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Theoretically Simulated and Experimental IR spectral study of some Schiff base compounds of 4-Dimethyl-aminoantipyrine

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ABSTRACT

Schiff base compounds were obtained using Salicylaldehyde, 3,4,5 Trimethoxybenzaldehyde, Benzaldehyde and 4-Dimethyl-aminoantipyrine. The structure of these synthesized compounds were stabilized by analytically studied through melting point along with element analysis. Spectral study of these Schiff base compounds were done by modern spectroscopic technique such as IR including far IR region. To perform theoretical studies of these compounds to get their spectral parameters viz. vibrational modes using appropriate software HYPERCHEM 8.0 VERSION and predict the results on the basis of statistical correlation.

Introduction

Infrared (IR) spectroscopy is one of the most common spectroscopic techniques used by organic and inorganic chemists. Simply, it is the absorption measurement of different IR frequencies by a sample positioned in the path of an IR beam. It covers a range of techniques, mostly based on absorption spectroscopy. Different functional groups absorb characteristic frequencies of IR radiation. Using various sampling accessories, IR spectrometers can accept a wide range of sample types such as gases, liquids, and solids. Thus, IR spectroscopy is an important and popular tool for structural elucidation and compound identification[1-4].

Semi-empirical quantum chemical calculations are widely used methods for simulating IR spectra of the molecules. Such simulations are indispensable tools to perform normal coordinate analysis. Modern vibrational spectroscopy would be unimaginable without involving them. In this study, we report the assignments of IR spectra of 2,3-Dimethyl-4-[Salicylidene]aminoantipyrine (SDMAAPy)[C-1], 2,3-Dimethyl-4-[(3,4,5-Trimethoxy)benzalidene] aminoantipyrine (DMTAApy)[C-2], 2,3-Dimethyl-4 [Benzalidene] aminoantipyrine (DMBAAPy)[C-3] Schiff base of 4-Dimethyl-aminoantipyrine supported by semi-empirical calculations[5-8].

Computational Detail: Computational chemistry may be defined as the application of mathematical and theoretical principles to the solution of chemical problems. Molecular modeling, a subset of computational chemistry, concentration on predicting the behavior of individual molecules within a chemical system. With the fast growing development of computer technology and constantly updated theoretical methods, quantum chemistry calculation has become a powerful tool for exploring and analysing problem of chemistry by various workers. In order to get a deeper insight into Schiff bases compounds Hyperchem 8.0 professional program package has been performed to investigate various property of compounds on the basis of experimental and theoretical work. The most common and popular computational (Semi-empirical) methods used today in the field of chemi-informatics are AM1, PM3, MNDO, ZINDO, MNDO/3, ZINDO1[9-10].

All the calculations were carried out on Pentium core – 2 Duo machine with configuration-

Intel (R) core™ 2 Duo CPU; T₅₄₅₀ @ 1.66 GHZ; 2 GB RAM; 250 GB HDD;

With window Microsoft windows XP software as an operating system.

Experimental Details :-

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 Tab.1. The FTIR spectra of the compounds were recorded on a Perkin Elmer Infrared Spectrophotometer in the range of 4000 to 400 cm^{-1} [11-13].

Synthesis of Compounds:-

A mixture of 4-Dimethylaminoantipyrene (1M mol) in absolute ethanol (30 ml) was slowly added to a solution of Salicylaldehyde, 3,4,5 tri-methoxybenzaldehyde and Benzaldehyde (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. Molecular structures of the compounds are given in fig.1[14-15].

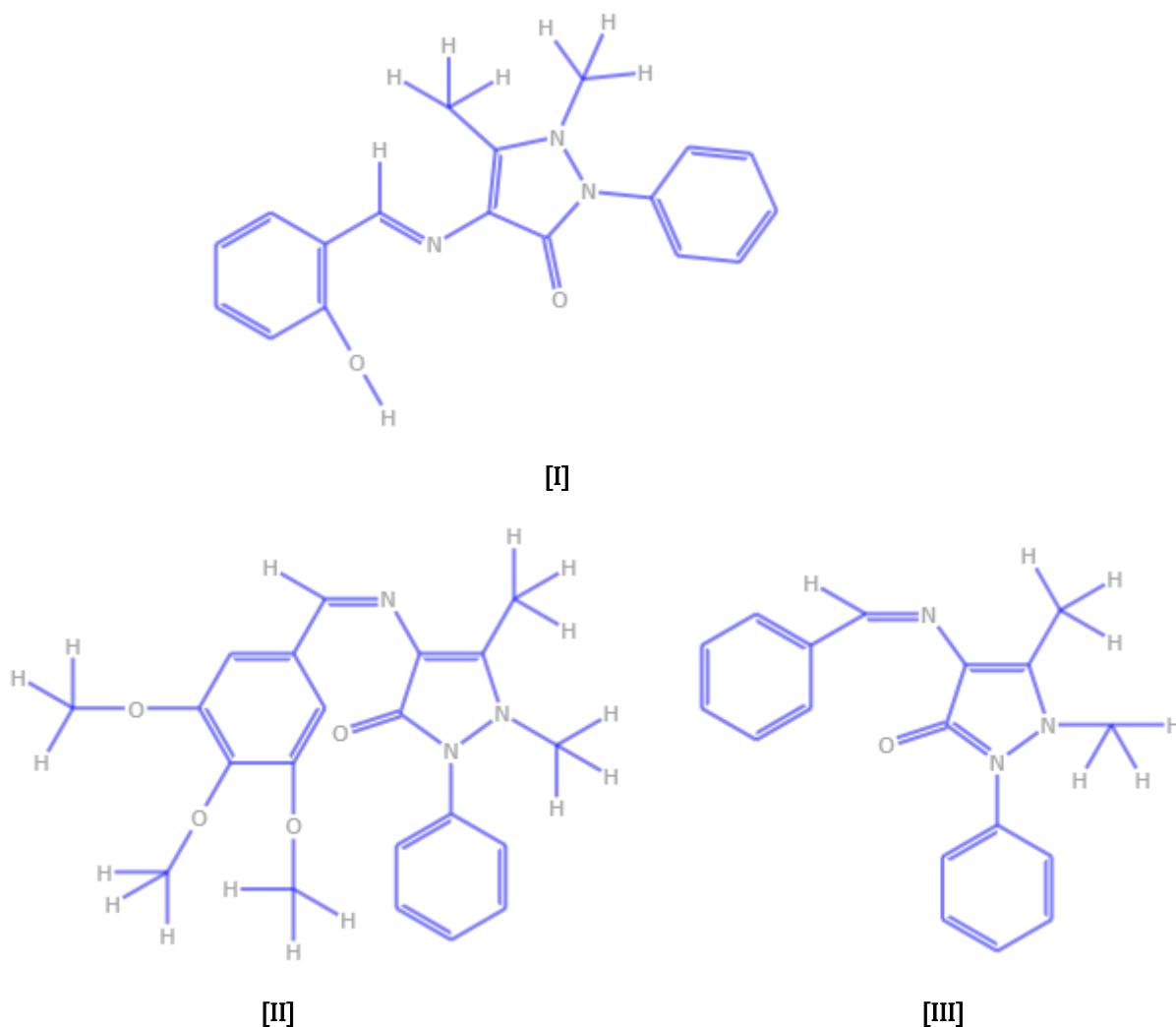


Fig.1 Molecular structure of 2,3-Dimethyl-4-[Salicyldene]aminoantipyrene (SDMAAPy) , 2,3-Dimethyl-4-[(3,4,5-Trimethoxy)benzalidene]aminoantipyrene (DMTAAAPy), 2,3-Dimethyl-4 [Benzalidene] aminoantipyrene (DMBAAPy) (I, II & III, respectively)

Results and Discussion:

The experimental and calculated IR fundamental vibration modes for 2,3-Dimethyl-4-[Salicyldene] aminoantipyrene (SDMAAPy) , 2,3-Dimethyl-4-[(3,4,5-Trimethoxy)benzalidene] aminoantipyrene (DMTAAAPy), 2,3-Dimethyl-4 [Benzalidene] aminoantipyrene (DMBAAPy) by AM1,PM3,MNDO &ZINDO1 semi-empirical methods are presented in tab.2,3 and 4 respectively. Experimental IR spectral results obtained are given in Fig.2,3&4

respectively. The differences between calculated and experimental frequencies are due to anharmonicity, intermolecular interaction, an approximation treatment of electron correlation effects and the limited basis sets [16-17]. To examine the usefulness of the calculation method for IR, a linearity between the experimental and calculated wave numbers has been derived by plotting the calculated versus experimental wave numbers and analyzing correlation coefficient value. Graphical correlation between experimental and calculated fundamental vibration frequencies are presented in fig. 5,6&7 respectively [18-19]. The cc values obtained for AM1, PM3, MNDO and ZINDO1 methods are discussed in Tab.5. It is evident that PM3 method gives most satisfactory correlation more than 0.9999 between experimental and calculated vibration frequencies.

Tab.1 Analytical data for Schiff base compounds

CODE	Melting Point (°c)	Elemental Analysis		
		C (In %)	H (In %)	N (In %)
C-1	95-98	67.17	7.81	19.18
C-2	65-70	63	7.08	7.48
C-3	62-65	76.34	7.04	17.44

Tab.2 Comparative study of Experimental and Calculated (AM1, PM3, MNDO, ZINDO1) Group frequencies (cm⁻¹) for 2,3-Dimethyl-4-[Salicyldene]aminoantipyrine (SDMAPy) [C-1]

S.N o.	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.	3320	3309	-	3370	-	ν_s (N-CH ₃)
2.	3056	3065	3057	-	-	ν (C-H)
3.	3023	3030	3027	-	-	ν (C-H)
4.	2969	-	-	-	-	ν (C-H)
5.	2863	-	-	-	-	ν (=C-H) Aldehyde
6.	2824	-	2839	-	2806	ν_{as} (C-H) in CH ₃
7.	2779	-	-	-	2720	ν_s (C-H) in CH ₃
8.	2226	-	-	-	-	ν_s (C-NH ₂)
9.	1625	1611	1640	1624	1628	ν (C=O)
10.	1593	1566	1579	-	1562	(NH ₂) Sci
11.	1497	-	-	1492	-	ν (C=C)
12.	1484	1488	-	1486	-	ν (C=C)
13.	1470	1476	-	1472	1474	ν (C=C)
14.	1448	1447	-	-	1453	ν (C=C)
15.	1411	-	1418	1420	-	ν_{as} (C-CH ₃)
16.	1341	-	1344	1338	1333	ν (C-N)
17.	1312	1319	1307	1317	1317	ν (C-C)
18.	1221	1237	1215	1236	1224	δ (C-H)
19.	1171	1178	-	1173	1167	δ (C-H)
20.	1076	1060	1068	1072	1075	δ (C-H)
21.	1036	1044	1040	1041	-	(NH ₂) Twi
22.	953	957	955	961	-	δ (C-H)

23.	909	-	912	916	903	δ (C-H)
24.	815	815	-	820	806	(CCC) rb
25.	753	762	-	753	758	δ (C-H)
26.	696	698	694	695	689	δ (CCC)
27.	674	681	679	685	664	δ (C=O)
28.	635	632	638	638	-	δ (CCC)
29.	502	507	510	500	-	δ (CNN)
30.	443	451	-	-	440	δ (CCN)

Tab.3 Comparative study of Experimental and Calculated (AM1, PM3, MNDO, ZINDO1) Group frequencies (cm^{-1}) for 2,3-Dimethyl-4-[(3,4,5-Trimethoxy)benzalidene]aminoantipyrine (DMTAApy) [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.	3349	3343	-	3322	-	ν_s (N-H) in NH_2
2.	3057	3074	3058	-	-	ν (C-H)
3.	2969	2990	2983	-	-	ν (C-H)
4.	2933	-	2955	-	-	ν (C-H)
5.	2862	-	2887	-	-	ν_{as} (C-H) in CH_3
6.	2780	-	-	-	-	ν_s (C-H) in CH_3
7.	1626	1621	-	1630	1635	ν (C=O)
8.	1590	1578	1587	1568	1587	(NH_2) Sci
9.	1499	1486	-	1497	-	ν (C=C)
10.	1392	1398	-	1369	1393	ν_s (C- CH_3)
11.	1325	1327	1328	1318	1323	ν (C-C)
12.	1235	1240	-	1232	1242	ν (C-H)
13.	1193	1197	1194	1197	1190	δ (C-H)
14.	1128	1126	1124	1117	1118	δ (C-H)
15.	1036	1042	1036	1038	1037	(NH_2) Twi
16.	991	999	999	990	-	(CCC) Tri
17.	954	960	951	940	-	δ (C-H)
18.	910	919	912	907	-	δ (C-H)
19.	816	827	821	805	814	(CCC) rb
20.	754	764	759	744	749	δ (C-H)
21.	697	682	-	682	-	δ (CCC)
22.	631	635	635	638	628	δ (CCC)
23.	502	505	507	504	503	δ (CNN)
24.	446	443	-	-	455	δ (CCN)

Tab.4 Comparative study of Experimental and Calculated (AM1, PM3, MNDO, ZINDO1) Group frequencies (cm^{-1}) for 2,3-Dimethyl-4-[Benzalidene]aminoantipyrine (DMBAAPy) [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.	3421	-	-	3420	-	ν_{as} (N-H) in NH_2
2.	3321	-	-	3347	-	ν_{s} (N- CH_3)
3.	3057	3073	3059	-	-	ν (C-H)
4.	3023	-	3025	-	-	ν (C-H)
5.	2969	-	2982	-	-	ν (C-H)
6.	2863	-	-	-	-	ν_{as} (C-H) in CH_3
7.	2779	-	-	-	2753	ν_{s} (C-H) in CH_3
8.	1626	1633	1167	1640	1630	$\nu(\text{C}=\text{O})$
9.	1593	1593	1585	1583	1549	(NH_2) Sci
10.	1496	-	-	1498	-	$\nu(\text{C}=\text{C})$
11.	1485	1488	-	1488	1480	$\nu(\text{C}=\text{C})$
12.	1470	-	-	-	1478	$\nu(\text{C}=\text{C})$
13.	1411	-	1418	1429	1422	$\nu_{\text{as}}(\text{C}-\text{CH}_3)$
14.	1341	1338	-	-	1344	ν (C-N)
15.	1313	1322	1313	1325	1327	ν (C-C)
16.	1222	1213	1218	-	1217	δ (C-H)
17.	1172	-	1167	1171	1162	δ (C-H)
18.	1098	-	1097	-	1097	δ (C=O)
19.	1076	1075	1082	1075	1069	δ (C-H)
20.	1036	-	1028	1034	-	(NH_2) Twi
21.	953	949	950	942	944	δ (C-H)
22.	909	-	911	911	-	δ (C-H)
23.	815	817	-	819	805	(CCC) rb
24.	753	-	758	-	-	δ (C-H)
25.	716	727	716	-	723	ν (N-N)
26.	696	-	-	687	686	δ (CCC)
27.	636	646	629	642	634	δ (CCC)
28.	502	502	506	502	-	δ (CNN)
29.	444	447	447	439	445	δ (CCN)

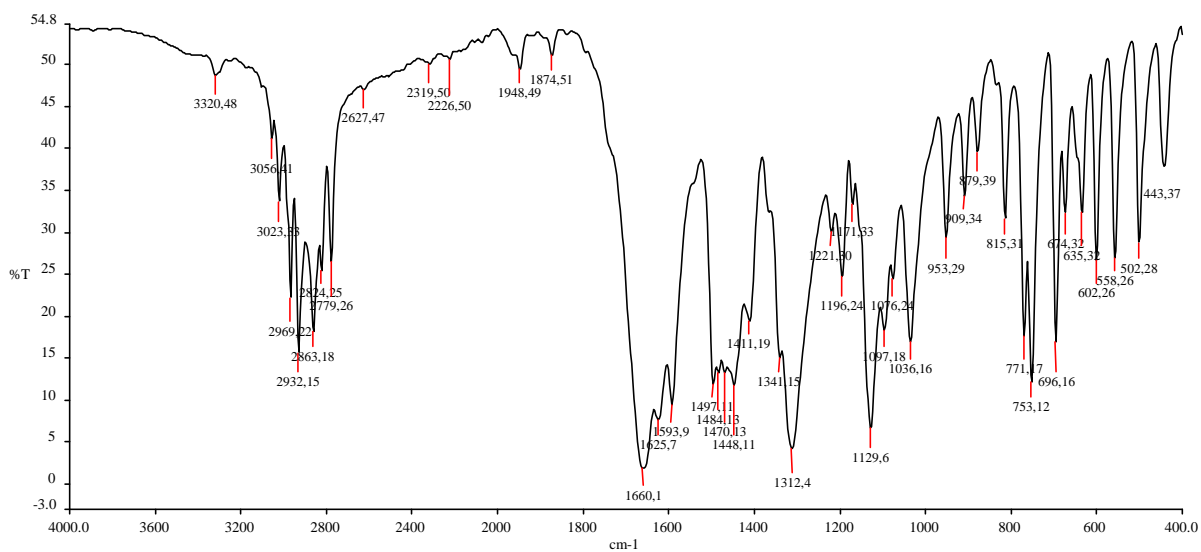


Fig. 2 Experimental spectra of 2,3-Dimethyl-4-[Salicyldene]aminoanti-pyrine (SDMAAPy)[C-1]

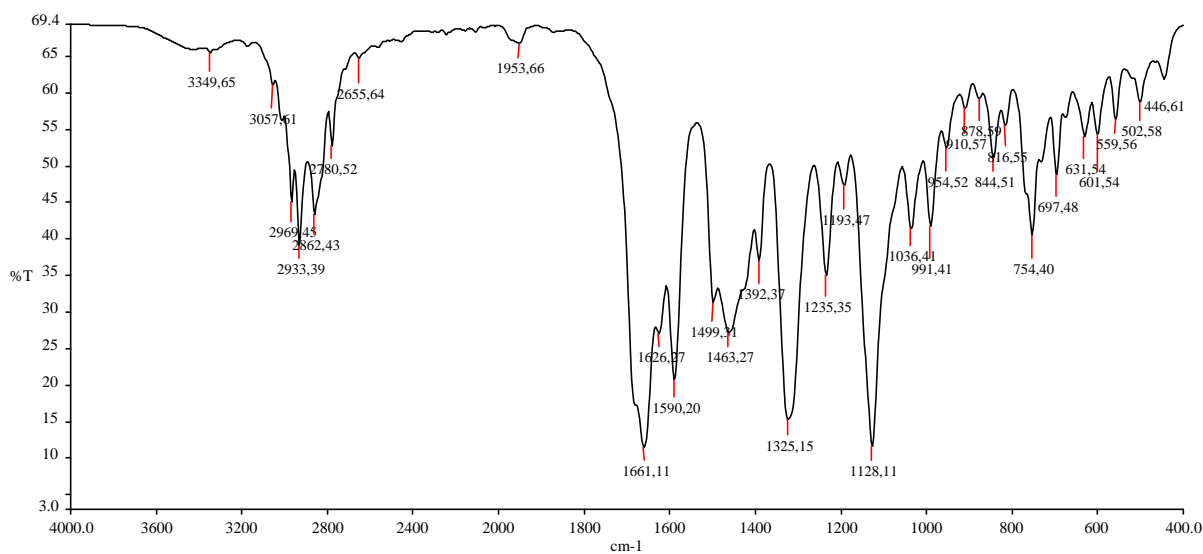


Fig.3 Experimental spectra of 2,3-Dimethyl-4-[(3,4,5- Trimethoxy) benzalidene] aminoantipyrine (DMTAAAPy)[C-2]

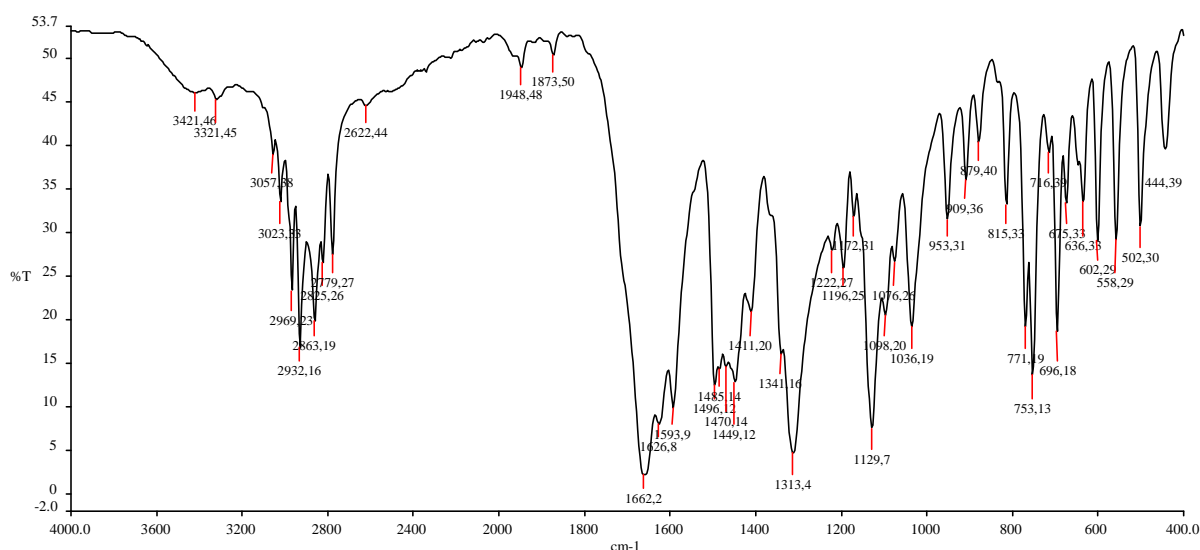


Fig. 4 Experimental spectra of 2,3-Dimethyl-4-[Benzalidene] amino- antipyrine (DMBAAPy) [C-4]

Tab.5 Correlation Coefficient between Experimental and Calculated (AM1, PM3, MNDO and ZINDO1) Vibration frequency for Schiff base compounds

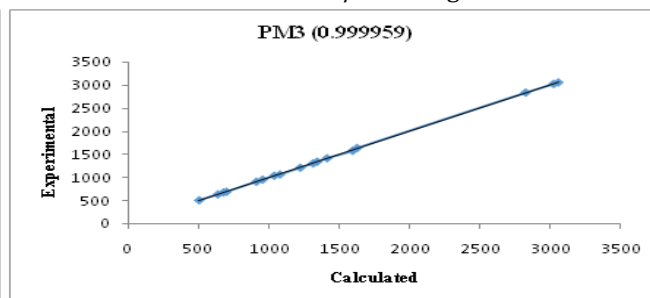
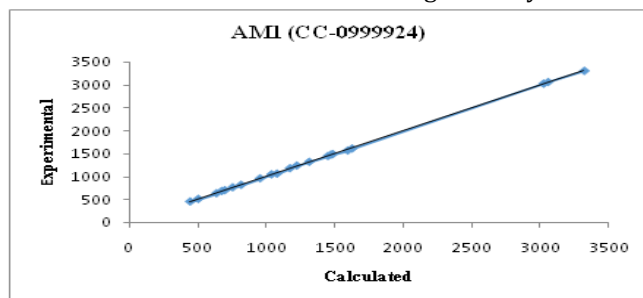
Schiff Base Compounds	Correlation Coefficient			
	AM1	PM3	MNDO	ZINDO1
C-1	0.999924	0.999959	0.999911	0.999799
C-2	0.99994	0.999974	0.999903	0.999897
C-3	0.999952	0.999979	0.999943	0.999675

Conclusion:

Semi-empirical AM1, PM3, MNDO & ZINDO1 calculations have been carried out on the vibration frequencies. A good matching between calculated and experimental vibration frequencies was observed by all theoretical methods (correlation coefficients more than 0.999). Any discrepancy noted between the observed and the calculated frequencies is due to the fact that calculations have been actually done on the single molecule in the gaseous state contrary to the experimental values recorded in the presence of intermolecular interactions.

At last it may be predicted that all the semi-empirical methods viz. AM1, PM3, MNDO, ZINDO1 are reasonably good and provide an excellently correlated results with experimental values so far as simulation of spectra is concern among all PM3 method is exceptionally good.

These studies are less time consuming and may be taken as alternate method of Studies/Teaching in this field.



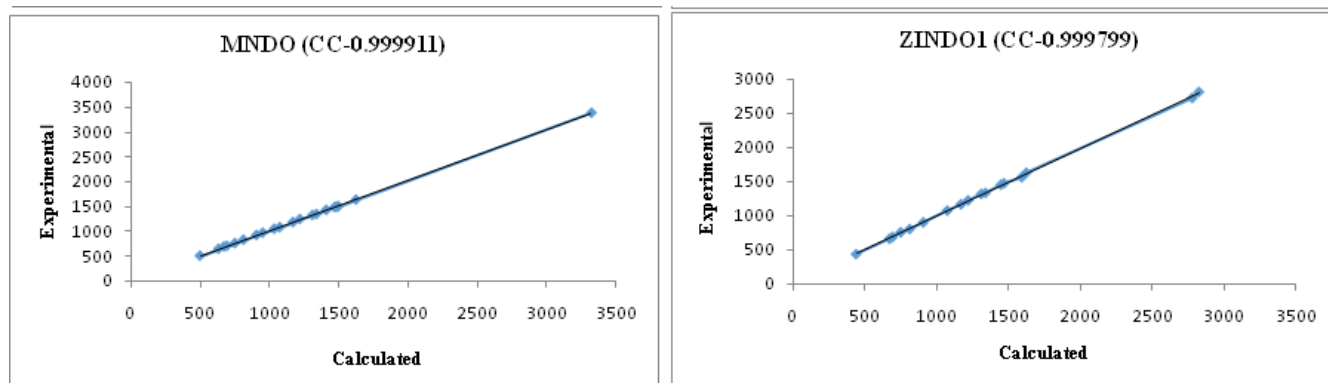


Fig.5 Graphical correlation between experimental and calculated fundamental vibration frequency obtained by AM1, PM3, MNDO and ZINDO1 Semi-empirical methods for 2,3-Dimethyl-4-[Salicyldene]aminoantipyrine (SDMAPy) [C-1] (CC-Correlation coefficient)

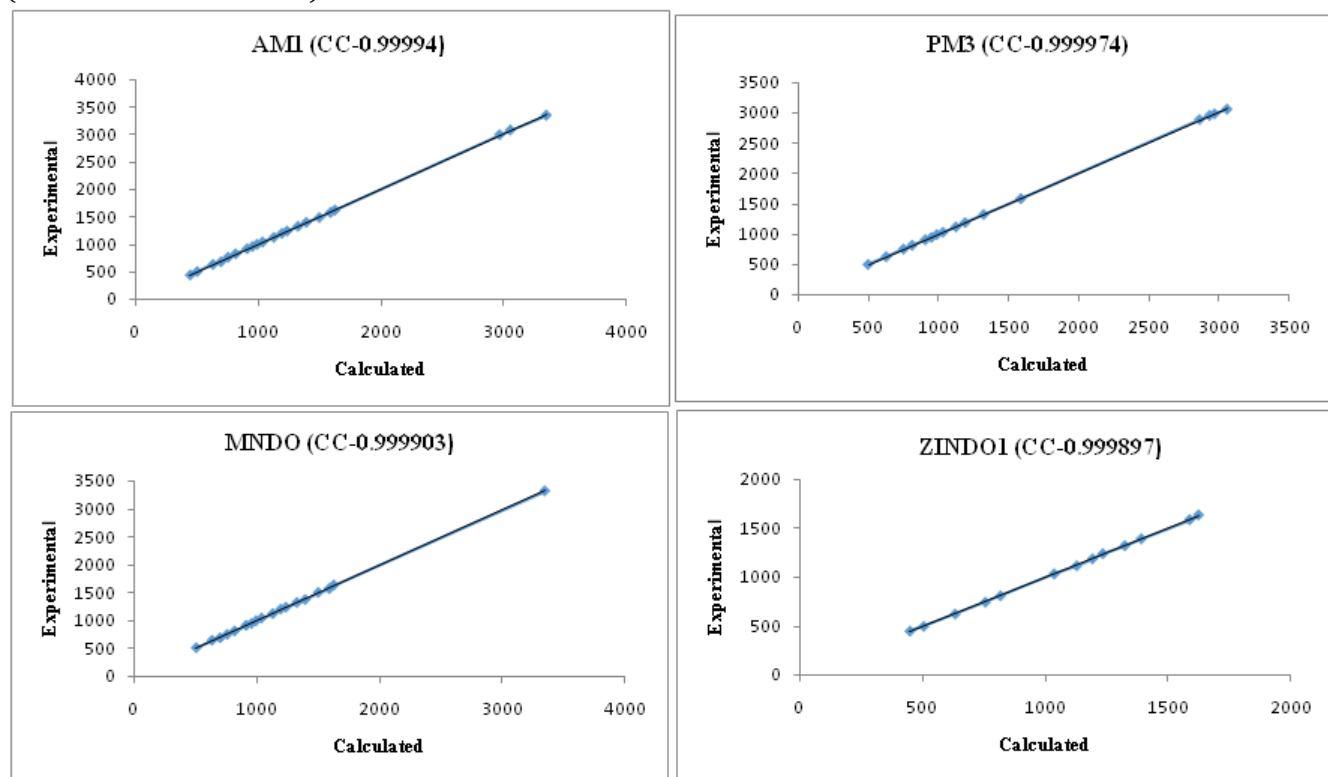
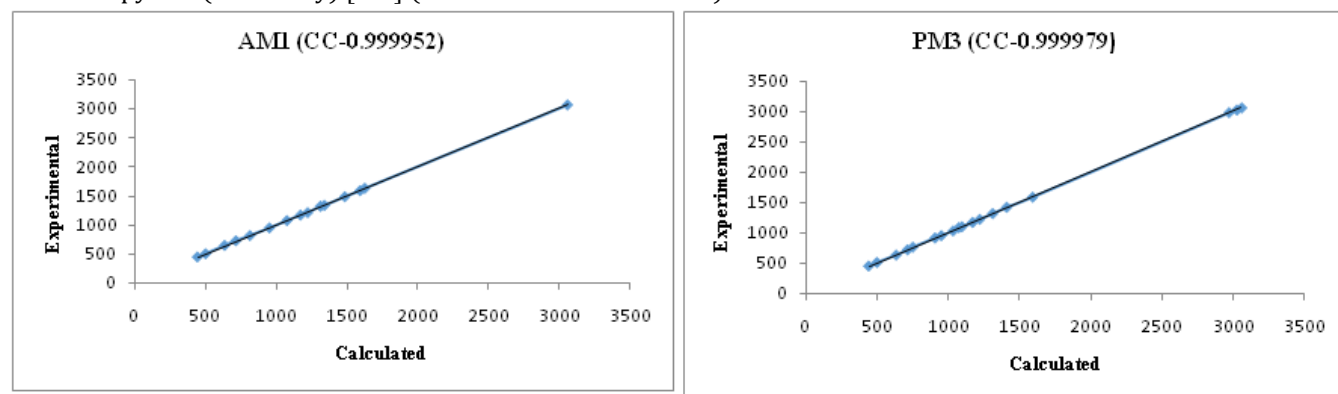


Fig.6 Graphical correlation between experimental and calculated fundamental vibration frequency obtained by AM1, PM3, MNDO and ZINDO1 Semi-empirical methods for 2,3-Dimethyl-4-[(3,4,5-Trimethoxy) benzalidene] aminoantipyrine (DMTAAPy) [C-2] (CC-Correlation coefficient)



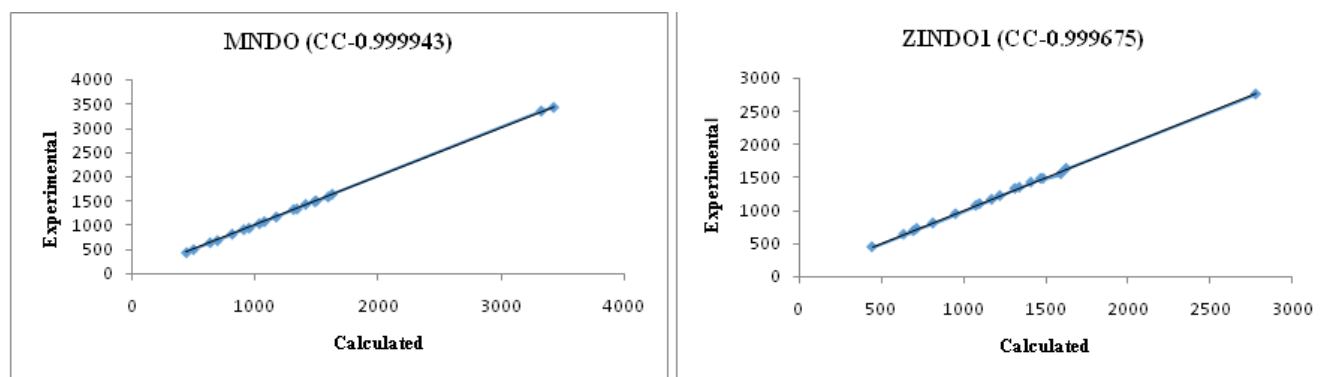


Fig. 7 Graphical correlation between experimental and calculated fundamental vibration frequency obtained by AM1, PM3, MNDO and ZINDO1 Semi-empirical methods for 2,3-Dimethyl-4-[Benzalidene]aminoantipyrine (DMBAAPy) [C-3] (CC-Correlation coefficient)

References:

- [1]. Raafat M. Issa, Abdalla M., Khedr and Helen Rizk. (2008) ^1H NMR, IR and UV/VIS Spectroscopic Studies of Some Schiff Bases Derived From 2-Aminobenzothiazole and 2-Amino-3-hydroxypyridine. Journal of the Chinese Chemical Society, 57: 875-884.
- [2]. A. Kulandaisamy, T. Kavitha, S. Angaiarkanni and P. Thillaiarasu. (2013) Synthesis and Spectroscopic Characterization of Blue Copper Model Schiff Base Complexes. Chem. Sci. Trans., 10, 2278-2278.
- [3]. Jimmy S. Hwang and M. O. Hamad Al-Turabi. (2000) EPR and Spectroscopic Studies of S-Methyl-N salicylidenehydrazinecarbothioatophenanthrolineoxovanadium(IV) as Model Compound for Vanadium Bound to Nitrogen and Sulfur Heteroatoms, American Chemical Society, 14:179-183.
- [4]. Azzouz A.S.P. et.al (2008) The UV and IR spectra of Some Schiff bases derived from salicylaldehyde and O-methoxybenzaldehyde. Study the influence of concentration of Schiff base on tautomerism reaction process. National Journal of Chemistry, 32:677-686.
- [5]. Kumar D., Agrawal M.C., Singh R. (2006) Computational Study of Benzaldehyde Thiosemicarbazone, Mat. Sci. Res. Ind. 3(1a), 37.
- [6]. Kumar D., Agrawal M. C., Singh R. (2007) Theoretical Investigation of IR and Geometry of the S-benzyl- β -N-(2-furylmethylketone)dithiocarbazate Schiff base by SemiEmpirical Methods, Asian J. Chem. 19 (5):3703.
- [7]. Arora Kishor, Kumar D., Burman K, Agnihotri S, Singh B. (2011) Theoretical studies of 2-nitrobenzaldehyde and furan-2-carbaldehyde Schiff base of 2-amino pyridine, J. Saudi Chem. Soc. 15:161.
- [8]. Singh R, Goswami Y C, Goswami R. (2011) Semiempirical & Experimental Investigation on Coordination behavior of S-methyl β -N-(4-methoxyphenylmethyl)methylene dithiocarbazate Schiff base towards Co(II), Ni(II) and Cu(II) metal ions, Journal of Chemistry, 2: 1.
- [9]. HyperChemTM Professional Release 8.0 for Window Molecular Modeling System, Dealer: Copyright © 2002 Hypercube, Inc (2002)
- [10]. Stewart J. J. P., Lipkowitz, K. B. Boyal, D. B. (Eds.); Reviews in Computational Chemistry, V.C.H. 1- 45 (1990).
- [11]. Marianne L. Mc Kelvy, Thomas R. Britt, Bradley L. Davis (1998). Infrared Spectroscopy, Anal. Chem., 70:119-177.
- [12]. H.A. Szymanski, R.E. Erickson (1970) Infrared Band Handbook. Plenum Press, New York.
- [13]. N.B. Colthrup, L.H. Daly, S.E. Wiberley (1990) Introduction to Infrared and Raman Spectroscopy. Academic Press, San Diego.
- [14]. N Raman, J Dhavethu Raja and A Sakthivel. (2007) Synthesis, spectral characterization of Schiff base transition metal complexes: DNA cleavage and antimicrobial activity studies, J. Chem. Sci., 119:303-310.
- [15]. Singh R & Surya Mani Upadhyay. (2012) Synthesis and spectral characterization of lanthanide metal complexes of Schiff base derived from substituted coumarin, ICRTE, 249-255.
- [16]. Arora Kishor, Kumar D., Burman K, Agnihotri S, Singh B. (2010) Vibration modes studies of 3,4,5-trimethoxy benzaldehyde, 4-hydroxy-3-methoxy benzaldehyde and 4-chloro benzaldehyde Schiff base of 2-amino pyridine- A quantum chemical study. Oriental Journal of Chemistry, 26(4):1361-1368.

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- [17]. Kishor Arora, Bhoop singh Yadav and S. K. Mishra. (2013) Theoretical Studies of Spectra of some Pyrazolone compounds, Research Journal of Pharmaceutical, Biological and Chemical Sciences,4(1):811-822.
- [18]. Ramesh S. Nirwan & Arun B. Sawant. (2011) Experimental And Theoretical Studies Of 6, 8-Dichloro-2-(4-Methoxyphenyl)-4h-Chromen- 4-One. J. Chem. Sci., 04:613-619.
- [19]. Kumar D., Agrawal M. C.,Singh R. (2006) Theoretical Study of Pyridine-2-Amidoxime by Semi-empirical Methods, Oriental J. Chem. 22(1):67.
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