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Full Length Research Paper

NMR and natural bond orbital (NBO) calculation of glyoxals: Nano physical parameter investigation

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

Key words: Glyoxals, physical parameter, NMR, natural bond orbital (NBO).

INTRODUCTION

Alicyclic and cyclic 1, 2-dicarbonyl and vicinal polycarbonyl compounds have been known for over 150 years. The properties of many of them have been well studied, and some have found practical use as biologically active compounds, intermediates in the synthesis of various heterocyclic compounds, analytical reagents, photopolymerisation initiators, etc (Filimonov et al., 1998a). The reagents known for the preparative oxidation of the methyl ketones are AlkONO, $NaNO_2$-HCl, HalNO, HSO_4NO, NH_4CrO_3Cl, nitrosonium salts, SeO_2, H_2SeO_3, PhSeSePh - $(NH)_4$ S_2O_8 - MeOH, HBr –DMSO. Some of aryl methyl ketones were oxidised with these reagents under mild conditions into arylglyoxals or their acetals. Heating of aryl methyl ketones with $NaNO_2$ in HCl at 60°C gives the corresponding arylglyoxals directly in yields higher than 60% (Filimonov et al., 1998b). A wide range of aryl methyl ketones with various donor and acceptor substituents in the ring are oxidised with SeO_2 to the corresponding arylglyoxals in yields usually exceeding 70%. It is reported in patent literature that the oxidation of acetophenone with SeO_2 in aliphatic alcohols at 100°C gives the corresponding phenyl-glyoxal acetals. Acetaldehyde is oxidised with H_2SeO_3 to glyoxal (isolated as a bisulfite derivative in 72 to 74% yield). It can be noted that glyoxal is also formed from acetone by refluxing the latter with SeO_2 in xylene in the presence of water (Filimonov et al., 1998b; Ronzio and Waugh, 1955).

Phenylglyoxal 1 was prepared by stirring dioxane (300 ml), pure selenium dioxide (0.5 mol.) and water (10 ml) in a 500 ml round bottom flask, heat the mixture to 50 to 55°C and stir until the solid has dissolved then add acetophenone (0.5 mol.) in one lot. Reflux the mixture with stirring for 4 h, after about 2 h the solution becomes clear and little further precipitation of selenium is observed. Decant the hot solution from the precipitate and remove the dioxane and water by distillation. The

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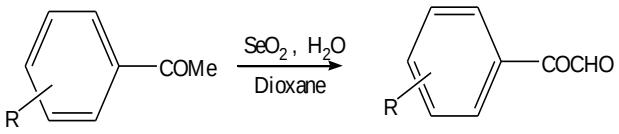
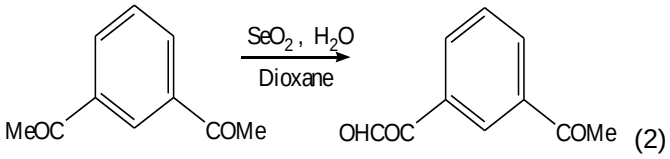
yield of pure phenylglyoxal (yellow liquid) is 48 g (72%), Rf value - 0.77, m. p - 54°C (Sushma et al., 2009)



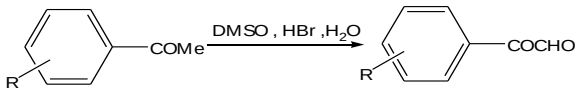
(R = H, Ph) (1)

Glyoxal 2 also can be prepared by similar process:



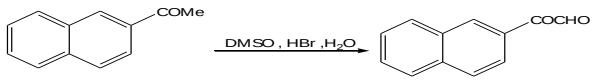
(2)

The DMSO-aqueous HBr system turned out to be very efficient in the transformation of acetylarenes to aryl-glyoxals 3. This is probably the most convenient reagent presently available for this transformation. The reaction is carried out at 55°C for 1 to 24 h to give the corresponding arylglyoxals in high yields (42 to 94%) (Floyd et al., 1985).



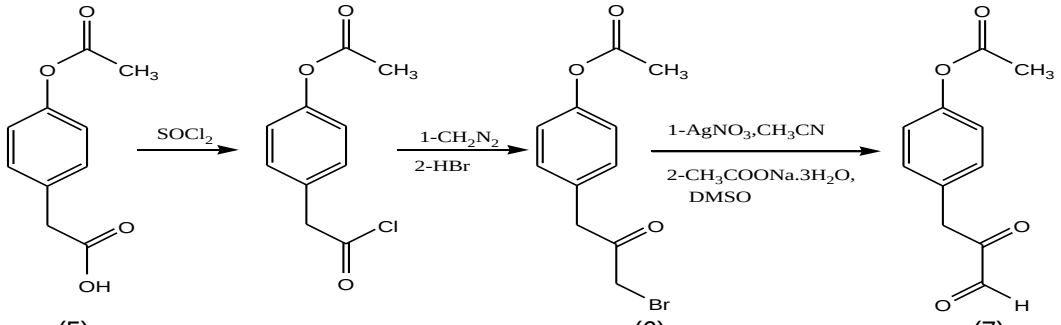
(R = 4-Ph, 4-MeO, 4-NO_2, 4-Br, 2-Ph) (3)

We can synthesiz arylglyoxal 4 by using this reagent.



(4)

Among the most promising antiviral agents mentioned in the literature are the glyoxals (against influenza virus) and certain derivatives of isatin /3-thiosemicarbazone (against vaccinia virus). The glyoxals are postulated as acting on the virus nucleic acid (de Bock et al., 1957), although at high concentrations there may be some effect on the neuraminidase system (Edmond et al., 1966). We have carried out experiments on some of the known anti-influenza virus glyoxals and have found that at levels of 1: 10,000 many showed marked neuraminidase inhibition (Edmond et al., 1966). One of the methods for synthesis of arylglyoxals is that phenylacetic acid 5 was transformed to the α-bromo-ketone 6, which was used to make 7 (Gonzalez, 2007):



(5) (6) (7)

COMPUTATIONAL 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 molecule applications; it 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 using the Hartree-Fock (HF) (Moller and Plesset, 1934), Becke's three-parameter hybrid method (Burke et al., 1998) with the Lee, Yang and Parr correlation functional methods (B3LYP) (Lee et al., 1988), Becke's exchange functional in combination with the Lee, Yang and Parr correlation functional methods (BLYP) (Lee et al., 1988; Becke, 1993), Becke's three parameter exchange functional combined with gradient corrected correlation functional of Perdew and Wang's 1991 (B3PW91) (Becke, 1993; Adamo and Barone, 1998) and 6-31G, 6-31G* and 6-31+G basis set. The calculation that you ask Gaussian to perform is distributed between many processors to get the answer faster. If

you want to optimize a 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” (Burke et al., 1998; Predew and Wang, 1992).

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 works best for calculating NMR properties. Finding a good geometry is called geometry optimization, so “opt” are used as the key word (Monajjemi et al.., 2010, 2007).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 are 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 Gaussian 98 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 key word. The calculation will generate an output file called “NMR out” (Monajjemi et al.., 2005a, b). 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 are 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 show 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 Eigen values (σ_{11}, σ_{22}, σ_{33}) (Monajjemi et al.., 2008). A perfect NBO analysis was obtained in Gaussian program when POP = NBO are used as the key word. 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 have calculated parameters like atomic charge, energy (ΔE), chemical shift (δ), asymmetry parameter (η), chemical shift anisotropy (Δσ), dipole moment (Table 1); isotropic (σ_{iso}) and anisotropic (σ_{aniso}) shielding, NMR determinant and distance matrix determinant (Table 2); natural bond orbital (NBO) (Table 3a, b) and GIAO magnetic shielding (Table 4) for several aryl glyoxals by using HF method with 6-31G,6-31G*, 6-31+G basis set and B3LYP, BLYP and B3PW91 methods with 6-31G basis set. HF method with 6-31+G basis set has not answered for molecules1, 3 and 5. The atoms that mentioned parameters have been calculated for them, and are related to $(-CO-CO-H)$ group. Here, we consider these parameters. As shown in Table 1, almost in all of the used methods, for all of the studied molecules, oxygen atoms in $(-CO-CO-H)$ group have negative atomic charge value, but in molecule 4, marked C atom in $(-CO-CO-H)$ group also has negative atomic charge value in HF/6-31+G level, and we have found that in many of levels except HF/6-31+G level, mentioned C atom has maximal positive atomic charge value, and in many of levels H atom in indicated group has minimal atomic charge value. We have seen that in Table 1, in many of levels and molecules, chemical shift (δ) and chemical shift anisotropy (Δσ) value for C atoms in $(-CO-CO-H)$ group is negative and in some of case for H atom in this group is negative. In general, in many of levels O atoms in $(-CO-CO-H)$ group has maximal positive value. As shown in Table 1, in many of used methods, marked C atom in $(-CO-CO-H)$ group has maximal asymmetry parameter (η). Dipole moment that was reported in Table 1, for molecule 3, in HF/6-31G and G* level, is the greatest than other molecule in the table, but in other methods, dipole orientation for molecule 2 is the greatest, and for molecule 5, is the least. ΔE (kcal/mol) that reported in Table 1, for all molecules in HF/6-31G level is zero. Also in all of the molecules, in B3LYP method, ΔE has the largest value.

Isotropic (σ_{iso}), anisotropic (σ_{aniso}) shielding, NMR determinant and distance matrix determinant have been reported in Table 2. As shown, σ_{iso} value for O atoms in $(-CO-CO-H)$ group in all of the molecules is negative, but in some of the levels and molecules, in addition to O atoms, σ_{iso} for one or both of C atoms in mentioned group also is negative. As defined in Table 2, the entire anisotropy amount is positive. In many of the methods, σ_{aniso} for marked O atom in $(-CO-CO-H)$ group is the largest amount, while the smallest one belongs to H atom in $(-CO-CO-H)$ group. We have seen that, in all of the methods for studied molecules, NMR determinant related to O atoms and H atom in mentioned group is maximal and minimal amount, respectively. The other parameter that was reported in Table 2 is distance matrix determinant for molecules. Molecule 1, in all of the methods, has positive distance matrix, but for molecule 2, in all of the methods except HF/6-31G level is positive, but for molecules 3, 4 and 5, in all of the methods is negative, in all of the molecules, calculated distance matrix determinant in BLYP method is the largest than other methods.

Table 3a and b shows share of contributor orbitals in bonds (BD for 2-center bond and BD* for 2-center

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

Method		HF																
Basis set		6-31G						6-31G*						6-31+G				
Name	Atom	Atomic charge	ΔE	δ	η	Δσ	Dipole moment	Atomic charge	ΔE	δ	η	Δσ	Dipole moment	Atomic charge	ΔE	δ	η	Δσ	Dipole moment
Molecule 1	C(7)	0.43		-131.49	0.89	-197.23		0.44		-104.37	0.89	-156.55		-		-	-	-	
	O(9)	-0.50		784.50	0.52	1176.74		-0.48		661.56	0.48	992.34		-		-	-	-	
	C(11)	0.28	0	-114.97	0.84	-172.45	4.65	0.25	-166.21	-89.33	0.74	-133.70	4.09	-		-	-	-	
	O(13)	-0.46		838.11	0.74	1257.17		-0.4		680.82	0.68	1021.23		-		-	-	-	
	H(18)	0.22		-0.59	0.12	-0.89		0.20		-1.67	0.68	-2.50		-	-	-	-	-	-
Molecule 2	C(8)	0.42		-133.89	0.89	-200.84		0.43		102.66	0.92	153.99		0.13		129.87	0.88	194.81	
	C(9)	0.26		-124.07	0.57	-186.11		0.24		-98.46	0.85	-147.70		0.19		-124.28	0.92	-186.43	
	O(10)	-0.52	0	770.74	0.48	1156.11	5.37	-0.50	-155.64	658.67	0.52	988.01	4.67	-0.4	-8.98	766.31	0.56	1149.47	5.62
	O(11)	-0.40		-980.47	0.99	-1470.70		-0.39		686.36	0.56	1029.54		-0.35		817.72	0.61	1226.58	
	H	0.21		-1.44	0.05	-2.16		0.19		1.19	0.97	1.78		0.22		2.80	0.17	4.21	
Molecule 3	C(9)	0.43		-127.65	0.93	-191.47		0.49		-102.50	0.88	-153.75		-		-	-	-	
	O(10)	-0.47		853.36	0.81	1280.05		-0.48		695.75	0.73	1043.62		-		-	-	-	
	C(11)	0.26		-122.43	0.89	-257.57	5.88	0.24	-176.70	-95.45	0.84	-143.17	5.39	-		-	-	-	-
	O(12)	-0.43		981.27	0.86	1471.90		-0.4		787.40	0.78	1181.09		-		-	-	-	
	H(21)	0.19	0	3.83	0.49	5.75		0.17		3.78	0.48	5.67		-	-	-	-	-	
Molecule 4	C(7)	0.43		-131.08	0.91	-196.62		0.44		-104.42	0.91	-156.64		-0.38		-131.70	0.91	-197.54	
	O(8)	-0.51		767.39	0.51	1151.08		-0.49		652.31	0.48	978.47		-0.40		755.95	0.50	1133.92	
	C(9)	0.28	0	-113.87	0.85	-170.81	2.70	0.2	-154.77	-88.58	0.74	-132.87	2.43	0.38	-9.49	-115.51	0.80	-173.27	2.73
	O(10)	-0.46		835.23	0.74	1252.85		-0.44		678.12	0.68	1017.18		-0.39		822.04	0.75	1233.07	
	H(18)	0.22		-0.53	0.55	-0.79		0.20		-1.83	0.63	-2.75		0.24		-0.75	0.70	-1.12	
Molecule 5	C(19)	0.42		-130.20	0.92	-195.30		0.44		-103.34	0.92	-155.01		-		-	-	-	
	C(20)	0.43	0	-130.20	0.92	-195.30	2.64	0.44	-292.73	-103.34	0.92	-155.01	2.41		-				-
	O(21)	-0.47		771.03	0.51	1156.55		-0.47		653.71	0.48	980.57							

Table 1. Cont'd.

	O(22)	-0.49		771.04	0.51	1156.56		-0.48		653.71	0.48	980.56		-		-	-	-	
	C(23)	0.28		-114.47	0.84	-171.71		0.26		-88.97	0.73	-133.46		-		-	-	-	
	C(24)	0.28		-114.47	0.84	-171.71		0.26		-88.97	0.73	-133.46		-		-	-	-	
	O(25)	-0.45		842.31	0.75	1263.47		-0.43		682.85	0.68	1024.27		-		-	-	-	
	O(26)	-0.45		842.32	0.75	1263.47		-0.43		682.85	0.68	1024.27		-		-	-	-	
	H(39)	0.22		-0.30	0.52	-0.45		0.20		-1.78	0.39	-2.67		-		-	-	-	
	H(40)	0.22		-0.30	0.51	-0.45		0.20		-1.78	0.39	-2.67		-		-	-	-	
Method				**B3LYP**						**BLYP**						**B3PW91**			
Basis set										**6-31G**									
Molecule 1	C(7)	0.29		-106.51	0.98	-159.77		0.25		-100.61	0.96	-150.91		0.30		-100.41	0.41	-150.62	
	O(9)	-0.37	-2320.23	754.48	0.73	1131.72		-0.33	-2211.04	745.56	0.80	1118.34		-0.38	-2170.40	613.47	0.49	920.21	
	C(11)	0.18		-87.81	0.98	-131.71	4.40	0.16		-81.71	0.94	-122.57	4.38	0.17		-88.90	0.64	-133.35	4.43
	O(13)	-0.33		765.47	0.91	1148.21		-0.29		734.84	0.97	1102.25		-0.34		690.59	0.74	1035.88	
	H(18)	0.16		0.44	0.75	0.66		0.13		0.57	0.45	0.86		0.19		0.80	0.96	1.21	
Molecule 2	C(8)	0.28		110.72	0.77	166.07		0.24		106.47	0.67	159.71		0.29		-95.89	0.27	-143.83	
	C(9)	0.17	-2016.26	99.41	0.96	149.11		0.15	-1920.32	95.52	0.90	143.29		0.16	-1887.59	-102.16	0.35	-153.25	
	O(10)	-0.38		742.83	0.74	1114.25	5.08	-0.3		715.70	0.77	1073.55	5.31	-0.39		596.71	0.44	895.06	5.20
	O(11)	-0.28		772.22	0.79	1158.34		-0.25		722.51	0.80	1083.77		-0.29		755.25	0.82	1132.87	
	H(19)	0.15		-2.42	1.00	-3.63		0.12		-2.74	0.89	-4.12		0.17		-1.66	0.44	-2.50	
Molecule 3	C(9)	0.33		-105.13	1.00	-157.69		0.30		-99.33	0.97	-149.00		0.33		104.90	0.99	157.35	
	O(10)	-0.34	-2498.83	-796.59	0.98	-1194.89		-0.30	-2372.71	-803.46	0.91	-1205.19		-0.35	-2341.20	-808.64	0.96	-1212.96	
	C(11)	0.18		97.73	0.85	146.60	4.84	0.16		91.03	0.83	136.54	4.50	0.17		99.52	0.83	149.28	4.90
	O(12)	-0.31		-899.42	0.98	-1349.13		-0.28		-883.09	0.94	-1324.64		-0.32		-908.45	0.97	-1362.68	
	H(21)	0.13		2.73	0.40	4.10		0.11		2.50	0.70	3.75		0.16		2.94	0.46	4.41	
Molecule 4	C(7)	0.29		-105.44	1.00	-158.17		0.25		-98.78	0.99	-148.16		0.30		-99.54	0.43	-149.31	
	O(8)	-0.38	-2391.29	735.19	0.73	1102.78		-0.34	-2268.31	727.81	0.80	1091.71		-0.39	-2242.47	606.12	0.49	909.17	
	C(9)	0.18		86.67	0.99	130.00	3.24	0.16		-79.95	0.97	-119.93	3.54	0.17		-88.10	0.66	-132.14	3.24

Table 1. Cont'd.

	O(10)	-0.33		759.16	0.92	1138.74		-0.29		726.34	0.97	1089.51		-0.34		690.13	0.74	1035.19	
	H(18)	0.15		0.62	0.30	0.93		0.12		0.75	0.10	1.12		0.18		0.93	0.73	1.40	
	C(19)	0.27		105.48	1.00	158.22		0.23		-99.39	0.98	-149.09		0.28		-84.39	0.72	-126.59	
	C(20)	0.28		105.48	1.00	158.22		0.24		-99.39	0.98	-149.08		0.29		-83.74	0.66	-125.61	
	O(21)	-0.35		738.21	0.72	1107.32		-0.31		729.04	0.79	1093.56		-0.35		628.33	0.77	942.50	
Molecule 5	O(22)	-0.36	4451.91	738.20	0.72	1107.30	2.68	-0.32	-4227.71	729.04	0.79	1093.56	2.81	-0.36	-4172.38	617.71	0.75	926.57	2.72
	C(23)	0.19		-86.87	1.00	-130.31		0.17		-80.62	0.96	-120.93		0.17		94.80	0.77	142.19	
	C(24)	0.19		-86.87	1.00	-130.31		0.17		-80.62	0.96	-120.93		0.18		92.60	0.83	138.89	
	O(25)	-0.33		767.05	0.92	1150.57		-0.29		735.48	0.97	1103.23		-0.33		768.50	0.86	1152.76	
	O(26)	-0.33		767.04	0.92	1150.57		-0.30		735.48	0.97	1103.22		-0.34		754.58	0.84	1131.87	
	H(39)	0.15		0.65	0.62	0.98		0.13		0.78	0.43	1.16		0.18		-3.20	0.89	-4.79	
	H(40)	0.15		0.65	0.62	0.98		0.13		0.78	0.43	1.16		0.18		2.80	0.88	4.20	

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

Method		**HF**											
Basis set		**6-31G**				**6-31G***				**6-31+G**			
Name	**Atom**	**Isotropic σ (ppm)**	**Anisotropy σ (ppm)**	**Determinant (NMR)**	**Distance matrix**	**Isotropic σ (ppm)**	**Anisotropy σ (ppm)**	**Determinant (NMR)**	**Distance matrix**	**Isotropic σ (ppm)**	**Anisotropy σ (ppm)**	**Determinant (NMR)**	**Distance matrix**
Molecule 1	C(7)	9.84	186.69	-2.4124e+005	1.5549e+007	24.47	147.87	-2.7758e+005	1.5439e+007	-	-	-	-
	O(9)	-377.20	1176.74	2.2487e+008		-251.80	992.34	1.2924e+008		-	-	-	
	C(11)	3.89	159.05	-1.5306e+005		19.24	116.80	-2.0853e+005		-	-	-	
	O(13)	-438.13	1257.17	2.5600e+008		-293.53	1021.24	1.3548e+008		-	-	-	
	H(18)	22.52	0.50	1.1506e+004		23.44	2.10	1.2839e+004		-	-	-	

Table 2. Cont'd.

Molecule 2	C(8)	7.17	190.17	-1.7867e+005	-8.1661e+005	15.57	153.99	-1.1293e+005	3.5284e+006	-1.91	194.81	1.5691e+005	3.5884e+006
	C(9)	13.65	144.85	-4.8596e+005		22.80	136.92	-2.5749e+005		6.75	178.78	-1.7201e+005	
	O(10)	-362.03	1156.11	2.1465e+008		-247.16	988.01	1.2355e+008		-360.49	1149.47	2.0402e+008	
	O(11)	-580.83	1467.40	3.6088e+008		-272.67	1029.54	1.4168e+008		-403.36	1226.58	2.4734e+008	
	H(19)	22.61	1.13	1.1697e+004		23.64	1.78	1.3237e+004		22.65	4.21	1.1672e+004	
Molecule 3	C(9)	6.96	184.92	-1.5465e+005	-1.6172e+008	23.08	144.58	-2.5774e+005	-1.5849e+008	-	-	-	-
	O(10)	-445.21	1280.05	2.6491e+008		-293.62	1043.62	1.4116e+008		-	-	-	
	C(11)	12.72	173.78	-2.5743e+005		28.86	131.47	-2.7054e+005		-	-	-	
	O(12)	-541.47	1471.90	3.9409e+008		-361.06	1181.09	2.0523e+008		-	-	-	
	H(21)	22.76	5.75	1.1680e+004		23.53	5.67	1.2839e+004		-	-	-	
Molecule 4	C(7)	9.29	187.42	-2.1630e+005	-2.4249e+007	23.58	149.53	-2.6065e+005	-2.4226e+007	10.23	188.17	-2.3792e+005	-2.4695e+007
	O(8)	-363.37	1151.08	2.1071e+0		-244.86	978.47	1.2359e+00		-349.75	1133.92	2.0150e+008	
	C(9)	3.44	158.14	-1.3999e+005		18.95	115.65	-2.0317e+005		3.95	156.01	-1.8146e+005	
	O(10)	-437.11	1252.85	2.5293e+008		-292.68	1017.18	1.3355e+008		-427.94	1233.07	2.4077e+008	
	H(18)	22.47	0.61	1.1437e+004		23.37	2.24	1.2717e+004		22.32	0.96	1.1203e+004	
Molecule 5	C(19)	8.99	187.50	-1.9305e+005	-2.1660e+013	23.54	149.04	-2.4814e+005	-2.1974e+013	-	-	-	-
	C(20)	8.99	187.51	-1.9302e+005		23.54	149.04	-2.4814e+005		-	-	-	
	O(21)	-364.81	1156.55	2.1375e+008		-244.61	980.57	1.2427e+008		-	-	-	
	O(22)	-364.82	1156.56	2.1375e+008		-244.60	980.56	1.2427e+008		-	-	-	
	C(23)	3.92	158.14	-1.5342e+005		19.35	115.79	-2.0883e+005		-	-	-	
	C(24)	3.92	158.14	-1.5343e+005		19.35	115.79	-2.0883e+005		-	-	-	
	O(25)	-442.93	1263.47	2.5907e+008		-296.13	1024.27	1.3654e+008		-	-	-	
	O(26)	-442.94	1263.47	2.5907e+00		-296.13	1024.27	1.3654e+008		-	-	-	
	H(39)	22.50	0.34	1.1489e+004		23.42	1.86	1.2810e+004		-	-	-	
	H(40)	22.50	0.34	1.1489e+004		23.42	1.86	1.2810e+004		-	-	-	
			B3LYP				**BLYP**				**B3PW91**		
Molecule 1	C(7)	7.84	158.39	-6.4337e+004	1.9150e+007	6.01	148.11	-4.1916e+004	2.2727e+007	7.01	106.41	-2.6100e+005	1.8623e+007
	O(9)	-384.25	1131.72	1.8756e+008		-392.91	1118.34	1.7720e+008		-279.35	920.21	1.0764e+008	
	C(11)	-1.49	130.72	6.8106e+003		-2.80	119.04	2.9215e+003		0.36	109.35	-1.0475e+005	

Table 2. Cont'd.

	O(13)	-410.37	1148.21	1.8059e+008		-401.45	1102.25	1.5546e+008		-376.7	1035.88	1.4334e+008	
	H(18)	22.14	0.66	1.0892e+004		22.02	0.86	1.0692e+004		21.53	1.21	1.0027e+004	
Molecule 2	C(8)	-6.22	166.07	2.0689e+005	4.3035e+006	-10.13	159.71	2.6139e+005	5.0464e+006	1.67	91.10	-2.1219e+005	4.1767e+006
	C(9)	1.86	149.11	-1.5759e+003		-0.92	143.29	4.2556e+004		8.20	103.70	-2.9225e+005	
	O(10)	-362.19	1114.25	1.7358e+008		-342.92	1073.55	1.5190e+008		-261.30	895.06	9.9559e+007	
	O(11)	-394.05	1158.34	1.9512e+008		-365.02	1083.77	1.5765e+008		-428.89	1132.87	1.8157e+008	
	H(19)	22.25	3.62	1.1003e+004		21.97	3.88	1.0564e+004		21.74	1.80	1.0344e+004	
Molecule 3	C(9)	-0.08	157.41	5.8937e+004	-2.0389e+008	-3.97	146.81	1.0345e+005	-2.4977e+008	2.76	157.35	4.2802e+004	-1.9714e+008
	O(10)	-419.77	1183.70	1.9103e+008		-419.97	1151.83	1.7047e+008		-420.68	1191.03	1.9268e+008	
	C(11)	4.81	146.60	7.8210e+004		2.10	136.54	1.3040e+005		6.37	149.28	7.8577e+004	
	O(12)	-492.97	1336.64	2.7500e+008		-478.43	1283.59	2.3888e+008		-491.64	1341.84	2.7626e+008	
	H(21)	22.11	4.10	1.0730e+004		21.96	3.75	1.0502e+004		22.06	4.41	1.0645e+004	
Molecule 4	C(7)	8.55	157.78	-6.5694e+004	-2.9941e+007	7.23	147.11	-4.5205e+004	-3.5509e+007	6.73	106.67	-2.4917e+005	-2.9186e+007
	O(8)	-368.42	1102.78	1.7331e+008		-378.68	1091.71	1.6402e+008		-272.08	909.17	1.0343e+008	
	C(9)	-1.95	129.10	1.8227e+004		-2.97	118.16	1.1283e+004		-0.09	109.75	-9.4521e+004	
	O(10)	-406.44	1138.74	1.7565e+008		-395.23	1089.51	1.4972e+008		-376.45	1035.19	1.4288e+008	
	H(18)	22.08	0.93	1.0796e+004		21.96	1.12	1.0605e+004		21.47	1.40	9.9391e+003	
Molecule 5	C(19)	7.73	158.22	-4.9044e+004	-2.6792e+013	6.20	147.61	-3.3770e+004	-3.5698e+013	-10.41	108.88	-6.6499e+003	-2.6315e+013
	C(20)	7.73	158.22	-4.9061e+004		6.20	147.61	-3.3776e+004		-8.27	104.41	-3.235e+004	
	O(21)	-368.66	1107.32	1.7606e+008		-376.94	1093.56	1.6611e+008		-342.24	942.50	1.0629e+008	
	O(22)	-368.65	1107.30	1.7605e+008		-376.94	1093.56	1.6611e+008		-325.69	926.57	1.0187e+008	
	C(23)	-1.74	130.12	1.2582e+004		-3.07	118.52	9.2878e+003		-8.21	142.19	1.4747e+005	
	C(24)		130.12	1.2564e+004		-3.07	118.52	9.2783e+003		-7.36	138.89	1.1737e+005	
	O(25)	-1.74	1150.57	1.8118e+008		-402.89	1103.23	1.5543e+008		-436.96	1152.76	1.8767e+008	
	O(26)	-412.78	1150.56	1.8117e+008		-402.89	1103.22	1.5543e+008		-423.83	1131.87	1.7915e+008	
	H(39)	-412.78	0.98	1.0853e+004		22.00	1.16	1.0649e+004		20.86	4.53	8.9711e+003	
	H(40)	22.12	0.98	1.0853e+004		22.00	1.16	1.0649e+004		20.98	4.20	9.1786e+003	

Table 3. 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		B3LYP		BLYP		B3PW91	
Basic set		6-31G					
Name	Bond	BD	BD*	BD	BD*	BD	BD*
Molecule 1	C7 – O9	0.5729 $sp^{2.14}$ + 0.8196 $sp^{1.39}$	0.8196 $sp^{2.14}$ - 0.5729 $sp^{1.39}$	0.5729 $sp^{2.16}$ + 0.8196 $sp^{1.41}$	0.8196 $sp^{2.16}$ - 0.5729 $sp^{1.41}$	0.5738 $sp^{2.14}$ + 0.8190 $sp^{1.40}$	0.8190 $sp^{2.14}$ - 0.5738 $sp^{1.40}$
	C7 – C11	0.7128 $sp^{2.14}$ + 0.7014 $sp^{2.13}$	0.7014 $sp^{2.14}$ - 0.7128 $sp^{2.13}$	0.7122 $sp^{2.13}$ + 0.7020 $sp^{2.11}$	0.7020 $sp^{2.13}$ - 0.7122 $sp^{2.11}$	0.7134 $sp^{2.13}$ + 0.7007 $sp^{2.14}$	0.7007 $sp^{2.13}$ - 0.7134 $sp^{2.14}$
	C11 – O13	0.5765 $sp^{2.17}$ + 0.8171 $sp^{1.48}$	0.8171 $sp^{2.17}$ - 0.5765 $sp^{1.48}$	0.5764 $sp^{2.18}$ + 0.8172 $sp^{1.50}$	0.8172 $sp^{2.18}$ - 0.5764 $sp^{1.50}$	0.5775 $sp^{2.17}$ + 0.8164 $sp^{1.49}$	0.8164 $sp^{2.17}$ - 0.5775 $sp^{1.49}$
	C8 – O10	0.5772 $sp^{2.25}$ + 0.8166 $sp^{1.37}$	0.8166 $sp^{2.25}$ - 0.5772 $sp^{1.37}$	0.5775 $sp^{2.26}$ + 0.8164 $sp^{1.39}$	0.8164 $sp^{2.26}$ - 0.5775$sp^{1.39}$	0.5781 $sp^{2.25}$ + 0.8160 $sp^{1.38}$	0.8160 $sp^{2.25}$ - 0.5781 $sp^{1.38}$
	C11 – H18	0.7832 $sp^{1.71}$ + 0.6217 s	0.6217 $sp^{1.71}$ - 0.7832 s	0.7813 $sp^{1.71}$ + 0.6242 s	0.6242 $sp^{1.71}$ - 0.7813 s	0.7853 $sp^{1.70}$ + 0.6191 s	0.6191 $sp^{1.70}$ - 0.7853 s
Molecule 2	C4 – C5	0.7106 $sp^{1.57}$ + 0.7036 $sp^{1.35}$	0.7036 $sp^{1.57}$ - 0.7106 $sp^{1.35}$	0.7109 $sp^{1.56}$ + 0.7033 $sp^{1.35}$	0.7033 $sp^{1.56}$ - 0.7109 $sp^{1.35}$	0.7106 $sp^{1.57}$ + 0.7036 $sp^{1.35}$	0.7036 $sp^{1.57}$ - 0.7106 $sp^{1.35}$
	C6 – O7	0.5799 $sp^{2.24}$ + 0.8147 $sp^{1.38}$	0.8147 $sp^{2.24}$ - 0.5799 $sp^{1.38}$	0.5798 $sp^{2.25}$ + 0.8148 $sp^{1.39}$	0.8148 $sp^{2.25}$ - 0.5798 $sp^{1.39}$	0.5808 $sp^{2.23}$ + 0.8141 $sp^{1.39}$	0.8141 $sp^{2.23}$ - 0.5808 $sp^{1.39}$
	C8 – O10	0.5718 $sp^{2.15}$ + 0.8204 $sp^{1.39}$	0.8204 $sp^{2.15}$ - 0.5718 $sp^{1.39}$	0.5719 $sp^{2.17}$ + 0.8203 $sp^{1.41}$	0.8203 $sp^{2.17}$ - 0.5719 $sp^{1.41}$	0.5726 $sp^{2.15}$ + 0.8198 $sp^{1.40}$	0.8198 $sp^{2.15}$ - 0.5726 $sp^{1.40}$
	C9 – O11	0.5792 $sp^{2.15}$ + 0.8152 $sp^{1.51}$	0.8152 $sp^{2.15}$ - 0.5792 $sp^{1.51}$	0.5792 $sp^{2.16}$ + 0.8152 $sp^{1.53}$	0.8152 $sp^{2.16}$ - 0.5792 $sp^{1.53}$	0.5803 $sp^{2.15}$ + 0.8144 $sp^{1.53}$	0.8144 $sp^{2.15}$ - 0.5803 $sp^{1.53}$
	C9 – H19	0.7817 $sp^{1.71}$ + 0.6237 s	0.6237 $sp^{1.71}$ - 0.7817 s	0.7799 $sp^{1.72}$ + 0.6259 s	0.6259 $sp^{1.72}$ - 0.7799 s	0.7837 $sp^{1.71}$ + 0.6212 s	0.6212 $sp^{1.71}$ - 0.7837 s
Molecule 3	C8 – O13	0.5865 sp2.38 + 0.8099 sp1.45	0.8099 sp2.38 - 0.5865 sp1.45	0.5868 sp2.40 + 0.8097 sp1.47	0.8097 sp2.40 - 0.5868 sp1.47	0.5874 sp2.38 + 0.8093 sp1.46	0.8093 sp2.38 - 0.5874 sp1.46
	C9 – O10	0.5869 sp2.28 + 0.8097 sp1.48	0.8097 sp2.28 - 0.5869 sp1.48	0.5870 sp2.29 + 0.8096 sp1.50	0.8096 sp2.29 - 0.5870 sp1.50	0.5878 sp2.28 + 0.8090 sp1.49	0.8090 sp2.28 - 0.5878 sp1.49
	C11– O12	0.5869 sp2.28 + 0.8097 sp1.56	0.8097 sp2.28 - 0.5869 sp1.56	0.5870 sp2.30 + 0.8096 sp1.58	0.8096 sp2.30 - 0.5870 sp1.58	0.5880 sp2.28 + 0.8089 sp1.57	0.8089 sp2.28 - 0.5880 sp1.57
	C9 – C11	0.7110 sp1.95 + 0.7032 sp1.73	0.7032 sp1.95 - 0.7110 sp1.73	0.7110 sp1.94 + 0.7031 sp1.71	0.7031sp1.94 - 0.7110 sp1.71	0.7113 sp1.95 + 0.7029 sp1.73	0.7029 sp1.95 - 0.7113 sp1.73
	C11 – H21	0.7761 sp2.03 + 0.6306 s	0.6306 sp2.03 - 0.7761 s	0.7747 sp2.03 + 0.6323 s	0.6323 sp2.03 - 0.7747 s	0.7779 sp2.02 + 0.6283 s	0.6283 sp2.02 - 0.7779 s
Molecule 4	C5 – C7	0.7112 sp2.89 + 0.7030 sp1.73	0.7030 sp2.89 - 0.7112 sp1.73	0.7127 sp2.89 + 0.7014 sp1.73	0.7014 sp2.89 - 0 .7127 sp1.73	0.7124 sp2.89 + 0.7018 sp1.73	0.7018 sp2.89 - 0.7124 sp1.73
	C7 – O8	0.5727 sp2.15 + 0.8198 sp1.38	0.8198 sp2.15 - 0.5727 sp1.38	0.5727 sp2.16 + 0.8198 sp1.40	0.8198 sp2.16 - 0.5727 sp1.40	0.5735 sp2.15 + 0.8192 sp1.39	0.8192 sp2.15 - 0.5735 sp1.39
	C7 - C9	0.7119 sp2.15 + 0.7023 sp2.12	0.7023 sp2.15 - 0.7119 sp2.12	0.7115 sp2.13 + 0.7027 sp2.10	0.7027 sp2.13 - 0.7115 sp2.10	0.7126 sp2.14 + 0.7016 sp2.13	0.7016 sp2.14 - 0.7126 sp2.13
	C9 - O10	0.5764 sp2.17 + 0.8172 sp1.48	0.8172 sp2.17 - 0.5764 sp1.48	0.5762 sp2.18 + 0.8173 sp1.49	0.8173 sp2.18 - 0.5762 sp1.49	0.5774 sp2.17 + 0.8165 sp1.49	0.8165 sp2.17 - 0.5774 sp1.49
	C9 - H18	0.7826 sp1.72 + 0.6225 s	0.6225 sp1.72 - 0.7826 s	0.7805 sp1.72 + 0.6252 s	0.6252 sp1.72 - 0.7805 s	0.7847 sp1.71 + 0.6199 s	0.6199 sp1.71 - 0.7847 s
Molecule 5	C19 - O21	0.5733 sp2.10 + 0.8193 sp1.42	0.8193 sp2.10 - 0.5733 sp1.42	0.5733 sp2.11 + 0.8193 sp1.44	0.8193 sp2.11 - 0.5733 sp1.44	0.5743 sp2.10 + 0.8187 sp1.44	0.8187 sp2.10 - 0.5743 sp1.44
	C20 - O22	0.5736 sp2.08 + 0.8192 sp1.41	0.8192 sp2.08 - 0.5736 sp1.41	0.5734 sp2.09 + 0.8192 sp1.43	0.8192 sp2.09 - 0.5734 sp1.43	0.5745 sp2.08 + 0.8185 sp1.42	0.8185 sp2.08 - 0.5745 sp1.42
	C23 - O2	0.5789 sp2.09 + 0.8154 sp1.54	0.8154 sp2.09 - 0.5789 sp1.54	0.5789 sp2.10 + 0.8154 sp1.57	0.8193 sp2.11 - 0.5733 sp1.44	0.5801 sp2.09 + 0.8146 sp1.57	0.8146 sp2.09 - 0.5801 sp1.57
	C24 - O26	0.5785 sp2.10 + 0.8157 sp1.53	0.8157 sp2.10 - 0.5785 sp1.53	0.5784 sp2.10 + 0.8157 sp1.55	0.8192 sp2.09 - 0.5734 sp1.43	0.5796 sp2.09 + 0.8149 sp1.55	0.8149 sp2.09 - 0.5796 sp1.55
	C23 - H39	0.7801 sp1.70 + 0.6256 s	0.6256 sp1.70 - 0.7801 s	0.7781 sp1.70 + 0.6282 s	0.8154 sp2.10 - 0.5789 sp1.57	0.7823 sp1.69 + 0.6229 s	0.6229 sp1.69 - 0.7823 s
	C24 - H40	0.7803 sp1.69 + 0.6254 s	0.6254 sp1.69 - 0.7803 s	0.7783 sp1.69 + 0.6279 s	0.8157 sp2.10 - 0.5784 sp1.55	0.7825 sp1.69 + 0.6227 s	0.6227 sp1.69 - 0.7825 s

Method		B3LYP		BLYP		B3PW91	
Basic set		6-31G					
Name	Bond	BD	BD*	BD	BD*	BD	BD*
Molecule 1	C7 - O9	0.5729 sp2.14 + 0.8196 sp1.39	0.8196 sp2.14 - 0.5729 sp1.39	0.5729 sp2.16 + 0.8196 sp1.41	0.8196 sp2.16 - 0.5729 sp1.41	0.5738 sp2.14 + 0.8190 sp1.40	0.8190 sp2.14 - 0.5738 sp1.40
	C7 - C11	0.7128 sp2.14 + 0.7014 sp2.13	0.7014 sp2.14 - 0.7128 sp2.13	0.7122 sp2.13 + 0.7020 sp2.11	0.7020 sp2.13 - 0.7122 sp2.11	0.7134 sp2.13 + 0.7007 sp2.14	0.7007 sp2.13 - 0.7134 sp2.14
	C11 - O13	0.5765 sp2.17 + 0.8171 sp1.48	0.8171 sp2.17 - 0.5765 sp1.48	0.5764 sp2.18 + 0.8172 sp1.50	0.8172 sp2.18 - 0.5764 sp1.50	0.5775 sp2.17 + 0.8164 sp1.49	0.8164 sp2.17 - 0.5775 sp1.49
	C8 - O10	0.5772 sp2.25 + 0.8166 sp1.37	0.8166 sp2.25 - 0.5772 sp1.37	0.5775 sp2.26 + 0.8164 sp1.39	0.8164 sp2.26 - 0.5775sp1.39	0.5781 sp2.25 + 0.8160 sp1.38	0.8160 sp2.25 - 0.5781 sp1.38

Table 3. Contd

	C11 - H18	0.7832 sp1.71 + 0.6217 s	0.6217 sp1.71 - 0.7832 s	0.7813 sp1.71 + 0.6242 s	0.6242 sp1.71 - 0.7813 s	0.7853 sp1.70 + 0.6191 s	0.6191 sp1.70 - 0.7853 s
Molecule 2	C4 - C5	$0.7106\ sp^{1.57} + 0.7036\ sp^{1.35}$	$0.7036\ sp^{1.57} - 0.7106\ sp^{1.35}$	$0.7109\ sp^{1.56} + 0.7033\ sp^{1.35}$	$0.7033\ sp^{1.56} - 0.7109\ sp^{1.35}$	$0.7106\ sp^{1.57} + 0.7036\ sp^{1.35}$	$0.7036\ sp^{1.57} - 0.7106\ sp^{1.35}$
	C6 – O7	$0.5799\ sp^{2.24} + 0.8147\ sp^{1.38}$	$0.8147\ sp^{2.24} - 0.5799\ sp^{1.38}$	$0.5798\ sp^{2.25} + 0.8148\ sp^{1.39}$	$0.8148\ sp^{2.25} - 0.5798\ sp^{1.39}$	$0.5808\ sp^{2.23} + 0.8141\ sp^{1.39}$	$0.8141\ sp^{2.23} - 0.5808\ sp^{1.39}$
	C8 – O10	$0.5718\ sp^{2.15} + 0.8204\ sp^{1.39}$	$0.8204\ sp^{2.15} - 0.5718\ sp^{1.39}$	$0.5719\ sp^{2.17} + 0.8203\ sp^{1.41}$	$0.8203\ sp^{2.17} - 0.5719\ sp^{1.41}$	$0.5726\ sp^{2.15} + 0.8198\ sp^{1.40}$	$0.8198\ sp^{2.15} - 0.5726\ sp^{1.40}$
	C9 – O11	$0.5792\ sp^{2.15} + 0.8152\ sp^{1.51}$	$0.8152\ sp^{2.15} - 0.5792\ sp^{1.51}$	$0.5792\ sp^{2.16} + 0.8152\ sp^{1.53}$	$0.8152\ sp^{2.16} - 0.5792\ sp^{1.53}$	$0.5803\ sp^{2.15} + 0.8144\ sp^{1.53}$	$0.8144\ sp^{2.15} - 0.5803\ sp^{1.53}$
	C9 – H19	$0.7817\ sp^{1.71} + 0.6237$ s	$0.6237\ sp^{1.71} - 0.7817$ s	$0.7799\ sp^{1.72} + 0.6259$ s	$0.6259\ sp^{1.72} - 0.7799$ s	$0.7837\ sp^{1.71} + 0.6212$ s	$0.6212\ sp^{1.71} - 0.7837$ s
Molecule 3	C8 – O13	$0.5865\ sp^{2.38} + 0.8099\ sp^{1.45}$	$0.8099\ sp^{2.38} - 0.5865\ sp^{1.45}$	$0.5868\ sp^{2.40} + 0.8097\ sp^{1.47}$	$0.8097\ sp^{2.40} - 0.5868\ sp^{1.47}$	$0.5874\ sp^{2.38} + 0.8093\ sp^{1.46}$	$0.8093\ sp^{2.38} - 0.5874\ sp^{1.46}$
	C9 – O10	$0.5869\ sp^{2.28} + 0.8097\ sp^{1.48}$	$0.8097\ sp^{2.28} - 0.5869\ sp^{1.48}$	$0.5870\ sp^{2.29} + 0.8096\ sp^{1.50}$	$0.8096\ sp^{2.29} - 0.5870\ sp^{1.50}$	$0.5878\ sp^{2.28} + 0.8090\ sp^{1.49}$	$0.8090\ sp^{2.28} - 0.5878\ sp^{1.49}$
	C11 –O12	$0.5869\ sp^{2.28} + 0.8097\ sp^{1.56}$	$0.8097\ sp^{2.28} - 0.5869\ sp^{1.56}$	$0.5870\ sp^{2.30} + 0.8096\ sp^{1.58}$	$0.8096\ sp^{2.30} - 0.5870\ sp^{1.58}$	$0.5880\ sp^{2.28} + 0.8089\ sp^{1.57}$	$0.8089\ sp^{2.28} - 0.5880\ sp^{1.57}$
	C9 – C11	$0.7110\ sp^{1.95} + 0.7032\ sp^{1.73}$	$0.7032\ sp^{1.95} - 0.7110\ sp^{1.73}$	$0.7110\ sp^{1.94} + 0.7031\ sp^{1.71}$	$0.7031sp^{1.94} - 0.7110\ sp^{1.71}$	$0.7113\ sp^{1.95} + 0.7029\ sp^{1.73}$	$0.7029\ sp^{1.95} - 0.7113\ sp^{1.73}$
	C11 – H21	$0.7761\ sp^{2.03} + 0.6306$ s	$0.6306\ sp^{2.03} - 0.7761$ s	$0.7747\ sp^{2.03} + 0.6323$ s	$0.6323\ sp^{2.03} - 0.7747$ s	$0.7779\ sp^{2.02} + 0.6283$ s	$0.6283\ sp^{2.02} - 0.7779$ s
Molecule 4	C5 – C7	$0.7112\ sp^{2.89} + 0.7030\ sp^{1.73}$	$0.7030\ sp^{2.89} - 0.7112sp^{1.73}$	$0.7747\ sp^{2.03} + 0.6323$ s	$0.7014\ sp^{2.89} - 0\ .7127\ sp^{1.73}$	$0.7124\ sp^{2.89} + 0.7018\ sp^{1.73}$	$0.7018\ sp^{2.89} - 0.7124\ sp^{1.73}$
	C7 – O8	$0.5727\ sp^{2.15} + 0.8198\ sp^{1.38}$	$0.8198\ sp^{2.15} - 0.5727sp^{1.38}$	$0.7127\ sp^{2.89} + 0.7014\ sp^{1.73}$	$0.8198\ sp^{2.16} - 0.5727\ sp^{1.40}$	$0.5735\ sp^{2.15} + 0.8192\ sp^{1.39}$	$0.8192\ sp^{2.15} - 0.5735\ sp^{1.39}$
	C7 – C9	$0.7119\ sp^{2.15} + 0.7023\ sp^{2.12}$	$0.7023\ sp^{2.15} - 0.7119sp^{2.12}$	$0.5727\ sp^{2.16} + 0.8198\ sp^{1.40}$	$0.7027\ sp^{2.13} - 0.7115\ sp^{2.10}$	$0.7126\ sp^{2.14} + 0.7016\ sp^{2.13}$	$0.7016\ sp^{2.14} - 0.7126\ sp^{2.13}$
	C9 – O10	$0.5764\ sp^{2.17} + 0.8172\ sp^{1.48}$	$0.8172\ sp^{2.17} - 0.5764sp^{1.48}$	$0.7115\ sp^{2.13} + 0.7027\ sp^{2.10}$	$0.8173\ sp^{2.18} - 0.5762\ sp^{1.49}$	$0.5774\ sp^{2.17} + 0.8165\ sp^{1.49}$	$0.8165\ sp^{2.17} - 0.5774\ sp^{1.49}$
	C9 – H18	$0.7826\ sp^{1.72} + 0.6225$ s	$0.6225\ sp^{1.72} - 0.7826$ s	$0.5762\ sp^{2.18} + 0.8173\ sp^{1.49}$	$0.6252\ sp^{1.72} - 0.7805$ s	$0.7847\ sp^{1.71} + 0.6199$ s	$0.6199\ sp^{1.71} - 0.7847$ s
Molecule 5	C19 – O21	$0.5733\ sp^{2.10} + 0.8193\ sp^{1.42}$	$0.8193\ sp^{2.10} - 0.5733sp^{1.42}$	$0.5733\ sp^{2.11} + 0.8193\ sp^{1.44}$	$0.8193\ sp^{2.11} - 0.5733\ sp^{1.44}$	$0.5743\ sp^{2.10} + 0.8187\ sp^{1.44}$	$0.8187\ sp^{2.10} - 0.5743\ sp^{1.44}$
	C20 – O22	$0.5736\ sp^{2.08} + 0.8192\ sp^{1.41}$	$0.8192\ sp^{2.08} - 0.5736sp^{1.41}$	$0.5734\ sp^{2.09} + 0.8192\ sp^{1.43}$	$0.8192\ sp^{2.09} - 0.5734\ sp^{1.43}$	$0.5745\ sp^{2.08} + 0.8185\ sp^{1.42}$	$0.8185\ sp^{2.08} - 0.5745\ sp^{1.42}$
	C23 – O25	$0.5789\ sp^{2.09} + 0.8154\ sp^{1.54}$	$0.8154\ sp^{2.09} - 0.5789sp^{1.54}$	$0.5789\ sp^{2.10} + 0.8154\ sp^{1.57}$	$0.8154\ sp^{2.10} - 0.5789\ sp^{1.57}$	$0.5801\ sp^{2.09} + 0.8146\ sp^{1.57}$	$0.8146\ sp^{2.09} - 0.5801\ sp^{1.57}$
	C24 – O26	$0.5785\ sp^{2.10} + 0.8157\ sp^{1.53}$	$0.8157\ sp^{2.10} - 0.5785sp^{1.53}$	$0.5784\ sp^{2.10} + 0.8157\ sp^{1.55}$	$0.8157\ sp^{2.10} - 0.5784\ sp^{1.55}$	$0.5796\ sp^{2.09} + 0.8149\ sp^{1.55}$	$0.8149\ sp^{2.09} - 0.5796\ sp^{1.55}$
	C23 – H39	$0.7801\ sp^{1.70} + 0.6256$ s	$0.6256\ sp^{1.70} - 0.7801$ s	$0.7781\ sp^{1.70} + 0.6282$ s	$0.6282\ sp^{1.70} - 0.7781$ s	$0.7823\ sp^{1.69} + 0.6229$ s	$0.6229\ sp^{1.69} - 0.7823$ s
	C24 – H40	$0.7803\ sp^{1.69} + 0.6254$ s	$0.6254\ sp^{1.69} - 0.7803$ s	$0.7783\ sp^{1.69} + 0.6279$ s	$0.6279\ sp^{1.69} - 0.7783$ s	$0.7825\ sp^{1.69} + 0.6227$ s	$0.6227\ sp^{1.69} - 0.7825$ s

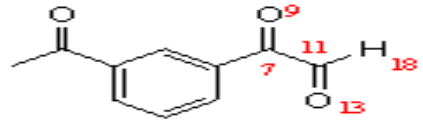
Table 4. Relative GIAO magnetic shielding for active site of studied molecules obtained using different methods.

Method		HF						B3LYP		BLYP		B3PW91	
Basis set		6-31G		6-31G*		6-31+G				6-31G			
Name	Atom / Parameter	Shielding (ppm)	Degeneracy	Shielding (ppm)	Degeneracy	Shielding (ppm)	Degeneracy	Shielding (ppm)	Degeneracy	Shielding (ppm)	Degeneracy	Shielding (ppm)	Degeneracy
Molecule 1	C(7)	10.11	1	24.27	1	-	-	7.87	1	6.18	1	7.19	1
	C(11)	3.93	1	19.33	1		-	-1.69	1	-2.81	1	0.45	1
	O(9)	-377.25	1	-251.81	1	-	-	-384.29	1	-392.91	1	-279.23	1
	O(13)	-438.19	1	-293.52	1	-	-	-410.36	1	-401.45	1	-376.75	1
	H(18)	22.51	1	23.42	1	-	-	22.14	1	22.03	1	21.54	1
Molecule 2	C(8)	7.19	1	15.73	1	-1.91	1	-6.18	1	-10.11	1	1.80	1
	C(9)	13.48	1	22.92	1	6.74	1	1.69	1	-1.12	1	8.09	1
	O(10)	-361.85	1	-247.22	1	-360.41	1	-362.21	1	-342.91	1	-261.29	1
	O(11)	-580.81	1	-272.69	1	-403.48	1	-394.04	1	-365.06	1	-428.78\	1
	H(19)	22.61	1	3.64	1	22.65	1	22.25	1	21.98	1	21.74	1
Molecule 3	C(9)	6.74	1	22.92		-	-	0	1	-3.93	1	2.81	1
	C(11)	12.92	1	28.76	1	-	-	5.06	1	2.25	1	6.18	1
	O(10)	-445.26	1	-293.68	1	-	-	-419.82	1	-419.87	1	-420.54	1
	O(12	-541.42	1	-361.22	1	-	-	-493.14	1	-478.38	1	-491.69	1
	H(21)	22.76	1	23.53	1	-	-	22.11	1	21.95	1	22.06	1
Molecule 4	C(7)	9.27	1	23.56	1	10.16	1	8.64	1	7.28	1	6.64	1
	C(9)	3.39	1	18.8	1	3.92	1	1.98	1	-3.05	1	-0.18	1
	O(8)	-363.43	1	-244.88	1	-349.75	1	-368.45	1	-378.67	1	-272.19	1
	O(10)	-437.11	1	-292.69	1	-427.97	1	-406.45	1	-395.20	1	-376.48	1
	H(18)	22.47	1	23.37	1	22.32	1	22.08	1	21.96	1	21.46	1

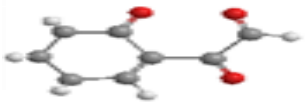
Table 4. Cont'd.

Molecule 5	C(19)	8.91	2	23.56	1	-	-	7.64	1	6.24	1	-10.39	1
	C(20)	8.91	1	23.56	2	-	-	7.64	2	6.24	2	-8.26	1
	C(23)	3.92	2	19.35	1	-	-	-1.7	1	-2.98	1	-8.20	1
	C(24)	3.92	1	19.35	2	-	-	-1.78	2	-2.98	2	-7.36	1
	O(21)	-364.88	2	-244.61	1	-	-	-368.67	1	-376.96	1	-342.21	1
	O(22)	-364.88	1	-244.61	2	-	-	-368.67	2	-376.96	2	-325.69	1
	O(25)	-442.89	2	-296.07	2	-	-	-412.82	1	-402.90	1	-437.02	1
	O(26)	-442.89	1	-296.07	1	-	-	-412.82	2	-402.90	2	-423.75	1
	H(39)	22.50	1	23.42	3	-	-	22.12	1	21.99	1	20.86	1
	H(40)	22.50	2	23.42	4	-	-	22.12	2	21.99	2	20.98	1

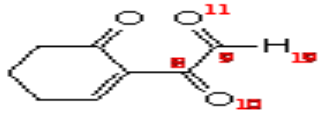
2-(3-acetylphenyl)-2-oxoacetaldehyde



molecule 1



2-oxo-2-(6-oxocyclohex-1-enyl) acetaldehyde



molecule 2

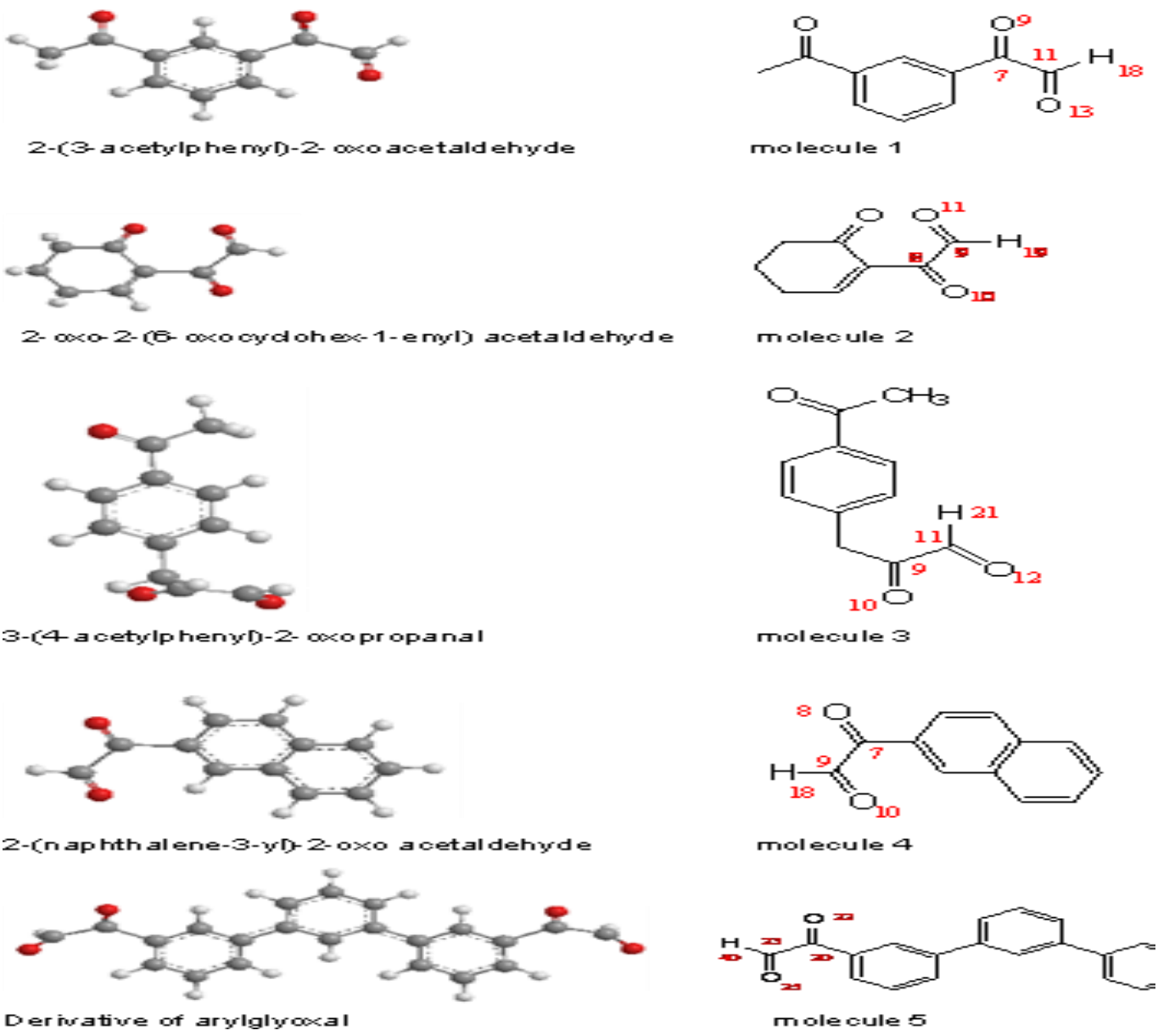


Figure 1. Optimized structure of studied molecules.

antibond). We have found that in HF/6-31G* level, in addition to (s) and (p) orbitals, (d) orbitals have contributed in reported bonds. In other words, the share of (p) orbital related to C atoms in mentioned bonds is the most than O and H atoms. Finally in Table 4, we have reported GIAO magnetic shielding for atoms related to $(-CO-CO-H)$ group. As shown in Table 4, in all of the methods, oxygen atoms in all of the molecules has negative magnetic shielding value and degeneracy value in molecules 1 to 4 for pointed atoms is equal to one. We have seen that magnetic shielding values for C atoms in $(-CO-CO-H)$ group are the least than other investigated atoms. We have found that in molecule 5, many of the calculated parameters in many of the methods, for C_{19}, C_{23}, O_{21}, O_{25} and H_{39} has been equal to C_{20}, C_{24}, O_{22}, O_{26} and H_{40}, respectively, because this molecule is symmetrical. The optimized structure of molecules that were studied in this work, have been shown in Figure 1, and diagrams of chemical shifts for each molecules have been shown In Figures 2 to 6. As reported in this figures,

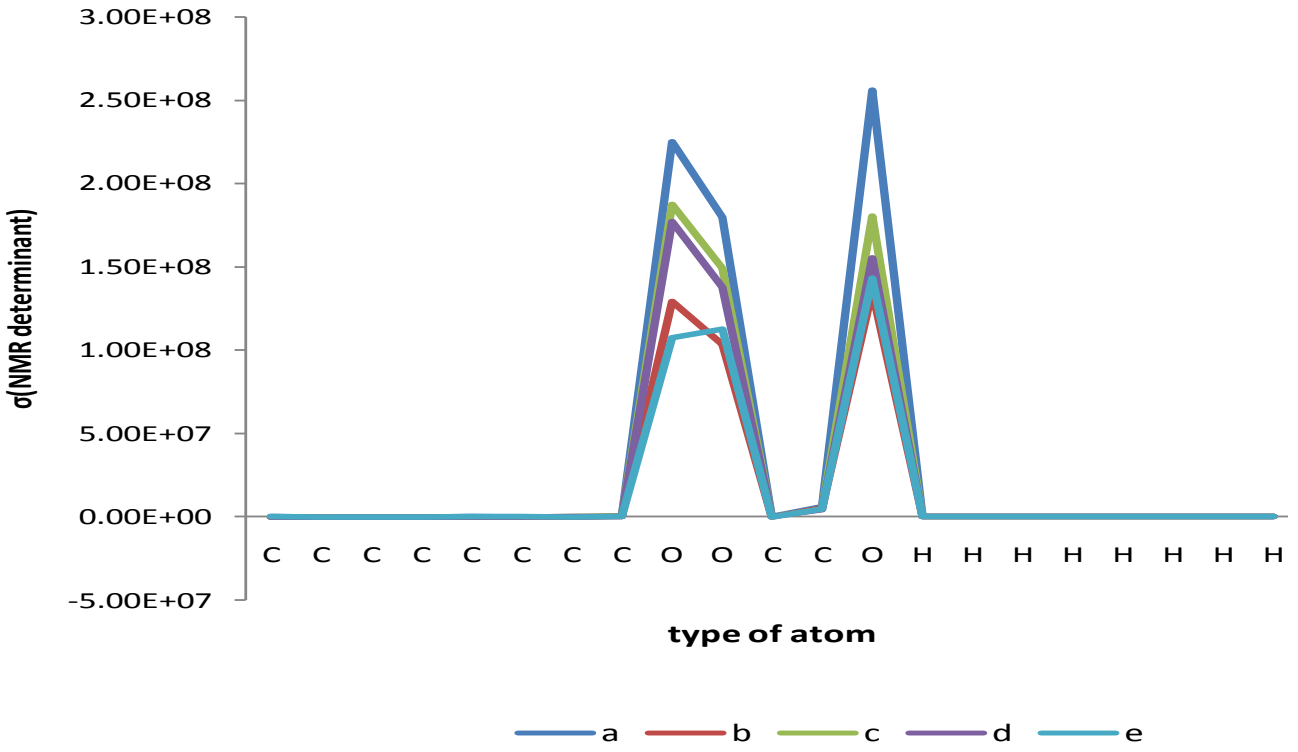


Figure 2. The graphs of chemical shifts for molecule 1: (a) HF/6-31g, (b) HF/6-31g*, (c) B3LYP/6-31g, (d) BLYP/6-31g, (e) B3PW91/6-31g.

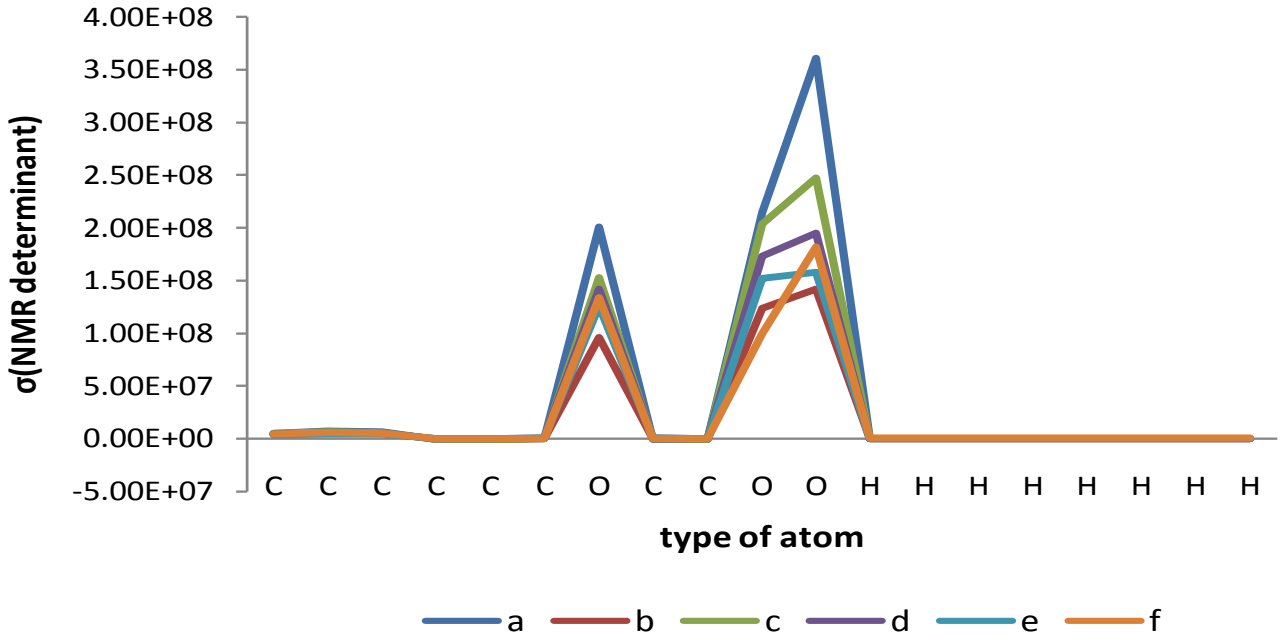


Figure 3. The graphs of chemical shifts for molecule 2: (a) HF/6-31g, (b) HF/6-31g*, (c) HF/6-31+g, (d) B3LYP/6-31g, (e) BLYP/6-31g, (f) B3PW91/6-31g.

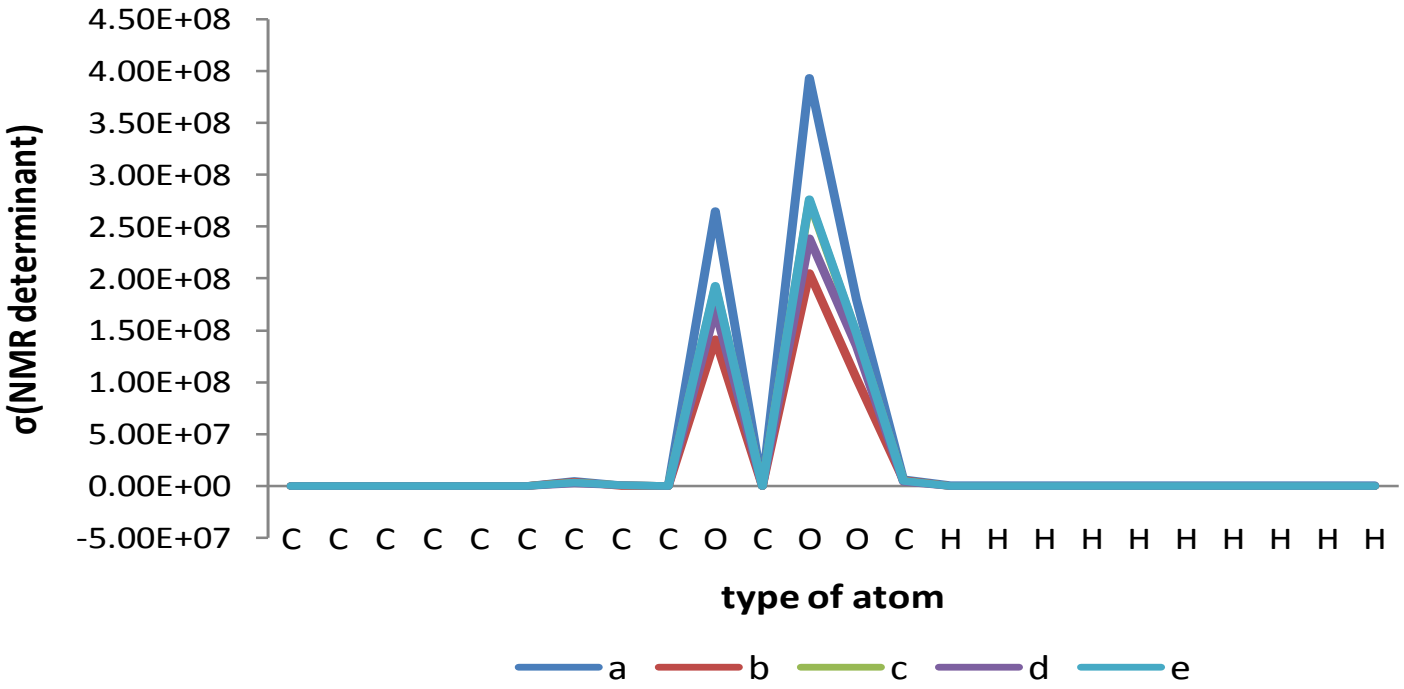


Figure 4. The graphs of chemical shifts for molecule 3: (a) HF/6-31g, (b) HF/6-31g*, (c) B3LYP/6-31g, (d) BLYP/6-31g, (e) B3PW91/6-31g.

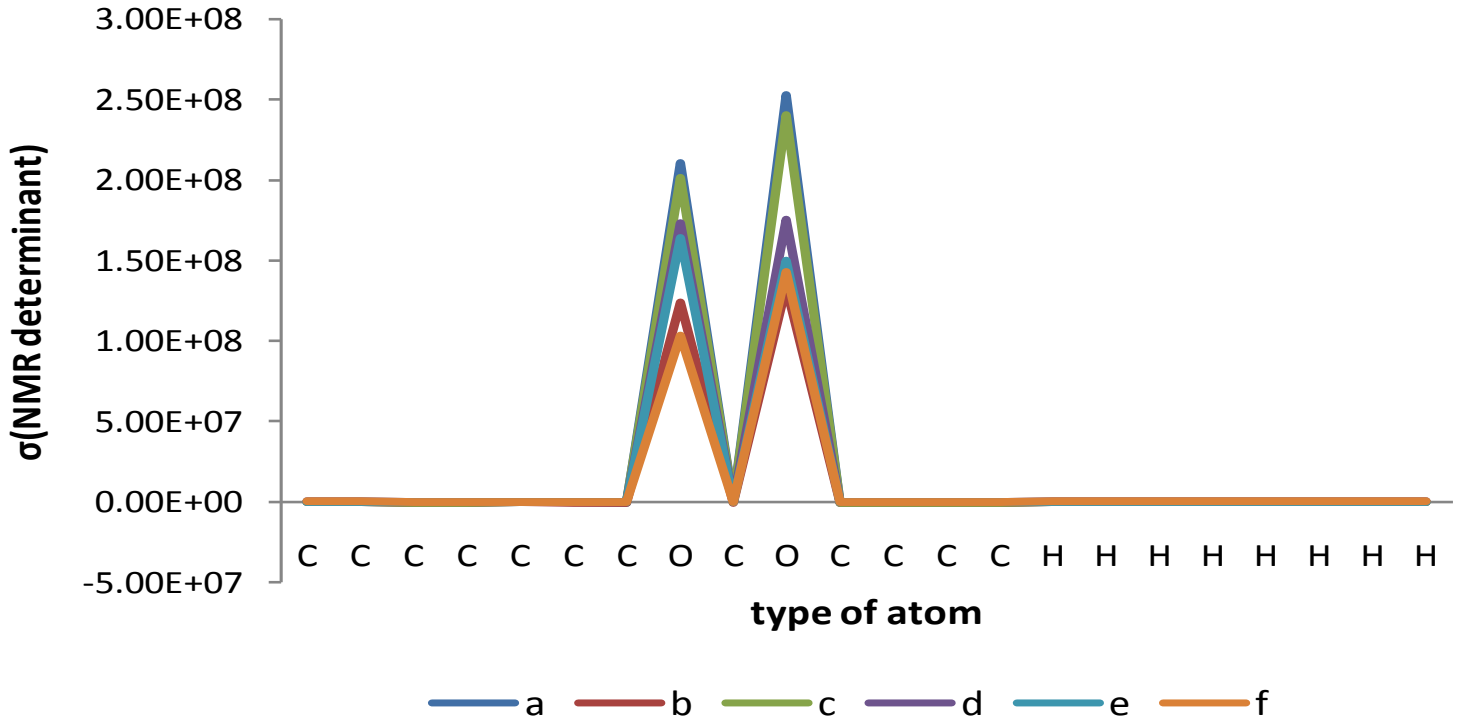


Figure 5. The graphs of chemical shifts for molecule 4: (a) HF/6-31g, (b) HF/6-31g*, (c) HF/6-31+g, (d) B3LYP/6-31g, (e) BLYP/6-31g, (f) B3PW91/6-31g.

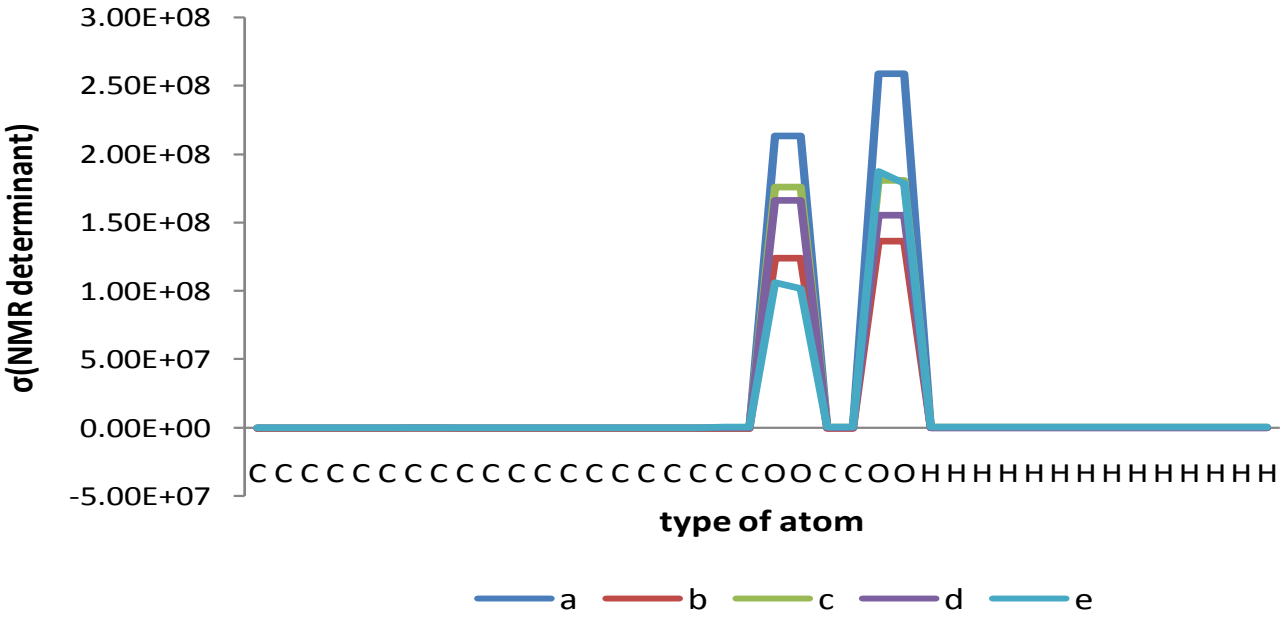


Figure 6. The graphs of chemical shifts for molecule 5: (a) HF/6-31g, (b) HF/6-31g*, (c) B3LYP/6-31g, (d) BLYP/6-31g, (e) B3PW91/6-31g.

in all of the methods and in all of the molecules, oxygen atoms related to mentioned group have maximal chemical shifts. Also we have found that in all of the molecules, chemical shift for oxygen atoms in HF/6-31g level is the largest than other used methods in this work.

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