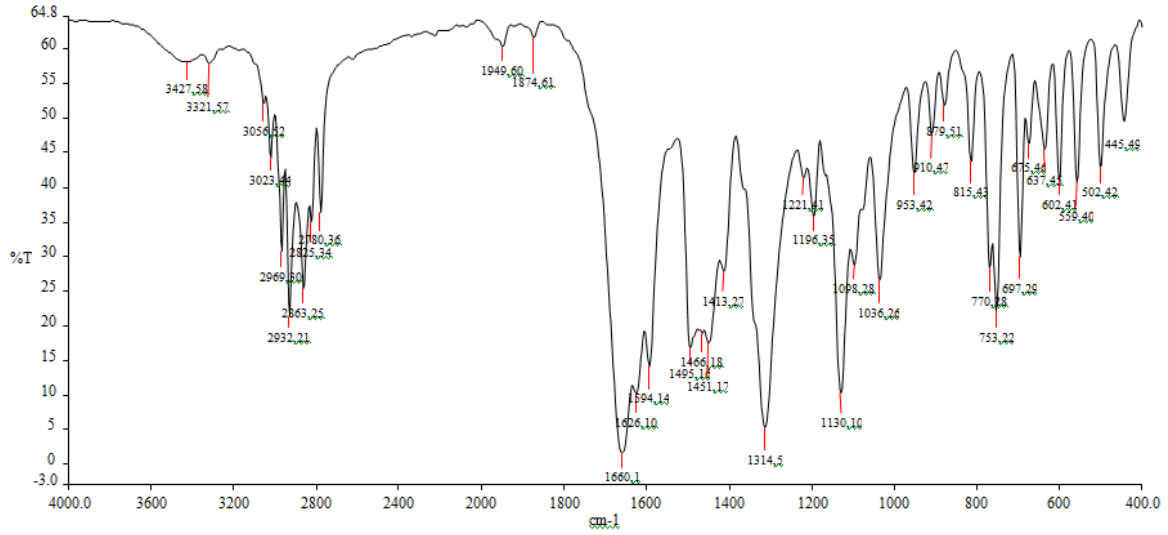


Fig. 2 Experimental spectra of 2,3-Dimethyl-4-[(þ-dimethoxy(amino)benzalidene] aminoantipyrine (DMDMBAAPy)[C-1]

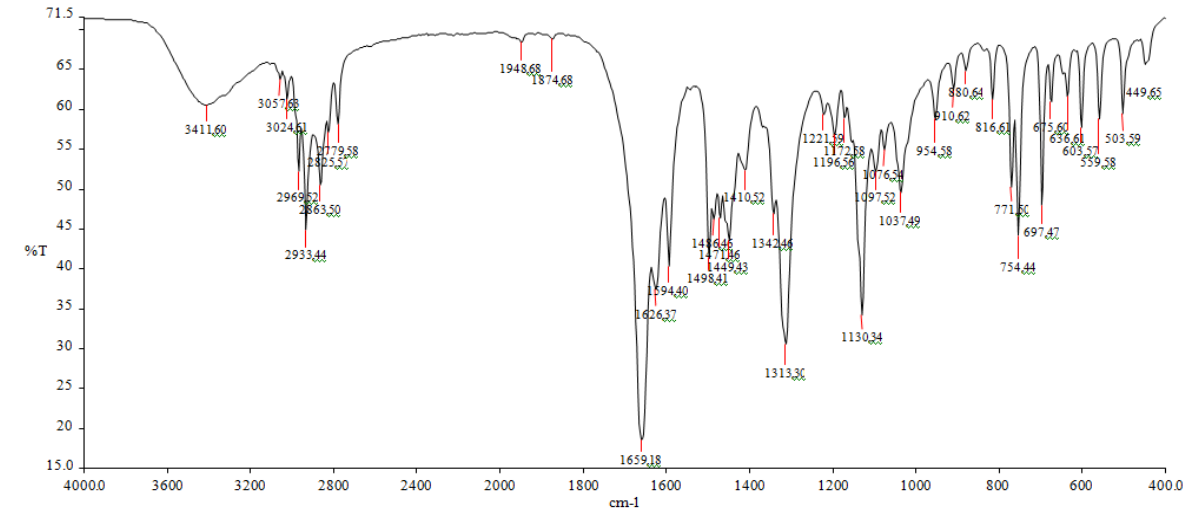


Fig.3 Experimental spectra of 2,3-Dimethyl-4-[Glutaralidene]aminoantipyrine (DMGAAPy)[C-2]

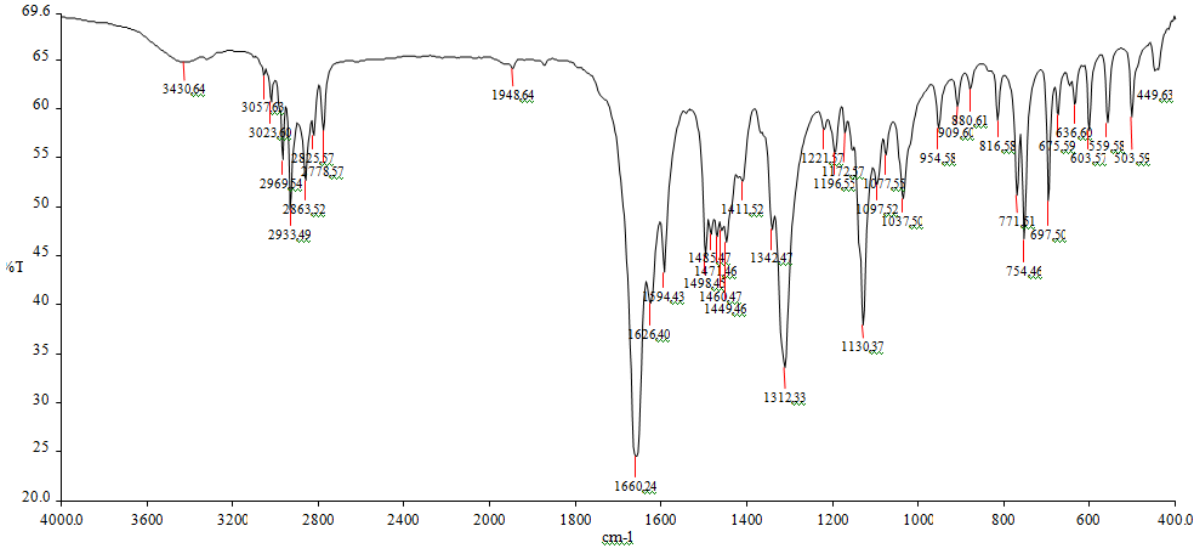
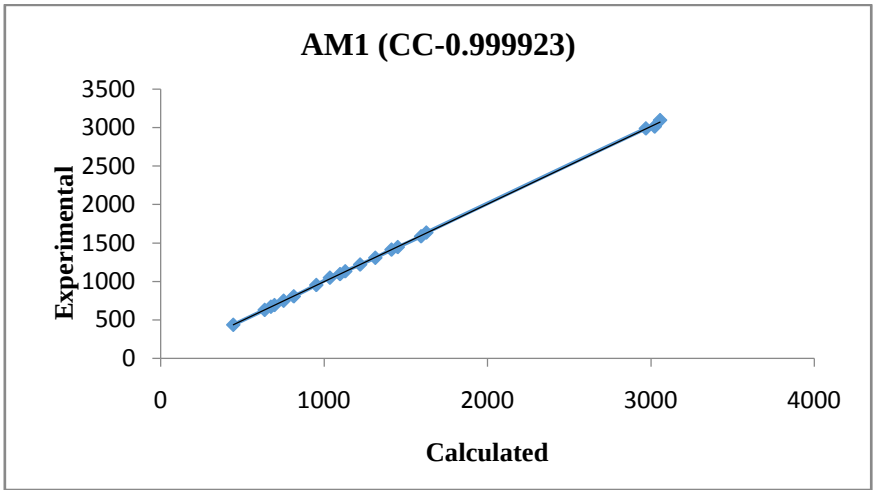
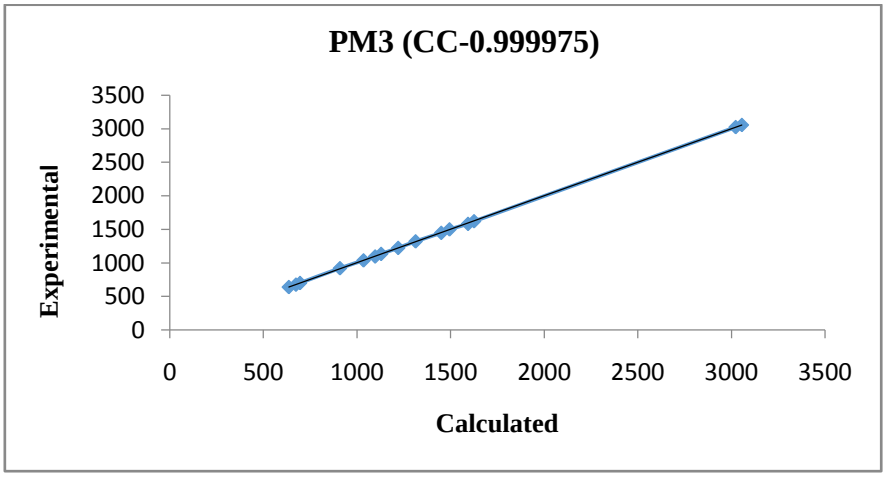
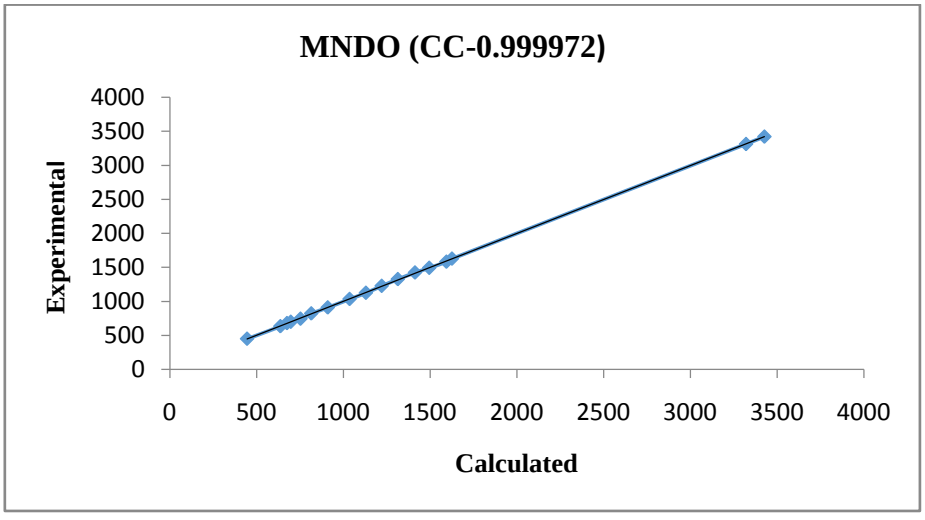


Fig.4 Experimental spectra of 2,3-Dimethyl-4-[Furfuralidene]aminoantipyrine (DMFAAPy)[C-4]


AM1 (CC-0.999923)
Experimental
Calculated
0
500
1000
1500
2000
2500
3000
3500
4000


PM3 (CC-0.999975)
Experimental
Calculated
0
500
1000
1500
2000
2500
3000
3500


MNDO (CC-0.999972)
Experimental
Calculated
0
500
1000
1500
2000
2500
3000
3500
4000

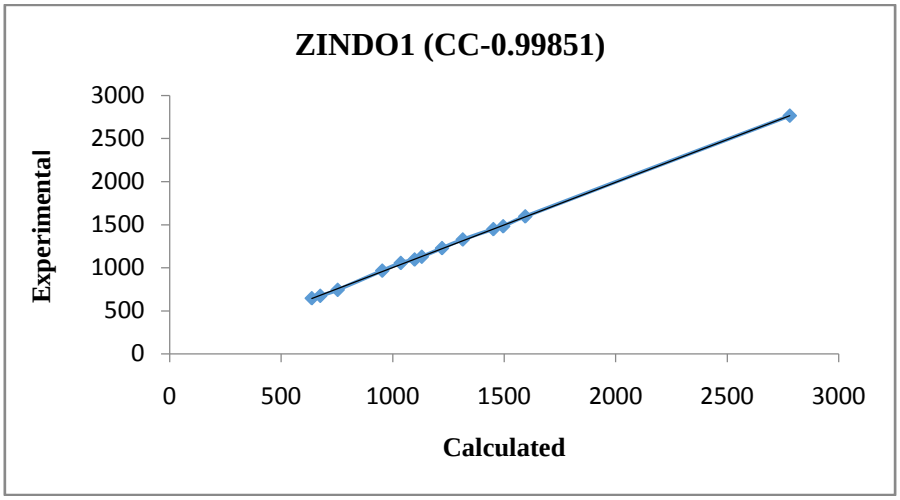
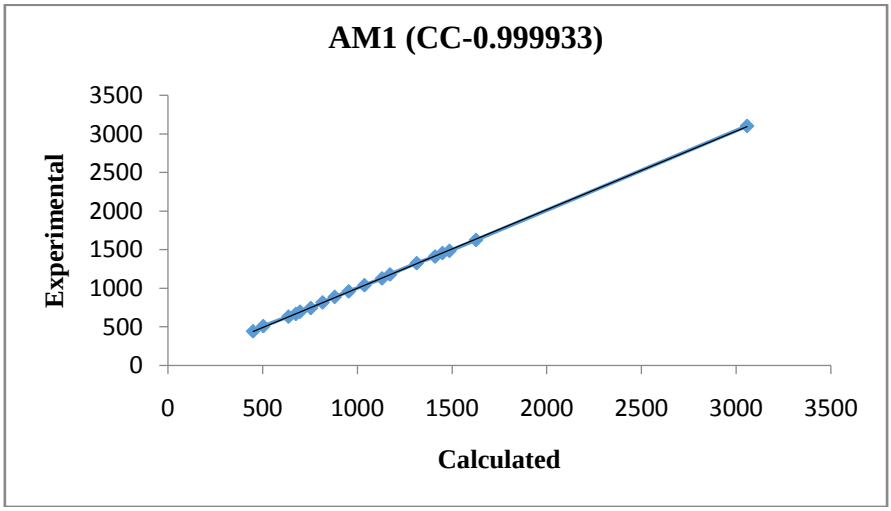
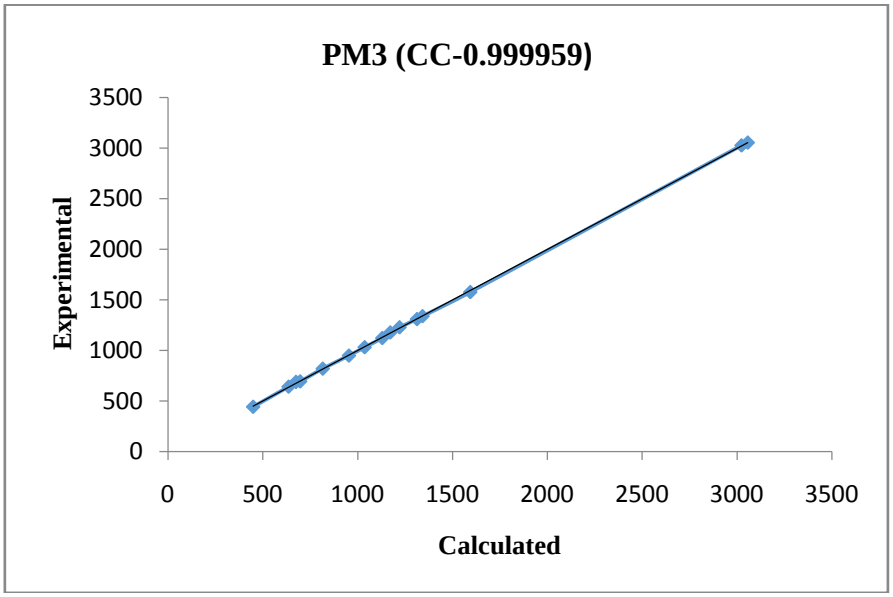
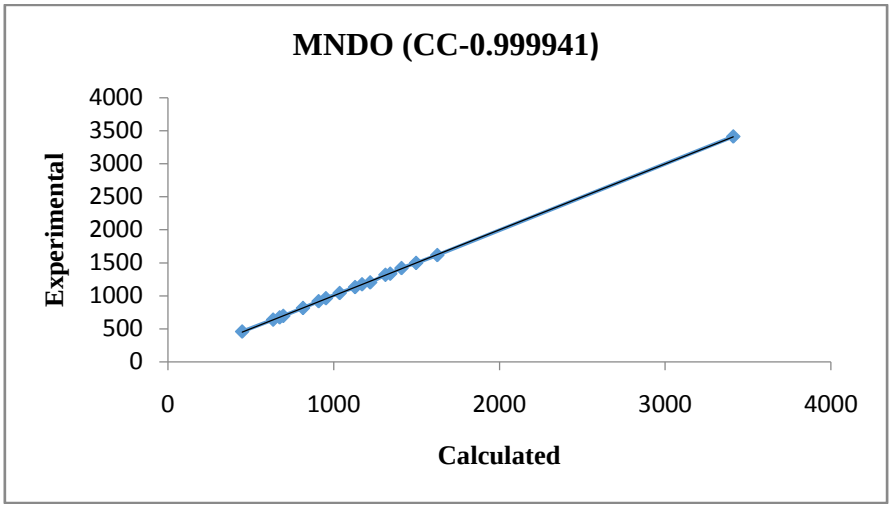


Fig.5 Graphical correlation between experimental and calculated fundamental vibration modes obtained by AM1, PM3, MNDO and ZINDO1 Semi-empirical methods for 2,3-Dimethyl-4-[(þ-dimethoxy(amino)benzalidene]aminoantipyrine (DMDMBAAPy)[C-1] (CC-Correlation coefficient)







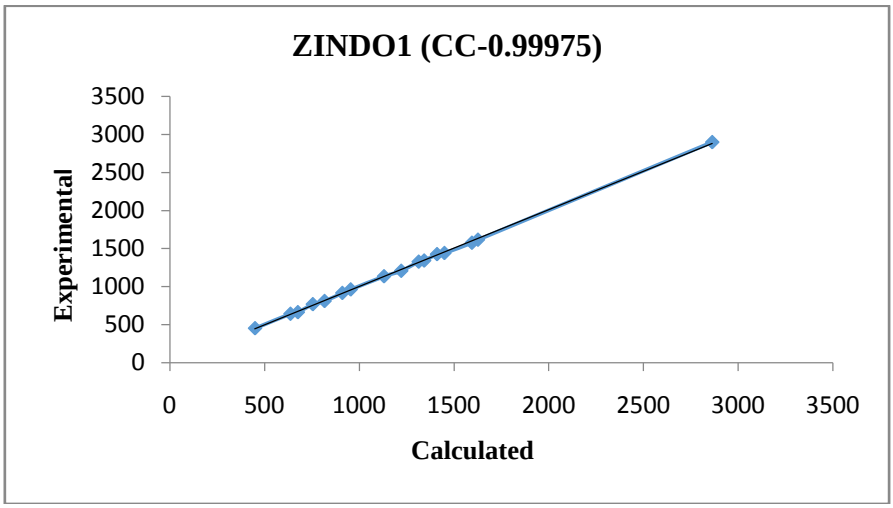
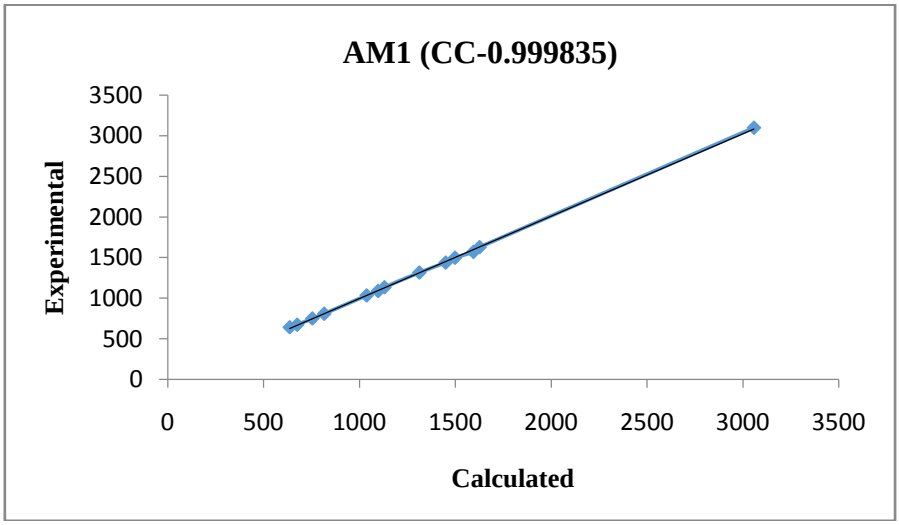
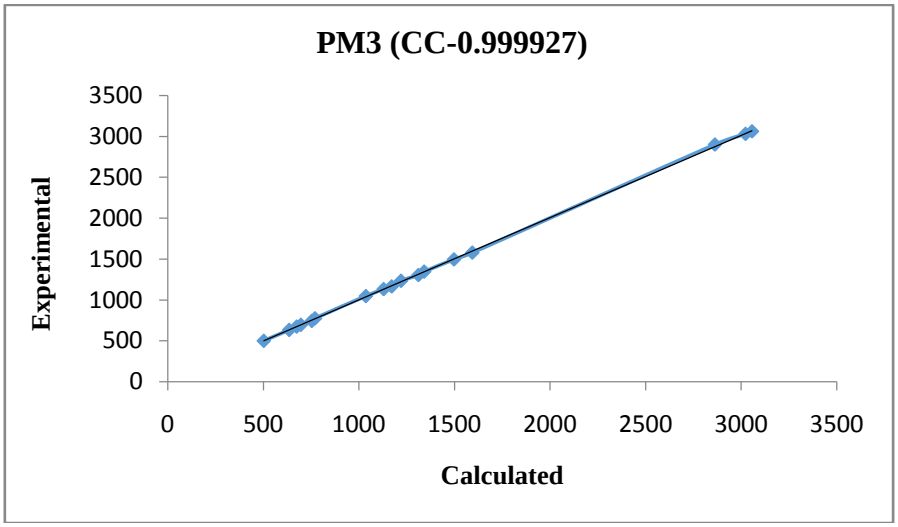
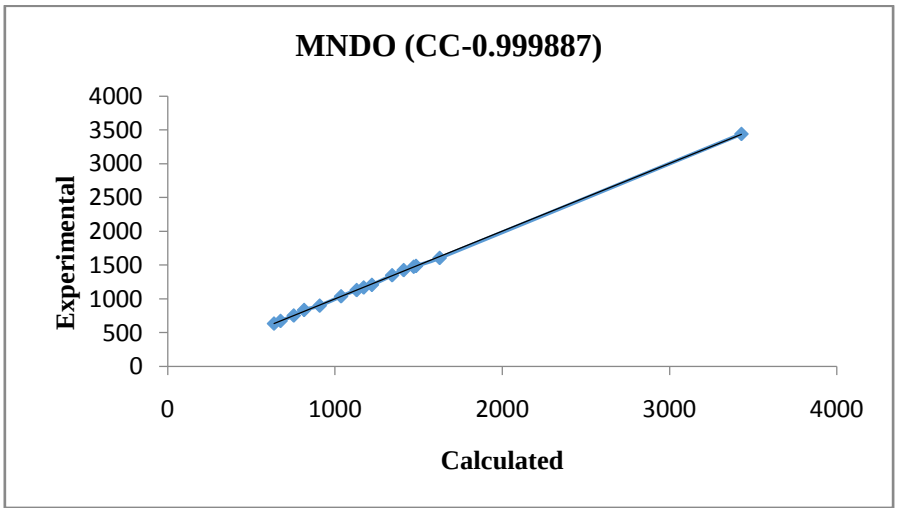


Fig.6 Graphical correlation between experimental and calculated fundamental vibration modes obtained by AM1, PM3, MNDO and ZINDO1 Semi-empirical methods for 2,3-Dimethyl-4-[Glutaralidene]aminoantipyrine (DMGAAPy) [C-2](CC-Correlation coefficient)







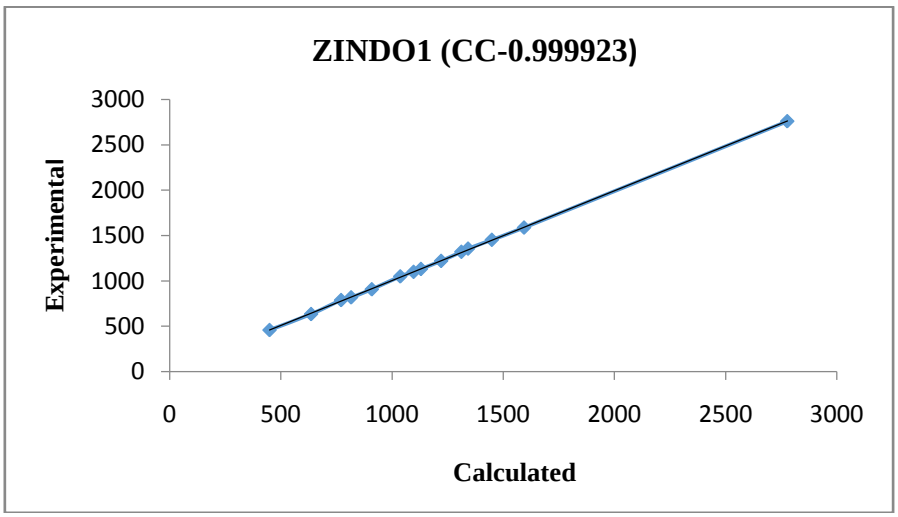


Fig. 7 Graphical correlation between experimental and calculated fundamental vibration modes obtained by AM1, PM3, MNDO and ZINDO1 Semi-empirical methods for 2,3-Dimethyl-4-[Furfuralidene]aminoantipyrine (DMFAAPy) [C-3] (CC-Correlation coefficient)

Table 5: Computed parameters for 2,3-Dimethyl-4-[(þdimethoxy(amino)benzalidene]aminoantipyrine

	AM1	PM3	MNDO	ZINDO1
TE(K.cal./Mol)	-92375.5	-84099.1	-92505.2	-128479.2
EE(K.cal/Mol)	-681014.2	-664688.9	-692104.9	-807448.0
CCI(K.cal/Mol)	588638.7	580589.7	599599.6	678968.7
HF(K.cal/Mol)	164.98	121.85	204.13	-9992.56
HOMO(eV)	-0.389	-0.115	-0.136	-5.784
LUMO(eV)	0.124	0.072	0.250	6.536
EG (eV)	-0.265	-0.043	0.114	0.752
DM(Debye)	2.982	2.336	4.278	6.532
ZPE(K.cal/Mol)	238.32	231.73	237.17	333.51

Table 6: Computed parameters for 2,3-Dimethyl-4-[Glutaralidene]aminoantipyrine

	AM1	PM3	MNDO	ZINDO1
TE(K.cal./Mol)	-82436.7	-74836.1	-82493.5	-115049.5
EE(K.cal/Mol)	-527501.1	-520173.6	-494475.2	-614328.6
CCI(K.cal/Mol)	445064.3	445337.5	411981.6	499279.1
HF(K.cal/Mol)	337.10	272.00	378.71	-7557.58
HOMO(eV)	-0.080	-0.356	-0.069	-2.891
LUMO(eV)	0.379	0.251	0.044	2.278
EG (eV)	0.299	-0.105	-0.025	-0.613
DM(Debye)	11.636	12.779	11.291	26.122
ZPE(K.cal/Mol)	146.42	144.06	146.53	204.11

Table 7: Computed parameters for2,3-Dimethyl-4-[Furfuralidene]aminoantipyrine

	AM1	PM3	MNDO	ZINDO1
TE(K.cal./Mol)	-79429.2	-72063.9	-79572.5	-11155.5
EE(K.cal/Mol)	-495795.1	-482811.4	-494579.1	-632602.9
CCI(K.cal/Mol)	416365.8	410747.5	415006.6	521447.3
HF(K.cal/Mol)	387.61	308.22	350.00	-7367.4
HOMO(eV)	-0.378	-0.113	-0.026	-2.839
LUMO(eV)	0.071	0.327	0.197	3.621
EG (eV)	-0.307	0.214	0.171	0.782
DM(Debye)	14.767	13.914	16.084	15.686
ZPE(K.cal/Mol)	142.66	140.87	145.84	204.50

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