

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Theoretical Investigations on the Structure, Geometry, Electron Densities and Thermodynamic Parameters of Terpyridine Molecule

HS Barhadiya^{1*} and D Kumar²

¹Post Graduate Department of Chemistry, Govt. P.G. College, Tikamgarh, India

²Centre of Research for Chemical Sciences, Post Graduate Department of Chemistry, SMS Govt. Model Science College, Gwalior, India.

ABSTRACT

The crystal structure of the terdentate ligand terpyridine (terpy) molecule was determined by single crystal x-ray diffraction methods. Experimental data of this compound is available however no theoretical study is reported which promoted us to study its theoretical parameters like molecular geometry, net atomic charge, electron density and general thermodynamic parameters using AM1, PM3, MNDO and MINDO/3 semi-empirical methods. For bond lengths, the correlation coefficient obtained for AM1, PM3, MNDO and MINDO/3 methods are 0.919, 0.919, 0.869 and 0.897 respectively. Out of the four semi-empirical methods AM1 and PM3 produces most satisfactory correlation (CC=0.919) between experimental and calculated bond length. In the case of bond angles, correlation coefficients are 0.754, 0.744, 0.839 and 0.739 for AM1, PM3, MNDO and MINDO/3 methods respectively. Thus MNDO method results most satisfactory correlation (CC=0.839) for bond angle. Electronic charge and atom electron density data reveal the potential coordination sites in terpyridine. Thus, performance of Semi-empirical AM1, PM3, MNDO and MINDO/3 methods has been tested to find the best auxiliary tool for geometry, electron density & thermodynamic parameters.

Keywords: Terpyridine molecule ($C_{15}H_{11}N_3$); Semi-empirical methods, AM1, PM3, MNDO and MINDO/3; Correlation Coefficient.

**Corresponding author*

INTRODUCTION

The Structure determination and x-ray study of terpyridine ($C_{15}H_{11}N_3$) molecule were conducted by Carol A. Bassel et al [1]. The terdentate meridieonally co-ordinating ligand terpyridine (terpy) was isolated by Morgan and Burstall [2]. The literature contains no computational study of this terdentate ligand, therefore, we report here the theoretical parameters of terpyridine by using different computational methods.

Though semi-empirical methods are approximate methods but these serve the purpose of calculation of wave function, energy and other properties like ionisation potential, heat of formation, molecular geometry, electron density distribution and interpretation of molecular spectra. In the present communication we report the quantum chemical calculations for terpy ligand using by AM1 [3], PM3 [4], MNDO [5] and MINDO/3 [6] methods. Geometrical parameters like bond length, bond angle, thermodynamic parameters like heat of formation, ionisation potential, electronic parameters like electronic charge and density, total energy, electronic energy and core-core repulsion have been calculated by semi-empirical AM1, PM3, MNDO and MINDO/3 methods. Correlation coefficients for bond length and bond angle have been reported [7-11].

COMPUTATIONAL DETAILS

Quantum chemical calculations were carried out by AM1, PM3, MNDO and MINDO/3 semi-empirical methods of MOPAC programs from Chemoffice 2004 package¹² and Hyperchem 7.5. The semi-empirical procedures, in general do not make use of symmetry in SCF cycles in economizing the CPU time. Therefore, all the geometries were fully optimized without any symmetry constraints using AM1, PM3, MNDO and MINDO/3 methods and stationary points were obtained on the potential energy surfaces. Bond length, bond angles, electron densities, net atomic charges, thermodynamic parameters were calculated with the help of standard parameters as implemented in the software. Intel based core i5-2450M HT3.2 machine having 800 FSB, 4GB RAM and 500 GB HDD was used to run all the programmes.

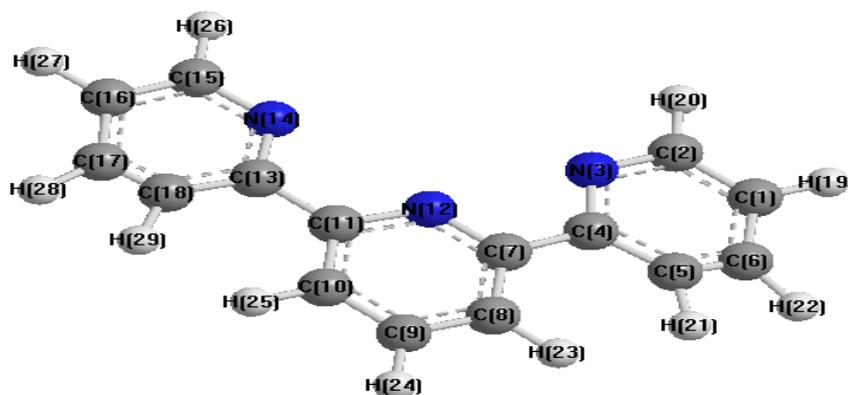


Fig 1: Terpyridine molecule showing atoms and their numbering

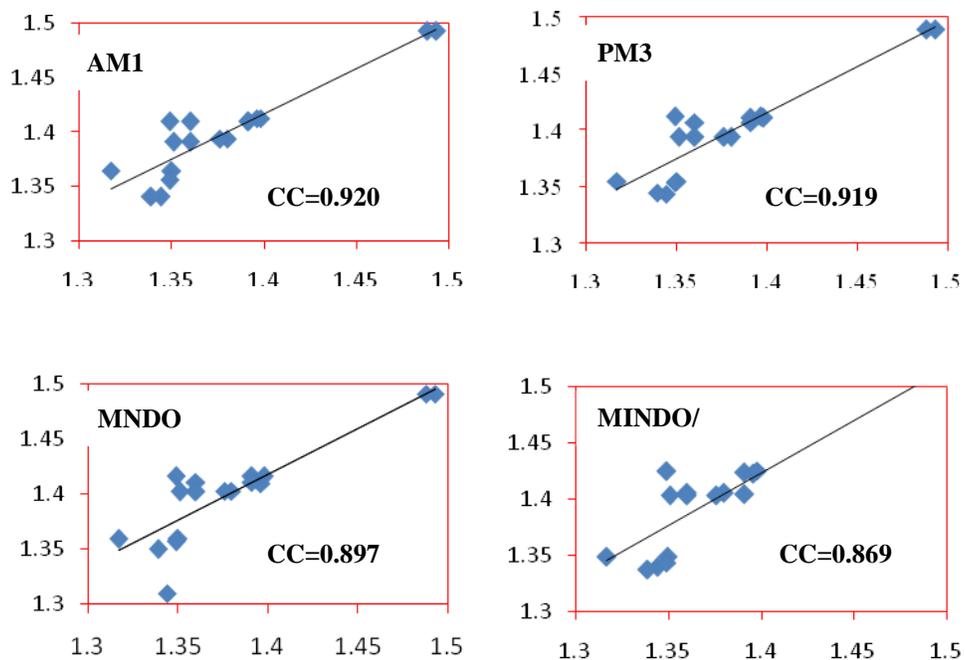
RESULTS AND DISCUSSION

Optimised Geometry

We examined the performance of semi-empirical AM1, PM3, MNDO and MINDO/3 methods in reproducing geometrical parameters. The calculated bond lengths are in good agreement with experimental values. The most suitable method was found by plotting the experimental versus calculated values and the obtained correlation coefficients were analysed. It is found that CC are not equal for different methods. The correlation coefficient for bond length obtained by AM1, PM3, MNDO and MINDO/3 methods are 0.920, 0.919, 0.869 and 0.897 respectively. It is evident that out of all the four methods AM1 method gives the maximum correlation for bond lengths (CC=0.920). In case of bond angles correlation coefficients are 0.790, 0.744, 0.839 and 0.739 for AM1, PM3, MNDO and MINDO/3 methods respectively. It is evident that MNDO methods gives satisfactory CC (CC=0.839). The calculated and experimental bond lengths and bond angles are given in tables 1 and 2, respectively and graph between experimental versus calculated bond length and bond angle are given in figures 2 and 3 respectively.

Table-1: Experimental and calculated bond lengths of Terpyridine molecule by AM1, PM3, MNDO and MINDO/3 Semi-empirical methods

Bond length	Experimental	AM1	PM3	MNDO	MINDO/3
C1-C2	1.360	1.410	1.407	1.411	1.405
C2-N3	1.344	1.341	1.344	1.310	1.339
N3-C4	1.350	1.364	1.355	1.359	1.348
C4-C5	1.391	1.410	1.411	1.416	1.423
C6-C1	1.360	1.391	1.394	1.402	1.403
C4-C7	1.493	1.493	1.489	1.491	1.503
N12-C7	1.349	1.356	1.354	1.357	1.343
C8-C9	1.380	1.394	1.394	1.403	1.405
C7-C8	1.396	1.413	1.412	1.410	1.422
C10-C9	1.376	1.394	1.394	1.403	1.403
C11-C10	1.398	1.413	1.411	1.416	1.425
N14-C13	1.317	1.365	1.355	1.359	1.348
N14-C15	1.339	1.341	1.345	1.350	1.337
C13-C11	1.488	1.493	1.489	1.491	1.502
C13-C18	1.349	1.410	1.412	1.416	1.424
C15-C16	1.391	1.410	1.407	1.411	1.404
C16-C17	1.351	1.391	1.394	1.402	1.403
CC	--	0.920	0.919	0.869	0.897



EXPERIMENTAL BOND LENGTHS

Fig. 2: Graphic correlation between the experimental and calculated bond lengths obtained by Semi-empirical methods AM1, PM3, MNDO & MINDO/3 for Terpyridine molecule

Table- 2: Experimental and calculated bond angles of Terpyridine molecule by AM1, PM3, MNDO and MINDO/3 Semi-empirical methods

Bond Angles	Experimental	AM1	PM3	MNDO	MINDO/3
N3-C2-C1	124.4	123.5	123.9	122.9	123.0
C4-N3-C2	115.4	118.5	117.0	118.6	119.9
N3-C4-C5	123.5	121.3	123.0	121.9	120.9
C6-C1-C2	119.8	117.9	118.2	118.5	118.2
C7-C4-N3	114.8	118.6	118.8	115.1	114.7
C9-C8-C7	120.0	118.7	118.5	118.7	118.8
C13-C11-C10	120.2	119.9	118.2	122.0	123.9
N12-C7-C4	116.7	118.2	118.4	115.0	115.9
N14-C13-C11	116.1	118.6	118.7	115.1	115.4
C13-N14-C15	118.4	118.6	117.0	118.6	119.7
N14-C16-C15	122.0	123.3	123.9	122.9	123.0
C11-C13-C18	120.5	120.0	118.2	122.8	123.9
CC	--	0.790	0.744	0.839	0.739

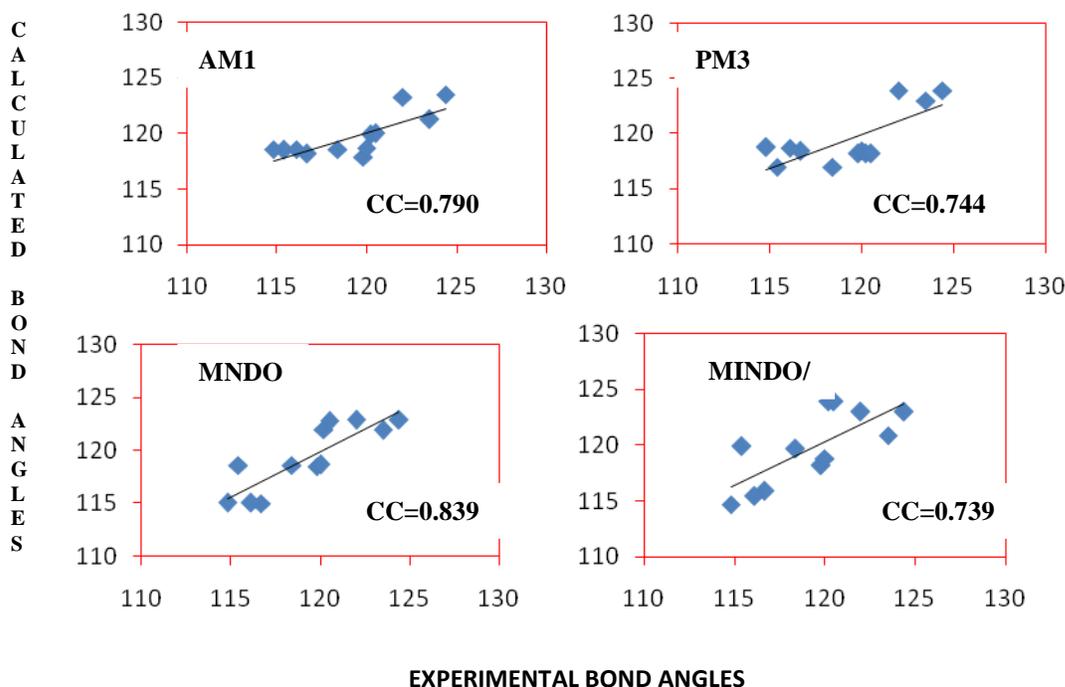


Fig. 3: Graphic correlation between the experimental and calculated bond angles obtained by semi-empirical methods AM1, PM3, MNDO, and MINDO/3 for Terpyridine molecule

ATOMIC CHARGE AND ELECTRON DENSITIES

Electron densities and net atomic charge on all atoms including nitrogen atoms of terpyridine molecule have been calculated by semi-empirical AM1, PM3, MNDO and MINDO/3 methods and are listed in table 3. The graphical presentation of electron densities on each atom is shown in figure 4. For stable complex formation it is of utmost importance to look for the bonding sites in ligand with which the metal ion will coordinate. In this regard the atom electron densities and net atomic charge become the vital parameters to assign the coordination sites of terpyridine molecule and stability of its complexes. The graphical representation (figure 4) of atom types and electron densities shows that N3, N12, and N14 may take part in coordination in complex formation as these atoms show maximum electron density. Electron densities and net atomic charge using by semi-empirical methods.

Table- 3: Net atomic charges (NAC) and Atom electron density (ED) calculated by semi-empirical Methods AM1, PM3, MNDO and MINDO/3 for Terpyridine molecule

Atom No.	AM1		PM3		MNDO		MINDO/3	
	NAC	ED	NAC	ED	NAC	ED	NAC	ED
C1	-0.1771	4.1771	-0.1450	4.1451	-0.1157	4.1157	-0.0621	4.0622
C2	-0.0710	4.0711	-0.0713	4.0714	0.0521	3.9479	0.1341	3.8658
N3	-0.1017	5.1017	-0.0230	5.0230	-0.2151	5.2152	-0.1738	5.1738
C4	0.0252	3.9747	-0.0099	4.0100	0.0813	3.9187	0.1347	3.8652
C5	-0.1670	4.1671	-0.1378	4.0379	-0.0861	4.0861	-0.0712	4.0713
C6	-0.0954	4.0955	-0.0699	4.0700	-0.0152	4.0861	0.0705	3.9294

C7	0.0275	3.9724	-0.0123	4.0123	0.0763	4.0153	0.1363	3.8637
C8	-0.1626	4.1627	-0.1324	4.1325	-0.0759	4.0759	-0.0655	4.0656
C9	-0.0967	4.0967	-0.0716	4.0717	-0.0228	4.0229	0.0696	3.9303
C10	-0.1617	4.1617	-0.1318	4.3190	-0.0753	4.0754	-0.0672	4.0673
C11	0.0276	3.9724	-0.0123	4.0123	0.0783	3.9216	0.1376	3.8623
N12	-0.0783	5.0783	0.0084	4.9916	-0.2060	5.2061	0.1935	5.1936
C13	0.0254	3.9746	-0.0096	4.0098	0.0811	3.9189	0.1330	3.8670
N14	-0.1031	5.1031	-0.0245	5.0246	-0.2157	5.2157	-0.1728	5.1728
C15	-0.0710	4.0710	-0.0711	4.0711	0.0520	3.9480	0.1337	3.8262
C16	-0.1771	4.1772	-0.0452	4.1453	-0.1155	4.0056	-0.0636	4.0636
C17	-0.0954	4.0954	-0.0700	4.0700	-0.0155	4.0155	0.0736	3.9264
C18	-0.1660	4.1660	-0.1366	4.1767	-0.0853	4.0853	-0.0670	4.0671

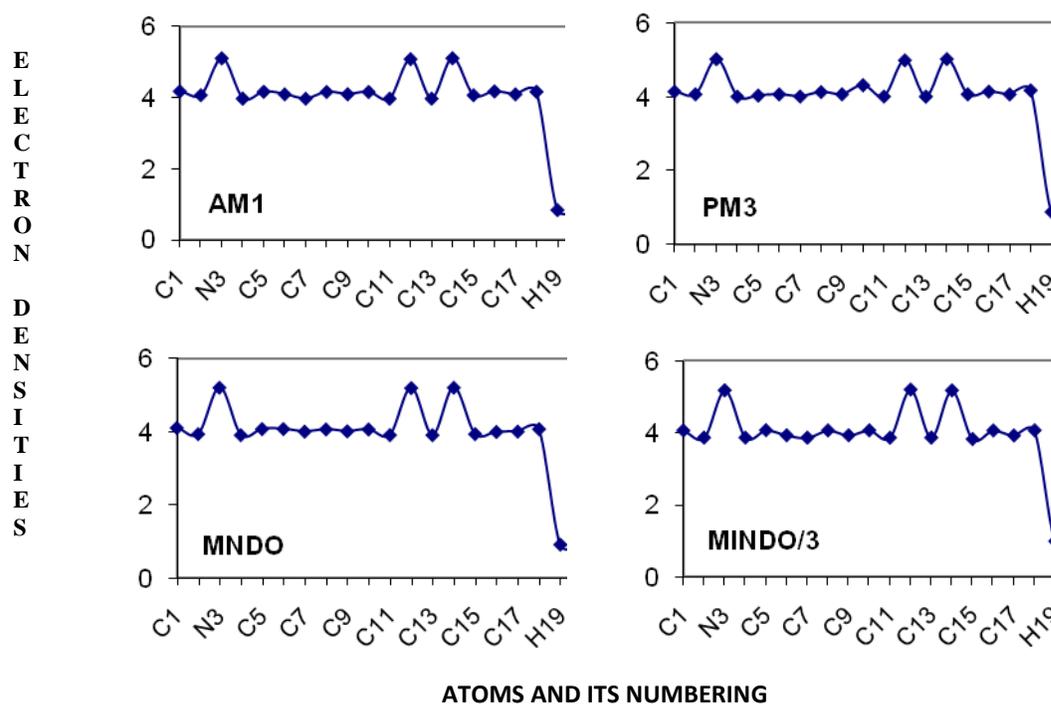


Fig. 4: Graphic presentation of calculated electron densities on all atoms obtained by AM1, PM3, MNDO and MINDO/3 semi-empirical methods

GENERAL THERMODYNAMIC PARAMETERS

The computed heat of formation, ionisation potential, total energy, electronic energy and core-core repulsion energy for terpyridine molecule (terpy) by semi-empirical methods AM1, PM3, MNDO and MINDO/3 are given in table 4. Heat of formation value for terpyridine molecule by all the four methods, AM1, PM3, MNDO and MINDO/3 shows its endothermic nature. PM3 gives highest ionisation potential value of 9.55624 and MINDO/3 gives lowest ionisation potential value of 8.17092. Core-core repulsion energy is given by total energy minus electronic energy. AM1 gives higher value of core-core repulsion while MINDO/3 gives lowest.

Table- 4: Computed heat of formation (kcal), ionisation potential, total energy, electronic energy, core- core repulsion energy predicted by AM1, PM3, MNDO & MINDO/3 semi-empirical methods

Parameters	AM1	PM3	MNDO	MINDO/3
Heat of formation (Kcal)	113.94	99.50	88.94	87.23
Ionisation Potential (eV)	9.48024	9.55624	9.33266	8.17092
Total energy (eV)	-2690.59	-2431.49	-2693.03	-2639.06
Electronic energy (eV)	-16297.67	-15843.20	-16299.83	-15914.41
Core-core repulsion (eV)	13607.08	13411.71	13606.80	13275.35

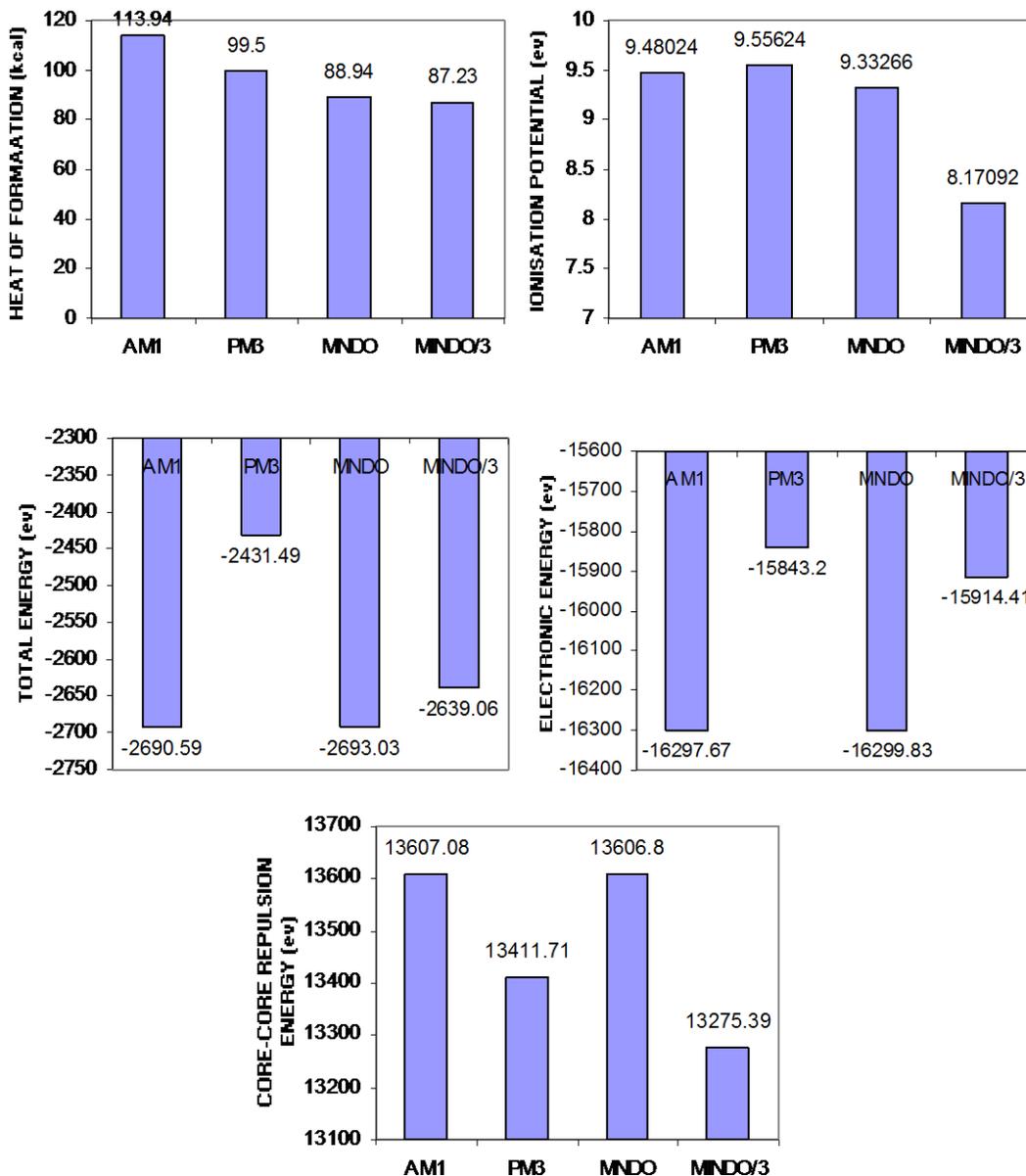


Fig. 5: Graphic presentation of heat of formation (kcal), ionisation potential, total energy, electronic energy, core-core repulsion energy obtained by AM1, PM3, MNDO and MINDO/3 semi-empirical methods



CONCLUSION

Semi-empirical methods AM1, PM3, MNDO and MNDO-d proved to be important auxiliary tools for geometry optimization, electronic structure and thermodynamic studies. The correlation coefficients for bond lengths for terpyridine molecule are 0.920, 0.919, 0.869 and 0.897 respectively for AM1, PM3, MNDO and MINDO/3 semi-empirical methods. AM1 method gives most satisfactory correlation (CC=0.920) and hence is most satisfactory methods. The correlation coefficients for bond angles are 0.790, 0.744, 0.839 and 0.739 for AM1, PM3, MNDO and MINDO/3 respectively and MNDO gives most satisfactory correlation (CC=0.839). In other methods, only few points are situated close to the trend line and many points are scattered away from trend line which shows bad graphical correlation. Atom electron densities and net atomic charge indicates the coordination sites during complex formation. Results from AM1, PM3 MNDO and MINDO/3 methods for electron density are supported by experimental data. Thus, semi-empirical quantum chemical calculations can successfully be used to predict the geometry, electronic structure and thermodynamic parameters.

REFERENCES

- [1] Carol A. Bassel and Takeuchi Kenneth. *J Chem Soc Dalton Trans* 1992; Issue 1.
- [2] GT Morgan and FH Burstall. *J Chem Soc* 1938; 1675.
- [3] MJS Dewar, EG Zoebisch, EF Healy and JJP Stewart. *J Am Chem Soc.* 1985; 107: 3902.
- [4] MJS Dewar and YC Yuan. *Inorg Chem* 1990; 29: 3881.
- [5] MJS Dewar, W Thiel. *J Am Chem Soc* 1977; 99: 4899.
- [6] RC Bingham, MJS Dewar and DH Lo. *J Am Chem Soc* 1975; 97: 1294.
- [7] D Kumar, Bhoop Singh and Hari Singh. *Asian J Chem* 2007; 19(5): 3703.
- [8] D Kumar and Hari Singh et al. *Orient J Chem* 2009; 25(1): 97.
- [9] D Kumar and Bhoop Singh. *J Saudi Chem Soc* 2011; 15: 165.
- [10] D Kumar et al. *Orient J Chem* 2010; 26(4): 1361.
- [11] Hari Singh Barhadiya and D Kumar. *J App Chem* 2012; 1(4): 575-582.
- [12] Hari Singh Barhadiya and D Kumar. *J App Chem* 2013; 2(1): 14-21.
- [13] Chemoffice (Trial version) Cambridge Soft Corporation 2004.
- [14] Hyperchem 7.5, (Trial version).