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Ab initio and DFT study of the thermodynamic properties and nuclear magnetic resonance of (4, 4) armchair AlN nanotubes

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Abstract: Ab initio and DFT calculation were used to study thermodynamic and nuclear magnetic resonance of AlN (4, 4) armchair nanotube. Geometry optimization was done in the level of B3LYP and 6-31G*. For this purpose, the Gaussian 03w program was used as a package of program and after geometry optimization thermodynamic, and NMR parameters including σ isotropic and σ anisotropic tensors and asymmetric parameters which were studied by nuclei with using GIAO method. The obtained outcome was shown for all ^{27}Al and ^{15}N atoms. It suggests that this nanotube can act as nanosensor and could be used as a trace in drug delivery system.

Keywords: *Ab initio*, Electronic structure, DFT, Nuclear magnetic resonance, Thermodynamic.

Introduction

In the past decade, investigation on carbon and non-carbon nanotubes due to their outstanding chemical and physical characteristics has been developed as well as their wide potential applications. When the carbon nanotubes (CNT) was discovered by Iijima in 1991 [1], nanotubes of other chemical compositions has been studied such as AlN [2]. Inorganic nanotubes such as AlN have drawn considerable attention to its unique structures and properties in the last few decades [3]. In a first theoretical research of AlN nanotubes in 2003, Zhang *et al*. have suggested a smooth surface and uniform width as a probable structure for AlN nanotubes [4]. From a practical viewpoint, this interest arises from the potentially enormous adsorptive capacity of the nanotubes, which makes them promising candidates for use in gas storage and sensor applications [5–7]. Tondare *et al*. have successfully synthesized AIN nanotubes (AlNNTs).

Moreover, other research groups [8, 9], and have been proposed as potential hydrogen storage media [10]. They are wide band gap semiconductors, representing excellent dielectric features, high thermal conductivity, and low thermal expansion coefficient [11] and their numerous technological applications in nanoengineering, such as optoelectronic devices in the ultraviolet (UV) and visible regions. Among these nanostructures, aluminum nitride (AlN) with a large band gap presents high-temperature resistance, significant thermal conductivity, low thermal expansion and high endurance towards chemicals and gases, and has been used in semiconductor processing due to its stable dielectric properties [12–15]. AlN nanostructures such as nanotubes, nanowires and nanocage have been concentrated for different studies in recent years [16-18]. The nuclear magnetic resonance (NMR) spectroscopy can be a powerful technique to characterize electronic property and structure of nanotubes [19-20]. Chemical shift in NMR which is represented by Chemical shielding (CS) tensors occur at the sites of half-spin nuclei, e.g. ^{27}Al

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and ^{15}N which has been greatly influenced by electronic density. Therefore, electrostatic properties of non-carbon nanotube could be obtained by calculating chemical shielding tensors. In this work, thermodynamic properties and theoretical calculations of NMR parameters are employed to examine the electronic structure and properties of consisting of (4, 4) AlN nanotube, by using Ab initio and DFT method, to assess these parameters after geometry optimization. These parameters have been calculated by different levels of DFT method and 6-31G* basis set by using Gaussian 03w package of the program.

Results and discussion

Thermodynamic property

Calculation of thermochemical data and total energies of armchair (4, 4) AlN nanotubes, after geometry optimization have been done by using B3LYP method and 6-31G* basis set, to consider the stability of the system at standard temperature (298.15 K) and pressure (1 atm.). Density functional theory is used to calculate geometry optimization and thermodynamic properties. Calculation of enthalpies, Gibbs free energies, entropy and total energies of this system carried out via Hartree-fuck and at the B3LYP, B1LYP, LSDA, BVP86, and B3PW91 levels of DFT theory which have shown in Table **1**.

We have obtained geometries, and computed enthalpies, entropies, and Gibbs free energy. To find the most stable structure at finite pressure and temperature, the Gibbs free energy G should be used. Relative values are reported in Table **1** where each terms are referred to 298.15 K. We analyzed the Gibbs free energy of the formation and found that among these methods, the results have obtained at the B3LYP level are more negative than those of the other calculations with -2990657.18 kcal/mol value, so it represents the best results for $Al_{16}H_{16}N_{16}$ structure which confirmed the structural stability. Also, the same relative trend observed for ΔH and ΔE with- -2990586.71 and -2990587.30 kcal/mol values, respectively. Moreover, according to the frequency calculation at the HF and B3LYP, B1LYP, LSDA, BVP86 and B3PW91 level of theory, we have observed no negative frequency which preferentially enhances the compound stability.

NMR

NMR parameters have given lots information about chemical medium around of nucleus and considered base on two basic parameters involving isotropic chemical shift (CSI) and anisotropic chemical shift. In this study, HF and DFT methods with 6-31G* basis set are used to obtain NMR parameters of AlN (4, 4) nanotube after geometry optimization which are considered by GIAO method. Obtained results which have shown in Table **2** are represented σ isotropic, σ anisotropic and asymmetric parameter for each atom of Al 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 Al atoms including Al25, Al29, Al33, Al35, Al37, Al41, Al43 and Al47 which are bonded to these saturated H atoms, respectively. On the other hand, atoms of 2N, 3N, 5N, 8N, 10 N, 11N, 13 N and 16N and also 27 Al, 28 Al, 31 Al, 32 Al, 39 Al, 40 Al, 45 Al and 46 Al 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, ^{27}Al nuclei are divided into two parts that the nuclei in each category have equivalent electrostatic properties. As have shown in Table **2**, it could be concluded that the AlNNTs 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 178.8 for N atom and 484.69 for Al atom at HF methods and the minimum amount is 89.41 for N atoms and 395.62 for Al atoms at LSDA levels of DFT theory. Investigation of AlN (4, 4) have shown that the maximum value of σ anisotropic among all chosen calculation methods have found for N atom which is 77.61 at LSDA level of theory and is 39.29 for Al atom at HF levels of theory and the minimum amount is 55.64 for N atom at BVP86 and 25.77 for Al atom at LSDA method which can be seen in Table **2** and also maximum value of asymmetric parameter is 0.78 for N atom and is 0.95 for Al atom at LSDA method and the minimum one is 0.78 for N atom at LSDA method and -0.85 for Al atom at HF 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 $Al_{16}H_{16}N_{16}$ system have different electronegativity, therefore, they have different charges. Hence, Al–N

bonds in $Al_{16}H_{16}N_{16}$ structures have ionic characters. The Mulliken population and atomic charge analysis were carried out for the $Al_{16}H_{16}N_{16}$ system, as displayed in Figure **2** which shown a color map of the charge distribution in the $Al_{16}H_{16}N_{16}$ nanotube. The atomic charge analysis of this system was done and presented in figure 3 as a function of atomic number for HF, B3LYP, B1LYP, BVP86 and LSDA levels of theory at 6-31G* basis set. It can be seen that HF method showed the most negative number for N atom and the most positive number for Al atom among all levels of theory. The atomic charge analysis versus σ isotropic was carried out for AlN (4, 4) system, as displayed in Figure 4 for HF, B3LYP, B1LYP, LSDA, BVP86 and B3PW91 levels of DFT theory for each atom of the compound.

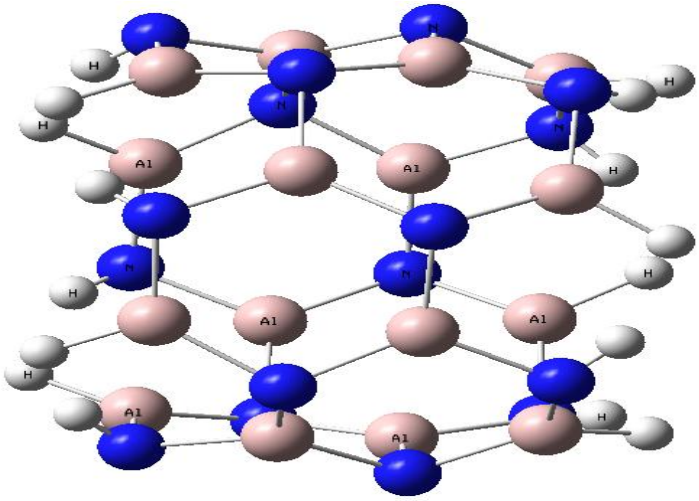

Figure1: The optimized Structures of AlN (4, 4) nanotube.

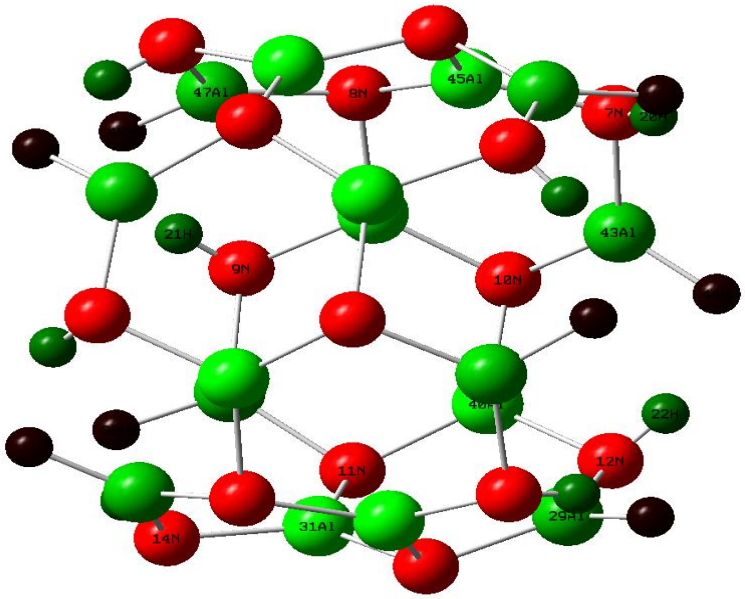

Figure 2: A color map of the charge distribution in the AlN (4, 4) nanotube

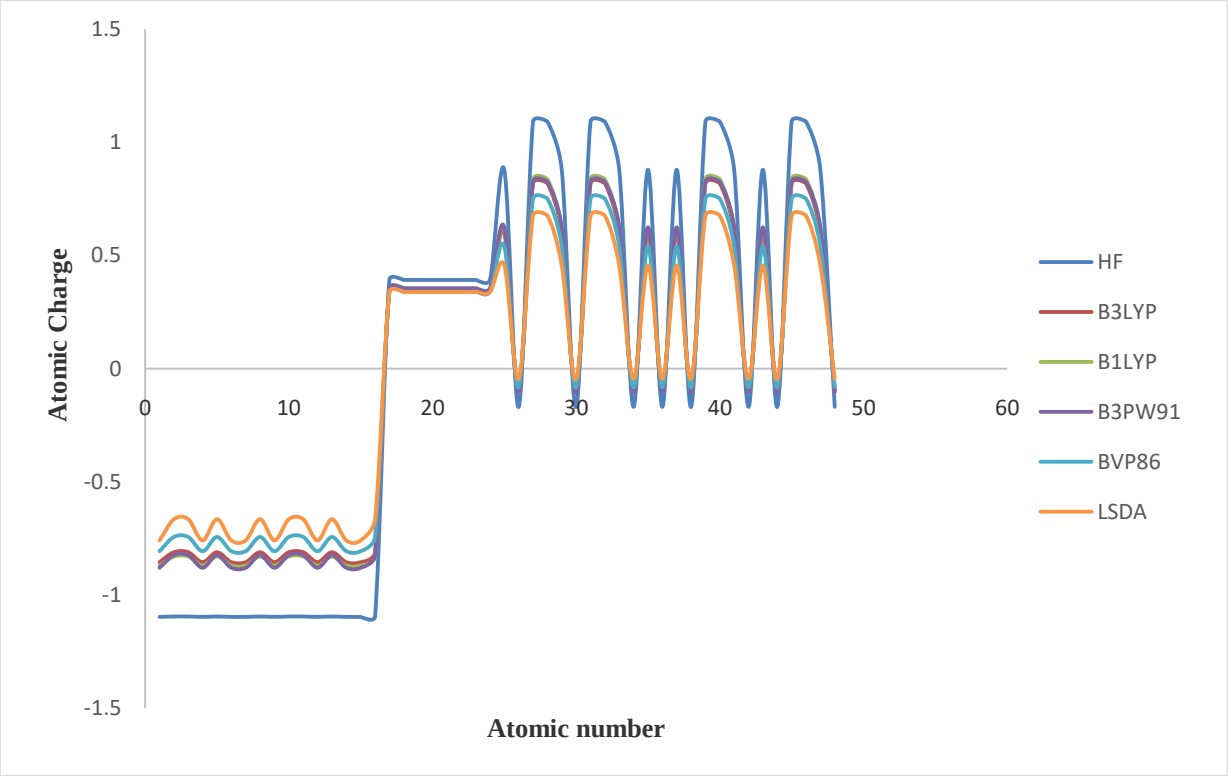

Figure 3. The atomic charge analysis versus atomic number for AlN (4, 4) nanotube.

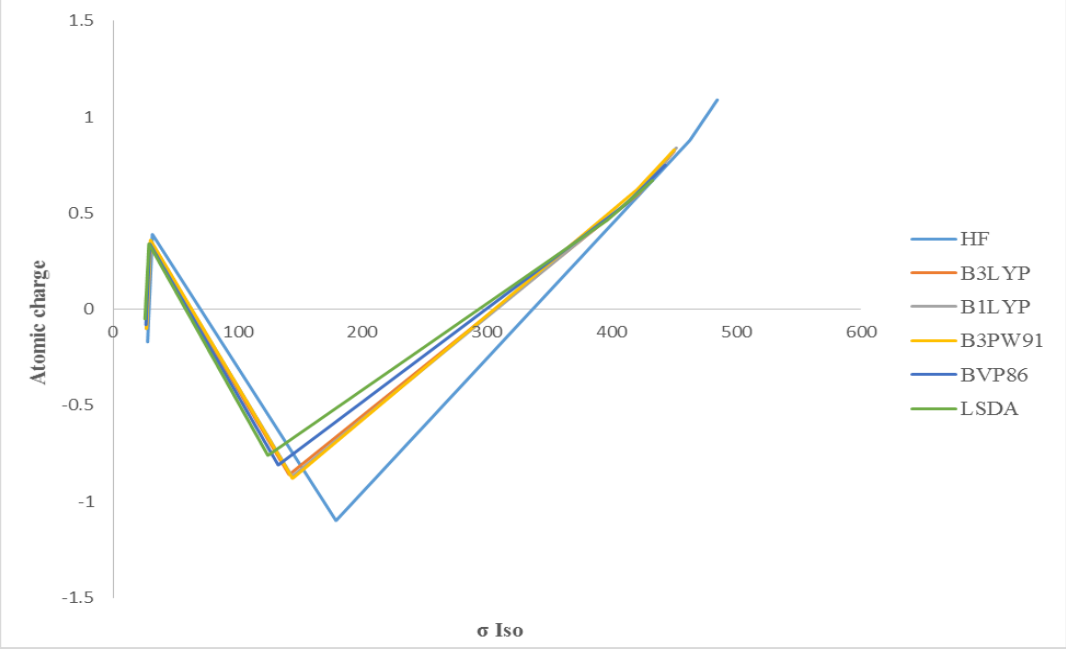

Figure 4. The atomic charge analysis versus σ isotropic for AlN (4, 4) nanotube

Table 1: Relative thermo chemical data (energy ΔE (Kcal/mol), enthalpy Δ H (Kcal/mol) and Gibbs free energy ΔG (Kcal/mol)) and antropy in cal/ (molk) obtained for AlN (4, 4) compound.

Basis set			**6-31G***		
Method	**ΔE**	**ΔH**	**ΔG**	***Zero-point correction***	***S***
HF	-8846.7	-8846.7	-8852.94	-870.35	215.45
B3LYP	0.00	0.00	0.00	0.00	236.38
B1LYP	226.47	-226.47	--223.88	-224.15	245.04
B3PW91	-894.27	-962.51	--964.16	-961.76	230.83
BPV86	-91.98	-91.98	-93.95	-91.41	229.77
LSDA	-11077.84	-11077.84	-11078.78	-11076.58	233.23

Table 2: NMR parameters of AlN (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	178.8	141.28	143.54	144.02	132.55	124.3	61.95	71.19	70.59	70.42	73.71	77.37	-0.08	-0.11	-0.11	-0.1	-0.13	-0.13
2N	150.76	108.93	111.41	111.21	99.68	89.41	76.57	61.03	62.18	65.06	57.05	59.05	0.28	0.6	-1.01	0.51	0.69	0.77
3N	150.76	109.61	112.03	111.89	100.45	90.23	76.57	59.7	60.93	63.93	55.64	57.6	0.28	0.61	0.58	0.52	0.7	0.78
4N	178.8	141.2	143.48	143.87	132.4	124.1	61.95	71.27	70.66	70.64	73.84	77.61	-0.08	-0.11	-0.11	-0.1	-0.13	-0.13
5N	150.76	108.93	111.41	111.21	99.68	89.41	76.57	61.03	62.18	65.06	57.05	59.05	0.28	0.6	0.58	0.51	0.69	0.77
6N	178.8	141.28	143.54	144.02	132.55	124.3	61.95	71.19	70.59	70.42	73.71	77.37	-0.08	-0.11	-0.11	-0.1	-0.13	-0.13
7N	178.8	141.28	143.48	143.87	132.4	124.1	61.95	71.27	70.66	70.64	73.84	77.61	-0.08	-0.11	-0.11	-0.1	-0.13	-0.13
8N	150.76	109.61	112.03	111.89	100.45	90.23	76.57	59.7	60.93	63.93	55.64	57.6	0.28	0.61	0.58	0.52	0.7	0.78
9N	178.8	141.28	143.54	144.02	132.55	124.3	61.95	71.19	70.59	70.42	73.71	77.37	-0.08	-0.11	-0.11	-0.1	-0.13	-0.13
10N	150.76	108.93	111.41	111.21	99.68	89.41	76.57	61.03	62.18	65.06	57.05	59.05	0.28	0.6	0	0.51	0.69	0.77
11N	150.76	109.61	112.03	111.89	100.45	90.23	76.57	59.7	60.93	63.93	55.64	57.6	0.28	0.61	0.58	0.52	0.7	0.78
12N	178.8	141.2	143.48	143.87	132.4	124.1	61.95	71.27	70.66	70.64	73.84	77.61	-0.08	-0.11	-0.11	-0.1	-0.13	-0.13
13N	150.76	108.93	111.41	111.21	99.68	89.41	76.57	61.03	62.18	65.06	57.05	59.05	0.28	0.6	0.58	0.51	0.69	0.77
14N	178.8	141.28	143.54	144.02	132.55	124.3	61.95	71.19	70.59	70.42	73.71	77.37	-0.08	-0.11	-0.11	-0.1	-0.13	-0.13
15N	178.8	141.2	143.48	143.87	132.4	124.1	61.95	71.27	70.66	70.64	73.84	77.61	-0.08	-0.11	-0.11	-0.1	-0.13	-0.13
16N	150.76	109.61	112.03	111.89	100.45	90.23	76.57	59.7	60.93	63.93	55.64	57.6	0.28	0.61	0.58	0.52	0.7	0.78
17H	31.49	30.05	30.18	29.95	29.49	28.74	12.6	8.94	9.14	9.25	8.15	7.86	0.58	0.8	0.78	0.77	0.87	0.9
18H	31.49	30.05	30.17	29.94	29.48	28.73	12.6	8.91	9.12	9.2	8.1	7.8	0.58	0.79	0.78	0.77	0.87	0.9
19H	31.49	30.05	30.18	29.95	29.49	28.74	12.6	8.94	9.14	9.25	8.15	7.86	0.58	0.8	0.78	0.77	0.87	0.9
20H	31.49	30.05	30.17	29.94	29.48	28.73	12.6	8.91	9.12	9.2	8.1	7.8	0.58	0.79	0.78	0.77	0.87	0.9
21H	31.49	30.05	30.18	29.95	29.49	28.74	12.6	8.94	9.14	9.25	8.15	7.86	0.58	0.8	0.78	0.77	0.87	0.9
22H	31.49	30.05	30.17	29.94	29.48	28.73	12.6	8.91	9.12	9.2	8.1	7.8	0.58	0.79	0.78	0.77	0.87	0.9
23H	31.49	30.05	30.18	29.95	29.49	28.74	12.6	8.94	9.14	9.25	8.15	7.86	0.58	0.8	0.78	0.77	0.87	0.9
24H	31.49	30.05	30.17	29.94	29.48	28.73	12.6	8.91	9.12	9.2	8.1	7.8	0.58	0.79	0.78	0.77	0.87	0.9
25Al	462.8	421.43	424.26	419.73	410.04	395.62	29.43	30.74	30.83	29.43	30.35	25.09	-0.85	0.67	0.66	0.61	0.69	0.95

26H	27.66	26.8	26.88	26.65	26.32	25.56	6.88	6.71	6.73	6.71	6.64	6.63	-0.8	-0.84	-0.84	-0.83	-0.83	-0.84
27Al	484.69	449.83	451.86	450.19	443.01	432.88	39.29	37.41	37.37	39.06	38.61	38.15	-0.45	-0.71	-0.69	-0.65	-0.79	-0.83
28Al	484.69	449.83	451.86	450.19	443.01	432.88	39.29	37.41	37.37	39.06	38.61	38.15	-0.45	-0.71	-0.69	-0.65	-0.79	-0.83
29Al	462.8	421.43	424.26	419.73	410.04	395.62	29.43	30.74	30.83	29.43	30.35	25.09	-0.85	0.67	0.66	0.61	0.69	0.95
30 H	27.66	26.8	26.88	26.65	26.32	25.56	6.88	6.71	6.73	6.71	6.64	6.63	-0.8	-0.84	-0.84	-0.83	-0.83	-0.84
31Al	484.69	449.68	451.73	450.07	442.82	432.64	39.29	37.16	37.15	38.83	38.26	37.72	-0.45	-0.69	-0.68	-0.64	-0.76	-0.8
32Al	484.69	449.68	451.73	450.07	442.82	432.64	39.29	37.16	37.15	38.83	38.26	37.72	-0.45	-0.69	-0.68	-0.64	-0.76	-0.8
33Al	462.8	421.63	424.44	419.9	410.27	395.81	29.43	31.15	31.17	29.87	30.94	25.77	-0.85	0.66	0.65	0.59	0.67	0.93
34H	27.66	26.79	26.88	26.65	26.31	25.54	6.88	6.73	6.74	6.73	6.66	6.65	-0.8	-0.84	-0.84	-0.83	-0.84	-0.850
35Al	462.8	421.63	424.44	419.9	410.27	395.81	29.43	31.15	31.17	29.87	30.94	25.77	-0.85	0.66	0.65	0.59	0.67	0.93
36H	27.66	26.79	26.88	26.65	26.31	25.54	6.88	6.73	6.74	6.73	6.66	6.65	-0.8	-0.84	-0.84	-0.83	-0.84	-0.85
37Al	462.8	421.63	424.44	419.9	410.27	395.81	29.43	31.15	31.17	29.87	30.94	25.77	-0.85	0.66	0.65	0.59	0.67	0.93
38H	27.66	26.79	26.88	26.65	26.31	25.54	6.88	6.73	6.74	6.73	6.66	6.65	-0.8	-0.84	-0.84	-0.83	-0.84	-0.85
39Al	484.69	449.68	451.73	450.07	442.82	432.64	39.29	37.16	37.15	38.83	38.26	37.72	-0.45	-0.69	-0.68	-0.64	-0.76	-0.8
40Al	484.69	449.83	451.86	450.19	443.01	432.88	39.29	37.41	37.37	39.06	38.61	38.15	-0.45	-0.71	-0.69	-0.65	-0.79	-0.83
41Al	462.8	421.43	424.26	419.73	410.04	395.62	29.43	30.74	30.83	29.43	30.35	25.09	-0.85	0.67	0.66	0.61	0.69	0.95
42H	27.66	26.8	26.88	26.65	26.32	25.56	6.88	6.71	6.73	6.71	6.64	6.63	-0.8	-0.84	-0.84	-0.83	-0.83	-0.84
43Al	462.8	421.43	424.26	419.73	410.04	395.62	29.43	30.74	30.83	29.43	30.35	25.09	-0.85	0.67	0.66	0.61	0.69	0.95
44H	27.66	26.8	26.88	26.65	26.32	25.56	6.88	6.71	6.73	6.71	6.64	6.63	-0.8	-0.84	-0.84	-0.83	-0.83	-0.84
45Al	484.69	449.83	451.86	450.19	443.01	432.88	39.29	37.41	37.37	39.06	38.61	38.15	-0.45	-0.71	-0.69	-0.65	-0.79	-0.83
46Al	484.69	449.68	451.73	450.07	442.82	432.64	39.29	37.16	37.15	38.83	38.26	37.72	-0.45	-0.69	-0.68	-0.64	-0.76	-0.8
47Al	462.8	421.63	424.44	419.9	410.27	395.81	29.43	31.15	31.17	29.87	30.94	25.77	-0.85	0.66	0.65	0.59	0.67	0.93
48H	27.66	26.79	26.88	26.65	26.31	25.54	6.88	6.73	6.74	6.73	6.66	6.65	-0.8	-0.84	-0.84	-0.83	-0.84	-0.85

Conclusion

The thermodynamic, stability and electronic structure of AlN (4, 4) explored by Hartee-Fock and DFT calculations after geometry optimization which has been reported. The NMR results indicate that nuclei of Al and N atoms are divided into two categories, and each of them has similar electronic property. AlN (4, 4) might be a good candidate as a nanosensor for adsorbing or detection of different gases, in drug delivery process by attaching different molecules on the external surface of AlN (4,4), semiconductor and also acting as a trace. We believe that the present results will provide helpful guidance to develop efficient nanoscale sensors for detection of gas molecules.

Calculation method

Armchair (4,4) Aluminum nitride nanotube with tube length of 5nm and with 16Al atoms and 16N atoms and 16H atoms (Fig. 1) which were examined by utilizing Hartree-Fock calculations and density functional theory (DFT) in level of B3LYP, B1LYP, LSDA, B3P86 and B3PW91 with 6-31G* basis set. Both ends of these systems are terminated with hydrogen atoms. For this purpose, the Gaussian 03w program of the package was used [21], and after final optimization, were studied structural and NMR parameters. Thermodynamic analysis and total energies at all levels of the theory 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 (AlNNTs) usage as nanosensors.

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