Volume : 4 | Issue : 10 | Special Issue Oct- 2015 • ISSN No 2277 - 8179

Molecular structure, vibrational spectroscopic and frontier molecular orbital studies of S-methyl β-N-(4-methoxyphenylmethyl)methylenedithiocarbazate and S-methyl β-N-(4-chlorophenylmethyl) methylenedithiocarbazate Schiff bases by quantum-chemical investigations

Chemistry

KEYWORDS: Semi-empirical methods; AM1; PM3; Vibration modes; Correlation coefficient

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ABSTRACT

In this study S-methyl β-N-(4-methoxyphenylmethyl)methylenedithiocarbazate andS-methyl β-N-(4-chlorophenylmethyl)methylenedithiocarbazate Schiff bases have 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. A good correlation has been observed between experimental and calculated values for vibration modes.

Introduction

Schiff bases derived from S-alkyl/aryl dithiocarbazate have been extensively studied over last decade (Ray et al., 2007; Konstantinos Tampouris et al., 2007; Ali et al., 2008; N. K. Singh at al., 2010). The attention of on these compounds arose mainly due to their potential biological activities (Hossian et al., 1993; Morya et al., 2003; Pavan Fernando R et al., 2008). Semi-empirical-quantum chemical calculations are widely used methods for simulating IR spectra of the molecules (Kumar et al., 2006a,b, 2007; Arora et al., 2011). 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 quantum-chemical investigations the Schiff bases of S-methylditiocarbazate by using AM1 and PM3 computational semi-empirical methods and compare with experimental data.

Experimental

General procedure for the synthesis of Schiff bases Ethanolic solution of appropriate ketone and S-methyl dithiocarbazate were mixed in 1:1 molar ratio. The mixture was made homogeneous by adding little more ethanol and then heated (refluxed) on a water bath for about 5-6 hrs. and then left to cool. The solid product was separated out which was filtered off and then recrystallized from ethanol. The recrystallized solid mass was dried in vacuum desiccator over P_4O_{10}.

For Schiff base I (MeSmdtCz: $C_{11}H_{14}N_2OS_2$): **Elemental analysis**; C:51.94 %, H: 5.55 %, N: 11.01% & S: 25.21 %. **IR**; n~/cm^{-1}: 3176 br and 2916 m (N-H), 1600 s (C=N), 1473 s (C=C), 1337 m (C-N), 1283 m (N-N), 956 s (C=S), 833 m (N-C-S). **^{1}H NMR** (DMSO-d_6); : 1.6 (s 0.6H); 2.3(s, 3H), 2.6(s, 3H), 3.8(s, 3H), 6.9(d, 2H), 7.7(d, 2H), & 9.9(s, 0.4H) ppm. **MS**; *m/z* (I_r/%): 255(100%), 254(23.3%), 207(72%),148(90%), 134(13%), & 133(7%), 107(5%).

For Schiff base II (ClSmdtCz: $C_{10}H_{11}ClN_2S_2$): **Elemental analysis**; C: 46.42 %, H: 4.25%, N: 10.38% & S: 25.21%. **IR**; /cm^{-1}: 3166 br and 2910 m (N-H); 1602s (C=N), 1474 s (C=C), 1335 m (C-N), , 1282 m (N-N), 957 s (C=S), 832 m (N-C-S). ^{1}H NMR (DMSO-d_6); : 2.3(s, 3H), 2.6(s, 3H), 7.3(d, 2H), 7.7(d, 2H), 11.57(s, 1H) ppm. MS; *m/z* (I_r/%): 258(15%), 259(78.37%), 261(32.43%), 211(50%), 213(17.5%), 152(100%), & 154(66%).

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™ 8.0 Molecular Modeling program (Stewart et al., 1990) with root mean square (RMS) gradient 0.1 k cal / mol using Polak-Ribiere algorithm.

Results and discussion

The Schiff bases derived from S-alkyl/aryldithiocarbazate have a thione group (C=S) and a proton adjacent to the thione group. It has been stated that the thione group (C=S) is relatively unstable in monomeric form and tends to form a more stable C-S single bond by enethiolization, if there is at least one hydrogen atom adjacent the thione (C=S) bond (Mayer R, 1967). The IR spectra of both the Schiff bases do not display (S-H) at *ca.* 2570 cm^{-1}, but (N-H) modes are present at *ca.* 3175 and 2917 cm^{-1}, indicating that the thione form predominates in the solid state. However, ^{1}H-NMR spectra in $CDCl_3$ of the Schiff base *I* in $CDCl_3$ supports the fact that the thione form (I) and the thiolo tautomeric form (II) are in equilibrium in solution by the presence of proton –N=C-SH (chemical shift 1.6) as shown in Fig. 2. The calculated fractions of the protons of –NH-C=S and –N=C-SH are *ca.* 0.4 and 0.6 respectively. This result indicates that in the solution Schiff bases I exists in thione and thiolo forms in the ratio of 4:6 respectively. But in case of Schiff base II, the ^{1}H NMR spectrum does not display the signal due to –SH proton, indicating that this Schiff base exists in thione form even in the solution.

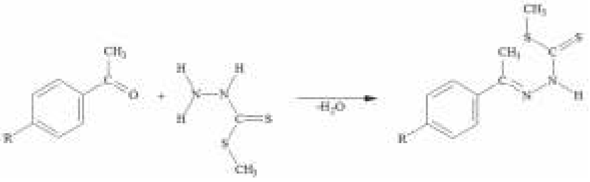

Fig. 1. Synthesis of Schiff bases.

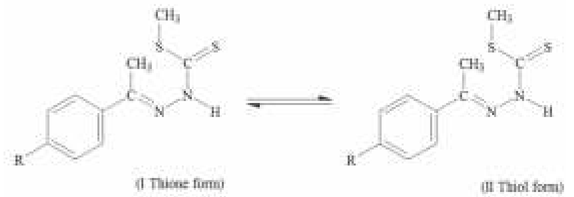

Fig. 2. Tautomeric forms of the Schiff bases (R = OCH_3/Cl).

Optimized geometry

The optimized structural parameters have been obtained by semi-empirical AM1 and PM3 methods and are given in Table 1 and 2 respectively . The optimized molecular geometries were obtained without symmetry constraints. The labeling of atoms in the Schiff base I and II are presented in Fig. 3 and 4 respectively.

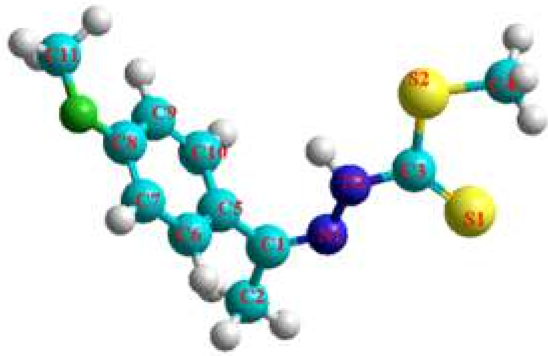

Fig. 3. MeSmdtCz (Schiff base I).

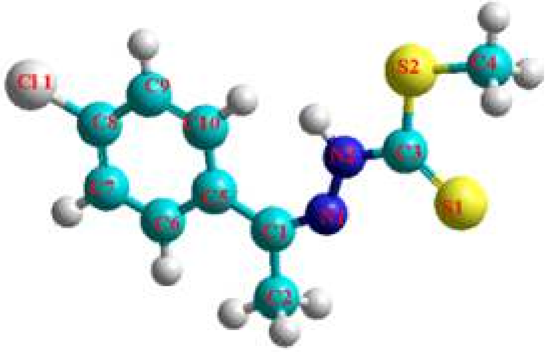

Fig. 4. ClSmdtCz (Schiff base II).

Table 1. Calculated bond lengths of MeSmdtCz and ClSmdtCz by AM1 and PM3 semi-empirical methods

	MeSmdtCz		ClSmdtCz	
Bond lengths	AM1	PM3	AM1	PM3
C1-C2	1.1515	1.4968	1.4986	1.4924
C1-N1	1.3109	1.3044	1.3115	1.3036
N1-N2	1.3269	1.3952	1.3363	1.3909
N3-C3	1.3908	1.4089	1.3886	1.4058
S1-C3	1.5602	1.6043	1.5624	1.6048
S2-C3	1.7614	1.8052	1.7643	1.8065
S2-C4	1.7536	1.8008	1.7518	1.8010
C1-C5	1.4753	1.4764	1.4782	1.4790
C5-C6	1.4045	1.3992	1.3998	1.3965
C6-C7	1.3902	1.3853	1.3932	1.3900
C7-C8	1.4039	1.4051	1.3989	1.3931
C8-C9	1.3991	1.3994	1.3988	1.3935
C9-C10	1.3911	1.3884	1.3931	1.3891
C5-C10	1.4091	1.3973	1.3996	1.3970
C8-O1	1.3783	1.3774	1.6985 (C8-Cl 1)	1.6825 (C8-Cl 1)
C11-O1	1.4238	1.4069	-	-

Table 2. Calculated bond angles of MeSmdtCz and ClSmdtCz by AM1 and PM3 semi-empirical methods

	MeSmdtCz		ClSmdtCz	
Bond angles	AM1	PM3	AM1	PM3
C2-C1-N1	112.283	116.582	119.193	118.386
C1-N1-N2	127.831	123.569	121.307	122.315
N1-N2-C3	121.198	118.950	121.674	120.016
N2-C3-S1	129.009	127.284	128.246	127.657
N2-C3-S2	108.623	108.361	108.252	108.136
S1-C3-S2	122.368	124.264	123.497	124.142
C3-S2-C4	102.997	104.822	103.931	104.740
N1-C1-C5	133.168	127.534	126.404	125.137
C2-C1-C5	114.547	115.881	114.402	116.472
C1-C5-C6	124.613	122.585	120.177	120.532
C1-C5-C10	118.615	118.197	120.094	119.270
C5-C6-C7	122.032	120.681	120.315	119.914
C6-C7-C8	119.795	119.492	119.557	119.546
C7-C8-C9	119.613	120.424	120.513	120.878
C8-C9-C10	119.492	119.168	119.596	119.476
C5-C10-C9	122.296	121.038	120.290	120.007
C7-C8-O1	115.294	114.048	119.742 (C7-C8-Cl 1)	119.563 (C7-C8-Cl 1)
C9-C8-O1	125.094	125.528	119.745 (C9-C8-Cl 1)	119.559 (C9-C8-Cl 1)
C8-O1-C11	116.228	117.607		

Vibration Frequencies

The experimental and calculated IR fundamental vibration modes for MeSmdtCz and ClSmdtCz by AM1 and PM3 semi-empirical methods are given in Table 3 and 4 respectively. 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 (Bingham et al., 1975) 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 Fig. 5 and 6 for Schiff base I and Schiff base II respectively. In case of Schiff base I, the correlation coefficient (cc) values obtained for AM1 and PM3 semi-empirical methods are 0.99881 and 0.99922 respectively. But in case of Schiff base II, the correlation coefficient (cc) values for AM1 and PM3 semi-empirical methods are 0.99954 and 0.99766 respectively It is evident that for Schiff base I, PM3 semi-empirical method gives more satisfactory correlation (cc=0.99922) than AM1 method, whereas for Schiff base II, AM1 semi-empirical method gives more satisfactory correlation (cc=0.99954) than PM3 method between experimental and calculated vibration frequencies as shown in Fig. 5 and 6.

Table 3. Experimental and calculated IR spectral frequencies of MeSmdtCz by AM1 and PM3 semi-empirical methods and their assignments.

Experimental (υ in cm^{-1})	Calculated in (υ in cm^{-1})		Assignments
	AM1	PM3	
3176 br,	3193,	3263,	υ(N-H) stretching
2916 m	3048	3010	
1600 s,	1625,	1626,	υ(C=N) coupled with N-H in plane and
1473 s	1526	1472	υ(C=C) aromatic ring
1418 s,	1437,	1425,	υ(C-N) stretching/C-H bending of C-H
1337 m	1409	1318	stretching, S-methyl, methyl linked with
			azomethine carbon
1283 m	1256	1278	υ (N-N) stretching
1099 m,	1115,	1109,	N-H out of plane deformation/Ring breathing
1059 m	1079	1026	of benzene
956 s	910	930	υ(C=S) stretching vibration
833 m	877	863	N-C-S stretching vibration
740 w	773	753	Out of plane ring deformation mode
625 w,	629	692	Out of plane bending of ring
Correlation coefficient (cc)	**0.99881**	**0.99922**	

Table 4. Experimental and calculated IR spectral frequencies of ClSmdtCz by AM1 and PM3 semi-empirical methods and their assignments.

Experimental (υ in cm^{-1})	Calculated in (υ in cm^{-1})		Assignments
	AM1	PM3	
3166 br,	3185,	3066,	υ(N-H) stretching
2910 m	2976	3010	
1602 s,	1629,	1600,	υ(C=N) coupled with N-H in plane and
1474 s	1520	1525	υ(C=C) aromatic ring
1419 s,	1426,	1440,	υ(C-N) stretching/C-H bending of C-H
1335 m	1354	1396	stretching /S-methyl, methyl linked with azomethine carbon
1282 m	1325	1389	υ (N-N) stretching
1089 m,	1099,	1118,	N-H out of plane deformation/Ring breathing
1058 m	1079	1095	of benzene
957 s	928	956	υ(C=S) stretching vibration
832 m	896	869	N-C-S stretching vibration
779 w	799,	751,	Out of plane ring deformation mode
698 m	701	688	
625 w,	635	633	Out of plane bending of ring
Correlation coefficient (cc)	**0.99954**	**0.99766**	

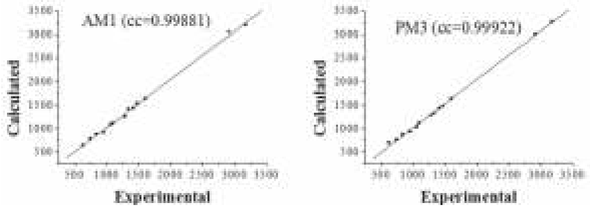

Fig. 5. Graphical correlations between the experimental and calculated vibration frequencies of MeSmdtCz obtained by AM1 and PM3 semi-empirical methods (cc= correlation coefficient).

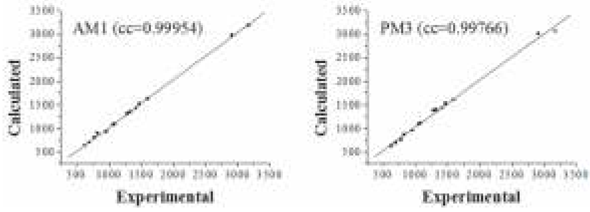

Fig. 6. Graphical correlations between the experimental and calculated vibration frequencies of ClSmdtCz obtained by AM1 and PM3 semi-empirical methods (cc = correlation coefficient).

Frontier Molecular Orbital Analysis

The frontier molecular orbital (HOMO and LUMO) of the chemical species are very important in defining its reactivity (Fukui et al., 1952; Huizar and Reys, 2011). Higher value of HOMO of a molecule has a tendency to donate electrons to appropriate acceptor molecule with low energy, empty molecular orbitals. The various parameters of frontier molecular orbital analysis for Schiff base I and Schiff base II have been calculated and are given in Table 5. An electronic system with a larger HOMO-LUMO gap should be less reactive than one having smaller gap (Kurtaran et al., 2007). In the present study, the HOMO-LUMO gap of Schiff base I is 7.71530 and 7.51723 eV for AM1 and PM3 respectively. In case of Schiff base II the HOMO-LUMO gap is 7.88010 and 7.52655 eV for AM1 and PM3 respectively, as shown in Table 7, which clearly indicates that both the Schiff base molecules are very stable. The ionization potential values obtained by AM1 and PM3 theoretical methods also support the stability of both the Schiff base molecules. The calculated dipole moment values show that the Schiff base molecules are highly polar in nature. 3D plots of the HOMO-LUMO and the corresponding energy levels for Schiff base I and Schiff base II obtained by and PM3 semi-empirical method are shown in Fig. 7 and 8 respectively.

Table 5. Comparison of various parameters for MeSmdtCz & ClSmdtCz obtained by semi-empirical AM1 and PM3 methods.

Energies	Schiff base *I*		Schiff base *II*	
	AM1	PM3	AM1	PM3
ϵ_{HOMO} (eV)	-8.53206	-8.77303	-8.69808	-8.84451
ϵ_{LUMO} (eV)	-0.81676	-1.25580	-0.81107	-1.31796
$\Delta\ \epsilon_{HOMO} - \epsilon_{LUMO}$	7.71530	7.51723	7.88010	7.52655
Hardness(η) = ½($\epsilon_{HOMO} - \epsilon_{LUMO}$)	3.85765	3.75861	3.94005	3.763275
IE = -ϵ_{HOMO}	8.53206	8.77303	8.69808	8.84451
EA = -ϵ_{LUMO}	0.81676	1.25580	0.81107	1.31796
Total Energy (au)	-100.03148	-92.13203	-95.78975	-86.93400
Dipole moment (Debyes)	2.857	4.067	1.251	3.101

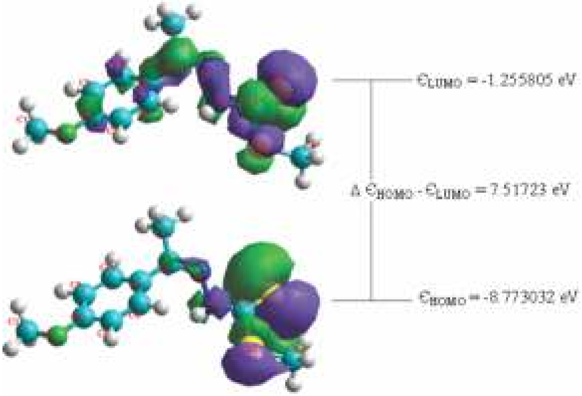

Fig. 7. Molecular orbital surface and HOMO-LUMO energy gap for HOMO and LUMO of MeSmdtCz obtained by PM3 semi-empirical method.

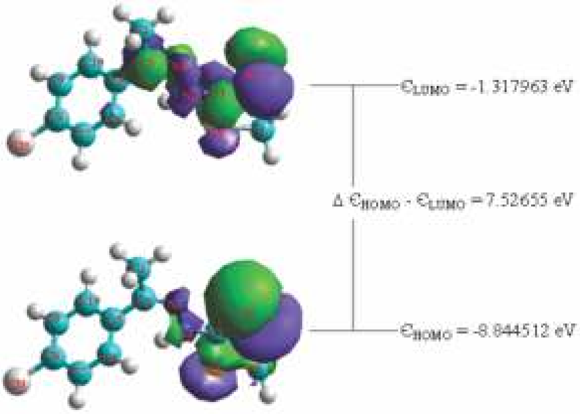

Fig. 8. Molecular orbital surface and HOMO-LUMO energy gap for HOMO and LUMO of ClSmdtCz by PM3 semi-empirical methods.

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.

We are greatly acknowledge the financial support for this work by the Madhya Pradesh Council of Science & Technology (MPCST), Bhopal for providing research grant no. 1076/CST/R&D/2012.

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