Theoretical Investigation of IR and Geometry of the S-benzyl-β-N-(2-furylmethylketone)dithiocarbazate Schiff Base by Semi-Empirical Methods

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Schiff bases of alkyl/aryl dithiocarbazate and their transition metal complexes have received much attention due to their biological activities. Performance of Semi-empirical AM1, PM3, MNDO, MNDO-d methods have been tested to find the best auxiliary tool for the IR frequencies, geometry and electron densities. For bond lengths, the correlation coefficient obtained for AM1, PM3, MNDO and MNDO-d methods are 0.96, 0.990, 0.983 and 0.976, respectively. Out of the four semi-empirical methods PM3 produces most satisfactory correlation (cc = 0.990) between experimental and calculated bond length. In the case of bond angles, correlation coefficients are 0.836, 0.742, 0.706 and 0.685 for AM1, PM3, MNDO and MNDO-d methods, respectively. Thus AM1 method gives most satisfactory correlation (cc = 0.836). Out of two nitrogen atoms azo-methine nitrogen carried more electron density. For fundamental vibrational frequencies, the correlation coefficient obtained for AM1, PM3, MNDO and MNDO-d methods are 0.926, 0.967, 0.760, and 0.969, respectively. Out of the four semi-empirical methods MNDO-d yields most satisfactory correlation (cc = 0.969) between experimental and calculated fundamental vibrational frequencies.

Key Words: Semi-empirical methods AM1, PM3, MNDO and MNDO-d, Correlation coefficient, Vibrational frequencies.

INTRODUCTION

Dithiocarbazic acid and its derivatives have been known for a long time and have been the subject of much experimental work[1-5]. Mixture of hydrazine hydrate, carbon disulphide and alc. KOH results in a condensation to form dithiocarbazate (**I**) salt which on reaction with alkyl/aryl halides yields alkyl/aryl dithiocarbazates (**II**).
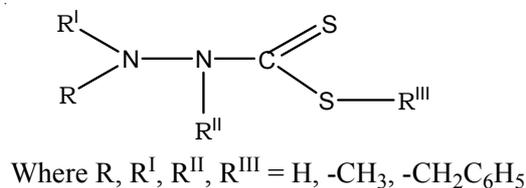
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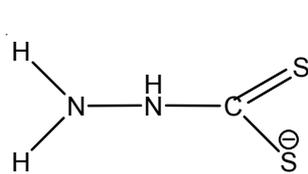
(I)

Where R, R^I, R^{II}, R^{III} = H, -CH$_3$, -CH$_2$C$_6$H$_5$

(II)

S-alkyl/aryl dithiocarbazates may undergo condensation with carbonyl compounds to form Schiff bases. Dithiocarbazates and their Schiff bases have four potential donor atoms and can, therefore, coordinate in several ways to transition metal ions depending on the influence of substituents present in the dithiocarbazates[6-10]. Various studies have shown that the >C=N- group present in Schiff base has considerable biological importance[11]. The Schiff bases of alkyl / aryl dithiocarbazate containing nitrogen and sulphur have been found to act as potential drugs against bacteria, virus and cancer[12-18] which have stimulated interest in their coordination chemistry studies. They have been found to possess carcinostatic activities against human tumor cells and also found to exhibit promising activity against leukemia cells[19]. This series of compounds received much attention and are subject of further study as they provide an interesting series of ligand whose properties can greatly be modified by introducing different organic substituents causing, thereby, a variation in their ultimate donor properties. In principle, bonding in dithiocarbazate complexes can occur either through the two sulphur atoms (**III**) or through the azomethine nitrogen and thiolo sulphur (**IV**).
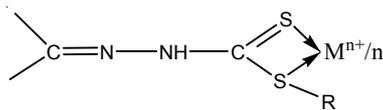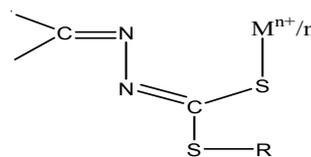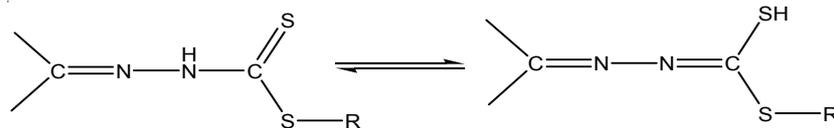

(III)   **(IV)**

Different modes of bonding produce marked change in the properties of the complex due to difference in geometry. Dithiocarbazates and their Schiff bases exhibit thione-thiol tautomerism and there exist a dynamic equilibrium between both these forms (**V** and **VI**).

Thione form
(V)

Thiol form
(VI)

These two forms of ligand can interact with metal ions in different ways to give metal complexes with different properties[20-25]. Electronic structure, spectral studies and geometry optimization are important tools to theoretically characterize these compounds. Semi-empirical molecular quantum mechanical methods are approximate methods but these serve the purpose of calculation of wave function, energy and other properties like ionization potential, heat of formation, molecular geometry, force constant, electron density distribution and interpretation of molecular spectra[26,27].

Semi-empirical methods use a simpler Hamiltonian than the correct molecular Hamiltonian and use parameters whose values are adjusted to fit experimental data. Because of the difficulties in applying *ab initio* methods to medium and large molecules many semi-empirical methods were developed to treat such molecules. All the geometries were fully optimized without any symmetry constraints using AM1, PM3, MNDO and MNDO-d methods and stationary points were obtained on the potential energy surfaces. The semi-empirical SCF procedures in general do not make use of symmetry in SCF cycles in economizing the CPU time.

Several semi-empirical two-electron MO generalizations of the PPP method were developed that are applicable to both planer and non-planer molecules. The complete neglect of differential overlap (CNDO)[28] and intermediate neglect of differential overlap (INDO)[29] both these methods treat only the valence electrons explicitly. The CNDO and INDO method 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)[30] 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[31-33] 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 1 kcal). 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)[34] 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[31] is based on the far more justifiable NDDO approximation and give better results as compared with MINDO/3.The MNDO valence electron Hamiltonian $\hat{H}_{val}$ is given by eqn. 1 and the Fock matrix elements are given by eqn. 2,

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

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

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 $\hat{H}_{val}$.

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

In MNDO, the core- core repulsion term is given by eqn. 3

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

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 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 eqn. 4.

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

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)[32,33] 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-core repulsion function in AM1 is given by eqn. 3 where f_{AB}^{AM1} value is given by eqn. 5.

$$f_{AB}^{AM1} = f_{AB}^{MNDO} + C_A C_B / R_{AB/Å} \Big(\sum_{K} a_{kA} \exp[-b_{kA}(R_{AB} - c_{kA})^2] +$$

$$\sum_{K} a_{kA} \exp[-b_{kB}(R_{AB} - c_{kB})^2] \Big) \tag{5}$$

AM1 is re-parameterized to give the PM3 method[35] (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-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 s and p valence A. Os only, so they can't be used with transition metal compounds (in Zn, Cd and Hg atoms the d-electrons are not valence electrons). Moreover, for compounds containing such second-row elements as S, the contributions of d-orbitals to MOs is significant, and these methods do not perform very well for such compounds.

MNDO/d is an improved method[36] 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. Semi-empirical methods are widely available in many programs/packages like MOPAC, Gaussian, Hyperchem, Chemoffice, *etc*.

2-Furylmethylketone Schiff base of S-benzyl dithiocarbazate (**VII**) has recently been synthesized[37]. This Schiff base and its complexes with metal ions (Pb^{2+}, Sn^{2+}, Fe^{2+}, Co^{2+} and Cd^{2+}) have been found to be biologically active. However, no theoretical quantum chemical study on this biologically important Schiff base has been reported in the literature so far. The Schiff base has 5 potential donor atoms (N, N, S, S and O) and electronic structure and IR spectral studies using computational methods are helpful in deciding the nature of Schiff base and its behavior while coordinating with metals.
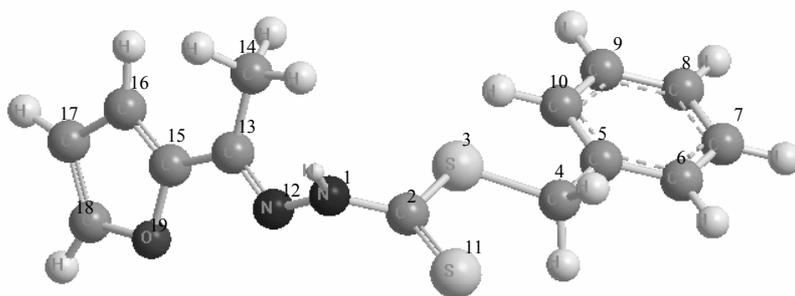

Fig. 1. S-Benzyl-β-N-(2-furylmethylketone)dithiocarbazate

Herein, a theoretical study to characterize the S-benzyl-β-N-(2-furyl methyl ketone) Schiff base by quantum chemical semi-empirical methods

is reported. The calculated data were compared with those obtained experimentally from X-ray and other spectroscopic techniques. This comparative study will enable us to determine the validity of theoretical methods to predict the geometrical and spectral features of dithiocarbazates and their coordination behaviours.

Computational details

Quantum chemical calculations were carried out by semi-empirical AM1, PM3, MNDO and MNDO-d methods of MOPAC programs of Chemoffice 2004 package[38]. Chemdraw was used to draw the structure of molecules. The semi-empirical procedures, in general do not make use of symmetry in SCF cycles in economizing the CPU time. Therefore, all the geometries were fully optimized without any symmetry constraints using AM1, PM3, MNDO and MNDO-d methods and stationary points were obtained on the potential energy surfaces. Bond lengths, bond angles, electron densities, net atomic charges and IR frequencies were calculated with the help of standard parameters as implemented in the software. Intel based Pentium IV, 630, HT3.2 machine having 800 FSB, 1 GB RAM, 7200 rpm HDD was used to run all the programmes.

RESULTS AND DISCUSSION

Optimized geometry

We examined the performance of semi-empirical AM1, PM3, MNDO and MNDO-d methods in reproducing structural/geometrical parameters. The calculated bond lengths are in good agreement with experimental values. The most suitable method was found by plotting the experimental values versus calculated values and the obtained correlation coefficients were analyzed. It is found that correlation coefficients (CC) are not equal for different methods. For bond length, the correlation coefficient obtained for AM1, PM3, MNDO and MNDO-d methods are 0.969, 0.990, 0.983 and 0.976, respectively. It is evident that PM3 method gives most satisfactory correlation (CC = 0.990) between experimental and calculated bond lengths. In the case of bond angle, correlation coefficients are 0.836, 0.742, 0.706 and 0.685 for AM1, PM3, MNDO and MNDO-d methods, respectively. It is evident that AM1 method gives most satisfactory correlation coefficient (CC = 0.836). The calculated and experimental (X-ray) bond lengths and bond angles are given in Tables 1 and 2, respectively and graph between experimental versus calculated bond length and bond angle are given in Figs. 2 and 3, respectively.

Electron densities and net atomic charge

Electron densities and net atomic charge on O, N and S atoms of S-benzyl β-*N*-(2-furylmethylketone)dithiocarbazate have been calculated by

semi-empirical AM1, PM3, MNDO and MNDO-d methods. The computed data are presented in the Table-3 and graphically it is shown in Fig. 4. For any ligand to be used for stable complex formation, it is of utmost importance to look for the bonding sited with which the metal ion will coordinate. In this regard the atomic electron density and net atomic charge become the vital parameters to assign the coordination site of a ligand and the stability of the complex.

TABLE-1

CALCULATED AND EXPERIMENTAL BOND LENGTHS OF
S-BENZYL-β-*N*-(2- FURYLMETHYL KETONE) DITHIOCARBAZATE
SCHIFF BASE OF S-BENZYL DITHIOCARBAZATE

Atoms	Experimental	AM1	PM3	MNDO	MNDO-d
S3-C2	1.7506	1.7615	1.7947	1.6973	1.7626
S3-C4	1.8197	1.7779	1.8304	1.7448	1.8110
C2-S11	1.6669	1.5641	1.6280	1.5653	1.6391
N1-N12	1.3820	1.3335	1.4090	1.3750	1.3774
N1-C2	1.3848	1.3889	1.3930	1.4252	1.4408
N12-C13	1.2750	1.3203	1.3110	1.3078	1.3078

TABLE-2

CALCULATED AND EXPERIMENTAL BOND ANGLES OF
S-BENZYL-β-N-(2-FURYLMETHYL KETONE) DITHIOCARBAZATE
SCHIFF BASE OF S-BENZYL DITHIOCARBAZATE

Atoms	Experimental	AM1	PM3	MNDO	MNDO-d
C2-S3-C4	102.37	104.20	105.3	110.2	111.3
C2-N1-N12	119.36	121.70	124.8	115.9	115.2
C13-N12-N1	115.86	120.80	124.3	118.8	118.3
C5-C4-S3	106.30	110.96	113.3	109.1	109.5
N1-C2-S11	121.74	128.10	126.5	123.0	122.7
N1-C2-S3	112.96	108.20	109.6	110.7	112.4
N12-C13-C15	121.32	116.10	114.1	112.7	–

S-benzyl-β-N-(2-furylmethylketone) Schiff base there are five atoms N1, N12, S3, S11, O19 which may be coordinated during complex formation with transition metal ion. Three methods AM1, MNDO and MNDO-d favour N2, S3 atom as coordination site in the ligand molecule while forming a complex, where as the PM3 method favours N12 and S3 atoms as coordination sites.

The computed coordination sites by PM3 method is supported by the experimental data[34] that suggest a considerable negative shift in the stretching vibration frequency of azo-methine group (C=N) and symmetric stretch-

ing of CSS groups after complexation. This observation is further supported by X-ray crystal structure of Cu and Fe complexes of the S-benzyl β -N-(2-furylmethylketone) Schiff base[34].
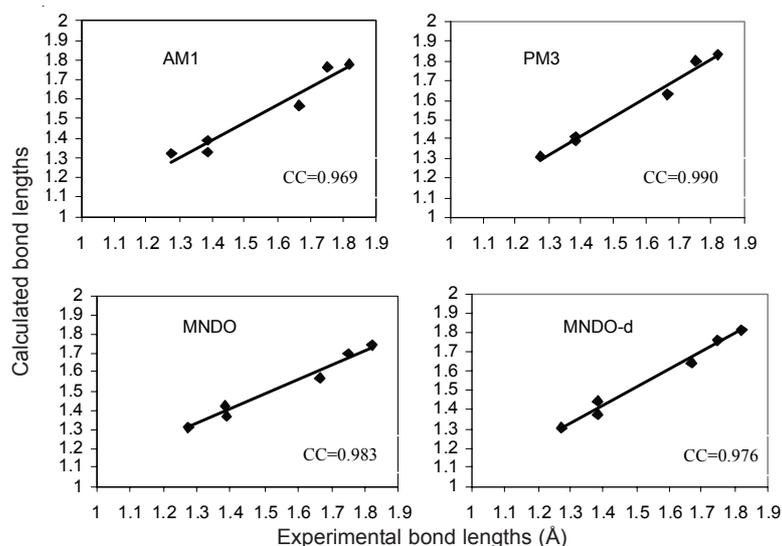

Fig. 2.   Graphic correlation between the experimental and calculated bond length obtained by the methods AM1, PM3, MNDO and MNDO-d for S-benzyl-β-*N*-2-furylmethylketone)dithiocarbazate Schiff base of S-benzyl dithiocarbazate (CC= correlation coefficient)
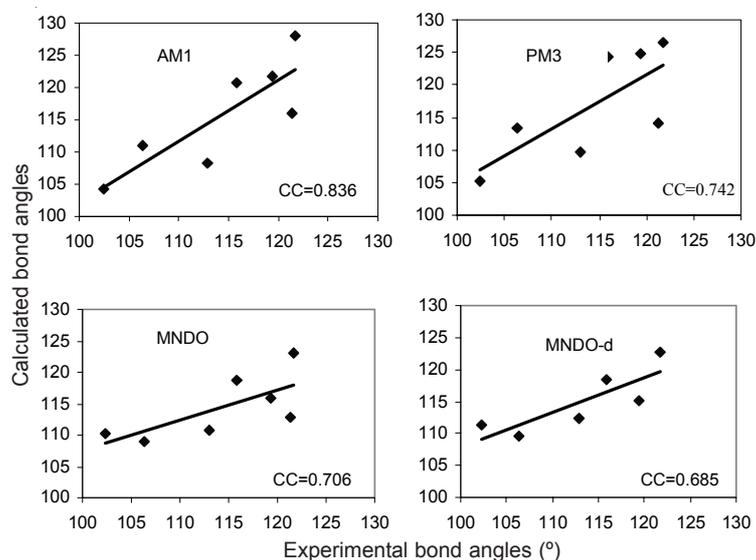

Fig. 3. Graphic correlation between the experimental and calculated bond angles obtained by different methods AM1, PM3, MNDO and MNDO-d for S-benzyl β-*N*-(2-furylmethylketone) dithiocarbazate Schiff base of S-benzyl dithiocarbazate (CC=correlation coefficient)

TABLE-3
CALCULATED NET ATOMIC CHARGES & ATOM ELECTRON
DENSITIES OF S-BENZYL-β-*N*-(2-FURYLMETHYLKETONE)
DITHIOCARBAZATE SCHIFF BASE OF SBDTC*

| Atoms	AM1	PM3	MNDO	MNDO-d
Net Atomic Charges				
N1	-0.232	-0.217	-0.194	-0.183
C2	-0.113	-0.220	-0.114	-0.045
S3	0.113	-0.040	-0.113	-0.101
C4	-0.235	-0.115	-0.010	-0.020
C5	-0.076	-0.089	-0.103	-0.098
C6	-0.111	-0.087	-0.022	-0.025
C7	-0.129	-0.101	-0.067	-0.066
C8	-0.122	-0.093	-0.039	-0.040
C9	-0.130	-0.103	-0.067	-0.066
C10	-0.116	-0.249	-0.023	-0.025
S11	-0.084	-0.249	-0.074	-0.139
N12	-0.015	-0.216	-0.149	-0.140
C13	-0.026	-0.137	0.133	0.122
C14	-0.215	-0.153	0.045	0.048
C15	-0.021	-0.070	-0.027	-0.024
C16	-0.131	-0.076	-0.070	-0.075
C17	-0.204	-0.199	-0.143	-0.141
C18	-0.078	-0.027	-0.010	-0.009
O19	-0.106	-0.055	-0.108	-0.107
H20	0.228	0.094	0.164	0.155
Atom Electron Densities				
N1	5.230	4.782	5.194	5.183
C2	4.113	4.221	4.114	4.045
S3	5.886	5.959	5.886	5.898
C4	4.235	4.115	4.010	4.020
C5	4.076	4.089	4.103	4.098
C6	4.111	4.087	4.022	4.025
C7	4.129	4.101	4.067	4.066
C8	4.122	4.093	4.039	4.040
C9	4.130	4.103	4.067	4.066
C10	4.116	4.084	4.023	4.025
S11	6.084	6.249	6.074	6.139
N12	5.015	5.216	5.149	5.140
C13	4.026	3.862	3.866	3.878
C14	4.215	4.153	3.954	3.951
C15	4.021	4.070	4.027	4.024
C16	4.131	4.076	4.070	4.075
C17	4.204	4.199	4.143	4.141
C18	4.078	4.027	3.989	3.990
O19	6.106	6.055	6.108	6.107
H20	0.771	0.903	0.835	0.844
H21	0.872	0.901	0.968	0.958
H22	0.835	0.869	0.965	0.956

*S-benzyl dithiocarbazate
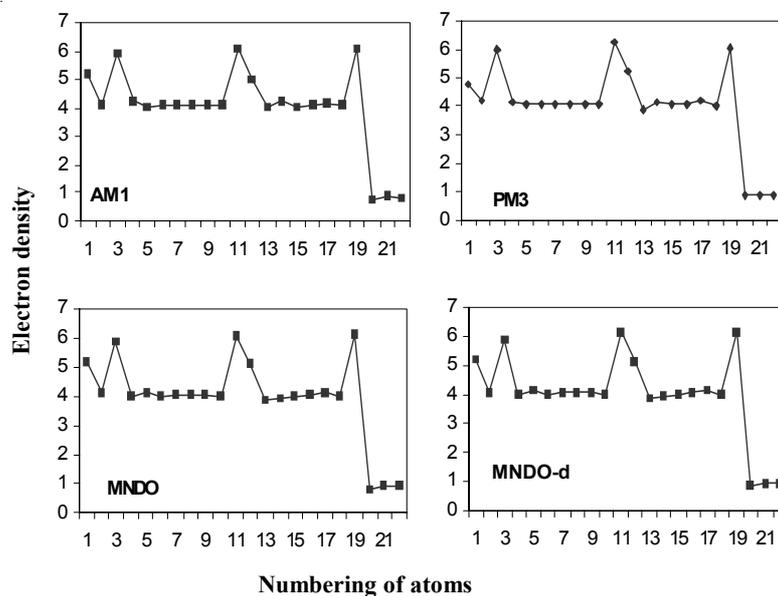
Fig. 4. Graphic presentation of calculated electron densities on each atom of
S-benzyl-B-*N*-(2-furylmethyl ketone)dithiocarbazate Schiff base obtained
by AM1, PM3, MNDO and MNDO-d semi-empirical methods

Vibration frequencies

The experimental and calculated IR fundamental vibrational frequen-
cies for the S-benzyl-β-N-(2-furylmethylketone) dithiocarbazate Schiff base
by AM1, PM3, MNDO & MNDO-d methods are presented in Table-4. To
examine the usefulness of the calculation method for IR, a linearity
between the experimental[35] & calculated wave numbers has been derived
by plotting the calculated versus experimental wave numbers and analyz-
ing correlation coefficients. Graphical correlation between experimental
and calculated fundamental vibration frequencies are presented in Fig. 5.
The correlation coefficients obtained for AM1, PM3, MNDO and MNDO-
d methods are 0.926, 0.967, 0760 and 0.969, respectively. It is evident that
MNDO-d method gives most satisfactory correlation (cc = 0.969) between
experimental and calculated vibrational frequencies.

TABLE-4
EXPERIMENTAL AND CALCULATED FUNDAMENTAL VIBRATIONAL
FREQUENCIES OF S-BENZYL-β-N-(2-FURYL METHYLKETONE)
DITHIOCARBAZATE SCHIFF BASE OF S-BENZYL DITHIOCARBAZATE
BY AM1, PM3, MNDO AND MNDO-d SEMI-EMPERICAL METHODS

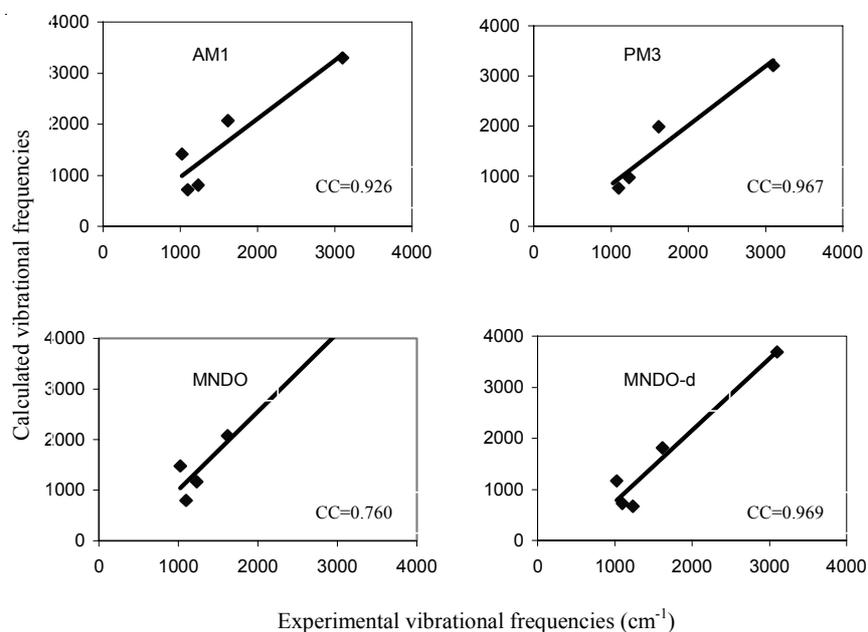| IR Bands	Experimental	AM1	PM3	MNDO	MNDO-d
N-H	3102	3301	3209	–	3692
C=N	1618	2071	1984	2075	1815
N-N	1023	1418	–	1478	1168
C=S	1096	717	763	796	726
C-O-C	1232	809	969	1166	668

Fig. 5.   Graphical correlation between experimental and calculated fundamental
            vibration frequencies obtained by semi-empirical methods AM1, PM3,
            MNDO and MNDO-d for S-benzyl-β-*N*-(2-furylmethyl-ketone)
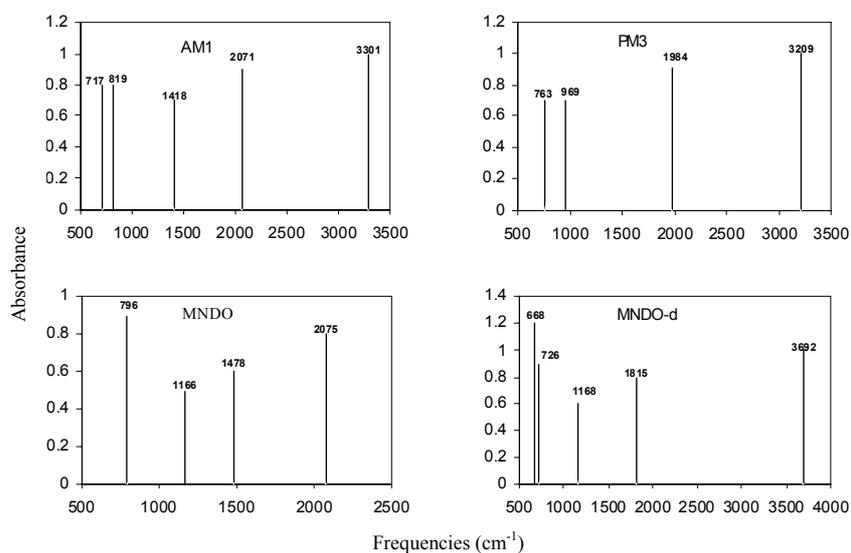   dithiocarbazate (CC=Correlation coefficient)

Fig. 6.   The simulated IR spectra for the S-benzyl-ß-N-(2-furylmethylketone)-
            dithiocarbazate Schiff base of S-benzyl dithiocarbazate by AM1, PM3,
            MNDO and MNDO-d methods

The simulated IR spectra for the S-benzyl-β-N-(2-furylmethylketone)-dithiocarbazate Schiff base of S-benzyl dithiocarbazate by AM1, PM3, MNDO & MNDO-d methods are presented in Fig. 6. Some vibrational frequencies in the experimental spectra could not be identified in the simulated counterparts and therefore have been omitted. There is a systematic error between the calculated and experimental values. It is due to the neglect of anharmonicity and electron correlation. The general view of the matching of simulated spectrum with experimental counterparts can be much more helpful for the compound identification (especially where fast screening of several possible isomers is necessary) than detailed analysis of the calculated spectra. The ν_{NH}, ν_{CN} and ν_{COC} frequencies which are well known are in good agreement with the experimental values. A good matching between calculated and experimental values was observed in some of the cases, however, some discrepancy was observed in case of (C=N) and (C=S) stretching frequencies.

Conclusion

AM1, PM3, MNDO and MNDO-d semi-empirical methods proved to be important auxiliary tool for geometry optimization, electronic structure and IR studies. The correlation coefficients for bond lengths for biologically active S-benzyl-β-*N*-(2-furylmethylketone) Schiff base molecule are 0.969, 0.990, 0.983 and 0.976 for AM1, PM3, MNDO and MNDO-d, respectively and PM3 gives most satisfactory correlation. The correlation coefficient for bond angles are 0.836, 0.742, 0.706 and 0.685 for AM1, PM3, MNDO and MNDO-d, respectively and AM1 gives most satisfactory correlation. PM3 method results for electron density are supported by experimental data. For vibrational frequencies the correlation coefficient are 0.926, 0.967, 0.760 and 0.969 for AM1, PM3, MNDO and MNDO-d, respectively. MNDO-d gives most satisfactory correlation for IR frequencies.

REFERENCES

1. K. Jensen and A. Holm, *Acta Chem. Scand.*, **23**, 1916, (1969).
2. C. Battistoni, G. Mattogno, A. Monaci and F. Tarli, *Inorg. Nucl. Chem. Lett.*, **7**, 981 (1971).
3. M.A. Ali, S.E. Livingstone and D.J. Phillips, *Inorg. Chim. Acta*, **5**, 119 (1971).
4. M.A. Ali, S.E. Livingstone and D.J. Phillips, *Inorg. Chim. Acta*, **6**, 39 (1972).
5. M.A. Ali, S.E. Livingstone and D.J. Phillips, *Inorg. Chim. Acta*, **7**, 179 (1973).
6. M. Das and S.E. Livingstone, *Inorg. Chim. Acta*, **19**, 5 (1976).
7. M.A. Ali, and M.T.H. Tarafder, *J. Inorg. Nucl. Chem.*, **39**, 1785 (1977).
8. M.A. Ali and S.G. Teoh, *J. Inorg. Nucl. Chem.*, **40**, 451 (1978).
9. M.T.H. Tarafder and M.A. Ali, *Can. J. Chem.*, **56**, 2000 (1978).
10. A. Amore-Bonepasta, C. Battistoni and A. Lapiccirell, *J. Mol. Struct.*, **63**, 93 (1980).
11. Patais, The Chemistry of Carbon-Nitrogen Double bond, Inter Science Publishers Inc., New Yark (1970).
12. H.G. Petering, H.H. Buskirk, J.A. Crim and G.J. Van giessen, *Pharmcologist*, **5**, 271 (1963).
13. Thiel and A.A. Voityuk, *J. Phys. Chem.*, **100**, 616 (1996).
14. G.D. Andretti, P. Domino, G. Fava, M. Nardelli and P. Sgarbotto, *Acta Crystallogr.*, *Sect.B*, **26**, 1005 (1970).
15. H.G. Petering and G.J. Van Giessen, *Fed. Proc. Am. Soc.Exp. Bio.*, **21**, 1970 (1965).
16. J.A. Crim and H.G. Petering, *Cancer Res.*, **27**, 1278 (1967).
17. H.G. Petering and G.J. Van Giessen, The Biochemistry of Copper, Acadimic Press Newyork., 197 (1966).
18. R. Jha *et al*, *Asian J. Chem.*, **10**, 717 (1998).
19. S. Kirschner, Y.K. Wei, D. Trancis and J.G. Berymen, *J. Med. Chem.*, **9**, 369 (1966).
20. S. Podhye and G.B. Kauffman, *J. Coord. Chem. Rev.*, **63**, 127 (1983).
21. A.E. Liberta and D.X. West, *Biometals*, **5**, 121 (1992).
22. J.G. Cory, A.H. Cory, G. Rappa, A. Lorico, M.C. Liu, T.S. Lin and A.C. Sartorelli, *Biochem. Pharmcol.*, **48**, 335 (1994).
23. E. Lukevics, D. Jansone, K. Rubina, E. Abele, S. Germane, L. Leite, M. Shymanska and J. Popelis, *Eur. J. Med. Chem.*, **30**, 983 (1995).
24. D. Yum-Ying, W. Bo-Mu and C.W.M. Thomas, *J. Chem. Soc. Dalton Trans.*, **12**, 3485 (1996).
25. G. Nocentini, F. Federci, P. Franchetti and A. Barzi, *Cancer Res.*, **53**, 19 (1993).
26. D. Kumar and K. Arora, *Asian J. Chem.*, **13**, 1325 (2001).
27. D. Kumar and K. Arora, *J. Indian Chem. Soc.*, **79**, 693 (2002).
28. J.A. Pople, D.P Santry and G.A. Segal, *J. Chem. Phys.*, **43**, 5129 (1965).
29. Pople, Biveridge and Dobosh in 1967.
30. J.A. Pople, D.P. Santry and G.A. Segal in 1965.
31. M.J.S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, **99**, 4899 (1977).
32. M.J.S. Dewar, E.G. Zoebisch, E.F. Healy and J.J.P. Stewart, *J. Am. Chem. Soc.*, **107**, 3902 (1985).
33. M.J.S. Dewar and Y.C. Yuan, *Inorg. Chem.*, **29**, 3881 (1990).
34. R.C. Bingham, M.J.S. Dewar and D.H. Lo, *J. Am. Chem. Soc.*, **97**, 1285, 1302 (1975).
35. J.J.P. Stewart, *J. Comp. Chem.*, **10**, 209 (1989)
36. W. Theil and A.A. Voityuk, *J. Am. Chem. Soc.*, **100**, 616 (1996).
37. M.T.H. Tarafder, Teng-Jin Khoo, K.A. Crouse, A.M. Ali, B.M. Yamin and H.K. Fun, *Polyhedron*, **21**, 2691 (2002).
38. Chemoffice 2004 (Trial Version) Cambridge Soft Corporation.