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COMPUTATIONAL STUDY OF BENZALDEHYDE THIOSEMICARBAZONE

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ABSTRACT

Benzaldehyde thiosemicarbazone, $C_8H_9N_3S$ crystals are rectangular plate-like ortho-rhombic structure. The compound undergoes complexation with transition metal ions. Experimental X-ray data of this compound is available which promoted us to study its theoretical parameters like bond length, bond angle, electron density, and general thermodynamic parameters using AM1, PM3, MNDO semi-empirical and 3-21G, 6-31G, and STO-3G ab-initio methods. For bond lengths, the correlation coefficient obtained for AM1, PM3, MNDO methods are 0.921**,** 0.929, 0.945 and for 3-21G, 6-31G, STO-3G methods are 0.984, 0.983, 0.906 respectively. Out of the three semi-empirical methods MNDO produces most satisfactory correlation (CC=0.945) between experimental and calculated bond length. In the case of bond angles, correlation coefficients are 0.423, 0.363, 0.551 for AM1, PM3, MNDO methods and for 3-21G, 6-31G, STO-3G methods the correlation coefficients are 0.547, 0.418 and 0.612 respectively. Thus for bond angles MNDO and STO-3G methods give most satisfactory correlation (CC=0.551, 0.612). Electronic charge and atom electron density data reveal the coordination sites of benzaldehyde thiosemicarbazone when it undergoes complexation with transition metal ions. Out of three nitrogen atoms N (9) thioamide nitrogen carried more electron density. Thus, performance of semi-empirical AM1, PM3, MNDO and 3-21G, 6-31G, STO-3G ab-initio methods has been tested to find the best auxiliary tool for geometry & electron densities.

Key words: Benzaldehyde thiosemicarbazone, Semi-empirical methods, AM1, PM3, MNDO, ab-initio, 3-21G, 6-31G, STO-3G basis-set and correlation coefficient.

INTRODUCTION

Thiosemicarbazones have attracted special attention on account of their biological activities. However, benzaldehyde thiosemicarbazone (BZTSC) is devoid of any biological activity and can function only as a bidentate ligand.[1] The structural determination & X-ray study of this compound were conducted by Bhatia *et al.*[2] The literature contains no computational study of this bidentate ligand ,therefore, we report here the theoretical parameters of benzaldehyde thiosemicarbazones (BZTSC) by using different computational methods.

The four main approaches for calculating molecular properties are ab-initio, semi-empirical,

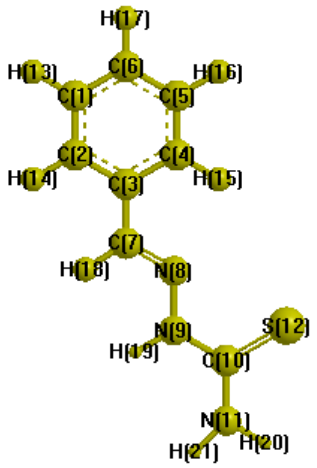

Fig. - 1: Benzaldehyde thiosemicarbazone ligand showing atoms and their numbering.

density functional and molecular–mechanics methods. These quantum chemical methods can provide informations regarding bond lengths, bond angles, electron density, dipole moment, vibrational frequencies etc.

Semi-empirical molecular quantum-mechanical methods use a simpler Hamiltonian than the correct molecular Hamiltonian and use parameters whose values are adjusted to fit experimental data or use the results of abinitio calculations. In contrast, an ab-initio (or first principles) calculation uses the correct Hamiltonian and does not use experimental data other than the values of the fundamental physical constants.

The most common type of ab-initio calculation is called a Hartree-Fock SCF calculation which seeks the antisymmetrized product Φ of one-electron functions that minimizes $\int \Phi^* \hat{H} \Phi d\tau$, where $\hat{H}$ is the true Hamiltonian, and is thus an ab-initio calculation. An ab-initio SCFMO calculation uses the approximation of taking Ψ as an antisymmetrized product of one-electron spin orbital and uses a finite (and hence incomplete) basis set. Accurate SCF molecular calculations on small to medium size molecules might use from 20 to 400 basis functions, producing from 2000 to $3x10^9$ electron – repulsion integrals. Computer evaluation of three- and four- centre integrals over STO basis functions is very time consuming.

To speed up molecular integral evaluation, Boys proposed in 1950 the use of Gaussian-type functions (GTFs) instead of STOs for the atomic orbitals in an LCAO wave function. Therefore, an LC-GTF SCF MO calculation involves evaluation of many many more integrals than the corresponding LC-STO SCF MO calculation, since the number of two electron integrals is proportional to the fourth power of the number of basis function. However, Gaussian integral evaluation takes much less computer time than Slater integral evaluation. Because of the difficulties in applying ab-initio methods to medium and large molecules many semi-empirical methods were developed to treat such molecules.

Though semi-empirical methods are approximate methods but these methods serve the purpose of calculation of wave function, energy and other properties like ionisation potentials, heat of formation, molecular geometry, force constant, electron density distribution, interpretation of molecular spectra etc.[3-8]

Several semi-empirical two-electron MO generalizations of the PPP method were developed that are applicable to both planer and nonplaner molecules. The complete neglect of differential overlap (CNDO)[9] and intermediate neglect of differential overlap (INDO)[10] both these methods treat only the valence electrons explicitly. The CNDO and INDO methods are SCF MO methods that iteratively solve the Roothan equations using approximations for the integrals in the Fock matrix elements. The neglect of diatomic differential overlap (NDDO)[9] is an improvement on INDO in which differential overlap is neglected only between atomic orbitals centered on different atoms.

Earlier attempt in devising CNDO and INDO was to reproduce as well as possible the results of minimal basis-set ab-initio SCF molecular orbital calculations. Dewar and co-workers devised several semi-empirical SCF MO theories that closely resemble the INDO and NDDO methods. However, Dewar's aim was not to reproduce ab-initio SCF wave functions and properties but to have a theory that would give molecular binding energies with chemical accuracy (within 1kcal/mole). Dewar type semi-empirical theories treat only the valence electrons and use a minimal basis set of valence Slater-type s and p atomic orbitals (with orbital exponents given values determined by parameterization) to expand the valence electron MOs. In ab-initio methods, the integrals occurring in the Fock matrix elements F_{rs} are evaluated accurately but this is not the approach used in Dewar type theories .

Third version of the modified INDO called (MINDO/3)[11] has been parameterized for compounds containing C, H, O, N, B, F, Cl, Si, P, and S atoms. MINDO/3 is based on the INDO approximation and the average absolute errors in calculated properties are large. MNDO method[12] is based on the far more justifiable NDDO approximation and give better results as compared with MINDO/3.

The MNDO valence electron Hamiltonian H_{val} is given by equation (1) and the Fock matrix elements are given by equation (2).

$$\hat{H}_{val} = \sum_{i=1}^{n_{val}} \hat{H}_{val}^{core}(i) + \sum_{i=1}^{n_{val}} \sum_{j>i} \frac{1}{r_{ij}} \quad (1)$$

Where $\hat{H}_{val}^{core}(i) = -\frac{1}{2}\nabla_i^2 + V(i)$

and n_{val} is the number of valence electrons in the molecule, V(i) is the potential energy of valence electron **i** in the field of nuclei and inner- shell (core) electrons, $\hat{H}_{val}^{core}(i)$ is the one-electron part of $\hat{H}_{val.}$

$$F_{val,rs} = H_{val,rs}^{core} + \sum_{t=1}^{b}\sum_{u=1}^{b} P_{tu}[(rs|tu) - \frac{1}{2}(ru|ts)] \quad (2)$$

In MNDO, the core- core repulsion term is given by equation (3)

$$V_{CC} = \sum_{B>A} \sum_{A} [C_A C_B (s_A s_A | s_B s_B) + f_{AB}] \quad (3)$$

Where $(s_A s_A | s_B s_B)$ is electron repulsion integral which involves the valence **s** orbitals of atoms A and B (and is approximately proportional to $1/R_{AB}$), and f_{AB} is a small term whose form differs in the various theories. f_{AB} is an empirical function of R_{AB} that finetunes interatomic attractions and repulsions in the molecule, so as to improve agreement with experiment. For MNDO method f_{AB}^{MNDO} is given by equation (4).

$$f_{AB}^{MNDO} = C_A C_B (s_A s_A | s_B s_B)\,(e^{-\alpha_A R_{AB}} + e^{-\alpha_B R_{AB}}) \quad (4)$$

where α_A and α_B are parameters for atoms A and B.

There are six parameters to be optimized for each kind of atoms in MNDO. MNDO method has been parameterized for compounds containing H, Li, Be, B, C, N, O, F, Al, Si, Ge, Sn, Pb, P, S, Cl, Br, I, Zn and Hg atoms.

Austin Model 1(AM1)[13-14] is an improved version of MNDO and it has been parameterized for H, B, Al, C, Si, Ge, Sn, N, P, O, S, Cl, I, Zn, and Hg atoms. The only differences between MNDO and AM1 are that the valence orbital exponents ζ_s and ζ_p on the same atom are allowed to differ and the core-repulsion function in AM1 is given by equation (3) wherevalue is given by equation (5).

$$f_{AB}^{AM1} = f_{AB}^{MNDO} + C_A C_B / R_{AB/Å} (\sum_K a_{kA} \exp[-b_{kA}(R_{AB} - c_{kA})^2] + \sum_K a_{kA} \exp[-b_{kB}(R_{AB} - C_{kB})^2]) \quad (5)$$

AM1 is re-parameterized to give the PM3 method[15] (Parametric method 3; 1 and 2 being MNDO and AM1). PM3 differs with AM1 in many ways. The one-center electron repulsion integrals are taken as parameters to be optimized (rather than being found from atomic spectral data).

The core-core repulsion function contains only two Gaussian terms per atom. A different method was used to find the optimized PM3 parameters. PM3 has been parameterized for H, C, Si, Ge, Sn, Pb, N, P, As, Sb, Bi, O, S, Se, Te, F, Cl, Br, Al, Ga, In, Tl, Be, Mg, Zn, Cd and Hg atoms.

A major limitation of the original versions of the MNDO, AM1, and PM3 methods is that they use a basis set of $\frac{1}{2}$ and $\frac{3}{4}$ valence A.Os only, so they can't be used with transition metal compounds (in Zn, Cd and Hg the d electrons are not valence electrons). Moreover, for compounds containing such second-row elements as **S**, the contributions of orbitals to MOs is significant, and these methods do not perform very well for such compounds.

MNDO/d is an improved method[16] over MNDO. It uses a basis set which includes d-orbitals for many second-row and later elements. MNDO/d does not add d-orbitals for first-row elements. Besides first-row elements MNDO/d has been parameterized for Al, Si, P, S, Cl, Br, I, and for several transition metals. Ab-intio and semi-empirical quantum chemical methods are widely available in many programs/packages viz. Gaussian, MOPAC, Hyperchem, Chemoffice etc.

These methods are designed to get the thermodynamic, spectral and structural parameters 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 the present communication we report the quantum chemical calculations for benzaldehyde thiosemicarbazones (BZTSC).

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 and MNDO methods and 3-21G, 6-31G and STO-3G ab-initio methods. Correlation coefficients for bond length and bond angle have been reported.

Computational Details

Quantum chemical calculations were carried out by semi-empirical AM1, PM3, MNDO and ab-initio 3-21G, 6-31G, STO-3G methods by Gaussian programs of Chemoffice 2004 package.[17] Chemdraw was used to draw the structure of molecules.

Bond lengths, bond angles, electron densities, net atomic charges, thermodynamic parameters like heat of formation, ionisation potential, total energy, electronic energy and core-core repulsion energy were calculated with the help of standard parameters as implemented in the software. Intel based Pentium IV, 630, HT3.2 machine having 800FSB, 1GB RAM, 7200rpm HDD was used to run all the programmes.

RESULTS AND DISCUSSION

Optimised Geometry

Bond length

Experimental and calculated bond lengths are presented in Table-1. We examined the performance of semi-empirical AM1, PM3, MNDO and 3-21G, 6-31G, STO-3G ab-initio methods in reproducing structural /geometrical parameters. Some of the calculated bond lengths are in good agreement with experimental values. The most suitable method is found by plotting the experimental verses calculated values and correlation coefficients[18] are calculated. For bond length, the correlation coefficients for AM1, PM3, MNDO methods are 0.921, 0.929 and 0.945, & for 3-21G, 6-31G, STO-3G methods are 0.984, 0.983, 0.906 respectively. It is evident that out of all the six

Table-1: Experimental and calculated bond lengths of benzaldehyde thiosemicarbazone by AM1, PM3, MNDO semi-empirical methods and 6-31G, STO-3G, 3-21G ab-initio methods

Bond Length	Experimental	AM1	PM3	MNDO	3-21G	6-31G	STO-3G
C(10)-S	1.686	1.607	1.644	1.581	1.733	1.728	1.603
C(10)-N(11)	1.321	1.382	1.393	1.385	1.340	1.344	1.401
C(10)-N(9)	1.343	1.414	1.416	1.41	1.345	1.351	1.42
N(8)-N(9)	1.389	1.333	1.342	1.382	1.393	1.365	1.405
N(8)-C(7)	1.28	1.301	1.31	1.301	1.261	1.265	1.287
C(3)-C(7)	1.46	1.465	1.476	1.464	1.470	1.467	1.491
C(5)-C(6)	1.417	1.394	1.407	1.393	1.379	1.383	1.383
C(1)-C(2)	1.38	1.392	1.403	1.388	1.384	1.387	1.385
C(2)-C(3)	1.390	1.404	1.401	1.42	1.386	1.391	1.393
C(3)-C(4)	1.427	1.402	1.398	1.417	1.390	1.395	1.395
C(4)-C(5)	1.394	1.394	1.391	1.407	1.379	1.383	1.384
Correlation Coefficient		0.921	0.929	0.945	0.984	0.983	0.906

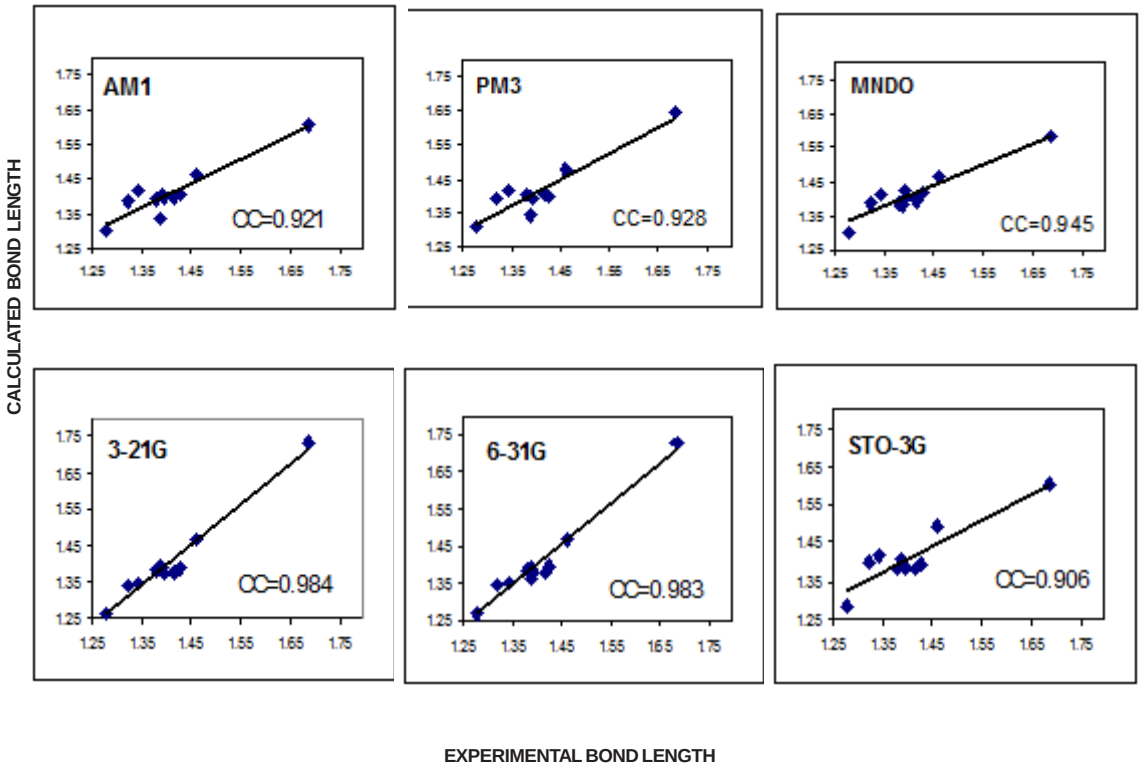

Fig. - 2: Graphic correlation between the experimental and calculated bond lengths obtained by the methods AM1, PM3, MNDO and 3-21G, 6-31G, STO-3G for benzaldehyde thiosemicarbazone(CC=Correlation Coefficient)

Table - 2: Experimental and calculated bond angles of benzaldehyde thiosemicarbazone by and AM1, PM3, MNDO semi empirical and 6-31G, STO-3G, 3-21G ab-initio methods

Bond Angle	Experimental	AM1	PM3	MNDO	3-21G	6-31G	STO-3G
N(9)-C(10)-N(11)	116.8	115.36	112.12	113.13	114.42	113.84	109.83
C(10)-N(9)-N(8)	119.1	120.46	120.55	118.7	120.91	122.13	120.47
N(9)-N(8)-C(7)	112.8	119.21	119.03	117.9	117.77	118.94	114.72
C(7)-C(3)-C(4)	117.0	119.15	118.8	119.02	119.56	119.25	119.74
C(4)-C(5)-C(6)	120.0	120.38	120.4	120.51	120.26	120.34	120.21
C(1)-C(2)-C(3)	122.5	120.22	120.19	121.17	120.24	120.51	120.47
C(4)-C(3)-C(2)	118.4	119.43	119.52	117.89	119.76	119.41	119.11
C(3)-C(4)-C(5)	119.5	119.96	119.87	120.77	119.86	119.97	120.28
Correlation Coefficient		0.423	0.363	0.551	0.548	0.418	0.612

Table-3: Net atomic charges (NAC) and Atom electron density (ED) calculated by AM1, PM3, MNDO semi-empirical and 3-21G, 6-31G, STO-3G abinitio methods

Atom No.	AM1 NAC	ED	PM3 NAC	ED	MNDO NAC	ED	3-21G NAC	ED	6-31-G NAC	ED	STO-3G NAC	ED
C(1)	-0.136	4.136	-0.111	4.112	-0.073	4.073	-0.235	4.237	-0.208	4.066	-0.064	4.872
C(2)	-0.117	4.117	-0.087	4.087	-0.035	4.035	-0.224	4.252	-0.206	4.084	-0.063	4.884
C(3)	-0.044	4.044	-0.071	4.071	-0.065	4.065	-0.168	4.414	-0.074	4.174	0.003	4.860
C(4)	-0.088	4.088	-0.051	4.052	-0.001	4.001	-0.198	4.263	-0.163	4.058	-0.055	4.876
C(5)	-0.136	4.136	-0.109	4.109	-0.074	4.074	-0.235	4.257	-0.208	4.074	-0.063	4.871
C(6)	-0.117	4.117	-0.085	4.085	-0.037	4.037	-0.232	4.242	-0.185	4.051	-0.060	4.874
C(7)	-0.129	4.129	-0.080	4.080	0.004	3.995	0.213	4.023	0.087	4.124	0.028	4.894
N(8)	0.015	4.984	-0.060	5.060	-0.043	5.043	-0.292	5.480	-0.174	5.226	-0.112	6.585
N(9)	-0.288	5.288	0.094	4.905	-0.289	5.289	-0.714	5.720	-0.711	5.716	-0.269	6.506
C(10)	0.175	3.824	-0.088	4.088	0.247	3.752	0.453	4.356	0.428	4.450	0.140	4.984
N(11)	-0.408	5.408	0.076	4.923	-0.390	5.390	-0.899	5.654	-0.904	5.571	-0.421	6.520
S(12)	-0.213	6.21	-0.278	6.278	-0.184	6.184	-0.072	14.617	-0.116	14.988	-0.047	16.999
H(18)	0.116	0.883	0.095	0.904	0.051	0.948	0.220	0.336	0.180	0.358	0.053	0.616
H(19)	0.206	0.793	0.060	0.939	0.175	0.824	0.355	0.248	0.370	0.269	0.189	0.5253
H(20)	0.260	0.739	0.097	0.902	0.208	0.791	0.401	0.202	0.416	0.215	0.209	0.490
H(21)	0.214	0.785	0.050	0.949	0.180	0.819	0.351	0.234	0.373	0.243	0.191	0.511

methods MNDO, 3-21G and 6-31G methods give the maximum correlation for bond length. From Figure-2 it is clear that in almost all methods only few points are diverted from trend line showing good results for bond length. In case of 3-21G and 6-31G maximum points are on trend line (cc=0.984, 0.983). AM1, PM3 and STO-3G graphical representation shows that few points are scattered away from trend line. And hence AM1, PM3 and STO-3G methods have less correlation coefficients (cc=0.921, 0.929 and 0.906 respectively). ab-initio methods (6-31G and 3-21G) yields maximum correlation among all the six methods.

Bond angle

Experimental and calculated bond angles have been presented in Table-2. In case of bond angles correlation coefficients are 0.423, 0.363, 0.551 for AM1, PM3, MNDO and 0.548, 0.418, 0.612 for 3-21G, 6-31G, STO-3G methods respectively. It is evident that in case of bond angles none of the method gave satisfactory correlation. STO-3G correlation coefficient (0.612) is maximum among all the semi-empirical and ab-initio methods. So in case of bond angles STO-3G is somewhat satisfactory among all the six methods. From Fig.-3 it is clear that only few points exists on the trend

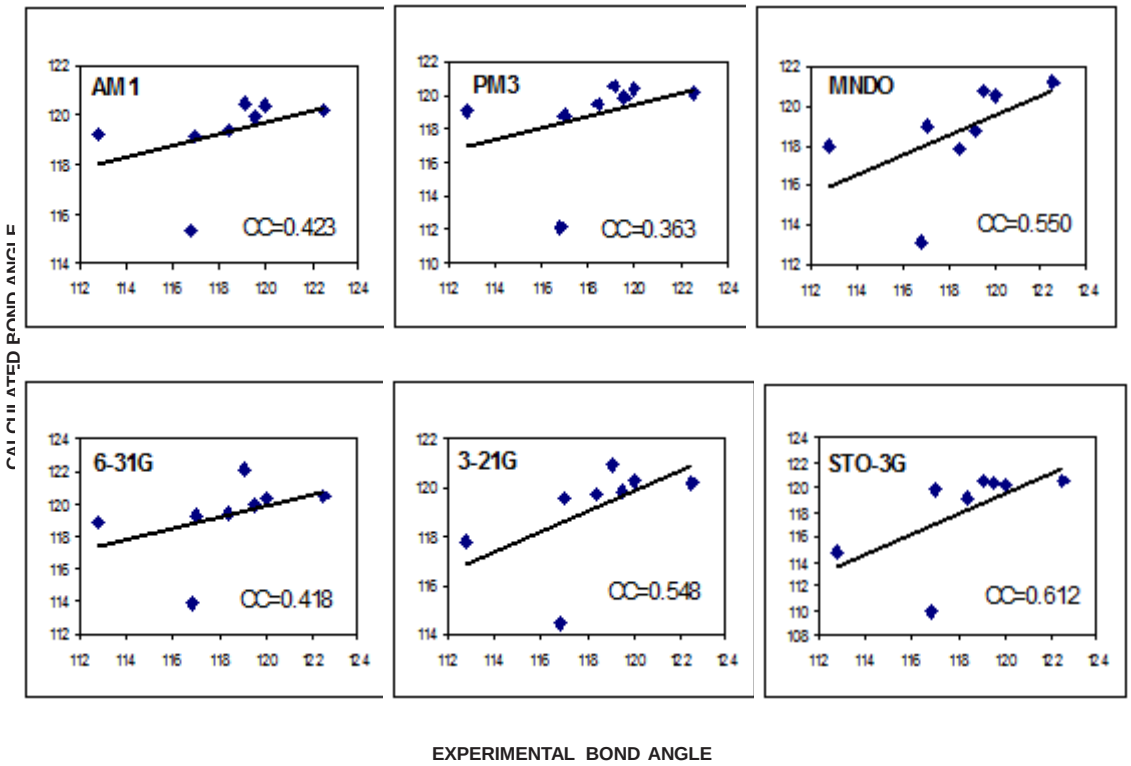

Fig. - 3 Graphic correlation between the experimental and calculated bond angle obtained by the methods AM1, PM3, MNDO and 3-21G, 6-31G, STO-3G for benzaldehyde thiosemicarbazone. (CC=Correlation Coefficient)

line and deviation is large showing that in case of bond angle no method yields satisfactory results. STO-3G gives maximum correlation (CC=0.612) while PM3 given minimum correlation (CC=0.363). MNDO and 3-21G results are very much close to each other.

Atomic charges and atom electron densitites

Calculated net atomic charges and atom electron densities are presented in table-3. The graphical presentation of electron density on each atom is shown in Figure-4. The graphical representation of atom type and electron density show that nitrogen and sulphur may take part in coordination in complex formation as these atoms show maximum net atomic charges and electron densities. For any ligand, to be used for stable complex formation, it the most common requirement to look for the bonding site with which the metal ion will coordinate. In this regard, the net atomic charge and the atomic electron density becomes useful parameters to look for the coordination sites of the ligand.

From table-3 and figure-4 it is clear that different methods predicted different net atomic charges and electron densities on N(8), N(9), N(11) and S(12) atoms and hence these atoms can act as coordination sites while forming complexes with transition metal ions.

General thermodynamic parameters

The computed heat of formation, ionisation potential, total energy, electronic energy and core-core repulsion energy for benzaldehyde

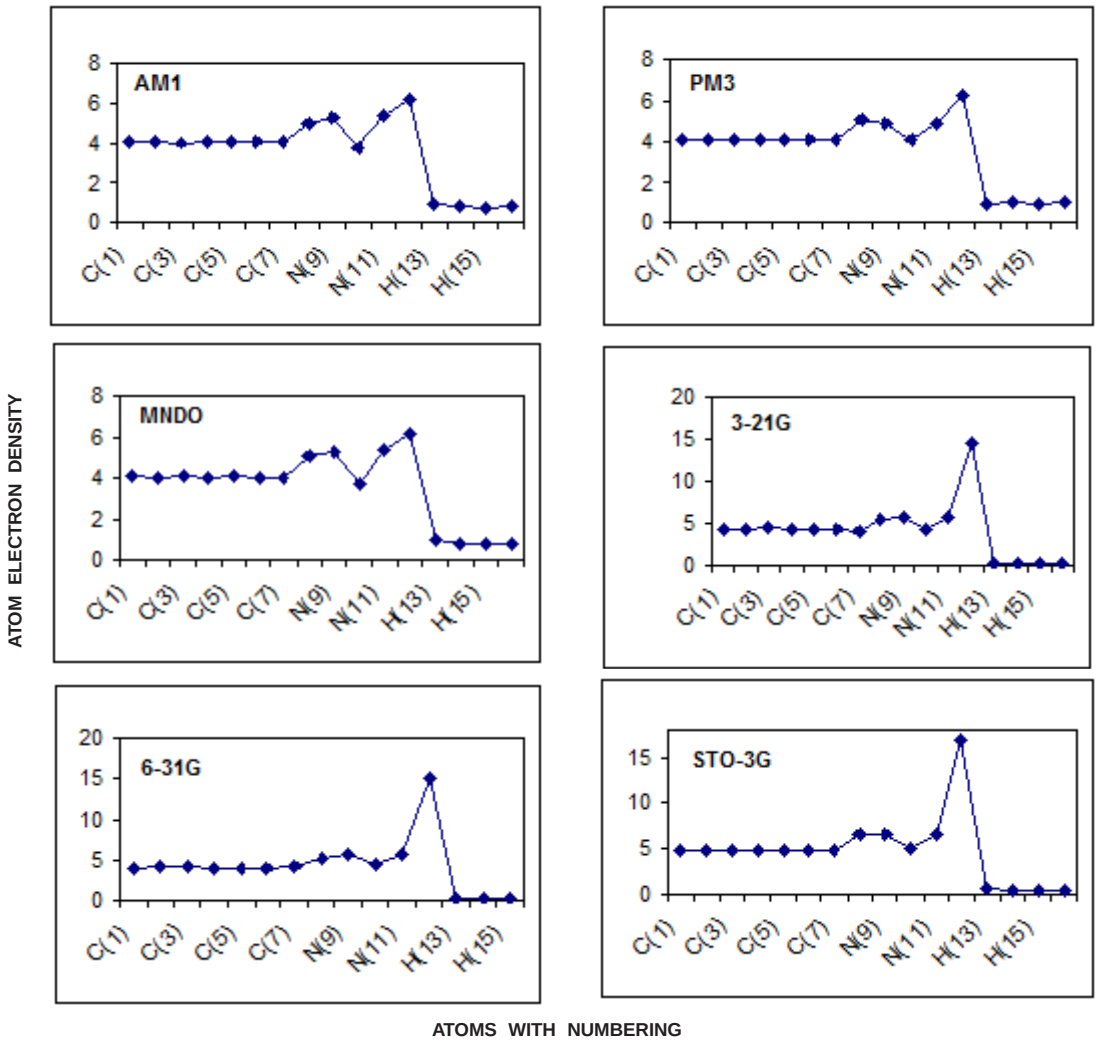

Fig. - 4: Graphic representation of calculated atom electron densities obtained by AM1, PM3 and MNDO semi-empirical methods for benzaldehyde thiosemicarbazone

Table - 4: Computed heat of formation, ionisation potential, total energy, electronic energy and core-core repulsion energies predicted by AM1, PM3, and MNDO semi-empirical methods

Parameters	AM1	PM3	MNDO
Heat of formation (Kcal)	90.221	99.656	79.372
Ionisation Potential (ev)	8.438	8.550	8.869
Total energy (ev)	-1961.335	-1756.670	-1998.628
Electronic energy (ev)	-9590.004	-9227.844	-9647.097
Core-core repulsion (ev)	7628.668	7471.173	7648.4689

thiosemicarbazone by semi-empirical methods AM1, PM3, MNDO are given in Table-4. Heat of formation value for benzaldehyde thiosemicarbazone by semi-empirical methods shows its endothermic nature. MNDO gives highest ionisation potential value of 8.869ev and AM1 gives lowest ionisation potential value of 8.438ev. Core-core repulsion energy is given by total energy minus electronic energy. MNDO gives higher value of core-core repulsion while PM3 gives lowest.

Conclusion

AM1, PM3, MNDO semi-empirical and 3-21G, 6-31G, STO-3G ab-initio methods proved to be important auxiliary tools for geometry optimization, electronic structure and thermodynamic studies and were used for bond length, bond angle, electron density, heat of formation, ionisation potential, total energy, electronic energy and core-core repulsion energy determination. The correlation coefficient for bond lengths for benzaldehyde thiosemicarbazone molecule are 0.921**,** 0.929, 0.945 respectively for AM1, PM3 and MNDO semi-empirical methods and 0.984, 0.983, 0.906 for 3-21G, 6-31G, STO-3G ab-initio methods. MNDO, 3-21G and 6-31G methods give best linearity between experimental and calculated bond lengths (CC=0.945, 0.984 and 0.983 respectively and hence are most satisfactory methods. Also ab-initio methods give better results than semi-empirical methods.

The correlation coefficients for bond angles are 0.423, 0.363, and 0.551 for AM1, PM3, MNDO and 0.548, 0.418, 0.612 for 3-21G, 6-31G and STO-3G respectively. MNDO and STO-3G give most satisfactory correlation. However STO-3G gives better correlation than MNDO method. Atom electron densities and net atomic charges indicate the coordination sites in the molecule during complex formation with transition metal ions. Results from AM1, MNDO and STO-3G methods for electron densities are supported by experimental data. Heat of formation value for benzaldehyde thiosemicarbazone by semi-empirical methods shows its endothermic nature. MNDO gives higher ionisation potential and core-core repulsion energy. Thus, computational quantum chemical calculations can successfully be used to predict the geometry, electronic structure and thermodynamic parameters.

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