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AB Initio Calculations of NMR Spectra for $H_{20}B_4C_9N_4$ As A New Nanosemiconductor Molecule

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ABSTRACT

BCN compounds have been researched theoretically and experimentally widely. In this paper, we introduce the theoretical prediction of ternary B-C-N compounds. NMR spectroscopy was employed extensively to study these ternary nanostructures. We discuss the utilization of chemical shift information as well as ab initio calculations of nuclear shielding for $H_{20}B_4C_9N_4$ structure determination. We calculated B NMR and N NMR spectra with computational aspects of the NMR spectra using the gauge-invariant atomic orbital (GIAO) and continuous set of gauge transformations (CSGT) methods at different DFT computational methods (B1LYP and LSDA), with a 6-31 G basis set at the GAUSSIAN 98 program package which are discussed. The purpose of this study is to carry out a more detailed analysis of the $H_{20}B_4C_9N_4$ as a new nanosemiconductor system.

Keywords: Dipeptide structures; *Ab initio*; DFT calculations; Conformational stability

INTRODUCTION

Graphite, hexagonal boron nitride (h-BN), diamond, cubic boron nitride (c-BN) and boron carbide play important roles in the areas of mechanical machining and as functional parts of an apparatus. These compounds consist of boron, carbon and nitrogen, which are three neighboring light elements in the second row of the periodic table of elements [1]. So far, the existence of ternary B-C-N compound is still an open question. It is well known that diamond and cubic boron nitride (c-BN) are the hardest materials among all known solids. They share a number of similar physical properties such as super hardness, wide band gap and high melting points. Therefore, a solid solution between C and B-N is anticipated to exist in the ternary B-C-N system according to their atom size. The similarity of the structure and phase diagram between C and B-N has motivated the synthesis of ternary B-C-N compounds. Since Liu and Cohen [2] predicted that β-C3N4 has hardness comparable to diamond in 1989, interests in the B-C-N system have been stimulated in the domains of materials, physics and chemistry. In the past two decades, the ternary B-C-N materials have been studied extensively. Theoretical and experimental results have revealed that in addition to the hardness comparable to diamond in the B-C-N system; the materials in the system with various structures may have unique physical and chemical properties. The novel B-C-N will

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have extensive applications in the mechanical, electronic, biological, physical and chemical fields. Hexagonal B–C–N compounds have been investigated both theoretically [3–5] and experimentally [6–8], and different methods have been used to the synthesis of the graphite-like B–C–N materials, such as nitriding of solid-phase at high temperatures [9], chemical vapor deposition (CVD) [10, 11], solvothermal method [12], chemical process [13], etc.

Over the past decades nuclear magnetic resonance (NMR) spectroscopy has established itself as a powerful technique to determine the three-dimensional (3D) structures of molecules at atomic resolution. For the immediate future, the inclusion of chemical shift information promises to become a very powerful addition to structure determination, making use of semi- empirical relationships as well as ab initio calculations. Recent progress in quantum chemical methods makes it possible to derive accurate relationships between calculated shielding parameters and 3D conformation and increases significantly the range of $H_{20}B_4C_9N_4$ that can be characterized structurally with NMR spectroscopy. There are two major routes of using the information from chemical shifts: (i) an empirical route based on the observation that similar structures produce similar chemical shifts, and (ii) a first principles modeling of chemical shifts in $H_{20}B_4C_9N_4$ structures. Recent theoretical and experimental study represent that the ternary B-C-N system may have many kinds of structures, with different characteristics. However, it is hard to synthesize the crystalline B-C-N phase with high purity [14]. In order to show the possible structures, several first- principles investigations on the structure of B-C-N compounds have been carried out [15-17]. The computational tools of quantum theory and molecular dynamics have been very useful for solving a number of substantial problems depended on the atomic structure, morphology, electronic structure, chemical bonding, and stability factors and for prediction of structures and properties of new assemblies [18–37]. Here, we represented the quantum-chemical simulation of structure, and calculation of the NMR chemical shifts of the $H_{20}B_4C_9N_4$. Today, NMR spectroscopy is especially attractive for ternary and quaternary systems, as they have different NMR active nuclei such as ^{13}C, ^{15}N and ^{11}B, which can be studied directly without further isotopic enrichment. The calculation of nuclear magnetic resonance (NMR) parameters using semi-empirical, *ab initio* and DFT techniques has become a major and powerful tool in the investigation to look at how difference in the molecular structure occurs [38]. In our current study, we performed quantum mechanical calculation of electronic structures of the $H_{20}B_4C_9N_4$ in three available methods using GAUSSIAN 98 program.

COMPUTATIONAL METHOD

We consider here recent, accurate programs to calculate chemical shifts from known 3D structures, which are freely distributed. Density functional theory was used to calculate ^{11}B, and ^{15}N chemical shifts from atomic coordinates. We carried out a quantum chemical calculation for $H_{20}B_4C_9N_4$. Full geometry optimization of present compound was performed as well as calculation of B NMR and N NMR spectra, which were carried out using the DFT method, Becke's One Parameter Hybrid Functional with LYP Correlation (B1LYP), local spin density approximation (LSDA) for the exchange and correlation term, with a 6-31G basis set at the GAUSSIAN 98 program package [39]. The optimized structures of $H_{20}B_4C_9N_4$ are given in Fig.1. Ab initio calculation may be used as a supplement to or in place of experimentation or to obtain information not accessible experimental [40]. Kohn-Sham equations produce exact electron density. The NMR spectra can be predicted using first principles computational methods that take into account both relativity and electron correlation using the gauge-invariant atomic orbital (GIAO) and continuous set of gauge transformations (CSGT) methods.

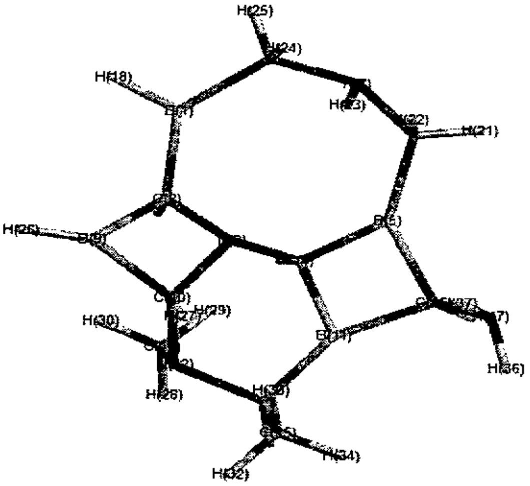

Fig. 1. Perspective view of $H_{20}B_4C_9N_4$ molecules.

RESULTS AND DISCUSSION

NMR Spectra

NMR spectroscopy is an integral part of modern chemistry. One of the most successful techniques for providing structural information including dynamic behavior, intermolecular interactions and kinetic information is NMR spectroscopy. As a consequence, NMR spectroscopy finds applications in several areas of science. All the parameters that can be measured by NMR spectroscopy are sensitive to molecular structure and dynamics and can be employed as restraints to construct models of the three dimensional structures of molecules. There are two major routes of using the information from chemical shifts: (i) an empirical route based on the observation that similar structures produce similar chemical shifts, and (ii) a first principles modeling of chemical shifts in specific molecule secondary structures [41]. The calculation of magnetic shielding and nuclear magnetic resonance (NMR) chemical shifts has substantially broadened the applicability of quantum chemical methods for practical purposes and is now an important asset of most quantum chemical investigations [42–45]. Gauge-invariant or at least approximately gauge-invariant methods at the electron correlation corrected *ab initio* levels have led to a wealth of reliable NMR chemical shift data concerning in particular first and second row nuclei [45–54]. Gauss and co-workers [45], [48–52] developed the gauge-including atomic orbitals (GIAO) method[56] previously applied only at the Hartree–Fock (HF) Level [56,57] at the *n*th order (*n*=2,3,4) many body perturbation theory with the Møller–Plesset perturbation (MPn) and at coupled cluster theory level yielding in this way GIAO-MP2[48] GIAO-MP3[49]GIAO-MP4[49] GIAO-CCSD[50] and GIAO-CCSD(T)[51] Later, GIAO was extended to the domain of density functional theory (DFT)[58, 59]. A cost-effective alternative to correlated wave function ab initio methods are provided by density functional theory (DFT). DFT represents an ingenious reformulation of the many-body problem in quantum mechanics whereby the problem of solving the Schrodinger equation for interacting electrons is cast in the form of a much simpler set of one electron equations, the so-called Kohn–Sham equations. The cost of a DFT calculation is roughly the same as the cost of a Hartree–Fock calculation. Modern density functional methods have been successful with regard to the calculation of molecular thermochemical and electronic properties such as equilibrium geometries, atomization energies, vibrational frequencies, dipole moments, excitation energies, etc [60, 61]. Circulation of current within electronic clouds of molecules gives rise to a local magnetic field at nuclei of interest, which is dependent on the molecular orientation relative to the applied magnetic field. The orientation dependence of this local field can be represented by a second rank chemical shift tensor. One of the major sources of chemical information is the measurement of chemical shifts in high-resolution NMR spectroscopy [62]. Recently DFT introduced exchange correlation functional [63] have proven very reliable and practical tools for the calculation of magnetic shielding. The calculation of the magnetic shielding can be performed using an optimized structure. We have been concentrated on chemical shifts as the results of the electronics field for $H_{20}B_4C_9N_4$ molecules. Atomic charge of $H_{20}B_4C_9N_4$ structure as a function of atomic number in B1LYP and LSDA methods with 6-31G basis set were shown in fig. 2 and displayed in table 1. Through atomic charge analysis, we find that the most negative charge belongs to N (17) at -0.66 and -0.65 in B1LYP and LSDA levels of theory and the most positive one belongs to B (5) at 0.55 and 0.42 in B1LYP and LSDA levels of theory, respectively.

We have been calculated NMR parameters for $H_{20}B_4C_9N_4$ using DFT method at different levels of theory including B1LYP and LSDA, with 6-31G basis set which were computed by gauge-including atomic orbital (GIAO) and continuous set of gauge transformations (CSGT) methods incorporated with the program Gaussian 98 package which are determined theoretically using DFT methods. 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 neighbour. 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 $H_{20}B_4C_9N_4$.

B NMR spectra

Boron has two naturally occurring NMR active nuclei. Both nuclei have spins of greater than ½ and are quadrupolar. ^{11}B has a spin of 3/2 and ^{10}B is spin 3. ^{11}B is the better nucleus in all respects, having the lower quadrupole moment and being more sensitive. Both nuclei have the same wide chemical shift range. Each type of signal has a characteristic chemical shift range which is the same for both nuclei. We represented BNMR spectra for $H_{20}B_4C_9N_4$ in absent of reference and in the present of B_2H_6 as a reference in fig 3, 4, 5, 6 in GIAO and CSGT methods. As can be seen in fig. 3 and 4 the shift of resonance is ~64.91 ppm and ~79.22 ppm downfield in LSDA/6-31G in comparison of HF/6-31G (d) in GIAO and CSGT methods in the presence of B_2H_6 as a references respectively for B(1) bond. It shown in Fig. 5 that the shift of resonance is ~ 50.03 ppm shifted to the lower field in the presence of B_2H_6 as a reference in HF/6-31G (d) methods in comparison of B1LYP/6-31G in GIAO methods, and fig. 6 shielding is ~ 62.41 ppm shifted to lower field for HF/6-31G (d) in the presence of B_2H_6 as references in comparison of B1LYP/6-31G in CSGT method for B (1).

Table 1. Calculated total atomic charge of system at B1LYP and LSDA methods with 6-31G basis set

Atomic number	Total atomic charge	
Method/Basis set	B1LYP/6-31G	LSDA/6-31G
1B	0.40	0.24
2C	-0.31	-0.28
3N	-0.52	-0.43
4C	-0.34	-0.33
5B	0.55	0.42
6C	-0.26	-0.32
7N	-0.56	-0.51
8C	-0.26	-0.32
9B	0.33	0.20
10C	0.01	-0.05
11B	0.50	0.36
12N	-0.44	-0.34
13C	-0.26	-0.37
14C	-0.15	-0.16
15C	-0.39	-0.49
16 C	-0.34	-0.32
17 N	-0.66	-0.65
18 H	-0.06	-0.01
19 H	0.15	0.18
20 H	0.11	0.14
21 H	0.13	0.17
22 H	0.14	0.17
23 H	0.26	0.29
24 H	0.13	0.17
25 H	0.13	0.17
26 H	-0.05	-0.01
27 H	0.15	0.18
28 H	0.14	0.17
29 H	0.12	0.15
30 H	0.14	0.18
31 H	0.13	0.16
32 H	0.14	0.18
33 H	0.12	0.15
34 H	0.12	0.16
35 H	0.13	0.16
36 H	0.28	0.29
37 H	0.28	0.29

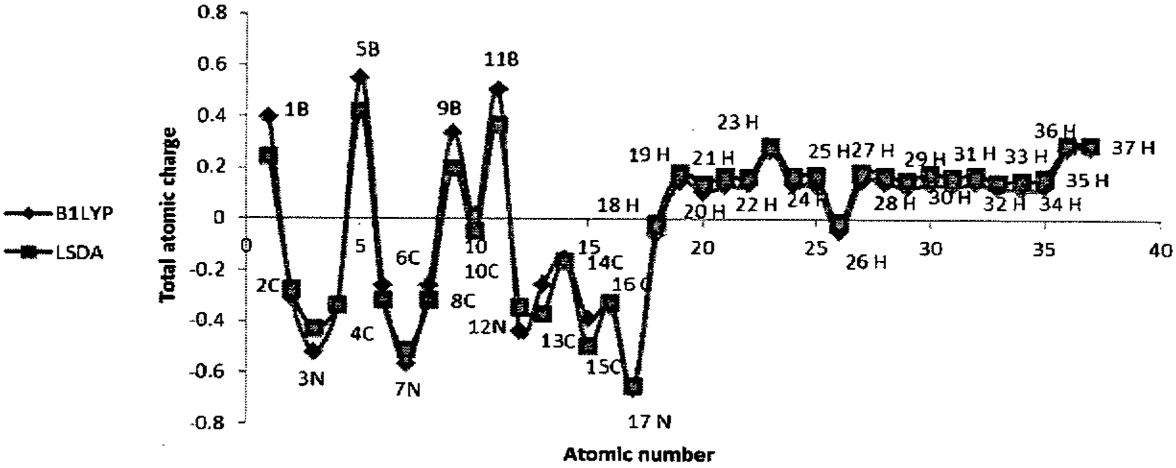

Fig. 2. Atomic charge of $H_{20}B_4C_9N_4$ structure as a function of atomic number.

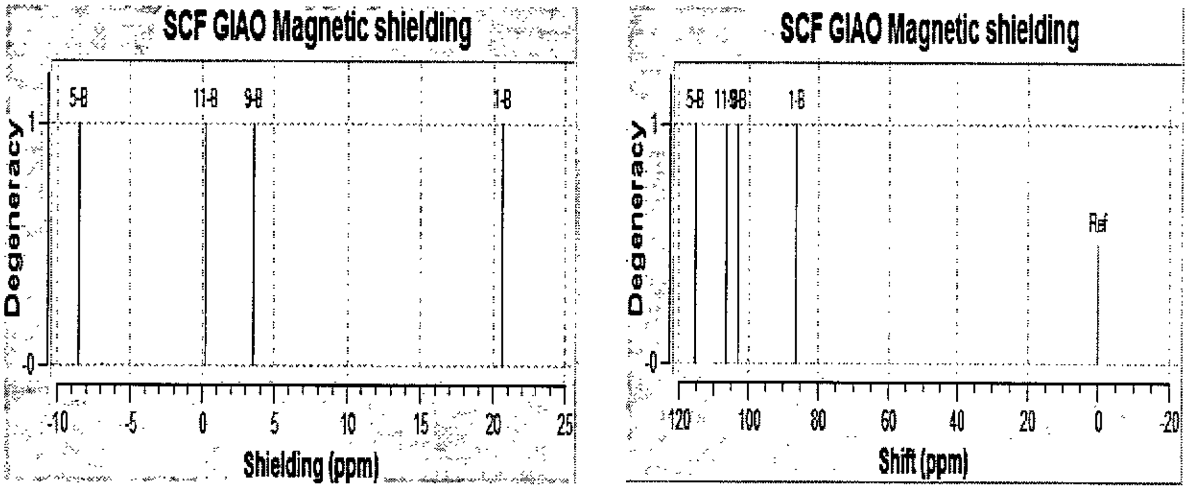

Fig. 3. B NMR shifts relative to LSDA/6-31G in GIAO methods (on the left side) and B NMR shifts relative to HF/6-31+G (d) GIAO in the presence of B_2H_6 as a reference (on the right side).

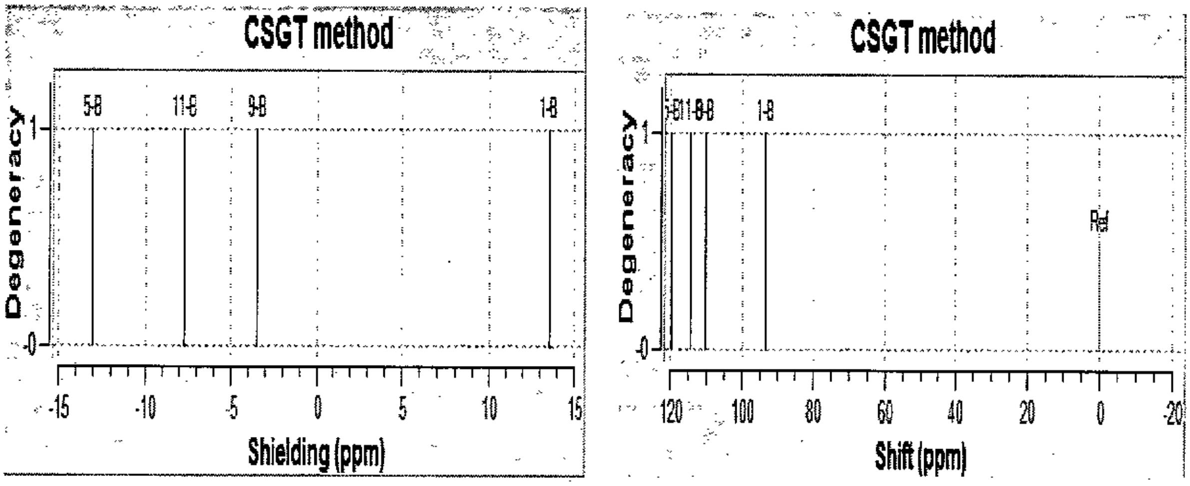

Fig. 4. B NMR shifts relative to LSDA/6-31G in CSGT methods (on the left side) and B NMR shifts relative to HF/6-31+G (d) GIAO in the presence of B_2H_6 as a reference (on the right side).

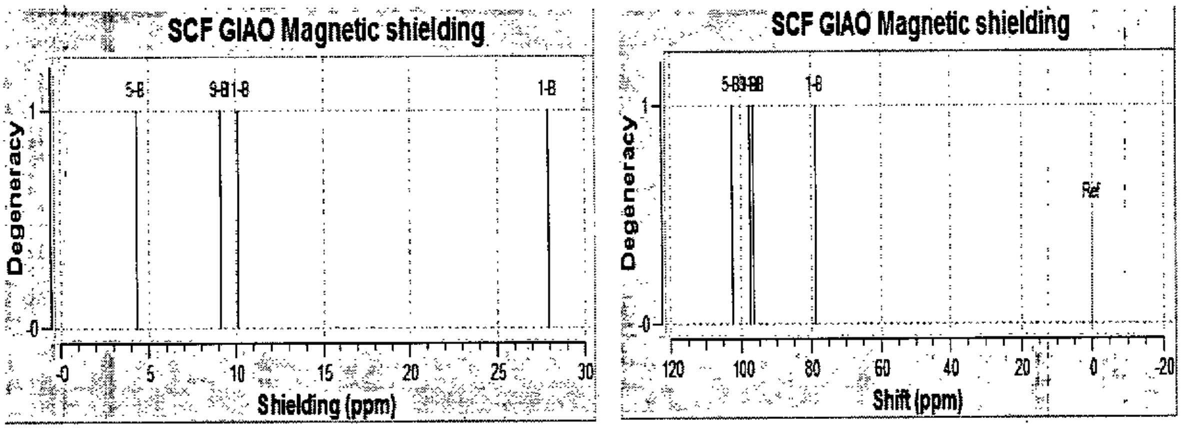

Fig. 5. B NMR shifts relative to B1LYP/6-31G in GIAO methods (on the left side) and B NMR shifts relative to HF/6-31+G (d) GIAO in the presence of B_2H_6 as a reference (on the right side).

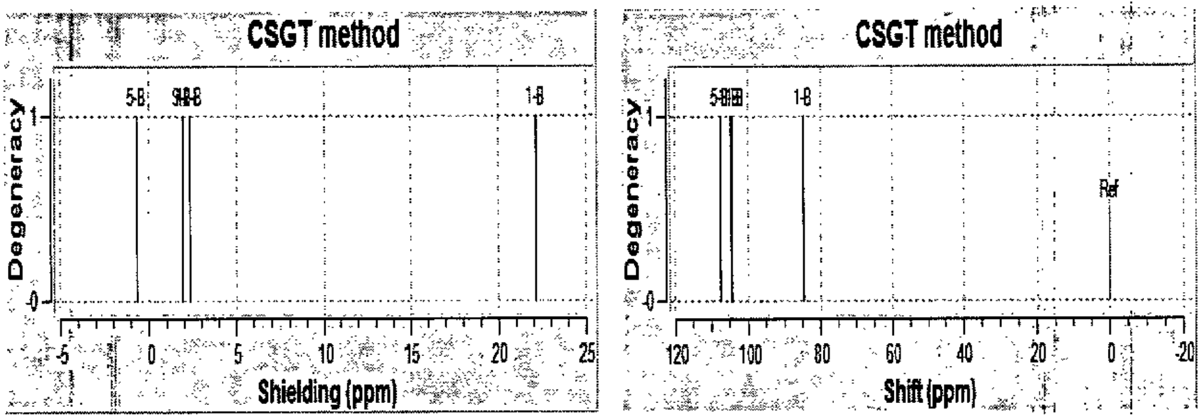

Fig. 6. B NMR shifts relative to B1LYP/6-31G in CSGT methods (on the left side) and B NMR shifts relative to HF/6-31+G (d) GIAO in the presence of B_2H_6 as a reference (on the right side).

N NMR spectra

The most easily accessible alternative probes of molecular conformation in $H_{20}B_4C_9N_4$ are the chemical shifts of ^{15}N nuclei. We have undertaken theoretical calculations of ^{15}N shielings in $H_{20}B_4C_9N_4$ at both the wave function ab initio level of theory GIAO-LSDA, CSGT-LSDA which are shown in fig. 7 and fig. 8 and GIAO-B1LYP and CSGT-B1LYP methods which are represented in fig. 9 and fig. 10 at the DFT levels of theory and in the presence of B_2H_6 as a reference. As can be seen in fig. 7 and fig.8 that the shift of resonance is ~-153.75 ppm and ~-87.87 ppm shifted to the upper field in the presence of B_2H_6 as a reference in HF/6-31G (d) methods in comparison of LSDA/6-31G methods, both for GIAO and CSGT methods for N(7), respectively. Fig. 9 and fig. 10 are represented ~-185.52 ppm and ~-114.73 ppm shifted to the upper field in the presence of B_2H_6 as a reference in HF/6-31G (d) methods in comparison of B1LYP/6-31G methods, both for GIAO and CSGT methods, respectively for N(7). N(3) atomic charge is -0.52 and -0.43 in B1LYP and LSDA levels of theory which is bonded to C(2), C(4) and C(10) with atomic charge of -0.31 and -0.28 for C(2), -0.34 and -0.33 for C(4), 0.01 and -0.05 for C(10) in B1LYP and LSDA levels of theory, respectively. it could be concluded that the most polar band in this structure is N (3)-C (10) band therefore N(3) has the highest electronic charge density which caused N(3) appeared in upfield of N NMR spectra related to other atoms.

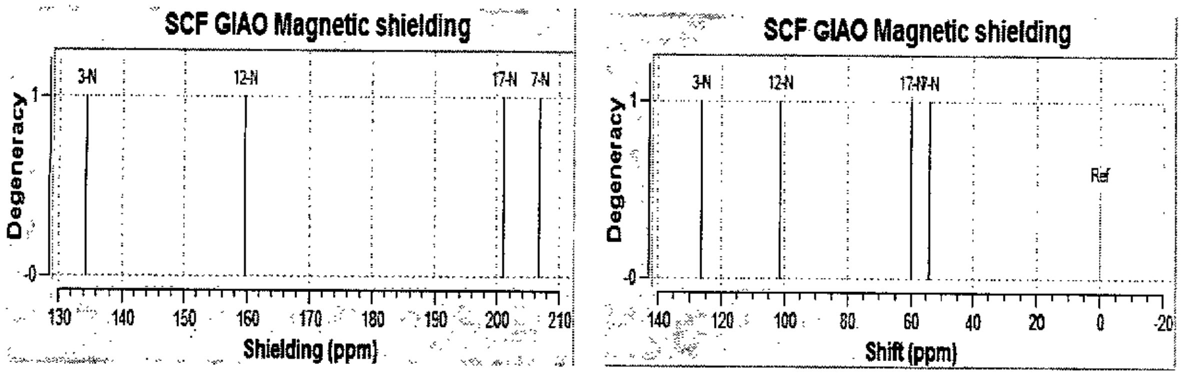

Fig. 7. N NMR shifts relative to LSDA/6-31G in GIAO methods (on the left side) and N NMR shifts relative to HF/6-31+G (d) GIAO in the presence of B_2H_6 as a reference (on the right side).

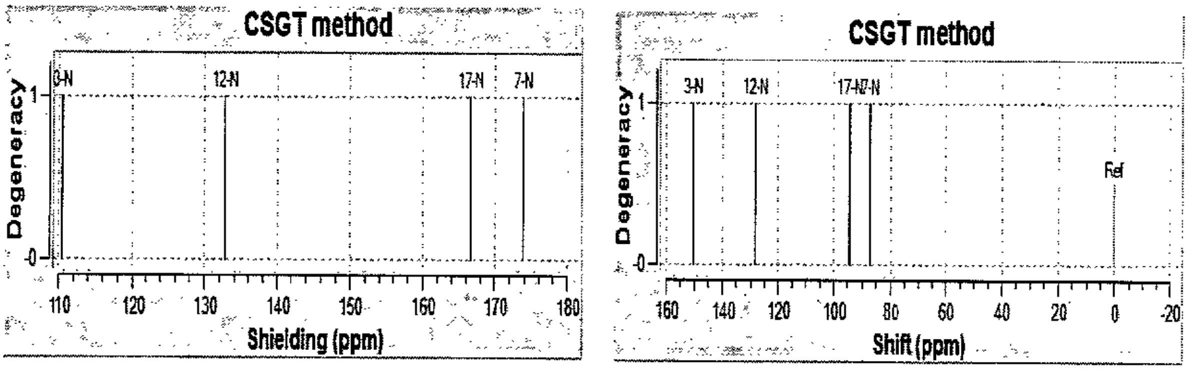

Fig. 8. N NMR shifts relative to LSDA/6-31G in CSGT methods (on the left side) and N NMR shifts relative to HF/6-31+G (d) GIAO in the presence of B_2H_6 as a reference (on the right side).

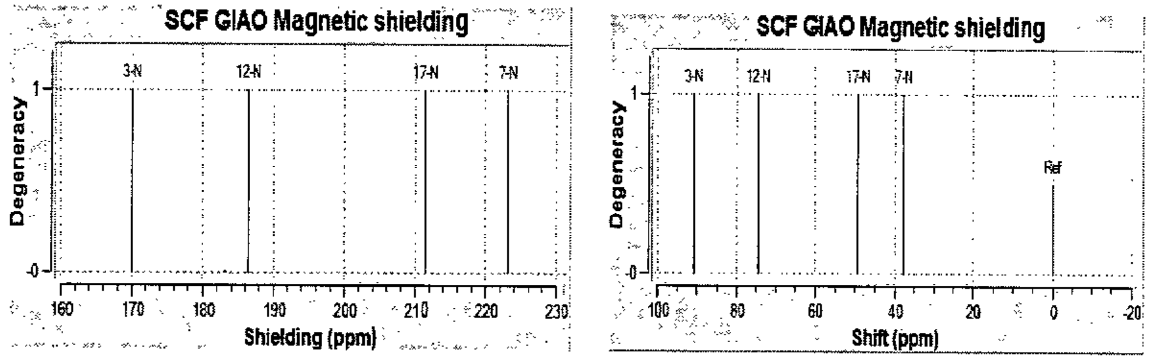

Fig. 9. N NMR shifts relative to B1LYP/6-31G in GIAO methods (on the left side) and N NMR shifts relative to HF/6-31+G (d) GIAO in the presence of B_2H_6 as a reference (on the right side).

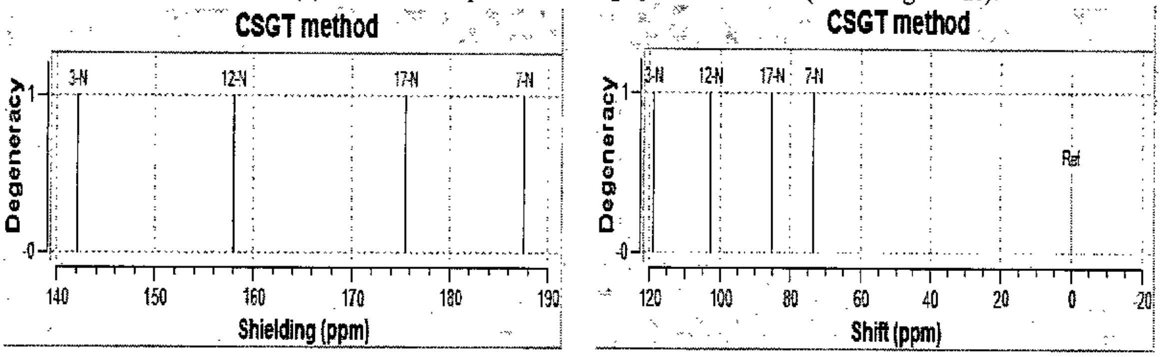

Fig. 10. N NMR shifts relative to B1LYP/6-31G in CSGT methods (on the left side) and N NMR shifts relative to HF/6-31+G (d) GIAO in the presence of B_2H_6 as a reference (on the right side).

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