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Semi-Empirical AM1 and PM3 Calculations for Electronic Structure of Some Simple Carbonyl Compounds

KISHOR ARORA
Department of Chemistry, Government (Autonomous) K.R.G. College, Gwalior, India
Email: kishorarora@rediffmail.com

Carbonyl ligands are in wide use for synthetic purposes in both organic synthesis and in coordination chemistry. These are reported as stable compounds which are in use as a ligand for synthesis of various complexes. Experimental data for some of these carbonyl molecules are available, so it prompted us to study the electronic structure of the compounds using semi-empirical AM1 and PM3 quantum chemical calculations. The theoretical studies were done for these carbonyl ligands to locate and confirm the site for coordination of the compounds to metal on the basis of electronic structure of these carbonyl ligands.

Key Words: Semi-empirical, AM1, PM3, Electronic structure, Carbonyl compounds.

INTRODUCTION

The semi-empirical methods that were introduced 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[1, 2] 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.

These methods are based on the Hartree Fock approach[3] whose matrix elements can be expressed as integral over atomic basis function as:

$$F_{uv} = \langle u | Fv \rangle = \langle u | \hat{H} | v \rangle + \sum_{\lambda\sigma} P_{\lambda,\sigma}[(uv/\lambda\sigma) - ½(u\lambda | u\sigma)]$$

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 the case of semi-empirical calculations, some approximations were made such as ZDO (Zero Differential Overlapp) approximation, *i.e.*,

$$\Phi_u(r)\ \Phi_v(r) = 0 \qquad \text{for } u \neq v$$

as

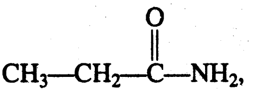
$$S_{uv} = \langle u | v \rangle = \delta_{uv}$$

where $\delta_{uv} = 0$ for $u \neq v$ and $\delta_{uv} = 1$ for $u = v$.

This case is same as orthogonalization 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.

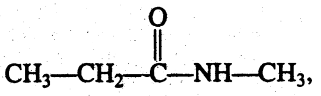
The most common and popular semi-empirical methods used today are MNDO, MNDO/3, AM1 and PM3 methods. These methods are designed to get the heat and formation and structures of large number of organic molecules. Practically it is experienced that for a particular problem one of these methods proved to be remarkably better than others. In general the most recent methods are AM1 and PM3 which are preferred by various workers[4-8] with small errors when PM3 is parametrized for systems with greater no. of electrons[1] no doubt that low-level *ab-initio* calculations are usually better, but very much time-consuming[9].

So AM1 methods are used to get reasonably good results[10-12]. In this present communication I wish to report the quantum chemical AM1 and PM3 calculations for simple carbonyl ligands that are in use for organic and co-ordination complex synthesis. The compounds chosen for study are given in Fig. 1.



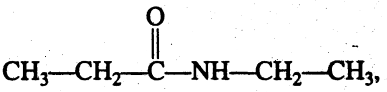
$CH_3{-}CH_2{-}\overset{\overset{O}{\|}}{C}{-}NH_2$,

(I)



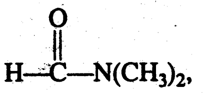
$CH_3{-}CH_2{-}\overset{\overset{O}{\|}}{C}{-}NH{-}CH_3$,

(II)



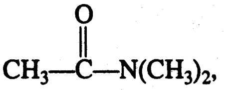
$CH_3{-}CH_2{-}\overset{\overset{O}{\|}}{C}{-}NH{-}CH_2{-}CH_3$,

(III)



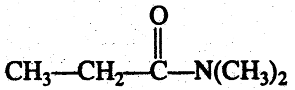
$H{-}\overset{\overset{O}{\|}}{C}{-}N(CH_3)_2$,

(IV)



$CH_3{-}\overset{\overset{O}{\|}}{C}{-}N(CH_3)_2$,

(V)



$CH_3{-}CH_2{-}\overset{\overset{O}{\|}}{C}{-}N(CH_3)_2$

(IV)

Fig. 1. Structures of the organic molecules under study

Computational details

The AM1 Hamiltonian[13] in the MOPAC package[14] 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[15] and then were optimized which is used as input for MOPAC[14]. 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 methdos 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 SIMPLE CARBONYL LIGANDS

Parameter	I		II		III		IV		V		VI	
	AM1	PM3	AM1	PM3	AM1	AM3	AM1	PM3	AM1	PM3	AM1	PM3
Heat of formation (kCal)	–4.66397	–4.98983	–5.39864	–9.81197	–11.21865	–14.46302	–36.8729	–44.6115	–41.3643	–51.9203	–12.7435	–14.9790
Total energy (eV)	–1467.372	–1379.257	–1623.164	–1528.771	–1778.954	–1678.278	–1007.857	–919.622	–1163.589	–1069.244	–1316.781	–1216.949
Electronic energy (eV)	–6552.441	–6413.962	–7819.317	–7671.980	–9170.707	–9007.216	–3394.029	–3270.975	–4485.922	–4343.175	–5537.130	–5380.920
Core-core repulsion energy (eV)	–5085.068	–5034.705	–6196.528	–6143.188	–7391.752	–7328.937	–2386.171	2351.352	3322.332	3273.930	4220.349	4163.970
Ionization potentials (eV)	–8.70765	–8.71751	–8.69584	–8.70707	–8.68177	–8.69895	–9.67002	9.55939	9.54165	9.50143	8.85983	7.81263
HOMO-LUMO (eV)	0.254–(–5.397)	0.133–(–5.465)	0.268–(–5.386)	0.145–(–5.456)	0.279–(–5.373)	0.144—5.444	1.486–(–9.670)	1.038–(–9.554)	1.435–(–9542)	0.994–(–9.501)	0.026–(–8.860)	0.807–(–0.439)

Heat of formation value for these carbonyl compounds 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 reuplsion and I.P. etc. are given in Table-1. The variation of heat of formation for these molecules is shown in Fig. 2.

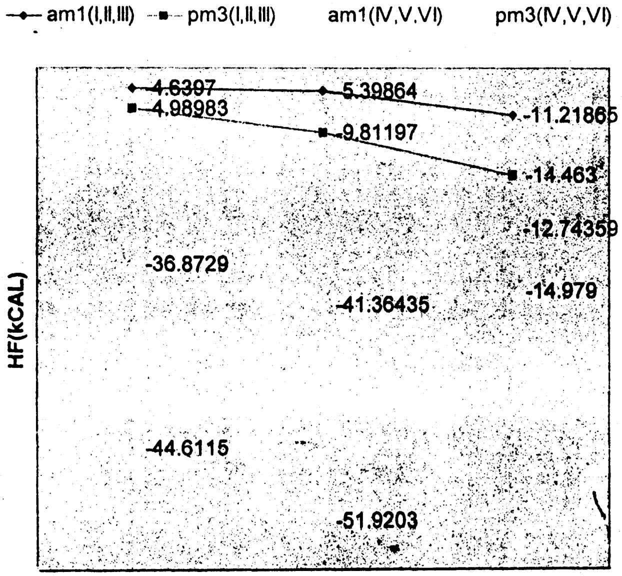


Fig. 2. Variation of heat of formation

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 carbonyl oxygen and the electron density are also given in Table-2. It is clear from the computed electron density on the carbonyl oxygen 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 these carbonyl compounds under study. The electron density values for these carbonyl compounds are in the range 6.2514 to 6.3696 (for carbonyl oxygens).

Same observation one can draw if he has a look on the net atomic charge on the carbonyl oxygen atom; it is highly negative in value (Table-2) as compared to other atoms of these Schiff bases.

Both of these facts support that in these carbonyl compounds the high elecron density is there on the carbonyl oxygen atom and it possess a high negative net atomic charge. So, these can coordinate to the metal atom through the carbonyl oxygen atom.

The observation is further supported by the experimental data[16] that suggest a considerable negative shift in the stretching vibrational frequency of the

(C=O), the carbonyl group on complex formation. This shift to the lower frequency is suggestive of co-ordination of (C=O) to the thorium(IV) metal atoms *via* carbonyl oxygen atom[16].

TABLE-2
AM1 AND PM3 COMPUTED NET ATOMIC CHARGES, ELECTRON DENSITY VALUES ON THE (C=O) OXYGEN ATOMS (CARBONYL) FOR DIFFERENT CARBONYL LIGAND MOLECULES

	Net atomic charge on oxygen (C=O) atom (AM1)	Net atomic charge on oxygen (C=O) atom (PM3)	Electron density on oxygen (C=O) atom (AM1)	Electron density on oxygen (C=O) atom (PM3)
I.	–0.2869	–0.3092	6.2869	6.3092
II.	–0.2873	–0.3094	6.2873	6.3094
III.	–0.2877	–0.3096	6.2877	6.3096
IV.	–0.3643	–0.3616	6.3643	6.3616
V.	–0.3696	–0.3625	6.3696	6.3625
VI.	–0.2941	–0.2514	6.2941	6.2514

It is clear from the above discussion and the values obtained for various parameters for these compounds that these can be used as effective (C=O) carbonyl ligand towards the metals for forming stable metal complexes.

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 discused here for a schiff base. However, the method adopted here for calculations (AM1) has proved to be good to give the optimized geometry and minimized energy for the compounds under study.

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