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Theoretical Studies on Stabilities of $C_{26}BN$ Isomers

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Abstract: The possible stable structures of substituted fullerene $C_{26}BN$ formed on the initial C_{28} cage with T_d symmetry have been systematically studied on UHF/3-21g level with constrained symmetry(C_s or C_1), the charge and multiplicity of all the isomers are zero and five, respectively. The geometry optimization and the vibrational frequencies analysis were performed on the same level with constrained symmetry(C_s or C_1). The results show that the most stable isomer of $C_{26}BN$ is formed by boron and nitrogen atoms doping at 5,2-sites.

Keywords: $C_{26}BN$ isomers, *ab initio*, stability.

Heterofullerenes which have one or more carbon atoms substituted by other elements such as boron and nitrogen are expected to be used as semiconductors and building materials for nanometer electronics due to their potential novel properties[1-3], such as superconductivity, hardness, photoinduced electron transfer and nonlinear optics. The first heterofullerenes of $C_{60-x}B_x$(x=1-6) were prepared by Smalley[4] and co-worker in 1991. Latter $C_{59}N$ was verified from experiment by Mattay[5] *et al*. in 1995, $(C_{59}N)_2$ and $(C_{69}N)_2$ were produced and isolated by Nuber[6] *et al*. in 1996. Recently, the structures and electronic spectrum of $C_{59}N$, $C_{69}N$ and their dimer $(C_{59}N)_2$, $(C_{69}N)_2$ have been studied on theoretical level by Ren[7] *et al*..

Considering BN and CC are isoelectronic species, substituted fullerene by B and N may be stable. In fact, BN substituted $C_{60-n}(BN)_n$ have already been reported by Piechota[8] early in 1996. The theoretical studies of $C_{34}BN$ and $C_{58}BN$ have been reported[9-10]. However, about $C_{26}BN$ we do not know very much.

Computational Methods

Ab initio calculations have been performed using Gaussian 98w package on P4 computer.

The geometries and the frequencies of the forty isomers of $C_{26}BN$ have been optimized at the UHF/3-21g level, the charge and the multiplicity of the forty isomers of $C_{26}BN$ are zero and five, respectively. Symmetry (C_s or C_1) of all the isomers was constrained during the optimizing process.

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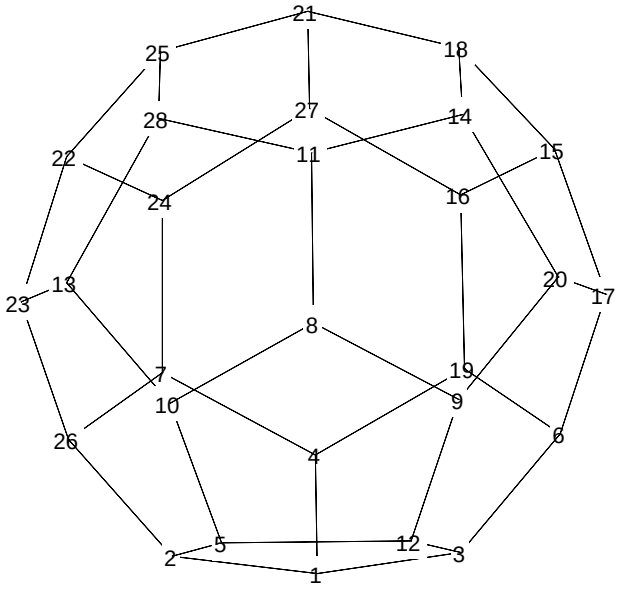
Figure 1 The structure and numbering of C_{28} with T_d symmetry



Results and Discussion

The geometry configuration of C_{28} with T_d symmetry[11] was shown in **Figure 1**. For the convenience of discussion, all the carbon atoms of C_{28} cage were numbered. Different $C_{26}BN$ isomers were marked as $C_{26}BN$: boron and nitrogen atoms substituted carbon atoms were labeled by *i* and *j*, respectively. Forty $C_{26}BN$ isomers with different energies were obtained. The symmetry and total energies at UHF/3-21g level, relative energies of all the isomers were listed in **Table 1**, and some structural parameters of $C_{28}(T_d)$ and two most stable $C_{26}BN$ isomers are listed in **Table 2**. The vibrational analysis indicated that all the isomers have no imaginative frequencies.

The mulliken charges of three kinds of carbon atoms C1, C2 and C5 of $C_{28}(T_d)$ cage are 0.004803, -0.003011 and 0.001411, which are different from $C_{36}(D_{6h}$ and $D_{3h})$ and $C_{60}(I_h)$. As far as $C_{26}BN$ isomers are concerned, the deformations brought by heteroatoms of $C_{26}BN$ isomers are different, depending on the substituted position of heteroatoms, the deformation of $C_{26}BN$ isomers with bonded heteroatoms is small, whereas the deformation of $C_{26}BN$ isomers with isolated heteroatoms is large. The $C_{26}BN$: 5-2 isomer has very similar structure to $C_{28}(T_d)$ and is the most stable one. The difference of boron and nitrogen atomic charge is affected by the distance of boron and nitrogen atoms, when boron and nitrogen are bonded or near, σ-bond inductive effect makes electron transfers from boron to nitrogen atom; on the other hand, when B and N are bonded, conjugate effect makes electron transfers from nitrogen to boron atom, due to the electron pair of nitrogen atom and the empty orbit of boron atom. It can be concluded that the stabilities of the $C_{26}BN$ isomers are affected by both inductive and conjugate effect, since the bonded boron and nitrogen atoms come up to one

carbon-carbon bond to a great extent. When nitrogen and boron atom substitute C2 and C5 atom, nitrogen atom can provide electron both to boron and C1 atom to form remarkable conjugate effect, and to keep the analogous structure of $C_{28}(T_d)$, especially to retain the similar structure of the three linked five-membered rings of $C_{28}(T_d)$ well; whereas, boron atom of another isomer $C_{26}BN$: 2-5 cannot provide electron to C1 atom to conjugate with it although nitrogen can provide electron to boron atom. From this point of view, the difference of energies between another pair of $C_{26}BN$: 1-2 and $C_{26}BN$: 2-1 isomers can also be explained. Due to lack of B-N σ-bond inductive and conjugate effect, the $C_{26}BN$ isomers with unbonded heteroatoms have much higher energies than the most stable one.

Table 1 The result energy for $C_{26}BN$ isomers at UHF/3-21g level

Isomers	Sym.	Total energies (/hartree)	Relative energy (kJ/mol)	Isomers	Sym.	Total energies (/hartree)	Relative energy (kJ/mol)
$C_{26}BN$: 1-2	C_s	-1057.2496	84.80	$C_{26}BN$: 11-2	C_1	-1057.1778	273.3
$C_{26}BN$: 1-5	C_1	-1057.1972	222.4	$C_{26}BN$: 13-2	C_s	-1057.2295	137.6
$C_{26}BN$: 2-5	C_1	-1057.2740	20.74	$C_{26}BN$: 14-2	C_1	-1057.1684	298.0
$C_{26}BN$: 2-6	C_1	-1057.2207	160.7	$C_{26}BN$: 14-3	C_s	-1057.2268	144.7
$C_{26}BN$: 2-7	C_1	-1057.2088	191.9	$C_{26}BN$: 8-4	C_s	-1057.1556	331.6
$C_{26}BN$: 2-1	C_s	-1057.2584	61.70	$C_{26}BN$: 9-4	C_1	-1057.1671	301.4
$C_{26}BN$: 5-1	C_1	-1057.2104	187.7	$C_{26}BN$: 11-4	C_s	-1057.1591	322.4
$C_{26}BN$: 2-3	C_1	-1057.1919	236.3	$C_{26}BN$: 13-4	C_1	-1057.2258	147.3
$C_{26}BN$: 5-2	C_1	-1057.2819	0	$C_{26}BN$: 10-6	C_1	-1057.2099	189.0
$C_{26}BN$: 6-2	C_1	-1057.1853	253.6	$C_{26}BN$: 12-5	C_s	-1057.2445	98.19
$C_{26}BN$: 7-2	C_1	-1057.2262	146.2	$C_{26}BN$: 13-5	C_1	-1057.2239	152.3
$C_{26}BN$: 5-6	C_1	-1057.1856	252.8	$C_{26}BN$: 14-5	C_1	-1057.1787	271.0
$C_{26}BN$: 8-1	C_s	-1057.1665	303.0	$C_{26}BN$: 8-6	C_s	-1057.1701	293.5
$C_{26}BN$: 10-1	C_1	-1057.2143	177.5	$C_{26}BN$: 9-6	C_s	-1057.2206	160.9
$C_{26}BN$: 11-1	C_s	-1057.2124	182.5	$C_{26}BN$: 13-6	C_1	-1057.1691	296.2
$C_{26}BN$: 13-1	C_s	-1057.1805	266.2	$C_{26}BN$: 14-6	C_1	-1057.1879	246.8
$C_{26}BN$: 14-1	C_s	-1057.1689	296.7	$C_{26}BN$: 8-7	C_s	-1057.1573	327.1
$C_{26}BN$: 8-2	C_1	-1057.1988	218.2	$C_{26}BN$: 9-7	C_1	-1057.2096	189.8
$C_{26}BN$: 9-2	C_1	-1057.1994	216.6	$C_{26}BN$: 10-7	C_s	-1057.1711	290.9
$C_{26}BN$: 10-2	C_1	-1057.2242	151.5	$C_{26}BN$: 13-7	C_1	-1057.1856	252.8

Table 2 Some structural parameters for $C_{28}(T_d)$ and two most stable $C_{26}BN$ isomers

Parameters	$C_{28}(T_d)$	$C_{26}BN$: 5-2	$C_{26}BN$: 2-5
R(1,2)/nm	0.14586	0.14703	0.15606
R(2,5)/nm	0.14337	0.14430	0.14413
R(5,12)/nm	0.15786	0.15891	0.15042
R(2,26)/nm	0.14337	0.14567	0.15545
D(1,2,3,4)/degree	35.414	35.402	38.194

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