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Computational study of energetic, stability, and nuclear magnetic resonance of BN nanotube as a nanosensor

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ABSTRACT

Now a day study on boron nitrid nanotubes are in considerable attetion due to their unique properties in different field of science. In this letter, after final optimization, thermodynamic properties analysis, stabilities, electronic structure and nuclear magnetic resonance parameters including σ isotropic and σ anisotropic tensors and asymmetric parameters of ^{15}N and ^{11}B nuclei are calculated. NMR spectrum of armchair boron nitrid nanotube (4, 4) with tube length of 5 nm consisting of equal numbers of 16 atoms of boron, 16 atoms of nitrogen and 16 atoms of hydrogen atoms by use of GIAO method are computed by using Hartee-Fock and different levels of density functional theory methods including B3LYP, B1LYP, LSDA, B3PW91 and BVP86 with 6-31g(d) basis set by employing Gaussian 03 package of program. Our study has revealed that this nanosemiconductor can act as a sensor in for different application, trace and also as the base of functionalizing in drug deliveries system.

Keywords: Boron-nitrid nanotube; Ab initio; DFT; Nuclear magnetic resonance; Thermodynamic properties.

INTRODUCTION

Inorganic nanotubes like BN have recived considerable attention due to their unparalleled structure and properties [1, 2]. In comparison with CNTs, BNNTs are more chemically and thermally stable and their electronic behavior is completely different from CNTs which caused BNTs to become more desirable for usage in nano devices, manufacturing and also high temperature environments [3, 4]. All BN nanotubes have wide band gap semiconductor properties about 5.5 eV [5-7]. Geometry optimization, stabilities and nuclear magnetic resonance parameters of BN armchair nanotubes were carried out by ab initio and different levels of DFT methods (B3LYP, B1LYP, B3PW91, BVP86 and LSDA) by using 6-31g (d) basis sets implemented in Gaussian 03 program to perform its application as a trace and the base of functionalizing in drug deliveries system. The calculations were done on armchair model of BN (4, 4) nanotubes which consist of 16 atoms of B, 16 atoms of N and 16 atoms of hydrogen. Geometric optimization of the nanotube carried out by the B3LYP method and 6-31G basis set. The energy gap and the thermodynamic properties of this nano semiconductor were reported. In addition,

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the chemical shielding (CS) tensors, isotropic and anisotropic tensors and asymmetric parameters of ^{15}N and ^{11}B nuclei are calculated which are sensitive to electronic density and also have shown important points to electrostatic properties of BN nanotubes. Comparison between different NMR values at different levels of DFT theory and ab initio method were done to evaluate the ^{15}N and ^{11}B NMR parameters.

CALCULATION METHOD

We report Armchair (4,4) Borom nitride nanotube with tube length of 5nm and with 16B atoms and 16N atoms and 16H atoms (Fig. 1) which were examined by using Hartree-Fock calculations and density functional theory (DFT) in level of B3LYP, B1LYP, LSDA, BVP86 and B3PW91 with 6-31G(d) basis set. Both ends of these systems are terminated with hydrogen atoms. For this purpose, the Gaussian 03w program of the package was used [8], and after final optimization, thermodynamic properties, , energy gap and NMR parameters were studied. Thermodynamic analysis and total energies at all levels of the theory of DFT methods were used to examine the stability of those optimized structures. GIAO method was used, and chemical shift anisotropic and chemical shift isotropic were considered. Obtained results were have been investigated through density functional calculations for exploring (BNNTs) usage as nanosensors.

RESULT AND DISCUSSION

1.Thermodynamic Properties

To confirm the stability of the (4,4) BNNTs system, after geometry optimization of this nanosemiconductor we performed ab initio and DFT methods for energy calculations and thermodynamic data by using 6-31G* basis set to considered the stability of the system at standard temperature (298.15 K) and pressure (1 atm.). Gibbs free energies, enthalpies, entropy and total energies of this system computed by using Hartree-fuck and at the B3LYP, B1LYP, LSDA, BVP86, and B3PW91 levels of DFT theory which have been revealed in table 1. In order to obtain the most stable structure, the Gibbs free energy should be used. Table 1 shown relative values for

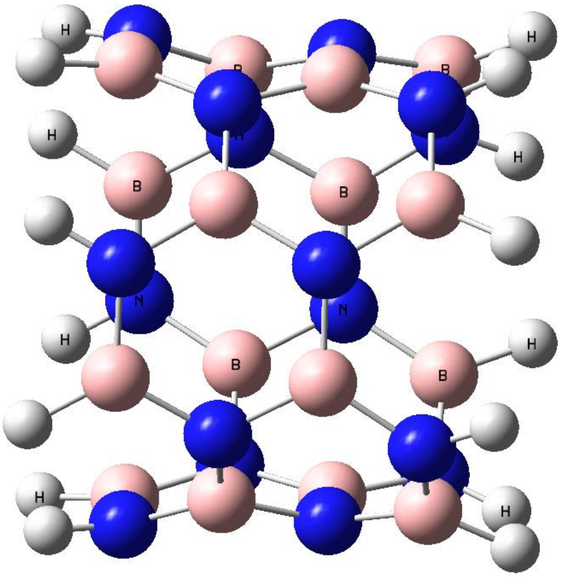

Fig. 1. The optimized Structures of B (4, 4) compound.

Table 1. Relative thermo dynamic data (energy ΔE (kcal/mol), enthalpy Δ H (kcal/mol) and Gibbs free energy ΔG (kcal/mol)) and antropy in cal/ (molK) obtained for B (4, 4) compound

Basis set	**6-31G***				
Method	**ΔE**	**ΔH**	**ΔG**	***Zero-point correction***	***S***
HF	0.00	0.00	0.00	0.00	151.53
B3LYP	-131423.51	-131423.47	-131423.74	-131423.41	150.76
B1LYP	-132180.74	-132180.74	-132180.75	-132180.04	151.51
B3PW91	-132134.96	-132134.96	-132132.92	-132133.69	158.35
BPV86	-131769.47	-131769.47	-131733.19	-131770.10	139.06
LSDA	-136377.12	-136377.12	-136409.81	-136376.53	148.83

thermodynamic data which each terms are referred to 298K. We analyzed the Gibbs free energy of the formation and found that among these methods, the results obtained at the HF level are more negative than those of the other calculations with -937466.02 kcal/mol value, so it represents the best results for $B_{16}H_{16}N_{16}$ structure which confirmed the structural stability. Also, the same relative trend observed for ΔH and ΔE with -937420.84 and -937421.43 kcal/mol values, respectively. Moreover, according to the frequency calculation at the HF and B3LYP, B1LYP, LSDA, BVP86 and B3PW91 level of theory, we observed no negative frequency which preferentially enhances the compound stability.

2. Nuclear Magnetic Resonance

Nuclear Magnetic Resonance (NMR) Spectroscopy is a non-destructive analytical technique that is used to probe the nature and characteristics of molecular structure. One of the most promising techniques used for studying the electronic properties of materials is based on Density Functional Theory (DFT) approach and its extensions. The fundamental parameters that reproduce a nuclear magnetic resonance (NMR) spectrum are the NMR chemical shift of the nucleus which is related to the local electronic structure at the nucleus. The theoretical methods used in calculating two basic parameters involving isotropic chemical shift (CSI) and anisotropic chemical shift. In this study, HF and DFT methods with 6-31G (d) basis set are used to obtain NMR parameters of BN (4, 4) nanotube after geometry optimization which are considered by GIAO method. Obtained results which are shown in Table.2 are represented σ isotropic, σ anisotropic and asymmetric parameter for each atom of B and N of this nanotube at Hartree-Fock and different levels of DFT including LSDA, B3LYP, B1LYP, BVP86 and B3PW91 methods. As can be seen in Table.2 all N atoms which are saturated at both ended of the tube with H atoms including N1, N4, N6, N7, N9, N12, N14 and N15 have the same values of σ isotropic, σ anisotropic and asymmetric parameters. The same trend can be seen in Table.2 for the B atoms including B25, B27, B32, B35, B37, B40, B42 and B45 which are bonded to these saturated H atoms, respectively. On the other hand, atoms of N2, N3, N5, N8, N10, N11, N13 and N16 and also B29, B30, B31, B34, B39, B44, B47 and 48B which are not bonded to any H atoms represented the same values of σ isotropic, σ anisotropic and asymmetric parameters in both Hartree-Fock and all calculated DFT methods which means that various ^{15}N, ^{11}B nuclei are divided into two parts that the nuclei in each category have equivalent electrostatic properties. As can be seen in Table.2 and Table.3, it could be concluded that the BNNTs is symmetric of chemical property therefore similar results are obtained for σ isotropic, σ anisotropic and asymmetric values in different parts of structure for all methods of calculation. Among all methods of maximum calculation amounts of σ isotropic is 134.98 for N atom and 80.31 for B atom at HF methods and the minimum amount is 80.83 for N atoms and 62.64 for B atoms at LSDA levels of DFT theory. Investigation of BN (4, 4) shown that the maximum value of σ anisotropic among all chosen calculation methods have found for N atom which is 209.43 at LSDA level of theory and is 60.46 for B atom at LSDA levels of theory and the minimum amount is 149.87 for N atom at HF and 33.6 for B atom at HF method which can be seen in table 2 and also maximum value of asymmetric parameter is 0.12 for N atom and is 0.58 for B atom at HF method and the minimum one is -0. 85 for N atom at LSDA method and 0.32 for B atom at LSDA method. The entire trend has not changed much in these levels of theory, and they are in good agreements with each other for each of calculated parameters. All obtained results depend on electron density of different nucleus. All atoms at $B_{16}H_{16}N_{16}$ system have different electronegativity, therefore, they have different charges. Hence, B–N bonds in $B_{16}H_{16}N_{16}$ structures have ionic characters. NMR shielding tensors of ^{15}N, ^{11}B nuclei are drastically affected by what it is bonded to and the type of bond to its neighbor. Our obtained results yielded strong evidence that intermolecular effects such as electron transfer interactions play very important role in determining the ^{15}N, ^{11}B -NMR chemical shielding tensors of $B_{16}H_{16}N_{16}$. One of the best techniques for considering structural information is NMR spectroscopy which is an integral part of modern chemistry. As a consequence, NMR spectroscopy finds applications in several areas of science. We indicated BNMR spectra for $B_{16}H_{16}N_{16}$ in absent of reference and in the present of B2H6 as a reference in fig. 2, fig. 3,fig 4, fig 5 in GIAO method for HF and B3LYP levels of theory. ^{11}B is the better nucleus in all respects in contrast of ^{10}B because of having the lower quadrupole moment and being more sensitive. As can be seen in fig. 2 and fig. 3 shielding is 106.7 ppm, and 106 ppm in the present of B2H6 as a reference for HF and B3LYP levels of theory respectively.

CONCLUSION

Ab initio and DFT theory with different levels of theory including B3LYP, B1LYP, B3PW91, BVP86 and LSDA by using 6-31d (g) basis set applied to study nanosemiconductor BN(4, 4). We performed optimization at B3LYP-DFT level using 6-31G (d) standard basis set on model of the considered BN nanotubes in order to calculate the minimum energy. Thermodynamic properties such as relative Gibss energy considered to find out system stability and nuclear magnetic resonance indicated electronic structure of the system. NMR shielding tensors of ^{15}N, ^{11}B nuclei are drastically affected by what it is bonded to and the type of bond to its neighbor. The NMR results show that nuclei of B and N atoms are divided into two categories, and each of them has similar electronic property. All N and B atoms of the system have different electronegativy, N atoms have the highest electron density and B atoms have the lowest electron density which represented they could be act as electron donor and electron acceptor atoms ,respectively, and are a good sites for bonding to different molecules to react as a nnanosensor or drug delivery system.

ACKNOWLEDGEMENTS

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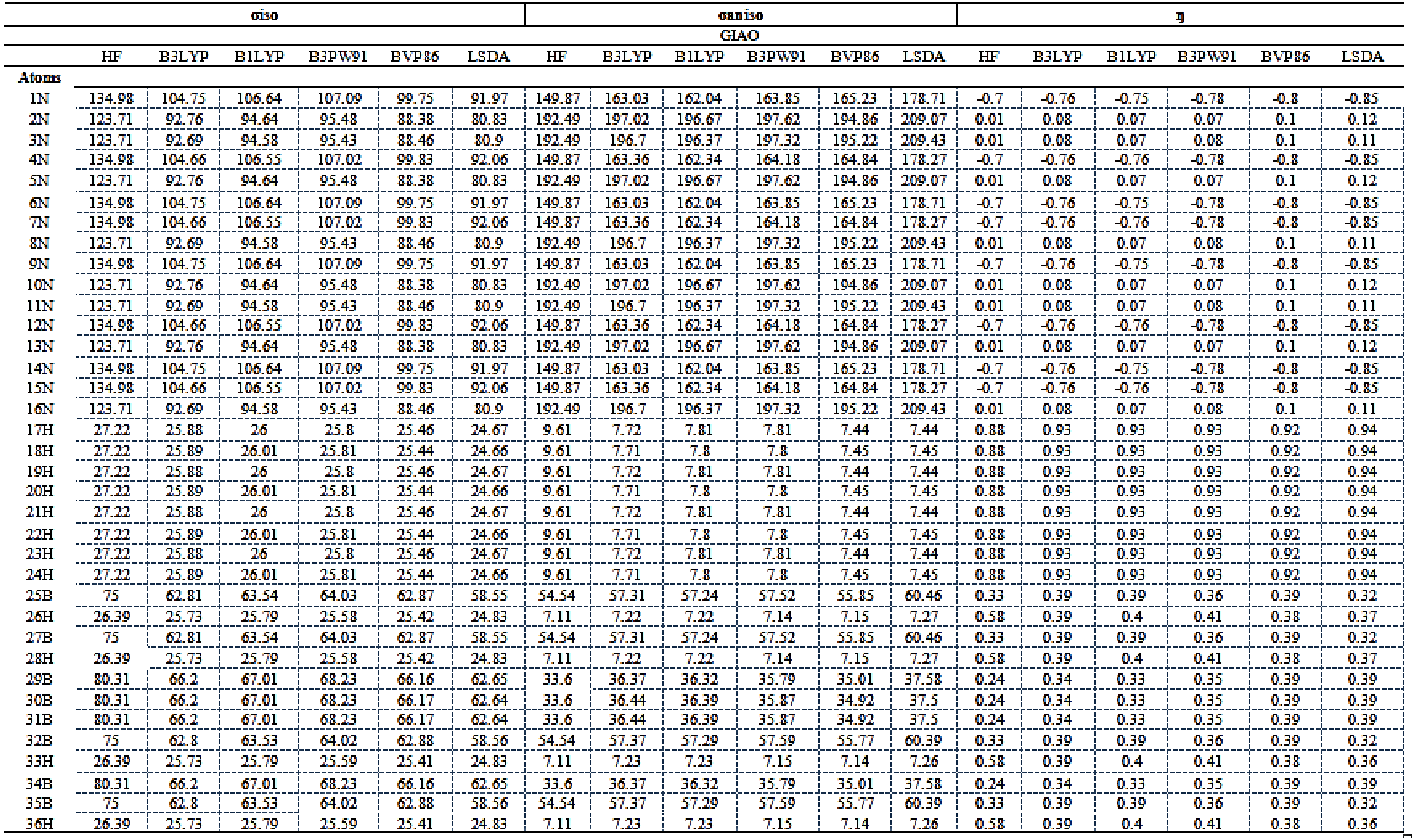
Table 2. NMR parameters of BN (4, 4) at HF and DFT levels with the 6-31G* basis sets in GIAO method



	σiso						σaniso						η					
									GIAO									
	HF	B3LYP	B1LYP	B3PW91	BVP86	LSDA	HF	B3LYP	B1LYP	B3PW91	BVP86	LSDA	HF	B3LYP	B1LYP	B3PW91	BVP86	LSDA
Atoms																		
1N	134.98	104.75	106.64	107.09	99.75	91.97	149.87	163.03	162.04	163.85	165.23	178.71	-0.7	-0.76	-0.75	-0.78	-0.8	-0.85
2N	123.71	92.76	94.64	95.48	88.38	80.83	192.49	197.02	196.67	197.62	194.86	209.07	0.01	0.08	0.07	0.07	0.1	0.12
3N	123.71	92.69	94.58	95.43	88.46	80.9	192.49	196.7	196.37	197.32	195.22	209.43	0.01	0.08	0.07	0.08	0.1	0.11
4N	134.98	104.66	106.55	107.02	99.83	92.06	149.87	163.36	162.34	164.18	164.84	178.27	-0.7	-0.76	-0.76	-0.78	-0.8	-0.85
5N	123.71	92.76	94.64	95.48	88.38	80.83	192.49	197.02	196.67	197.62	194.86	209.07	0.01	0.08	0.07	0.07	0.1	0.12
6N	134.98	104.75	106.64	107.09	99.75	91.97	149.87	163.03	162.04	163.85	165.23	178.71	-0.7	-0.76	-0.75	-0.78	-0.8	-0.85
7N	134.98	104.66	106.55	107.02	99.83	92.06	149.87	163.36	162.34	164.18	164.84	178.27	-0.7	-0.76	-0.76	-0.78	-0.8	-0.85
8N	123.71	92.69	94.58	95.43	88.46	80.9	192.49	196.7	196.37	197.32	195.22	209.43	0.01	0.08	0.07	0.08	0.1	0.11
9N	134.98	104.75	106.64	107.09	99.75	91.97	149.87	163.03	162.04	163.85	165.23	178.71	-0.7	-0.76	-0.75	-0.78	-0.8	-0.85
10N	123.71	92.76	94.64	95.48	88.38	80.83	192.49	197.02	196.67	197.62	194.86	209.07	0.01	0.08	0.07	0.07	0.1	0.12
11N	123.71	92.69	94.58	95.43	88.46	80.9	192.49	196.7	196.37	197.32	195.22	209.43	0.01	0.08	0.07	0.08	0.1	0.11
12N	134.98	104.66	106.55	107.02	99.83	92.06	149.87	163.36	162.34	164.18	164.84	178.27	-0.7	-0.76	-0.76	-0.78	-0.8	-0.85
13N	123.71	92.76	94.64	95.48	88.38	80.83	192.49	197.02	196.67	197.62	194.86	209.07	0.01	0.08	0.07	0.07	0.1	0.12
14N	134.98	104.75	106.64	107.09	99.75	91.97	149.87	163.03	162.04	163.85	165.23	178.71	-0.7	-0.76	-0.75	-0.78	-0.8	-0.85
15N	134.98	104.66	106.55	107.02	99.83	92.06	149.87	163.36	162.34	164.18	164.84	178.27	-0.7	-0.76	-0.76	-0.78	-0.8	-0.85
16N	123.71	92.69	94.58	95.43	88.46	80.9	192.49	196.7	196.37	197.32	195.22	209.43	0.01	0.08	0.07	0.08	0.1	0.11
17H	27.22	25.88	26	25.8	25.46	24.67	9.61	7.72	7.81	7.81	7.44	7.44	0.88	0.93	0.93	0.93	0.92	0.94
18H	27.22	25.89	26.01	25.81	25.44	24.66	9.61	7.71	7.8	7.8	7.45	7.45	0.88	0.93	0.93	0.93	0.92	0.94
19H	27.22	25.88	26	25.8	25.46	24.67	9.61	7.72	7.81	7.81	7.44	7.44	0.88	0.93	0.93	0.93	0.92	0.94
20H	27.22	25.89	26.01	25.81	25.44	24.66	9.61	7.71	7.8	7.8	7.45	7.45	0.88	0.93	0.93	0.93	0.92	0.94
21H	27.22	25.88	26	25.8	25.46	24.67	9.61	7.72	7.81	7.81	7.44	7.44	0.88	0.93	0.93	0.93	0.92	0.94
22H	27.22	25.89	26.01	25.81	25.44	24.66	9.61	7.71	7.8	7.8	7.45	7.45	0.88	0.93	0.93	0.93	0.92	0.94
23H	27.22	25.88	26	25.8	25.46	24.67	9.61	7.72	7.81	7.81	7.44	7.44	0.88	0.93	0.93	0.93	0.92	0.94
24H	27.22	25.89	26.01	25.81	25.44	24.66	9.61	7.71	7.8	7.8	7.45	7.45	0.88	0.93	0.93	0.93	0.92	0.94
25B	75	62.81	63.54	64.03	62.87	58.55	54.54	57.31	57.24	57.52	55.85	60.46	0.33	0.39	0.39	0.36	0.39	0.32
26H	26.39	25.73	25.79	25.58	25.42	24.83	7.11	7.22	7.22	7.14	7.15	7.27	0.58	0.39	0.4	0.41	0.38	0.37
27B	75	62.81	63.54	64.03	62.87	58.55	54.54	57.31	57.24	57.52	55.85	60.46	0.33	0.39	0.39	0.36	0.39	0.32
28H	26.39	25.73	25.79	25.58	25.42	24.83	7.11	7.22	7.22	7.14	7.15	7.27	0.58	0.39	0.4	0.41	0.38	0.37
29B	80.31	66.2	67.01	68.23	66.16	62.65	33.6	36.37	36.32	35.79	35.01	37.58	0.24	0.34	0.33	0.35	0.39	0.39
30B	80.31	66.2	67.01	68.23	66.17	62.64	33.6	36.44	36.39	35.87	34.92	37.5	0.24	0.34	0.33	0.35	0.39	0.39
31B	80.31	66.2	67.01	68.23	66.17	62.64	33.6	36.44	36.39	35.87	34.92	37.5	0.24	0.34	0.33	0.35	0.39	0.39
32B	75	62.8	63.53	64.02	62.88	58.56	54.54	57.37	57.29	57.59	55.77	60.39	0.33	0.39	0.39	0.36	0.39	0.32
33H	26.39	25.73	25.79	25.59	25.41	24.83	7.11	7.23	7.23	7.15	7.14	7.26	0.58	0.39	0.4	0.41	0.38	0.36
34B	80.31	66.2	67.01	68.23	66.16	62.65	33.6	36.37	36.32	35.79	35.01	37.58	0.24	0.34	0.33	0.35	0.39	0.39
35B	75	62.8	63.53	64.02	62.88	58.56	54.54	57.37	57.29	57.59	55.77	60.39	0.33	0.39	0.39	0.36	0.39	0.32
36H	26.39	25.73	25.79	25.59	25.41	24.83	7.11	7.23	7.23	7.15	7.14	7.26	0.58	0.39	0.4	0.41	0.38	0.36

Table 3. NMR parameters of BN (4, 4) at HF and DFT levels with the 6-31G* basis sets in GIAO method

	σiso						σaniso						η					
	GIAO																	
	HF	B3LYP	B1LYP	B3PW91	BVP86	LSDA	HF	B3LYP	B1LYP	B3PW91	BVP86	LSDA	HF	B3LYP	B1LYP	B3PW91	BVP86	LSDA
Atoms																		
37B	75	62.8	63.53	64.02	62.88	58.56	54.54	57.37	57.29	57.59	55.77	60.39	0.33	0.39	0.39	0.36	0.39	0.32
38H	26.39	25.73	25.79	25.59	25.41	24.83	7.11	7.23	7.23	7.15	7.14	7.26	0.58	0.39	0.4	0.41	0.38	0.36
39B	80.31	66.2	67.01	68.23	66.16	62.65	33.6	36.37	36.32	35.79	35.01	37.58	0.24	0.34	0.33	0.35	0.39	0.39
40B	75	62.81	63.54	64.03	62.87	58.55	54.54	57.31	57.24	57.52	55.85	60.46	0.33	0.39	0.39	0.36	0.39	0.32
41H	26.39	25.73	25.79	25.58	25.42	24.83	7.11	7.22	7.22	7.14	7.15	7.27	0.58	0.39	0.4	0.41	0.38	0.37
42B	75	62.81	63.54	64.03	62.87	58.55	54.54	57.31	57.24	57.52	55.85	60.46	0.33	0.39	0.39	0.36	0.39	0.32
43H	26.39	25.73	25.79	25.58	25.42	24.83	7.11	7.22	7.22	7.14	7.15	7.27	0.58	0.39	0.4	0.41	0.38	0.37
44B	80.31	66.2	67.01	68.23	66.16	62.65	33.6	36.37	36.32	35.79	35.01	37.58	0.24	0.34	0.33	0.35	0.39	0.39
45B	75	62.8	63.53	64.02	62.88	58.56	54.54	57.37	57.29	57.59	55.77	60.39	0.33	0.39	0.39	0.36	0.39	0.32
46H	26.39	25.73	25.79	25.59	25.41	24.83	7.11	7.23	7.23	7.15	7.14	7.26	0.58	0.39	0.4	0.41	0.38	0.36
47B	80.31	66.2	67.01	68.23	66.17	62.64	33.6	36.44	36.39	35.87	34.92	37.5	0.24	0.34	0.33	0.35	0.39	0.39
48B	80.31	66.2	67.01	68.23	66.17	62.64	33.6	36.44	36.39	35.87	34.92	37.5	0.24	0.34	0.33	0.35	0.39	0.39

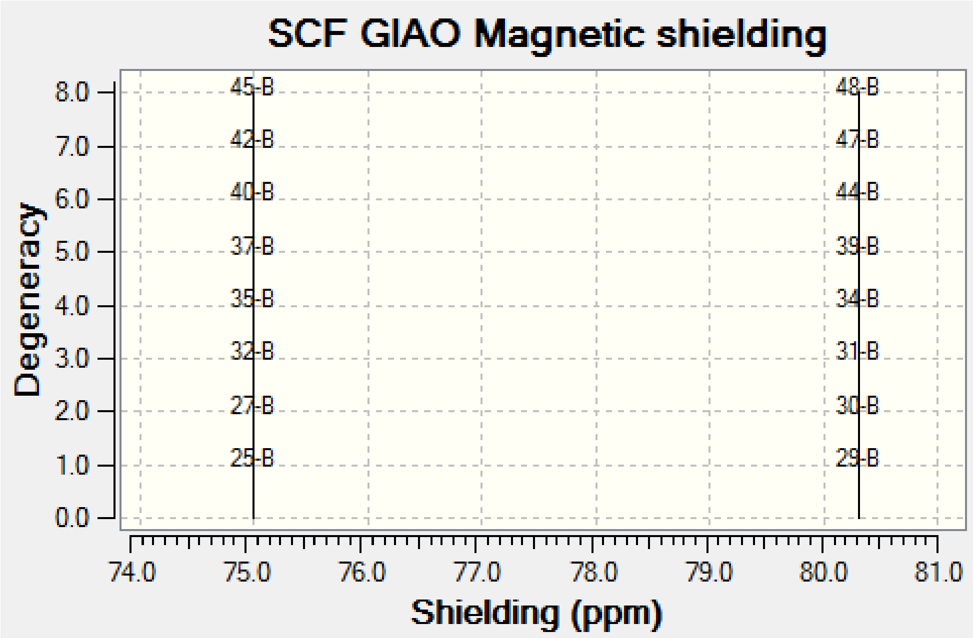


Fig. 2. B NMR shifts relative to HF/6-31G* in GIAO methods.

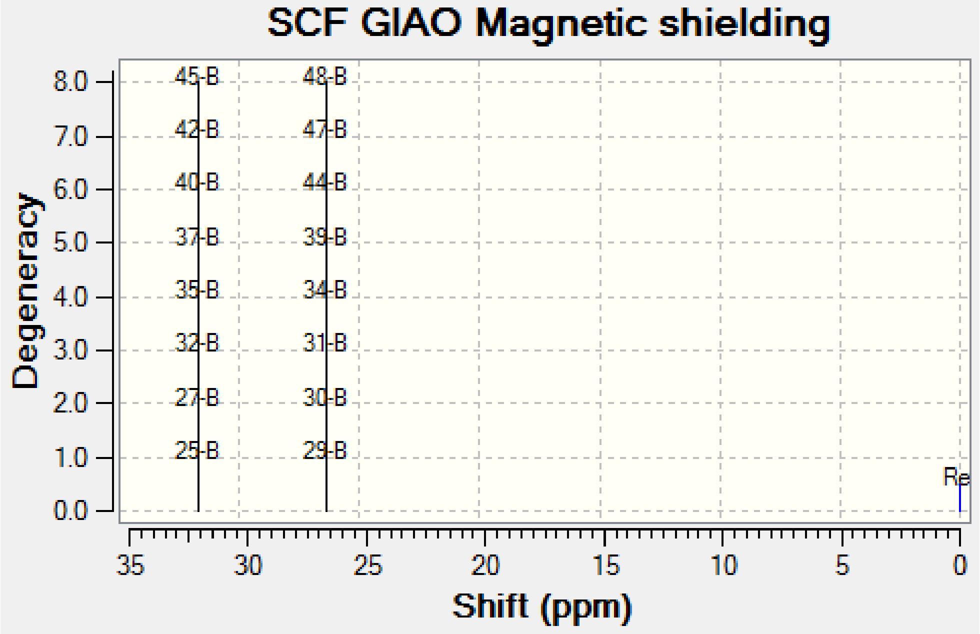


Fig. 3. B NMR shifts relative to HF/6-31G* in GIAO methods in the presence of B_2H_6 as a reference.

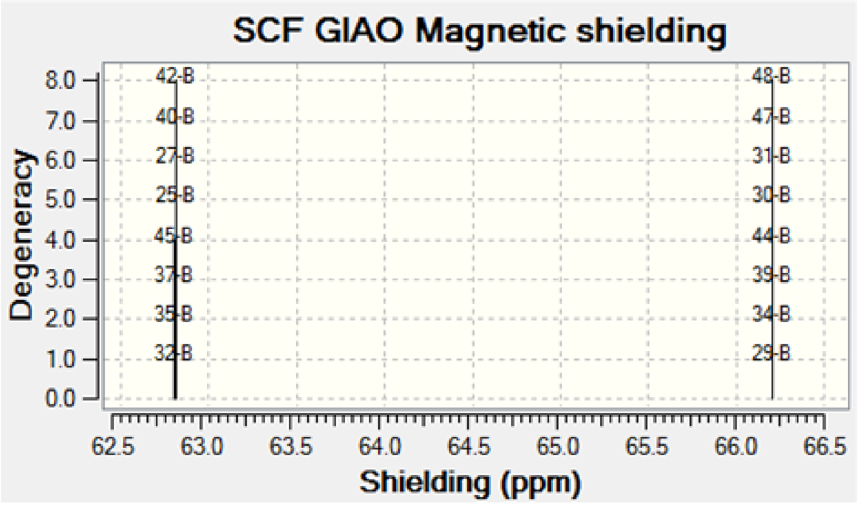


Fig. 4. B NMR shifts relative to B3LYP/6-31G* in GIAO methods.

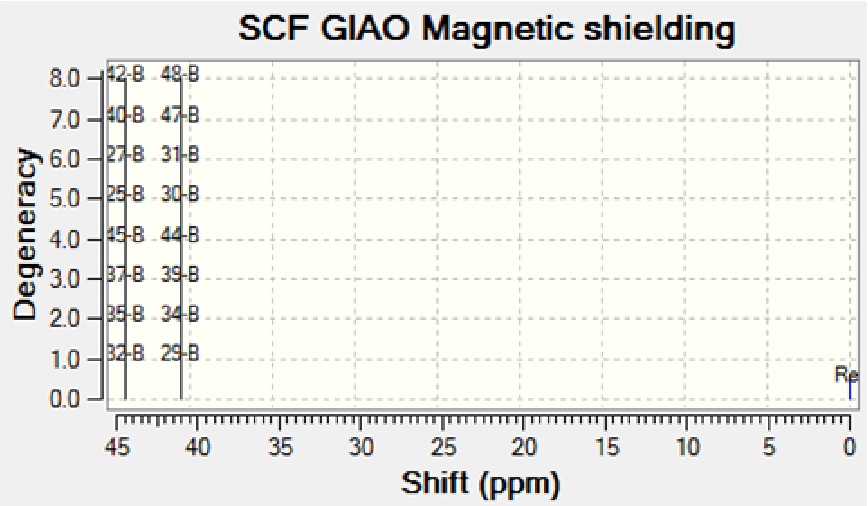


Fig. 5. B NMR shifts relative to HF/6-31G* in GIAO methods in the presence of B_2H_6 as a reference.

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