STRUCTURAL PROPERTIES,THEORY FUNCTIONAL CALCULATIONS (DFT), NATURAL BOND ORBITAL AND ENERGIES FOR THE N-(3-CHLORO-1H-INDAZOL-5-YL)-4-METHOXYBENZENESULFONAMIDE

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ABSTRACT

B3LYP/3-21G calculation results indicated that some selected bond length and bond angles values for the C14H12ClN3O3S In this paper, the optimized geometries and frequencies of the stationary point and the minimum-energy paths of new compound with C14H12ClN3O3S chemical formula are calculated by using the DFT methods with 3-21G basis set. The detail group points of compound is C1

Keywords: Methoxybenzenesulfonamide, Electronic structure, DFT Calculations, Vibrational analysis, B3LYP level.

INTRODUCTION

In the title compound, C14H12ClN3O3S, the fused five- and sixmembered ring are folded slightly along the common edge,forming a dihedral angle of 3.2(1)° The mean plane through the indazole system makes a dihedral angle of 30.75(7)° with the distant benzene ring. In the crystal, N—H_ _ _O hydrogen bonds link the molecules, forming a two-dimensional network[1].Sulfonamide derivatives are well known pharmaceutical agents since this group has been the main functional part of the most of the drug structures due to stability and tolerance in human beings. These compounds exhibit a wide range of biological activities such as anticancer, anti-inflammatory, and antiviral functions[2].Sulfonamides are antimicrobial agents widely employed in animal production and their residues in food could be an important risk to human health. In the dairy industry, large quantities of milk are monitored daily for the presence of sulfonamides. A simple and low-cost extraction protocol followed by a liquid chromatographic–tandem mass spectrometry method was developed for the simultaneous detection of nine sulfonamides in whole milk. The method was validated at the maximum residue limits established by European legislation.During this study we report the optimized geometries, assignments and electronic structure calculations for the compound. The structure of the compound has been optimized by using the DFT (B3LYP) method with the 3-21G basis sets, using the Gaussian 09 program. The comparison between theory and experiment is made. Density functional theory methods were employed to determine the optimized structures of C14H12ClN3O3S and Initial calculations were performed at the DFT level and split- valence plus polarization 3-21G basis sets were used. Local minima were obtained by full geometrical optimization have all positive frequencies[3]. Density functional theory (DFT) is a quantum mechanical modelling method used in physics and chemistry to investigate the electronic structure (principally the ground state) of many-body systems, in particular atoms, molecules, and the condensed phases. With this theory, the properties of a many-electron system can be determined by using functionals, i.e. functions of another function, which in this case is the spatially dependent electron density. Hence the name density functional theory comes from the use of functionals of the electron density. DFT is among the most popular and versatile methods available in

condensed-matter physics, computational physics, and computational chemistry.DFT has been very popular for calculations in solid-state physics since the 1970s. However, DFT was not considered accurate enough for calculations in quantum chemistry until the 1990s, when the approximations used in the theory were greatly refined to better model the exchange and correlation interactions. In many cases the results of DFT calculations for solid-state systems agree quite satisfactorily with experimental data. Computational costs are relatively low when compared to traditional methods, such as Hartree–Fock theory and its descendants based on the complex many-electron wavefunction.Despite recent improvements, there are still difficulties in using density functional theory to properly describe intermolecular interactions, especially van der Waals forces (dispersion); charge transfer excitations; transition states, global potential energy surfaces and some other strongly correlated systems; and in calculations of the band gap in semiconductors. Its incomplete treatment of dispersion can adversely affect the accuracy of DFT (at least when used alone and uncorrected) in the treatment of systems which are dominated by dispersion (e.g. interacting noble gas atoms) or where dispersion competes significantly with other effects (e.g. in biomolecules). The development of new DFT methods designed to overcome this problem, by alterations to the functional or by the inclusion of additive terms, is a current research topic.[4-17]

Chemicals and reagents

The optimized structural parameters were used in the vibrational frequency calculations at the DFT level to characterize all stationary points as minima. All computational are carried out using Gaussian 09w program. Harmonic vibrational frequencies (ν) in cm-1 and infrared intensities (int) in Kilometer per mole of all compounds were performed at the same level on the respective fully optimized geometries. Energy minimum molecular geometries were located by minimizing energy, with respect to all geometrical coordinates without imposing any symmetrical constraints.

NBO (Natural bond orbital) study on structures

NBO Calculated Hybridizations are significant parameters for our investigation. The structure of the compound has been optimized by using the DFT (B3LYP) method with 3-21G basis sets, using the Gaussian 09w program. Density functional theory methods were employed to determine the optimized structures of $C_{14}H_{12}ClN_3O_3S$ (Table 1, Figure 1,Table 1-1,Figure 1-1).This work we calculation selected bond length and bond angles values for the $C_{14}H_{12}ClN_3O_3S$ by mercury and Gaussian software. Natural Bond Orbital's (NBOs) are localized few-center orbital's that describe the Lewis-like molecular bo nding pattern of electron pairs in optimally compact form. More precisely, NBOs are an orthonormal set of localized "maximum occupancy" orbital's whose leading N/2 members (or N members in the open-shell case) give the most accurate possible Lewis-like description of the total N-electron density. This analysis is carried out by examining all possible interactions between "filled" (donor) Lewis-type NBOs and "empty" (acceptor) non-Lewis NBOs, and estimating their energetic importance by 2nd-order perturbation theory. Since these interactions lead to donation of occupancy from the localized NBOs of the idealized Lewis structure into the empty non-Lewis orbitals (and thus, to departures from the idealized Lewis structure description), they are referred to as "delocalization" corrections to the zeroth-order natural Lewis structure.

Natural charges have been computed using natural bond orbital (NBO) module implemented in Gaussian 09w. The. These quantities are derived from the NBO population analysis. The

former provides an orbital picture that is closer to the classical Lewis structure. The NBO analysis involving hybridizations of selected bonds are calculated at B3LYP methods and 3-21G level of theory (Tables 2, 3).

These data shows the hyper conjugation of electrons between ligand atoms with central metal atom. These conjugations stand on the base of p-d π-bonding. The NBO calculated hybridization for C14H12ClN3O3S shows that all of compounds have SPX hybridization and non planar configurations. The total hybridization of these molecules are SPX that confirmed by structural. The amount of bond hybridization showed the in equality between central atoms angles (Table 2) shown distortion from normal VSEPR structures and confirmed deviation from VSEPR structures. (Figure 2). Some thermodynamic parameters Frequencies for C14H12ClN3O3S Zero-point Energy, correction Energy, Enthalpy lengths, Gibbs free Energy are calculated and confirmed with other published theoretical data (Table 4).

Frontier molecular orbital

The HOMO represents the ability to donate an electron, LUMO as an electron acceptor represents the ability to obtain an electron. The HOMO and LUMO energy were calculated by B3LYP/3-21G method. This electronic absorption corresponds to the transition from the ground to the first excited state and is mainly described by one electron excitation from the highest occupied molecular or orbital (LUMO) both the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are the main orbital take part in chemical stability.. Therefore, while the energy of the HOMO is directly related to the ionization potential, LUMO energy is directly related to the electron affinity. Energy difference between HOMO and LUMO orbital is called as energy gap that is an important stability for structures. In addition, 3D plots of highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) are shown in Figure 2. The HOMO–LUMO energies were also calculated at the 3-21G and the values are listed in Figure 2, respectively.

RESULTS
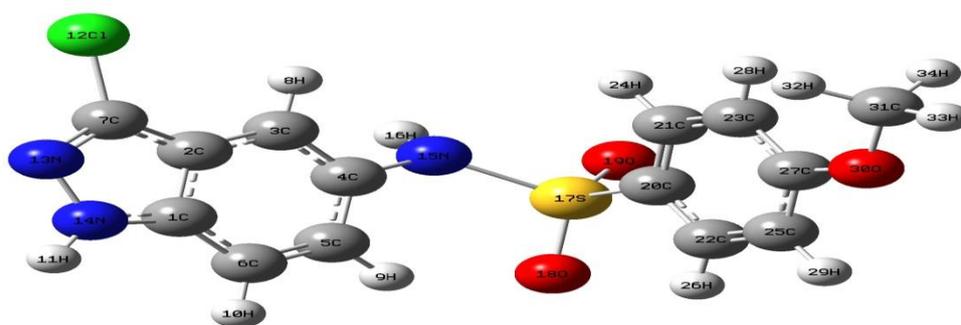
Figure 1. The schematic structure *of* $C_{14}H_{12}ClN_3O_3S$ at B3LYP/3-21G level of theory
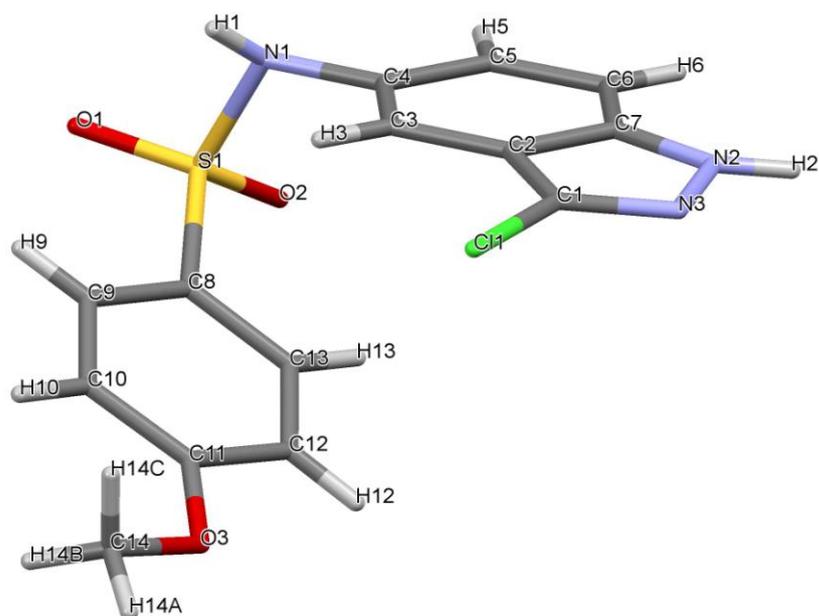
Figure 1-1. The schematic structure *of* $C_{14}H_{12}ClN_3O_3S$ at exprimenal[1]

$E_{LUMO=}-0.03607$

$\Delta E=0.21659$

$E_{HOMO=}-0.2526$
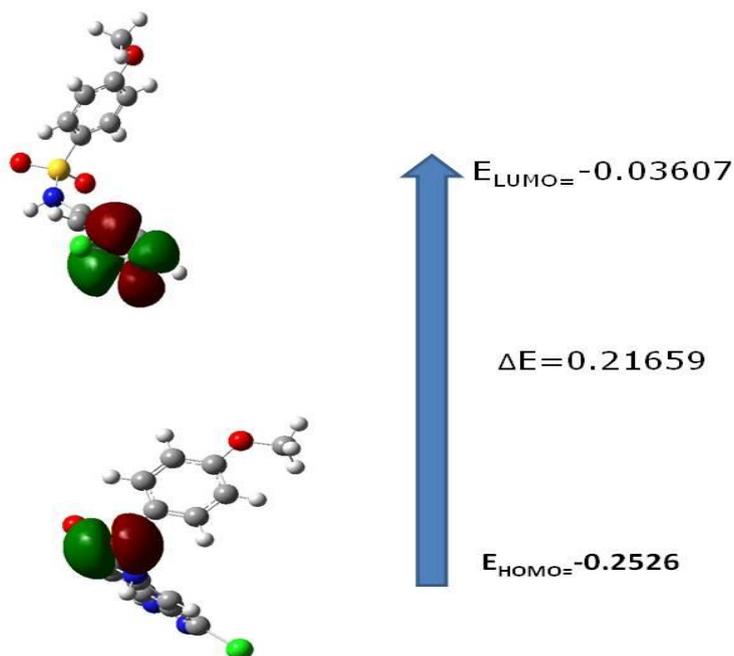
Figure 2. The atomic orbital of the frontier molecular orbital for C14H12ClN3O3S at B3LYP/3-21gG level of theory
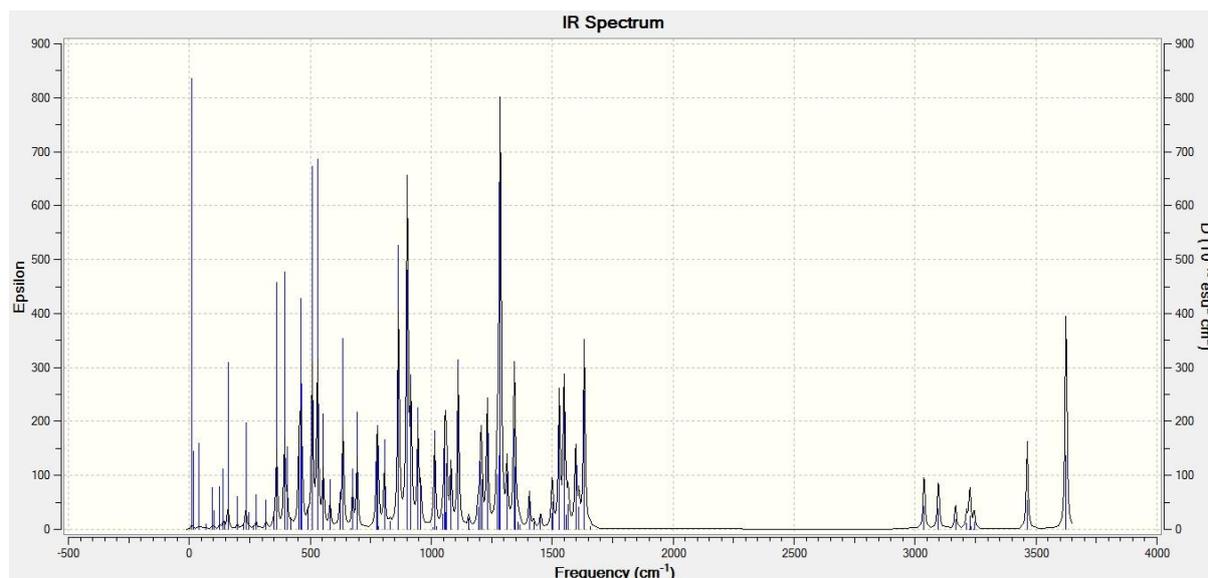
Figure 3. IR spectroscopy for $C_{14}H_{12}ClN_3O_3S$

Table 1: Geometrical parameters optimized for C14H12ClN3O3S some selected bond lengths (Å) and bond angles (°)(by Gaussian)

Method	B3lyp/3-21G	C14H12ClO3N3S	
Bond length(A°)			**Bond length(A°)**
$N_{15}-H_{16}$	1	C_1-N_{14}	1.4577
$S_{17}-O_{18}$	1.4696	C_4-N_{15}	1.47
$S_{17}-O_{19}$	1.4696	C_7-Cl_{12}	1.76
$S_{17}-C_{20}$	1.78	C_7-N_{13}	1.4077
$C_{27}-O_{30}$	1.43	$O_{30}-C_{31}$	1.43
H_9-O_{18}	1.763	$H_{11}-N_{14}$	1.0875
$N_{15}-S_{17}$	1.71	$N_{13}-N_{14}$	1.4072
Bond angles			**Bond angles**
$C_6-C_1-N_{14}$	132.5625	$C_3-C_4-N_{15}$	119.1113
$C_2-C_7-Cl_{12}$	124.7422	$O_{18}-S_{17}-O_{19}$	109.4712
$C_2-C_7-N_{13}$	108.1756	$O_{18}-S_{17}-C_{20}$	109.4712
$Cl_{12}-C_7-N_{13}$	127.0822	$O_{19}-S_{17}-C_{20}$	109.4712
$C_7-N_{13}-N_{14}$	109.5728	$S_{17}-C_{20}-C_{21}$	120.0113
$C_1-N_{14}-H_{11}$	124.7225	$S_{17}-C_{20}-C_{22}$	119.984
$C_1-N_{14}-N_{13}$	108.183	$C_{23}-C_{27}-O_{30}$	119.9957
$H_{11}-N_{14}-N_{13}$	127.0945	$C_{25}-C_{27}-O_{30}$	119.9957
$C_4-N_{15}-S_{17}$	109.4712	$O_{30}-C_{31}-H_{32}$	109.4712
$H_{16}-N_{15}-S_{17}$	109.4712	$N_{15}-S_{17}-O_{19}$	109.4712

Table 1-1: Geometrical parameters optimized for $C_{14}H_{12}ClN_3O_3S$ some selected bond lengths (Å) and angles (°)(experimental)

Method	B3lyp/3-21G	C14H12ClO3N3S	
Bond length(A°)		**Bond length(A°)**	
C_4-N_1	1.446	C_7-N_2	1.361
C_1-N_3	1.314	C_1-C_{11}	1.704
C_3-C_{l3}	1.398	C_3-S_1	1.751
C_{11}-O_3	1.363	C_{14}-O_3	1.421
N_1-H_1	0.823	N_1-S_1	1.639
N_2-H_2	0.880	N_2-N_3	1.354
O_1-S_1	1.436	O_2-S_1	1.434
Bond angles		**Bond angles**	
C_5-C_4-N_1	118.2	C_3-C_4-N_1	119.9
C_6-C_7-N_2	132.0	C_2-C_1-Cl_1	126.5
N_3-C_1-Cl_1	120.7	C_9-C_8-S_1	119.9
C_{13}-C_8-S_1	119.2	C_{10}-C_{11}-O_3	124.4
C_{12}-C_{11}-O_3	115.1	H_{14A}-C_{14}-O_3	109.5
C_4-N_1-S_1	116.70	H_1-N_1-S_1	109.8
C_7-N_2-H_2	128.2	C_7-N_2-N_3	112.5
H_2-N_2-N_3	118.6	C_1-N_3-N_2	105.0
C_8-S_1-O_1	109.65	C_8-S_1-O_2	108.27
N_1-S_1-O_1	105.16	O_1-S_1-O_2	118.65

Table2.The *NBO* Calculated Hybridizations for $C_{14}H_{12}ClN_3O_3S$ B3LYP/321G.

Bond	Atom	B3LYP	Bond	Atom	B3LYP
C-N	C_1-N_{14}	$S^1P^{2.73}$,$S^1P^{1.50}$	N-H	N_{15}-H_{16}	$S^1P^{4.51}$,$S^1P^{2.72}$
C-N	C_4-N_{15}	$S^1P^{2.87}$,$S^1P^{1.48}$	N-S	N_{15}-S_{17}	$S^1P^{2.41}$,S^1
C-Cl	C_7-Cl_{12}	$S^1P^{2.85}$,$S^1P^{6.01}$	S-O	S_{17}-O_{18}	$S^1P^{2.81}$,$S^1P^{8.82}$
C-N	C_7-N_{13}	$S^1P^{2.09}$,$S^1P^{1.55}$	S-O	S_{17}-O_{19}	$S^1P^{2.61}$,$S^1P^{8.73}$
H-N	H_{11}-N_{14}	S,$S^1P^{2.03}$	S-C	S_{17}-C_{20}	$S^1P^{2.73}$,$S^1P^{3.50}$
N-N	N_{13}-N_{14}	$S^1P^{4.51}$,$S^1P^{2.72}$	C-O	C_{27}-O_{30}	$S1P^{3.12}$,$S1P^{2.16}$

Table 3. Second order perturbation theory *of Fock matrix in NBO basis for $C_{14}H_{12}ClN_3O_3S$ E(2)a means energy of hyper conjugative interaction (stabilization energy); b Energy difference between donor and acceptor i and j NBO orbital's; c F(i, j) is the Fock matrix element between i and j NBσO orbital's

(i)Dono	Type	Acceptor(j)	Type	E(2) Kcal/mo	E(j)-E(i) a.u.	F(i,j) a.u.
C_1-N_{14}	σ	C_1-C_2	σ*	0.98	1.37	0.033
C_4-N_{15}	σ	C_2-C_3	σ*	1.46	1.38	0.040
C_7-Cl_{12}	σ	N_{13}-N_{14}	σ*	2.18	0.96	0.041
C_7-N_{13}	σ	H_{11}-N_{14}	σ*	1.75	1.30	0.043
N_{15}-S_{17}	σ	S_{17}-O_{18}	σ*	4.29	0.79	0.054
C_{27}-O_{30}	σ	C_{21}-C_{23}	σ*	0.95	1.48	0.034
H_{11}-N_{14}	σ	C_1-N_{14}	σ*	0.79	1.13	0.027

Table 4. Some thermodynamic parameters Frequencies for $C_{14}H_{12}ClN_3O_3S$ Zero-point Energy,correction Energy, Enthalpy lengths, Gibbs free Energy

$C_{14}H_{12}ClN_3O_3S$	
Zero-point correction=	0.248043 (Hartree/Particle)
Thermal correction to Energy=	0.267452
Thermal correction to Enthalpy=	0.268396
Thermal correction to Gibbs Free Energy=	0.197526

CONCLUSIONS

In this paper we are interested and studied on C14H12ClN3O3S was chosen to theoretical studies. The optimized geometries and frequencies of the stationary point and the minimum-energy paths are calculated by using the DFT (B3LYP) methods with 3-21G basis sets. B3LYP/3-21G calculation results indicated that some selected bond length and bond angles values for the C14H12ClN3O3S. The group point of compound is C1. Infrared spectra may be obtained from samples in all phases (liquid, solid and gaseous). Liquids are usually examined as a thin film sandwiched between two polished salt plates (note that glass absorbs infrared radiation, whereas NaCl is transparent). If solvents are used to dissolve solids, care must be taken to avoid obscuring important spectral regions by solvent absorption. Perchlorinated solvents such as carbon tetrachloride, chloroform and tetrachloroethene are commonly used. Alternatively, solids may either be incorporated in a thin KBr disk, prepared under high pressure, or mixed with a little non-volatile liquid and ground to a paste (or mull) that is smeared between salt plates but,in this paper we obtained IR spectrum theoretically by use Gaussian 09.frequencies of functional group showed in figure3.

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