ISSN: 0975-8585

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Theoretical Studies of Spectra of some Pyrazolone compounds

Kishor Arora*[1], Bhoop singh Yadav[2] and SK Mishra[1]

[1]Department of Chemistry, Govt. P.G. Autonomous College, Datia, (M.P)
[2]Department of chemistry, S.M.S Govt. Science College, Gwalior (M.P)

ABSTRACT

The vibration modes of some pyrazolone compounds were examined experimentally and theoretically using Semi-empirical AM1 and PM3 methods. Apart from giving the comparison of the significant part of the spectra, the statistical correlation was also calculated for the theoretical spectra and methods to establish the use of these methods as alternative and supportive tool in analytical chemistry. Vibration modes for the compounds under study show a perfect correlation between theoretically and experimentally observed values.

***Corresponding author**

INTRODUCTION

Pyrazolone compounds refer to the class of compounds characterized by 5- membered ring structurecomposed of three carbon and two nitrogen atoms in the adjacent position, out of which one is basic nitrogen and other is neutral nitrogen. The aromatic nature these compounds arises from the four electrons and the unshared pair of electrons on th NH nitrogen (1).Pyrazole derivative have a long history of application in agrochmicals as herbicidesand insecticide and in pharmaceutical industry as antipyratic and anti- inflammatory drugs. Antipyrine is one of the earliest synthetic drug and is named after its antipyratic properties.

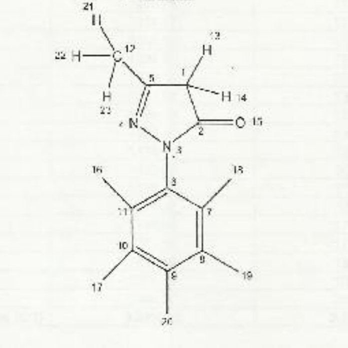
Pyrazolone compounds also have complex formation property. They can coordinate to metal ions via carbonyl oxygen atom and may be considered as a good oxygen donor ligands. This fact has been established by various workers(1-3). Some of the pyrazolone compounds have also found to show drug property(4-5).

Due to its wide range of biological activity, pyrazoles have received a considerable interest in the field of drug discovery and therefore, pyrazole ring constitutes a relevant synthetic target in pharma ceutical industry. In fact, such a heterocyclic moiety represents the core structure of a number of drugs (6).

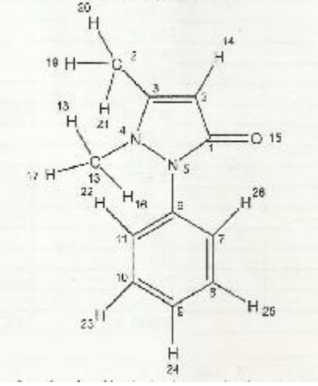
DFT, molecular mechanics, semi-empirical and ab-initio methods are often employed to calculate molecular properties. These methods give information regarding vibration modes, molecular geometry, heat of formation, force constants, electron densities, dipole moments, population analysis, chemical reaction pathways and thermodynamic properties etc.

Semi-empirical methods provide the information of approximate calculations of different chemical properties using different methods viz. AM1, PM3, MNDO and ZINDO (7-8). Since the ab-initio calculation methods are time consuming, so, semi-empirical AM1 and PM3 methods are in use with reasonably good results.

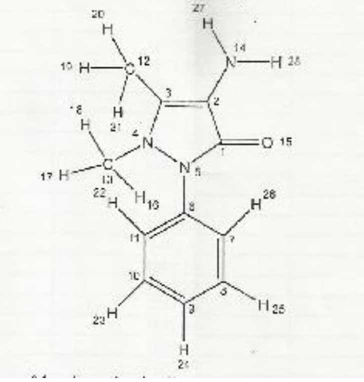
MPP(I)



Antipy(IV)



4-Amantipy(V)



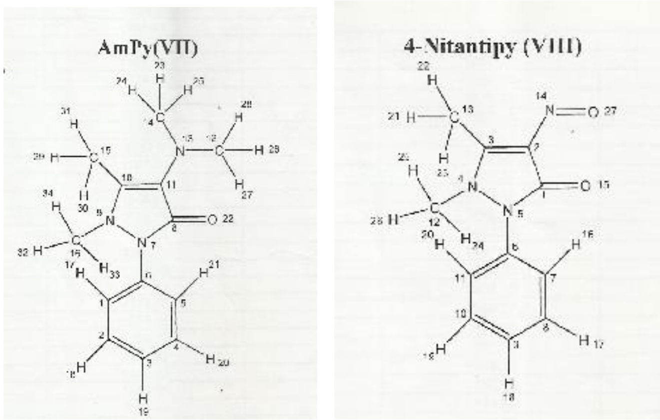


Figure 1: Structures of pyrazolone compounds under study

In this paper we wish to report the vibration modes analysis of some selected pyrazolone compounds using AM1 and PM3 methods and their comparison with their real spectra. Compounds taken for the studies here are (i) Methyl phenyl – 5- pyrazolone (MPP); (ii) Antipyrine (Antipy); (iii) 4- Amino antipyrine (4-Amantipy); (iv) Amino pyrine (Ampy) and (v) 4-Nitrosoantipyrine (4-Nitantipy). Structures of these compounds are given in figure 1.

EXPERIMENTAL

The compounds under study were procured from the reliable sources as E-merck, Loba Chemie and C.D.H. etc. Their purities were checked by checking their melting points.

The I.R. spectral studies of these compounds were carried out at Sophisticated Analytical Instrumentation Facility (S.A.I.F), Central Drugs Research Institute (C.D.R.I.) Lucknow using KBr/ CsI pallets in the range 4000- 400 cm^{-1} (9).

Computational details: The AM1 and PM3 methods in MOPAC package were used to calculate the bond lengths, bond angles, heat of formations, core-core repulsion energies, ionization potentials etc.. The calculations for vibration modes of the pyrazolone compounds under study were also done using same package. Structures of the compounds were drawn on the PCMODEL package of Serena software and then were optimized which were then used as input to MOPAC . All these calculations were done on the Pentium – III machine with configuration: P-III/866Mhz/20GB/52X/SCROLL MOUSE/ 56 KBPS.

RESULTS AND DISCUSSION

The computed heat of formation, total energy, electronic energy, core-core repulsion energy, ionization potential and other computed results are of theoretical interest. The computed vibration modes along with their experimental values are given in the tables 1-5. It has also been tried to match the computed spectral peaks with their experimental values.

Recorded spectral data match well with the theoretically computed data for the compounds under study. The observed results are well within range (10-11).

Table 1: Computed and observed vibration modes values (cm^{-1}) for Methyl phenyl-5- pyrazolone (MPP) compound.

Experimental (cm^{-1})	AM1	PM3
------	414.42	386.99
------	488.21	474.48
499	508.36	496.39
------	553	551.54
570	593.35	569
616	650.11	626.38
689	657.07	642.52
757	726.06	673.7
800	806.55	774.89
------	884.71	812.14
917	916.53	845.39
-----	945.08	901.58
------	954.93	933.27
------	984.9	945.02
------	1003.29	976.49
1025	1044.47	994.47
------	1049.11	1005.32
1076	1089.63	1015.29
------	1109.55	1043.62
------	1131.54	1050.62
------	1196.33	1111.18
1198	1197.69	1123.59
------	1248.52	1155.52
------	1280.74	1171.79
------	1304.47	1205.69
------	1338.62	1215.08
------	1364.62	1233.17
------	1378.12	1340.38
1394	1387.52	1364.85
1397	1408.99	1385.47
------	1430.45	1386.84
1457	1474.08	1392.44
1522	1553.86	1475.41
1610	1578.08	1544.97
------	1674.82	1587.7
------	1745.91	1771.46

Table 2: Computed and observed vibration modes values (cm^{-1}) for Antipyrine (Antipy) compound

Experimental (cm^{-1})	AM1	PM3
-----	476.13	461.64
-----	526.75	484.82
575	595.73	559.85

-----	633.81	581.28
665	655.14	594.68
-----	677.92	634.44
-----	698.54	645.61
750	713.28	684.1
-----	814.5	773.33
-----	848.84	777.72
-----	891.1	874.95
920	952.7	889.9
-----	979.51	910.35
-----	988.88	948.19
-----	1046.96	983.38
-----	1054.66	989.61
-----	1073.07	1007.89
1115	1110.41	1016.89
-----	1134.22	1035.42
1178	1178.51	1075.74
------	1196.39	1106.7
1250	1252.97	1163.07
	1319.89	1204.05
1350	1365.59	1247.80
------	1372.81	1349.14
-----	1378.3	1368.77
-----	1410.39	1376.68
1444	1453.82	1388.65
-----	1487.49	1392.53
-----	1503.02	1453.83
1594	1566	1538.81
1649	1639.06	1584.44
-----	1746.23	1769.37
-----	1774.38	1782.66
-----	1793.32	1823.82
------	2074.67	1982.65

Table 3: Computed and observed vibration modes values (cm^{-1}) for 4-Aminoantipyrine (4-Amantipy) compound.

Experimental (cm^{-1})	AM1	PM3
-----	423	396.26
-----	481.69	460.46
-----	520.24	493.39
572	599.01	536.17
-----	630.76	580.44
-----	641.99	609.59
661	663.46	629.27
-----	680.24	634.17
-----	717.14	660.97
753	739.89	725.81
-----	784.04	766.76
-----	812.05	779.68
-----	825.62	847.23
-----	887.71	857.88

920	945.59	900.65
-----	955.44	932.02
-----	988.56	956.14
-----	1006.05	979.06
-----	1030.86	989.8
-----	1060.2	1008.71
------	1067.27	1032.16
------	1099.67	1017.14
1115	1131.96	1032.16
------	1144.69	1047.06
1178	1177	1070.63
-----	119.94	1102.64
-----	1196.47	1105.58
1250	1259.91	1153.28
-----	1302.97	1157.71
-----	1325.46	1203.09
	1339.28	1222.61
1350	1366.51	1230.32
-----	1370.35	1301.23
-----	1382.03	1369.99
-----	1393.31	1377.02
1444	1449.04	1386.14
-----	1469.67	1388.1
-----	1493.4	1405.07
-----	1566.74	1492.65
1594	1585.22	1541.26
1649	1641.54	1588.51
-----	1710.35	1652.73

Table 4: Computed and observed vibration modes values (cm^{-1}) for Aminopyrine (Ampy) compound.

Experimental (cm^{-1})	AM1	PM3
------	433.62	439.25
------	484.1	467.62
500	503.17	493.76
559	507.4	506.75
604	601.8	545.82
------	623.26	586.12
------	646.92	629.22
------	657.54	636.45
695	692.14	652.08
------	732.83	681.81
750	759.76	720.29
------	789.62	778.35
------	809.39	788.34
------	885.4	842.28
------	923.36	857.38
954	946.78	905.32
------	985.17	936.35
------	1002.74	949.49
------	1019.1	954.80

------	1062.6	959.5
------	1065.52	984.73
------	1084.67	989.21
------	1101.58	1003.86
1111	1114.46	1015.14
------	1123.57	1021.8
------	1135.17	1029.18
------	1179.33	1044.77
------	1187.5	1096.68
1198	1197.05	1104.83
------	1201.95	1119.54
------	1246.87	1146.28
------	1285.75	1174.63
1317	1332.34	1185.45
------	1365.76	1218.42
------	1368.35	1248.02
------	1371.23	1303.95
------	1373.76	1331.85
------	1453.53	1382.82
1474	1489.02	1392.29
------	1576.49	1488.1
1657	1608.47	1543.05

Table 5: Computed and observed vibration modes values (cm^{-1}) for 4-Nitroso antipyrine (4-Nitantipy) compound.

Experimental (cm^{-1})	AM1	PM3
------	456.74	430.92
499	478.12	439.66
------	502.48	484.08
564	531.54	499.9
601	615.89	586.25
------	650.04	603.84
658	655.72	626
------	672.86	831.81
------	702.41	632.88
------	720.25	667.87
765	746.43	723.97
------	805.94	741.33
------	829.98	786.45
------	848.58	836.74
872	885.6	847.91
------	949.77	859.77
980	986.69	933.22
------	1005.99	954.06
1034	1037.99	980.38
------	1066.52	1000.81
1089	1100.66	1020.64
------	1142.89	1030.73
1168	1176.57	1064.81
------	1195.89	1102.48

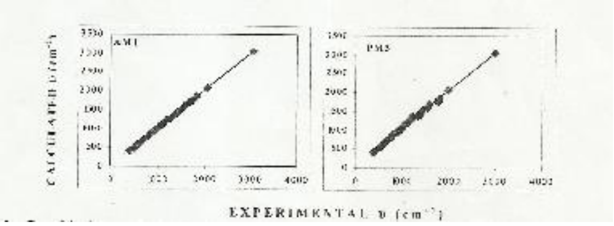
------	1207.51	1104.59
------	1242.76	1153.09
------	1270.73	1157.11
1290	1292.43	1172.66
------	1335.11	1204.41
------	1359.25	1301.84
------	1367.02	1322.11
1371	1375.26	1362.84
------	1408.15	1368.19
------	1433.34	1370.07
------	1447.62	1371.71
1466	1484.36	1385.36
------	1503.13	1399.1
1515	1550.27	1491.92
1562	1574.26	1539.51
1615	1690.16	1586.1
------	1748.11	1603.77

The notable peaks in these compounds are carbonyl stretching frequency υ (C=O); υ (C=N); υ(C-N-C) bending; ring breathing and deformation and ring stretching etc (10-12) which appear well within the range as reported by earlier workers (10-12).

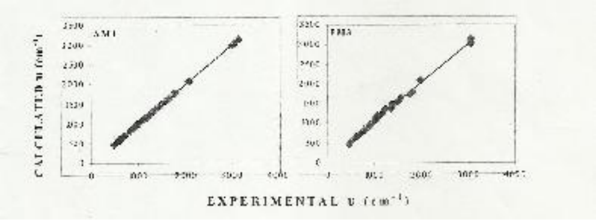
Correlation coefficient between computed and experimental vibration modes for the different pyrazolone compounds under study using AM1 and PM3 methods respectively are computed and are listed here:

(i) Methyl phenyl – 5- pyrazolone (MPP)-- **0.99995** (AM1) and **0.99747**(PM3) ;
(ii) Antipyrine (Antipy**)--** **0.99997** (AM1) and **0.998748** (PM3) ;
(iii) 4- Amino antipyrine (4-Amantipy)-- **0.99993** (AM1) and **0.99524**(PM3) ;
(iv) Amino pyrine (Ampy) -- **0.999243** (AM1) and **0.992732**(PM3)
(v) 4- Nitrosoantipyrine (4-Nitantipy)-- **0.99998** (AM1) and **0.993373** (PM3) .

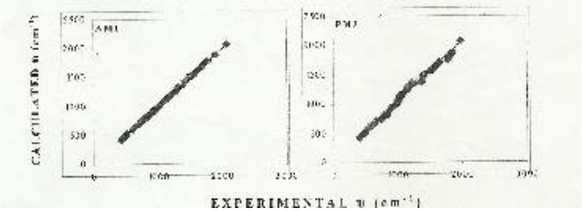
These correlation coefficient values among computed and experimental vibration modes for the pyrazolone compounds under study clearly indicates that computed values are approximately in correlation with the experimental values. The linear graphs between computed and experimental values for vibration modes for the pyrazolone compounds under studies are given in the figure 2.



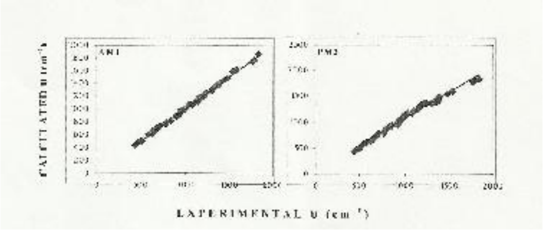
MPP



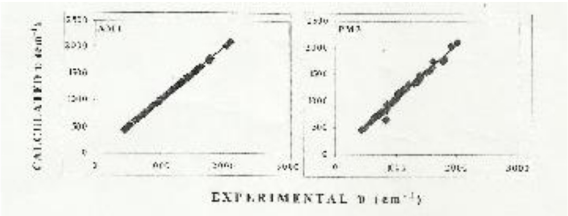
Antiapy



Amantiapy



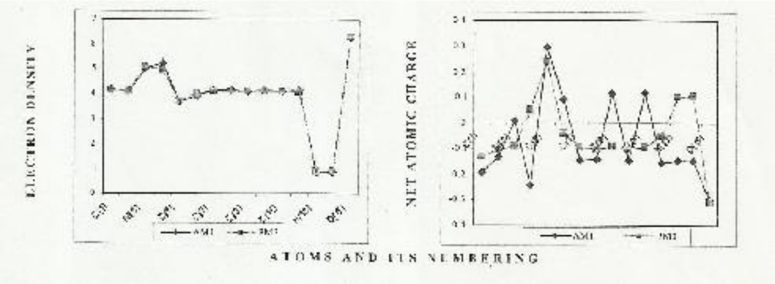
Ampy



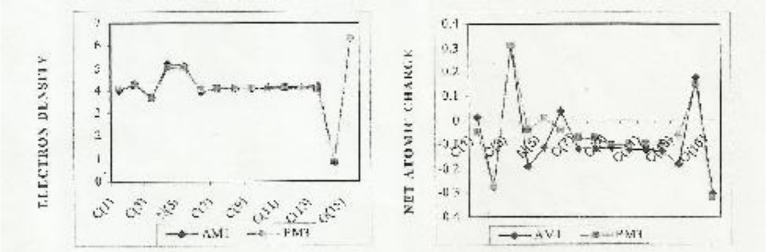
Nitantipy

Figure 2. Correlation graphs between Computed and experimental values of vibration modes of various pyrazolone compounds under study

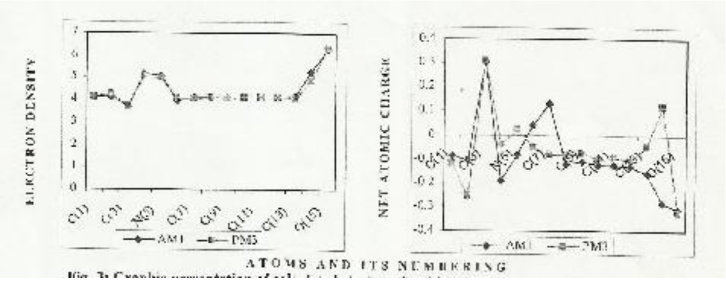
Net atomic charge (NAC) and electron density (ED) on different atoms were also computed using this semi-empirical methods of the pyrazolone compounds under study. Their variation graphs are plotted and are shown in the figure 3 for various pyrazolone compounds.



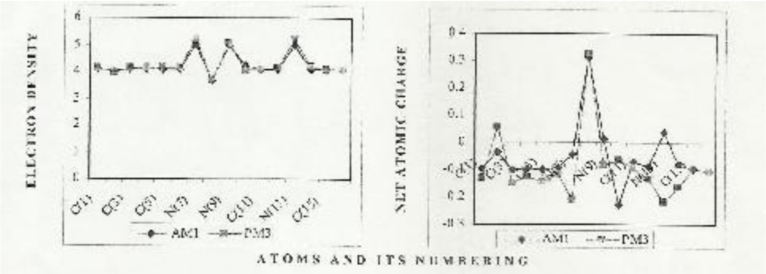
MPP



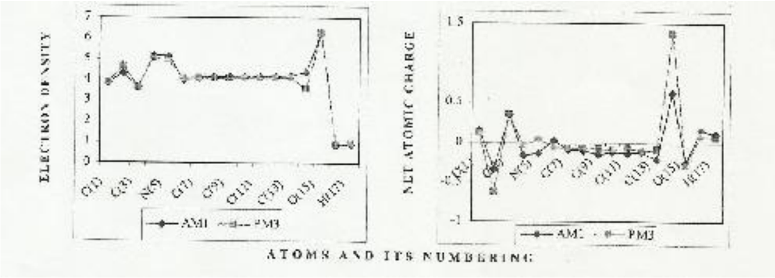
Antipy



Amantipy



Ampy



Nitantipy

Figure 3 Computed values for Net Atomic Charge (NAC) and Electron Density (ED) of various pyrazolone compounds under study

CONCLUSIONS

On comparison among the AM1 and PM3 semi-empirical methods tested in the present study for the title compounds, AM1 semi-empirical method can be considered as the most appropriate method to facilitate the vibration frequencies identifications of such compounds as I.R. frequencies simulated by this method exhibit the best linearity between computed and experimental frequencies data. Thus this may be concluded that Quantum- chemical semi-empirical calculations can be successfully used for the prediction of vibration modes and simulation of I.R. spectra for making more effective ligands and other organic compounds.

ACKNOWLEDGEMENTS

One of the Authors Kishor Arora (KA) sincerely acknowledges University Grants Commission, Central regional office UGC – CRO Bhopal for the financial support as MRP.

REFERENCES

[1] Chande MS, Thakkar NV and Patil DV. Acta Poloniae Drug Research 1999; 56(3): 207-10.
[2] Attby FA, Elneairy MAA and Elsayed MS. Arch Pharma Research 1999; 222(2): 194-201.
[3] Thakkar KM, Ghateya RM, Tala SD, Dobiya BL, Joshi KA, Dubal KL and Joshi HS. Indian J Chem 2011; 50B(5):738-44.
[4] Singh N, Sangwan NK, Dhindsa KS. Pesticide Science 2000; 56(3):284-88.
[5] Zhao PL, Wang F, Zhang MZ, Liu ZM, Huang W, Yang GF. J Agri Food Chemistry 2008; 56(22): 19767-73.
[6] Bondock S, Khalifa W, Fadda AA. Eur J Chem 2011; 46(6): 2555-61.
[7] U Deva Priya Kumar and G Narharisastry. Indian J Chem 2000; 39(A): 92.
[8] J Laxmi kanth and K Bhanu prakash. Indian J Chem 2000; 39(A): 114.
[9] K Arora and D Kumar. Asian J Chem 2001; 13(4): 1325.
[10] Kishor Arora, D Kumar, Kiran Burman, Sonal Agnihotri and Bhoop Singh. J Saudi Chem Soc 2011; 15:161-165.
[11] Kishor Arora, D Kumar, Kiran Burman, Sonal Agnihotri and Bhoop Singh. Oriental J Chem 2010; 26(4): 1361-1368.

[12] D Kumar, MC Agrawal, Radha Tomar, Kaman Singh, Kishor Arora, Rajeev Singh MK, Bhardwaj, Bhoop Singh, HS Barahdiya, RK Taiger and Anjana Gupta. ASIAN J CHEM 2007; 19(5): 3703.