Research Journal of Chemical Sciences ____ ISSN 2231-606X
Vol. **3(2),** 79-84, February **(2013)** *Res. J. Chem. Sci.*

Molecular structure, vibrational spectroscopic and HOMO, LUMO studies of S-2-picolyl-β-N-(2-acetylpyrrole) dithiocarbazate Schiff base by Quantum Chemical investigations

Singh Rajeev[1], Kumar D.[2], Singh Bhoop[1], Singh V.K.[1] and Sharma Ranjana[3]
[1]Department of Chemistry, Institute of Information Technology and Management, Gwalior, INDIA
[2]Center of Research for Chemical Sciences, PG Department of Chemistry, SMS Govt. College, Jiwaji University, Gwalior, INDIA
[3]Department of Chemistry, Institute of Technology and Management, Gwalior, INDIA

Available online at: www.isca.in
Received 21st December 2012, revised 31st December 2012, accepted 5th January 2013

Abstract

In this study S-2-picolyl-β-N-(2-acetylpyrrole) dithiocarbazate Schiff base has been subjected to theoretical studies by using Semi-empirical AM1 and PM3 quantum chemical methods. The molecular geometry, vibration frequencies, HOMO-LUMO energy gap, molecular hardness (η), ionization energy (IE), electron affinity (EA), total energy and dipole moment were analyzed. The theoretically obtained results were found to be consistent with the experimental data reported. A good correlation has been observed between experimental and calculated values for vibration modes.

Keywords: Semi-empirical methods, AM1, PM3, Vibration modes, correlation coefficient, hardness (η).

Introduction

Schiff bases derived from S-alkyl/aryl dithiocarbazate have been extensively studied over last decade[1-4]. The attention of on these compounds arose mainly due to their potential biological activities[5-7]. Bioactivity of S-2-picolyl-β-N-(2-acetylpyrrole) dithiocarbazate Schiff base has been reported by Crouse et al[8]. Semi-empirical quantum chemical calculations are widely used methods for simulating IR spectra of the molecules[9-13]. Such simulations are indispensible tools to perform normal coordinate analysis. Modern vibrational spectroscopy would be unimaginable without involving them. In this study, we report the assignments of IR spectra, molecular geometry, HOMO-LUMO energy gap, molecular hardness (η), ionization energy (IE), electron affinity (EA), total energy and dipole moment of S-2-picolyl-β-N-(2-acetylpyrrole)dithiocarbazate Schiff base supported by semi-empirical calculations.

Methodology

Computational details: Intel based Pentium IV, 630, HT3.2 machine having 800 FSB, 1GB RAM, 7200rpm HDD was used to run all the calculations. Semi-empirical AM1 and PM3 quantum chemical calculations were carried out by the HyperChem^{TM} 8.0 Molecular Modeling program[14,15] with root mean square (RMS) gradient 0.1 k cal /Å mol using Polak-Ribiere algorithm.

Results and Discussion

Optimized Structure: The optimized structural parameters (bond lengths and bond angles) of S-2-picolyl-β-N-(2-acetylpyrrole) dithiocarbazate have been obtained by semi-empirical AM1 and PM3 methods. The optimized molecular geometry was obtained without symmetry constraints and it is presented in figure-1. Comparison for the calculated bond lengths and angles for the S-benzyldithiocarbazate with those of experimentally available x-ray[8] diffraction data are listed in the table 1. We examined the performance of semi-empirical AM1 and PM3 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 and PM3 are 0.958 and 0.966 respectively. It is evident that PM3 method gives most satisfactory correlation (CC=0.966) between experimental and calculated bond lengths. In the case of bond angle, correlation coefficients are 0.506 and 0.474 for AM1 and PM3 methods respectively. For bond angles none of the methods produce excellent correlation but out the two methods AM1 method gives slightly better results than PM3 methods (correlation coefficients, cc=0.506). The graph between experimental versus calculated bond length and bond angle are given in figure-2 and 3 respectively. From the theoretical values, we can find that most of the optimized bond angles are slightly larger than the experimental values. It is due to the fact that theoretical calculations of the molecules are performed in gaseous phase and the experimental results of molecules are recorded in solid phase. In spite of the differences, calculated geometric parameters represent a good approximation and they are the basis for calculating other parameters such as vibration frequencies and thermodynamic properties.

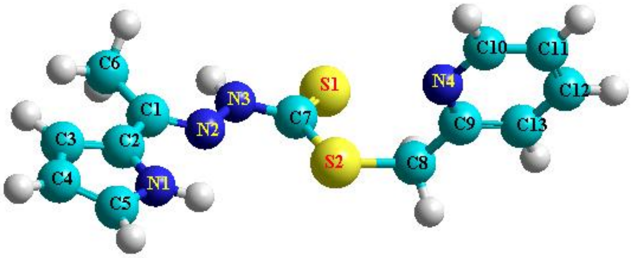

Figure-1
PM3 Optimized geometry of S-2-picolyl-β-N-(2-acetylpyrrole) dithiocarbazate

Table-1
Calculated and experimental selected bond lengths (Å) and angles (°) for S-2-picolyl-β-N-(2-acetylpyrrole) dithiocarbazate by AM1 and PM3 method

Bond lengths (Å)	Experimental	Calculated	
		AM1	PM3
S2-C7	1.751	1.717	1.777
S2-C8	1.815	1.761	1.821
S1-C7	1.699	1.595	1.643
N4-C10	1.389	1.345	1.315
N4-C9	1.422	1.355	1.357
N3-C7	1.308	1.389	1.391
N2-N3	1.382	1.334	1.388
N2-C1	1.314	1.318	1.314
C8-C9	1.504	1.494	1.494
C1-C2	1.426	1.462	1.448
C1-C6	1.474	1.497	1.493
Correlation coefficient (cc)	-	**0.958**	**0.966**
Bond Angles (°)			
C7-S2-C8	104.6	103.2	103.6
C1-N2-N3	124.3	121.9	122.6
C7-N3-N2	112.4	122.7	121.4
N4-C9-C8	120.1	120.5	120.5
N3-C7-S1	127.5	119.1	118.4
N3-C7-S2	117.8	115.6	116.6
C9-C8-S2	114.0	103.2	118.2
N2-C1-C2	124.8	118.0	116.4
N2-C1-C6	115.1	126.5	126.4
C1-C2-C6	120.1	115.4	117.2
Correlation coefficient (cc)	-	**0.506**	**0.474**

Vibration Frequencies: The experimental and calculated IR fundamental vibration modes for S-2-picolyl-β-N-(2-acetylpyrrole)dithiocarbazate by AM1 and PM3 semi-empirical methods are presented in table-2 and 4 respectively. Because of both symmetry and large size of the system, many vibrations are difficult to describe, in particular those involving the coupled movement of several parts of groups. Some vibrations identified in the solid phase experimental spectra could not be identified in the simulated counterpart and therefore, have been omitted. The differences between calculated and experimental frequencies are due to anharmonicity, intermolecular interaction, an approximation treatment of electron correlation effects and the limited basis sets. To examine the usefulness of the calculation method for IR, a linearity between the experimental[16] and calculated wave numbers has been derived by plotting the calculated versus experimental wave numbers and analyzing correlation coefficient value. Graphical correlation between experimental and calculated fundamental vibration frequencies are presented in figure-4. The cc values obtained for AM1 AND PM3 methods are 0.999 and 0.995 respectively. It is evident that AM1 method gives most satisfactory correlation (cc value=0.999) between experimental and calculated vibration frequencies.

Table-2
Experimental and calculated fundamental vibration frequencies of S-2-picolyl-β-N-(2-acetylpyrrole) dithiocarbazate by AM1 and PM3 methods

IR Bands	Experimental (cm^{-1})	Calculated	
		AM1	PM3
ν(N-H)	3084	3290	3113
ν(C=N)	1524	1617	1714
ν(N-N)	1050	1103	1043
ν(C=S)	1046	1036	1022
ν(CSS)	996	1005	969
Correlation coefficient (cc)	-	**0.999**	**0.995**

Frontier Molecular Orbital Analysis: The frontier orbital (HOMO and LUMO) of the chemical species are very important in defining its reactivity[17,18]. Higher value of HOMO of a molecule has a tendency to donate electrons to appropriate acceptor molecule with low energy, empty molecular orbitals. The highest occupied molecular orbital (HOMO) energies, the lowest unoccupied molecular orbital (LUMO) energies, hardness (η), ionization energy (IE), total energy and dipole moment have been calculated and are given in Table-3. Based on AM1 and PM3 optimized geometry, the total energy of the compound has been calculated by these methods, which are -112.851 and -101.950 au respectively. An electronic system with a larger HOMO-LUMO gap should be less reactive than one having smaller gap[19]. The ionization energy (IE) can be expressed through HOMO orbital energies as IE = $-E_{HOMO}$ and electron affinity (EA) can be expressed through LUMO orbital energies[20] as EA = $-E_{LUMO}$. The hardness (η) corresponds to the gap between the HOMO and LUMO orbital energies. The larger the HOMO-LUMO orbital energy gap, the harder the molecule. The hardness has been associated with the stability of the chemical system. In the present study, the HOMO-LUMO gap of the molecule is 7.555429 and 7.27366 eV for AM1 and PM3 respectively as shown in table 3, which clearly indicates that the molecule is very stable. The ionization potential values obtained by all the four theoretical methods also support the stability of the title molecule. The calculated dipole moment values show that the molecule is highly polar in nature. 3D plot of the HOMO, LUMO and the corresponding energy levels for S-2-picolyl-β-N-(2-acetylpyrrole) dithiocarbazate obtained by AM1 and PM3 methods are shown in figure-5 and 6 respectively.

Table-3
Comparison of HOMO-LUMO energy, hardness (η), ionization energy (IE), electron affinity (EA), total energy and dipole moment of S-2-picolyl-β-N-(2-acetylpyrrole)dithiocarbazate obtained by AM1 and PM3 methods

Energies	**Semi empirical Methods**	
	AM1	**PM3**
ϵ_{HOMO} (eV)	-8.369117	-8.59651
ϵ_{LUMO} (eV)	-0.813688	-1.32285
$\epsilon_{HOMO} - \epsilon_{LUMO}$	7.555429	7.27366
Hardness(η) = ½($\epsilon_{HOMO} - \epsilon_{LUMO}$)	3.777714	3.63683
IE = $-\epsilon_{HOMO}$	8.369117	8.59651
EA = $-\epsilon_{LUMO}$	0.813688	1.32285
Total Energy (au)	-112.851	-101.950
Dipole moment (Debyes)	3.384	4.033

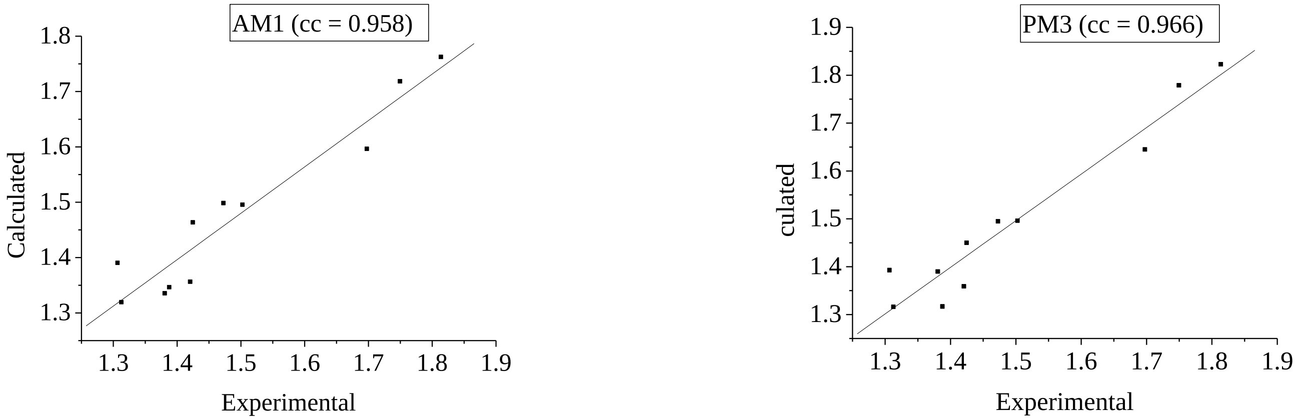

Figure-2
Graphical correlations between the experimental and calculated bond lengths of S-2-picolyl-β-N-(2-acetylpyrrole) dithiocarbazate obtained by AM1 and PM3 methods (CC= correlation coefficient)

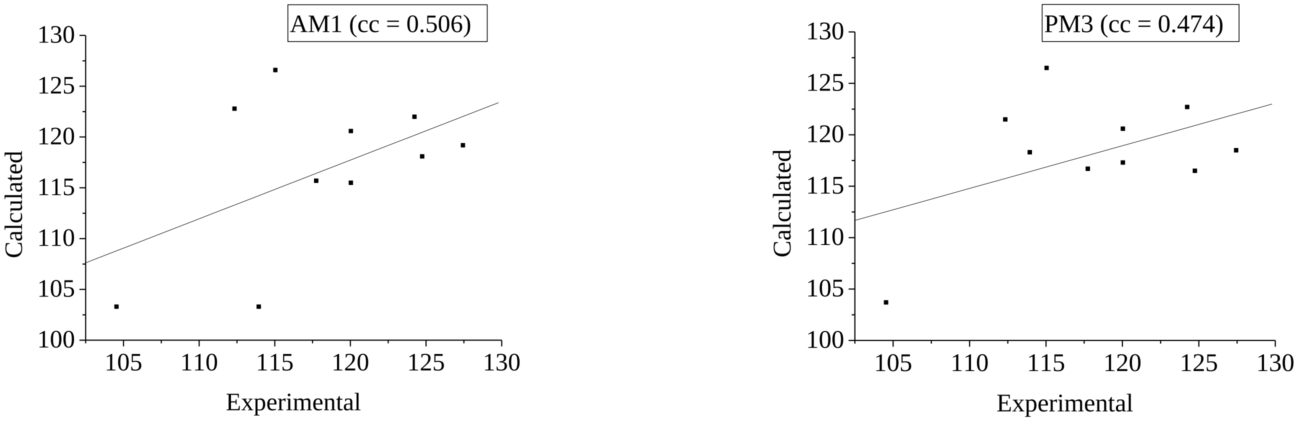

Figure-3
Graphical correlations between the experimental and calculated bond angles of S-2-picolyl-β-N-(2-acetylpyrrole) dithiocarbazate obtained by AM1 and PM3 methods (CC= correlation coefficient)

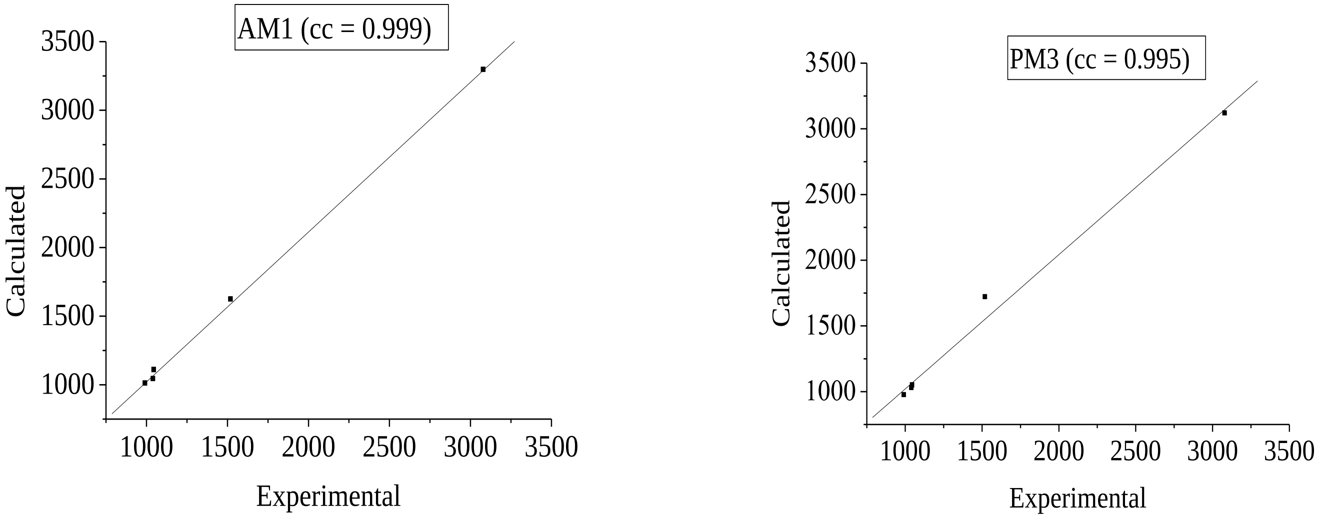

Figure-4
Graphical correlations between the experimental and calculated fundamental vibration frequencies of S-2-picolyl-β-N-(2-acetylpyrrole)dithiocarbazate obtained by AM1 and PM3 methods (CC= correlation coefficient)

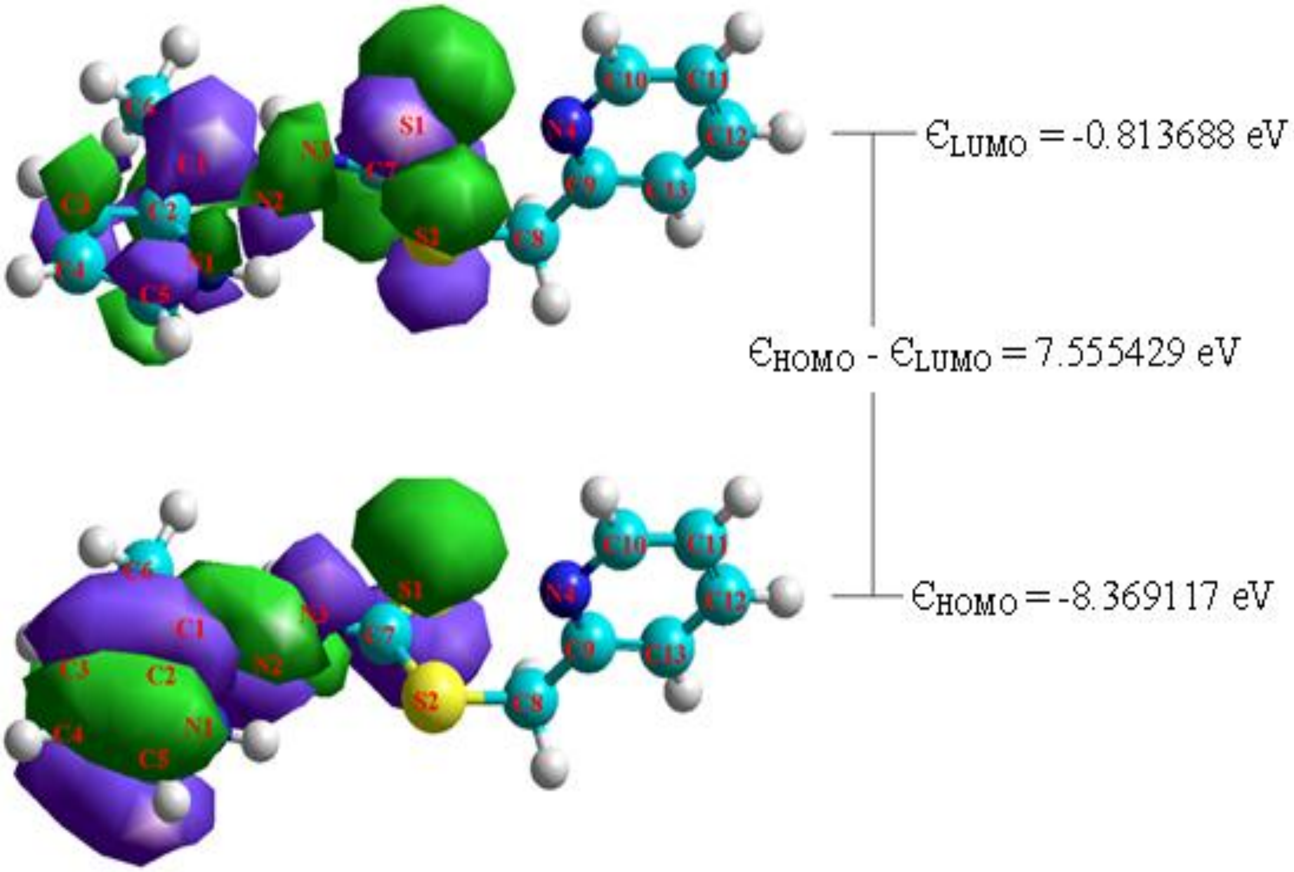

Figure-5
Molecular orbital surface and HOMO-LUMO energy gap for HOMO and LUMO of S-2-picolyl-β-N-(2-acetylpyrrole) dithiocarbazate obtained by AM1 semi-empirical method

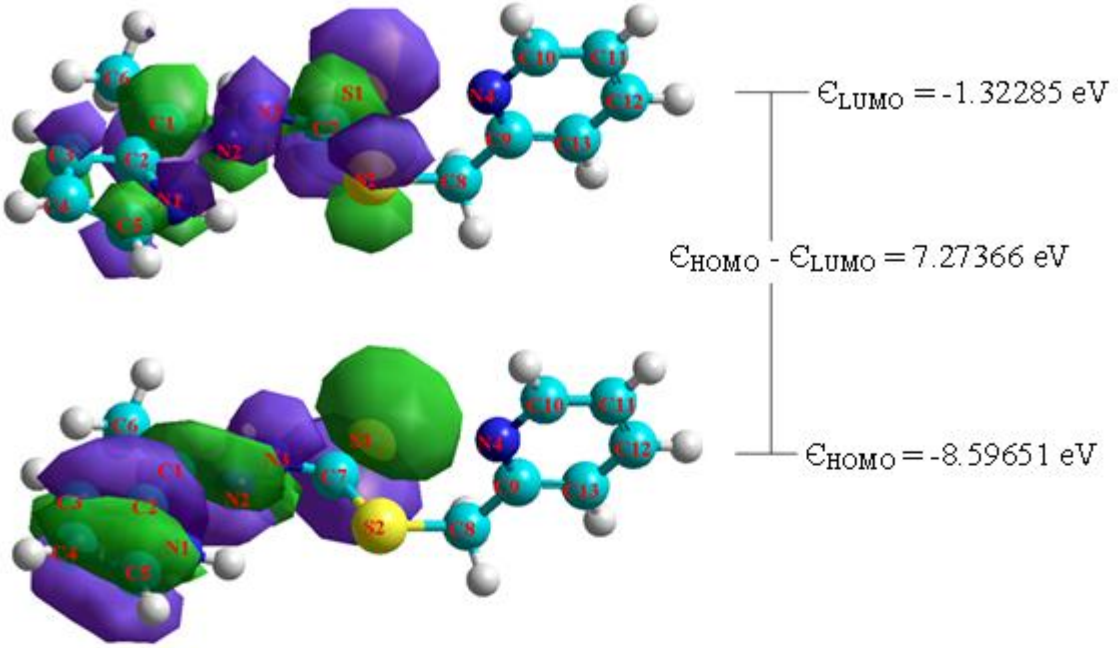

Figure-6
Molecular orbital surface and HOMO-LUMO energy gap for HOMO and LUMO of S-2-picolyl-β-N-(2-acetylpyrrole) dithiocarbazate obtained by PM3 semi-empirical method

Conclusion

Semi-empirical AM1 and PM3 calculations have been carried out on the molecular geometry, vibration frequencies, HOMO-LUMO energy gap, molecular hardness, ionization energy, electron affinity, total energy, and dipole moment. A good matching between calculated and experimental vibration frequencies was observed by both theoretical methods (correlation coefficients more than 0.99). Any discrepancy noted between the observed and the calculated frequencies is due to the fact that calculations have been actually done on the single molecule in the gaseous state contrary to the experimental values recorded in the presence of intermolecular interactions. Therefore, the assignments made with minimal basis set and reasonable deviations from the experimental values seem to be correct. The calculated HOMO-LUMO orbital energies can be used to estimate the ionization energy, molecular hardness and other physical parameters semiquantitatively. HOMO-LUMO energy gap, molecular hardness, ionization energy, electron affinity and total energy are very important physical parameters for chemical reactivity and biological activities of the studied compound.

Acknowledgements

One of the authors Rajeev Singh acknowledges M. P. Council of Science and Technology, Bhopal for the financial support as Research Project. Authors are thankful to Dr. B. K. Singh, The Director, Institute of Information Technology and Management, Gwalior (India) for providing laboratory facilities.

References

1. Ray S., Mandal T.N., Barik A.K., Pal S., Gupta S., Hazara A., Butcher R. J., Hunter A. D., Zeller M. and Kar S. K.; Metal complexes of pyrimidine derived ligand – Synthesis, characterization and X-ray crystal structures of Ni(II), Co(III) and Fe(III) complexes of Schiff base ligand derived from S-methyl/benzyl dithiocarbazate and 2-S-methylmercapto - 6 - methylpyrimidine-4-carbaldehyde, *Polyhedron*, **26,** 2603 **(2007)**

2. Konstantinos Tampouris, Silverio Coco, Athanasios Yannopoulos, Spyros Koinis, Palladium(II) complexes with *S*-benzyldithiocarbazate and *S*-benzyl-*N*-isopropylidenedithiocarbazate; Synthesis, spectroscopic properties and X-ray crystal structures, *Polyhedron*, **26,** 4269 **(2007)**

3. Ali M. Akbar, Hjh Junaidah Hj Abu Bakar, A.H. Mirza S.J. Smith L.R. Gahan Paul V., Bernhardt; Preparation, spectroscopic characterization and X-ray crystal and molecular structures of nickel(II), copper(II) and zinc(II) complexes of the Schiff base formed from isatin and *S*-methyldithiocarbazate (Hisa-sme), *Polyhedron*, **27,** 71 **(2008)**

4. N.K. Singh, P. Tripathi, M.K. Bharty, A.K. Srivastava, Sanjay Singh, R.J. Butcher; Ni(II) and Mn(II) complexes of NNS tridentate ligand N′-[(2-methoxyphenyl) carbonothioyl] pyridine-2-carbohydrazide (H_2mcph):

Synthesis, spectral and structural characterization, *Polyhedron,* **29 (8),** 1993 **(2010)**

5. Hossian Mir Ezharul, Jairpa Bengum, Mohammad Nurul Alam, Mohamed Nazimuddin and Mohammad Akbar Ali.; Synthesis, characterization and biological activities of some nickel (II) complexes of tridentate NNS ligand formed condensation of 2-acetyl- and2- benzoylpyridine with S-alkyldithiocarbazate, *Transi. Met. Chem.,* **18 (5),** 497 **(1993)**

6. Morya M. R., Khurana S., Shailendra S., Azam A., Zhang W., Rehdar D.; Synthesis, Characterisation and Antiamoebic Studies of Dioxovanadium(V) Complexes Containing ONS Donor Ligands Derived from *S*-Benzyldithiocarbazate, *Eur. J. Inorg. Chem.*, 1966 **(2003)**

7. Pavan Fernando R., Pedro I.da S. Maia, Sergio R.A. Leite, Victor M. Deflon, Alzir A. Batista, Daisy N. Sato, Scott G. Franzblau, Clarice Q.F. Leite; Thiosemicarbazones, semicarbazones, dithiocarbazates and hydrazide/hydrazones: Anti – Mycobacterium tuberculosis activity and cytotoxicity, *Polyhedron,* **27 (17),** 3433 **(2008)**

8. Karan A Crouse, Kar-Beng Chew, M. T. H. Tarafeder, A. Kasbollah, A. M. Ali, B. M. Yamin, H.-K. Fun; Synthesis, characterization and bioactivity of S-2-picolyldithiocarbazate (S2PDTC), some of its Schiff bases and their Ni(II) complexes and X-ray structure of S-2-picolyl-β-N-(2-acetylpyrrole)dithiocarbazate, *Polyhedron,* **23,** 161 **(2004)**

9. Kumar D., Agrawal M. C., Rajeev Singh; Theoretical Study of Pyridine-2-Amidoxime by Semi-empirical Methods, *Oriental J. Chem.* **22(1),** 67 **(2006)**

10. Kumar D., Agrawal M.C., Rajeev Singh; Computational Study of Benzaldehyde Thiosemicarbazone, *Mat. Sci. Res. Ind.* **3(1a),** 37 **(2006)**

11. Kumar D., Agrawal M. C., Rajeev Singh; Theoretical Investigation of IR and Geometry of the S-benzyl-β-N-(2-furylmethylketone)dithiocarbazate Schiff base by Semi-Empirical Methods, *Asian J. Chem.* **19 (5),** 3703 **(2007)**

12. Arora Kishor, Kumar D., Kiran Burman, Sonal Agnihotri, Bhoop Singh; Theoretical studies of 2-nitrobenzaldehyde and furan-2-carbaldehyde Schiff base of 2-amino pyridine, *J. Saudi Chem. Soc.* **15,** 161 **(2011)**

13. Rajeev Singh, Y. C. Goswami, Ranjana Goswami; Semi-empirical & Experimental Investigation on Coordination behavior of S-methyl –β -N-(4-methoxyphenylmethyl)methylenedithiocarbazate Schiff base towards Co(II), Ni(II) and Cu(II) metal ions; *Journal of Chemistry,* **2**, 1, **(2011)**

14. HyperChem™ Professional Release 8.0 for Window Molecular Modeling System, Dealer: Copyright © **2002** Hypercube, Inc **(2002)**

15. Stewart J. J. P., Lipkowinz, K. B. Boyal, D. B. (Eds.); Reviews in Computational Chemistry, V.C.H. **1**, 45 **(1990)**

16. Bingham Richard C., Dewar M. J. S., Lo D. H.; Ground state of molecules. XXV. MINDO/3, Improved version of the MINDO Semi-empirical SCF-MO method, *J. Am. Chem. Soc.* **97 (6),** 1285 **(1975)**

17. Fukui K., Yonezaw T., Shingu; A Molecualr Orbital Theory of Reactivity in Aromatic Hydrocarbons, *J. Chem. Phy.* **20,** 722 **(1952)**

18. Huizar Luis Humberto-Mendoza and Reyes Clara Hilda Rios; Chemical Reactivity of Atrazine Employing the Fukui Function, *J. Mex. Chem. Soc.* **55(3),** 142 **(2011)**

19. Kurtaran Raif, Sinem O., Akin Azizoglu; Experimental and Computational study on [2,6-bis(3,5-dimethyl-N-pyrazolyl) pyridine] - (dithiocyanato) mercury (II), *Polyhedron,* **26,** 5069 **(2007)**

20. Dixon A. David, Chang-Guo Zhan, Jeffrey A. Nicholos; Ionization Potential, Electron Affinity, Electronegativity, Hardness, and Electron Excitation Energy: Molecular Properties from Density Functional Theory Orbital Eneries, *J. Phys. Chem. A.* **107,** 4184 **(2003)**