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Semi-Empirical AM1 and PM3 Calculations for Electronic Structure of Schiff Base[‡]

KISHOR ARORA*, AARTI GUPTA and D.D. AGARWAL[†]
Department of Chemistry, Government Autonomous K.R.G. College, Gwalior, India.
Email: kishorarora@rediffmail.com

Schiff bases are widely in use for synthetic purposes both by organic and inorganic chemists. These are stable compounds which are in use for synthesis of many complexes as ligands such as in the synthesis of complexes of transition metals, lanthanides and actinide metal ions. Experimental data for such compounds are reported by various workers, which prompted us to study the electronic structure of some Schiff basdses using semi-empirical AMI and PM3 quantum chemical calculations. The theoretical studies were done on the Schiff bases of 2-amino pyridine and this study reveals that it is the azomethine group of these Schiff bases which act as a site for coordination to metal as it is reported by the coordination chemists.

Key Words: Schiff Base, Electronic structure, Quantum chemical calculations.

INTRODUCTION

In recent years it has been shown that *ab initio* quntum chemical methods which utilize the SCF approach within the Hartree-Fock-Roothan approximation are limited in their practical approach as they are restricted to very small molecules[1, 2] and they require calculation of a very large number of many-centre integrals and hence require high CPU time and large storage space on the disk in the computer memory. Therefore 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 methoda[3, 4] are approximate methods but these methods serve the purpose of calculation of wave function and energy and to get other properties like ionization potentials, heats of formation, molecular geometries, force constant, electron density distribution, dipole moments, population analysis, conformation analysis, investigation of chemical reaction path and transition states, interpretation of molecular spectra from them and nonlinear optical properties etc.

[†] School of Studies in Chemistry, Jiwaji University, Gwalior, India

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

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

Where

P is the density matrix, $P_{\lambda\sigma} = 2\,2\sum_{i} C_{i\lambda}C_{i\sigma}$

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

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

as $\quad Suv = \langle u\,|\,v\rangle = \delta uv$

where $\quad \delta uv = 0; \quad u \neq v$

$\delta uv = 1; \quad u = v$

This case is same as orthogon-alization of atomic basis orbitals, as because of ZDO approximation many two-electronic integrals vanish in the HF problem.

Another common feature of semi-empirical methods is that they only consider valence electrons.

The most common and popular semi-empirical methods used today are MNDO, MNDO/3, AMI & 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, the most recent methods are AM1 and PM3 which are preferred by various workers[6–10] with small errors when PM3 is parametrized 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].

So, AMI methods are used to get reasonably good results[12]. In this present communication we wish to report the quantum chemical AM1 and PM3 calculations for a Schiff base of 2-amino pyridine. The compounds chosen for study are BAPY(I), PBAPY(II) and SALAPY(III) whose structure are given in Fig. 1.

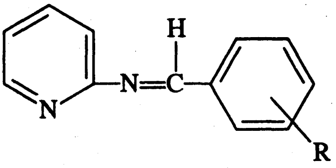

Fig. 1
I R = H (BAPY)
II R = p-N(CH_3)$_2$ (PBAPY)
III R = o-OH (SALAPY)

Computational details

The AMI Hamiltonian[15] in the MOPAC package[16] was used to calculate the bond lengths, bond angles, heat of formation, core-core repulsion energies, ionization potential, etc. Structures of molecules were drawn on the PCMODEL package of Serena software[17] and then were optimized which is used as input for MOPAC[16]. These calculations were done for the compound given in Fig. 1.

RESULTS AND DISCUSSION

The computed heat of formation, total energy, electronic energy, core-core repulsion energy, ionization potential and other computed results on the basis of AM1 and PM3 methods are given in Table-1.

TABLE-1
AM1 AND PM3 COMPUTED HEAT OF FORMATION (kcal/mol), TOTAL ENERGY, ELECTRONIC ENERGIES, CORE-CORE REPULSION ENERGIES AND I.P.'s FOR FOR SCHIFF BASE LIGANDS

Parameters	BAPY AM1	BAPY PM3	PBAPY AM1	PBAPY PM3	SALAPY AM1	SALAPY PM3
Heat of formation (kcal/mol)	86.1560	94.2237	94.7779	72.0271	42.6498	36.5359
Total energy (eV)	–2086.15	–1898.71	–2617.81	–2375.37	–2406.71	–2192.58
Electronic Energy (eV)	–11531.79	–11152.53	–16290.72	–15880.99	–13348.39	–13049.81
Core-Core Repulsion (eV)	9445.646	9253.825	13672.908	13504.993	10941.669	10857.233
I.P.	9.22073	9.21710	8.51662	8.55851	9.09934	9.117317
No. of Filled Levels	34	34	43	43	37	37

Heat of formation value for the schiff bases by both the methods, *viz.*, AM1 and PM3 shows that it is endothermic (Table-1) and all other computed parameters such as total energy, electronic energy, core-core repulsion and I.P. etc. are also given in Table-1.

For any ligand, to be used for stable complex formation, the most common requirement is to locate the bonding site, with which the metal ion will react. In this regard, the net atomic charge and the atomic electron density become useful parameters to look for the coordination site of a ligand and the stability of the complex.

The net atomic charge at azomethine nitrogen and the electron density is also given in Table-2. It is clear from the computed electron density on the azomethine nitrogen that this nitrogen would be the coordination site to the metal ions, as this value is higher as compared to all other atoms present in the Schiff bases under study. The electron density values on nitrogen atoms (azomethine) are in the range 5.03 to 5.17.

Same observation one can draw if have a look on the net atomic charge on the azomethine nitrogen atom; it is highly negative value (Table-2) as compared to other atoms of these Schiff bases. The net atomic charges are in the range –0.0366 to –0.1649 for N-atoms (azomethine).

Both of these facts support that in these Schiff bases, there is high electron density on the azomethine nitrogen and it possesses a high negative net atomic charge. So, it can coordinate to the metal atom through the azomethine nitrogen atom.

This observation is further supported by the experimental data[18,19] that suggest a considerable negative shift in the stretching vibrational frequency of the (—C=N—), the azomethine group on complex formation from 1660–1590 cm^{-1} in the case of ligand to 1630–1540 cm^{-1} in the complexes. This shift to the lower frequency is suggestive of coordination of (—C=N—) to the thorium(IV) metal atoms *via* azomethine nitrogen atom[18,19].

TABLE-2

AM1 AND PM3 COMPUTED NET ATOMIC CHARGES, ELECTRON DENSITY VALUES AND DIPOLE MOMENT ON THE (—C=N—) NITROGEN ATOMS (AZOMETHINE) FOR DIFFERENT SCHIFF BASE LIGANDS.

	Net atomic Charge on Nitrogen (—C=N—) Atom	Net atomic Charge on Nitrogen (—C=N—) Atom	Electron Density on Nitrogen (—C=N—) Atom	Electron Density on Nitrogen (—C=N—) Atom	Dipole Moment (Debye)
	AM1	**PM3**	**AM1**	**PM3**	
BAPY	–0.1558	–0.0907	5.1558	5.0907	4.186
PBAPY	–0.1649	–0.0983	5.1649	5.0983	4.479
SALAPY	–0.1706	–0.1002	5.1706	5.1002	4.974

It is clear from the above discussion and the values obtained for various parameters for this compound that this can be used as an effective (—C=N—) azomethine ligand towards the metals for forming stable metal complexes. On substitution of different groups of different electronic effects on the phenyl ring, there is some change in the net atomic charge and elecron density on the nitrogen atom of the (—C=N—) azomethine group. These are AM1 computed values and these values are a little bit higher in the case of electron donating hydroxyl group when it is *ortho* substituted on the phenyl ring and in case of *para* substituted dimethyl amino group. So, it can be concluded that SALAPY with *ortho* substituted hydroxyl group on the phenyl ring and PBAPY *para* substituted dimethyl amino group can also be used for the purpose of complex formation, they would prove to be effective ligands.

The dipole moment plays an important role in the establishment of the active site for coordination in the ligands, and hence these values are also given in Table-2, further support the fact that on substitution of hydroxyl, particularly, ligand can be made more effective for the purpose of complexation.

Conclusion

The quantum chemical calculations can be successfully used to predict the stability of the complex and making more active ligands, used for complex formation which may be a work of interest for coordination and bioinorganic chemists, as it is discussed here for a Schiff bases.

However, 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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