

## 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 sulforaphane and several similar compounds. We calculated physical parameters like atomic charges, energy ( $\Delta E$ ), chemical shift anisotropy ( $\delta$ ), asymmetry parameter ( $\eta$ ), chemical shift anisotropy ( $\Delta\sigma$ ), 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 ( $\Delta E$ ), 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  $\sigma$  Isotropic (ppm) and  $\sigma$  Anisotropic (ppm) that listed in the "GIAO Magnetic shielding tensor (ppm)", and  $\sigma$  determinant was calculated by using Matlab program. Molecular orbital

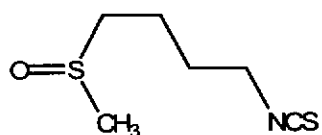
calculations can be used to get good estimates for chemical shifts. In this exercise, we calculated chemical shifts for each atom, then draw diagrams that shown chemical shifts for each atom by using Excel program. parameters such as  $\delta$ ,  $\eta$  and  $\Delta\sigma$  were calculated by using  $\sigma$  Isotropic (ppm),  $\sigma$  Anisotropic (ppm) and Eigenvalues( $\sigma_{11}$ ,  $\sigma_{22}$ ,  $\sigma_{33}$ ) [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.

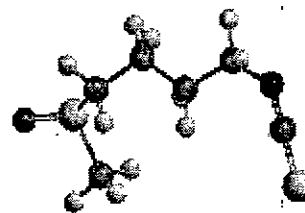
## RESULTS AND DISCUSSION

In this work ,we calculated parameters like atomic charges, energy ( $\Delta E$ ), chemical shift anisotropy ( $\delta$ ), asymmetry parameter ( $\eta$ ), chemical shift anisotropy ( $\Delta\sigma$ ), 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).

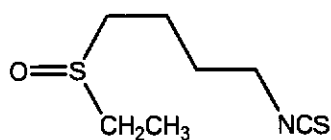
The optimized structure of molecules that studied in this work, have been shown in Fig.1.



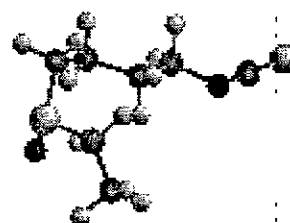
1-isothiocyano-4-(methylsulfinyl) butane



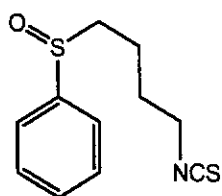
molecular (1)



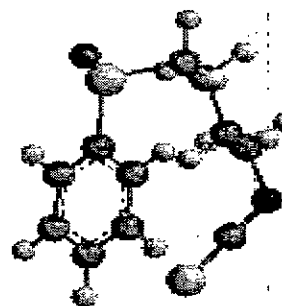
1-(ethylsulfinyl)-4-isothiocyano butane



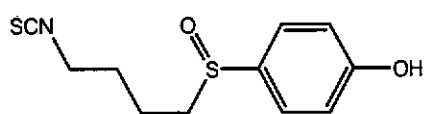
molecular (2)



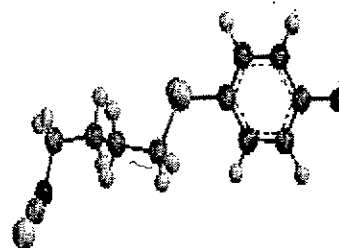
1-(4-isothiocyano-butylsulfinyl) benzene



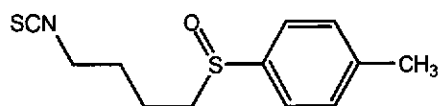
molecular (3)



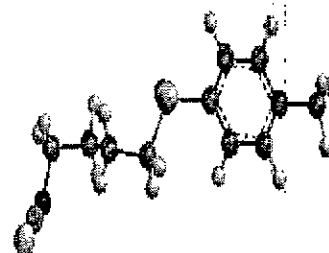
4-(4-isothiocyano-butylsulfinyl) phenol



molecular (4)



1-(4-isothiocyano-butylsulfinyl)-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 ( $\delta$ ) and ( $\Delta\sigma$ ) value for S atom in (- C - SO -) group is negative but other studied atoms is positive and  $\delta_O$  in (-C - SO-) group is the most positive value, while in HF/6-31G\* for molecular 2,  $\delta_O$  in (-C - SO-) group is negative but in other molecules is positive, also in all of the molecules,  $\delta_C$  in (-NCS) group is the greatest value. B3LYP and B3PW91 methods for all of the molecules,  $\delta_O$  in (-C - SO-) group is negative but in BLYP method  $\delta_O$  in (- C - SO -) group in molecular 2,4 and 5 is negative, also in B3LYP, BLYP and B3PW91 methods,  $\delta_S$  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,  $\eta_C$  in (- C - SO -) group is the greatest value, but in molecular1,  $\eta_S$  in (- C - SO -) group is the greatest, while in HF/6-31G\*,  $\eta_C$  in (-NCS) group has the greatest value, and in HF/6-31+G level  $\eta_C$  in (- C - SO -) group is the most amount, and in B3LYP and B3PW91 methods,  $\eta_S$  in (- C - SO -) group has the most value. But in BLYP

method  $\eta_O$  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.

$\Delta E$  (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,  $\Delta E$  has the most value, but in molecular3,  $\Delta E$  related to BLYP method, is the greatest.

As shown in table 2, in all of the methods for all of the molecules,  $\sigma_{iso}$  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,  $\sigma_{iso}$  for O atom in (- C - SO -) group is negative. In other hands, in HF/6-31G\*  $\sigma_{iso}$  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,  $\sigma_{aniso}$  for O atom in (- C - SO -) group is the most value, while HF/6-31G\*,  $\sigma_{aniso}$  related to C atom in (-NCS) group is the most, and in B3LYP, BLYP and B3PW91 methods,  $\sigma_{aniso}$  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,  $\Delta E$  (kcal/mol), chemical shift ( $\delta$ ), asymmetry parameter ( $\eta$ ), and chemical shift anisotropy ( $\Delta\sigma$ ), dipole moment for active site of studied molecules obtained using different methods

Method	Basis set	Name	HF										B3lyp					BLYP					B3PW91											
			6-31G					6-31G*					6-31+G					6-31G					6-31G					6-31G						
			Atomic charges	atomic charges	$\Delta E$ (kcal/mol)	$\delta$	$\eta$	$\Delta\sigma$	Dipole moment	atomic charges	atomic charges	$\Delta E$ (kcal/mol)	$\delta$	$\eta$	$\Delta\sigma$	Dipole moment	atomic charges	atomic charges	$\Delta E$ (kcal/mol)	$\delta$	$\eta$	$\Delta\sigma$	Dipole moment	atomic charges	atomic charges	$\Delta E$ (kcal/mol)	$\delta$	$\eta$	$\Delta\sigma$	Dipole moment	atomic charges	atomic charges	$\Delta E$ (kcal/mol)	$\delta$
Molecular 1	C(1) S(3) N(7) O(8) O(16)	Molecular 1	C(1) S(3) N(7) O(8) O(16)	atomic charges	$\Delta E$ (kcal/mol)	$\delta$	$\eta$	$\Delta\sigma$	Dipole moment	atomic charges	$\Delta E$ (kcal/mol)	$\delta$	$\eta$	$\Delta\sigma$	Dipole moment	atomic charges	$\Delta E$ (kcal/mol)	$\delta$	$\eta$	$\Delta\sigma$	Dipole moment	atomic charges	$\Delta E$ (kcal/mol)	$\delta$	$\eta$	$\Delta\sigma$	Dipole moment	atomic charges	$\Delta E$ (kcal/mol)	$\delta$	$\eta$	$\Delta\sigma$	Dipole moment	
																																		atomic charges
Molecular 2	C(1) S(3) N(7) O(8) O(16)	Molecular 2	C(1) S(3) N(7) O(8) O(16)	atomic charges	$\Delta E$ (kcal/mol)	$\delta$	$\eta$	$\Delta\sigma$	Dipole moment	atomic charges	$\Delta E$ (kcal/mol)	$\delta$	$\eta$	$\Delta\sigma$	Dipole moment	atomic charges	$\Delta E$ (kcal/mol)	$\delta$	$\eta$	$\Delta\sigma$	Dipole moment	atomic charges	$\Delta E$ (kcal/mol)	$\delta$	$\eta$	$\Delta\sigma$	Dipole moment	atomic charges	$\Delta E$ (kcal/mol)	$\delta$	$\eta$	$\Delta\sigma$	Dipole moment	
Molecular 3	C(1) S(3) N(7) O(8) O(16)	Molecular 3	C(1) S(3) N(7) O(8) O(16)	atomic charges	$\Delta E$ (kcal/mol)	$\delta$	$\eta$	$\Delta\sigma$	Dipole moment	atomic charges	$\Delta E$ (kcal/mol)	$\delta$	$\eta$	$\Delta\sigma$	Dipole moment	atomic charges	$\Delta E$ (kcal/mol)	$\delta$	$\eta$	$\Delta\sigma$	Dipole moment	atomic charges	$\Delta E$ (kcal/mol)	$\delta$	$\eta$	$\Delta\sigma$	Dipole moment	atomic charges	$\Delta E$ (kcal/mol)	$\delta$	$\eta$	$\Delta\sigma$	Dipole moment	
Molecular 4	C(1) S(3) N(7) O(8) O(16)	Molecular 4	C(1) S(3) N(7) O(8) O(16)	atomic charges	$\Delta E$ (kcal/mol)	$\delta$	$\eta$	$\Delta\sigma$	Dipole moment	atomic charges	$\Delta E$ (kcal/mol)	$\delta$	$\eta$	$\Delta\sigma$	Dipole moment	atomic charges	$\Delta E$ (kcal/mol)	$\delta$	$\eta$	$\Delta\sigma$	Dipole moment	atomic charges	$\Delta E$ (kcal/mol)	$\delta$	$\eta$	$\Delta\sigma$	Dipole moment	atomic charges	$\Delta E$ (kcal/mol)	$\delta$	$\eta$	$\Delta\sigma$	Dipole moment	
Molecular 5	C(1) S(3) N(7) O(8) O(16)	Molecular 5	C(1) S(3) N(7) O(8) O(16)	atomic charges	$\Delta E$ (kcal/mol)	$\delta$	$\eta$	$\Delta\sigma$	Dipole moment	atomic charges	$\Delta E$ (kcal/mol)	$\delta$	$\eta$	$\Delta\sigma$	Dipole moment	atomic charges	$\Delta E$ (kcal/mol)	$\delta$	$\eta$	$\Delta\sigma$	Dipole moment	atomic charges	$\Delta E$ (kcal/mol)	$\delta$	$\eta$	$\Delta\sigma$	Dipole moment	atomic charges	$\Delta E$ (kcal/mol)	$\delta$	$\eta$	$\Delta\sigma$	Dipole moment	

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

Molecular 5	Molecular 4	Molecular 3	Molecular 2	Molecular 1	Name	Method		
						Basis set		
C(1) N(2) O(3) S(4) O(10) O(11)	C(1) N(2) O(3) S(4) O(10)	C(1) N(2) O(3) S(4) O(10)	C(1) N(2) O(3) S(4) O(10)	C(1) N(2) O(3) S(4) O(10)	6-31G	$\sigma$ Isotropic(ppm)	175.05	
							$\sigma$ Anisotropy (ppm)	311.8
							Determinan(NMR)	5.22E+06
							Distance matrix	3.8532E+007
							$\sigma$ Isotropic(ppm)	164.16
							$\sigma$ Anisotropy (ppm)	47.68
							Determinan(NMR)	4.46E+05
							Distance matrix	2.9587E+007
							$\sigma$ Isotropic(ppm)	...
							$\sigma$ Anisotropy (ppm)	...
Determinan(NMR)	...							
Distance matrix	...							
C(1) N(2) O(3) S(4) O(10)	C(1) N(2) O(3) S(4) O(10)	C(1) N(2) O(3) S(4) O(10)	C(1) N(2) O(3) S(4) O(10)	C(1) N(2) O(3) S(4) O(10)	6-31G*	$\sigma$ Isotropic(ppm)	149.79	
							$\sigma$ Anisotropy (ppm)	51.84
							Determinan(NMR)	6.33E+06
							Distance matrix	-3.6807E+005
							$\sigma$ Isotropic(ppm)	159.34
							$\sigma$ Anisotropy (ppm)	48.89
							Determinan(NMR)	3.89E+05
							Distance matrix	-1.1757E+008
							$\sigma$ Isotropic(ppm)	...
							$\sigma$ Anisotropy (ppm)	...
Determinan(NMR)	...							
Distance matrix	...							
C(1) N(2) O(3) S(4) O(10)	C(1) N(2) O(3) S(4) O(10)	C(1) N(2) O(3) S(4) O(10)	C(1) N(2) O(3) S(4) O(10)	C(1) N(2) O(3) S(4) O(10)	B3LYP	$\sigma$ Isotropic(ppm)	147.15	
							$\sigma$ Anisotropy (ppm)	69.16
							Determinan(NMR)	2.29E+06
							Distance matrix	-2.9234E+008
							$\sigma$ Isotropic(ppm)	122.94
							$\sigma$ Anisotropy (ppm)	72.51
							Determinan(NMR)	1.69E+06
							Distance matrix	-3.4432E+008
							$\sigma$ Isotropic(ppm)	...
							$\sigma$ Anisotropy (ppm)	...
Determinan(NMR)	...							
Distance matrix	...							
C(1) N(2) O(3) S(4) O(10)	C(1) N(2) O(3) S(4) O(10)	C(1) N(2) O(3) S(4) O(10)	C(1) N(2) O(3) S(4) O(10)	C(1) N(2) O(3) S(4) O(10)	B3PW91	$\sigma$ Isotropic(ppm)	151.09	
							$\sigma$ Anisotropy (ppm)	64.59
							Determinan(NMR)	3.93E+06
							Distance matrix	4.3525E+007
							$\sigma$ Isotropic(ppm)	128.31
							$\sigma$ Anisotropy (ppm)	112.04
							Determinan(NMR)	3.92E+06
							Distance matrix	7.6409E+010
							$\sigma$ Isotropic(ppm)	...
							$\sigma$ Anisotropy (ppm)	...
Determinan(NMR)	...							
Distance matrix	...							

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 molecules 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 <sup>1.44</sup> + 0.6843 sp <sup>4.15</sup>	0.6843 sp <sup>1.44</sup> - 0.7292 sp <sup>4.15</sup>	0.7437 sp <sup>1.18</sup> d <sup>0.01</sup> + 0.6686 sp <sup>4.10</sup> d <sup>0.05</sup>	0.6686 sp <sup>1.18</sup> d <sup>0.01</sup> - 0.7437 sp <sup>4.10</sup> d <sup>0.05</sup>	-	-
	S2 - O10	0.6171 sp <sup>2.95</sup> + 0.7869 sp <sup>3.04</sup>	0.7869 sp <sup>2.95</sup> - 0.6171 sp <sup>3.04</sup>	0.5752 sp <sup>3.10</sup> d <sup>0.08</sup> + 0.8180 sp <sup>2.38</sup> d <sup>0.04</sup>	0.8180 sp <sup>3.10</sup> d <sup>0.08</sup> - 0.5752 sp <sup>2.38</sup> d <sup>0.04</sup>	-	-
	S2 - C3	0.6828 sp <sup>4.13</sup> + 0.7306 sp <sup>3.03</sup>	0.7306 sp <sup>4.13</sup> - 0.6828 sp <sup>3.03</sup>	0.6666 sp <sup>4.10</sup> d <sup>0.09</sup> + 0.7454 sp <sup>3.38</sup> d <sup>0.01</sup>	0.7454 sp <sup>4.10</sup> d <sup>0.09</sup> - 0.6666 sp <sup>3.38</sup> d <sup>0.01</sup>	-	-
	C6 - N7	0.6113 sp <sup>3.37</sup> + 0.7914 sp <sup>2.19</sup>	0.7914 sp <sup>3.37</sup> - 0.6113 sp <sup>2.19</sup>	0.6102 sp <sup>3.33</sup> d <sup>0.01</sup> + 0.7923 sp <sup>2.13</sup> d <sup>0.01</sup>	0.7923 sp <sup>3.33</sup> d <sup>0.01</sup> - 0.6102 sp <sup>2.13</sup> d <sup>0.01</sup>	-	-
	N7 - C8	0.7663 sp <sup>1.35</sup> + 0.6425 sp <sup>1.19</sup>	0.6425 sp <sup>1.35</sup> - 0.7663 sp <sup>1.19</sup>	0.7672 sp <sup>1.35</sup> d <sup>0.01</sup> + 0.6414 sp <sup>1.17</sup>	0.6414 sp <sup>1.35</sup> d <sup>0.01</sup> - 0.7672 sp <sup>1.17</sup>	-	-
	C8 - S9	0.7434 sp <sup>1.19</sup> + 0.6689 sp <sup>4.39</sup>	0.6689 sp <sup>1.19</sup> - 0.7434 sp <sup>4.39</sup>	0.7468 sp <sup>1.16</sup> d <sup>0.01</sup> + 0.6651 sp <sup>3.98</sup> d <sup>0.05</sup>	0.6651 sp <sup>1.16</sup> d <sup>0.01</sup> - 0.7468 sp <sup>3.98</sup> d <sup>0.05</sup>	-	-
Molecular 2	C1 - S3	0.7257 sp <sup>3.08</sup> + 0.6880 sp <sup>3.75</sup>	0.6880 sp <sup>3.08</sup> - 0.7257 sp <sup>3.75</sup>	0.7409 sp <sup>3.41</sup> d <sup>0.01</sup> + 0.6716 sp <sup>3.75</sup> d <sup>0.08</sup>	0.6716 sp <sup>3.41</sup> d <sup>0.01</sup> - 0.7409 sp <sup>3.75</sup> d <sup>0.08</sup>	-	-
	S3 - O11	0.6136 sp <sup>2.92</sup> + 0.7896 sp <sup>3.30</sup>	0.7896 sp <sup>2.92</sup> - 0.6136 sp <sup>3.30</sup>	0.5728 sp <sup>3.09</sup> d <sup>0.08</sup> + 0.8197 sp <sup>3.01</sup> d <sup>0.02</sup>	0.8197 sp <sup>3.09</sup> d <sup>0.08</sup> - 0.5728 sp <sup>3.01</sup> d <sup>0.02</sup>	-	-
	S3 - C4	0.6851 sp <sup>3.79</sup> + 0.7285 sp <sup>3.07</sup>	0.7285 sp <sup>3.79</sup> - 0.6851 sp <sup>3.07</sup>	0.6693 sp <sup>3.77</sup> d <sup>0.08</sup> + 0.7430 sp <sup>3.41</sup> d <sup>0.01</sup>	0.7430 sp <sup>3.77</sup> d <sup>0.08</sup> - 0.6693 sp <sup>3.41</sup> d <sup>0.01</sup>	-	-
	C7 - N8	0.6102 sp <sup>3.38</sup> + 0.7922 sp <sup>2.19</sup>	0.7922 sp <sup>3.38</sup> - 0.6102 sp <sup>2.19</sup>	0.6093 sp <sup>3.34</sup> d <sup>0.01</sup> + 0.7930 sp <sup>2.13</sup> d <sup>0.01</sup>	0.7930 sp <sup>3.34</sup> d <sup>0.01</sup> - 0.6093 sp <sup>2.13</sup> d <sup>0.01</sup>	-	-
	N8 - C9	0.7663 sp <sup>1.35</sup> + 0.6425 sp <sup>1.18</sup>	0.6425 sp <sup>1.35</sup> - 0.7663 sp <sup>1.18</sup>	0.7672 sp <sup>1.35</sup> d <sup>0.01</sup> + 0.6414 sp <sup>1.17</sup>	0.6414 sp <sup>1.35</sup> d <sup>0.01</sup> - 0.7672 sp <sup>1.17</sup>	-	-
	C9 - S10	0.7424 sp <sup>1.20</sup> + 0.6700 sp <sup>4.39</sup>	0.6700 sp <sup>1.20</sup> - 0.7424 sp <sup>4.39</sup>	0.7459 sp <sup>1.17</sup> d <sup>0.01</sup> + 0.6660 sp <sup>3.98</sup> d <sup>0.05</sup>	0.6660 sp <sup>1.17</sup> d <sup>0.01</sup> - 0.7459 sp <sup>3.98</sup> d <sup>0.05</sup>	-	-
Molecular 3	C1 - S2	0.7408 sp <sup>2.92</sup> + 0.6717 sp <sup>3.14</sup>	0.6717 sp <sup>2.92</sup> - 0.7408 sp <sup>3.14</sup>	0.7565 sp <sup>2.76</sup> d <sup>0.01</sup> + 0.6540 sp <sup>3.16</sup> d <sup>0.09</sup>	0.6540 sp <sup>2.76</sup> d <sup>0.01</sup> - 0.7565 sp <sup>3.16</sup> d <sup>0.09</sup>	-	-
	S2 - O10	0.6161 sp <sup>2.95</sup> + 0.7877 sp <sup>3.29</sup>	0.7877 sp <sup>2.95</sup> - 0.6161 sp <sup>3.29</sup>	0.5746 sp <sup>3.10</sup> d <sup>0.08</sup> + 0.8184 sp <sup>2.34</sup> d <sup>0.02</sup>	0.8184 sp <sup>3.10</sup> d <sup>0.08</sup> - 0.5746 sp <sup>2.34</sup> d <sup>0.02</sup>	-	-
	S2 - C3	0.6849 sp <sup>3.11</sup> + 0.7286 sp <sup>3.06</sup>	0.7286 sp <sup>3.11</sup> - 0.6849 sp <sup>3.06</sup>	0.6687 sp <sup>3.09</sup> d <sup>0.09</sup> + 0.7435 sp <sup>3.40</sup> d <sup>0.01</sup>	0.7435 sp <sup>3.09</sup> d <sup>0.09</sup> - 0.6687 sp <sup>3.40</sup> d <sup>0.01</sup>	-	-
	C6 - N7	0.6110 sp <sup>3.37</sup> + 0.7916 sp <sup>2.18</sup>	0.7916 sp <sup>3.37</sup> - 0.6110 sp <sup>2.18</sup>	0.6100 sp <sup>3.33</sup> d <sup>0.01</sup> + 0.7924 sp <sup>2.14</sup> d <sup>0.01</sup>	0.7924 sp <sup>3.33</sup> d <sup>0.01</sup> - 0.6100 sp <sup>2.14</sup> d <sup>0.01</sup>	-	-
	N7 - C8	0.7663 sp <sup>1.35</sup> + 0.6424 sp <sup>1.18</sup>	0.6424 sp <sup>1.35</sup> - 0.7663 sp <sup>1.18</sup>	0.7673 sp <sup>1.34</sup> d <sup>0.01</sup> + 0.6413 sp <sup>1.17</sup>	0.6413 sp <sup>1.34</sup> d <sup>0.01</sup> - 0.7673 sp <sup>1.17</sup>	-	-
	C8 - S9	0.7443 sp <sup>1.17</sup> + 0.6679 sp <sup>4.27</sup>	0.6679 sp <sup>1.17</sup> - 0.7443 sp <sup>4.27</sup>	0.7482 sp <sup>1.14</sup> d <sup>0.01</sup> + 0.6635 sp <sup>3.88</sup> d <sup>0.03</sup>	0.6635 sp <sup>1.14</sup> d <sup>0.01</sup> - 0.7482 sp <sup>3.88</sup> d <sup>0.03</sup>	-	-
Molecular 4	C1 - S2	0.7396 sp <sup>2.89</sup> + 0.6730 sp <sup>4.07</sup>	0.6730 sp <sup>2.89</sup> - 0.7396 sp <sup>4.07</sup>	0.7547 sp <sup>2.74</sup> d <sup>0.01</sup> + 0.6560 sp <sup>3.07</sup> d <sup>0.09</sup>	0.6560 sp <sup>2.74</sup> d <sup>0.01</sup> - 0.7547 sp <sup>3.07</sup> d <sup>0.09</sup>	-	-
	S2 - O10	0.6143 sp <sup>3.04</sup> + 0.7891 sp <sup>3.56</sup>	0.7891 sp <sup>3.04</sup> - 0.6143 sp <sup>3.56</sup>	0.5726 sp <sup>3.19</sup> d <sup>0.08</sup> + 0.8198 sp <sup>2.32</sup> d <sup>0.02</sup>	0.8198 sp <sup>3.19</sup> d <sup>0.08</sup> - 0.5726 sp <sup>2.32</sup> d <sup>0.02</sup>	-	-
	S2 - C3	0.6875 sp <sup>3.01</sup> + 0.7262 sp <sup>3.08</sup>	0.7262 sp <sup>3.01</sup> - 0.6875 sp <sup>3.08</sup>	0.6707 sp <sup>2.98</sup> d <sup>0.09</sup> + 0.7417 sp <sup>3.40</sup> d <sup>0.01</sup>	0.7417 sp <sup>2.98</sup> d <sup>0.09</sup> - 0.6707 sp <sup>3.40</sup> d <sup>0.01</sup>	-	-
	C6 - N7	0.6079 sp <sup>3.41</sup> + 0.7940 sp <sup>2.21</sup>	0.7940 sp <sup>3.41</sup> - 0.6079 sp <sup>2.21</sup>	0.6071 sp <sup>3.37</sup> d <sup>0.01</sup> + 0.7946 sp <sup>2.17</sup> d <sup>0.01</sup>	0.7946 sp <sup>3.37</sup> d <sup>0.01</sup> - 0.6071 sp <sup>2.17</sup> d <sup>0.01</sup>	-	-
	N7 - C8	0.7670 sp <sup>1.31</sup> + 0.6416 sp <sup>1.19</sup>	0.6416 sp <sup>1.31</sup> - 0.7670 sp <sup>1.19</sup>	0.7680 sp <sup>1.32</sup> d <sup>0.01</sup> + 0.6404 sp <sup>1.17</sup>	0.6404 sp <sup>1.32</sup> d <sup>0.01</sup> - 0.7680 sp <sup>1.17</sup>	-	-
	C8 - S9	0.7428 sp <sup>1.19</sup> + 0.6695 sp <sup>4.41</sup>	0.6695 sp <sup>1.19</sup> - 0.7428 sp <sup>4.41</sup>	0.7458 sp <sup>1.17</sup> d <sup>0.01</sup> + 0.6662 sp <sup>4.01</sup> d <sup>0.03</sup>	0.6662 sp <sup>1.17</sup> d <sup>0.01</sup> - 0.7458 sp <sup>4.01</sup> d <sup>0.03</sup>	-	-
Molecular 5	C1 - S2	0.7383 sp <sup>2.92</sup> + 0.6744 sp <sup>4.07</sup>	0.6744 sp <sup>2.92</sup> - 0.7383 sp <sup>4.07</sup>	0.7541 sp <sup>2.76</sup> d <sup>0.01</sup> + 0.6567 sp <sup>3.08</sup> d <sup>0.09</sup>	0.6567 sp <sup>2.76</sup> d <sup>0.01</sup> - 0.7541 sp <sup>3.08</sup> d <sup>0.09</sup>	-	-
	S2 - O10	0.6138 sp <sup>3.05</sup> + 0.7895 sp <sup>3.55</sup>	0.7895 sp <sup>3.05</sup> - 0.6138 sp <sup>3.55</sup>	0.5723 sp <sup>3.20</sup> d <sup>0.08</sup> + 0.8200 sp <sup>2.32</sup> d <sup>0.02</sup>	0.8200 sp <sup>3.20</sup> d <sup>0.08</sup> - 0.5723 sp <sup>2.32</sup> d <sup>0.02</sup>	-	-
	S2 - C3	0.6865 sp <sup>3.05</sup> + 0.7272 sp <sup>3.07</sup>	0.7272 sp <sup>3.05</sup> - 0.6865 sp <sup>3.07</sup>	0.6701 sp <sup>3.01</sup> d <sup>0.09</sup> + 0.7423 sp <sup>3.40</sup> d <sup>0.01</sup>	0.7423 sp <sup>3.01</sup> d <sup>0.09</sup> - 0.6701 sp <sup>3.40</sup> d <sup>0.01</sup>	-	-
	C6 - N7	0.6076 sp <sup>3.41</sup> + 0.7943 sp <sup>2.20</sup>	0.7943 sp <sup>3.41</sup> - 0.6076 sp <sup>2.20</sup>	0.6069 sp <sup>3.38</sup> d <sup>0.01</sup> + 0.7948 sp <sup>2.17</sup> d <sup>0.01</sup>	0.7948 sp <sup>3.38</sup> d <sup>0.01</sup> - 0.6069 sp <sup>2.17</sup> d <sup>0.01</sup>	-	-
	N7 - C8	0.7670 sp <sup>1.32</sup> + 0.6417 sp <sup>1.18</sup>	0.6417 sp <sup>1.32</sup> - 0.7670 sp <sup>1.18</sup>	0.7680 sp <sup>1.32</sup> d <sup>0.01</sup> + 0.6405 sp <sup>1.17</sup>	0.6405 sp <sup>1.32</sup> d <sup>0.01</sup> - 0.7680 sp <sup>1.17</sup>	-	-
	C8 - S9	0.7425 sp <sup>1.19</sup> + 0.6698 sp <sup>4.41</sup>	0.6698 sp <sup>1.19</sup> - 0.7425 sp <sup>4.41</sup>	0.7456 sp <sup>1.17</sup> d <sup>0.01</sup> + 0.6663 sp <sup>4.01</sup> d <sup>0.03</sup>	0.6663 sp <sup>1.17</sup> d <sup>0.01</sup> - 0.7456 sp <sup>4.01</sup> d <sup>0.03</sup>	-	-



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 <sup>1.43</sup> + 0.6889 sp <sup>4.29</sup>	0.6889 sp <sup>1.25</sup> - 0.7248 sp <sup>1.49</sup>	0.7233 sp <sup>1.41</sup> + 0.6905 sp <sup>4.20</sup>	0.6905 sp <sup>1.41</sup> - 0.7233 sp <sup>4.20</sup>	0.7246 sp <sup>1.47</sup> + 0.6891 sp <sup>4.26</sup>	0.6891 sp <sup>1.37</sup> - 0.7246 sp <sup>4.26</sup>
	S2 - O10	0.6116 sp <sup>3.18</sup> + 0.7912 sp <sup>3.73</sup>	0.7912 sp <sup>3.16</sup> - 0.6116 sp <sup>3.73</sup>	0.6093 sp <sup>3.20</sup> + 0.7930 sp <sup>3.73</sup>	0.7930 sp <sup>3.20</sup> - 0.6093 sp <sup>3.73</sup>	0.6132 sp <sup>3.19</sup> + 0.7899 sp <sup>3.73</sup>	0.7899 sp <sup>3.19</sup> - 0.6132 sp <sup>3.73</sup>
	S2 - C3	0.6880 sp <sup>4.27</sup> + 0.7257 sp <sup>3.63</sup>	0.7257 sp <sup>4.27</sup> - 0.6880 sp <sup>3.63</sup>	0.6897 sp <sup>4.38</sup> + 0.7241 sp <sup>3.62</sup>	0.7241 sp <sup>4.38</sup> - 0.6897 sp <sup>3.62</sup>	0.6878 sp <sup>4.43</sup> + 0.7259 sp <sup>3.62</sup>	0.7259 sp <sup>4.43</sup> - 0.6878 sp <sup>3.62</sup>
	C6 - N7	0.6244 sp <sup>3.32</sup> + 0.7811 sp <sup>2.43</sup>	0.7811 sp <sup>3.32</sup> - 0.6244 sp <sup>2.43</sup>	0.6277 sp <sup>3.31</sup> + 0.7785 sp <sup>2.30</sup>	0.7785 sp <sup>3.31</sup> - 0.6277 sp <sup>2.30</sup>	0.6250 sp <sup>3.33</sup> + 0.7806 sp <sup>2.44</sup>	0.7806 sp <sup>3.33</sup> - 0.6250 sp <sup>2.44</sup>
	N7 - C8	0.7669 sp <sup>1.51</sup> + 0.6418 sp <sup>1.17</sup>	0.6418 sp <sup>1.51</sup> - 0.7669 sp <sup>1.17</sup>	0.7672 sp <sup>1.50</sup> + 0.6414 sp <sup>1.16</sup>	0.6414 sp <sup>1.50</sup> - 0.7672 sp <sup>1.16</sup>	0.7667 sp <sup>1.52</sup> + 0.6420 sp <sup>1.16</sup>	0.6420 sp <sup>1.52</sup> - 0.7667 sp <sup>1.16</sup>
C8 - S9	0.7388 sp <sup>1.17</sup> + 0.6739 sp <sup>4.37</sup>	0.6739 sp <sup>1.17</sup> - 0.7388 sp <sup>4.37</sup>	0.7375 sp <sup>1.16</sup> + 0.6753 sp <sup>4.37</sup>	0.6753 sp <sup>1.16</sup> - 0.7375 sp <sup>4.37</sup>	0.7375 sp <sup>1.18</sup> + 0.6753 sp <sup>4.33</sup>	0.6753 sp <sup>1.18</sup> - 0.7375 sp <sup>4.33</sup>	
Molecular 2	C1 - S3	0.7219 sp <sup>1.68</sup> + 0.6920 sp <sup>3.03</sup>	0.6920 sp <sup>1.68</sup> - 0.7219 sp <sup>3.03</sup>	0.7206 sp <sup>1.67</sup> + 0.6934 sp <sup>3.12</sup>	0.6934 sp <sup>1.67</sup> - 0.7206 sp <sup>3.12</sup>	0.7220 sp <sup>1.71</sup> + 0.6919 sp <sup>3.00</sup>	0.6919 sp <sup>1.71</sup> - 0.7220 sp <sup>3.00</sup>
	S3 - O11	0.6086 sp <sup>3.15</sup> + 0.7933 sp <sup>3.63</sup>	0.7933 sp <sup>3.15</sup> - 0.6086 sp <sup>3.63</sup>	0.6063 sp <sup>3.24</sup> + 0.7951 sp <sup>3.63</sup>	0.7951 sp <sup>3.24</sup> - 0.6063 sp <sup>3.63</sup>	0.6103 sp <sup>3.15</sup> + 0.7922 sp <sup>3.63</sup>	0.7922 sp <sup>3.15</sup> - 0.6103 sp <sup>3.63</sup>
	S3 - C4	0.6898 sp <sup>4.07</sup> + 0.7240 sp <sup>3.66</sup>	0.7240 sp <sup>4.07</sup> - 0.6898 sp <sup>3.66</sup>	0.6913 sp <sup>4.16</sup> + 0.7226 sp <sup>3.66</sup>	0.7226 sp <sup>4.16</sup> - 0.6913 sp <sup>3.66</sup>	0.6897 sp <sup>4.04</sup> + 0.7241 sp <sup>3.70</sup>	0.7241 sp <sup>4.04</sup> - 0.6897 sp <sup>3.70</sup>
	C7 - N8	0.6237 sp <sup>3.33</sup> + 0.7816 sp <sup>2.43</sup>	0.7816 sp <sup>3.33</sup> - 0.6237 sp <sup>2.43</sup>	0.6270 sp <sup>3.32</sup> + 0.7791 sp <sup>2.30</sup>	0.7791 sp <sup>3.32</sup> - 0.6270 sp <sup>2.30</sup>	0.6243 sp <sup>3.34</sup> + 0.7812 sp <sup>2.44</sup>	0.7812 sp <sup>3.34</sup> - 0.6243 sp <sup>2.44</sup>
	N8 - C9	0.7670 sp <sup>1.51</sup> + 0.6417 sp <sup>1.16</sup>	0.6417 sp <sup>1.51</sup> - 0.7670 sp <sup>1.16</sup>	0.7672 sp <sup>1.50</sup> + 0.6414 sp <sup>1.16</sup>	0.6414 sp <sup>1.50</sup> - 0.7672 sp <sup>1.16</sup>	0.7668 sp <sup>1.52</sup> + 0.6419 sp <sup>1.16</sup>	0.6419 sp <sup>1.52</sup> - 0.7668 sp <sup>1.16</sup>
C9 - S10	0.7382 sp <sup>1.17</sup> + 0.6746 sp <sup>4.36</sup>	0.6746 sp <sup>1.17</sup> - 0.7382 sp <sup>4.36</sup>	0.7371 sp <sup>1.16</sup> + 0.6757 sp <sup>4.33</sup>	0.6757 sp <sup>1.16</sup> - 0.7371 sp <sup>4.33</sup>	0.7369 sp <sup>1.18</sup> + 0.6760 sp <sup>4.34</sup>	0.6760 sp <sup>1.18</sup> - 0.7369 sp <sup>4.34</sup>	
Molecular 3	C1 - S2	-	-	0.7309 sp <sup>3.00</sup> + 0.6825 sp <sup>4.36</sup>	0.6825 sp <sup>3.00</sup> - 0.7309 sp <sup>4.36</sup>	0.7333 sp <sup>2.99</sup> + 0.6799 sp <sup>4.44</sup>	0.6799 sp <sup>2.99</sup> - 0.7333 sp <sup>4.44</sup>
	S2 - O10	-	-	0.6081 sp <sup>3.21</sup> + 0.7938 sp <sup>3.71</sup>	0.7938 sp <sup>3.21</sup> - 0.6081 sp <sup>3.71</sup>	0.6121 sp <sup>3.21</sup> + 0.7908 sp <sup>3.72</sup>	0.7908 sp <sup>3.21</sup> - 0.6121 sp <sup>3.72</sup>
	S2 - C3	-	-	0.6910 sp <sup>4.23</sup> + 0.7229 sp <sup>3.66</sup>	0.7229 sp <sup>4.23</sup> - 0.6910 sp <sup>3.66</sup>	0.6897 sp <sup>4.39</sup> + 0.7241 sp <sup>3.70</sup>	0.7241 sp <sup>4.39</sup> - 0.6897 sp <sup>3.70</sup>
	C6 - N7	-	-	0.6273 sp <sup>3.31</sup> + 0.7788 sp <sup>2.40</sup>	0.7788 sp <sup>3.31</sup> - 0.6273 sp <sup>2.40</sup>	0.6247 sp <sup>3.33</sup> + 0.7809 sp <sup>2.43</sup>	0.7809 sp <sup>3.33</sup> - 0.6247 sp <sup>2.43</sup>
	N7 - C8	-	-	0.7673 sp <sup>1.50</sup> + 0.6413 sp <sup>1.16</sup>	0.6413 sp <sup>1.50</sup> - 0.7673 sp <sup>1.16</sup>	0.7667 sp <sup>1.52</sup> + 0.6420 sp <sup>1.16</sup>	0.6420 sp <sup>1.52</sup> - 0.7667 sp <sup>1.16</sup>
C8 - S9	-	-	0.7379 sp <sup>1.14</sup> + 0.6749 sp <sup>4.25</sup>	0.6749 sp <sup>1.14</sup> - 0.7379 sp <sup>4.25</sup>	0.7382 sp <sup>1.16</sup> + 0.6746 sp <sup>4.24</sup>	0.6746 sp <sup>1.16</sup> - 0.7382 sp <sup>4.24</sup>	
Molecular 4	C1 - S2	0.7316 sp <sup>2.96</sup> + 0.6818 sp <sup>4.40</sup>	0.6818 sp <sup>2.96</sup> - 0.7316 sp <sup>4.40</sup>	0.7291 sp <sup>2.98</sup> + 0.6844 sp <sup>4.30</sup>	0.6844 sp <sup>2.98</sup> - 0.7291 sp <sup>4.30</sup>	0.7317 sp <sup>2.97</sup> + 0.6816 sp <sup>4.37</sup>	0.6816 sp <sup>2.97</sup> - 0.7317 sp <sup>4.37</sup>
	S2 - O10	0.6090 sp <sup>3.20</sup> + 0.7932 sp <sup>3.67</sup>	0.7932 sp <sup>3.20</sup> - 0.6090 sp <sup>3.67</sup>	0.6066 sp <sup>3.40</sup> + 0.7950 sp <sup>3.66</sup>	0.7950 sp <sup>3.40</sup> - 0.6066 sp <sup>3.66</sup>	0.6107 sp <sup>3.30</sup> + 0.7919 sp <sup>3.70</sup>	0.7919 sp <sup>3.30</sup> - 0.6107 sp <sup>3.70</sup>
	S2 - C3	0.6916 sp <sup>4.31</sup> + 0.7223 sp <sup>3.68</sup>	0.7223 sp <sup>4.31</sup> - 0.6916 sp <sup>3.68</sup>	0.6928 sp <sup>4.41</sup> + 0.7211 sp <sup>3.67</sup>	0.7211 sp <sup>4.41</sup> - 0.6928 sp <sup>3.67</sup>	0.6917 sp <sup>4.26</sup> + 0.7222 sp <sup>3.71</sup>	0.7222 sp <sup>4.26</sup> - 0.6917 sp <sup>3.71</sup>
	C6 - N7	0.6216 sp <sup>3.34</sup> + 0.7834 sp <sup>2.45</sup>	0.7834 sp <sup>3.34</sup> - 0.6216 sp <sup>2.45</sup>	0.6249 sp <sup>3.31</sup> + 0.7807 sp <sup>2.32</sup>	0.7807 sp <sup>3.31</sup> - 0.6249 sp <sup>2.32</sup>	0.6221 sp <sup>3.33</sup> + 0.7829 sp <sup>2.46</sup>	0.7829 sp <sup>3.33</sup> - 0.6221 sp <sup>2.46</sup>
	N7 - C8	0.7676 sp <sup>1.48</sup> + 0.6410 sp <sup>1.17</sup>	0.6410 sp <sup>1.48</sup> - 0.7676 sp <sup>1.17</sup>	0.7680 sp <sup>1.47</sup> + 0.6405 sp <sup>1.15</sup>	0.6405 sp <sup>1.47</sup> - 0.7680 sp <sup>1.15</sup>	0.7673 sp <sup>1.49</sup> + 0.6413 sp <sup>1.16</sup>	0.6413 sp <sup>1.49</sup> - 0.7673 sp <sup>1.16</sup>
C8 - S9	0.7393 sp <sup>1.15</sup> + 0.6734 sp <sup>4.36</sup>	0.6734 sp <sup>1.15</sup> - 0.7393 sp <sup>4.36</sup>	0.7379 sp <sup>1.14</sup> + 0.6749 sp <sup>4.33</sup>	0.6749 sp <sup>1.14</sup> - 0.7379 sp <sup>4.33</sup>	0.7379 sp <sup>1.16</sup> + 0.6749 sp <sup>4.34</sup>	0.6749 sp <sup>1.16</sup> - 0.7379 sp <sup>4.34</sup>	
Molecular 5	C1 - S2	0.7310 sp <sup>2.98</sup> + 0.6824 sp <sup>4.41</sup>	0.6824 sp <sup>2.98</sup> - 0.7310 sp <sup>4.41</sup>	0.7286 sp <sup>3.00</sup> + 0.6849 sp <sup>4.31</sup>	0.6849 sp <sup>3.00</sup> - 0.7286 sp <sup>4.31</sup>	0.7311 sp <sup>2.99</sup> + 0.6823 sp <sup>4.38</sup>	0.6823 sp <sup>2.99</sup> - 0.7311 sp <sup>4.38</sup>
	S2 - O10	0.6087 sp <sup>3.21</sup> + 0.7934 sp <sup>3.66</sup>	0.7934 sp <sup>3.21</sup> - 0.6087 sp <sup>3.66</sup>	0.6065 sp <sup>3.41</sup> + 0.7951 sp <sup>3.66</sup>	0.7951 sp <sup>3.41</sup> - 0.6065 sp <sup>3.66</sup>	0.6104 sp <sup>3.31</sup> + 0.7921 sp <sup>3.67</sup>	0.7921 sp <sup>3.31</sup> - 0.6104 sp <sup>3.67</sup>
	S2 - C3	0.6910 sp <sup>4.25</sup> + 0.7229 sp <sup>3.68</sup>	0.7229 sp <sup>4.25</sup> - 0.6910 sp <sup>3.68</sup>	0.6923 sp <sup>4.44</sup> + 0.7216 sp <sup>3.67</sup>	0.7216 sp <sup>4.44</sup> - 0.6923 sp <sup>3.67</sup>	0.6911 sp <sup>4.31</sup> + 0.7228 sp <sup>3.71</sup>	0.7228 sp <sup>4.31</sup> - 0.6911 sp <sup>3.71</sup>
	C6 - N7	0.6214 sp <sup>3.34</sup> + 0.7835 sp <sup>2.45</sup>	0.7835 sp <sup>3.34</sup> - 0.6214 sp <sup>2.45</sup>	0.6248 sp <sup>3.32</sup> + 0.7808 sp <sup>2.32</sup>	0.7808 sp <sup>3.32</sup> - 0.6248 sp <sup>2.32</sup>	0.6220 sp <sup>3.35</sup> + 0.7831 sp <sup>2.46</sup>	0.7831 sp <sup>3.35</sup> - 0.6220 sp <sup>2.46</sup>
	N7 - C8	0.7676 sp <sup>1.48</sup> + 0.6409 sp <sup>1.17</sup>	0.6409 sp <sup>1.48</sup> - 0.7676 sp <sup>1.17</sup>	0.7679 sp <sup>1.47</sup> + 0.6406 sp <sup>1.16</sup>	0.6406 sp <sup>1.47</sup> - 0.7679 sp <sup>1.16</sup>	0.7673 sp <sup>1.49</sup> + 0.6413 sp <sup>1.16</sup>	0.6413 sp <sup>1.49</sup> - 0.7673 sp <sup>1.16</sup>
C8 - S9	0.7391 sp <sup>1.15</sup> + 0.6736 sp <sup>4.36</sup>	0.6736 sp <sup>1.15</sup> - 0.7391 sp <sup>4.36</sup>	0.7378 sp <sup>1.14</sup> + 0.6750 sp <sup>4.33</sup>	0.6750 sp <sup>1.14</sup> - 0.7378 sp <sup>4.33</sup>	0.7378 sp <sup>1.17</sup> + 0.6751 sp <sup>4.34</sup>	0.6751 sp <sup>1.17</sup> - 0.7378 sp <sup>4.34</sup>	

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.

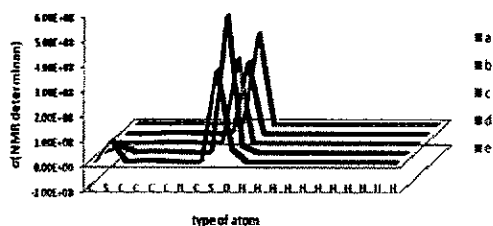


Fig. 2. The graphs of chemical shifts for molecular 1. (a) HF/6-31g, (b) HF/6-31g\*, (c) B3LYP/6-31g, (d) BLYP/6-31g, (e) B3PW91/6-31g.

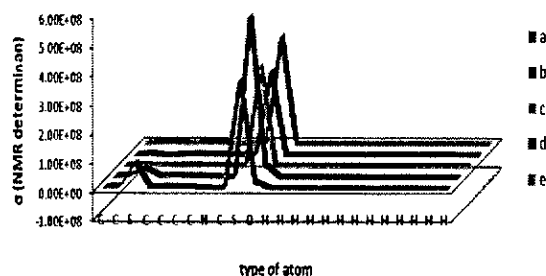


Fig. 3. The graphs of chemical shifts for molecular 2.(a) HF/6-31g, (b) HF/6-31g\*, (c) B3LYP/6-31g, (d) BLYP/6-31g, (e) B3PW91/6-31g.

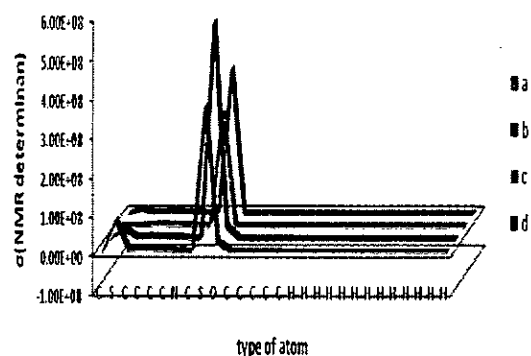


Fig. 4. The graphs of chemical shifts for molecular 3. (a) HF/6-31g, (b) HF/6-31g\*, (c) BLYP/6-31g, (d) B3PW91/6-31g.

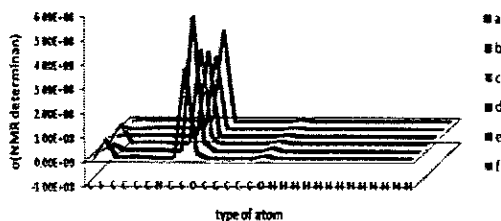


Fig. 5. The graphs of chemical shifts for molecular 4.(a) HF/6-31g, (b) HF/6-31g\*, (c) HF/6-31+g, (d) B3LYP/6-31g, (e) BLYP/6-31g, (f) B3PW91/6-31g.

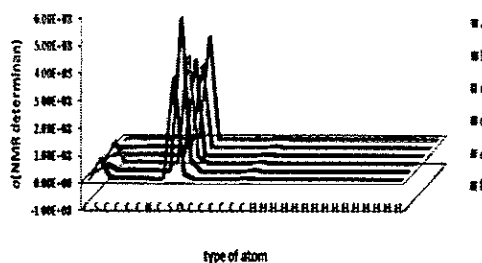


Fig. 6. The graphs of chemical shifts for molecular 5.(a) HF/6-31g, (b) HF/6-31g\*, (c) HF/6-31+g, (d) B3LYP/6-31g, (e) BLYP/6-31g, (f) B3PW91/6-31G.

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.

## REFERENCES

- [1] Y. Zhang, Proc. Natl. Acad. Sci., 91 (1994) 3147.
- [2] E. Giovannucci, E. B. Rimm, Y. Liu, M. J. Stampfer, W. C. Willett, K. Yoshizawa, A. Ascherio, J. S. Morris, C. K. Baskett and J. Chen, Cancer Epidemiol Biomarkers Prev, (12) 2003, 1403.
- [3] Y. Zhang, Proc. Natl. Acad. Sci. 89 (1992) 2399.
- [4] J. W. Chiao, F. L. Chung, R. Kancherla, T. Ahmed, A. Mittelman and D. D. Conaway, Int J Oncol. 20 (2002) 631.
- [5] L. Gamet-Payrastre, P. Li, S. Lumeau, G. Cassar, M. A. Dupont, S. Chevolleau, N. Gase, J. Tulliez and F. Terce, Cancer Res. 60 (2000) 1426.
- [6] J. W. Fahey, X. Haristoy, P. M. Dolan, T. W Kensler, I. Scholtus, K. Stephenson, P. Talalay and A. Lozniewski, Proceedings of the National Academy of Sciences of the United States of America. 99 (2002) 7610.
- [7] S A Ritz, Am J Physiol Lung Cell Mol Physiol. 292 (2007) 33.
- [8] R. H. Dashwood, J Nutr. 136 (2006) 2681S.
- [9] J. M. Han, P J Pharmacol Exp Ther. 321 (2007) 249.
- [10] Z. Healy, Proc Nat. Acad. Sci. 102 (2005) 10410.
- [11] L. Wu, 101 (2004) 7094.
- [12] A. H. Conney, Cancer Res. 63 (2003) 7005.
- [13] S. J. T. Jackson and K. W. Singletary, J Nutr. 134 (2004) 2229.
- [14] S. Choi and S. V. Singh, Cancer Res. 65 (2005) 2035.
- [15] C. Adamo and V. Barone, J. Chem. Phys. 108 (1998) 664.
- [16] K. Burke, J. P. Perdew and Y. Wang. Electronic Density Functional Theory: Recent Progress and New Directions: New York, 1998.
- [17] J. P. Perdew and Y. Wang. Phys. Rev. B. 45 (1992) 13244.
- [18] M. Monajjemi, B. Honaparvar, B. Khalili Hadad, A. R. Ilkhani and F. Mollaamin, African Journal of Pharmacy and Pharmacology. 4 (2010) 521.
- [19] M. Monajjemi, S. Afsharnejad, M. R. Jaafari, T. Abdolahi, A. Nikosade and H. Monajemi, Russian Journal of Physical Chemistry A, 81 (2007) 1956.
- [20] M. Monajjemi, Sajadi, M.A.S. Sayadia, Main group metal chemistry, 28 (2005) 71.
- [21] M. Monajjemi, R. Sayyadia, G. Ghasemi, Kh. Lalateh, A. Nouria and F. Naderi main group metal chemistry, 28 (2005) 247.
- [22] M. Monajjemi, E. Rajaecian, F. Mollamin, F. Naderi and S. Saki, 46 (2008) 299.