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NMR and NBO Calculation of Broccoli Calm: Nano Physical Parameter Study

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ABSTRACT

Sulforaphane, an isothiocyanate found in broccoli and other cruciferous vegetables, it is an anti-oxidant and anti-cancer agent, and reduces blood pressure, and also has anti-allergic Effects.

In this article, six theoretical methods have been used for calculation of physical parameters in solforaphane and several similar compounds. We calculated physical parameters like atomic charges , energy (ΔE) , chemical shift anisotropy (δ) , asymmetry parameter (η) , chemical shift anisotropy (Δσ) , dipole moment , isotropic , anisotropic , NMR determinant and distance matrix determinant, and in this work we used Gaussian 98 at NMR and natural bond orbital(NBO) calculation by using HF method with 6-31G,6-31G* and 6-31+G basis set and B3LYP , BLYP and B3PW91 methods with 6-31G basis set. The GIAO magnetic shielding for studied molecules was obtained by using Gauss view program. Chemical shift curve was drawn for all of the atoms in each molecular.

Keywords: Broccoli; Isothiocyanates; Sulforaphane; Cruciferous vegetables; Physical parameter; NMR; Natural bond orbital (NBO)

INTRODUCTION

Sulforaphane is a naturally occurring isothiocyanate found in high concentrations in the SAGA (Mariner) variety of broccoli (*Brassica oleracea italica*). It is an anti-oxidant and a potent monofunctional inducer, which accounts for its anticarcinogenic properties in animal models. Studies have documented important antibiotic activities. L-Sulforaphane is the biologically active isomer [1].

Sulforaphane has been extensively researched for its health-promoting benefits. In fact, there is *no* Sulforaphane found in Broccoli or any other Cruciferous Vegetable. The plant cell contains 2 different types of sacs that contain the two substances that produce Sulforaphane only when mixed together [2].

When the plant is cut or chewed, the contents of the 2 sacs combine, producing a chemical reaction that leads to the production of the Sulforaphane. Sulforaphane itself is not stable for longer than about 30 minutes; therefore, the Sulforaphane must be produced just before consuming the broccoli. It is the effect of the enzyme, *Myrosinase* in one sac on the compound, on the *Glucoraphanin* in the other sac that produces the Sulforaphane [3].

Enzymes such as *Myrosinase* can only react when they are in contact with water. Because the powder is dry, there can be no reaction.

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However, when the powder is added to a glass of water, the chemical reaction begins immediately and the sulforaphane is produced [3, 4].

Sulforaphane exerts anti-oxidant, antiinflammatory, anti-cancer and radio sensitizing activities.

Free radicals or reactive oxygen species are created by toxins and carcinogens as well as by the body as a byproduct of various chemical reactions, especially in the mitochondria. These reactive species readily attack various tissues in the body causing disease and aging. Sulforaphane is a potent quencher of such species, acting by stimulating various enzymes and compounds that neutralize these reactive species effectively [5, 6, 7].

Inflammation is now considered the hallmark of a number of diseases like diabetes, allergies, cardiovascular disease and even obesity. Sulforaphane has an anti inflammatory effect via a number of different mechanisms including the inhibition of COX 2 enzymes and NF-kappaB, a molecule associated with inflammation, and the promotion of Nrf2, a powerful molecule that inhibits inflammation. In a number of studies sulforaphane has been shown to clinically reduce inflammation and pain in osteo-arthritic patients as well as improving the repair of damaged cartilage [8].

High blood pressure has been linked to high amounts of reactive oxygen species. Animal studies have demonstrated that sulforaphane significantly reduces blood pressure and improves other cardiovascular health conditions [9].

Sulforaphane has been shown to reduce symptoms of allergies including sneezing, watery eyes, itchy and runny nose caused by a variety of allergens like different types of pollen, dust, diesel fuel etc. A recent human study showed that sulforaphane greatly increased antioxidant status of the patients and the authors suggested a potential application of sulforaphane in conditions like asthma [10].

Perhaps the most widely studied effect of sulforaphane for over 20 years is in the field of cancer research in a number of diverse species as well as variety of tissues like prostate, skin, colon, breast, uterine, ovarian, bladder, pancreas etc. No human studies are available due to the large number of subjects required, length of study (over 20-30 years) and the cost [11].

The anti-cancer effect is attributed to a number of mechanisms including the stimulation of phase II enzymes, apoptosis (cell suicide), cell cycle arrest (preventing replication), reduction of the spread of tumors (metastases) and the inhibition of blood supply to cancer cells (angiogenesis)[12,13,14].

COMPUTATION METHODS

Stage 1: Start ChemDraw and construct molecules. Save the results as a ChemDraw file.

Stage 2: Reopen this file using Chem3D and perform an energy minimization. Then save the results as a gjc file.

Stage 3: Reopen this file using Gaussian98 and the calculations were performed using the *Gaussian® 98* program suite.

Gaussian is one of the most widely used quantum chemical program packages for molecular applications, and is used both in industry and in many scientific areas in academia. we have calculated the geometric parameters of the compounds in the ground state the using the Hartree-Fock (HF) , Becke’s three-parameter hybrid method with the Lee, Yang, and Parr correlation functional methods (B3LYP) , Becke’s exchange functional in combination with the Lee, Yang and Parr correlation functional methods (BLYP) , Becke's three parameter exchange functional combined with gradient corrected correlation functional of Perdew and Wang's 1991 (B3PW91) , and 6-31G, 6-31G* and 6-31+G basis set [15,16].

The calculation that you ask Gaussian to perform is distributed between many

processors to get the answer faster. If you want to optimize geometry, it means that you want Gaussian to adjust the bond lengths, angles, and dihedrals to find the lowest energy conformation of the molecule. The command to tell Gaussian to optimize the molecular geometry is "opt" [17].

The Gaussian program does semi-empirical and *ab initio* calculations. In *ab initio* calculations the important integrals are done directly from first principles. First principles means that the integrals are done either using closed formulas or by doing the integrals numerically. The particular *ab initio* method was accomplished best for calculating NMR properties. Finding a good geometry is called geometry optimization, so "OPT" are used as the keyword [18, 19].

The calculation will generate an output file called *filename.out.*

The output file (*filename.out*) contains a lot of information about the calculation and the results. The content depends on what type of calculation that has been performed and on what print options that was specified. The units are usually Hartree (atomic unit) for energy and Ångström for distance. There are several different pieces of data that you may need from this. The important information is the Hartree-Fock energy (ΔE), the Mulliken charges, Distance matrix (angstroms), Dipole moment (Debye) and Atomic charge. Distance matrix value is determined using Matlab program.

We used Gaussian98 in calculation of NMR chemical shift by using HF, B3LYP, BLYP, B3PW91 methods and 6-31G, 6-31G* and 6-31+G basis set. Therefore "NMR" is used as keyword. The calculation will generate an output file called *NMR.out* [20].

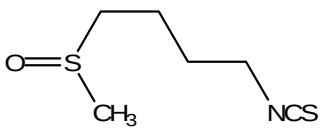
The output file (*NMR.out*) contains a lot of information about NMR chemical shift calculation and parameters such as σ Isotropic (ppm) and σ Anisotropic (ppm) that listed in the "GIAO Magnetic shielding tensor (ppm)", and σ determinant was calculated by using Matlab program. Molecular orbital calculations can be used to get good estimates for chemical shifts. In this exercise, we calculated chemical shifts for each atom, then draw diagrams that shown chemical shifts for each atom by using Excel program. parameters such as δ, η and Δσ were calculated by using σ Isotropic (ppm), σ Anisotropic (ppm) and Eigenvalues(σ_{11}, σ_{22}, σ_{33}) [21,22].

A perfect NBO analysis was obtained in *Gaussian* program when POP=NBO are used as the keyword. NBO analysis was performed by using HF method with 6-31G, 6-31G* and 6-31+G basis set and B3LYP, BLYP and B3PW91 methods with 6-31G basis set and the output was obtained for each molecule.The main list of NBOs, displays the form and occupancy of the complete set of NBOs that span the input AO space and for each orbital gives the type of orbital and the occupancy. We have extracted just BD for 2-center bond and BD* for 2-center antibond from NBO output.

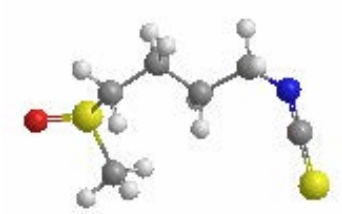
RESULTS AND DISCUSSION

In this work ,we calculated parameters like atomic charges, energy (ΔE), chemical shift anisotropy (δ), asymmetry parameter (η), chemical shift anisotropy (Δσ), dipole moment, isotropic, anisotropic, NMR determinant and distance matrix determinant and natural bond orbital(NBO), and GIAO magnetic shielding for solforaphane and several similar compounds by using HF method with 6-31G,6-31G* and 6-31+G basis set and B3LYP, BLYP and B3PW91 methods with 6-31G basis set. HF method with 6-31+G basis set didn't answer for molecular1,2,3,and B3LYP method with 6-31G basis set wasn't performed for molecular3.The atoms that mentioned parameters calculated for them, are related to (- C – SO -) and (-NCS) groups. These parameters are reported in Table (1-5).

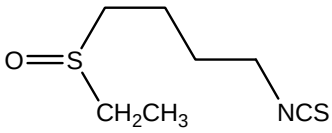
The optimized structure of molecules that studied in this work, have been shown in Fig.1.



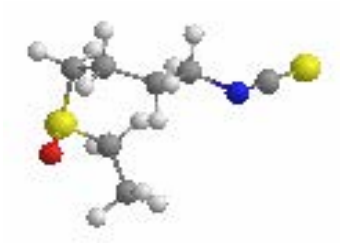
1-isothiocyanato-4-(methylsulfinyl) butane



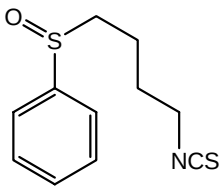
molecular (1)



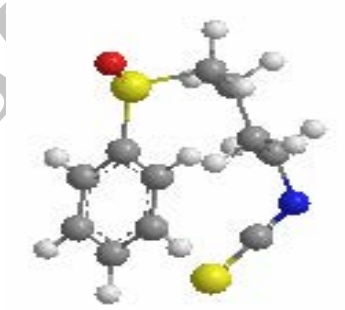
1-(ethylsulfinyl)-4-isothiocyanatobutane



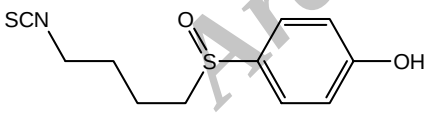
molecular (2)



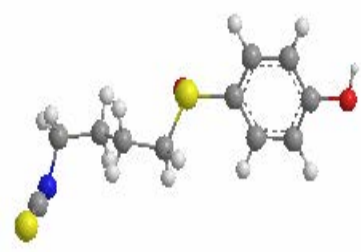
1-(4-isothiocyanatobutylsulfinyl) benzene



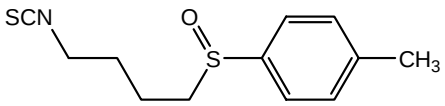
molecular (3)



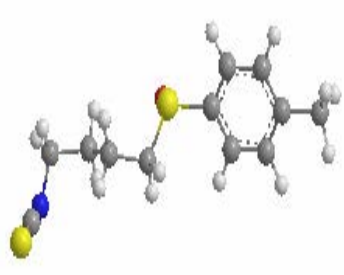
4-(4-isothiocyanatobutylsulfinyl) phenol



molecular (4)



1-(4-isothiocyanatobutylsulfinyl)-4-methylbenzene



molecular (5)

Fig. 1. Optimized structure of studied molecular.

At present, in this section, we considered these parameters.

As shown in table 1, in HF/6-31G and HF/6-31G* levels for all of the studied molecular, C and O atoms in (- C – SO -) group and N and S atoms in $(-NCS)$ group have negative atomic charge value, but in B3LYP, BLYP and B3PW91 methods C and O atoms in (- C – SO -) group and N and C atoms in $(-NCS)$ group have negative atomic charge value, and in all of the used methods S atom in (- C – SO -) group has the most atomic charge value.

As pointed in table 1, in HF/6-31G level for all of the molecules and in HF/6-31+G for molecular 4 and 5, chemical shift anisotropy (δ) and (Δσ) value for S atom in (- C – SO -) group is negative but other studied atoms is positive and δ_O in $(-C-SO-)$ group is the most positive value, while in HF/6-31G* for molecular 2, δ_O in $(-C-SO-)$ group is negative but in other molecules is positive, also in all of the molecules, δ_C in $(-NCS)$ group is the greatest value. B3LYP and B3PW91 methods for all of the molecules, δ_O in $(-C-SO-)$ group is negative but in BLYP method δ_O in (- C – SO -) group in molecular 2,4 and 5 is negative, also in B3LYP , BLYP and B3PW91 methods, δ_S in $(-NCS)$ group for all of the molecules is the most positive value.

As reported in table 1, in HF/6-31G level for all of the molecules except molecular 1, η_C in (- C – SO -) group is the greatest value, but in molecular1, η_S in (- C – SO -) group is the greatest, while in HF/6-31G*, η_C in $(-NCS)$ group has the greatest value, and in HF/6-31+G level ηC in (- C – SO -) group is the most amount, and in B3LYP and B3PW91 methods, η_S in (- C – SO -) group has the most value. But in BLYP method η_O in (- C – SO -) group is the greatest value.

Dipole moment that reported in Table 1, dipole moment for molecular 1, in BLYP method, is the greatest than other used methods, but in other molecules, dipole moment in HF/6-31G level is the greatest.

ΔE (kcal/mol) that reported in Table 1, for all molecules in HF/6-31G level is zero. Also in all of the molecules except molecular3, in B3LYP method, ΔE has the most value, but in molecular3, ΔE related to BLYP method, is the greatest.

As shown in table 2, in all of the methods for all of the molecules, σ_{iso} for S atom in $(-NCS)$ group is the greatest value, and in HF/6-31G and HF/6-31+G and BLYP methods for all of the molecules, and in B3LYP and B3PW91 methods for molecular1, σ_{iso} for O atom in (- C – SO -) group is negative. In other hands, in HF/6-31G* σ_{iso} for all of the atoms in all of the molecules is positive.

As defined in table 2, the entire anisotropy amount is positive. In HF/6-31G and HF/6-31+G, for all of the molecules, σ_{aniso} for O atom in (- C – SO -) group is the most value, while HF/6-31G*, σ_{aniso} related to C atom in $(-NCS)$ group is the most, and in B3LYP, BLYP and B3PW91 methods, σ_{aniso} related to S atom in $(-NCS)$ group is the most.

As reported in table 2, in all of the methods for all of the molecules, NMR determinant relative to (S) atoms is the greatest value.

The other parameter that reported in table 2 is distance matrix determinant for molecules. Molecules 1, 4, 5 in all of the methods, has positive distance matrix, but distance matrix for molecules 2, 3, in all of the methods is negative. In the entire molecular, calculated distance matrix determinant in BLYP method is the largest than other methods.

Table 1. Values of parameters like atomic charges, ΔE (kcal/mol), chemical shift (δ), asymmetry parameter (η), and chemical shift anisotropy (Δσ), dipole moment for active site of studied molecules obtained using different methods

Method: HF — Basis set: 6-31G

Name	Atoms	atomic charges	ΔE(kcal/mol)	δ	η	Δσ	Dipole moment
Molecular 1	C(1) S(2) N(7) C(8) S(9) O(10)	-0.71 0.87 -0.60 0.10 -0.01 -0.76	-	34.12 -141.33 218.26 218.56 290.01 489.44	0.16 0.64 0.05 0.002 0.002 0.43	51.18 -212.00 327.39 327.84 435.02 734.16	3.50
Molecular 2	C(1) S(3) N(8) C(9) S(10) O(11)	-0.56 0.89 -0.59 0.09 -0.03 -0.77	-	34.56 -155.85 221.96 217.47 292.56 393.71	0.79 0.10 0.05 0.003 0.004 0.32	51.84 -233.78 332.93 326.21 438.84 590.56	8.28
Molecular 3	C(1) S(2) N(7) C(8) S(9) O(10)	-0.46 0.99 -0.60 0.09 -0.02 -0.77	-	98.37 -145.04 220.41 218.01 291.24 399.64	0.86 0.51 0.05 0.002 0.002 0.30	147.56 -217.56 330.61 327.01 436.86 599.46	8.48
Molecular 4	C(1) S(2) N(7) C(8) S(9) O(10)	-0.47 1.00 -0.58 0.10 -0.02 -0.77	-	90.33 -122.59 219.76 218.73 292.46 390.89	0.89 0.30 0.05 0.02 0.01 0.39	135.49 -183.89 329.64 328.10 438.69 586.34	6.42
Molecular 5	C(1) S(2) N(7) C(8) S(9) O(10)	-0.46 0.99 -0.58 0.10 -0.03 -0.77	-	94.34 -123.18 219.86 218.61 292.11 381.51	0.86 0.30 0.05 0.02 0.01 0.39	141.51 -184.77 329.79 327.91 438.16 572.27	6.74

Method: HF — Basis set: 6-31G*

Name	Atoms	atomic charges	ΔE(kcal/mol)	δ	η	Δσ	Dipole moment
Molecular 1	C(1) S(2) N(7) C(8) S(9) O(10)	-0.71 0.96 -0.46 0.29 -0.20 -0.79	-167.43	31.73 209.86 191.10 211.64 201.70 189.23	0.55 0.21 0.06 6.4e-4 9.0e-4 0.66	47.60 314.79 286.66 317.47 302.56 283.85	3.14
Molecular 2	C(1) S(3) N(8) C(9) S(10) O(11)	-0.54 0.98 -0.45 0.29 -0.22 -0.81	-175.60	26.73 168.52 193.87 210.99 202.76 -169.25	0.81 0.22 0.06 0.002 0.004 0.93	40.09 252.78 290.81 316.48 304.13 -253.87	6.86
Molecular 3	C(1) S(2) N(7) C(8) S(9) O(10)	-0.29 1.00 -0.46 0.29 -0.21 -0.80	-203.02	108.65 191.84 192.07 211.37 202.48 157.10	0.55 0.13 0.05 0.006 0.002 0.70	162.97 287.76 288.10 317.05 303.72 235.66	3.40
Molecular 4	C(1) S(2) N(7) C(8) S(9) O(10)	-0.32 1.00 -0.45 0.30 -0.22 -0.81	-227.27	93.88 154.98 191.38 211.83 202.19 164.19	0.62 0.16 0.05 0.02 0.01 0.73	140.81 232.47 287.07 317.75 303.29 246.28	5.66
Molecular 5	C(1) S(2) N(7) C(8) S(9) O(10)	-0.30 1.00 -0.45 0.30 -0.22 -0.80	-216.02	100.11 158.60 191.35 211.76 202.08 162.65	0.58 0.15 0.05 0.02 0.01 0.76	150.16 237.89 287.03 317.64 303.11 243.97	5.58

Method: HF — Basis set: 6-31+G

Name	Atoms	atomic charges	ΔE(kcal/mol)	δ	η	Δσ	Dipole moment
Molecular 1	C(1) S(2) N(7) C(8) S(9) O(10)	- - - - - -	-	- - - - - -	- - - - - -	- - - - - -	-
Molecular 2	C(1) S(3) N(8) C(9) S(10) O(11)	- - - - - -	-	- - - - - -	- - - - - -	- - - - - -	-
Molecular 3	C(1) S(2) N(7) C(8) S(9) O(10)	- - - - - -	-	- - - - - -	- - - - - -	- - - - - -	-
Molecular 4	C(1) S(2) N(7) C(8) S(9) O(10)	0.17 0.85 -0.53 0.17 0.09 -0.66	-13.03	91.67 -116.59 221.23 217.36 283.87 397.08	0.88 0.30 0.05 0.02 0.02 0.35	[illegible]	6.27
Molecular 5	C(1) S(2) N(7) C(8) S(9) O(10)	-0.02 0.93 -0.53 0.17 0.09 -0.66	-11.38	95.18 -116.23 221.41 217.40 283.77 392.12	0.86 0.30 0.05 0.02 0.02 0.35	[illegible]	6.60

Method: B3lyp — Basis set: 6-31G

Name	Atoms	atomic charges	ΔE(kcal/mol)	δ	η	Δσ	Dipole moment
Molecular 1	C(1) S(2) N(7) C(8) S(9) O(10)	-0.64 0.76 -0.36 -0.04 0.04 -0.66	-2354.82	46.04 246.58 205.69 208.45 286.16 -108.86	0.12 0.63 0.04 0.01 0.02 0.22	69.06 369.87 308.54 312.67 429.24 -163.29	3.28
Molecular 2	C(1) S(3) N(8) C(9) S(10) O(11)	-0.48 0.76 -0.35 -0.04 0.02 -0.67	-2535.17	44.11 185.8791 208.97 207.96 287.78 -103.10	0.69 0.92 0.04 0.00 9 0.02 0.33	66.16 278.82 313.45 311.94 431.68 -154.65	6.69
Molecular 3	C(1) S(2) N(7) C(8) S(9) O(10)	- - - - - -	-	- - - - - -	- - - - - -	- - - - - -	-
Molecular 4	C(1) S(2) N(7) C(8) S(9) O(10)	-0.30 0.81 -0.35 -0.04 0.02 -0.66	-3367.08	77.17 156.86 206.99 208.60 286.93 -114.86	0.57 0.92 0.05 0.02 0.02 0.80	115.75 235.28 310.48 312.90 430.39 -172.29	6.07
Molecular 5	C(1) S(2) N(7) C(8) S(9) O(10)	-0.30 0.81 -0.35 -0.04 0.02 -0.66	-3316.53	80.49 159.02 207.07 208.60 287.01 -113.00	0.54 0.91 0.05 0.02 0.01 0.80	120.73 238.53 310.60 312.89 430.52 -169.49	6.02

Method: BLYP — Basis set: 6-31G

Name	Atoms	atomic charges	ΔE(kcal/mol)	δ	η	Δσ	Dipole moment
Molecular 1	C(1) S(2) N(7) C(8) S(9) O(10)	-0.57 0.69 -0.31 -0.05 0.03 -0.60	-2250.49	50.96 292.61 209.03 207.91 307.81 99.35	0.08 0.38 0.01 0.04 0.09 0.78	76.44 438.92 313.55 311.87 461.71 149.02	7.55
Molecular 2	C(1) S(3) N(8) C(9) S(10) O(11)	-0.42 0.68 -0.31 -0.05 0.03 -0.61	-2410.57	48.35 236.47 209.00 207.85 307.88 -86.95	0.66 0.58 0.001 0.04 0.10 0.80	72.53 354.71 313.49 311.78 461.82 -130.42	5.88
Molecular 3	C(1) S(2) N(7) C(8) S(9) O(10)	-0.24 0.72 -0.31 -0.05 0.03 -0.60	-2983.19	80.54 229.24 209.13 207.75 307.97 76.47	0.29 0.32 0.01 0.04 0.09 0.56	120.82 343.86 313.70 311.62 461.96 114.71	8.30
Molecular 4	C(1) S(2) N(7) C(8) S(9) O(10)	-0.24 0.73 -0.31 -0.05 0.03 -0.60	-3209.97	72.97 210.59 207.48 208.38 305.47 -71.85	0.39 0.66 0.03 0.04 0.05 0.76	109.46 315.89 311.22 312.57 458.21 -107.78	5.46
Molecular 5	C(1) S(2) N(7) C(8) S(9) O(10)	-0.24 0.73 -0.31 -0.05 0.03 -0.60	-3145.34	76.06 212.87 207.50 208.36 305.46 -70.03	0.37 0.65 0.03 0.04 0.05 0.79	114.10 319.31 311.25 312.54 458.19 -105.05	5.24

Method: B3PW91 — Basis set: 6-31G

Name	Atoms	atomic charges	ΔE(kcal/mol)	δ	η	Δσ	Dipole moment
Molecular 1	C(1) S(2) N(7) C(8) S(9) O(10)	-0.72 0.80 -0.39 -0.04 0.06 -0.68	-2205.37	44.40 242.60 202.30 204.91 271.32 -101.90	0.17 0.63 0.05 0.00 6 0.01 0.47	66.59 363.90 303.45 307.36 406.98 -152.85	3.30
Molecular 2	C(1) S(3) N(8) C(9) S(10) O(11)	-0.55 0.80 -0.38 -0.04 0.04 -0.68	-2377.21	42.35 186.78 205.64 204.12 272.33 -97.95	0.70 0.89 0.05 0.00 3 0.00 3 0.05	63.52 280.17 308.46 306.17 408.49 -146.92	6.72
Molecular 3	C(1) S(2) N(7) C(8) S(9) O(10)	-0.35 0.85 -0.39 -0.04 0.05 -0.68	-2941.71	84.56 191.55 204.93 204.37 272.27 -92.70	0.53 0.63 0.05 0.00 3 0.00 6 0.49	126.84 287.32 307.40 306.56 408.40 -139.05	7.91
Molecular 4	C(1) S(2) N(7) C(8) S(9) O(10)	-0.34 0.85 -0.38 -0.04 0.04 -0.67	-3154.01	76.68 156.06 203.61 205.14 271.82 -102.09	0.60 0.91 0.05 0.02 0.01 0.63	115.03 234.09 305.41 307.71 407.74 -153.14	6.11
Molecular 5	C(1) S(2) N(7) C(8) S(9) O(10)	-0.34 0.85 -0.38 -0.04 0.04 -0.67	-3112.95	80.21 158.07 203.50 205.06 271.60 -99.86	0.56 0.89 0.05 0.02 0.01 0.63	120.31 237.10 305.25 307.59 407.40 -149.78	6.00

Table 2. Values of parameters like isotropic (σ_{iso}), anisotropic (σ_{aniso}) shielding, NMR determinant and distance matrix determinan for active site of studied **molecules** obtained using different methods

Method	Basis set	Name	Molecular 1	Molecular 2	Molecular 3	Molecular 4	Molecular 5
HF	6-31G	Atoms	C(1) S(2) N(7) C(8) S(9) O(10)	C(1) S(2) N(8) C(9) S(10) O(11)	C(1) S(2) N(7) C(8) S(9) O(10)	C(1) S(2) N(7) C(8) S(9) O(10)	C(1) S(2) N(7) C(8) S(9) O(10)
		σ Isotropic(ppm)	175.05 441.51 155.51 58.32 745.52 -195.84	164.79 460.05 151.99 59.25 745.14 -64.17	67.43 445.65 153.62 58.84 745.68 -80.87	75.69 434.92 151.00 58.59 746.23 -86.77	70.38 433.18 151.06 58.70 746.59 -77.33
		σ Anisotropy(ppm)	51.18 171.49 327.39 327.84 435.02 734.16	51.84 128.59 332.93 326.21 438.84 590.56	147.56 163.81 330.61 327.01 436.86 599.46	135.49 119.87 329.64 328.10 438.69 586.34	141.51 120.38 329.79 327.91 438.16 572.27
		Determinan(NMR)	5.12E+06 9.01E+07 7.94E+08 7.18E+08 3.78E+08 5.37E+07	4.30E+06 8.93E+07 6.13E+08 6.77E+08 3.72E+08 2.11E+07	-2.42E+06 8.04E+07 6.99E+08 6.99E+08 3.73E+08 2.39E+07	-1.14E+06 7.71E+07 6.32E+08 7.13E+08 3.74E+08 2.25E+07	-1.81E+06 7.62E+07 6.18E+08 7.05E+08 3.75E+08 2.02E+07
		Distance matrix	3.8532e+007	-2.6807e+008	-8.8008e+009	1.5368e+010	6.6443e+010
	6-31G*	σ Isotropic(ppm)	166.16 316.90 178.52 66.60 832.72 334.72	159.94 337.82 175.89 67.10 833.04 372.74	62.50 312.76 177.91 67.15 833.00 334.69	73.47 316.27 175.52 66.71 834.56 354.88	65.75 316.27 175.50 66.70 834.56 356.64
		σ Anisotropy(ppm)	47.60 314.69 286.66 317.47 300.56 283.85	40.09 252.78 290.81 316.48 304.13 246.48	161.97 287.76 288.10 317.05 300.72 235.66	140.81 233.47 287.07 317.75 300.29 264.28	150.16 237.89 287.03 317.64 300.11 243.97
		Determinan(NMR)	4.45E+06 2.65E+07 2.54E+08 4.29E+08 5.54E+08 2.84E+07	3.99E+06 3.25E+07 2.30E+08 4.09E+08 5.55E+08 4.22E+07	-1.37E+05 2.43E+07 2.47E+08 4.13E+08 5.55E+08 3.11E+07	-2.03E+04 2.77E+07 2.38E+08 4.27E+08 5.58E+08 3.70E+07	-9.39E+04 2.68E+07 2.39E+08 4.26E+08 5.58E+08 3.77E+07
		Distance matrix	2.9587e+007	-2.1757e+008	-3.8247e+009	1.2455e+010	5.5554e+010
	6-31+G	σ Isotropic(ppm)	. . . . . .	. . . . . .	. . . . . .	74.63 440.33 148.61 60.10 755.17 -105.85	69.43 438.51 148.49 60.14 755.36 -101.41
		σ Anisotropy(ppm)	. . . . . .	. . . . . .	. . . . . .	137.50 113.91 331.85 326.04 425.91 595.62	142.77 112.96 332.12 326.10 425.65 588.18
		Determinan(NMR)	. . . . . .	. . . . . .	. . . . . .	-1.34E+05 8.05E+07 5.24E+08 6.53E+08 3.91E+08 2.55E+07	-1.39E+05 7.59E+07 5.18E+08 6.53E+08 3.91E+08 2.44E+07
		Distance matrix	-	-	-	1.5836e+010	6.8672e+010
B3LYP	6-31G	σ Isotropic(ppm)	147.55 208.20 158.21 69.09 724.73 -37.33	135.21 211.46 155.70 69.18 725.17 32.74	. . . . . .	53.95 208.78 155.08 70.02 730.07 9.96	48.75 207.33 155.92 70.04 730.05 11.83
		σ Anisotropy(ppm)	69.06 369.07 308.54 312.67 432.24 99.24	66.16 278.82 313.45 311.94 431.68 103.15	. . . . . .	115.75 235.28 310.48 312.90 430.39 155.11	120.73 238.53 310.60 312.89 430.52 152.76
		Determinan(NMR)	3.00E+06 2.22E+07 1.14E+08 3.41E+08 3.42E+08 -5.22E+04	2.26E+06 2.27E+07 9.61E+07 3.33E+08 3.42E+08 -2.79E+05	. . . . . .	-2.35E+04 4.47E+06 9.91E+07 3.26E+08 3.50E+08 -2.49E+05	-4.86E+04 4.23E+06 9.87E+07 3.25E+08 3.50E+08 -2.58E+05
		Distance matrix	4.4765e+007	-2.9234e+008	-	1.9076e+010	8.3310e+010
	BLYP	σ Isotropic(ppm)	138.33 144.31 149.21 67.39 692.23 -41.59	122.84 112.21 148.79 67.00 691.11 -10.70	33.93 148.70 149.46 67.68 692.93 -26.50	44.12 116.94 149.41 68.27 698.14 -25.64	38.64 115.57 149.40 68.29 698.18 -23.59
		σ Anisotropy(ppm)	76.44 438.91 313.55 311.87 461.71 149.02	72.53 354.71 313.49 311.78 461.82 117.62	120.82 343.86 313.70 311.62 461.96 114.71	109.46 315.89 311.22 312.57 458.21 94.84	114.10 319.31 311.25 312.54 458.19 93.84
		Determinan(NMR)	2.41E+06 -1.34E+06 7.53E+05 3.85E+05 2.93E+08 4.12E+05	1.63E+06 -1.57E+06 7.42E+05 3.66E+05 2.88E+08 2.71E+05	-9.67E+03 -6.50E+04 7.57E+05 3.85E+05 2.91E+08 1.78E+05	-1.45E+04 -1.40E+06 7.72E+05 3.49E+05 2.99E+08 6.37E+04	-1.98E+04 -1.45E+06 7.71E+05 3.48E+05 2.99E+08 6.43E+04
		Distance matrix	5.6723e+007	-3.4432e+008	-1.1790e+010	2.3015e+010	1.0102e+011
B3PW91		σ Isotropic(ppm)	152.68 234.75 163.75 73.09 740.02 -3.56	141.17 242.43 160.19 74.09 742.28 65.66	50.45 251.80 160.92 73.89 741.73 59.48	59.39 237.44 159.86 73.75 745.21 43.48	53.98 236.33 159.52 73.39 744.68 46.36
		σ Anisotropy(ppm)	66.59 301.90 303.45 307.36 406.68 112.01	63.52 280.17 308.46 306.17 408.49 77.20	126.84 287.32 307.40 306.56 408.40 103.74	115.03 234.09 306.41 307.71 407.74 125.04	120.31 237.10 307.25 307.59 407.40 122.06
		Determinan(NMR)	3.35E+06 1.33E+06 1.33E+06 2.38E+05 3.69E+08 -1.57E+05	2.61E+06 6.61E+06 1.20E+06 2.17E+05 3.73E+08 -7.43E+04	-5.52E+04 9.26E+06 1.25E+06 2.22E+05 3.72E+08 -2.92E+05	-8.05E+03 8.22E+06 1.22E+06 2.33E+05 3.78E+08 -4.45E+05	-3.91E+04 7.98E+06 1.21E+06 2.34E+05 3.77E+08 -4.27E+05
		Distance matrix	4.3626e+007	-2.8415e+008	-1.0161e+010	1.7749e+010	7.6094e+010

Table 3a, 3b have been shown share of orbitals contribute in bonds (BD for 2-center bond and BD* for 2-center antibond).

Table 3a. Relative natural bond orbital (NBO) for several active bond in studied moleculars by **a)** HF method with 6-31G, 6-31G* and 6-31+G basis set **b)** B3LYP, BLYP and B3PW91 methods with 6-31G

Method		**HF**					
Basis set		**6-31G**		**6-31G***		**6-31+G**	
Name	**Bond**	**BD**	**BD***	**BD**	**BD***	**BD**	**BD***
Molecular 1	C1 – S2	$0.7292\ sp^{3.44} + 0.6843\ sp^{4.13}$	$0.6843\ sp^{3.44} - 0.7292\ sp^{4.15}$	$0.7437\ sp^{3.18}\ d^{0.01} + 0.6686\ sp^{4.10}\ d^{0.09}$	$0.6686\ sp^{3.18}\ d^{0.01} - 0.7437\ sp^{4.10}\ d^{0.09}$	-	-
	S2 – O10	$0.6171 sp^{2.93} + 0.7869\ sp^{3.62}$	$0.7869\ sp^{2.93} - 0.6171\ sp^{3.62}$	$0.5752\ sp^{3.10}\ d^{0.08} + 0.8180\ sp^{2.36}\ d^{0.02}$	$0.8180\ sp^{3.10}\ d^{0.08} - 0.5752\ sp^{2.36}\ d^{0.02}$	-	-
	S2 – C3	$0.6828\ sp^{4.13} + 0.7306\ sp^{3.63}$	$0.7306\ sp^{4.13} - 0.6828\ sp^{3.63}$	$0.6666\ sp^{4.10}\ d^{0.09} + 0.7454\ sp^{2.38}\ d^{0.01}$	$0.7454\ sp^{4.10}\ d^{0.09} - 0.6666\ sp^{2.38}\ d^{0.01}$	-	-
	C6 – N7	$0.6113\ sp^{3.37} + 0.7914\ sp^{2.19}$	$0.7914\ sp^{3.37} - 0.6113\ sp^{2.19}$	$0.6102\ sp^{3.33}\ d^{0.01} + 0.7923\ sp^{2.15}\ d^{0.01}$	$0.7923\ sp^{3.33}\ d^{0.01} - 0.6102\ sp^{2.15}\ d^{0.01}$	-	-
	N7 – C8	$0.7663\ sp^{1.55} + 0.6425\ sp^{1.19}$	$0.6425\ sp^{1.55} - 0.7663\ sp^{1.19}$	$0.7672\ sp^{1.55}\ d^{0.01} + 0.6414\ sp^{1.17}$	$0.6414\ sp^{1.55}\ d^{0.01} - 0.7672\ sp^{1.17}$	-	-
	C8 – S9	$0.7434\ sp^{1.19} + 0.6689\ sp^{4.39}$	$0.6689\ sp^{1.19} - 0.7434\ sp^{4.39}$	$0.7468\ sp^{1.16}\ d^{0.01} + 0.6651\ sp^{3.98}\ d^{0.03}$	$0.6651\ sp^{1.16}\ d^{0.01} - 0.7468\ sp^{3.98}\ d^{0.03}$	-	-
Molecular 2	C1 – S3	$0.7257\ sp^{3.68} + 0.6880\ sp^{3.75}$	$0.6880\ sp^{3.68} - 0.7257\ sp^{3.75}$	$0.7409\ sp^{3.41}\ d^{0.01} + 0.6716\ sp^{3.75}\ d^{0.08}$	$0.6716\ sp^{3.41}\ d^{0.01} - 0.7409\ sp^{3.75}\ d^{0.08}$	-	-
	S3 – O11	$0.6136\ sp^{2.92} + 0.7896\ sp^{3.30}$	$0.7896\ sp^{2.92} - 0.6136\ sp^{3.30}$	$0.5728\ sp^{3.09}\ d^{0.08} + 0.8197\ sp^{3.30}\ d^{0.02}$	$0.8197\ sp^{3.09}\ d^{0.08} - 0.5728\ sp^{3.30}\ d^{0.02}$	-	-
	S3 – C4	$0.6851\ sp^{3.79} + 0.7285\ sp^{3.67}$	$0.7285\ sp^{3.79} - 0.6851\ sp^{3.67}$	$0.6693\ sp^{3.77}\ d^{0.08} + 0.7430\ sp^{3.41}\ d^{0.01}$	$0.7430\ sp^{3.77}\ d^{0.08} - 0.6693\ sp^{3.41}\ d^{0.01}$	-	-
	C7 – N8	$0.6102\ sp^{3.38} + 0.7922\ sp^{2.19}$	$0.7922\ sp^{3.38} - 0.6102\ sp^{2.19}$	$0.6093\ sp^{3.34}\ d^{0.01} + 0.7930\ sp^{2.15}\ d^{0.01}$	$0.7930\ sp^{3.34}\ d^{0.01} - 0.6093\ sp^{2.15}\ d^{0.01}$	-	-
	N8 – C9	$0.7663\ sp^{1.55} + 0.6425\ sp^{1.18}$	$0.6425\ sp^{1.55} - 0.7663\ sp^{1.18}$	$0.7672\ sp^{1.55}\ d^{0.01} + 0.6414\ sp^{1.17}$	$0.6414\ sp^{1.55}\ d^{0.01} - 0.7672\ sp^{1.17}$	-	-
	C9 – S10	$0.7424\ sp^{1.20} + 0.6700\ sp^{4.39}$	$0.6700\ sp^{1.20} - 0.7424\ sp^{4.39}$	$0.7459\ sp^{1.17}\ d^{0.01} + 0.6660\ sp^{3.98}\ d^{0.03}$	$0.6660\ sp^{1.17}\ d^{0.01} - 0.7459\ sp^{3.98}\ d^{0.03}$	-	-
Molecular 3	C1 – S2	$0.7408\ sp^{2.92} + 0.6717\ sp^{4.14}$	$0.6717\ sp^{2.92} - 0.7408\ sp^{4.14}$	$0.7565\ sp^{2.76}\ d^{0.01} + 0.6540\ sp^{4.16}\ d^{0.09}$	$0.6540\ sp^{2.76}\ d^{0.01} - 0.7565\ sp^{4.16}\ d^{0.09}$	-	-
	S2 – O10	$0.6161\ sp^{2.95} + 0.7877\ sp^{3.59}$	$0.7877\ sp^{2.95} - 0.6161\ sp^{3.59}$	$0.5746\ sp^{3.10}\ d^{0.08} + 0.8184\ sp^{2.34}\ d^{0.02}$	$0.8184\ sp^{3.10}\ d^{0.08} - 0.5746\ sp^{2.34}\ d^{0.02}$	-	-
	S2 – C3	$0.6849\ sp^{4.11} + 0.7286\ sp^{3.66}$	$0.7286\ sp^{4.11} - 0.6849\ sp^{3.66}$	$0.6687\ sp^{4.08}\ d^{0.09} + 0.7435\ sp^{3.40}\ d^{0.01}$	$0.7435\ sp^{4.08}\ d^{0.09} - 0.6687\ sp^{3.40}\ d^{0.01}$	-	-
	C6 – N7	$0.6110\ sp^{3.37} + 0.7916\ sp^{2.18}$	$0.7916\ sp^{3.37} - 0.6110\ sp^{2.18}$	$0.6100\ sp^{3.33}\ d^{0.01} + 0.7924\ sp^{2.14}\ d^{0.01}$	$0.7924\ sp^{3.33}\ d^{0.01} - 0.6100\ sp^{2.14}\ d^{0.01}$	-	-
	N7 – C8	$0.7663\ sp^{1.55} + 0.6424\ sp^{1.18}$	$0.6424\ sp^{1.55} - 0.7663\ sp^{1.18}$	$0.7673\ sp^{1.54}\ d^{0.01} + 0.6413\ sp^{1.17}$	$0.6413\ sp^{1.54}\ d^{0.01} - 0.7673\ sp^{1.17}$	-	-
	C8 – S9	$0.7443\ sp^{1.17} + 0.6679\ sp^{4.27}$	$0.6679\ sp^{1.17} - 0.7443\ sp^{4.27}$	$0.7482\ sp^{1.14}\ d^{0.01} + 0.6635\ sp^{3.86}\ d^{0.05}$	$0.6635\ sp^{1.14}\ d^{0.01} - 0.7482\ sp^{3.86}\ d^{0.05}$	-	-
Molecular 4	C1 – S2	$0.7396\ sp^{2.89} + 0.6730\ sp^{4.07}$	$0.6730\ sp^{2.89} - 0.7396\ sp^{4.07}$	$0.7547\ sp^{2.74}\ d^{0.01} + 0.6560\ sp^{4.07}\ d^{0.09}$	$0.6560\ sp^{2.74}\ d^{0.01} - 0.7547\ sp^{4.07}\ d^{0.09}$	-	-
	S2 – O10	$0.6143\ sp^{3.04} + 0.7891\ sp^{3.56}$	$0.7891\ sp^{3.04} - 0.6143\ sp^{3.56}$	$0.5726\ sp^{3.19}\ d^{0.08} + 0.8198\ sp^{2.32}\ d^{0.02}$	$0.8198\ sp^{3.19}\ d^{0.08} - 0.5726\ sp^{2.32}\ d^{0.02}$	-	-
	S2 – C3	$0.6875\ sp^{4.01} + 0.7262\ sp^{3.68}$	$0.7262\ sp^{4.01} - 0.6875\ sp^{3.68}$	$0.6707\ sp^{3.98}\ d^{0.09} + 0.7417\ sp^{3.40}\ d^{0.01}$	$0.7417\ sp^{3.98}\ d^{0.09} - 0.6707\ sp^{3.40}\ d^{0.01}$	-	-
	C6 – N7	$0.6079\ sp^{3.41} + 0.7940\ sp^{3.21}$	$0.7940\ sp^{3.41} - 0.6079\ sp^{3.21}$	$0.6071\ sp^{3.37}\ d^{0.01} + 0.7946\ sp^{3.17}\ d^{0.01}$	$0.7946\ sp^{3.37}\ d^{0.01} - 0.6071\ sp^{3.17}\ d^{0.01}$	-	-
	N7 – C8	$0.7670\ sp^{1.51} + 0.6416\ sp^{1.19}$	$0.6416\ sp^{1.51} - 0.7670\ sp^{1.19}$	$0.7680\ sp^{1.52}\ d^{0.01} + 0.6404\ sp^{1.17}$	$0.6404\ sp^{1.52}\ d^{0.01} - 0.7680\ sp^{1.17}$	-	-
	C8 – S9	$0.7428\ sp^{1.19} + 0.6695\ sp^{4.41}$	$0.6695\ sp^{1.19} - 0.7428\ sp^{4.41}$	$0.7458\ sp^{1.17}\ d^{0.01} + 0.6662\ sp^{4.01}\ d^{0.05}$	$0.6662\ sp^{1.17}\ d^{0.01} - 0.7458\ sp^{4.01}\ d^{0.05}$	-	-
Molecular 5	C1 – S2	$0.7383\ sp^{2.92} + 0.6744\ sp^{4.07}$	$0.6744\ sp^{2.92} - 0.7383\ sp^{4.07}$	$0.7541\ sp^{2.76}\ d^{0.01} + 0.6567\ sp^{4.08}\ d^{0.09}$	$0.6567\ sp^{2.76}\ d^{0.01} - 0.7541\ sp^{4.08}\ d^{0.09}$	-	-
	S2 – O10	$0.6138\ sp^{3.05} + 0.7895\ sp^{3.55}$	$0.7895\ sp^{3.05} - 0.6138\ sp^{3.55}$	$0.5723\ sp^{3.20}\ d^{0.08} + 0.8200\ sp^{2.32}\ d^{0.02}$	$0.8200\ sp^{3.20}\ d^{0.08} - 0.5723\ sp^{2.32}\ d^{0.02}$	-	-
	S2 – C3	$0.6865\ sp^{4.03} + 0.7272\ sp^{3.67}$	$0.7272\ sp^{4.03} - 0.6865\ sp^{3.67}$	$0.6701\ sp^{4.01}\ d^{0.09} + 0.7423\ sp^{3.40}\ d^{0.01}$	$0.7423\ sp^{4.01}\ d^{0.09} - 0.6701\ sp^{3.40}\ d^{0.01}$	-	-
	C6 – N7	$0.6076\ sp^{3.41} + 0.7943\ sp^{2.20}$	$0.7943\ sp^{3.41} - 0.6076\ sp^{2.20}$	$0.6069\ sp^{3.38}\ d^{0.01} + 0.7948\ sp^{2.17}\ d^{0.01}$	$0.7948\ sp^{3.38}\ d^{0.01} - 0.6069\ sp^{2.17}\ d^{0.01}$	-	-
	N7 – C8	$0.7670\ sp^{1.52} + 0.6417\ sp^{1.18}$	$0.6417\ sp^{1.52} - 0.7670\ sp^{1.18}$	$0.7680\ sp^{1.52}\ d^{0.01} + 0.6405\ sp^{1.17}$	$0.6405\ sp^{1.52}\ d^{0.01} - 0.7680\ sp^{1.17}$	-	-
	C8 – S9	$0.7425\ sp^{1.19} + 0.6698\ sp^{4.41}$	$0.6698\ sp^{1.19} - 0.7425\ sp^{4.41}$	$0.7456\ sp^{1.17}\ d^{0.01} + 0.6663\ sp^{4.01}\ d^{0.05}$	$0.6663\ sp^{1.17}\ d^{0.01} - 0.7456\ sp^{4.01}\ d^{0.05}$	-	-

Table 3b.

Basis set		6-31G					
Method		B3LYP		BLYP		B3PW91	
Name	Bond	BD	BD*	BD	BD*	BD	BD*
Molecular 1	C1 – S2	0.7248 $sp^{3.43}$ + 0.6889 $sp^{4.49}$	0.6889 $sp^{3.43}$ - 0.7248 $sp^{4.49}$	0.7233 $sp^{3.41}$ + 0.6905 $sp^{4.60}$	0.6905 $sp^{3.41}$ - 0.7233 $sp^{4.60}$	0.7246 $sp^{3.47}$ + 0.6891 $sp^{4.46}$	0.6891 $sp^{3.47}$ - 0.7246 $sp^{4.46}$
	S2 – O10	0.6116 $sp^{3.19}$ + 0.7912 $sp^{3.73}$	0.7912 $sp^{3.19}$ - 0.6116 $sp^{3.73}$	0.6093 $sp^{3.20}$ + 0.7930 $sp^{3.75}$	0.7930 $sp^{3.39}$ - 0.6093 $sp^{3.75}$	0.6132 $sp^{3.19}$ + 0.7899 $sp^{3.75}$	0.7899 $sp^{3.19}$ - 0.6132 $sp^{3.75}$
	S2 – C3	0.6880 $sp^{4.47}$ + 0.7257 $sp^{3.63}$	0.7257 $sp^{4.47}$ - 0.6880 $sp^{3.63}$	0.6897 $sp^{4.38}$ + 0.7241 $sp^{3.62}$	0.7241 $sp^{4.38}$ - 0.6897 $sp^{3.62}$	0.6878 $sp^{4.43}$ + 0.7259 $sp^{3.66}$	0.7259 $sp^{4.43}$ - 0.6878 $sp^{3.66}$
	C6 – N7	0.6244 $sp^{3.32}$ + 0.7811 $sp^{3.45}$	0.7811 $sp^{3.32}$ - 0.6244 $sp^{3.45}$	0.6277 $sp^{3.31}$ + 0.7785 $sp^{3.50}$	0.7785 $sp^{3.31}$ - 0.6277 $sp^{3.50}$	0.6250 $sp^{3.33}$ + 0.7806 $sp^{3.44}$	0.7806 $sp^{3.33}$ - 0.6250 $sp^{3.44}$
	N7 – C8	0.7669 $sp^{1.51}$ + 0.6418 $sp^{1.17}$	0.6418 $sp^{1.51}$ - 0.7669 $sp^{1.17}$	0.7672 $sp^{1.50}$ + 0.6414 $sp^{1.16}$	0.6414 $sp^{1.50}$ - 0.7672 $sp^{1.16}$	0.7667 $sp^{1.52}$ + 0.6420 $sp^{1.16}$	0.6420 $sp^{1.52}$ - 0.7667 $sp^{1.16}$
	C8 – S9	0.7388 $sp^{2.17}$ + 0.6739 $sp^{3.37}$	0.6739 $sp^{2.17}$ - 0.7388 $sp^{3.37}$	0.7375 $sp^{2.16}$ + 0.6753 $sp^{3.37}$	0.6753 $sp^{2.16}$ - 0.7375 $sp^{3.37}$	0.7375 $sp^{2.18}$ + 0.6753 $sp^{3.25}$	0.6753 $sp^{2.18}$ - 0.7375 $sp^{3.25}$
Molecular 2	C1 – S3	0.7219 $sp^{3.68}$ + 0.6920 $sp^{4.03}$	0.6920 $sp^{3.68}$ - 0.7219 $sp^{4.03}$	0.7206 $sp^{3.67}$ + 0.6934 $sp^{4.12}$	0.6934 $sp^{3.67}$ - 0.7206 $sp^{4.12}$	0.7220 $sp^{3.71}$ + 0.6919 $sp^{4.00}$	0.6919 $sp^{3.71}$ - 0.7220 $sp^{4.00}$
	S3 – O11	0.6086 $sp^{3.15}$ + 0.7935 $sp^{3.63}$	0.7935 $sp^{3.15}$ - 0.6086 $sp^{3.63}$	0.6065 $sp^{3.24}$ + 0.7951 $sp^{3.65}$	0.7951 $sp^{3.24}$ - 0.6065 $sp^{3.65}$	0.6103 $sp^{3.15}$ + 0.7922 $sp^{3.65}$	0.7922 $sp^{3.15}$ - 0.6103 $sp^{3.65}$
	S3 – C4	0.6898 $sp^{4.07}$ + 0.7240 $sp^{3.68}$	0.7240 $sp^{4.07}$ - 0.6898 $sp^{3.68}$	0.6913 $sp^{4.16}$ + 0.7226 $sp^{3.66}$	0.7226 $sp^{4.16}$ - 0.6913 $sp^{3.66}$	0.6897 $sp^{4.04}$ + 0.7241 $sp^{3.70}$	0.7241 $sp^{4.04}$ - 0.6897 $sp^{3.70}$
	C7 – N8	0.6237 $sp^{2.33}$ + 0.7816 $sp^{2.43}$	0.7816 $sp^{2.33}$ - 0.6237 $sp^{2.43}$	0.6270 $sp^{2.32}$ + 0.7791 $sp^{2.50}$	0.7791 $sp^{2.32}$ - 0.6270 $sp^{2.50}$	0.6243 $sp^{2.34}$ + 0.7812 $sp^{2.44}$	0.7812 $sp^{2.34}$ - 0.6243 $sp^{2.44}$
	N8 – C9	0.7670 $sp^{1.31}$ + 0.6417 $sp^{1.16}$	0.6417 $sp^{1.31}$ - 0.7670 $sp^{1.16}$	0.7672 $sp^{1.30}$ + 0.6414 $sp^{1.16}$	0.6414 $sp^{1.30}$ - 0.7672 $sp^{1.16}$	0.7668 $sp^{1.32}$ + 0.6419 $sp^{1.16}$	0.6419 $sp^{1.32}$ - 0.7668 $sp^{1.16}$
	C9 – S10	0.7382 $sp^{1.17}$ + 0.6746 $sp^{4.36}$	0.6746 $sp^{1.17}$ - 0.7382 $sp^{4.36}$	0.7371 $sp^{1.16}$ + 0.6757 $sp^{4.33}$	0.6757 $sp^{1.16}$ - 0.7371 $sp^{4.33}$	0.7369 $sp^{1.18}$ + 0.6760 $sp^{4.34}$	0.6760 $sp^{1.18}$ - 0.7369 $sp^{4.34}$
Molecular 3	C1 – S2	-	-	0.7309 $sp^{3.00}$ + 0.6825 $sp^{4.59}$	0.6825 $sp^{3.00}$ - 0.7309 $sp^{4.59}$	0.7333 $sp^{3.59}$ + 0.6799 $sp^{4.44}$	0.6799 $sp^{3.59}$ - 0.7333 $sp^{4.44}$
	S2 – O10	-	-	0.6081 $sp^{3.31}$ + 0.7938 $sp^{3.71}$	0.7938 $sp^{3.31}$ - 0.6081 $sp^{3.71}$	0.6121 $sp^{3.21}$ + 0.7908 $sp^{3.72}$	0.7908 $sp^{3.21}$ - 0.6121 $sp^{3.72}$
	S2 – C3	-	-	0.6910 $sp^{4.33}$ + 0.7229 $sp^{3.66}$	0.7229 $sp^{4.33}$ - 0.6910 $sp^{3.66}$	0.6897 $sp^{4.39}$ + 0.7241 $sp^{3.70}$	0.7241 $sp^{4.39}$ - 0.6897 $sp^{3.70}$
	C6 – N7	-	-	0.6273 $sp^{3.31}$ + 0.7788 $sp^{2.48}$	0.7788 $sp^{3.31}$ - 0.6273 $sp^{2.49}$	0.6247 $sp^{3.33}$ + 0.7809 $sp^{2.43}$	0.7809 $sp^{3.33}$ - 0.6247 $sp^{2.43}$
	N7 – C8	-	-	0.7673 $sp^{1.50}$ + 0.6413 $sp^{1.16}$	0.6413 $sp^{1.50}$ - 0.7673 $sp^{1.16}$	0.7667 $sp^{1.52}$ + 0.6420 $sp^{1.16}$	0.6420 $sp^{1.52}$ - 0.7667 $sp^{1.16}$
	C8 – S9	-	-	0.7379 $sp^{1.14}$ + 0.6749 $sp^{4.25}$	0.6749 $sp^{1.14}$ - 0.7379 $sp^{4.25}$	0.7382 $sp^{1.16}$ + 0.6746 $sp^{4.24}$	0.6746 $sp^{1.16}$ - 0.7382 $sp^{4.24}$
Molecular 4	C1 – S2	0.7316 $sp^{2.96}$ + 0.6818 $sp^{4.40}$	0.6818 $sp^{2.96}$ - 0.7316 $sp^{4.40}$	0.7291 $sp^{2.98}$ + 0.6844 $sp^{4.50}$	0.6844 $sp^{2.98}$ - 0.7291 $sp^{4.50}$	0.7317 $sp^{2.97}$ + 0.6816 $sp^{4.37}$	0.6816 $sp^{2.97}$ - 0.7317 $sp^{4.37}$
	S2 – O10	0.6090 $sp^{2.20}$ + 0.7932 $sp^{3.67}$	0.7932 $sp^{2.30}$ - 0.6090 $sp^{3.67}$	0.6066 $sp^{2.40}$ + 0.7950 $sp^{3.69}$	0.7950 $sp^{2.40}$ - 0.6066 $sp^{3.69}$	0.6107 $sp^{2.20}$ + 0.7919 $sp^{3.70}$	0.7919 $sp^{2.20}$ - 0.6107 $sp^{3.70}$
	S2 – C3	0.6916 $sp^{4.31}$ + 0.7223 $sp^{3.68}$	0.7223 $sp^{4.31}$ - 0.6916 $sp^{3.68}$	0.6928 $sp^{4.41}$ + 0.7211 $sp^{3.67}$	0.7211 $sp^{4.41}$ - 0.6928 $sp^{3.67}$	0.6917 $sp^{4.28}$ + 0.7222 $sp^{3.71}$	0.7222 $sp^{4.28}$ - 0.6917 $sp^{3.71}$
	C6 – N7	0.6216 $sp^{3.24}$ + 0.7834 $sp^{2.45}$	0.7834 $sp^{3.24}$ - 0.6216 $sp^{2.45}$	0.6249 $sp^{3.31}$ + 0.7807 $sp^{2.32}$	0.7807 $sp^{3.31}$ - 0.6249 $sp^{2.32}$	0.6221 $sp^{3.35}$ + 0.7829 $sp^{2.46}$	0.7829 $sp^{3.35}$ - 0.6221 $sp^{2.46}$
	N7 – C8	0.7676 $sp^{1.48}$ + 0.6410 $sp^{1.17}$	0.6410 $sp^{1.48}$ - 0.7676 $sp^{1.17}$	0.7680 $sp^{1.47}$ + 0.6405 $sp^{1.16}$	0.6405 $sp^{1.47}$ - 0.7680 $sp^{1.16}$	0.7673 $sp^{1.49}$ + 0.6413 $sp^{1.16}$	0.6413 $sp^{1.49}$ - 0.7673 $sp^{1.16}$
	C8 – S9	0.7393 $sp^{1.15}$ + 0.6734 $sp^{4.36}$	0.6734 $sp^{1.15}$ - 0.7393 $sp^{4.36}$	0.7379 $sp^{1.14}$ + 0.6749 $sp^{4.35}$	0.6749 $sp^{1.14}$ - 0.7379 $sp^{4.35}$	0.7379 $sp^{1.16}$ + 0.6749 $sp^{4.34}$	0.6749 $sp^{1.16}$ - 0.7379 $sp^{4.34}$
Molecular 5	C1 – S2	0.7310 $sp^{2.96}$ + 0.6824 $sp^{4.41}$	0.6824 $sp^{2.98}$ - 0.7310 $sp^{4.41}$	0.7286 $sp^{3.00}$ + 0.6849 $sp^{4.51}$	0.6849 $sp^{3.00}$ - 0.7286 $sp^{4.51}$	0.7311 $sp^{2.99}$ + 0.6823 $sp^{4.38}$	0.6823 $sp^{2.99}$ - 0.7311 $sp^{4.38}$
	S2 – O10	0.6087 $sp^{3.31}$ + 0.7934 $sp^{3.66}$	0.7934 $sp^{3.31}$ - 0.6087 $sp^{3.66}$	0.6065 $sp^{3.41}$ + 0.7951 $sp^{3.69}$	0.7951 $sp^{3.41}$ - 0.6065 $sp^{3.69}$	0.6104 $sp^{3.31}$ + 0.7921 $sp^{3.69}$	0.7921 $sp^{3.31}$ - 0.6104 $sp^{3.69}$
	S2 – C3	0.6910 $sp^{4.35}$ + 0.7229 $sp^{3.68}$	0.7229 $sp^{4.35}$ - 0.6910 $sp^{3.68}$	0.6923 $sp^{4.44}$ + 0.7216 $sp^{3.67}$	0.7216 $sp^{4.44}$ - 0.6923 $sp^{3.67}$	0.6911 $sp^{4.31}$ + 0.7228 $sp^{3.71}$	0.7228 $sp^{4.31}$ - 0.6911 $sp^{3.71}$
	C6 – N7	0.6214 $sp^{3.34}$ + 0.7835 $sp^{2.45}$	0.7835 $sp^{3.34}$ - 0.6214 $sp^{2.45}$	0.6248 $sp^{3.32}$ + 0.7808 $sp^{2.32}$	0.7808 $sp^{3.32}$ - 0.6248 $sp^{2.32}$	0.6220 $sp^{3.35}$ + 0.7831 $sp^{2.46}$	0.7831 $sp^{3.35}$ - 0.6220 $sp^{2.46}$
	N7 – C8	0.7676 $sp^{1.48}$ + 0.6409 $sp^{1.17}$	0.6409 $sp^{1.48}$ - 0.7676 $sp^{1.17}$	0.7679 $sp^{1.47}$ + 0.6406 $sp^{1.16}$	0.6406 $sp^{1.47}$ - 0.7679 $sp^{1.16}$	0.7673 $sp^{1.48}$ + 0.6413 $sp^{1.16}$	0.6413 $sp^{1.48}$ - 0.7673 $sp^{1.16}$
	C8 – S9	0.7391 $sp^{1.15}$ + 0.6736 $sp^{4.36}$	0.6736 $sp^{1.15}$ - 0.7391 $sp^{4.36}$	0.7378 $sp^{1.14}$ + 0.6750 $sp^{4.33}$	0.6750 $sp^{1.14}$ - 0.7378 $sp^{4.33}$	0.7378 $sp^{1.17}$ + 0.6751 $sp^{4.34}$	0.6751 $sp^{1.17}$ - 0.7378 $sp^{4.34}$

Finally Table 4 shows GIAO magnetic shielding for some of the atoms. As shown in table 4, in HF/6-31G and HF/6-31+G and BLYP methods for all of the molecules, and in B3LYP and B3PW91 methods for molecular1, oxygen atom in $(-C-SO-)$ group has negative magnetic shielding value, and in all of the methods for all of the atoms in all of the molecular, degeneracy value is equal to one.

Table 4. Relative GIAO Magnetic shielding for active site of studied molecules obtained using different methods

Method		**HF**						**B3LYP**		**BLYP**		**B3PW91**	
Basis set		**6-31G**		**6-31G***		**6-31+G**		**6-31G**					
Name	**atoms**	**Shielding (ppm)**	**Degeneracy**	**Shielding (ppm)**	**Degeneracy**	**Shielding (ppm)**	**Degeneracy**	**Shielding (ppm)**	**Degeneracy**	**Shielding (ppm)**	**Degeneracy**	**Shielding (ppm)**	**Degeneracy**
Molecular 1	C(1)	175.19	1	166.02	1	-	-	147.64	1	138.20	1	152.76	1
	S(2)	461.46	1	325.62	1	-	-	202.70	1	144.49	1	233.71	1
	N(7)	155.51	1	178.52	1	-	-	158.72	1	149.31	1	162.75	1
	C(8)	58.34	1	66.61	1	-	-	69.17	1	67.28	1	73.21	1
	S(9)	745.96	1	832.58	1	-	-	724.50	1	691.91	1	740.67	1
	O(10)	-195.84	1	334.72	1	-	-	-37.33	1	-41.59	1	-3.56	1
Molecular 2	C(1)	164.79	1	159.94	1	-	-	135.21	1	122.94	1	141.17	1
	S(3)	462.14	1	337.75	1	-	-	212.14	1	112.14	1	241.80	1
	N(8)	152.00	1	175.89	1	-	-	155.70	1	148.79	1	160.19	1
	C(9)	59.42	1	67.24	1	-	-	69.12	1	67.01	1	74.16	1
	S(10)	745.28	1	832.58	1	-	-	725.84	1	690.56	1	742.02	1
	O(11)	-64.17	1	372.74	1	-	-	32.74	1	-10.70	1	65.66	1
Molecular 3	C(1)	67.33	1	62.52	1	-	-	-	-	34.02	1	50.38	1
	S(2)	445.62	1	312.14	1	-	-	-	-	148.54	1	251.24	1
	N(7)	153.63	1	177.91	1	-	-	-	-	149.46	1	160.92	1
	C(8)	58.70	1	67.24	1	-	-	-	-	67.68	1	73.90	1
	S(9)	746.07	1	832.58	1	-	-	-	-	693.26	1	742.02	1
	O(10)	-80.87	1	334.69	1	-	-	-	-	-26.50	1	59.48	1
Molecular 4	C(1)	75.69	1	73.47	1	74.62	1	53.80	1	44.22	1	59.51	1
	S(2)	434.61	1	316.18	1	440.45	1	209.44	1	117.53	1	237.75	1
	N(7)	151.09	1	175.52	1	148.61	1	155.98	1	149.41	1	159.86	1
	C(8)	58.70	1	66.71	1	60.13	1	70.02	1	68.13	1	73.74	1
	S(9)	746.07	1	833.93	1	755.06	1	729.89	1	698.65	1	744.72	1
	O(10)	-86.63	1	354.88	1	-105.96	1	9.89	1	-25.84	1	43.64	1
Molecular 5	C(1)	70.38	1	65.75	1	69.43	1	48.81	1	38.70	1	53.84	1
	S(2)	433.03	1	316.18	1	438.65	1	206.74	1	116.18	1	236.40	1
	N(7)	151.06	1	175.50	1	148.49	1	155.92	1	149.40	1	159.52	1
	C(8)	58.70	1	66.70	1	60.13	1	70.04	1	68.28	1	73.40	1
	S(9)	746.85	1	833.93	1	755.06	1	729.89	1	698.65	1	744.72	1
	O(10)	-77.33	1	356.64	1	-101.41	1	11.83	1	-23.59	1	46.36	1

Diagrams of chemical shifts for each molecule have been shown In Figures 2-6. As reported in this Figures, in all of the methods and in all of the molecules, S atom related to (- NCS) group has maximal chemical shifts. Also we have found that in all of the molecules, chemical shift for mentioned atom, in HF/6-31g* level is the largest than other used methods in this work.

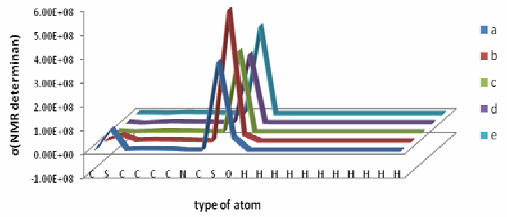


Fig. 2. The graphs of chemical shifts for molecular 1. (a) HF/6-31g, (b) HF/6-31g*, (c) B3LYP/6-31g, (d) BLYP/6-31g, (e) B3PW91/6-31g.

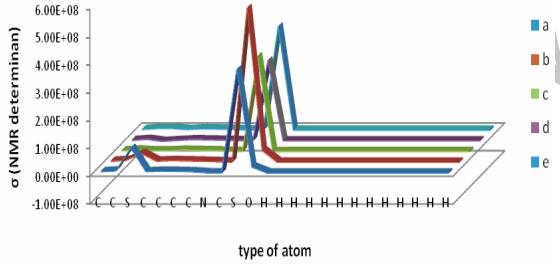


Fig. 3. The graphs of chemical shifts for molecular 2.(a) HF/6-31g , (b) HF/6-31g* , (c) B3LYP/6-31g, (d) BLYP/6-31g , (e) B3PW91/6-31g.

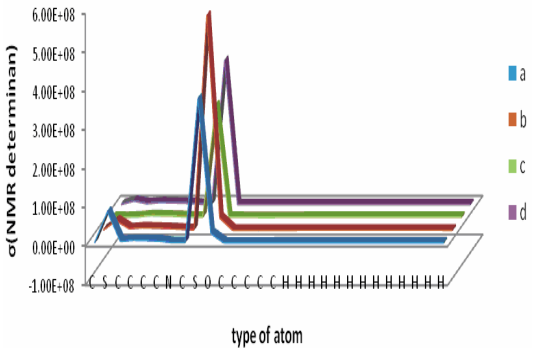


Fig. 4. The graphs of chemical shifts for molecular 3. (a) HF/6-31g, (b) HF/6-31g*, (c) BLYP/6-31g, (d) B3PW91/6-31g.

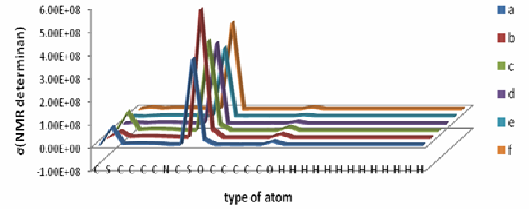


Fig. 5. The graphs of chemical shifts for molecular 4.(a) HF/6-31g , (b) HF/6-31g* , (c) HF/6-31+g , (d) B3LYP/6-31g , (e) BLYP/6-31g , (f) B3PW91/6-31g.

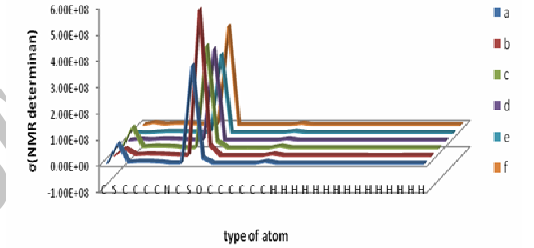


Fig. 6. The graphs of chemical shifts for molecular 5.(a) HF/6-31g , (b) HF/6-31g* , (c) HF/6-31+g , (d) B3LYP/6-31g , (e) BLYP/6-31g , (f) B3PW91/6-31G.

Finally Table 4 shows GIAO magnetic shielding for some of the atoms. As shown in table 4, in HF/6-31G and HF/6-31+G and BLYP methods for all of the molecules, and in B3LYP and B3PW91 methods for molecular1, oxygen atom in $(-C-SO-)$ group has negative magnetic shielding value, and in all of the methods for all of the atoms in all of the molecular, degeneracy value is equal to one.

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