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Experimental and Theoretical Vibrational Spectroscopic Study of Schiff base Derived from 4-Amino Antipyrine- A Quantum Chemical Study

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Abstract: ***In the present work Experimental IR Spectral study and theoretical study of three Schiff base organic compounds, 4-N-[Furfuralidene]aminoantipyrine(FAAPy), 4-N-[(3,4,5-Trimethoxy)benzalidene] amino antipyrine(TMBAAPy), 4-N-[Glutaralidene]aminoantipyrine (GAAPy) of 4-Aminoantipyrine has been performed by using semi-empirical methods AM1, PM3, MNDO and ZINDO1 in order to elucidate the correlation coefficient between experimental and theoretical vibration modes. The efficiency of Schiff base compounds relate to some 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) were calculated. All calculations has been performed by considering semi-empirical methods AM1, PM3, MNDO and ZINDO1 using program HYPERCHEM 8.0 version. The calculated results are in agreement with the experimental data on the whole.***

Keywords: Vibration Modes, Semi-empirical, AM1, PM3, MNDO, ZINDO1, Correlation.

1. Introduction

Schiff's bases are an important class of organic compounds [1]. They were first reported by Hugo Schiff in 1864 [2]. Schiff's bases are condensation products of primary amines with carbonyl compounds. The common structural feature of these compounds is the azomethine group with the general formula RHC = N-R1, where R and R1 are alkyl, aryl, cycloalkyl, or heterocyclic groups. Structurally, a Schiff's base (also known as imine or azomethine) is a nitrogen analogue of an aldehyde or ketone in which the carbonyl group (>C = O) is replaced by an imine or azomethine group[3-4].

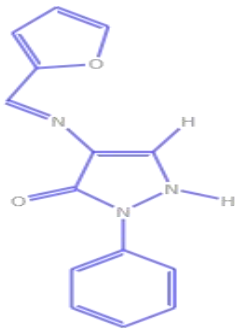
In this respect we reported here the synthesis of 4-N-[Furfuralidene] amino anti pyrine(FAAPy),4-N-[(3,4,5-Trimethoxy)benzalidene]aminoantipyrine(TMBAAPy) , 4-N-[Glutaralidene]aminoantipyrine (GAAPy) of 4-Aminoantipyrine and find out their experimental and theoretical spectra and some important parameters related to its efficiency.

2. Materials and Methods

All the chemicals used were of AR grade and were used with further purification where ever required. Fourier transform infrared (FTIR) spectra were registered on a Perkin Elmer Infrared Spectrophotometer in the range of 4000 to 400 cm-1 at SAIF Panjab University, Chandigarh. Melting Point of the compounds are noted by usual method in chemistry research laboratory, Department of chemistry, Govt. K.R.G. P.G. Autonomous college, Gwalior (M.P.)

Synthesis of Compounds

A mixture of 4-Aminoantipyrine (1M mol) in absolute ethanol(30ml) was slowly added to a solution of Furfuraldehyde, 3,4,5 tri methoxybenzaldehyde and Glutaraldehyde (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[5-6]. Molecular structure of the compounds are given in fig.1.



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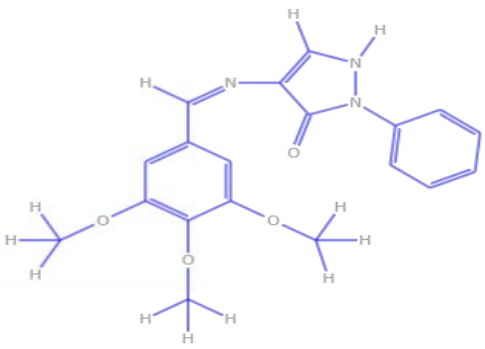

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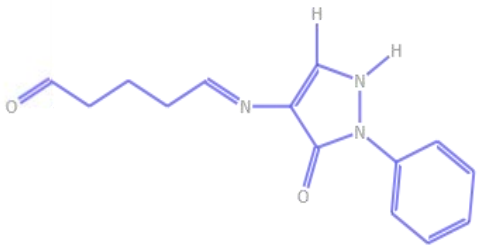


[III]

Figure 1: Molecular structure of 4-N-[Furfuralidene]aminoantipyrine(FAAPy)[C-1],4-N-[(3,4,5-Trimethoxy) benzalidene] aminoantipyrine (TMBAAPy)[C-2], 4-N-[Glutaralidene] aminoanti- pyrine (GAAPy)[C-3] of 4-Aminoantipyrine.

Computational Detail

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[7-8] and calculated parameters such as frequency of 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).

3. Results and Discussion

The Experimental and Theoretical vibration modes for 4-N-[Furfuralidene] aminoantipyrine (FAAPy) [C-1], 4-N-[(3,4,5-Trimethoxy) benzalidene]amino antipyrine (TMBAA Py)[C-2], 4-N-[Glutaralidene]aminoantipyrine(GAAPy)[C-3] Schiff base compounds by semi-empirical methods[9-11] AM1, PM3,MNDO and ZINDO1 are given in Table-2, 3 & 4 respectively and the Experimental results are discussed in fig. 2, 3 & 4.

In case of compound 1 the correlation coefficient obtained for AM1, PM3, MNDO and ZINDO1 are 0.999863, 0.999859, 0999921 and 0.999579 respectively. It is evident that MNDO method give most satisfactory result of correlation coefficient (CC) between experimental and calculated vibration frequencies.

In case of compound 2 the correlation coefficient obtained for AM1, PM3, MNDO and ZINDO1 are 0.999958, 0.999885, 0.999966 and 0.999898 respectively. It is evident that MNDO method give most satisfactory result of correlation coefficient (CC) between experimental and calculated vibration frequencies.

In case of compound 3 the correlation coefficient obtained for AM1, PM3, MNDO and ZINDO1 are 0.999877, 0.999859, 0.999942 and 0. 999917 respectively. It is evident that MNDO method give most satisfactory result of correlation coefficient (CC) between experimental and calculated vibration frequencies.

It is evident that MNDO 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. Theoretically simulated spectra for Schiff base compounds by AM1, PM3, MNDO and ZINDO1 semi-empirical methods are given in fig. 8,9 & 10 respectively[12-13].

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-4, 5 and 6 respectively[14-15].

4. Conclusion

AM1, PM3, MNDO and ZINDO1 semi-empirical methods tested in the presented study on Schiff base compounds. MNDO 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 4-N-[Furfuralidene]aminoantipyrine(FAAPy)[C-1], 4-N-[(3,4,5-Trimethoxy) benzalidene]aminoantipyrine(TMBAAPy)[C-2], 4-N-[Glutaralidene] aminoanti- pyrine (GAAPy)[C-3] 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[15-19].

Table 1: Experimental and Theoretical simulated (AM1, PM3, MNDO, ZINDO1) frequency of vibration modes(cm^{-1}) for 4-N-[Furfuralidene]aminoantipyrine (FAAPy)

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.	3421	3442	-	3421	-	υ_{as} (N-H) in NH_2
2.	3110	3159	-	-	-	υ_s (N-CH_3)
3.	3046	-	3055	-	3006	υ_s (C-H)
4.	2958	-	-	-	-	υ (C-H)
5.	2924	-	-	-	-	υ (C-H)
6.	1647	1645	1683	1649	1698	υ (C=O)
7.	1603	-	-	-	-	υ(C=C)
8.	1592	1599	1582	1590	-	(NH_2) Sci
9.	1575	1579	-	-	1544	(NH_2) Sci
10.	1487	1473	-	1492	1479	υ (C=C)
11.	1456	-	-	1452	-	υ(C=C)
12.	1444	1449	1443	1439	1423	υ(C=C)
13.	1380	1368	-	1369	1384	υ(N-C)
14.	1351	1344	-	-	1346	υ(C-N)
15.	1331	-	1339	-	-	υ(C-N)
16.	1305	1310	1318	-	1301	υ(C-C)
17.	1266	1242	-	1273	1265	υ(C-H)
18.	1212	1209	-	1211	1213	δ (C-H)
19.	1151	-	1154	1159	-	δ (C-H)
20.	1135	-	-	-	-	δ (C-H)
21.	1074	1072	1077	1069	-	δ (C-H)
22.	1054	-	-	-	-	δ (C-H)
23.	1014	1004	1008	1004	-	δ (C-N)
24.	951	-	-	-	-	δ (C-H)
25.	928	930	931	916	912	δ (C-H)
26.	867	868	-	866	864	δ (C-H)
27.	820	-	-	-	-	(CCC) rb
28.	760	-	766	-	758	δ (C-H)
29.	750	-	-	-	-	δ (C-H)
30.	701	705	-	705	-	δ (CCC)
31.	664	675	-	-	674	δ (C=O)
32.	628	627	627	620	628	δ (CCC)
33.	435	-	439	-	431	τ (NH_2)

Table 2: Experimental and Theoretical Simulated (AM1, PM3, MNDO, ZINDO1) frequency of vibration modes (cm^{-1}) for 4-N-[(3,4,5-Trimethoxy)benzalidene] aminoantipyrine (TMBAAPy)

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.	3437	-	3392	3445	-	υ_{as} (N-CH_3)
2.	3080	3078	3079	-	-	υ (C-H)
3.	3014	3022	-	-	-	υ (C-H)
4.	2994	2992	2994	-	-	υ (C-H)
5.	2961	-	2955	-	-	υ (C-H)
6.	2934	-	-	-	-	υ (C-H)
7.	2834	-	-	-	2805	(=C-H) Aldehyde
8.	2238	-	-	-	2245	υ_s (C-NH_2)
9.	1649	1658	1676	1641	1649	υ (C=O)
10.	1579	1578	1587	1583	-	(NH_2) Sci
11.	1489	1480	-	-	1480	υ(C=C)
12.	1452	1451	1446	1450	1438	υ(C=C)
13.	1411	1402	-	1416	-	υ_{as} (C-CH_3)
14.	1379	1381	1378	-	1383	υ(N-C)
15.	1365	1364	-	1362	1366	υ(C-C)
16.	1327	1331	1325	1325	1328	υ(C-C)
17.	1290	1288	-	1282	1295	υ(C-N)
18.	1228	1211	1225	1229	1228	δ (C-H)
19.	1183	1188	1168	1179	1197	δ (C-H)
20.	1069	1078	1074	1068	1082	δ (C-H)
21.	1041	-	-	1041	-	NH_2 Twi
22.	1023	-	1021	-	-	δ (C-N)
23.	1002	1004	-	1000	-	(CCC) Tri

24.	952	962	970	963	955	δ (C-H)
25.	859	865	851	854	861	δ (C-H)
26.	827	821	823	-	831	(CCC) rb
27.	753	763	-	-	-	δ (C-H)
28.	730	-	736	725	734	δ (C-H)
29.	651	658	-	-	658	ω (NH_2)
30.	630	628	626	623	628	δ (CCC)
31.	526	519	519	518	-	δ (CCC)
32.	503	504	-	510	502	δ (CNN)
33.	428	430	423	-	-	τ (NH_2)

Table 3: Experimental and Theoretical simulated (AM1, PM3, MNDO, ZINDO1) frequency of vibration (cm^{-1}) for 4-N-[Glutaralidene]aminoantipyrine (GAAPy)

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.	3401	-	-	3405	-	υ_{as} (N-H) in NH_2
2.	3322	3351	3385	-	-	υ_s (N-CH_3)
3.	3062	-	3062	-	-	υ (C-H)
4.	2984	-	-	-	2938	υ (C-H)
5.	1656	1636	-	1661	1648	υ(C=O)
6.	1593	1576	1585	1586	-	(NH_2) Sci
7.	1496	1496	-	1486	1481	υ (C=C)
8.	1456	-	1456	-	1450	υ (C=C)
9.	1350	1353	-	-	1349	υ(C-C)
10.	1310	-	1303	1300	-	υ(C-C)
11.	1294	-	-	-	1295	υ (C-N)
12.	1181	1176	1173	1188	-	δ (C-H)
13.	1165	1162	1168	1166	1174	δ (C-H)
14.	1134	-	1149	-	1138	δ (C-H)
15.	1105	1105	1113	-	1108	δ (C=O)
16.	1075	1067	1071	1065	-	δ (C-H)
17.	925	932	920	-	-	δ (C-H)
18.	905	910	-	912	-	δ (C-H)
19.	836	829	846	834	-	(CCC) rb
20.	758	769	752	770	750	δ (C-H)
21.	697	-	-	686	-	δ (CCC)
22.	664	666	655	673	-	δ (C=O)
23.	645	648	646	-	647	δ (CCC)
24.	502	501	-	-	507	δ (CNN)
25.	451	-	453	450	441	δ (CCN)

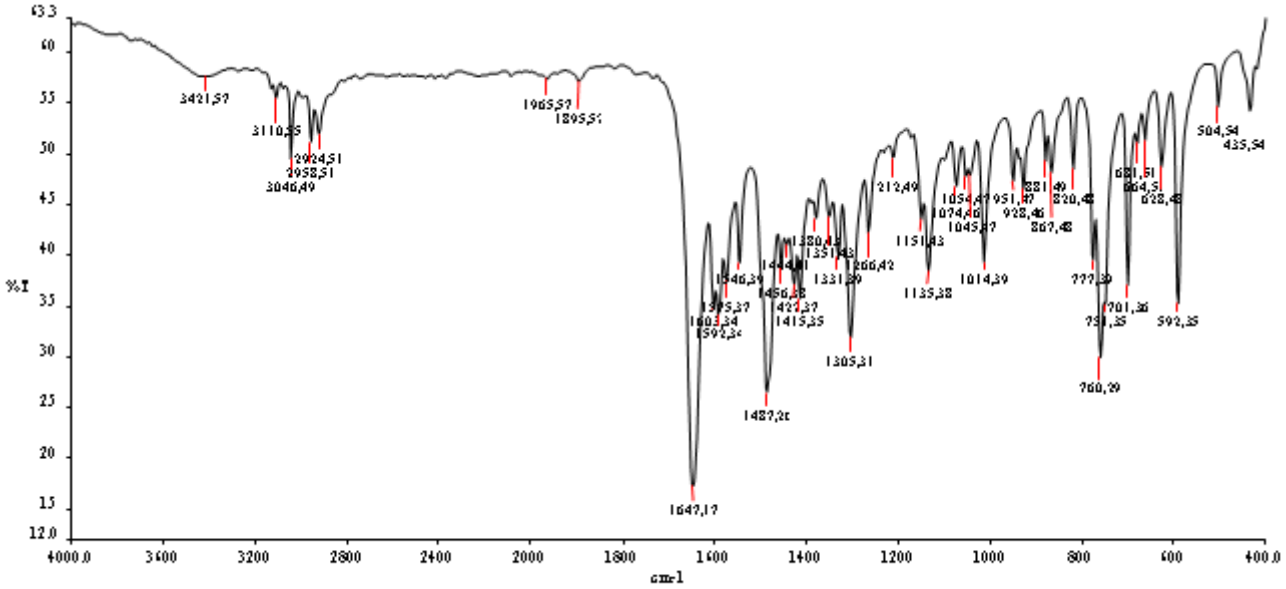


Fig. 2 Experimental spectra of 4-N-[Furfuralidene]aminoantipyrine (FAAPy)

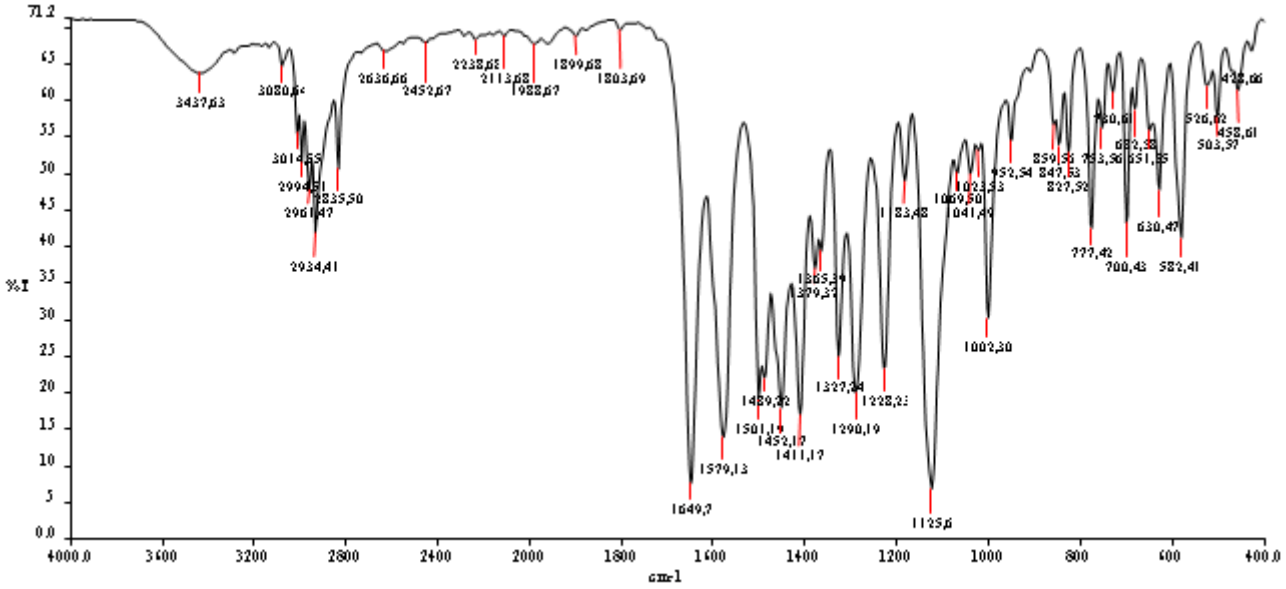


Fig. 3 Experimental spectra of 4-N-[(3,4,5-Trimethoxy)benzalidene]aminoantipyrene (TMBAAPy)

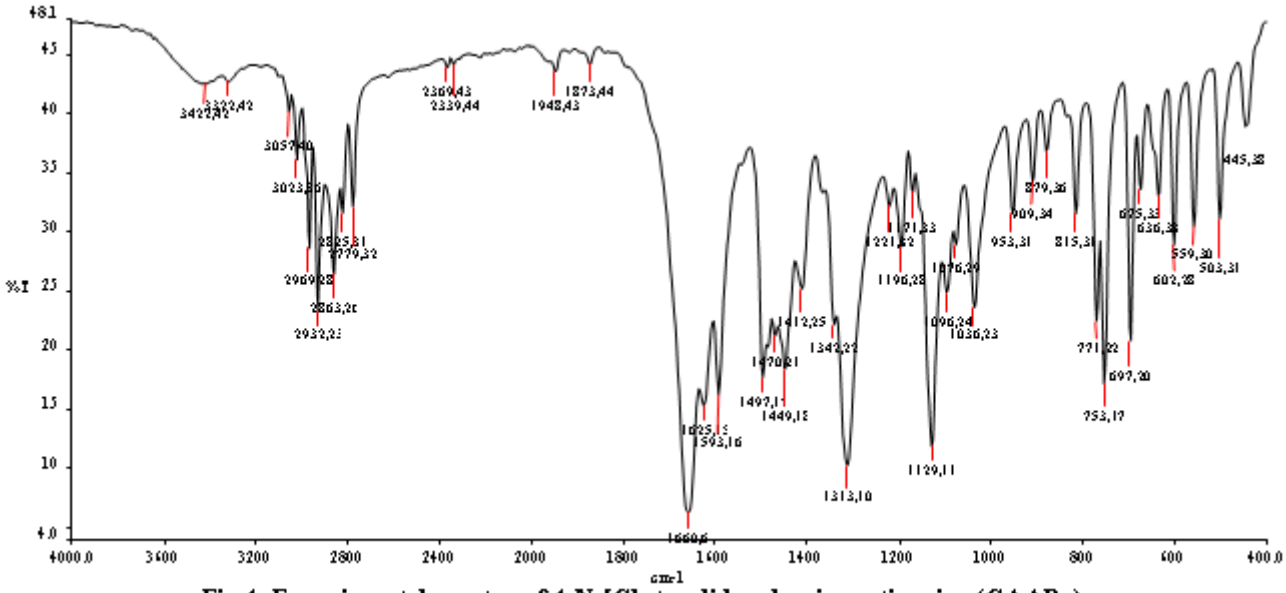
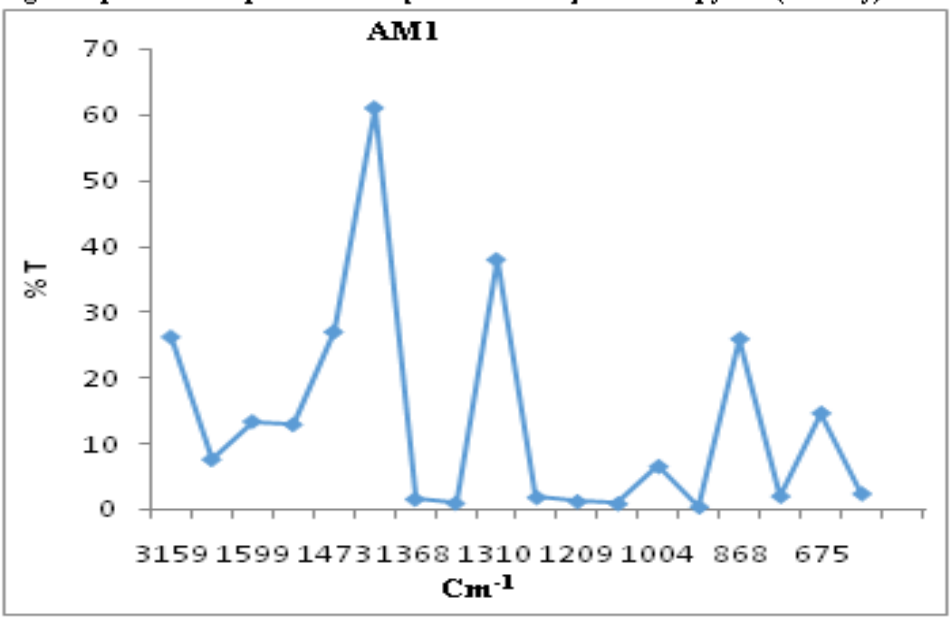
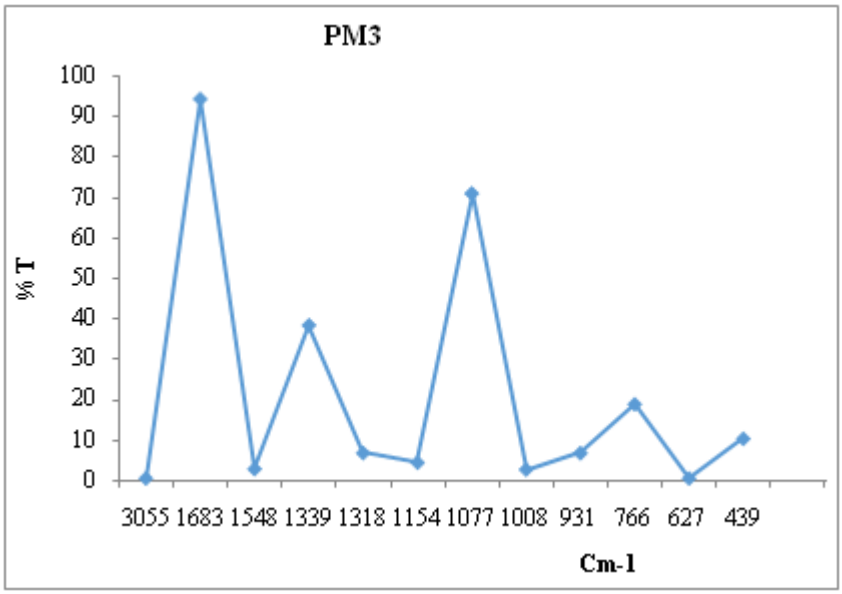
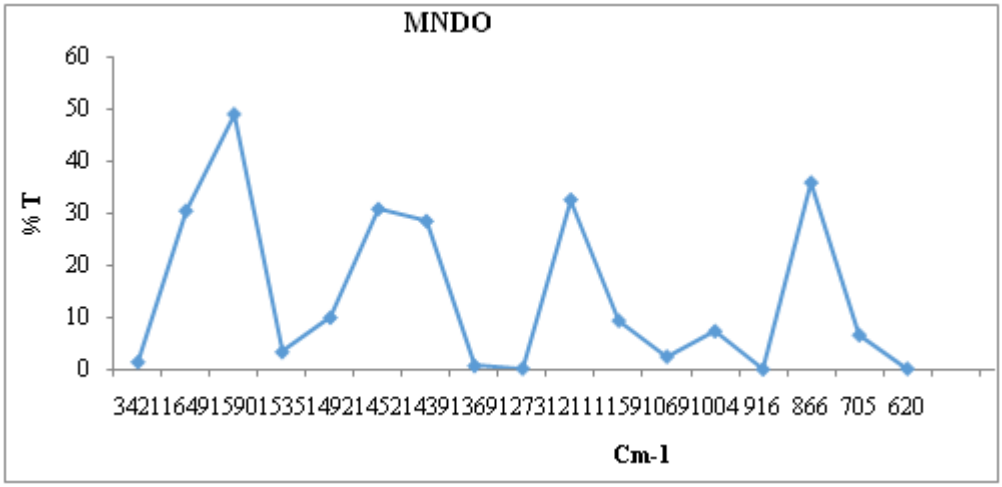


Fig.4 Experimental spectra of 4-N-[Glutaralidene]aminoantipyrine (GAAPy)







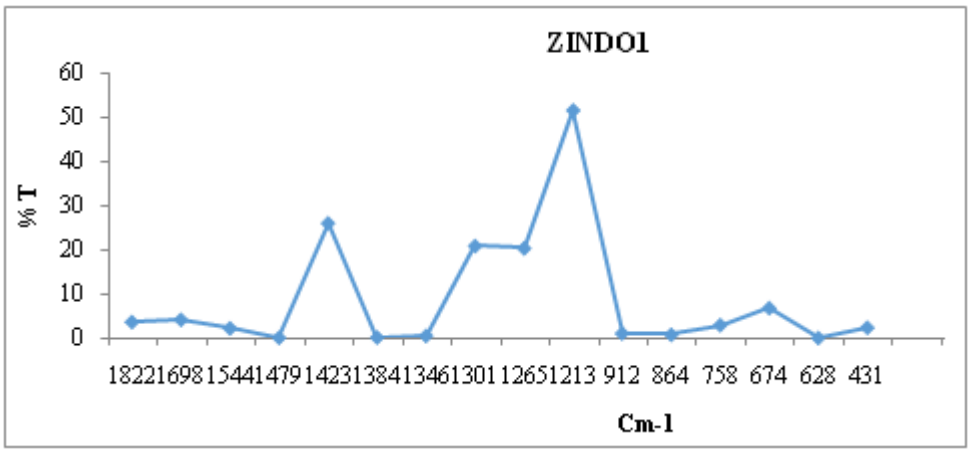
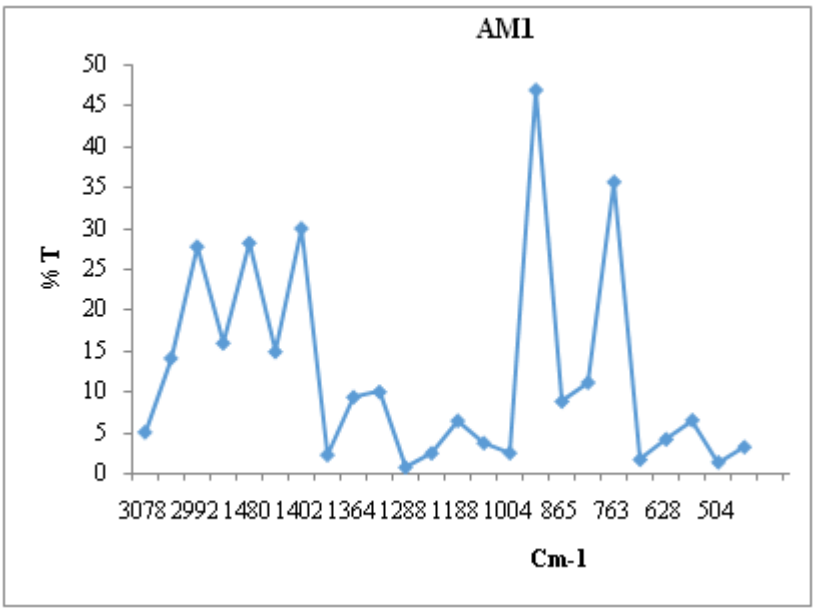
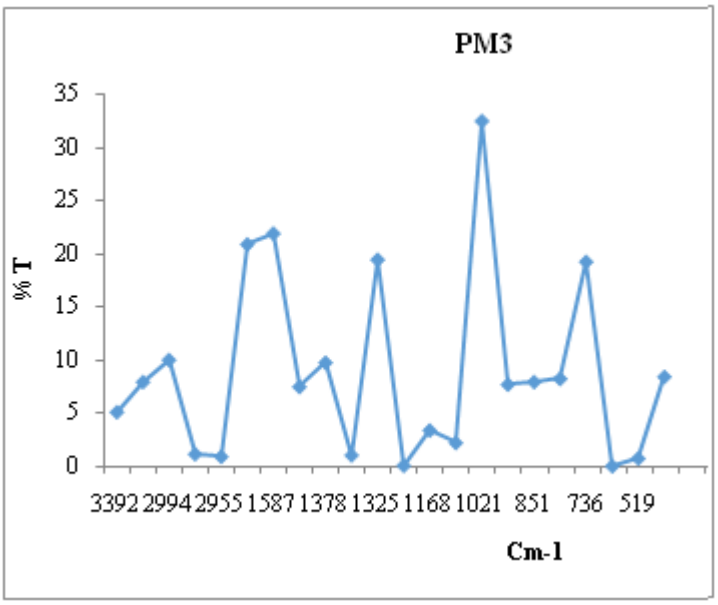
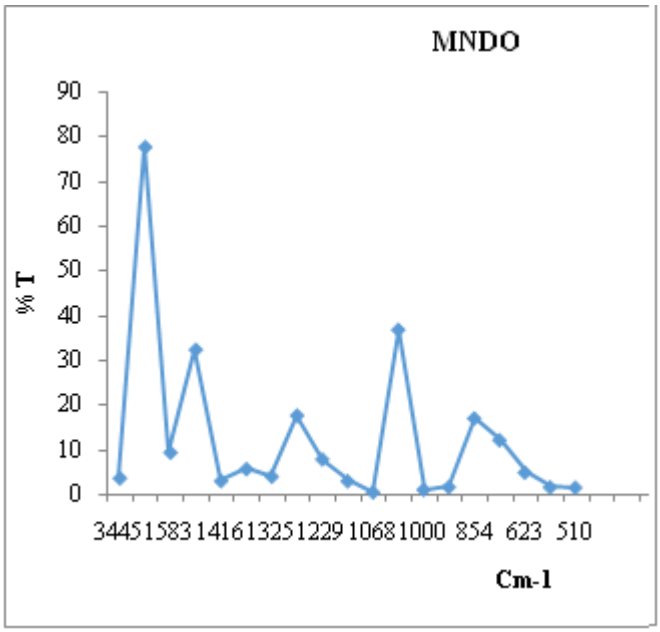
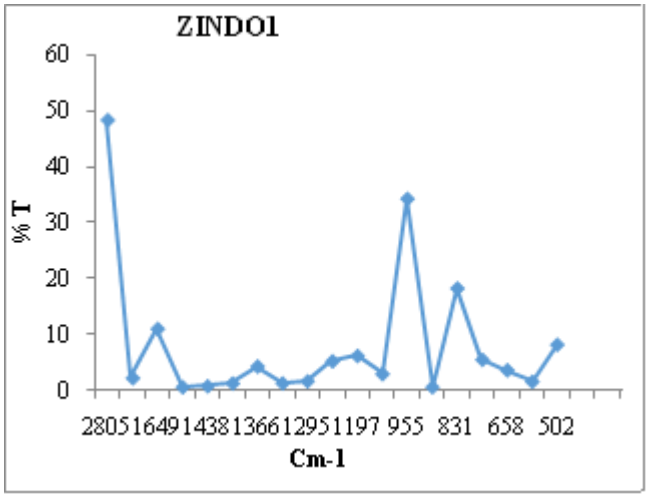


Figure 5: Theoretically AM1, PM3, MNDO & ZINDO1 Simulated spectra for 4-N-[Furfuralidene] aminoantipyrine (FAAPy)[C-1]









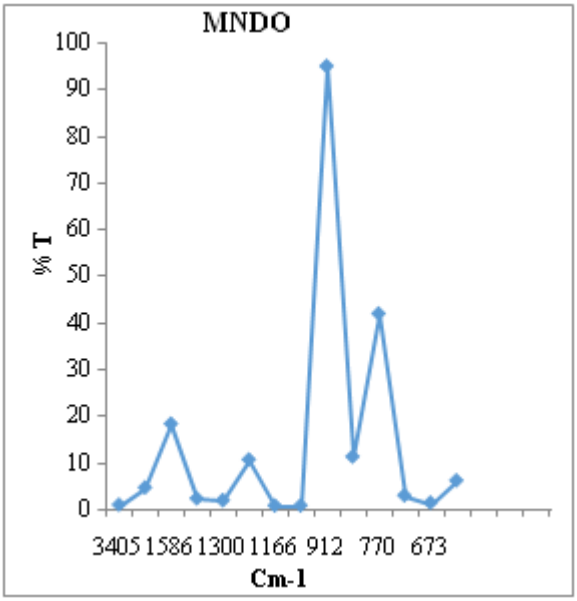
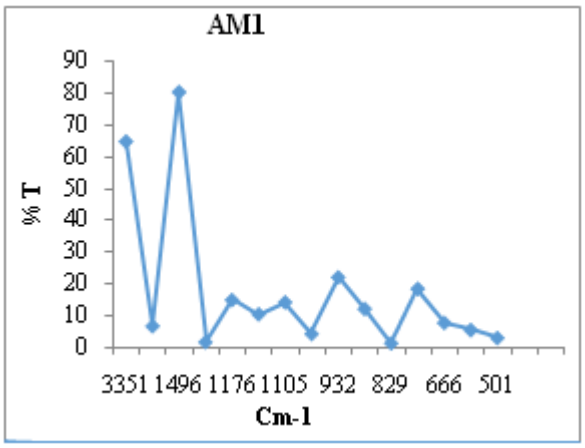
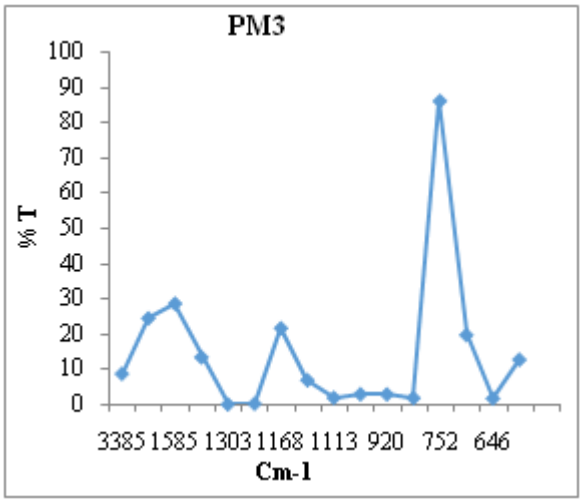


Figure 6: Theoretically AM1, PM3, MNDO & ZINDO1 Simulated spectra for 4-N-[(3,4,5-Trimethoxy) benzalidene]aminoantipyrine (TMBAAPy)[C-2]





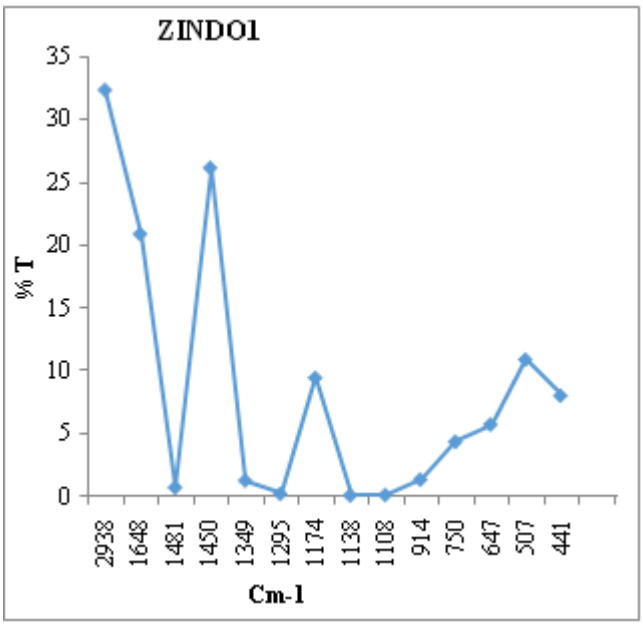


Figure 7: Theoretically AM1, PM3, MNDO & ZINDO1 Simulated spectra for 4-N-[Glutaralidene] aminoantipyrine (GAAPy)[C-3]

Table 4: Computed parameters for 4-N-[Furfuralidene] aminoantipyrine (FAAPy)[C-1]

	AM1	PM3	MNDO	ZINDO1
TE(K.cal./Mol)	-72369.0	-65179.5	-72476.7	-101018.8
EE(K.cal/Mol)	-396679.3	-381962.6	-385494.7	-491035.6
CCI(K.cal/Mol)	324310.2	316783.0	313017.9	390016.7
HF(K.cal/Mol)	274.10	306.33	239.56	-6051.80
HOMO(eV)	-0.051	-0.450	-0.124	-5.625
LUMO(eV)	0.041	0.273	0.079	4.931
EG (eV)	-0.01	-0.177	-0.045	-0.694
DM(Debye)	9.307	4.147	4.996	5.030
ZPE(K.cal/Mol)	111.51	111.03	115.60	156.71

Table- 5: Computed parameters for 4-N-[(3,4,5-Trimethoxy) benzalidene]aminoanti- pyrine (TMBAAPy)[C-2]

	AM1	PM3	MNDO	ZINDO1
TE(K.cal./Mol)	-105754.6	-96769.5	-106125.7	-148318.8
EE(K.cal/Mol)	-766206.6	-749280.8	-756394.4	-885679.9
CCI(K.cal/Mol)	660451.9	652511.3	650268.7	737361.0
HF(K.cal/Mol)	150.79	103.29	39.326	-9533.27
HOMO(eV)	-0.154	-0.009	-0.124	-5.560
LUMO(eV)	0.359	0.185	0.123	4.326
EG (eV)	0.205	0.176	-0.001	-1.234
DM(Debye)	3.406	5.301	2.995	7.589
ZPE(K.cal/Mol)	214.40	205.12	225.49	307.99

Table 6: Computed parameters for 4-N-[Glutaralidene] aminoantipyrine (GAAPy)[C-3]

	AM1	PM3	MNDO	ZINDO1
TE(K.cal./Mol)	-75304.1	-67982.3	-75347.6	-105276.9
EE(K.cal/Mol)	-440416.1	-426863.0	-422222.7	-516602.3
CCI(K.cal/Mol)	365112.0	358880.6	346875.0	411325.35
HF(K.cal/Mol)	296.10	239.51	318.45	-6605.96
HOMO(eV)	-0.034	-0.212	-0.030	-5.978
LUMO(eV)	0.208	0.012	0.135	5.129
EG (eV)	0.174	-0.2	0.105	-0.849
DM(Debye)	4.879	4.939	3.270	11.551
ZPE(K.cal/Mol)	120.67	115.81	119.56	165.38

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