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Semi-Empirical Study of Schiff base Compounds Derived from 4-Dimethylaminoantipyrine

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Abstract: ***In this study 2,3-Dimethyl-4-N-[(þ-chloro)benzalidene]aminoantipyrine,2,3-Dimethyl-4-[(2-Nitro) benzalidene] aminoantipyrine , 2, 3-Dimethyl-4-[(4-Hydroxy-3-methoxy) benzalidene]aminoantipyrine Schiff base of 4-Dimethylaminoantipyrine has been subjected to semi-empirical study by using AM1, PM3, MNDO and ZINDO1 quantum chemical methods. 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 have been also reported. A good correlation has been observed between different quantum chemical methods.***

Keywords: Semi-empirical, AM1, PM3 , MNDO , ZINDO1,Normal modes Frequency, correlation.

1. 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[1-2]. In this present work three Schiff base are reported which were derived from 4-Dimethylaminoantipyrine and þ-chloro benzaldehyde, 2-Nitro benzaldehyde and Vanilline[3] . 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 2,3-Dimethyl-4-N-[(þ-chloro)benzalidene]aminoantipyrine(þ-CBDMAAPy),2,3-Dimethyl-4-[(2-Nitro)benzalidene] amino anti pyrine(NBDMAAPy),2,3-Dimethyl-4-[(4-Hydroxy-3-methoxy)benzalidene]aminoantipyrine (HMBDMAAPy). A good correlation has been observed between different quantum chemical methods.

2. Experiment

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}[4].

3. Synthesis of Compounds

A mixture of 4-Dimethylaminoantipyrine (1M mol) in absolute ethanol(30ml) was slowly added to a solution of þ-Chlorobenzaldehyde, 2-nitrobenzaldehyde,Vaniline, (1.1M mol) in absolute ethanol(20 ml).The stirred reaction mixture 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 figure-1.

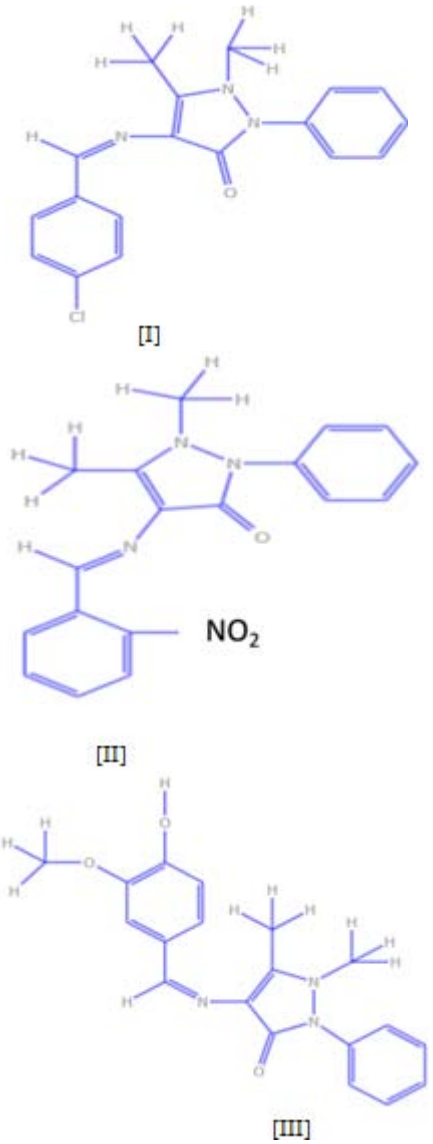

Figure 1: Molecular structure of 2,3-Dimethyl-4-N-[(þ-chloro)benzalidene]aminoantipyrine(þ-CBDMAAPy),2,3-Dimethyl-4-[(2-Nitro)benzalidene] amino anti pyrine(NBDMAAPy),2,3-Dimethyl-4-[(4-Hydroxy-3-

methoxy)benzalidene]aminoantipyrine (HMBDMAAPy) (I, II & III, respectively)

Computational details:-

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[7-8].

4. Result and Discussion

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[9-10] and given in Table 1,2 & 3 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.

Table 1: Computed parameters by using semi-empirical methods AM1 , PM3 , MNDO , ZINDO1 for Compound 2,3-Dimethyl-4-N-[(þ-chloro)benzalidene]aminoantipyrine :-

	AM1	**PM3**	**MNDO**	**ZINDO1**
TE(K.cal./Mol)	-88404.1	-79960.0	-88064.5	-12078.9
EE(K.cal/Mol)	-599395.6	-575246.6	-586344.4	-712719.5
CCI(K.cal/Mol)	510991.5	495286.6	498279.9	592440.6
HF(K.cal/Mol)	164.40	217.54	173.19	-8461.11
HOMO(eV)	-0.065	-0.011	-0.084	-4.963
LUMO(eV)	0.016	0.834	0.049	4.256
EG (eV)	-0.049	0.823	0.035	-0.707
DM(Debye)	3.051	7.690	5.693	7.952
ZPE(K.cal/Mol)	186.80	172.80	191.14	260.01

Table 2: Computed parameters by using semi-empirical methods AM1 , PM3 , MNDO , ZINDO1 for Compound 2,3-Dimethyl-4-[(2-Nitro)benzalidene]aminoantipyrine :-

	AM1	PM3	MNDO	ZINDO1
TE(K.cal./Mol)	-99886.1	-90686.4	-100161.4	-139895.9
EE(K.cal/Mol)	-714764.6	-675379.1	-712153.9	-852429.5
CCI(K.cal/Mol)	614878.5	584592.6	611992.5	712533.5
HF(K.cal/Mol)	179.01	112.48	121.59	-9170.79
HOMO(eV)	-0.074	-0.031	-0.219	-5.389
LUMO(eV)	0.186	0.206	0.128	4.360
EG (eV)	0.112	0.175	-0.091	-1.029
DM(Debye)	5.091	3.084	4.149	6.929
ZPE(K.cal/Mol)	204.17	198.69	208.49	284.16

Table 3: Computed parameters by using semi-empirical methods AM1 , PM3 , MNDO , ZINDO1 for Compound 2,3-Dimethyl-4-[(4-Hydroxy-3-methoxy)benzalidene]aminoantipyrine :-

	AM1	**PM3**	**MNDO**	**ZINDO1**
TE(K.cal./Mol)	-98451.2	-90016.4	-98513.9	-137718.4
EE(K.cal/Mol)	-683533.8	-698656.5	-686606.1	-866255.7
CCI(K.cal/Mol)	585082.6	608656.5	588092.1	728537.2
HF(K.cal/Mol)	105.05	124.33	261.15	-9462.65
HOMO(eV)	-0.108	-0.218	-0.052	-4.363
LUMO(eV)	0.036	0.082	0.136	5.908
EG (eV)	-0.072	-0.136	0.084	1.545
DM(Debye)	2.906	3.231	4.694	15.670
ZPE(K.cal/Mol)	208.51	201.26	201.85	298.27

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}. Simultaneously Normal mode frequency of vibration were also recorded with the semi-empirical methods AM1,PM3,MNDO &ZINDO1[11-13]. The results obtained are discussed in Table 4,5 & 6 & the experimental results are given in figure 2,3&4.

Table 4: Comparative study of Experimental and Computed (AM1, PM3, MNDO, ZINDO1) Group frequencies (cm^{-1}) for 2,3-Dimethyl-4-N-[(þ-chloro)benzalidene]aminoantipyrine (þ-CBDMAAPy) [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.	3422	-	-	-	-	υ_{as} (N-H) in NH_2
2.	3322	-	-	3309	-	υ_{s} (N-CH_3)
3.	3057	3069	3056	-	-	υ (C-H)
4.	3023	-	3018	-	-	υ (C-H)
5.	2969	-	2968	-	-	υ (C-H)
6.	2863	-	-	-	-	υ (=C-H) Aldehyde
7.	2825	-	-	-	-	υ_{as} (C-H) in CH_3
8.	2779	-	-	-	-	υ_{s} (C-H) in CH_3
9.	1625	1627	1641	1640	1661	υ(C=O)
10.	1593	-	1592	-	1571	(NH_2) Sci
11.	1497	-	-	1488	1483	υ (C=C)
12.	1470	1474	-	-	1469	υ(C=C)
13.	1449	1447	-	1447	1446	υ(C=C)
14.	1412	1422	1423	-	-	υ_{as}(C-CH_3)
15.	1342	1334	-	1335	1352	υ(C-N)

16.	1313	1323	1314	1327	1312	-CH_2Cl
17.	1221	1225	1228	1244	1219	δ (C-H)
18.	1171	1167	1166	1168	1175	δ (C-H)
19.	1076	-	1072	1070	-	δ (C-H)
20.	1036	1048	1047	1039	1045	(NH_2) Twi
21.	953	956	961	-	-	δ (C-H)
22.	909	-	906	915	901	δ (C-H)
23.	815	807	812	808	820	(CCC) rb
24.	753	-	755	740	-	δ (C-H)
25.	697	-	-	-	691	δ (CCC)
26.	636	638	634	633	632	δ (CCC)
27.	559	560	556	563	-	δ (CCC)
28.	445	-	444	-	-	δ (CCN)

Table 5: Comparative study of Experimental and Computed (AM1, PM3, MNDO, ZINDO1) Group frequencies (cm^{-1}) for 2,3-Dimethyl-4-[(2-Nitro)benzalidene]aminoantipyrine (NBDMAAPy) [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.	3387	3318	-	3398	-	υ_{as} (N-H) in NH_2 Group
2.	3059	3060	3061	-	-	υ (C-H)
3.	3025	-	3028	-	-	υ (C-H)
4.	2970	-	2999	-	-	υ (C-H)
5.	2865	-	2898	-	-	υ (=C-H) Aldehyde
6.	2829	-	-	-	-	υ_{as} (C-H) in CH_3
7.	2782	-	-	-	2713	υ_s (C-H) in CH_3
8.	2487	-	-	-	2491	υ_{as} (C- NH_2)
9.	2228	-	2231	-	2255	υ_s (C- NH_2)
10.	1627	1629	1610	1630	-	υ(C=O)
11.	1576	1578	1578	1583	1561	(NH_2) Sci
12.	1529	-	-	1525	-	NO_2
13.	1497	1494	-	1496	1488	υ(C=C)
14.	1473	-	-	-	1474	υ(C=C)
15.	1452	1446	1452	1454	-	υ(C=C)
16.	1419	1420	1421	-	1411	υ_{as}(C-CH_3)
17.	1346	1334	1352	1349	1349	υ (C-N)
18.	1315	-	1306	1306	1323	υ (C-C)
19.	1272	1266	-	1273	1276	υ (C-H)
20.	1192	1193	-	1192	1172	δ (C-H)
21.	1132	1121	1134	1137	-	δ (C-H)
22.	1097	-	-	-	1085	δ (C=O)
23.	1075	1074	-	1068	-	δ (C-H)
24.	1037	1033	1026	1038	-	(NH_2) Twi
25.	955	952	961	-	962	δ (C-H)
26.	912	913	908	915	908	δ (C-H)
27.	856	-	856	852	864	δ (C-H)
28.	820	824	819	811	815	(CCC) rb
29.	755	-	-	763	-	δ (C-H)
30.	742	737	739	-	738	δ (C-H)
31.	698	692	697	697	-	δ (CCC)
32.	639	640	634	632	628	δ (CCC)
33.	602	601	602	-	614	δ (CCC)
34.	503	514	513	500	-	δ (CNN)
35.	445	447	-	-	442	δ (CCN)

Table 6: Comparative study of Experimental and Computed (AM1, PM3, MNDO, ZINDO1) Group frequencies (cm^{-1}) for2,3-Dimethyl-4-[(4-Hydroxy-3-methoxy)benzalidene]aminoantipyrine(HMBDMAAPy)[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.	3069	3066	3067	-	-	υ (C-H)
2.	2970	-	2973	-	-	υ (C-H)
3.	2937	-	-	-	-	υ_{as} (C-H) in CH_3
4.	2868	-	-	-	-	υ (=C-H) Aldehyde
5.	2834	-	-	-	-	υ_{as} (C-H) in CH_3
6.	2786	-	-	-	-	υ_s (C-H) in CH_3
7.	2732	-	-	-	2713	υ_s (C-H) in CH_3

8.	1652	1644	1633	-	1662	υ(C=O)
9.	1592	1569	1584	1576	1587	(NH_2) Sci
10.	1497	1498	-	1492	1494	υ (C=C)
11.	1455	1460	-	1445	1465	υ(C=C)
12.	1433	1436	-	-	1428	$υ_{as}(C\text{-}CH_3)$
13.	1402	-	1402	1413	-	$υ_s(C\text{-}CH_3)$
14.	1293	1290	1293	1290	1286	υ(C-N)
15.	1268	-	1269	1273	1253	υ(C-H)
16.	1217	1218	1217	1223	-	δ (C-H)
17.	1153	1171	1155	1152	-	δ (C-H)
18.	1074	1076	-	1076	1072	δ (C-H)
19.	1032	-	1038	1034	-	(NH_2) Twi
20.	958	961	961	958	-	δ (C-H)
21.	910	-	904	910	918	δ (C-H)
22.	868	858	869	-	855	δ (C-H)
23.	820	830	-	819	808	(CCC) rb
24.	756	-	744	758	758	δ (C-H)
25.	729	-	-	704	727	δ (C-H)
26.	697	683	700	-	-	δ (CCC)
27.	603	616	612	612	-	δ (CCC)
28.	536	-	536	529	536	δ (CCC)
29.	459	460	462	463	466	δ (CCC)

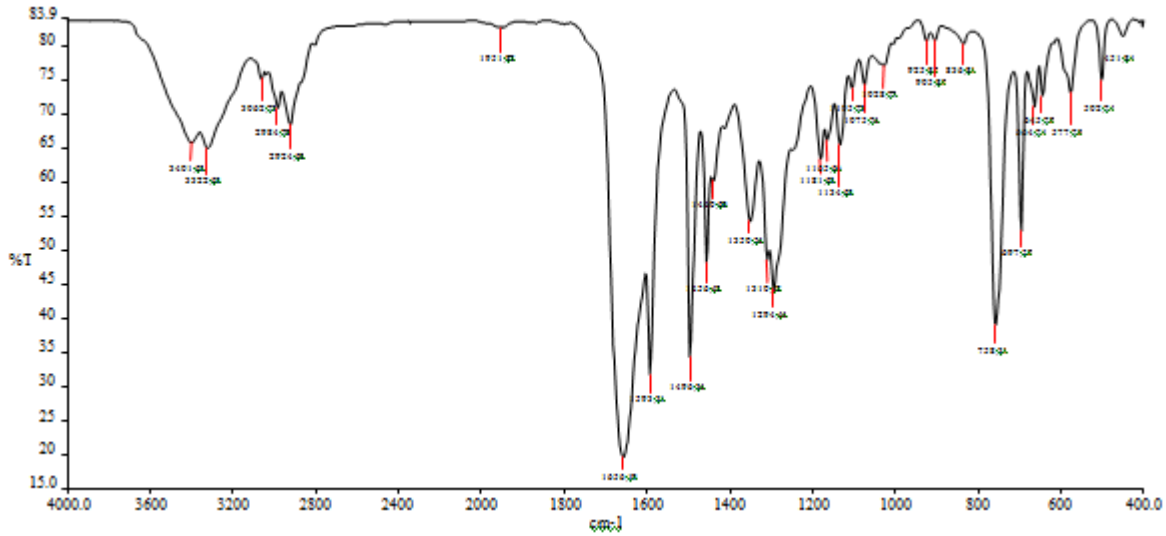

Figure 2: Experimental Spectra of 2,3-Dimethyl-4-N-[(þ-chloro)benzalidene]aminoantipyrine

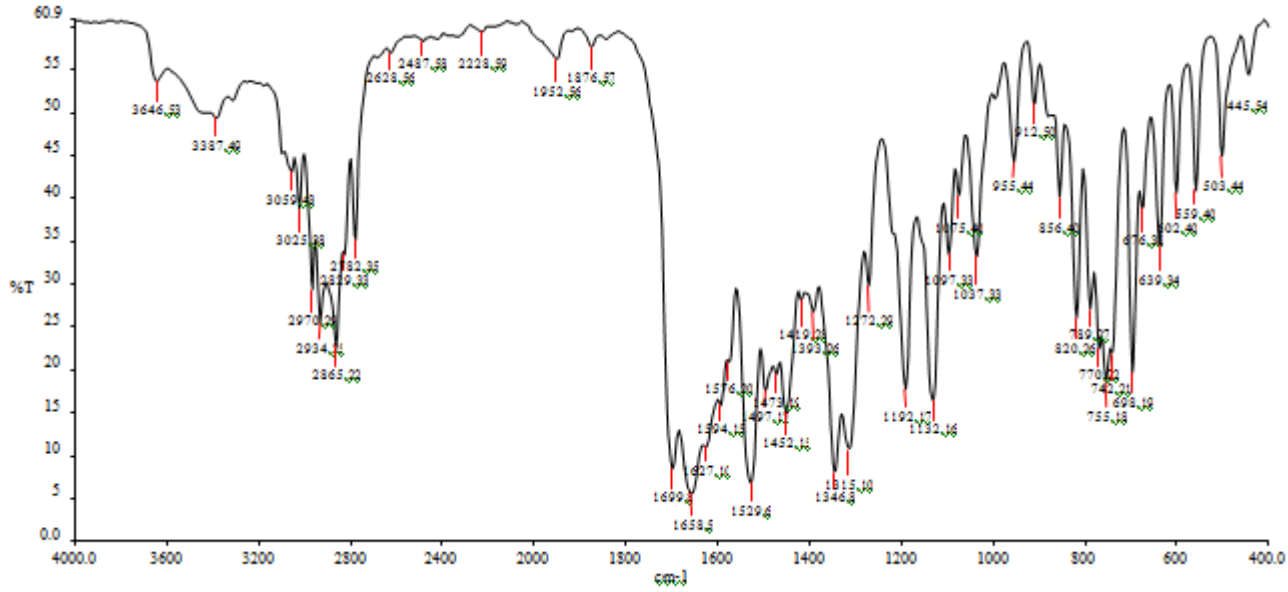

Figure 3: Experimental Spectra of 2,3-Dimethyl-4-[(2-Nitro)benzalidene]aminoantipyrine

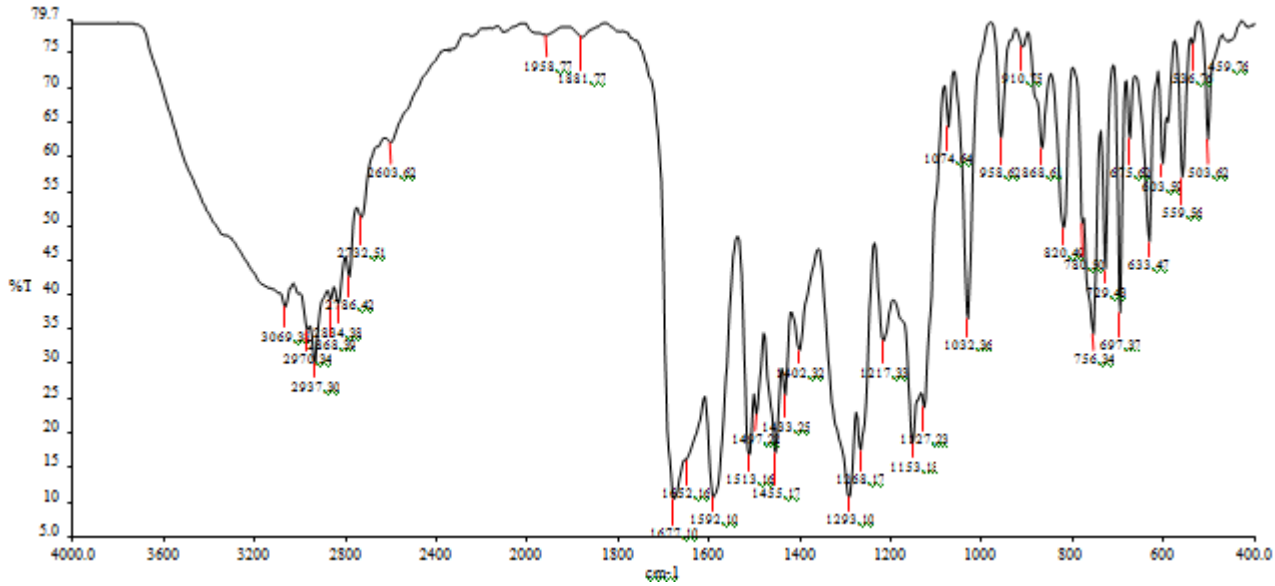

Figure 4: Experimental Spectra of 2,3-Dimethyl-4-[(4-Hydroxy-3-methoxy)benzalidene]aminoantipyrine

5. Conclusions

Semi-empirical AM1, PM3, MNDO and ZINDO1 calculations have been carried out on the vibration mode frequencies. In case of 2,3-Dimethyl-4-N-[(þ-chloro)benzalidene]aminoantipyrine the correlation coefficient obtained for AM1, PM3, MNDO and ZINDO1 are 0.999949 ,0.999966, 0.999867 and 0.999622 respectively. In case of 2,3-Dimethyl-4-[(2-Nitro)benzalidene]aminoantipyrine the correlation coefficient obtained for AM1, PM3, MNDO and ZINDO1 are 0.999858, 0.999198, 0.999658 and 0.999596 respectively, In case of 2,3-Dimethyl-4-[(4-Hydroxy-3-methoxy)benzalidene]aminoantipyrine the correlation coefficient obtained for AM1, PM3, MNDO and ZINDO1 are 0.999869 0.99996 ,0.999801 and 0.999884 respectively.PM3 Semi-empirical method can be considered as the most appropriate quantum chemical method to facilitate the vibrational frequencies identification of such compounds. Semi-empirical method can be considered as the most appropriate quantum chemical method to facilitate the vibrational frequencies identification of such compounds because the correlation coefficient obtained is more than 0.999[14-15].The semi empirical methods also provide good results of 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).

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