

Density functional theory calculations of vibrational frequencies and molecular structure of s-methyl β -n-(4-nitro benzal) methylene dithiocarbazate

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ABSTRACT

The vibrational frequencies and molecular geometry of the title compound are examined theoretically using the density functional theory (DFT) B1LYP, B3LYP, B3P86 and B3PW91 methods. For vibrational frequencies, the correlation coefficients obtained for B1LYP, B3LYP, B3P86, and B3PW91 methods are 0.998, 0.999, 0.998 and 0.998, respectively. B3LYP method provides most satisfactory correlation (CC=0.999) between experimental and calculated fundamental vibrational frequencies. For bond length correlation coefficients for B1LYP, B3LYP, B3P86 and B3PW91 methods are 0.997, 0.996, 0.994 and 0.995, respectively. For bond angle correlation coefficients for B1LYP, B3LYP, B3P86 and B3PW91 methods are 0.954, 0.952, 0.978 and 0.976, respectively. B1LYP and B3P86 yields highest correlation (CC=0.997 and 0.978) for bond length and bond angle, respectively.

Key words: Density functional theory (DFT) methods, B1LYP, B3LYP, B3P86, and B3PW91; Correlation Coefficient (CC).

INTRODUCTION

Nitrogen and sulphur containing Schiff bases derived from S-alkyl dithiocarbazate and their complexes show biological activities^{1,2}. These compounds have NNCSS back bone and four donor atoms and can act as multidentate ligand whose ligand properties can be modified by introducing organic substituents into the molecule. Such substituted ligands induce different stereochemistry in their coordination compounds^{3,4}. Synthesis and characterization of biological active 4-nitro benzaldehyde Schiff base of S-methyl dithiocarbazate was first reported by Duan et al^[4] and due to our interest in its theoretical studies, we report here the vibrational frequencies and other

structural parameters calculated by density functional methods.

The four main approaches for calculating molecular properties are ab-initio, semi-empirical, density functional theory and molecular mechanics methods.^[5-8] These quantum chemical methods can provide informations regarding bond length, bond angle, electron density, dipole moment, thermodynamic properties and vibrational frequencies etc.⁹⁻¹⁴. However, density functional theory approach has become increasing successful and important in quantum chemistry. This approach has as its objective the direct determination of the exact ground state energy and electron density, without the intermediary of a many-electron wave function¹⁵.

In the present study, we have been employed several gradient-corrected functionals in the density functional theory (DFT)^[16] calculations. The first one, denoted BLYP, consist of the Becke exchange functional with the correlation functional of Lee, Yang and Parr.^[17] In the second one, the hybrid Becke exchange functional has been used with the LYP correlation functional (B3LYP).^[18] In the third one, B3P86.^[19] Finally, the Becke exchange functional has also been used with the correlation functional of Perdew and Wang (BPW91).^[20] All calculations have been done using the standard 6-31G^[21] basis set. Thus, we report here the vibrational frequencies, geometrical parameters like as bond length and bond angle, electron densities and net atomic charges computed by B1LYP, B3LYP, B3P86 and B3PW91 density functionals with 6-31G basis set.

Computational details

An Intel based Pentium IV machine with HT3.2 technology having 800 FSB, 1GB RAM, 7200 RPM HDD was used to run all the calculations. Quantum chemical calculations were carried out by the density functional theory using the B1LYP, B3LYP, B3P86 and B3PW91 functionals with 6-31G basis set by Gaussian03 series of Chemoffice 2004^[22] program with root mean square (RMS) gradient 0.00001 kcal (Dmol⁻¹) using Polak-Ribiere algorithm. Chemdraw^[23] was used to draw the structure of molecule. Bond lengths, bond angles, vibrational frequencies, electron densities and net atomic charges were calculated with the help of standard parameters as implemented in the software.

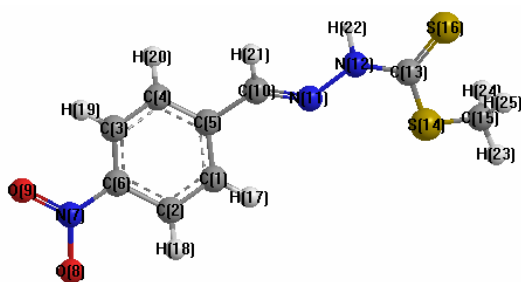


Fig. 1: Molecular structure of S-methyl β -N-(4-nitro benzal) methylene dithiocarbazate Schiff base ligand with numbering atoms adopted in the calculation

RESULT AND DISCUSSION

Vibrational frequencies

The experimental and calculated IR fundamental vibrational frequencies for the S-methyl β -N-(4-nitro benzal) methylene dithiocarbazate Schiff base by B1LYP, B3LYP, B3P86 and B3PW91 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 analysing correlation coefficients⁷. Graphical correlations between experimental and calculated fundamental vibrational frequencies are presented in Fig.-3. The correlation coefficients obtained for B1LYP, B3LYP, B3P86 and B3PW91 methods are 0.998, 0.999, 0.998 and 0.998, respectively. It is evident that B3LYP method gives most satisfactory correlation (CC=0.999), while B1LYP, B3P86 and B3PW91 method show same correlation coefficients (CC=0.998) between experimental and calculated vibrational frequencies.

The simulated IR frequencies for the S-methyl β -N-(4-nitro benzal) methylene dithiocarbazate Schiff base by B1LYP, B3LYP, B3P86 and B3PW91 methods are presented in Fig. 2. Some vibrational frequencies in the experimental frequencies 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 frequencies 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 frequency. The ν_{NH} , ν_{CN} and ν_{CSS} 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.

Optimised geometry

Bond length and Bond angle

We examined the performance of the density functional theory calculations in reproducing structural/ geometrical parameters by using B1LYP, B3LYP, B3P86 and B3PW91 methods. The geometrical parameters like bond lengths and bond

angles are compared with the experimental data^[4] in Table 2. The corresponding labelling scheme is given in Fig. 4. As it was observed in the earlier cases^{7,8}, the correlation coefficients are not equal for different methods. Thus, we can see from Fig. 5 the correlation coefficients for bond length are the highest one 0.997 has been obtained for B1LYP; a little lower value of 0.996 for B3LYP; 0.995 for

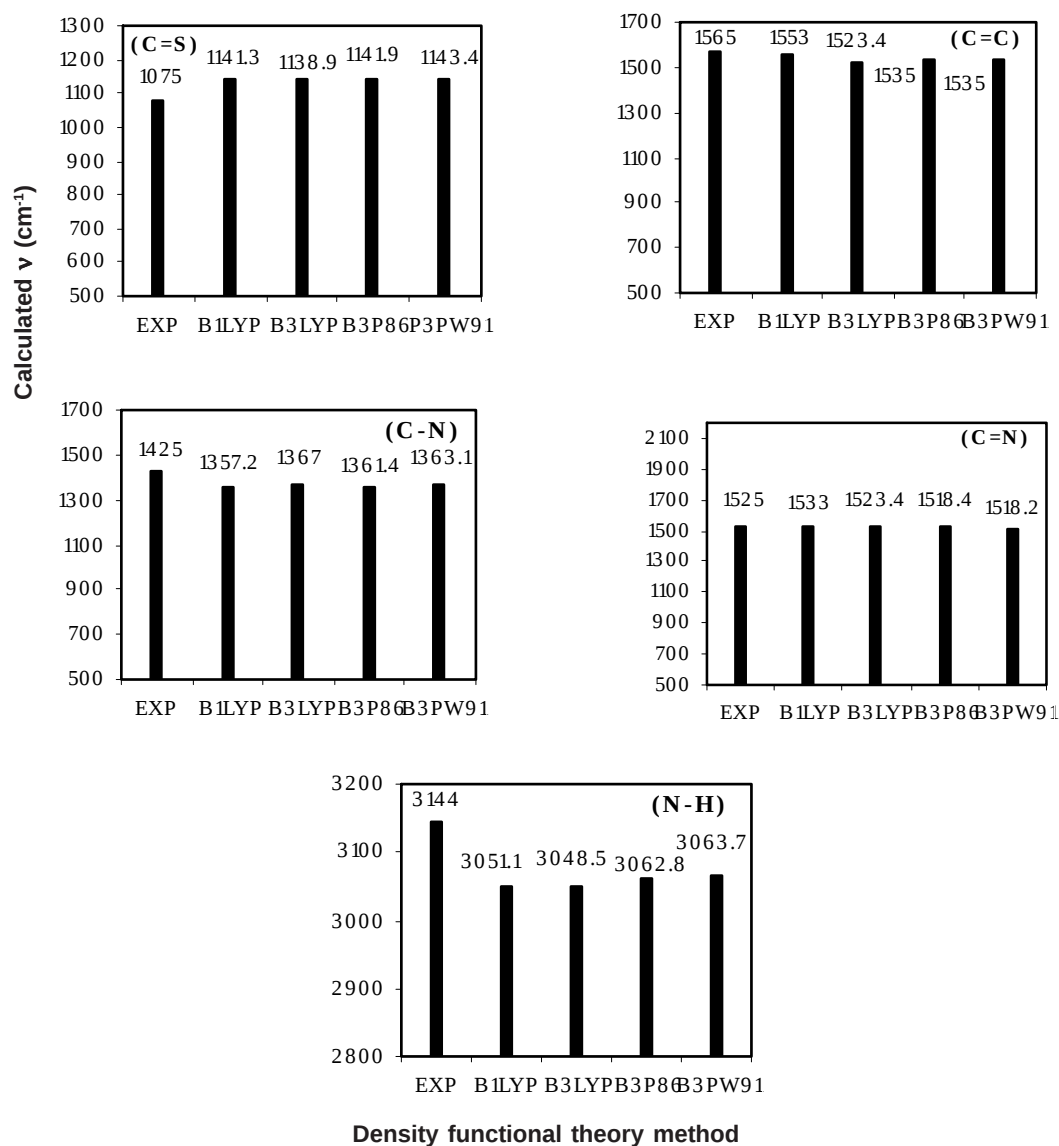


Fig. 2: The simulated IR frequencies for the S-methyl β-N-(4-nitro benzal) methylene dithiocarbamate by B1LYP, B3LYP, B3P86 and B3PW91 density functional theory methods

B3PW91; and 0.994 for B3P86. It is found here B1LYP accurately reproduce the geometrical parameters as the bond lengths calculated for title compound using this method compare favourably with the experimental observations with correlation coefficients of 0.997.

In the case of bond angle, the graphical representation of selected atom is shown in Fig. 6. The correlation coefficients from the experimental and calculated data for title molecule are found as 0.954 for B1LYP, 0.952 for B3LYP, 0.978 for B3P86 and 0.976 for B3PW91 method. It is clear that bond

Table1: Experimental and Calculated fundamental vibrational frequencies of S-methyl β -N-(4-nitro benzal) methylene dithiocarbazate ligand by B1LYP, B3LYP, B3P86 and B3PW91 density functional theory methods

Atom Pair	Vibration	B1LYP	B3LYP	B3P86	B3PW91	Experimental
C(13)—S(16)	$\nu(\text{C}=\text{S})$	1141.33	1138.94	1141.92	1143.35	1075
C(3)—C(6)	$\nu(\text{C}=\text{C})$	1357.21	1367.04	1361.38	1363.10	1425
C(13)—N(12)	$\nu(\text{C}-\text{N})$	1533.02	1523.39	1518.38	1518.24	1525
N(11)—C(10)	$\nu(\text{C}=\text{N})$	1553.00	1523.39	1535.73	1535.56	1565,s
N(12)—H(22)	$\nu(\text{N}-\text{H})$	3051.13	3048.46	3062.78	3063.72	3144,m
CC		0.998	0.999	0.998	0.998	

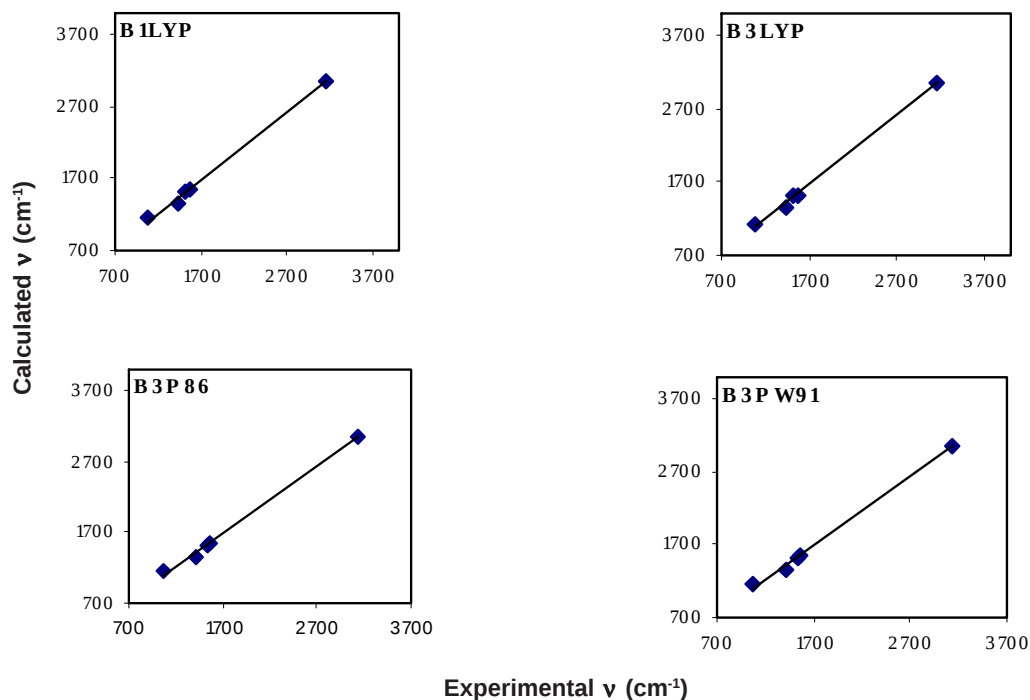


Fig. 3: Graphical correlation between experimental and calculated fundamental vibration frequencies obtained by density functional theory methods B1LYP, B3LYP, B3P86 and B3PW91 for S-methyl β -N-(4-nitro benzal) methylene dithiocarbazate (CC=Correlation Coefficient)

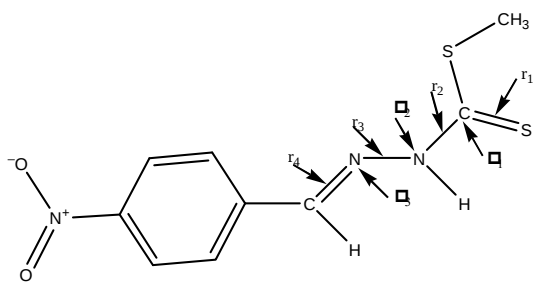


Fig. 4: Labelling scheme for the geometrical parameters of S-methyl β -N-(4-nitro benzal) methylene dithiocarbazate used in Table 2

angle from B3P86 method and experimental are in good accord with each other.

Atomic charge and electron density

Electron density (ED) and net atomic charge (NAC) on Nitrogen, Sulfur, and Oxygen atoms of title compound have been calculated by density functional theory B1LYP, B3LYP, B3P86, and B3PW91 methods and are listed in Table 3. The graphical presentation of electron density on N, S, and O atoms are shown in Fig. 7. For stable complex formation it is of almost importance to look for the bonding sites in ligand with which the metal ion will

Table 2: Experimental and Optimized geometries of S-methyl β -N-(4-nitro benzal) methylene dithiocarbazate ligand by AM1, PM3, MNDO, MINDO/3 semi-empirical methods. ^a Values from X-ray diffraction experiment: ref. 4

Designation	Bond length (in D)				(CC)	Bond angle (inE)			(CC)
	r_1	r_2	r_3	r_4		$\angle_1$	$\angle_2$	$\angle_3$	
Experimental ^a Method	1.661	1.343	1.367	1.265	-	121.2	115.7	120.2	-
B1LYP	1.7041	1.3668	1.3676	1.2954	0.9965	120.09	122.58	118.48	0.9541
B3LYP	1.7041	1.3687	1.3669	1.2978	0.9960	120.09	122.56	118.46	0.9524
B3P86	1.6952	1.3649	1.3588	1.2954	0.9945	120.19	122.24	118.70	0.9778
B3PW91	1.6971	1.3664	1.3574	1.2965	0.9945	120.11	122.39	118.68	0.9762

Table 3: Net atomic charges (NAC) and Atom electron density (ED) calculated by four density functional theory methods B1LYP, B3LYP, B3P86, and B3PW91 for S-methyl β -N-(4-nitro benzal) methylene dithiocarbazate

Atom number	B1LYP		B3LYP		B3P86		B3PW91	
	NAC	ED	NAC	ED	NAC	ED	NAC	ED
S(14)	0.37760	14.8554	0.37568	14.85961	0.41000	14.86562	0.41142	14.86306
S(16)	-0.05427	14.96333	-0.05072	14.96158	-0.03202	14.96715	-0.03081	14.96499
N(12)	-0.42832	5.61556	-0.41954	5.61065	-0.44086	5.66190	-0.44048	5.66146
N(11)	-0.16697	5.29647	-0.16497	5.30303	-0.17942	5.31058	-0.18197	5.31268
N(7)	0.05950	5.50784	0.04921	5.51681	0.03847	5.55610	0.04222	5.55200
O(9)	-0.29690	6.40102	-0.29061	6.39710	-0.29102	6.42258	-0.29214	6.42377
O(8)	-0.29449	6.39976	-0.28827	6.39585	-0.28859	6.42124	-0.28974	6.42244

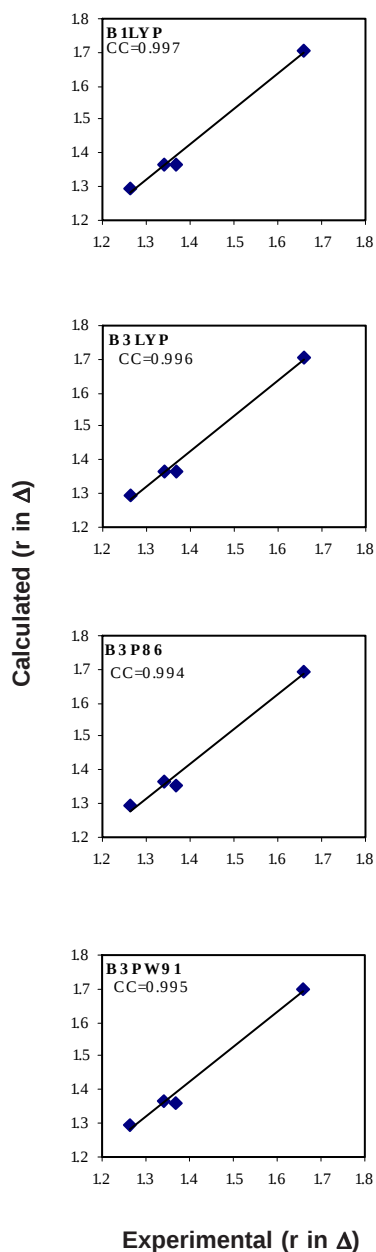


Fig. 5: Graphic correlation between the experimental and calculated bond lengths obtained by density functional theory methods B1LYP, B3LYP, B3P86, and B3PW91 for S-methyl β -N-(4-nitro benzal) methylene dithiocarbazate (CC=Correlation Coefficient)

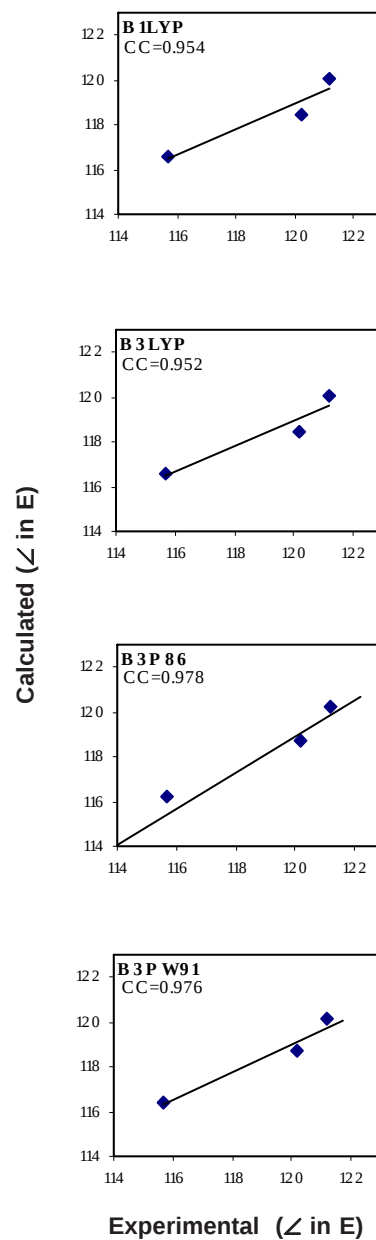


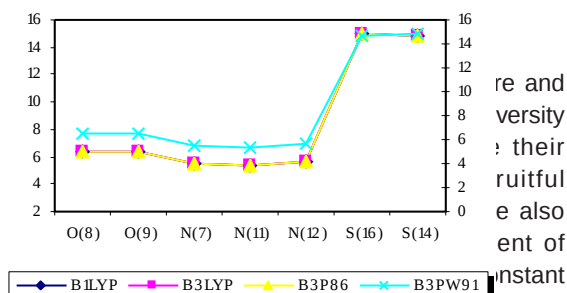
Fig. 6: Graphic correlation between the experimental and calculated bond angles obtained by the density functional theory methods B1LYP, B3LYP, B3P86, and B3PW91 for S-methyl β -N-(4-nitro benzal) methylene dithiocarbazate. (CC=Correlation Coefficient)

coordinate.^[6] In this regard the atom electron density and net atomic charge become the vital parameters to assign the coordination site of title compound and stability of the complex. The graphical representation (Fig. 7) of atom types and electron density shows that Nitrogen (12) and Sulphur (16) may take part in coordination in complex formation as these atoms shows maximum electron density. This fact is also supported by the experiment ^[11] which shows that Cu^{II} ion forms square-planar complex with title Schiff base via coordination through Nitrogen (12) and Sulfur (16). This result is accurately predicted by B1PLY, B3LYP, B3P86, and B3PW91 density functional methods.

Electron Duty

Atoms and its numbering

Fig. 7: Graphic presentation of calculated electron densities on all atoms obtained by B1LYP, B3LYP, B3P86, and B3PW91 density functional theory methods for S-methyl β -N-(4-nitro benzal) methylene dithiocarbazate



CONCLUSION

Of the four density functional methods tested in the present study on title compound, B3LYP can be considered as the most appropriate method to facilitate the vibrational frequencies identification of such compounds, since the IR frequencies simulated by this method best match the experimental frequencies and this method provides the best linearity between the calculated and experimental frequencies data (CC=0.999). In case of molecular geometry, B1LYP method (CC=0.997) for bond length & B3P86 method for bond angle give optimum satisfactory correlation between the experimental and calculated data. Atom electron densities (ED)/ Net atomic charges (NAC) indicate the coordination sites during complex formation. Result from; all density functional method is supported by experimental aspect. Thus, density functional quantum chemical calculations can successfully be used to predict the vibrational frequencies, geometry and other mentioned parameters in present of communication.

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