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Full Length Research Paper

NMR shielding tensors and thermodynamic investigation of $B_{10}N_{11}$ nanocone structures

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Density functional theory (DFT) and HF are carried out at B3LYP/3-21G/6-31G/6-31G*/6-311G* level of theory to investigate the stability and ground state of $B_{10}N_{11}$ nanocone. In present work, NMR shielding parameters were calculated based on each atom to study the active sites in this system. In thermochemistry part of study, it was found that the best molecular orbital description for this molecule is 6-311G* level of theory.

Key words: Nanocone, NMR shielding tensors, density functional theory (DFT).

INTRODUCTION

Since the discovery of C60, there are many researches on higher fullerenes (Kroto et al., 1985), carbon nanotubes (Iijima, 1991), and other nanostructures such as BN nanotubes (Chopra et al., 1995). Curved nanoscale structures of which the best known examples are carbon fullerenes and nanotubes, have been concentrated in many technological and scientific interests, due to their unique electronic and mechanical properties (Kroto et al., 1985; Iijima, 1991).

One of the important groups of nanocones is Boron nitride nanocones. Although these structures have been known since 1994, Rubio et al. (1994) observation recently has been experimented (Bourgeois et al., 2000; Sachdeva et al., 2010).A complete analogy between C and BN structures is not possible, since, for instance, a pentagonal ring made by B and N atoms will introduce at least one homonuclear bond (Machado et al., 2003). Then, in general, the situation, concerning electronic and structural properties, is less focused for BN than for C cones (Machado et al., 2003). Boron nitride nanocones are made of B and N atoms, it can be seen that there is a negative charge at nitrogen atom and a positive charge at boron atom. In addition this negative and positive charges and unique properties such as reactivity and polarity show that we can apply an electrophilic or nucleophilic reagent as a solution for these structures (Iijima et al., 1992). Taking into account the chemical and mechanical stability of nanocones and little tip degradation, BN nanocones can be applied as good candidates for field emitters (Machado et al., 2003). The properties of BN and carbon nanocones are very fascinating than other nano structures (Nirmala and Kolandaivel, 2007).

Recently, scientists have focused more on these novel researches (Iijima et al., 1992) because these structures can open a vast field of nanoscience both theoretical and experimental. Theoretical investigations on $(BN)_n$ nanocones have been performed in vast field which shows that they are better candidates than carbon nanotubes when there is not any experimental results (Kroto et al., 1985; Bourgeois et al., 2000).Most of the researches about carbon structures have been done with these nanocones (Charlier and Rignanese, 2001). A comparison between boron nitride nanocones and carbon nanotubes has led to the understanding that these novel structures have more interesting characteristics than the carbon nanotubes (Nirmala and Kolandaivel, 2007; Oku et al., 2003). In the present study, we address the relative stability and NMR parameters of $B_{10}N_{11}$ nanocone in different methods and basis sets.

COMPUTATIONAL DETAILS

The Gaussian 98 program was run to obtain the best prediction of this particular structure (Monajjemi et al., 2008a) in the electronic grand state. This program was applied to study many specific properties of $B_{10}N_{11}$ such as thermodynamic properties, atomic charges, multipole moment and NMR shielding in gas phase

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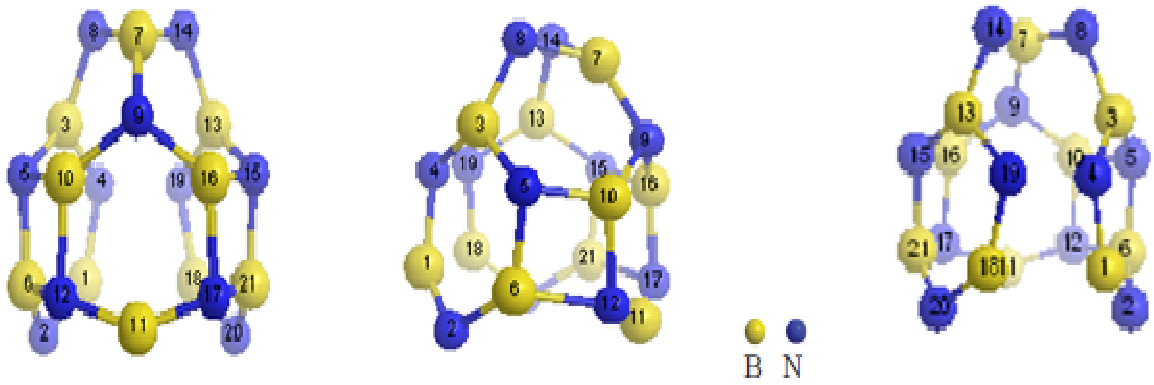

Figure 1. BN nanocone in three lateral views, rotated by 90º one from another.

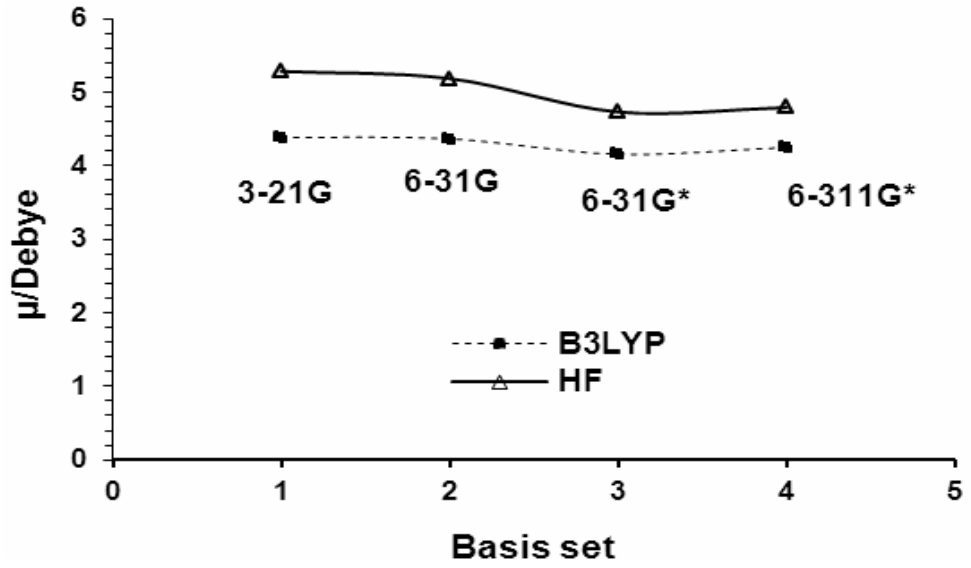

Figure 2. Calculated dipole moment μ (Debye) versus methods and basis sets.

(Monajjemi et al., 2010a). The adopted tools of full survey of the geometric structure optimization and computing properties of $B_{10}N_{11}$ nanocone are the hartree fock and density-functional theory (Hohenberg and Kohn, 1964; Kohn and Sham, 1965; Slater, 1964; Pople et al., 1992; Monajjemi et al., 2010b; Monajjemi et al., 2008b) .Primary basis sets describe the atomic orbitals and also shows the best description of the electronic structures. B3LYP (Becke, 1993, 1992, 1992) and HF methods with split valence basis sets (3-21G, 6-31G) and polarized basis sets (6-31G*, 6-311G*) were used in this study. Frequency analyses were carried out at the same theoretical level to show that the optimized structures are true minima and wave function is ground state, without imaginary frequencies (Monajjemi et al., 2010c, 2011a).

The chemical shielding shows the phenomenon which is dependent on the secondary magnetic field which is built by the induced movements of the electrons that encompass the nuclei (De Dios et al., 1999). The structure of molecules widely revolutionizes NMR spectroscopy, thus, NMR parameters can be calculated to predict the active sites of molecules (Hohenberg and Kohn, 1964; Czernek et al., 2000; Monajjemi et al., 2011, 2007, 2008c, 2010). All of the NMR shielding tensors are calculated in the basis of gauge-including atomic orbital (GAIO) method.

RESULTS AND DISCUSSION

We selected a particular nanocone as $B_{10}N_{11}$ in this study. All calculations were performed to study the relative stability of boron nitride nanocone $B_{10}N_{11}$ especially thermodynamic properties in different methods and basis sets. Our *ab initio* methodology is based on HF and B3LYP in different basis sets such as 3-21G, 6-31G, 6-31G* and 6-311G*. The geometry optimization for $B_{10}N_{11}$ nanocone has been carried out to clarify ground state structure. The results are summarized in four tables and five figures as follow. The optimization structure is shown in Figure 1. Figure 2 shows the relation between

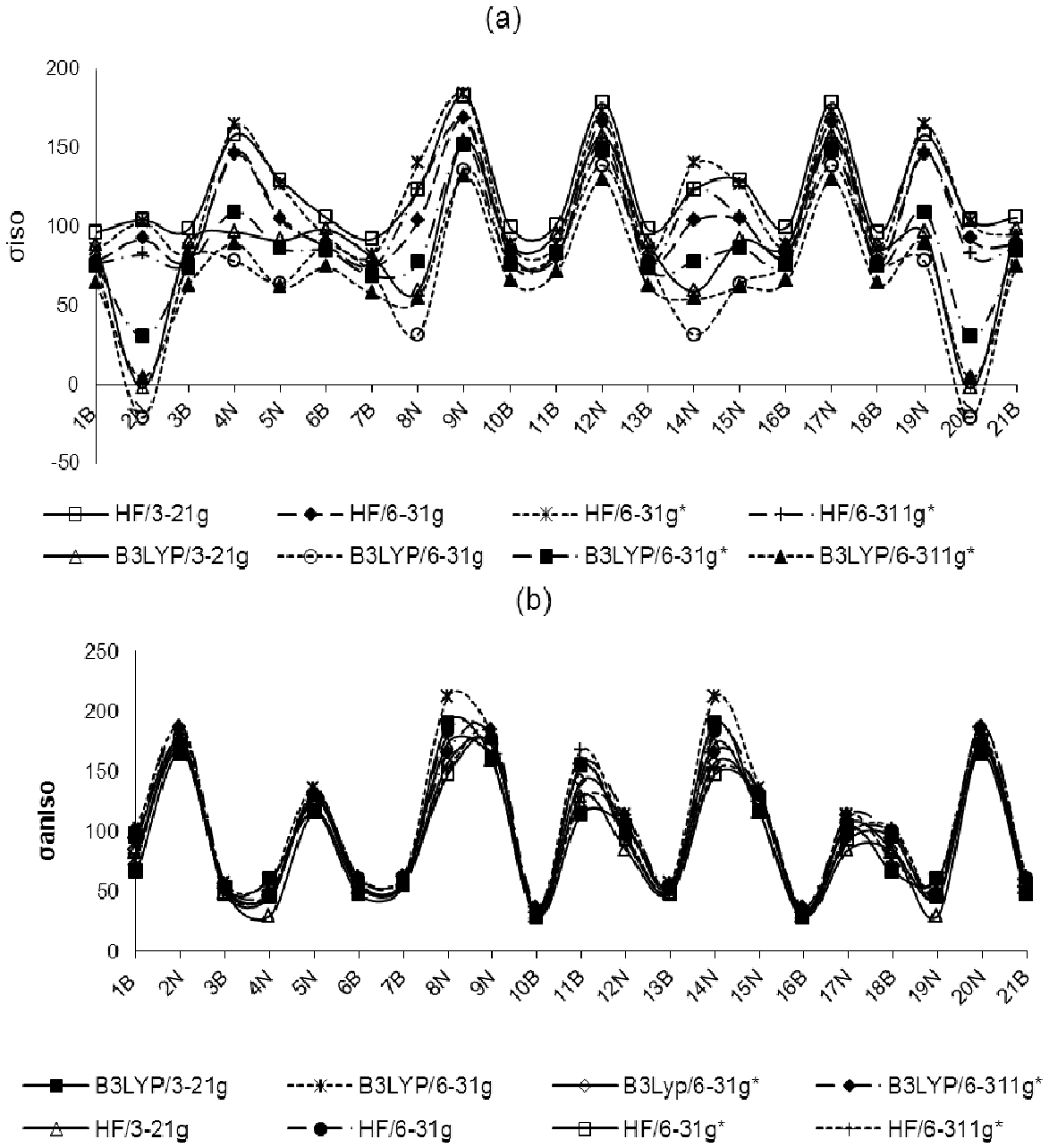

Figure 3. NMR parameters calculated (in different methods and basis sets) of $B_{10}N_{11}$ for (a) σiso, (b) σaniso.

dipole moment and basis sets and also Figures 3, 4 and 5 indicates NMR parameters and Mulliken charges per atom of this structure and thermodynamic parameters in different methods and basis sets, respectively. Thermodynamic parameters, which were computed in different methods and basis sets, were containing internal energy (E) , enthalpy (H), Gibbs free energy (G),entropy (S) and E[SCF(Done)]. These results are shown in Table 1. In Table 2, the values of dipole moments (Debye) in the same methods and basis sets are given. NMR parameters were summarized with concentration on active sites, and the results are given in Table 3. In Table 4, average Mulliken charge values per atom for $B_{10}N_{11}$ in different methods and basis sets are reported.

Conclusion

In this present study, we have applied a structure of substitutional atoms in carbon structures with disclination,

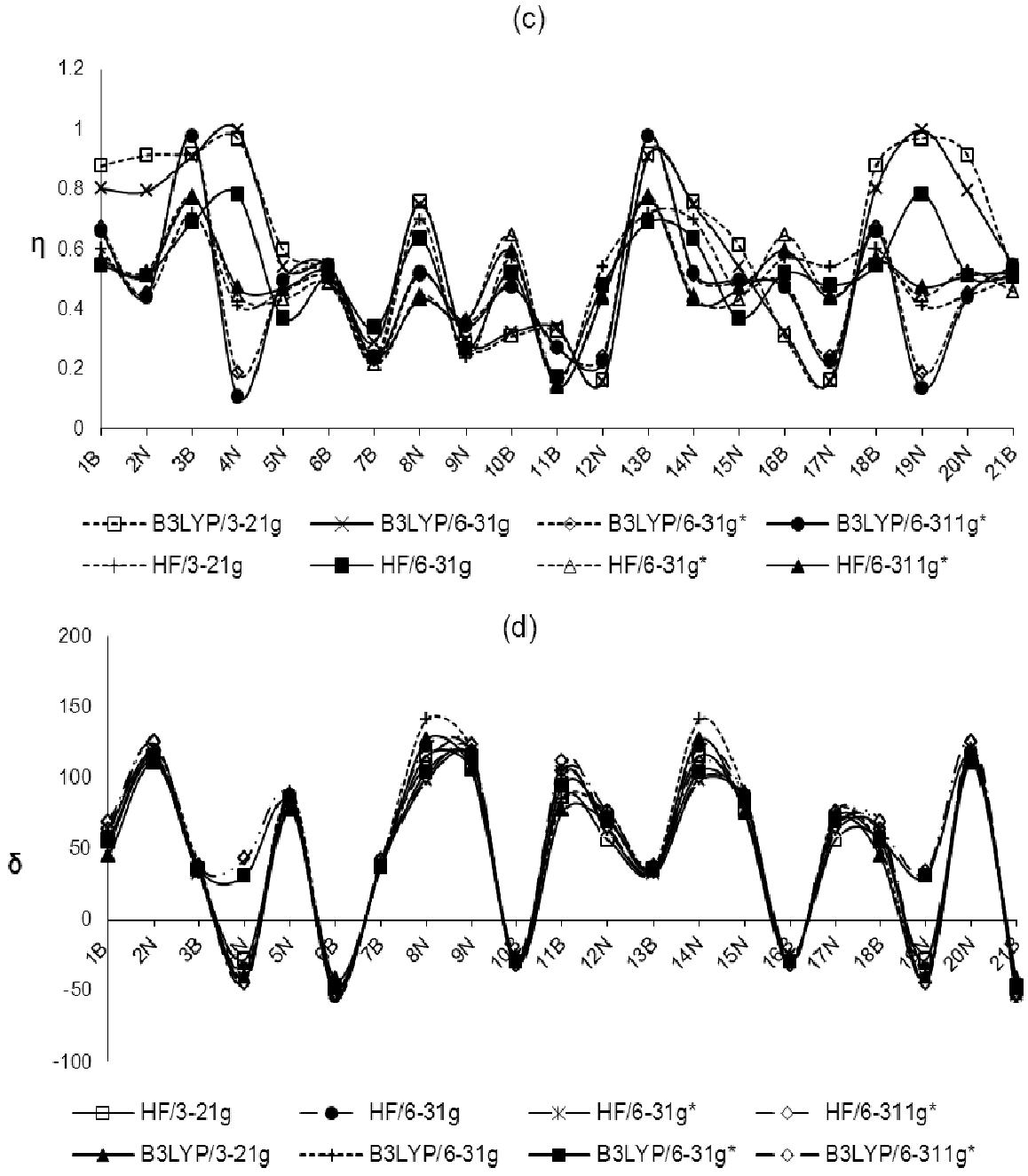

Figure 3. NMR parameters calculated (in different methods and basis sets) of B10N11 for (c)η(d)δ.

called nanocones. This structure, used in this work, was $B_{10}N_{11}$ nanocone. In summary, an analysis of DFT and HF calculations at the level of B3LYP/3-21G/6-31G/6-31G*/6-311G*and HF/3-21G/6-31G/6-31G*/6-311G* on this particular structure have been performed. Furthermore we have calculated the stability of this nanocone and the computed energy shown the high stability of this system without distortion in different methods and basis sets. The most stability of this nanoscale cone was investigated in B3LYP/6-311G*. A good agreement was observed between Mulliken charges and NMR parameters. On the other hand, to show the location of active sites, NMR parameters and Mulliken charges can be applied. Finally, our results confirm the role of $B_{10}N_{11}$ nanocone as a good candidate in biological systems and drug delivery than the other nanostructures.

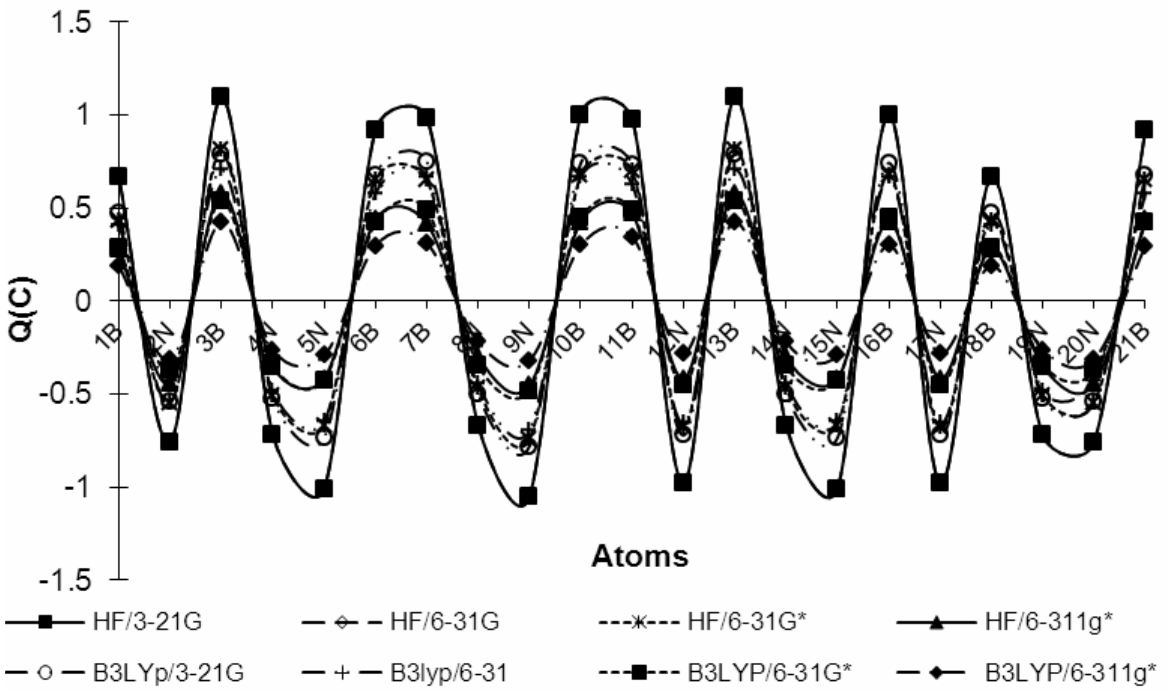

Figure 4. Average Mulliken charge values for per atom of $B_{10}N_{11}$ in different methods and basis sets.

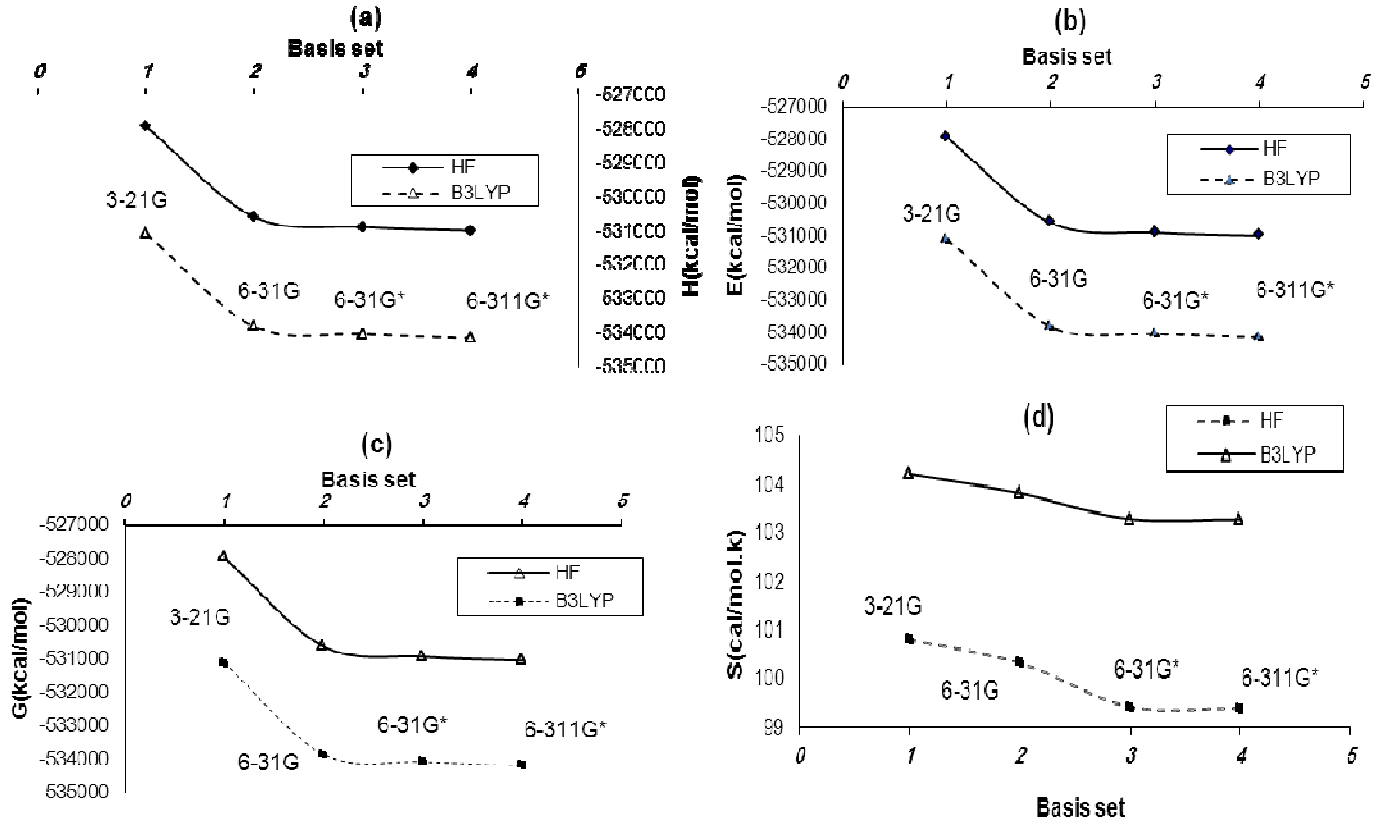

Figure 5. The values of thermodynamic parameters of $B_{10}N_{11}$nanocone (in different methods and basis sets) (a) Enthalpy, (b) Internal energy, (c) Gibbs free energy, (d) Entropy.

Table 1. Computed energetic data, enthalpy H (kcal/mol), internal energy E (kcal/mol), Gibbs free energy G (kcal/mol) and entropy for $B_{10}N_{11}$.

Methods	Basis set	-E(kcal/mol)	-G(kcal/mol)	-H(kcal/mol)	S(cal/mol.k)	-E[SCF(Done)]
HF	3-21G	527931	527960	527930	100.8	527931
	6-31G	530593	530622	530592	100.32	530593
	6-31G*	530897	530926	530896	99.413	530974
	6-311G*	530999	531028	530999	99.385	531076
B3LYP	3-21G	531082	531113	531082	104.22	531153
	6-31G	533821	533852	533821	103.81	533892
	6-31G*	534038	534069	534038	103.28	534110
	6-311G*	534153	534183	534152	103.27	534225

Table 2. Calculated dipole moment μ (Debye) versus methods and basis sets for $B_{10}N_{11}$.

Method		Basis set			
		3-21G	6-31G	6-31G*	6-311G*
HF	μ (Debye)	5.2819	5.1844	4.7309	4.7906
B3LYP		4.3860	4.3652	4.1569	4.2491

Table 3. Computed NMR parameters for $B_{10}N_{11}$ in different methods and basis sets.

Method		HF										
		B3LYP										
Atoms		2N	4N	6B	9N	11B	12N	15N	17N	18B	19N	20N
	3-21g	104.62	158.3905	*105.96*	183.2758	101.18	178.5	129.72	178.51	96.6258	158.38	104.615
σiso		-2.238	96.3587	98.355	154.1968	95.437	157.41	91.312	157.41	88.1406	*96.358*	-2.24
		168.08	29.6173	52.612	158.849	129.67	84.758	115.74	84.757	82.9801	29.596	168.0773
σaniso		164.96	60.2289	47.477	159.8339	114.39	*103.56*	*115.76*	103.56	66.643	60.231	164.9617
		168.08	-41.9937	-70.11	158.849	129.67	84.758	115.74	84.757	82.9801	-41.97	168.0773
Δσ		164.96	-61.1677	-62.43	159.8189	114.39	103.56	113.76	103.56	66.643	-61.17	164.9616
		0.446	0.4105616	0.5009	0.236826	0.1536	0.5423	0.4597	0.5424	0.5997361	0.4103	0.4459824
η		0.9137	0.9693049	0.5209	0.282194	0.3283	0.1621	0.6134	0.1621	0.8773743	0.9693	0.9137554
		112.05	-27.9958	-46.74	105.8993	86.45	56.505	77.158	56.505	55.32	-27.98	112.0515
δ		109.97	-40.7785	-41.62	106.556	76.262	69.039	75.17	69.039	44.4287	-40.78	109.9744
	6-31g	92.035	145.6934	88.207	168.4834	80.5	165.65	104.55	165.66	78.0459	145.69	92.0344
σiso		-20.69	78.3361	88.269	136.3965	83.361	139.1	64.294	139.1	77.4832	78.335	-20.7015
		173.99	46.9912	60.275	176.8854	155.51	96.371	130.1	96.372	99.5756	46.989	173.9868
σaniso		179.03	59.4266	54.563	179.6602	126.75	113.24	135.59	113.24	76.455	59.428	179.0306
		173.99	-52.6948	-79.99	176.8854	155.51	96.371	130.1	96.372	99.4728	-52.68	173.9869
Δσ		179.03	-59.52595	-70.56	179.6601	126.75	113.24	135.59	113.24	76.455	-59.53	179.0306
		0.5132	0.7835206	0.5071	0.266489	0.1739	0.4784	0.3681	0.4785	0.5441637	0.7838	0.5131488
η		0.793	0.9966636	0.5465	0.29533	0.3381	0.157	0.5396	0.157	0.80211	0.9966	0.7930772
		115.99	-35.1299	-53.33	117.9227	103.67	64.247	86.735	64.248	66.3837	-35.12	115.9913
δ		119.35	-39.6839	-47.04	119.7734	84.502	75.491	90.393	75.491	50.97	-39.69	119.3537

Table 3. contd.

		102.87	164.1998	94.086	183.491	88.416	172.08	126.17	172.08	85.1665	165.2	102.8714
Σiso		30.644	109.5776	84.821	152.0903	83.155	148.16	86.679	148.16	75.5576	109.58	30.6423
		174.73	45.1429	56.61	170.839	155.15	93.091	127.8	93.091	95.2791	45.136	174.7254
σaniso		172.2	46.2034	54.295	171.0078	141.84	106.69	125.58	106.69	85.0405	46.202	172.1955
	6-31g*	174.73	-62.44345	-76.21	170.8389	155.15	93.091	127.8	93.091	95.2792	-62.44	174.7254
Δσ		172.2	46.20345	-71.54	171.0079	141.84	106.69	125.58	106.69	85.04055	46.202	172.1956
		0.5263	0.4458791	0.4856	0.358038	0.1477	0.4452	0.4311	0.4452	0.5636946	0.4458	0.5262148
η		0.4522	0.1860413	0.5179	0.356298	0.2676	0.2428	0.4873	0.2428	0.6739708	0.186	0.4522252
		116.48	-41.629	-50.81	113.8927	103.44	62.06	85.198	62.061	63.5195	-41.62	116.4836
δ		114.8	30.8023	-47.69	114.0053	94.562	71.126	83.719	71.127	56.6937	30.801	114.797
		82.316	147.8946	86.982	167.4394	79.595	155.28	106.29	155.28	76.9387	147.9	82.3146
σiso		4.3795	89.3302	74.282	132.368	71.366	129.17	61.601	129.17	63.6642	89.329	4.3778
		186.64	49.7418	62.076	178.0013	167.6	97.352	129.76	97.353	103.3537	49.733	186.6411
σaniso		186.97	50.1931	60.95	184.6001	156.26	114.01	132.27	114.01	94.831	50.19	186.9744
	6-311g*	186.64	-67.56005	-81.68	178.0013	167.6	97.352	129.76	97.353	103.3537	-67.55	186.6411
Δσ		186.97	50.1932	-78.91	184.6002	156.26	114.01	132.27	114.01	94.831	50.19	186.9744
		0.5113	0.47252	0.52	0.363672	0.1422	0.4373	0.4677	0.4373	0.5629368	0.4724	0.5112781
η		0.4411	0.1064903	0.5449	0.342492	0.2723	0.2246	0.4971	0.2246	0.6586419	0.1351	0.4411358
		124.43	-45.04	-54.45	118.6675	111.73	64.902	86.504	64.909	68.9024	-45.03	124.4274
δ		124.65	42.4621	-52.6	123.0668	104.17	76.007	88.177	76.008	63.2207	33.46	124.6496

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