Asian Journal of Chemistry; Vol. 24, No. 12 (2012), 5522-5524

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in

Synthesis, Spectral and Quantum-Chemical Calculations on 5-Bromo-4-hydroxy-3-methoxy-2-nitro Benzaldehyde Schiff Base of S-Benzyldithiocarbazate†

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AJC-11684

A new Schiff base has been synthesized by the 1:1 condensation of 5-bromo-4-hydroxy-3-methoxy-2-nitro benzaldehyde and S-benzyldithiocarbazate. The structure of this Schiff base was determined by FT-IR and ^{1}H NMR and mass spectroscopic data. The synthesized Schiff base has been subjected to theoretical studies by using Semi-empirical AM1, PM3, MNDO and MNDO/d quantum-chemical methods. The vibration frequencies, HOMO-LUMO energy gap, molecular hardness (η), ionization energy, electron affinity, total energy and dipole moment and molecular electrostatic potential surface 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.

Key Words: Semi-empirical methods, Vibration modes, Molecular electrostatic potential surface, Hardness.

INTRODUCTION

Schiff bases derived from S-alky/aryl esters of dithiocarbazic acid[1-3] and some of their metal complexes have beeen found to exhibit interesting physico-chemical properties[4,5] and biological activities[6,7]. In the present investigation we have synthesized the 5-bromo-4-hydroxy-3-methoxy-2-nitro benzaldehyde Schiff base of S-benzyldithiocarbazate and the synthesized Schiff base was characterized with the aid of IR, NMR and mass spectral analysis. The synthesized Schiff bases was also undertaken to theoretically characterize by quantum chemical AM1, PM3, MNDO and MNDO/d semi-empirical investigations. Electronic structure, spectral studies and geometry optimization are important tools to theoretically characterize these compounds[8-12].

EXPERIMENTAL

All chemicals were of either BDH/Merck (A.R.) grade and were used as such without further purification. The IR spectrum in KBr pellets (500-4000 cm^{-1}) was recorded using Shimadzu 8201 PC FT-IR spectrophotometer. The ^{1}H NMR spectrum in $CDCl_3$ was recorded on Bruker DRX-300 FT NMR. The FAB mass spectra of the compound was recorded on a JEOL SX 102/DA-6000 mass spectrometer/Data system using Argon/Xenon (6kV, 10 mA) as FAB gas.

Synthesis of 5-bromo-4-hydroxy-3-methoxy-2-nitro benzaldehyde Schiff base of S-benzyldithiocarbazate: S-benzyldithiocarbazate (0.02 mol) dissolved in hot absolute ethanol (30-40 mL) was added to the solution of an equimolar amount of carbonyl compound in hot absolute ethanol (20 mL). The mixture was heated for 5 h and then cooled to room temperature. The product was filtered, washed with absolute ethanol, recrystallized from absolute ethanol and dried over silica gel. Yield, 58 %, m.p. 169 ºC. IR (KBr, cm^{-1}): 1029 ν(C=S), 1068 ν(N-N), 1365 ν(C-N), 1523 ν(C=N), 3267 ν(N-N); ^{1}H NMR ($CDCl_3$), δ: 4.02 (s, 3H), 4.59 (s, 2H), 7.39-7.45 (m, 6H), 7.66 (s, 1H), 7,95 (s, 1H) ppm; Mass, *m/z*: 458 (98 %), 459 (25 %), 456 (100 %), 334 (7 %) and 332 (9 %).

Computational details: Quantum chemical calculations were carried out by semi-empirical AM1 and PM3 methods by using hyperchem 8.0 software[13] Intel based Pentium IV, 630, HT 3.2 machine having 800 FSB, 2 GB RAM, 7200 rpm HDD was used to run all the programmes.

†Presented at International Conference on Global Trends in Pure and Applied Chemical Sciences, 3-4 March, 2012; Udaipur, India

RESULTS AND DISCUSSION

The title Schiff base has 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[14] (Fig. 1). The IR spectra of the Schiff base dose not display ν(S-H) at *ca*. 2570 cm^{-1}, but ν(N-H) modes are present at *ca*. 3267 cm^{-1}, indicating that the thione form predominates in the solid state (Fig. 1). The ^1H NMR spectra of the Schiff base in $CDCl_3$ exhibit the -NH proton signal at 10.15 ppm, indicating that even in solution it exists as thione form. The optimized molecular geometry was obtained without symmetry constraints and is given in Fig. 2.

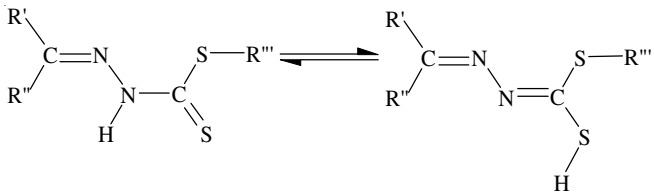

Fig. 1. Tautomeric forms (a) thione form (b) thiolo form

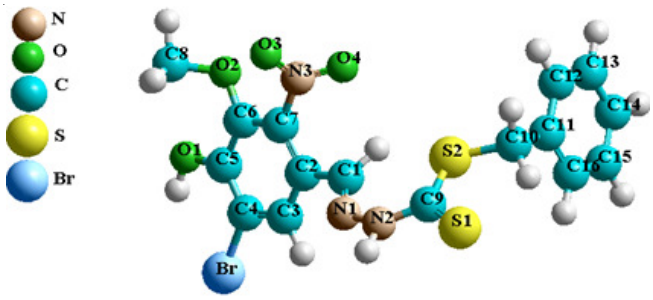

Fig. 2. Optimized molecular structure of the title Schiff base

Quantum-chemical Semi-empirical investigations on vibration frequencies: The experimental and calculated IR fundamental vibration frequencies for the 5-bromo-4-hydroxy-3-methoxy-2-nitro benzaldehyde Schiff base of S-benzyl-dithiocarbazate by AM1, PM3, MNDO and MNDO/d methods are presented in Table-1. To examine the usefulness of the calculation method for IR, a linearity between the experimental and calculated wave numbers has been derived by plotting the calculated *versus* experimental wave numbers and analyzing correlation coefficient value[15]. The correlation coefficient (cc) values obtained for AM1, PM3, MNDO and MNDO/d methods are 0.999, 0.999, 0.998 and 0.998 respectively. It is evident that AM1 and PM3 method gives more satisfactory correlation (cc value = 0.999) between experimental and calculated vibration frequencies. A good matching between calculated and experimental values was observed in most of the cases.

Molecular electrostatic potential: The molecular electrostatic potential is related to the electronic density and is a very useful descriptor for determining sites for electrophilic attack and nucleophilic reactions as well as hydrogen-bonding interactions[16,17]. To predict reactive sites for electrophilic and nucleophilic attack for the title molecule, molecular electrostatic potential were calculated at AM1, PM3, MNDO and MNDO/d optimized geometries. The presented molecular electrostatic potential surface, an overlying of the electrostatic potential (the attraction or repulsion of a positive charge for a molecule) is valuable for describing overall electronic distribution as well as anticipating sites for electrophilic attack. The red colour in the Fig. 3 represents negatively charged areas of surface (*i.e.* those areas where attack of an electrophile is most favourable) and blue colour represents positively charged areas. As can be seen from the Fig. 3, there are six possible sites in the compound for electrophilic attack. The negative region is localized on N1, S1, O1, O2, O3 and O4. However, maximum negative region is localized on O3 and O4.

TABLE-1
EXPERIMENTAL AND CALCULATED IR SPECTRAL FREQUENCIES OF TITLE SCHIFF BASE

Experimental freq. (cm^{-1})	Semi empirical methods			
	AM1	PM3	MNDO	MNDO/d
3267	3386	3285	3391.92	3340.71
1524	1654	1606	1672.40	1638.15
1473	1595	1518	1515.53	1513.61
1416	1481	1456	1479.45	1467.61
1365	1399	1367	1392.68	1371.14
1296	1358	1300	1315.51	1355.08
1068	1136	1097	1106.66	1165.53
1029	1030	1029	1071.08	1109.33
929	998	946	958.74	940.77
709	748	722	724.44	755.18
621	677	635	694.14	661.22
Correlation coefficient (cc)	0.999	0.999	0.998	0.998

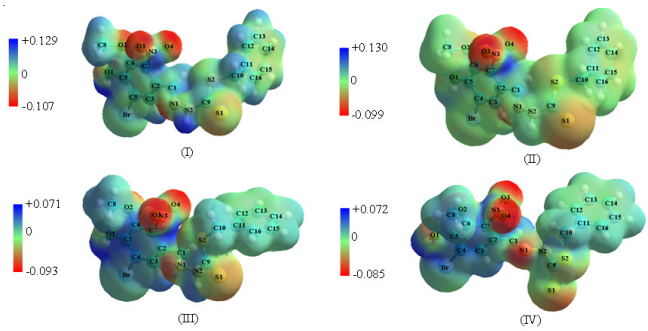

Fig. 3. Molecular electrostatic potential surface diagram of the title Schiff base obtained from AM1 (I), PM3 (II), MNDO (III) and MNDO/d (IV)

Frontier molecular orbital analysis of 5-bromo-4-hydroxy-3-methoxy-2-nitro benzaldehyde Schiff base of S- benzyldithiocarbazate: The frontier orbital (HOMO and LUMO) of the chemical species are very important in defining its reactivity[18,19]. 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 energies, the lowest unoccupied molecular orbital energies, hardness (η), ionization energy, total energy and dipole moment have been calculated and are given in Table-2. Based on AM1, PM3, MNDO and MNDO/d optimized geometry, the total energy of the compound has been calculated by these methods, which are -179.340819, -165.069986, -182.019135 and -175.383586 au respectively. An electronic system with a larger HOMO-LUMO gap should be less reactive than one having smaller gap[20]. The ionization energy can be expressed through HOMO orbital energies as IE =

TABLE-2
COMPARISON OF DIFFERENT ENERGIES OF THE TITLE SCHIFF BASE OBTAINED BY SEMIEMPIRICAL METHODS

Energies	Semi empirical methods			
	AM1	PM3	MNDO	MNDO/d
E_{HOMO} (eV)	-9.005302	-9.030843	-9.306012	-8.74024
E_{LUMO} (eV)	-1.45669	-1.930736	-1.458588	-1.422235
E_{HOMO} - E_{LUMO}	7.548612	7.100107	7.847424	7.318005
Hardness(η)	3.774306	3.5500535	3.923712	3.6590025
IE = $-E_{HOMO}$	9.005302	9.030843	9.306012	8.74024
EA = $-E_{LUMO}$	1.45669	1.930736	1.458588	1.422235
Total energy (au)	-179.340819	-165.069986	-182.019135	-175.383586
Dipole moment (Debyes)	5.173	5.764	4.436	2.335

$-E_{HOMO}$ and electron affinity can be expressed through LUMO orbital energies[21] 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 are 7.548612, 7.100107, 7.847424 and 7.318005 eV for AM1, PM3, MNDO and MNDO/d respectively as shown in Table-2, which clearly indicates that the molecule is very stable. The ionization potential values obtained by both the theoretical methods also support the stability of the title molecule. The calculated dipole moment values show that the molecule is highly polar in nature.

Conclusion

We have synthesized a new Schiff base of S-benzyldithiocarbazate. The IR and ^{1}H NMR spectra of the Schiff base indicate that in solid state it remains in the thione form even in the solution. A good linearity between calculated and experimental vibration frequencies was observed. 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, total energy and dipole moment are very important physical parameters for chemical reactivity and biological activities of the studied compound.

ACKNOWLEDGEMENTS

The authors are thankful to The Principal, Institute of Information Technology and Management, Gwalior (India) for providing laboratory facilities. Authors are also thankful to Dr. K.P. Madhusudan, CDRI, Lucknow (India) for providing instrumentation facilities.

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