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Theoretical Semi-Empirical Studies of Electronic Structures of Schiff Bases of Cyanoethylatedbenzaldehyde

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Present communication reports theoretical semi-empirical AM1 studies of some Schiff bases of 2-methyl-4-NN-*bis*-2'- cyano ethylaminobenzaldehyde along with their comparison with their parent compounds. Theoretical studies reveal that it is azomethine group in the Schiff bases under study, that acts as site for coordination to metals as reported by many coordination and bioinorganic chemists.

Key Words: Semi-empirical studies, Electronic structure, Schiff base, Cyanoethylatedbenzaldehyde.

INTRODUCTION

In the recent years, it has been shown that *ab initio* quantum chemical methods which utilize the SCF-approach within the Hartree-Fock Roothan approximation are limited in their practical approach as they are restricted to small molecules[1,2]. The methods require calculations of a very large number of many centre integrals and hence needed high CPU time and large storage on the disk of computer memory.

In view of the above semi-empirical methods were introduced that retain characteristics of quantum-chemical approach in the calculation of wave function from which electronic and other properties can be obtained.

Though semi-empirical methods[3,4] are approximate methods they serve the purpose of calculation of heat of formation, molecular geometries, force constants, electron density distribution, dipole moments, population analysis and conformation analysis. Investigation of chemical reaction path-ways and transition states, interpretation of molecular spectra from them and non-linear optical properties etc. have also been studied by these methods.

Semi-empirical methods are based on the Hartree-Fock approach[5] whose matrix elements can be expressed as integral over atomic basis function as:

$$F_{uv} = \langle u \mid \hat{F} \mid v \rangle = \langle u \mid \hat{H} \mid v \rangle + \sum_{\lambda,\sigma} P_{\lambda,\sigma}\left[(uv \mid \lambda\sigma) - \frac{1}{2}(u\lambda \mid u\sigma)\right]$$

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where P is the density matrix

$$P_{\lambda\sigma} = 2\sum_{i} C_{i\lambda} C_{i\sigma}$$

In order to simplify the matters and to solve the equations in semi-empirical calculations, some approximations were made such as zero differential overlap (ZDO).

$$\phi_u(r) \quad \phi_v(r) = 0 \qquad \text{for } u \neq v$$

as

$$\delta uv = \langle u|v\rangle = \delta uv$$

where

$$\delta uv = 0 \quad : \quad u \neq v$$
$$\delta uv = 1 \quad : \quad u = v$$

This case is same as orthogonalization of atomic basis orbitals because of ZDO approximation many two electronic integrals vanish in the Hartree-Fock problem.

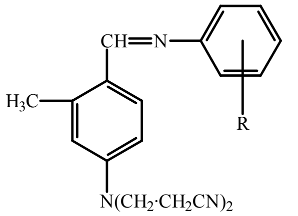
The most common and popular MNDO, MNDO/3, AM1 and PM3 methods. These methods are designed to get the heat of formation and structures of large number of organic molecules.

Practically it is experienced that for a particular problem one of these methods proved to be remarkably better than others.

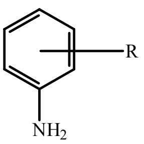
In general most recent methods AM1 and PM3 which are preferred by various workers[6-10], with small errors when PM3 is parameterized for systems with greater number of electrons[3]. No doubt the low-level *ab initio* calculations are usually better, but very much time consuming[11].

In this present communication we wish to report the quantum chemical AM1 calculations for Schiff-bases of 2-methyl-4-N,N-*bis*-2'-cyanoethylaminobenzaldehyde. The compounds chosen for the study are (MCEABAB) (**I**); (MCEABFAB) (**II**); (MCEABCAB) (**III**); (MCEABEAB) (**IV**); (MCEABPT) (**V**) and (MCEABMT) (**VI**).

Semi-empirical quantum chemical calculations for corresponding amines *viz*. aniline (**VII**); 4-fluoroaniline (**VIII**), 4-chloro aniline (**IX**); Ethyl-4-amino benzoate (**X**); *p*-toluidine (**XI**) and *m*-toluidine (**XII**) along with the aldehyde (**XIII**) were also done and compared with the above mentioned Schiff bases.



(I) R = H (MCEAB AB) (II) R = 4 - Flouro (MCEAB FAB) (III) R = 4 - Chloro (MCEAB CAB) (IV) R = *p*-($COOC_2H_2$) (MCEAB EAB) (V) R = *p*-CH_3(MCEAB PT) (VI) R = *m*-CH_3 (MCEAB MT)



(VII) R = H (Aniline) (VIII) R = 4-Flouro(4-Flouro aniline) (IX) R = 4 - Chloro (4-Chloro aniline) (X) R = *p*-($COOC_2H_5$) (Ethylaminobenzoate) (XI) R = *p*-CH_3 (*p*-Toluidine) (XII) R = *m*-CH_3 (*m*-Toluidine)

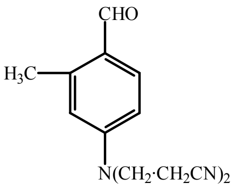


Fig. 1

Computational Details: The AM1 Hamiltonian in the MOPAC package was used to calculate the bond lengths, bond angles, heat of formation, core-core repulsion energies, ionization potentials *etc*. The structures of the molecules were drawn on the PCMODEL package of Serena software and then were optimized which is used as input for MOPAC[12-15]. These calculations were done for the compounds given in Fig. 1.

RESULTS AND DISCUSSION

The computed heat of formation, (H.F.) total energy (T.E.) electronic energy (E.E.), core-core repulsion energy, ionization potential (I.P.) and other computed results for compounds (**I-XIII**) on the basis of AM1 methods are given in Table-1. Variation of heat of formation for the compounds is shown in the Fig. 2.

TABLE-1
SEMI-EMPIRICAL AM1 COMPUTED PARAMETERS FOR COMPOUNDS (**I-XIII**) UNDER STUDY

Compd. No.	H.F. (kcal)	E.E. (eV)	T.E. (eV)	Corecore (eV)	I.P.	E.D.	N.A.C.	Dipole Moment
I	127.698	-26956.58	-3661.33	23295.25	8.92329	5.2622	-0.2622	0.668
II	82.448	-29162.26	-4132.74	25029.51	8.99121	5.2617	-0.2617	1.509
III	120.578	-29000.43	-4021.43	24978.99	8.99433	5.2597	-0.2597	1.395
IV	39.195	-36430.88	-4741.83	31689.05	8.99527	5.2627	-0.2627	2.118
V	120.045	-28830.07	-3817.20	25012.87	8.90757	5.2602	-0.2602	0.696
VI	141.91	-29063.89	-3817.18	25246.70	8.91796	5.2612	-0.2612	0.540
VII	20.493	-4358.84	-1071.36	3287.47	8.52290	-	-	1.542
VIII	-24.611	-5760.51	-1542.77	4217.74	8.54981	-	-	2.800
IX	50.309	-5540.21	-1431.48	4108.72	8.57723	-	-	2.624
X	-62.586	-10786.90	-2151.63	8635.27	8.98879	-	-	5.610
XI	12.960	-5460.35	-1227.23	4223.12	8.35807	-	-	1.446
XII	13.000	-5473.34	-1227.22	4246.11	8.47534	-	-	1.523
XIII	45.315	-18200.34	-2938.64	15261.69	9.05984	5.2634	-0.2634	1.493

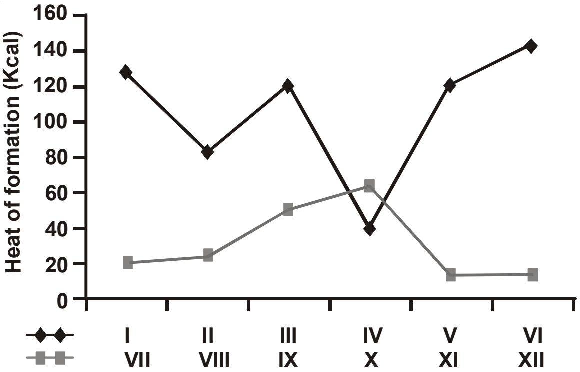


Fig. 2. Variation of heat of formation (Kcal) of compounds **I-XII**

Heat of formation values for schiff base compounds **I-VI** are higher than parent amines **VII-XII** and aldehyde **XIII** which indicates the stability of Schiff bases (**I-VI**).

For any ligand to be used to form a stable complex, the prime requirement is to locate the binding site with which metal ion can react to locate the coordination site of the ligand net atomic charge (NAC) and atomic electron density (ED) on the atoms of the ligand prove to be important parameters on which the formation and stability of the complex depends.

The net atomic charge (NAC) on the azomethine nitrogen and electron density on the azomethine nitrogen in case of schiff bases are appreciably higher as compared to others (Table-1).

Appreciable negative values for atomic charges NAC of the schiff bases also reveal azomethine nitrogen would be the coordination site in case of Schiff bases. Same conclusion one can draw if have a look of electron density values on azomethine nitrogen. This observation is similar to the observation made by previous workers[16-18].

The dipole moment also plays a key role in establishing the active site of the ligand for complex formation and hence these values are also given in Table-1 for Schiff bases along with the other parent compounds under study. The variation of dipole moment for the compounds (**I-XIII**) (Fig. 3), shows that this parameters also has appreciable value for Schiff bases which also support the fact that these Schiff bases prove to be effective ligands for the purpose of complex formation.

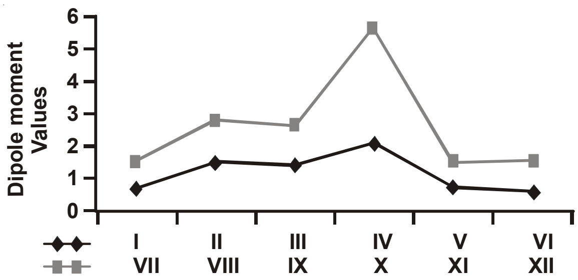


Fig. 3. Variation of dipole moment of the compounds **I-XII**

Conclusion

The quantum chemical semi-empirical calculations can be successfully used for the predictions of making more active ligands and hence for the formation of stable complexes which may be the work of interest of coordination and bioinorganic chemists, as it is discussed here for Schiff base ligands. The method adopted here for calculations (AM1) is proved to be good to give the optimized geometry and minimized energy for the compounds under study.

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