Oriental Journal of Chemistry Vol. **26**(4), 1361-1368 (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

KISHOR ARORA[1]*, D. KUMAR[2], KIRAN BURMAN[1], SONAL AGNIHOTRI[1] and BHOOP SINGH[2]

[1]Department of Chemistry, Govt. Kamla Raja Girls Auto. Post Graduate College, Gwalior (India).
[2]Centre of Research for Chemical Sciences, Post Graduate Department of Chemistry, SMS Govt. Model Science College, Gwalior (India).

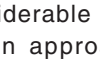
(Received: July 02, 2010; Accepted: August 11, 2010)

ABSTRACT

The vibration modes of the title compounds are examined by experimentically and theoretically using the Semi-empirical AM1 and PM3 computational methods. Vibration modes for 2N-(3, 4, 5-trimethoxy benzalidine) aminopyridine (TMBAPy), the correlation coefficients obtained for AM1 and PM3 methods are 0.999587and 0.999712, respectively. However, vibration modes for 2N-(4-hydroxy-3-methoxy benzalidine) aminopyridine (HMBAPy), the correlation coefficients for AM1 and PM3 methods are 0.986742 and 0.98184, respectively. As well as correlation coefficient for 2N-(4-chlorobenzalidine) aminopyridine (p-ClBAPy) Schiff base compound are 0.999646 and 0.999714 by AM1 and PM3 Semi-empirical methods, respectively. PM3 method provides most satisfactory correlations between experimental and calculated fundamental vibration modes of 2N-(3, 4, 5-trimethoxy benzalidine) aminopyridine (TMBAPy) and 2N-(4-chlorobenzalidine) aminopyridine (p-ClBAPy) compounds (CC = 0.999712_and 0.999714, respectively). AM1 Semi-empirical method yields highest correlation (0.986742) for 2N-(4-hydroxy-3-methoxy benzalidine) aminopyridine (HMBAPy) Schiff base compound.

Key words: Semi-empirical methods, AM1, PM3 and Vibration modes.

INTRODUCTION

The condensation of primary amines with carbonyl compounds was first reported by Schiff [1] and the condensation products are often referred to as Schiff bases. Various studies have shown that the  group has considerable biological importance[2]. 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, molecular geometry, ionization potential, heat of formation, force constant, electron density, dipole moments, population analysis, conformation analysis, chemical reaction pathways and thermodynamic properties etc. Though, Semi-empirical methods are not so accurate methods these serve the purpose of approximate calculation of different chemical properties[3-7]. The Semi-empirical methods are usually Self Consistent Field methods developed in minimal basis sets under neglect of some empirical parameters of a part of Fock-matrix elements. Among the popular Semi-empirical methods are AM1[8], PM3[9], MNDO[10], MINDO/3[11], SINDO[12] and INDO/S[13], these all methods are parameterized for ground-state properties and spectra. Out of these methods AM1 and PM3 methods are most recent and are preferred by

various workers [14-19] and the resulting these methods are with small errors PM3 methods is parameterized for system with greater number of electrons [20]. No doubt the low-level ab-initio calculations are usually better but are considerably time consuming. Therefore AM1 methods are used to get reasonably good results [21, 22].

In this respect, we report here the vibration modes of 3, 4, 5-trimethoxy benzaldehyde, 4-hydroxy-3-methoxy benzaldehyde and 4-chloro benzaldehyde Schiff bases with 2-Amino pyridine by using AM1 and PM3 computational Semi-empirical methods and compare with experimental data.

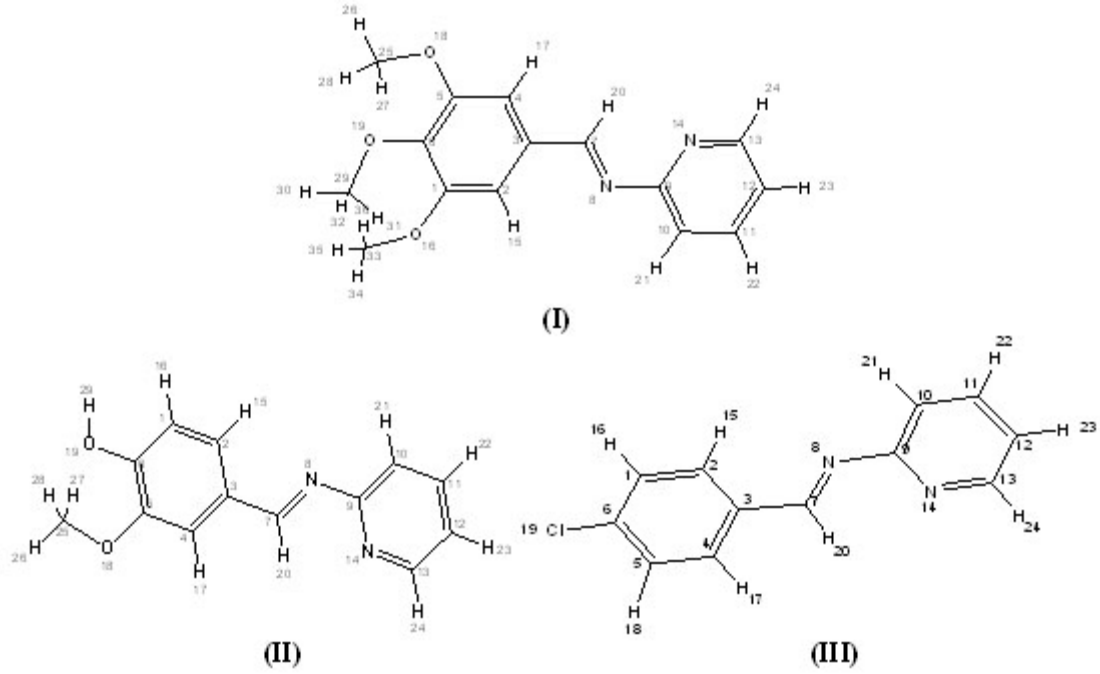


Fig. 1: Molecular structure of 3, 4, 5-trimethoxy benzaldehyde, 4-hydroxy-3-methoxy benzaldehyde and 4-chloro benzaldehyde Schiff base with 2- Amino pyridine (I, II & III, respectively) with numbering atoms adopted in the calculation

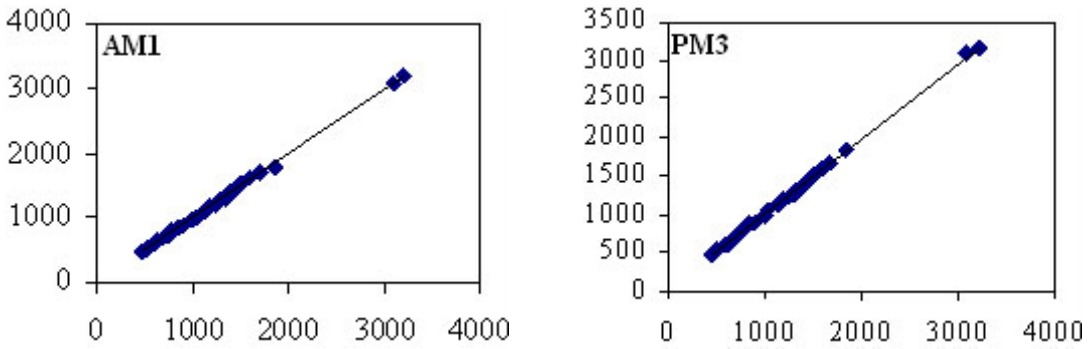


Fig. 2: Graphical correlation between experimental and calculated fundamental vibration modes obtained by AM1 and PM3 Semi-empirical methods for 2N-(3, 4, 5-Trimethoxy benzalidine) amino pyridine (TMBAPy) (CC=Correlation Coefficient)

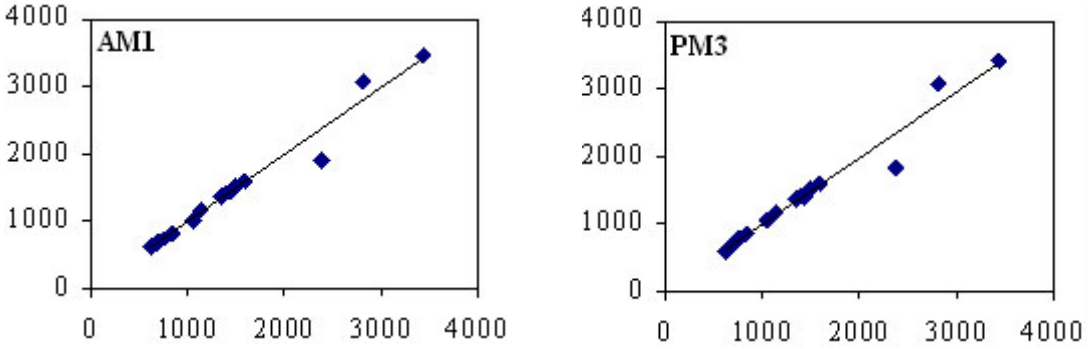


Fig. 3: Graphical correlation between experimental and calculated fundamental vibration modes obtained by AM1 and PM3 Semi-empirical methods for 2N-(4-hydroxy-3-methoxy benzalidene) amino pyridine (HMBAPy) (CC=Correlation Coefficient)

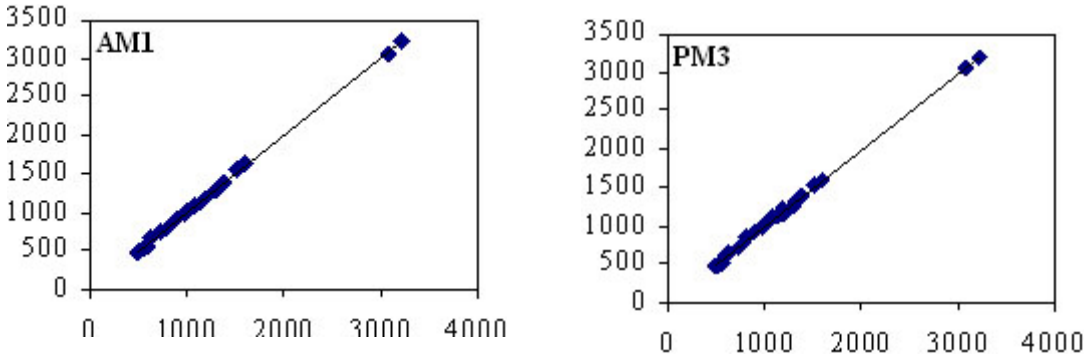


Fig. 4: Graphical correlation between experimental and calculated fundamental vibration modes obtained by AM1 and PM3 Semi-empirical methods for 2N-(4-chloro benzalidine) amino pyridine (p-ClBAPy) (CC=Correlation Coefficient)

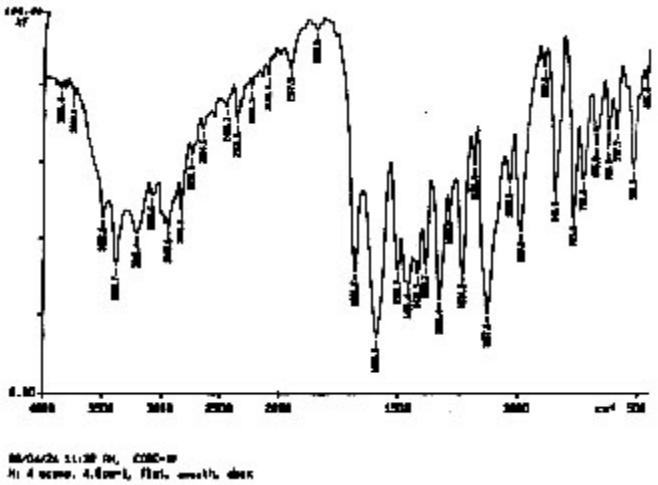


Fig. 5: Experimental IR Spectra of 2N-(3, 4, 5-tri methoxy benzalidine) amino pyridine (TMBAPy) Schiff base compound

Computational Methodology

An Intel based CORE 2DUO, DUALCORE machine with HT 3.2 technology having 800 FSB, 1GB RAM, 7200 RPM HDD was used to run all the calculations. AM1 & PM3 Semi-empirical quantum chemical calculations were carried out by the HyperChem™ 8.0 Molecular Modeling program[23] with root mean square (RMS) gradient 0.00001 kcal ($Åmol^{-1}$) using Polak-Ribiere algorithm. ACD/ ChemSketch 8.17[24] was used to draw the structure of molecules.

Table 1: Experimental and Calculated fundamental vibrational modes of 2N-(3,4, 5-Trimethoxy benzalidine) amino pyridine (TMBAPy) by AM1 and PM3 Semi-empirical methods

Experimental	AM1	PM3
465.4	481.03	477.60
522.1	530.75	542.33
592.9	611.45	597.67
626.5	626.82	618.56
676.8	678.42	662.83
730.4	733.36	748.65
769.8	797.19	786.59
845.3	856.34	883.53
892.8	888.25	886.75
989.8	979.68	993.61
1038.0	1016.92	1039.84
1127.6	1102.71	1130.44
1186.4	1183.62	1173.34
1234.5	1227.56	1221.95
1288.9	1299.07	1264.26
1330.4	1309.11	1319.46
1389.7	1399.43	1369.76
1460.4	1464.12	1469.17
1503.7	1545.23	1519.94
1592.8	1604.36	1587.48
1686.7	1682.52	1669.62
1850.0	1784.03	1834.24
3086.6	3085.36	3082.24
3215.4	3210.65	3143.66
Correlation Coefficient (CC)	0.999587	0.999712

RESULT AND DISCUSSION

The experimental and calculated IR fundamental vibration modes for the 2N-(3, 4, 5-trimethoxy benzalidine) aminopyridine (TMBAPy), 2N-(4-hydroxy-3-methoxy benzalidine) aminopyridine (HMBAPy) and 2N-(4-chlorobenzalidine) aminopyridine (p-ClBAPy) Schiff base by AM1 and PM3 Semi-empirical methods are presented in Table 1, 2 & 3, respectively and molecular structure of these compounds are presented in Figure-1. The correlation coefficients obtained for 2N-(3, 4, 5-trimethoxy benzalidine) aminopyridine (TMBAPy) are 0.999587and 0.999712_by using AM1 and PM3 Semi-empirical methods, respectively. It is evident that PM3 Semi-empirical method gives most satisfactory correlation (CC = 0.999712) between experimental and calculated vibration modes. In the case of 2N-(4-hydroxy-3-methoxy benzalidine) aminopyridine (HMBAPy) Schiff base compound, the correlation

Table 2: Experimental and Calculated fundamental vibrational modes of 2N-(4-hydroxy-3-methoxy benzalidene) amino pyridine (HMBAPy) by AM1 and PM3 Semi-empirical methods

Experimental	AM1	PM3
615.6	605.73	591.43
675.3	676.81	663.01
711.3	710.86	702.69
764.6	734.83	785.64
833.6	827.86	843.35
1057.2	1016.81	1048.06
1140.7	1164.57	1146.03
1352.6	1364.29	1363.26
1383.3	1394.14	1386.97
1425.6	1429.45	1413.16
1461.3	1464.33	1487.29
1492.3	1524.80	1526.32
1594.3	1583.26	1573.36
2366.2	1921.64	1825.53
2819.0	3062.06	3060.13
3428.9	3449.17	3425.20
Correlation Coefficient (CC)	0.986742	0.98184

coefficients (CC) of AM1 and PM3 methods are 0.986742 and 0.98184, respectively. However, the correlation coefficients for 2N-(4-chlorobenzalidine) aminopyridine (p-ClBAPy) Schiff base compound are 0.999646 and 0.999714 by using AM1 and PM3 Semi-empirical methods, respectively. It is evident that PM3 method gives most satisfactory correlation (CC = 0.999714). Graphical correlations between experimental and calculated fundamental vibrational modes are presented in Figure-2, 3 & 4 for the title Schiff base compounds, respectively.

Theoretically, Important band that occur at 1686-1594 cm^{-1} is attributed to õ(C=N) mode. In the case of 2N-(3, 4, 5-tri methoxy benzalidine) amino pyridine (TMBAPy) this band is appear at 1686.7 cm^{-1}. By using AM1 and PM3 semi-empirical methods the calculated fundamental vibrational modes are 1682.52 and 1669.62 cm^{-1}. In the case of 2N-(4-hydroxy-3-methoxy benzalidine) amino pyridine (HMBAPy) this band is shifted to lower wave number and appears at 1594.3 cm^{-1} involvement of Nitrogen atom of azomethine group in coordination. By using AM1 calculation the calculated vibrational mode is 1583.26 cm^{-1} and calculated vibrational mode obtained by PM3 methods is 1575.36 cm^{-1}. In 2N(4-chloro benzalidine) amino pyridine (p-ClBAPy) this band is shifted to lower wave number and appear at 1598.8 cm^{-1} indicating the involvement of Nitrogen atom of azomethine group in coordination. Calculated fundamental vibrational mode of p-ClBAPy by AM1 and PM3 methods are

Table 4: Experimental and Calculated IR Spectral frequencies of 2N-(3, 4, 5-trimethoxy benzalidine) aminopyridine (TMBAPy), 2N-(4-hydroxy-3-methoxy benzalidine) aminopyridine (HMBAPy) and 2N-(4-chloro benzalidine) amino pyridine (p-ClBAPy) by AM1 and PM3 Semi-empirical methods and their assignments

Schiff bases with abbreviation	Experimental (υ in cm^{-1})	Calculated (υ in cm^{-1}) AM1	PM3	Assignments
TMBAPy	1686-1594	1682.52	1669.62	υ(C=N) stretching
HMBAPy	1594.3	1583.26	1575.30	azomethine
p-ClBAPy	1598	1614.65	1600.30	
TMBAPy	1686	1682.52	1669.62	υ(C=N)/ υ(C=C)
HMBAPy	1594.3	1583.26	1573.36	pyridine ring
p-ClBAPy	1598.8	1614.65	1600.30	deformation
TMBAPy	1389, 1330.4, 1288.9	1399.4, 1309.1, 1299.1	1369.8, 1319.5, 1264.3	Ring stretching
HMBAPy	1594.3	1583.26	1573.36	
p-ClBAPy	1598	1614.65	1600.30	
TMBAPy	1186.4, 1127.6	1183.62, 1102.71	1173.32, 1130.44	N-phenyl stretching
HMBAPy	1140.00	1164.57	1146.03	
p-ClBAPy	1135.70	1118.99	1127.85	
TMBAPy	1038.00, 989.00	1016.92, 979.68	1039.84, 993.61	Ring breathing of
HMBAPy	1057.20	1016.81	1048.06	benzene
p-ClBAPy	1598.00	1614.65	1600.30	
TMBAPy	769.00, 730.00	797.19, 733.36,	786.59, 748.65	C-N-C bending
HMPBAPy	833.00, 764.00	827.86, 734.83	843.35, 785.64	
p-ClBAPy	773.00, 719.00	781.99, 735.17	786.00, 709.05	
TMBAPy	676.00	678.42	662.83	Out of plane
HMPBAPy	771.30	710.86	702.69	deformation mode
p-ClBAPy	625.80	665.95	637.91	

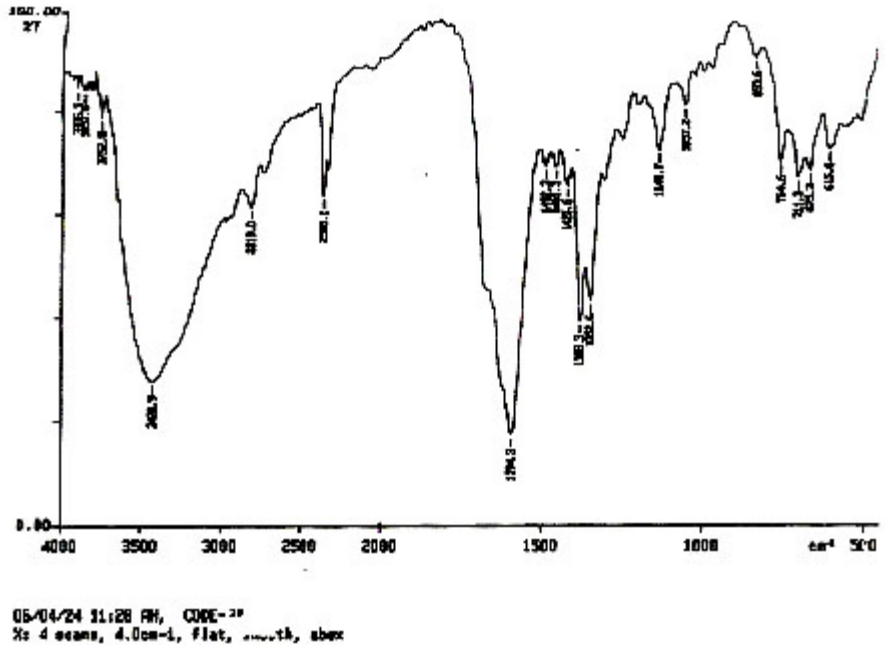


Fig. 6: Experimental IR Spectra of 2N-(4-hydroxy-3-methoxy benzalidine) amino pyridine (HMBAPy) Schiff base compound

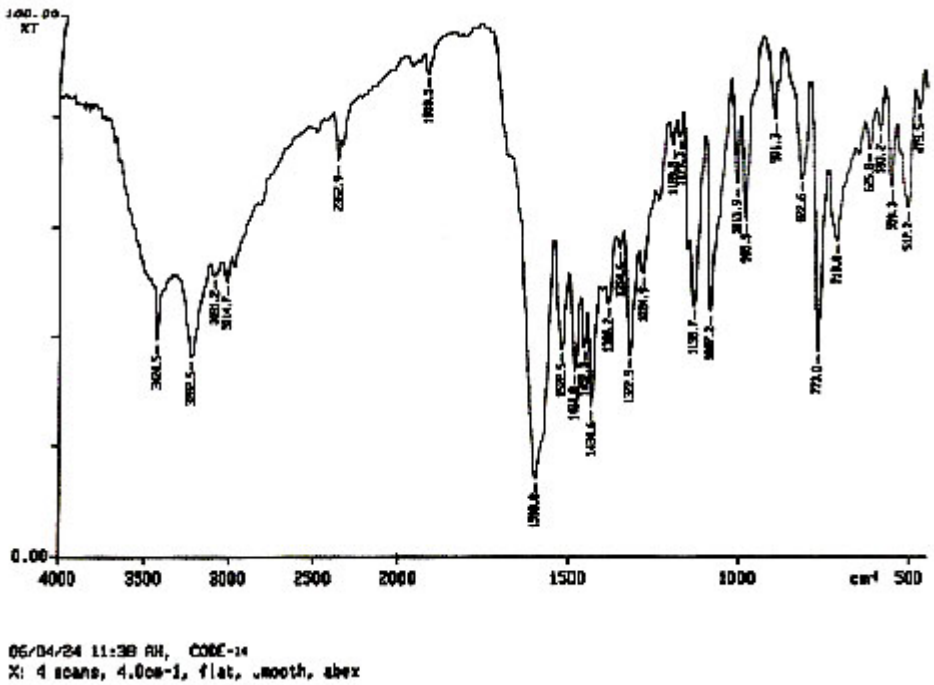


Fig. 7: Experimental IR Spectra of 2N-(4-chloro benzalidine) amino pyridine (p-CIBAPy) Schiff base compound

Table-3: Experimental and Calculated fundamental vibrational modes of 2N-(4-chloro benzalidine) amino pyridine (p-ClBAPy) by AM1 and PM3 Semi-empirical methods

Experimental	AM1	PM3
479.5	485.64	478.74
512.2	501.58	491.13
559.3	535.67	525.74
593.2	547.03	605.33
625.8	665.95	637.91
719.0	735.17	709.05
773.0	781.99	786.00
822.6	827.33	845.37
901.3	923.38	918.82
985.5	981.28	980.39
1011.9	1020.08	1011.81
1087.2	1100.33	1105.48
1135.7	1118.99	1127.85
1179.3	1182.66	1164.60
1199.5	1205.80	1207.21
1284.9	1285.88	1245.12
1322.9	1319.16	1325.27
1354.6	1355.78	1349.00
1386.2	1396.52	1397.15
1522.5	1549.30	1529.19
1598.8	1614.65	1600.30
3091.2	3061.16	3070.38
3222.5	3211.88	3182.20
Correlation Coefficient (CC)	0.999646	0.999714

1614.6 cm^{-1} and 1600.30 cm^{-1} which is in accordance with experimental value 1598.8 cm^{-1}. In addition to other important IR spectral frequencies of title Schiff base compounds are presented in below Table-4. The scan copies of the IR spectrum are also given in Fig.-5, 6 and 7.

CONCLUSION

Of the AM1 and PM3 semi-empirical methods tested in the presented study on title 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 (0.999712, 0.999714, respectively) used in 2N-(3, 4, 5-trimethoxy benzalidine) aminopyridine (TMBAPy) and 2N-(4-chlorobenzalidine) aminopyridine (p-ClBAPy) Schiff base compounds. But AM1 Semi-empirical method gives most satisfactory correlation (0.986742) in the case of 2N-(4-hydroxy-3-methoxy benzalidine) aminopyridine (HMPBAPy) compound. Thus, Quantum chemical Semi-empirical calculation can be successfully used for the prediction of vibration modes of making more active ligands and other molecules.

ACKNOLEDGEMENTS

One of the authors Kishor Arora acknowledges UGC for financial support as MRP. Thanks are also thankful to Prof. P. Mehta, the Head, Department of Chemistry and The Principal, Govt. Kamla Raja Girls Auto. Post Graduate College, Gwalior (India).

REFERENCES

1. H. Schiff, *Annls Chem.*, **131**: 118 (1864).
2. S. Patai, The chemistry of carbon-nitrogen double bond (*interscience Publishers Inc.*, New York) (1970).
3. Kishor Arora and D. Kumar, *Asian J. Chem.*, **13** (4): 1325 (2001).
4. Kishor Arora and D. Kumar, J. *Indian Chem. Soc.*, **79**: 693 (2002).
5. D. Kumar, Kishor Arora and Bhoop Singh, *Asian J. Chem.*, **19**(5): 3703 (2007).
6. D. Kumar, M. C. Agrawal, Bhoop Singh, Hari Singh, Radha Tomar and Kaman Singh, *Mat. Sci. Ind.*, **5**(1): 139 (2008).
7. D. Kumar, M. C. Agrawal, Bhoop Singh, Hari Singh, Radha Tomar and Kaman Singh, *Mat. Sci. Ind.*, **5**(2): 485 (2008).

8. M. J. S. Dewar, E. G. Zoebisch, E. F. Healy and J. J. P. Stewart, *J. Am. Chem. Soc.* **107**: 3202 (1985).
9. J. J. P. Stewart, *J. Comp. Chem.* **10**: 210 (1989).
10. M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.* **99**: 4899 (1977).
11. R. C. Bingham, M. J. S. Dewar and D. H. Lo, *J. Am. Chem. Soc.* **97**: 1285 (1975).
12. D. N. Nanda and K. Jung, *Theor. Chim. Acta* **57**: 95 (1980).
13. J. E. Ridley and M. C. Zerner, *Theor.Chim. Acta* **32**: 111 (1973).
14. Kishor Arora, R. C. Goyal and D. D. Agrawal, *Asian J. Chem.*, **12**: 893 (2000).
15. Kishor Arora, R. C. Goyal and D. D. Agrawal, *Oriental J. Chem.*, **16**: 105 (2000).
16. Kishor Arora, A. R. Khan and K. P. Sharma, *Oriental J. Chem.*, **18**(2): 319 (2002).
17. Kishor Arora, Aarti Gupta and D. D. Agrawal, *Asian J. Chem.*, **14**: 1611 (2002).
18. Kishor Arora and Sonal Agnihotri, *J. Saudi Chem. Soc.*, **7**: 221 (2003).
19. Kishor Arora and Kiran Burman, *J. Saudi Chem. Soc.*, **9**(2): 297 (2005).
20. J. J. P. Stewart, K. B. Lipkowitz and D. B. Boyal (Eds), *Reviews in Computational Chemistry*, V. C. H., **1**: 45 (1990).
21. J. Laxmikanth and K. Bhanu Prakash, *Indian J. Chem.*, **39**A: 114 (2000).
22. Kishor Arora and D. Kumar, *J. Ind. Chem. Soc.*, **79**: 693 (2002).
23. HyperChem Professional Release 8.0 Molecular Modeling System.
24. ACD/Labs Release 8.17 Molecular Drawing System.