ORIGINAL PAPER

Bonding analysis and stability on alternant $B_{16}N_{16}$ cage and its dimers

Bing Yin · Guo Wang · Niya Sa · Yuanhe Huang

Abstract Bonding analysis is performed on alternant $B_{16}N_{16}$ cage based on a combined study of DFT with NBO method. The main feature of such analysis is the separation of bonding structure into two components: σ skeleton and π bond system. Each component is further decomposed into contributions from various NBOs, thus we obtain the details of bonding interactions of every BN unit. Based on these results, relative stability of four covalent dimers of $B_{16}N_{16}$ is predicted and this prediction is verified by DFT calculations. So the possibility of forecasting properties of oligomers just from analysis on monomer is highlighted in this way.

Keywords DFT · Bonding analysis · NBO · Relative stability

Introduction

Due to its role of isoelectronic species to carbon fullerene, stoichiomeric boron nitride cage $(BN)_n$ have been investigated extensively both in experiments and calculations to exploit their electronic, optical and magnetic properties [1–15]. There are mainly two structural classes for $(BN)_n$ cages [6, 12]: One is constructed from alternant BN units and governed by an isolated square rule [14, 15], which is the counterpart of isolated pentagon rule [16] of carbon fullerenes. Another class is of fullerene-like structures, based on combination of 5- and 6-membered rings, with the existence of N-N and B-B bonds.

According to our best knowledge, detailed bonding analysis is still infrequent in theoretical works on $(BN)_n$ cages. On the other hand, the oligomers and solids of $(BN)_n$ cages have attracted the interest of theorists [8]. Due to the enlarged-size of such systems, the cost of direct calculations is quite high and the possibility of predicting properties of oligomers just from studies on monomer is of great interest. So the purpose of this paper is, first, to analyse the details of bonding of alternant $B_{16}N_{16}$ cage [6, 8, 15], which is shown to be the most stable isomer [6]. Second, as a preliminary step to explore the possibility of forecasting properties of oligomers just from studies on monomer, we predict the relative stability of four dimers of alternant $B_{16}N_{16}$ cage, just from bonding analysis on single cage, and examine the validity of this prediction.

DFT [17] has become an efficient tool for theoretical studies on $(BN)_n$ cage [3, 4, 6–11] and NBO analysis [18–21] has been successfully applied into various molecular systems [22–34]. One thing worth noting is that conjugated systems, such as benzene and π-conjugated linear molecules, have been well studied with NBO analysis [32–34]. This fact points out the possibility of application of NBO analysis into alternant $B_{16}N_{16}$ cage since this cage is the boron-nitride analogy of curved π-conjugated carbon fullerene. So bonding analysis in this paper is based on a combined study of DFT with NBO method. This combination has been shown to provide significant improvement over NBO analysis at HF level [20, 35, 36]. To ensure the reliability of such analysis, four DFT functionals, together with HF and MP2 [37] methods, are applied in this paper.

Theoretical methods and computational details

NBO method transforms atomic orbitals into a new basis set of localized lewis(core, bonding) and non-lewis(mainly

B. Yin · G. Wang · N. Sa · Y. Huang (✉)
College of Chemistry, Beijing Normal University,
Beijing 100875, People's Republic China
e-mail: yuanhe@bnu.edu.cn

antibonding) NBO orbitals [18–20]. In closed-shell systems, lewis NBOs are nearly double-occupied [18] and provide the most accurate natural Lewis structure(NLS) description of the system [19].

Since antibonding NBO is of non-zero occupancy and leads to certain energetic stabilization [18], it contributes to bonding interaction between bond-connected atoms as well as bonding NBO. Lower orbital energy(OE) means occupying electrons are more stable at zeroth-order approximation, thus stronger bonding NBO is related to lower OE. Since occupancies(Q) of various NBOs are different, orbital energy multiplied with its occupancy(OEMO) is more suitable to measure the strength of bonding NBO. The strength of antibonding NBOs can be measured by deletion energy(DE) [21, 27] and second-order interaction energy (SOIE) [34] quantitatively. Higher value of DE or SOIE corresponds to stronger antibonding NBO.

Alternant $B_{16}N_{16}$ cage is fully optimized by B3LYP [38, 39], BLYP [39, 40], MPW1PW91 and MPWPW91 [41, 42], together with HF and MP2 [37] method. 6-31G* basis set, which is proven to be suitable for $(BN)_n$ cages [9, 10], is used in this paper. The local minimum character of optimized structures is confirmed by frequency analysis [43]. Gaussian 03 program [44] with NBO 5.0 code [45] is used for all calculations and analysis.

Results and discussions

The decomposion of bonding structure

The bonding structure of $B_{16}N_{16}$ cage could be decomposed into σ skeleton, shown in Fig. 1, and π bond system.

The σ skeleton is considered as being constructed from sp^2 hybrids and can be described by σ bonding and σ antibonding(σ*) NBOs. Similarly, the π bond system, constructed from remaining π-type atomic orbitals, could be characterized in terms of π and π* NBOs. Because of the cage curvature, π bond system should be partially conjugated.

In order to simplify the bonding analysis, full usage of molecular symmetry is necessary. Due to the Td symmetry of the cage [15], confirmed by frequency analysis of optimized structures, both nitrogen and boron atoms can be separated into two types as shown in σ skeleton in Fig. 1: type i-atoms lying on C_3 axes(atom 25-atom 32 in slanted text) and type j-atoms constituting 4-membered rings(atom 1-atom 24 in normal text). So there are only three types of BN units: N(i)-B(j), B(i)-N(j) and N(j)-B(j), noted as BN(1), BN(2), BN(3) respectively in this paper.

As shown in Table 1, the optimized bond lengths for alternant $B_{16}N_{16}$ cage are shorter than BN single bond in H_3B-NH_3 but longer than double bond in $H_2B=NH_2$, supporting the existence of partially conjugated π bond system. The order of bond lengths is: BN(3)>BN(2)> BN(1).

As a matter of fact, an alternant $B_{16}N_{16}$ cage with equal BN bonds is also obtained from point-wise optimization at B3LYP/6-31G* level. The calculations show that the energy of this structure is 200.91 kcal/mol higher than that of the minimum calculated here. Hence the monomeric $B_{16}N_{16}$ cage should be favorable to a distorted structure from a geometry with perfectly square B_2N_2 and perfectly hexagonal B_3N_3 faces. This is in accordance with the previous calculations for alternant $(BN)_n$ cages with more than 20 atoms [4–6]. Moreover, 4-membered ring B_2N_2 and
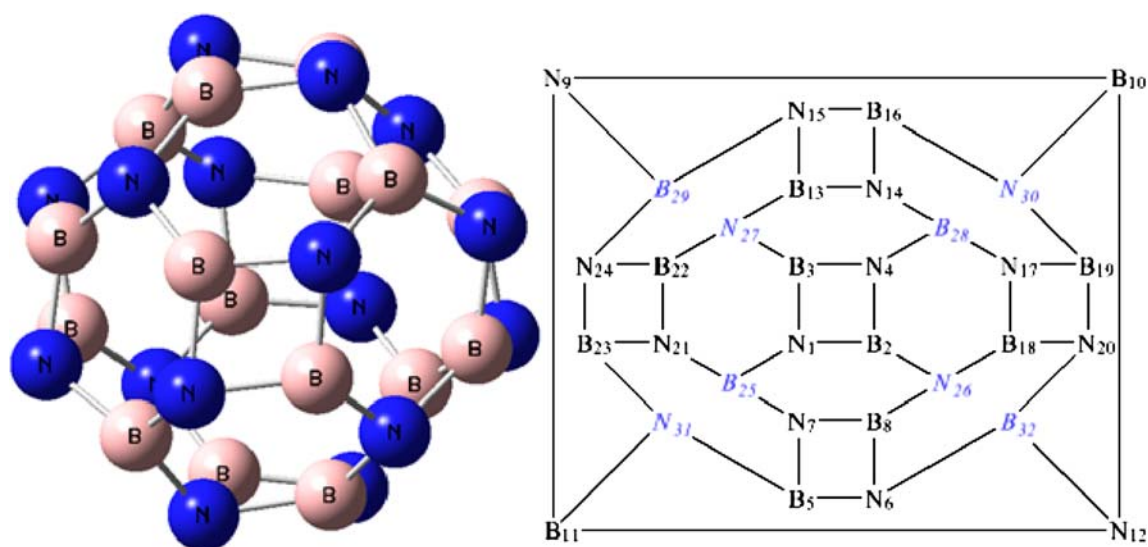

Fig. 1 Optimized geometry and σ skeleton of alternant $B_{16}N_{16}$ cage

Table 1 Optimized bond lengths for alternant $B_{16}N_{16}$ cage[a]

	B3LYP	BLYP	MPW1	MPW	HF	MP2
BN(3)	1.473	1.485	1.469	1.480	1.463	1.476
BN(2)	1.458	1.469	1.454	1.464	1.452	1.460
BN(1)	1.456	1.466	1.452	1.461	1.450	1.456
B-N[b]	1.669	1.684	1.651	1.660	1.688	1.665
B=N[c]	1.392	1.401	1.389	1.397	1.389	1.394

[a] Bond lengths in Å. [b] length of BN single bond in H_3B-NH_3. [c] length of BN double bond in $H_2B=NH_2$

6-membered ring B_3N_3 are also distorted by the same calculations. The deviation may be due to different geometry preference for B and N atoms which have different configurations of valent electron. Borons prefer planar geometry and nitrogens prefer pyramidalization [15]. However, for the 6-membered ring $B_3N_3H_6$, a recent optimization leads to perfectly hexagonal structure [46]. As to the 4-membered ring $B_2N_2H_4$, i.e., 1,3-diazadiboretidine, the optimized structures are also deviated from perfectly square faces [47].

By the way, experiments have shown the existence of boron-nitride analogy of graphite [48]. This kind of graphite-like boron nitride could be constructed from not only hexagonal but also rhombohedral rings [49, 50]. This reflects the diversity of boron nitride structures which is worth exploration.

Further decomposition into contributions from various NBOs

Selection of natural Lewis structure(NLS) Default NLS with different methods are not unique. Even nitrogen lone pairs and five-valency boron atoms exist in the default NLS of DFT calculations. For the consistency of consequent bonding analysis, a uniform NLS is necessary. Since there are three different types of BN unit and only 16 double bonds are available for 48 BN units of the $B_{16}N_{16}$ cage, a suitable NLS, without lone pairs and violations of lewis octet rule, is selected. In this NLS, one third of every distinct type of BN units are connected with double bonds as shown in Fig. 2.

Details of bonding interaction of BN units For a certain BN unit, its bonding interaction is determined by all the NBOs within this unit as shown in Sect.2; thus it can be analyzed with the parameters of NBO as shown in Tables 2 and 3. Since only one third of BN units of one given type are connected with double bonds, shown by selected NLS (Fig. 2), π and π^* NBOs should be considered as orbitals into which π bond system is condensed. In most cases, maximum relative deviations of parameters for NBOs of a certain type BN units are less than 2%; thus this fact provides

the validity of selected NLS and only averaged values of these parameters are tabulated. From Tables 2 and 3, all the methods show consistent characters, though actual values are some different with different calculations.

Lower occupancy (Q) of bonding NBO means more electrons have been donated into antibonding NBOs [18], thus lower occupancy leads to stronger donor-ability. From Table 2, it can be seen that the values of occupancy are 1.910-1.972 and 1.667-1.785 for σ and π bonding NBOs respectively. Therefore, π bonding NBOs possess higher donor-ability than σ bonding NBOs. The order of occupancies of a given type of bonding NBOs with different methods is HF≥Hybrid functionals≥GGA functionals≥ MP2. The lowest value of MP2 occupancies is due to the multi-determinant wavefunction in which the limiting value of occupancy is less than 2 for closed-shell system [18, 21, 51]. It is easy to understand the intermediate results provided by hybrid functional since it can be considered as combination of pure GGA and HF.

For the energetic parameters in Table 2, σ-BN(1) and σ-BN(2) are of nearly the same magnitude for OE and OEMO. However this magnitude is significantly lower than that of σ-BN(3) by ~50 kcal/mol and ~100 kcal/mol for OE and
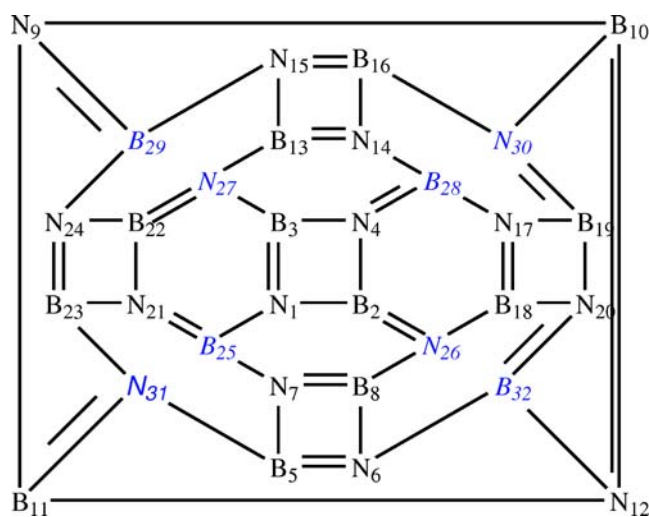

Fig. 2 Selected NLS for alternant $B_{16}N_{16}$ cage

Table 2 Calculated parameters of bonding NBOs of alternant $B_{16}N_{16}$ cage

		B3LYP	BLYP	MPW1	MPW	HF	MP2
σ-BN(1)	Q[a]	1.960	1.959	1.959	1.958	1.963	1.927
	OE[b]	−433.55	−387.75	−477.68	−396.09	−569.13	
	OEMO[c]	−849.99	−760.00	−877.17	−775.68	−1117.16	
σ-BN(2)	Q	1.972	1.972	1.971	1.971	1.972	1.938
	OE	−430.08	−384.34	−444.45	−393.11	−565.57	
	OEMO	−847.99	−757.81	−876.02	−774.81	−1114.94	
σ-BN(3)	Q	1.946	1.945	1.945	1.943	1.951	1.910
	OE	−381.87	−338.43	−394.98	−346.39	−510.46	
	OEMO	−743.22	−658.13	−768.31	−673.01	−996.03	
π-BN(1)	Q	1.741	1.727	1.741	1.724	1.785	1.710
	OE	−211.51	−183.22	−220.74	−190.70	−288.15	
	OEMO	−368.21	−316.45	−384.31	−320.80	−514.24	
π-BN(2)	Q	1.701	1.688	1.697	1.680	1.747	1.667
	OE	−215.32	−187.46	−224.60	−195.46	−290.24	
	OEMO	−366.27	−316.42	−381.15	−328.37	−507.03	
π-BN(3)	Q	1.709	1.694	1.706	1.688	1.758	1.678
	OE	−226.13	−197.50	−235.92	−205.89	−303.29	
	OEMO	−386.45	−334.60	−402.58	−347.50	−533.16	

[a] Occupancy in electron number [b] Orbital energy in kcal/mol [c] Orbital energy multiplied with its occupancy in kcal/mol

OEMO respectively. The values of OE and OEMO of π-BN (1) are very close to those of π-BN(2) and higher than those of π-BN(3) by ~13 kcal/mol and ~20 kcal/mol for OE and OEMO respectively. For σ bonding NBOs, the shorter the bond length is, the lower the OE and OEMO are. However it is just contrary for π bonding NBOs. It seems that different types of bonding NBOs have different relation-ship with bond lengths and this may be the result of curvature structure of this cage. Finally the order of strength of bonding NBOs is $\sigma-BN(1) \simeq \sigma-BN(2) \gg \sigma-BN(3) \gg \pi-BN(3) > \pi-BN(1) \simeq \pi-BN(2)$.

As to the parameters of antibonding NBOs shown in Table 3, the occupancies of π* NBOs are much larger than those of σ* NBOs, i.e., π* NBOs have stronger acceptor-

Table 3 Calculated parameters of antibonding NBOs of alternant $B_{16}N_{16}$ cage

		B3LYP	BLYP	MPW1	MPW	HF	MP2
σ*-BN(1)	Q	0.055	0.057	0.056	0.059	0.048	0.075
	DE[a]	38.99	36.51	40.95	38.15	45.53	
	SOIE[b]	50.98	46.57	53.98	48.67	61.89	
σ*-BN(2)	Q	0.041	0.045	0.042	0.045	0.036	0.061
	DE	27.10	25.32	28.61	26.45	32.52	
	SOIE	30.91	27.83	32.41	28.85	39.25	
σ*-BN(3)	Q	0.051	0.056	0.052	0.056	0.043	0.072
	DE	31.12	26.74	29.92	28.14	32.82	
	SOIE	34.79	31.38	36.83	32.86	44.46	
π*-BN(1)	Q	0.244	0.256	0.244	0.261	0.200	0.261
	DE	86.94	85.58	89.64	88.62	88.06	
	SOIE	128.50	117.22	133.31	119.98	157.39	
π*-BN(2)	Q	0.229	0.243	0.228	0.244	0.186	0.240
	DE	67.28	66.28	68.69	67.58	69.36	
	SOIE	72.58	62.46	75.73	63.42	101.36	
π*-BN(3)	Q	0.233	0.244	0.233	0.246	0.196	0.249
	DE	81.32	79.41	83.65	81.72	85.80	
	SOIE	101.62	89.58	106.34	92.17	137.44	

[a] Deletion energy in kcal/mol [b] Second-order interaction energy in kcal/mol

ability compared to σ* NBOs. DE values demonstrate that the strength of π*-BN(3) is close to that of π*-BN(1) while markedly stronger than π*-BN(2) by 15~20 kcal/mol. σ*-BN(3) and σ*-BN(2) are of comparable strengths and weaker than σ*-BN(1) by ~10 kcal/mol. Although SOIE values are higher than corresponding DE values, especially for π* NBOs, it is consistent with DE in the aspect of relative strength of different antibonding NBOs.

Summary of bonding analysis The order of strengths is $\sigma-BN(1) \simeq \sigma - BN(2) \gg \sigma - BN(3) \gg \pi - BN(3) > \pi- BN(1) \simeq \pi - BN(2)$ for bonding NBOs and $\pi* - BN(1) \simeq \pi* -BN(3) > \pi* -BN(2) \gg \sigma - BN(1) > \sigma - BN(3) \simeq \sigma - BN(2)$ for antibonding NBOs. So for σ bonding interaction, it is BN(1)>BN(2)>BN(3) and for π bonding interaction it is BN(3)>BN(1)>BN(2).

Bonding index analysis

In order to provide sufficient description on alternant $B_{16}N_{16}$ cage, wiberg bond index (WBI) [21, 52] and overlap-weighted NAO bond order (OWBO) [21] are calculated and shown in Table 4.

The calculated values in Table 4 indicate that the B-N bonds of alternant $B_{16}N_{16}$ cage are just between the typical single and double BN bond, thus bond index also support that the $B_{16}N_{16}$ cage is a partially conjugated system. It should be pointed out that the order of bond index are not exactly matched with bond lengths. Especially, WBI of BN(3) with longer bond length is larger than that of BN(1) with shorter bond length. Although WBI has been used in the study of $(BN)_{10}$ [3], the results here suggest that bond indexes can only provide a primitive description of $(BN)_n$ cage

Predicting relative stability of dimers

Based on the above bonding analysis we now discuss the possible stability for two cages joining to form covalent dimers $(B_{16}N_{16})_2$. Four linking patterns, which are $BN(1)_a = BN(1)_b$, $BN(2)_a = BN(2)_b$, $BN(3)_a = BN(3)_b$ and $BN(1)_a = BN(2)_b$, with a, b denoting different $B_{16}N_{16}$ cages, are considered. These four dimers are abbreviated as D1, D2, D3, D4, shown in Fig. 3.

Assuming the reservation of σ skeletons of monomer cages, the main change, after the formation of dimers, is that π bonds of two BN units of original $B_{16}N_{16}$ cages are broken and replaced by two inter-cage single bonds. If the strength of inter-cage bonds were almost the same, the relative stability of the dimers should be determined mainly by the relative strength of replaced π bonds. Since the order of the strength of π bond is BN(3)>BN(1)>BN(2) from bonding analysis on monomer, the relative stability of the $(B_{16}N_{16})_2$ dimers is predicted as D2>D4>D1>D3.

To verify this prediction, we optimized the four dimers at B3LYP/ 6-31G* level. The calculations give the stable order of D3>D2>D4>D1 as shown in Table 5. It can be seen that only D3 is not in accordance with the predicted order. This exception is because the σ skeletons of monomer cages have been broken after the formation of D3. The lengths of original BN units, connected by inter-cage BN bonds, change to 2.586Å and is much longer than that of a usual single BN bond. Moreover, the inter-cage BN bonds are of nearly the same length as the double bond in $H_2B=NH_2(1.392Å)$ as shown in Table 5. Therefore in the case of D3, both σ and π bonding interactions of two original BN units are broken and replaced by two inter-cage double bonds. Although BN(3) is the strongest in the aspect of π bonding interaction, its σ bonding interaction is quite weaker than other types of BN units, considering the OEMO of σ-BN(3) is ~100 kcal/mol higher than other two types of σ NBOs (Table 2). This may be the reason why D3 becomes the most stable dimer.

The main difference between π bond of BN(1) and BN (2) is that the contribution from π*-BN(1) is stronger than that of π*-BN(2) by 6.55 kcal/mol on average [53]. There are moderate deviations of calculated relative energies

Table 4 Calculated bond index for alternant $B_{16}N_{16}$ cage

		B3LYP	BLYP	MPW1	MPW	HF	MP2
BN(1)	WBI	0.857	0.867	0.869	0.867	0.818	0.798
	OWBO	0.900	0.902	0.905	0.904	0.882	0.883
BN(2)	WBI	0.875	0.886	0.889	0.888	0.828	0.814
	OWBO	0.903	0.906	0.909	0.908	0.884	0.887
BN(3)	WBI	0.870	0.878	0.882	0.880	0.832	0.812
	OWBO	0.884	0.884	0.888	0.887	0.873	0.870
H_3B-NH_3[a]	WBI	0.608	0.626	0.634	0.619	0.559	0.572
	OWBO	0.594	0.610	0.615	0.598	0.558	0.580
$H_2B=NH_2$[b]	WBI	1.261	1.266	1.303	1.281	1.148	1.183
	OWBO	1.048	1.052	1.059	1.051	1.016	1.029

[a] Bond index for BN unit of H_3B-NH_3 [b] Bond index for BN unit of $H_2B=NH_2$

Fig. 3 Optimized structures of the four $(B_{16}N_{16})_2$
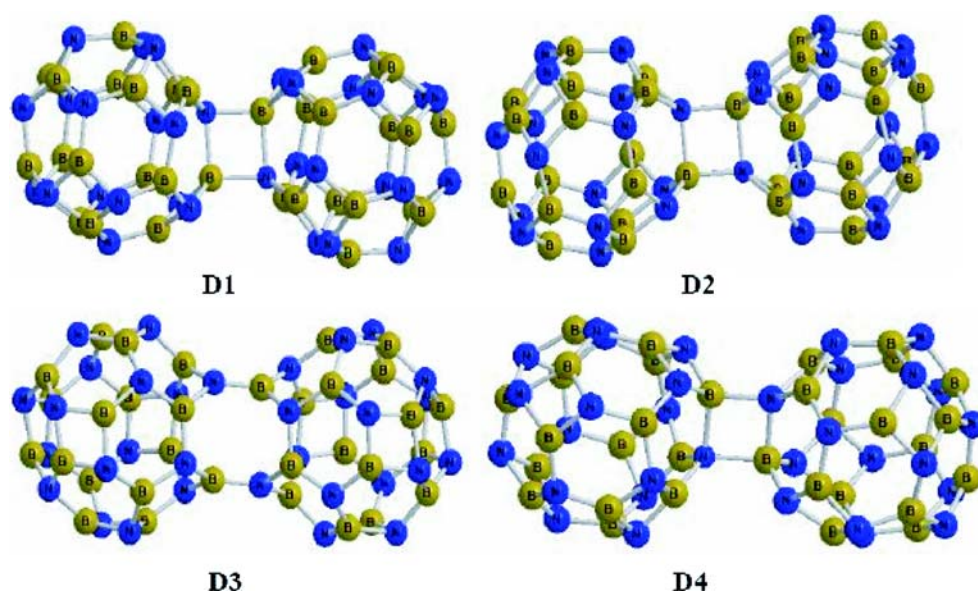
from the estimation based on DE as shown in Table 5. This is because various inter-cage bonds are not exactly the same and monomers are deformed during the formation of dimer. From Table 5, D4 is less deformed than D2 and the strength of inter-cage bonds of D4 is stronger than that of D2, shown by bond lengths. Even though, D4 is still less stable than D2 and this fact stresses the possibility of forecasting properties of oligomers just from studies on monomer.

As a comparison, we also explored the dimerization of 1,3-diazadiboretidine. Here, only one isomer of $B_4N_4H_8$, which is a cage structure with alternant BN units [54], was considered. Our calculations show that, this dimerization is exothermic, about 24.49 kcal/mol, which is consistent with MP2 calculations [54]. The dimerization of alternant $B_{16}N_{16}$ cage is also exothermic, 11.92-55.88 kcal/mol for the dimers studied here. Previous work reported the possibility of delocalization of electrons in 1,3-diazadiboretidine [47], which may result into the partially conjugated π bond system similar to alternant $B_{16}N_{16}$ cage. However, both boron and nitrogen atoms in the cage structure of $B_4N_4H_8$ are 4-coordinated, thus this structure excludes the possibility

for conjugated π bond. This is different from the dimers of $B_{16}N_{16}$ cage.

Conclusions

Based on a combined study of DFT with NBO method, a detailed bonding analysis on alternant $B_{16}N_{16}$ cage is performed. First the bonding structure is seperated into two components: σ skeleton and π bond system. Then bonding interaction of one single BN unit is decomposed into contributions from various NBOs. Results with different methods agree with each other well and details of bonding interactions of any BN unit are obtained in this way.

Relative stability of four covalent dimers of the $B_{16}N_{16}$ cage is predicted from bonding analysis on monomers. Moreover, direct calculations on dimers verify this prediction if the σ skeletons of monomer cages are not broken. Hence the possibility of forecasting properties of oligomers just from studies on the monomer, which is a more efficient way compared to direct calculations on oligomers, is highlighted by this study.

Table 5 Relative energies and bond lengths of the four dimers[a]

	D1	D2	D3	D4
Relative energy	0.00(0.00)	−8.96(-13.10)	−43.96	−5.45(-6.55)
Inter-cage BN	1.613/1.613	1.596/1.596	1.404/1.404	1.581/1.581
Deformation energy[b]	51.26	56.02		53.79

[a] Energy in kcal/mol and bond length in Å. Relative energies, based on DE estimation exclusively, are shown in parenthesis. [b] The difference between energy of two monomers with structures fixed as in dimers and that of two monomers with optimal structures

Bond index analysis is also carried out with the conclusion that bond indexes can only provide a primitive description of boron nitride cages.

References

1. Golberg D, Bando Y, Stephan O, Kurashima K (1998) Appl Phys Lett 73:2441–2443
2. Oku K, Nishiwaki A, Narita I, Gonda M (2003) Chem Phys Lett 380:620–623, and references cited
3. Xu SH, Zhang MY, Zhao YY, Cheng BG, Zhang J, Sun CC (2006) Chem Phys Lett 418:297–301
4. Strout DL (2000) J Phys Chem A 104:3364–3366
5. Strout DL (2001) J Phys Chem A 105:261–263
6. Strout DL (2004) Chem Phys Lett 383:95–98, and references cited
7. Alexandre SS, Mazzoni MSC, Chacham H (1999) Appl Phys Lett 75:61–63
8. Alexandre SS, Nunes RW, Chacham H (2002) Phys Rev B 66:085–406
9. Wu HS, Xu XH, Zhang FQ, Jiao HJ (2003) J Phys Chem A 107:6609–6612, and references cited
10. Wu HS, Jiao HJ (2004) Chem Phys Lett 386:369–372
11. Wu HS, Xu XH, Strout DL, Jiao HJ (2005) J Mol Model 12:1–8
12. Rogers KW, Fowler PW, Seifert G (2000) Chem Phys Lett 332:43–50
13. Zope RR, Dunlap BI (2004) Chem Phys Lett 386:403–407
14. Sun ML, Slanina Z, Lee SL (1995) Chem Phys Lett 233:279–283
15. Zhu HY, Schmalz TG, Klein DJ (1997) Int J Quantum Chem 63:393–401
16. Manolopoulos DE, Fowler PW (1991) Chem Phys Lett 187:1–7
17. Koch W, Holthausen MC (2000) A chemist's guide to density functional theory.Wiley, Weinheim
18. Reed AE, Curtiss LA, Weinhold F (1988) Chem Rev 88:899–926
19. Weinhold F, Landis CR (2001) Chem Educ Res Pract Eur 2:91–104
20. Weinhold F (1998) Natural bond orbital methods. In: Schleyer PvR, Allinger NL, Clark T, Gasteiger J, Kollman PA (eds) Encyclopedia of computational chemistry. Wiley, Chichester UK
21. Weinhold F (2001) NBO 5.0 Program manual. Theoretical Chemistry Institute and Department of Chemistry, University of Wisconsin, Madison, WI, p 53706
22. Pophristic V, Goodman L (2001) Nature 411:565–568
23. Goodman L, Pophristic V, Weinhold F (1999) Acc Chem Res 32:983–993
24. Reed AE, Weinhold F (1985) J Am Chem Soc 107:1919–1921
25. Reed AE, Weinhold F (1986) J Am Chem Soc 108:3586–3593
26. Alabugin IV, Manoharan M, Peabody S, Weinhold F (2003) J Am Chem Soc 125:5973–5987
27. Reed AE, Weinhold F, Curtiss LA, Pochatko DJ (1986) J Chem Phys 86:5687–5705
28. Reed AE, Schleyer PvR (1987) J Am Chem Soc 109:7362–7373
29. Salzner U, Schleyer PvR (1993) J Am Chem Soc 115:10231–10236
30. Suárez D, Sordo TL, Sordo JA (1996) J Am Chem Soc 118:9850–9854
31. Banavali NK, MacKerell AD Jr (2001) J Am Chem Soc 123:6747–6755
32. Glendening ED, Faust R, Streitwieser A, Vollhardt KPC, Weinhold F (1993) J Am Chem Soc 115:10952–10957
33. Bruschi M, Giuffreda MG, Lüthi HP (2002) Chem Eur J 8:4216–4227
34. Giuffreda MG, Bruschi M, Lüthi HP (2004) Chem Eur J 10:5671–5680
35. Zierkiewicz W, Hobza P (2004) Phys Chem Chem Phys 6:5288–5296
36. Parreira RLT, Galembeck SE, Hobza P (2007) ChemPhysChem 8:87–92
37. Møller C, PLesset MS (1934) Phys Rev 46:618–622
38. Becke AD (1993) J Chem Phys 98:5648–5652
39. Lee C, Yang W, Parr RG (1988) Phys Rev B 37:785–789
40. Becke AD (1988) Phys Rev A 38:3098–3100
41. Adamo C, Barone V (1998) J Chem Phys 108:664–675
42. Perdew JP, Chevary JA, Vosko SH, Jackson KA, Pederson MR, Singh DJ, Fiolhais C (1992) Phys Rev B 46:6671–6687
43. Foresman JE, Frisch Æ (1996) Exploring chemistry with electronic structure methods, 2nd edn. Gaussian Inc, Pittsburgh PA
44. Frisch MJ, Trucks GW, Schlegel HB et al (2003) Gaussian 03. Gaussian Inc, Pittsburgh PA
45. Glendening ED, Badenhoop JK, Reed AE, Carpenter JE, Bohmann JA, Morales CM, Weinhold F (2001) NBO 5.G. Theoretical Chemistry Institute, University of Wisconsin, Madison,WI
46. Rehaman A, Datta A, Mallajosyula SS, Pati SK (2006) J Chem Theory Comput 2:30–36
47. Tricamo AJ, Knaus KJ, Ball DW (2007) J Mol Struct (Theochem) 807:67–72
48. Britun VF, Kurdyumov AV, Borimchuk NI, Yarosh VV (2007) Diamond Relat Mater 16:267–276
49. Le Godec Y, Martinez_Garcia D, Solozhenko VL, MezouarM, Syfosse G, Besson JM (2000) J Phys Chem Solids 61:1935–1938
50. Solozhenko VL, Lazarenko AG, Petitet JP, Kanaev AV (2001) J Phys Chem Solids 62:1331–1334
51. Lödwin PR (1955) Phys Rev 97:1474–1489
52. Wiberg KB (1968) Tetrahedron 24:1083–1096
53. This is one third of the difference between π* DE of these two types of BN unit since only one third of BN units of a given type are dispensed with π* NBOs
54. Minyaev RM (2000) J Struct Chem 41:1–10