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$B_{28}N_{28}$ 笼的稳定性及笼中四元环间键联类型对笼稳定性的影响

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摘要 采用密度泛函方法对四、六元环组成的所有可能的 23 个笼状 $B_{28}N_{28}$ 结构进行了理论计算和拓扑学特性研究, 用三个指标 $N_{4x}(x=0, 1, 2)$ 来描述相邻四元环间的键联类型, 结果发现 $B_{28}N_{28}$ 笼的相对能量随 N_{4x} 值的增大而增大, 且 N_{404} 对稳定性的影响起主导作用. 这一简单的拓扑学标准可以给出所有四六结构 $B_{28}N_{28}$ 异构体的大致能量顺序, 并从 ISR 结构中挑选出能量较低的结构, 因此有望用于挑选大尺寸氮化硼团簇的热力学稳定结构.

关键词: 氮化硼, 稳定性, 拓扑学, 密度泛函理论

中图分类号: O641

Stability of $B_{28}N_{28}$ Alternant Cages and Their Dependence on Bonds between Squares

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Abstract The structures and stabilities of twenty-three $B_{28}N_{28}$ alternant structures have been investigated at the B3LYP/6-31G* level of density functional theory. It is found that stability index of all the isomers obey a simple N_{4x} ($x=0, 1, 2$) topological rule characterizing the number of bonds between squares. The relative energies show an increasing tendency with the rising of x in N_{4x} ($x=0, 1, 2$), in which N_{404} is dominant. The present study provides a simple topological criterion that can be used to sort an approximate stability order of all the isomers and select the more stable candidate from the ISR(isolated square rule) structures. The simple filtering scheme is ideally suited for prescreening the thermodynamically viable structures of large boron nitride clusters.

Keywords: Boron nitride, Stability, Topology, Density functional theory

As the isoelectronic analogues to carbon fullerene, boron nitride nanomaterials with a band-gap energy of ~6 eV and non-magnetism are also expected to show various electronic, optical and magnetic properties such as Coulomb blockade, photo luminescence, and super paramagnetism^[1]. Up to now, extensive studies have been reported on the structure and stability of boron nitrides (BN)_n as nanotubes^[2] and cages^[3]. Experimentally, Stéphan *et al.*^[4] synthesized the small singer-layer and nested BN cages under electron irradiation of nanotubes and bulk material. More recently, Oku *et al.*^[5] synthesized and detected the $B_{24}N_{24}$

and $B_{28}N_{28}$ clusters by means of an arc-melting method and laser desorption time-of-flight mass spectrum. Computationally, it has been found that the small molecules (BN)_x ($x=3\sim 10$) favor ring structures while those with $x > 10$ prefer forming cages^[6]. As for the caged BN structures, there exist two major classes^[7] that exhibit quite different structural features, i.e., fullerene-like structures consisting of pentagons and hexagons, and alternant structures consisting of squares and hexagons. Fowler and co-workers^[8] suggested that the fullerene-like class was systematically more stable than the alternant class over the entire range of

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molecule size. Conversely, other theoretical studies conclude that alternant class would be preferred^[24, 7], and these findings agreed with the more recent study of Strout^[9] on $B_{13}N_{13}$, $B_{14}N_{14}$, and $B_{16}N_{16}$. Interestingly, our previous studies showed that the medium-sized structures^[10] comprising octagons also exhibited comparable stability. However, the traditional square-hexagon systems were still more stable for the large cages^[11].

By now we know that the stability of carbon fullerenes obeys the isolated pentagon rule (IPR)^[12] and the stability of alternant boron nitrides is dominated by the isolated square rule (ISR)^[13]. Besides, a theoretical study of the even subset^[14] of isomers up to 70 atoms has verified that isolated-pentagon-pair (IPP) B_xN_{x+4} cages are especially stable. Furthermore, it is noteworthy that the number of possible isomers of $(BN)_x$ is an increasing function of x , and systematic calculations performed on all of the isomers are difficult and time-consuming. The filtering principles must therefore be used. The well-known ISR has helped to filter out a large number of less stable isomers, however, the calculations are still expensive for the large-sized structure. For the BN alternant class, does it exist any other useful filtering principles for the large-sized isomers?

In this article, a study of density functional theory at B3LYP/6-31G* level on the structures and energies of all the possible isomers of the $B_{23}N_{23}$ is presented. It is found that the most stable isomer always has all the least number of N_{4x} ($x=0, 1, 2$) which topologically characterize the bonds between squares. And with increased number of the N_{4x} , the relative energies

increase consistently. The result provides useful information to experimentalists on the formation of other BN clusters.

1 Computational details

All structures of the $B_{23}N_{23}$ isomers were optimized at the B3LYP/6-31G* level of density functional theory, and the corresponding vibrational frequency calculations at the same level were used to characterize the optimized structure to be energy minima without imaginary frequencies. Single-point energies at B3LYP/6-311G* level of are used for discussion. The vertical ionization potentials are calculated to aid experimental study. All neutral cages were treated as closed-shell singlet configurations by using the Gaussian 03 program^[15].

2 Results and discussion

2.1 Structures

All the isomers of $B_{23}N_{23}$ were generated based on the fullerene spiral algorithms^[16], and the total number was 23. Each isomer has 84 B—N bonds without direct B—B and N—N connections. Topologically, these neutral cages can be viewed as polyhedra containing squares (f_4) and hexagons (f_6), and all of them have 6 f_4 and 24 f_6 . For simplicity, only the more stable 10 optimized structures are shown in Fig.1.

In order to get the location of f_4 in an easy way, a N_{4x} ($x=0, 1, 2$) nomenclature is introduced to characterize bonds between f_4 , in which N_{40} is the number of shared square B—N bonds among fused f_4 , N_{41} is the number of B—N bonds that connected

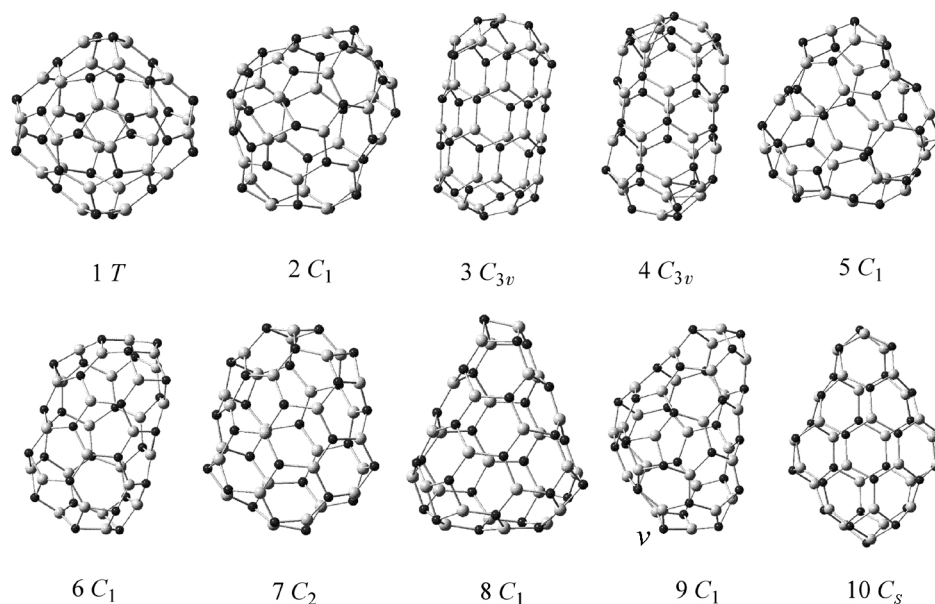


Fig.1 B3LYP/6-31G* optimized $B_{23}N_{23}$ isomers (1~10)

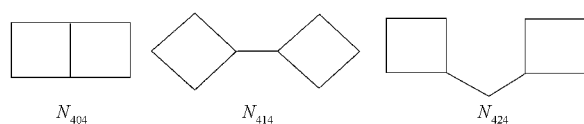


Fig.2 Structure motifs of the nomenclature $N_{4x4}(x=0, 1, 2)$

two isolated f_4 , and N_{424} is the number of B—N—B and N—B—N linker that bridged two isolated f_4 (Fig.2).

The nomenclature can characterize different isomers very well. For example, isomer 1 in T symmetry is an octahedron-like structure with all the f_4 and f_6 arranged in the most symmetric way. There are no fused f_4 ($N_{404}=0$) in the structure and the numbers of B—N bonds that connected any two-neighborhood f_4 are all 3 ($N_{414}=0$, $N_{424}=0$). Isomers 3 and 4 are both tube-like with all the f_4 dispersed averagely in the two caps. In each cap, 3 f_4 are separated by 3 fused f_6 ($N_{404}=0$, $N_{414}=0$), all the 3 f_4 in each cap are bridged by B—N—B and N—B—N ($N_{424}=12$). Isomer 10 is an oblate structure with C_s symmetry, in which 2 fused f_4 ($N_{404}=1$) locate at one side of the cage, 2 B—N bridged f_4 ($N_{414}=1$) locate at another side, and the left 2 f_4 are well isolated ($N_{424}=0$).

The nomenclature for other structures is given in Table 1.

2.2 Stability

The B3LYP/6-311G* single-point energies of all structures and their relative energies are summarized in Table 1. The vertical ionization energies (VIP) are also listed to aid experimental study. Isomer 1 in T symmetry with $N_{404}=0$ is the most stable $B_{28}N_{28}$ not only in this study but also in literature^[11a]. The least stable isomer 23 with $N_{404}=6$ is higher in energy than isomer 1 by $3368.67 \text{ kJ} \cdot \text{mol}^{-1}$. It can be seen clearly that the most stable structure has the minimal value of N_{404} while the least stable isomer has the maximum N_{404} . Additionally, considering all isomers with $N_{404}=0$, almost all of them have lower energies than those isomers with $N_{404} \geq 1$. The result is satisfied with the simple rule of thumb ISR^[13], namely, the most stable isomer at any given N is one that minimizes the number of square adjacencies.

Examination of the full set of optimized geometries shows that the relative energies of the $B_{28}N_{28}$ isomers increase steadily and considerably with rising of N_{404} . For example, among those structures with $N_{404}=1$, isomer 8 is the most stable one that is

Table 1 B3LYP/6-311G* single-point energies E_T , relative energies E_{rel} , ZPE, vertical ionization energy (E_{VIP}), energy gaps

E_g and the topological nomenclature (N_{4x4}) number of $B_{28}N_{28}$									
$B_{28}N_{28}$	Sym.	E_T (a.u.)	$E_{rel}/(\text{kJ} \cdot \text{mol}^{-1})$	ZPE ($\text{kJ} \cdot \text{mol}^{-1}$)	$E_{VIP}/(\text{kJ} \cdot \text{mol}^{-1})$	E_g / eV	N_{404}	N_{414}	N_{424}
1	T	-2232.12845	0.00	820.32	37.15	6.84	0	0	0
2	C_1	-2232.08464	115.02	819.27	37.24	6.54	0	0	4
3	C_{3c}	-2232.06334	170.95	818.14	36.61	5.51	0	0	12
4	C_{3c}	-2232.06124	176.46	817.85	36.61	5.51	0	0	12
5	C_1	-2232.04317	223.90	817.55	36.65	6.16	0	1	4
6	C_1	-2232.03620	242.20	816.76	36.48	6.07	0	2	4
7	C_2	-2232.02092	282.32	816.42	37.20	6.54	0	0	8
8	C_1	-2232.02358	275.34	813.79	37.11	5.77	1	0	4
9	C_1	-2232.00740	317.82	816.13	36.94	5.85	1	1	0
10	C_s	-2231.97233	409.89	815.50	36.78	5.90	1	1	0
11	C_1	-2231.97109	413.15	814.16	36.40	5.86	1	1	2
12	C_3	-2231.95583	453.21	814.37	36.74	5.80	0	3	0
13	C_1	-2231.94816	473.35	813.45	36.57	5.75	1	1	2
14	C_1	-2231.92389	537.07	812.20	36.69	5.69	2	0	0
15	C_1	-2231.91552	559.05	812.03	36.40	5.47	2	0	0
16	C_1	-2231.90262	592.92	811.15	36.44	5.44	2	0	0
17	C_1	-2231.90101	597.14	811.03	36.69	5.43	2	0	0
18	C_1	-2231.84597	741.65	809.73	36.19	5.84	2	0	4
19	C_i	-2231.83400	773.08	808.81	36.11	5.81	2	0	4
20	C_3	-2231.83376	773.71	805.21	36.74	5.83	3	0	0
21	C_1	-2231.74823	998.27	808.68	35.61	4.94	2	2	2
22	S_4	-2231.30319	2166.72	786.13	35.02	5.52	4	0	0
23	C_{3c}	-2230.84539	3368.67	766.38	35.31	2.61	6	0	0

275.34 kJ·mol⁻¹ higher than isomer 1; while isomer 14, the most stable structure of those with $N_{404}=2$, is 537.07 kJ·mol⁻¹ higher than isomer 1 and 261.73 kJ·mol⁻¹ higher than isomer 8. The similar behavior is also found in other isomers. It is also not claimed that all isomers with less N_{404} value will have lower energies than all isomers with high N_{404} value. As the energy range spanned when the number of isomers grow, some overlaps occur. However, most of them obey this rule and the most stable isomers can be surely included and selected. Thus, we can get a few likely stable isomers based on the N_{404} number of all isomers of a given size alternant BN cluster.

Additionally, we studied the other two merits N_{414} and N_{424} in detail. For all the isomers with $[a, b, c]$ (a, b, c in $[a, b, c]$ denotes $N_{404}, N_{414}, N_{424}$ respectively), the isomers 5 [0, 1, 4], 6 [0, 2, 4], 12 [0, 3, 0] is higher in energy than isomer 1 [0, 0, 0] by 223.90, 242.20, and 453.21 kJ·mol⁻¹, respectively, demonstrating an increasing tendency of relative energy with increasing of N_{414} . The similar trend is also found in other isomers sharing the same N_{404} number but different N_{414} numbers, e.g., isomer 9 with [1, 1, 0] is 42.48 kJ·mol⁻¹ higher than isomer 8 with [1, 0, 4]; isomer 21 [2, 2, 2] is higher in energy than the isomer 14 with [2, 0, 0] by 461.20 kJ·mol⁻¹. This result can help us to reduce the likely candidates again from the sorted ISR structures, and can also give a mainly picture of all isomers' relative stability order.

Furthermore, the merit N_{424} can provide more detailed information when isomers have the same N_{404} and N_{414} values. As shown in Table 1, the first four likely isomers all have [0, 0, c] nomenclature. Among of them, isomers 3 and 4 that sharing the same nomenclature [0, 0, 12] are both in C_{3v} symmetry and very close in energy. The observed stability order is [0, 0, 12] (isomers

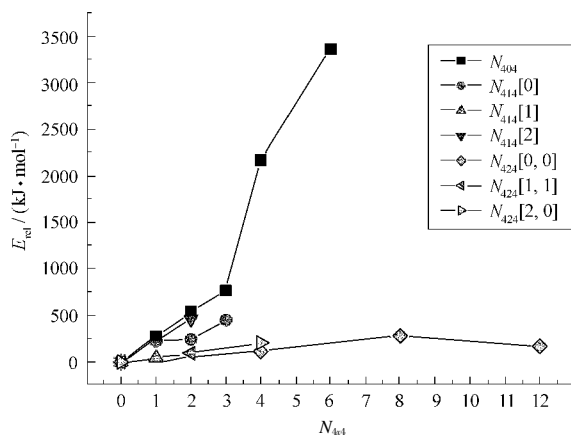


Fig.3 Variation of relative energy with number of N_{4x4} ($x=0, 1, 2$) nomenclature

3, 4) < [0, 0, 4] (isomer 2) < [0, 0, 0] (isomer 1). The same tendency can be found in other isomers with the same N_{404} and N_{414} but different N_{424} , such as [1, 1, 2] (isomer 11) > [1, 1, 0] (isomers 9, 10), [2, 0, 4] (isomers 18, 19) < [2, 0, 0] (isomers 14-17).

It should be noted that the isomer 7 with [0, 0, 8] in C_2 symmetry is higher in energy than the two [0, 0, 12] isomers 3 and 4. As shown in Fig.1, isomers 3 and 4 are both tube-like, however, isomer 7 is oblate. The 6 f_4 of isomers 3 and 4 are all dispersed in the two caps while the f_4 of isomer 7 are all located in the belt and make the cage very flat with large strain in the structure. These energetic differences are very similar to those of fullerenes obeying the isolated pentagons rule (IPR)^[17], and the relative stability of BN cages reflects the intimate interplay between strains of individual rings, conjugations and curvatures of the cages. For the similar reason, isomers 5 [0, 1, 4] and 6 [0, 2, 4] with N_{414} of 1 and 2 are also lower in energy than isomer 7.

Based on the discussion above, it can be concluded that, in general, relative energies show an increasing tendency with N_{4x4} ($x=0, 1, 2$) nomenclature. And the penalty caused by N_{404} is larger than those caused by N_{414} and N_{424} . To make the tendency clearer and more visible, Fig.3 shows the variation of relative energies with numbers of topological merit N_{4x4} ($x=0, 1, 2$). From the gradient of N_{4x4} ($x=0, 1, 2$) against the relative energy, it can be found that, the relative order of the three kinds of gradients is $N_{404} > N_{414} > N_{424}$, i.e., the penalty caused by N_{404} , N_{414} , and N_{424} decreases gradually. Therefore, N_{404} is further confirmed to be dominant in affecting the relative energies of isomers.

3 Conclusion

In summary, the topological properties and stabilities of all 23 $B_{20}N_{20}$ alternant cages have been investigated at the B3LYP level systemically. It is found that relative energies show a tendency to rise with N_{4x4} ($x=0, 1, 2$). The most stable isomer has the least number of N_{4x4} ($x=0, 1, 2$). N_{404} is dominant in affecting the relative energies of isomers, but the influences of the N_{414} and N_{424} are also significant. The present study suggests a simple topological criterion that can be used to select the ISR isomers and choose the more stable candidate from the sorted ISR structures. The simple filtering scheme is ideally suited for prescreening the thermodynamically viable structures of large boron nitride clusters. It may also give us a guideline for designing and synthesis of the BN clusters.

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