Asian Journal of Chemistry Vol. 13, No. 4 (2001), 1325–1329

Semi-Empirical AM1 and PM3 Calculations for Electronic Structure of a Pyrazolone

KISHOR ARORA* and D. KUMAR†
Department of Chemistry, Government KR.G. (Autonomous) College, Gwalior, India
E-mail: kishorarora@usa.net

Pyrazolones and substituted pyrazolones are widely in use for the synthetic purposes. These are stable compounds, which are in use for synthesis of many complexes like complexes of transition metals, thorium(IV) and dioxouranium(VI) metals. Experimental data for this compound is available, so it prompted us to study the electronic structure of this compound using semi-empirical AM1 and PM3 quantum chemical calculations. The theoretical study reveals that it is the carbonyl group of the pyrazolone under study which act as a site for coordination to metal as it is reported by the experimental chemist.

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 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 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 methods[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 non-linear optical properties, etc. These methods are also used as the basis of quantitative structure-property (or activity) relationships to predict a wide variety of biological and other propoerties including carcinogenicity, vapour pressure, water solubility and reaction rates etc.

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

---

†Department of Chemistry, Govt. Science (Autonomous) College, Gwalior, India.

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

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 Zero Differential Overlap (ZDO) approximation, *i.e.*,

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

as

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

where $\delta_{uv} = 0$; $u \neq v$

$\delta_{uv} = 1$; $u = v$

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 valance 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 of formation and structure 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[6–8] with samll errors when PM3 is parameterized for systems with large number of electrons[3] no doubt that low-level *ab-initio* calculations are usually better, but time consuming[9].

Thus, AM1 methods are used to get reasonably good results[10–12]. In this present communication we report the quantum chemical AM1 and PM3 calculations for a pyrazolone. The compound chosen for study is 3-methyl-1-phenyl-5-pyrazolone (MPP) whose structure is given below:

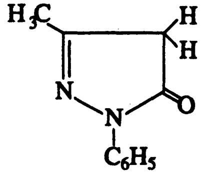

Fig. 1 3-Methyl-1-phenyl-5-pyrazolone (MPP)

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 the figure.

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.

For any ligand, to be used for stable complex formation, it is the most common requirement to look for 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 co-ordiantion site of a ligand and the stability of the complex.

TABLE-1
AM1 AND PM3 COMPUTED HEATS OF FORMATION (kcal/mol), TOTAL ENERGY, ELECTRONIC ENERGIES, CORE-CORE REPULSION ENERGIES, AND I.P.'s FOR MPP AND NET ATOMIC CHARGE AND ELECTRON DENSITY ON THE CARBONYL OXYGEN ATOM OF MPP

Parameters	AM1 calculated values	PM3 calculated values
Heat of formation (kcal/mol)	45.08464	20.03987
Total energy (eV)	–2150.17225	–1955.31250
Eectronic energy (eV)	–11303.97038	–10985.06074
Core-core repulsion (eV)	9158.79812	9029.24824
I.P.	8.68971	8.95353
No. of filled levels	33	33
Electron density on (C═O) oxygen	6.2986	6.3099
Net atomic charge on (C═O) oxygen	–0.2986	–0.3099
Dipole moment (μ) (Debye)	2.58	3.86

The net atomic charge at carbonyl oxygen and the electron density is also given in Table-1. It is clear from the computed electron density on the carbonyl oxygen that this oxygen would be the co-ordiantion site to the metal ions, as this value is higher as compared to all other atoms present in pyrazolone. The electron density values on all other atoms are in the range 4.09 to 4.14 on the C-atoms and 4.95 to 5.09 on the N-atoms.

Same observation can be drawn through net atomic charge on this carbonyl oxygen; it is highly negative in value (Table-1) as compared to other atoms of pyrazolone. The net atomic charges are in the range –0.0415 to –0.134 for C-atoms and –0.905 to 0.487 for N-atoms.

Both of these facts support that in this pyrazolone the high electron density is there on the carbonyl oxygen and it posseses a high negative net atomic charge. So, it can co-ordinate to the metal atom through the carbonyl oxygen atom.

This observation is further supported by the experimetal data[16, 17] that suggest a considerable negative shift in the stretching vibrational frequency of (C═O), the carbonyl group on complex formation from 1625 cm^{-1} in the case of ligand to 1600–1590 cm^{-1} in the complexes. This shift to the lower frequency is suggestive of co-ordination of (C=O) to the thorium(IV) and uranyl(VI) metal atoms *via* oxygen[16, 17].

Heat of formation value for the pyrazolone by both the methods, *viz.*, AM1 and PM3 shows that it is endothermic (Table-1)*, but the more reliable results are obtained with AM1 method. So, it can be said that Austin model-1 (AM1) method is good for the purpose of quantum chemical calculations.

It is clear from the above discussion and the values obtained for various parameters for this compound that MPP can be used as effective (C=O) 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 electron density on the oxygen atom of the (C=O) group as shown in Table-2.† These are AM1 computed values and these values are a little bit higher in the case of electron donating hydroxyl group when it is *para*-substituted on the phenyl ring. So, it can be concluded that if MPP with substituted hydroxyl group on the phenyl ring is used for the purpose of complex formation, it would prove to be an effective ligand.

TABLE-2
AM1 COMPUTED NET ATOMIC CHARGES AND ELECTRON DENSITY VALUES ON THE (C=O) OXYGEN ATOM OF SUBSTITUTED PYRAZOLONE, *i.e.*, MPP

Substitution on the phenyl ring of the MPP pyrazolone	Net atomic charge on the (C=O) oxygen atom	Dipole moment (Debye)
o-Chloro	–0.2966	0.019
m-Chloro	–0.2956	1.245
p-Chloro	–0.2960	2.230
o-Hydroxyl	–0.2456	1.782
m-Hydroxyl	–0.2518	2.102
p-Hydroxyl	–0.3017	2.475

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 co-ordination and bioinorganic chemists, as it is discussed here for a pyrazolone.

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

---

†The dipole moment plays a key role in establishing the active sites on the ligands, for the complex formation. Hence, on substituting —OH gp at the phenyl ring of the compound, increases the electronic charge on the carbonyl oxygen. It further supports the fact the ligand can be made more active for complexation. The dipole moment values calculated by AM1 method are given in Table-2.

REFERENCES

1. W.G. Richards, T.E.H. Walker and R.K. Hinkley, A. Biblography of Ab-initio Molecular Wave Functions, Clarendon Press, Oxford (1971).
2. L. Random and J.A. Pople, in: W. Byers-Brown (Ed.), MTP International Reviews of Science, Physical Chemistry, 1, Series-1, Butterworths, London, p. 71 (1972).
3. Spartan User's Guide, Version 3.0, Wave Function, Inc. (1993).
4. J.J.P. Stewart, in: K.B. Lipkowitz and D.B. Boyd (Eds.), Reviews in Computational Chemistry, V.C.H., Vol. 1, p. 45 (1990).
5. I.L. Lavine, Quantum Chemistry, 4th Edn. (1991).
6. Animesh Pramanik, *J. Indian Chem. Soc.*, **77,** 402 (2000).
7. U. Deva Priyakumar and G. Naraharisastry, *Indian. J. Chem.*, **39A,** 92 (2000).
8. J. Laxmikanth and K. Bhanuprakash, *Indian J. Chem.*, **39A,** 114 (2000).
9. W.J. Hehre, L. Random, P. Von, R. Schleyer and J.A. Pople, Ab-initio Molecular Orbital Theory, Wiley (1986).
10. Palas Gangopadhyaya, M. Ravi and T.P. Radhakrishanan, *Indian J. Chem.*, **39A,** 106 (2000).
11. S.N. Datta and Abhishek Jha, *Indian J. Chem.*, **39A,** 120 (2000).
12. P.V. Bhartam, *Indian J. Chem.*, **39A,** 100 (2000).
13. M.J.S. Dewer, E.G. Zoebisch, E.F. Healy and J.J.P. Stewart, *J. Am. Chem. Soc.*, **107,** 3902 (1985).
14. MOPAC 93 @ Fujitsu Inc.
15. N.L. Allinger, *J. Am. Chem. Soc.*, **113,** 1907 (1977).
16. R.K. Agarwal and K. Arora, *Polish J. Chem.*, **67,** 25 (1993).
17. R.K. Agarwal and K. Arora, *Synth. React. Inorg. Met-Org. Chem.*, **23,** 653 (1993).

(*Received:* 20 March 2001; *Accepted:* 9 June 2001) AJC-2376