

# BN-naphthalene and carbon-containing derivatives: an ab initio study

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## Abstract

Ab initio calculations are used to examine the stability of various isomers of benzene and naphthalene after substitution of pairs of carbon atoms by the isoelectronic boron–nitrogen (BN) tandem. It is found that stability is enhanced by keeping the B and N atoms adjacent to one another. When multiple pairs of BN are present, these pairs prefer to be consecutive with one another. The energy is also lowered by maintaining the heteroatoms on the same ring of naphthalene. Another factor is the preference that consecutive carbon atoms be grouped into even numbers. Successively higher degrees of substitution lead to a regular drop in the molecular valency, as well as increased hardness. © 1997 Elsevier Science B.V.

**Keywords:** Azaborine; Borazine; Molecular valency; Hardness

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## 1. Introduction

The chemistry of the boron atom is dominated by its so-called electron deficiency when incorporated into molecular systems, as in compounds containing boron bonded to N, P, etc. Molecules of the type  $R_3N-BR_3$  have attracted a great deal of attention by both experimental and theoretical chemists, especially because of the similarities of the BN unit to the isoelectronic CC unit of conventional organic compounds. One such interesting compound is borazine,  $B_3N_3H_6$  [1,2]. Owing to its formal structural resemblance to benzene and their very similar physical properties [3], borazine is sometimes referred to as “inorganic benzene”. Laubengayer et al. [4] proposed that the biphenyl analogue  $B_6N_6H_{10}$  and the

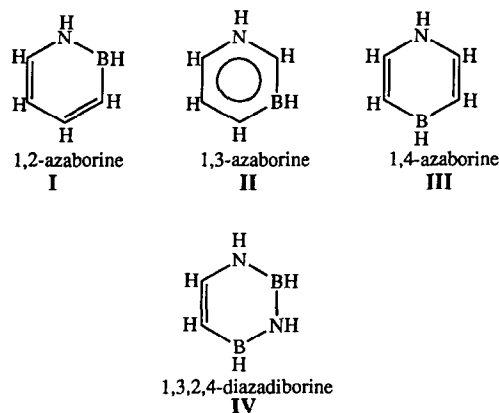
naphthalene analogue  $B_5N_5H_8$  were formed during the gas-phase pyrolysis of borazine. These species were then identified by Manatov and Margrave [5] in gas-phase mass spectrometric analysis. Recently, Sneddon and co-workers [6] reported the experimental (X-ray) geometries of  $B_6N_6H_{10}$  and  $B_5N_5H_8$ , and concluded that these are the primary structural units of the BN polymer. Another interesting compound is boron nitride (BN), the non-oxide ceramic, which is similar to graphite in physical properties and has a graphite-like layer structure of alternating B and N. Like the conversion of graphite to diamond, the layer structure of BN can be converted to a tetrahedral diamond-like structure which is known as boraxon. These two compounds are sometimes referred to as “inorganic graphite” and “inorganic diamond”, respectively. Paine and Narula [7], in a review article, pointed out that boron nitride is a fascinating ceramic with a potentially bright future in advanced materials.

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Chart 1



Scheme 1.

The replacement of a pair of carbon atoms in benzene by B and N leads to a series of heterocyclic molecules. Of the three structural isomers (Scheme 1), 1,2-azaborine (**I**) where B and N atoms are adjacent, is found to be most stable by MNDO [8] and ab initio calculations [9]. MNDO has also been

applied by Massey and Zoellner [10] to diazadiborine, where two CC units are replaced by two BN pairs. The authors considered 11 possible six-membered ring isomers and found that the 1,3,2,4-diazadiborine (**IV** in Scheme 1) is the most stable. These studies indicate that BN-substituted benzene molecules are most stable when the BN replacements are consecutive, with alternating boron and nitrogen atoms. The present study continues this work by using a more accurate ab initio method to investigate the effect of successive BN replacement in six-membered rings. The theoretical framework is extended beyond the benzene paradigm by considering a pair of fused rings as in naphthalene derivatives. We enquire into the energetic effects of various BN-substitutions on one or both rings simultaneously.

## 2. Method of calculation

The six-membered rings and fused-ring systems were optimized at the SCF/6-31G\* level. To assess the role of

Table 1

Total energies ( $E/\text{au}$ ), relative energies ( $E_{\text{rel}}/\text{kcal mol}^{-1}$ ), zero-point energies ( $\text{ZPE}/\text{kcal mol}^{-1}$ ), molecular valencies ( $V_M$ ) and hardness ( $\eta/\text{eV}$ ) of the six-membered ring systems (see Fig. 1)

System	$E^a$	$E_{\text{rel}}^a$	$\text{ZPE}^{a,b}$	$V_M$	$\eta$
<b>A</b>	–230.70314		67.57(0)	14.50	6.53
	–230.71109		67.50(0)		
	–231.48719		63.21(0)		
<b>B</b>	–234.13353		65.65(0)	13.68	5.85
	–234.14229		65.56(0)		
	–234.90424		62.10(0)		
<b>C</b>	–237.62167	0.0	63.72(0)	12.88	6.29
	–237.63110	0.0	63.66(0)		
	–238.37175	0.0	60.71(0)		
<b>D</b>	–237.55484	41.94	63.53(0)	13.10	5.32
	–237.56526	41.32	63.42(0)		
	–238.31452	35.91	60.42(0)		
<b>E</b>	–237.52311	61.85	63.62(0)	13.15	4.33
	–237.53349	61.25	63.61(0)		
	–238.31122	37.98	60.54(0)		
<b>F</b>	–241.15101		62.01(0)	12.16	7.89
	–241.16121		62.00(0)		
	–241.88248		59.42(0)		

<sup>a</sup> The three values correspond to HF/6-31G\*, HF/6-31 + G\* and MP2/6-31G\*, respectively.

<sup>b</sup> Number of imaginary frequency.

diffuse functions, the geometries of the smaller single rings were also optimized with the 6-31+G\*\* basis set. Electron correlation was considered using second-order Møller–Plesset (MP2) theory. Stationary points for all systems were characterized as minima by harmonic vibrational frequency calculations.

### 3. Results and discussion

#### 3.1. Six-membered ring

Fig. 1 shows the geometric parameters of benzene (A), BN-substituted benzene (B–E) and borazine (F).

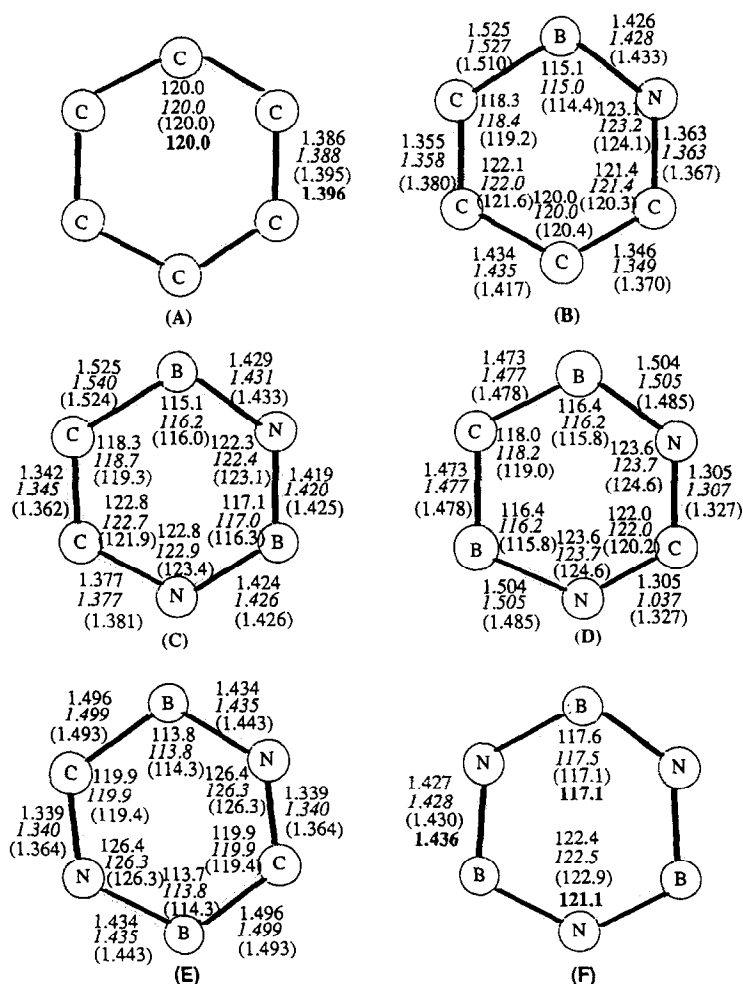


Fig. 1. Six-membered ring geometries (in Å and degrees). Hydrogen atoms are not shown in the diagrams. Plain, RHF/6-31G<sup>+</sup>; italics, RHF/6-31+G<sup>+</sup>; parentheses, MP2/6-31G<sup>+</sup>; bold, experimental.

optimized at the HF/6-31G<sup>+</sup>, HF/6-31+G<sup>+</sup> and MP2/6-31G<sup>+</sup> levels. Since previous studies [8,9] had already confirmed that the 1,2-azaborine (**B** in Fig. 1) is the most stable isomer, we have not considered other isomers of azaborines in the present investigation. Those earlier studies indicate that the isomer with adjacent B and N atoms is the most stable. In the case of diazaborines, three isomeric forms (C–E) were considered. It can be seen from Table 1 that the 1,3,2,4-diazaborine (C), where BN groups are consecutive, is the most stable.

Comparing the 6-31G<sup>+</sup> and 6-31+G<sup>+</sup> results (Fig. 1 and Table 1), it can be concluded that diffuse functions have only a negligible effect on the geometries

and relative energies of the isomers, suggesting that 6-31G\* is a satisfactory basis set for systems containing B and N. On the other hand, electron correlation can be important for certain aspects of the present systems. Experimental geometries of benzene (**A**) [11] and borazine (**F**) [12] are particularly well reproduced by MP2/6-31G\* (see Fig. 1).

The MP2/6-31G\* optimized BN single and double bond lengths in ammoniaborane ( $\text{H}_3\text{N}-\text{BH}_3$ ) and aminoborane ( $\text{H}_2\text{N}=\text{BH}_2$ ), respectively, are 1.661 and 1.393 Å. The corresponding experimental values are 1.61 [13] and 1.40 Å [14], respectively. The BN bonds in borazine, 1.430 Å, are slightly longer than

the double bond in aminoborane. In fact, the BN distances in all stable isomers (**B** and **C**) of azaborine and diazadiborine are in the 1.425–1.433 Å range, similar to borazine.

Besides the energies of the systems, their molecular valency ( $V_M$ ) [15] and hardness [16] values are listed in the last two columns of Table 1. The molecular valency is a measure of the covalent character of a given system, i.e.  $V_M$  is equal to the sum of the covalent bond orders. As an example, benzene contains six CH single bonds, and six CC single bonds. Adding the three classical double bonds leads to a total sum of purely covalent CC and CH bond orders of 15. (The

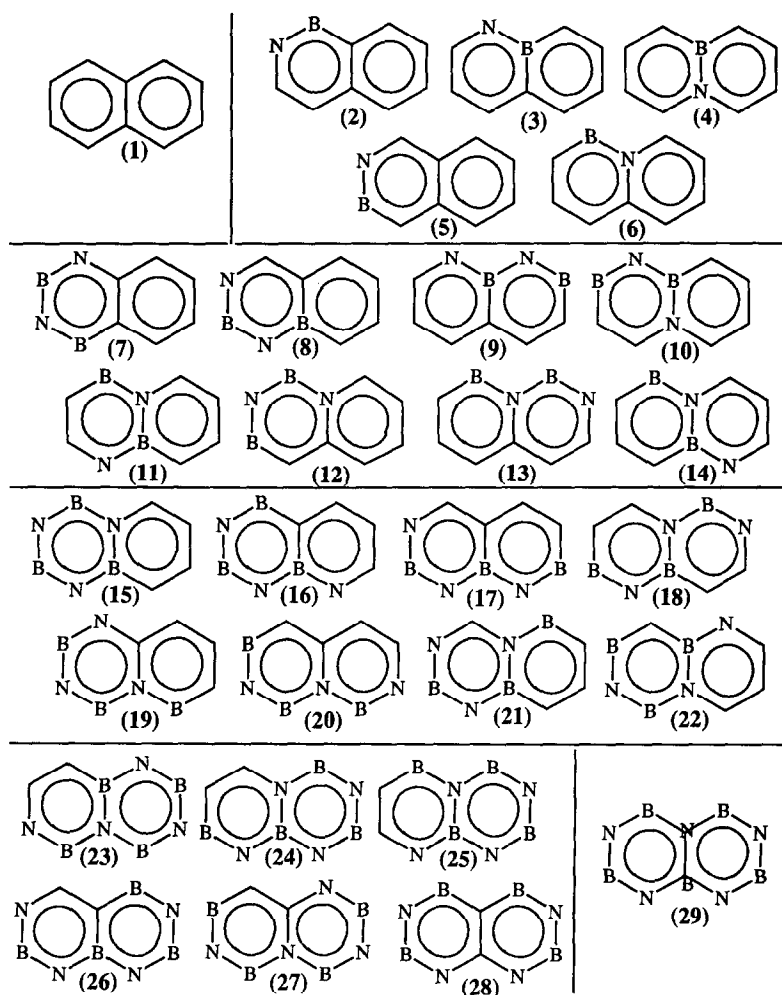


Fig. 2. Fused ring isomers optimized at the RHF/6-31G\* level. Hydrogen atoms are omitted for clarity.

actual  $V_M$  is slightly lower than 15 due to the partial ionic character of the CH bonds.) As is evident from Table 1,  $V_M$  decreases as the number of BN groups in the six-membered ring increases. This change is due to the partial ionic character of each BN bond, in addition to heteronuclear BH and NH bonds. In the series, running from benzene to borazine, the molecular valence undergoes a progressive decrease.

The maximum hardness principle for molecular systems was originally introduced by Pearson [17]: “there seems to be a rule of nature that molecules arrange themselves so as to be as hard as possible”. Hardness has been conceived as a measure of the stability of a system. Numerical results indicate that

higher  $\eta$  is associated with a lower energy of the isomer. In the case of diazadiborane the highest  $\eta$  value of 6.29 is found for the most stable isomer C, confirming this presumption.

Pearson [17] also pointed out that a hard molecule resists distortions in its electronic charge cloud. Not only are changes in the total amount of charge resisted, but the same is true for changes in the charge distribution in space. Borazine is found to be harder than benzene, with  $\eta$  equal to 7.89 and 6.53, respectively. This distinction may be understood on the basis that the electronegativity difference between B and N causes the electron pairs to shift towards the N atoms, thus forming the polar covalent BN bonds in borazine.

Table 2

Total energies ( $E/\text{au}$ ), relative energies ( $E_{\text{rel}}/\text{kcal mol}^{-1}$ ), zero-point energies (ZPE/ $\text{kcal mol}^{-1}$ ), molecular valencies ( $V_M$ ) and hardness ( $\eta/\text{kcal mol}^{-1}$ ) of the most stable isomers of BN-naphthalenes (see Fig. 2)

System	$E$	$E_{\text{rel}}$	ZPE	$V_M$	$\eta$
1	-383.35505		99.24	23.32	5.31
2	-386.79679	0.0	97.43	22.41	5.40
3	-386.77584	13.13	98.11	22.37	4.85
4	-386.77238	15.30	97.85	22.40	5.64
5	-384.77219	15.42	97.21	22.51	4.65
6	-386.76303	21.17		22.37	4.88
7	-390.28805	0.0	95.41	21.57	5.54
8	-390.26198	16.36	96.23	21.58	4.96
9	-390.26189	16.42	96.08	21.53	5.01
10	-390.25885	18.32	95.92	21.60	5.52
11	-390.25780	18.98			
12	-390.24839	24.09			
13	-390.24716	25.66			
14	-390.20608	51.44			
15	-393.78665	0.0	94.30	20.86	5.63
16	-393.75531	19.67	94.36	20.73	5.36
17	-393.75303	21.10	94.26	20.76	5.32
18	-393.74924	23.47	94.19	20.79	6.12
19	-393.74315	27.30			
20	-393.73769	30.72			
21	-393.69694	56.29			
22	-393.69350	58.45			
23	-397.27625	0.0	92.49	20.05	6.26
24	-397.27624	0.01	92.38	20.05	6.15
25	-397.27064	3.52	92.21	19.99	6.06
26	-397.25099	15.85	92.63	19.96	5.97
27	-397.23795	24.03			
28	-397.21962	35.54			
29	-400.80437		90.72	19.32	7.35

This interpretation is in accordance with the lower  $V_M$  value of borazine compared to benzene. Since the electron pairs are more delocalized in benzene, compared to borazine, the former can be thought of as softer than the latter.

### 3.2. Fused-ring systems

The fused-ring isomers studied are shown in Fig. 2. Beginning with naphthalene **1**, various pairs of C atoms have been replaced by the B–N combination, all the way up to total replacement in compound **29**. The computed data for these species are organized in Table 2 into groups, depending upon the number of B–N pairs. Molecules **2–6** all contain one such pair, **7–14** contain two, and so on. The most stable of each set is assigned a relative energy of zero. For the sake of simplicity, hydrogens are omitted from Fig. 2.

Since the results obtained in the previous section for six-membered ring systems indicate that diffuse functions have little effect on the geometric parameters and relative energies, only the 6-31G\* basis set is used for geometry optimization here. Electron correlation at the MP2 level is employed to further refine the geometries of the most stable isomer in each group of BN-substituted fused ring systems. Vibrational frequency analyses confirm the planarity of all BN-substituted naphthalene.

Isomers obtained by replacing one CC unit of naphthalene by one BN unit are referred to as mono-azamonoboranaphthalene, or simply 1-BN-naphthalene. Only those isomeric forms (**2–6**) where B and N are adjacent were considered because that arrangement was found to be most stable. It can be seen from Table 2 that isomer **2**, 1-bora-2-azanaphthalene, is most stable out of the five isomers considered. When the B atom is situated at a ring fusion position, as in **3**, the system is less stable by 13 kcal mol<sup>-1</sup>. Higher in energy by another 2 kcal mol<sup>-1</sup> are isomers **4** and **5** where the B and N atoms are both at fusion positions or both at  $\beta$ -positions. It is interesting that isomer **6** is even less stable; **6** is similar to **3** except that the B and N atoms switch positions.

The fourth column of Table 2 reports the total zero-point vibrational energy (ZPE) of the first few stable isomers in each group of BN-substituted naphthalene. The results indicate there are no dramatic differences from one isomer to the next in any group, and cer-

tainly not enough to reverse any of the conclusions derived from analysis of electronic energies alone. There is a pattern evident that each substitution of a pair of C atoms by B–N yields a slight reduction in the ZPE, of roughly 2 kcal mol<sup>-1</sup>.

Another property that shows little sensitivity to the specific isomer in each group is  $V_M$ . For example, this quantity varies only between 22.37 and 22.51 for the five isomers **2–6**. It is not a good indicator of the energy, since the most stable structure **2** takes a value of 22.41, not on either extreme of the range.  $V_M$  does show a pattern of steady reduction as the C–C units are replaced by B–N. This reduction is something less than one unit for each such replacement. Nor does  $\eta$  serve as a good indicator of the stability of the various isomers. While there is some tendency for this quantity to be larger for the most stable isomer, there are examples where a less stable isomer is associated with an even larger value of  $\eta$ .

Previous MNDO [10] and our own ab initio calculations on six-membered ring systems demonstrated the greater stability of consecutive BN units when there are more than one. The present study is hence limited to isomers where the B–N pairs are consecutive. Nevertheless, even this limitation leads to eight interesting isomeric forms of diazadiboranaphthalene (2-BN-naphthalene). Isomer **7** places all four heteroatoms in  $\alpha$  or  $\beta$  positions, i.e. the fused-ring positions are occupied by C only. It is this particular isomer that is found to be most stable in this group. Allowing a B

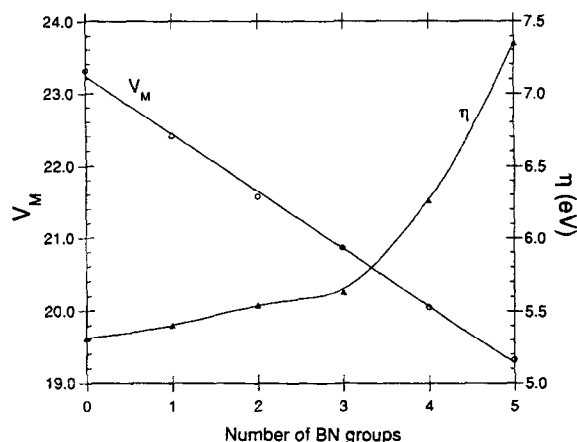


Fig. 3. Molecular valency ( $V_M$ ) and hardness ( $\eta$ ) of the most stable isomers in the substituted fused-ring systems versus the number of BN groups in the ring.

atom to occupy one of the fused-ring positions leads to a 16 kcal mol<sup>-1</sup> higher energy, as noted in Table 2 for isomers **8** and **9**. Even less stable are isomers **12** and **13** where the fused-ring position is occupied by nitrogen. Isomers **10**, **11** and **14** share the feature that they all permit occupation of both fused-ring positions by B and N. The energies of **10** and **11** are only 18 or 19 kcal mol<sup>-1</sup> higher than the most stable isomer, whereas the relative energy of **14** is fully 51 kcal mol<sup>-1</sup>. The principal distinction is that the former two isomers place all four of the heteroatoms on a single ring, whereas the B and N atoms are located

on both rings in **14**. An alternate means of understanding the high energy of **14** is via the organization of carbon atoms. Whereas all the other 2-BN-naphthalenes examined permit the carbons to either all be consecutive with one another (**7–9**, **12** and **13**) or to occur in a group of two and a group of four (**10** and **11**); the carbon atoms are grouped in two sets of three in isomer **14**.

The latter themes are carried over into the 3-BN-naphthalenes **15–22** where the most stable isomer (**15**) places all six heteroatoms on the same ring. If this is not the case, then occupation of a single

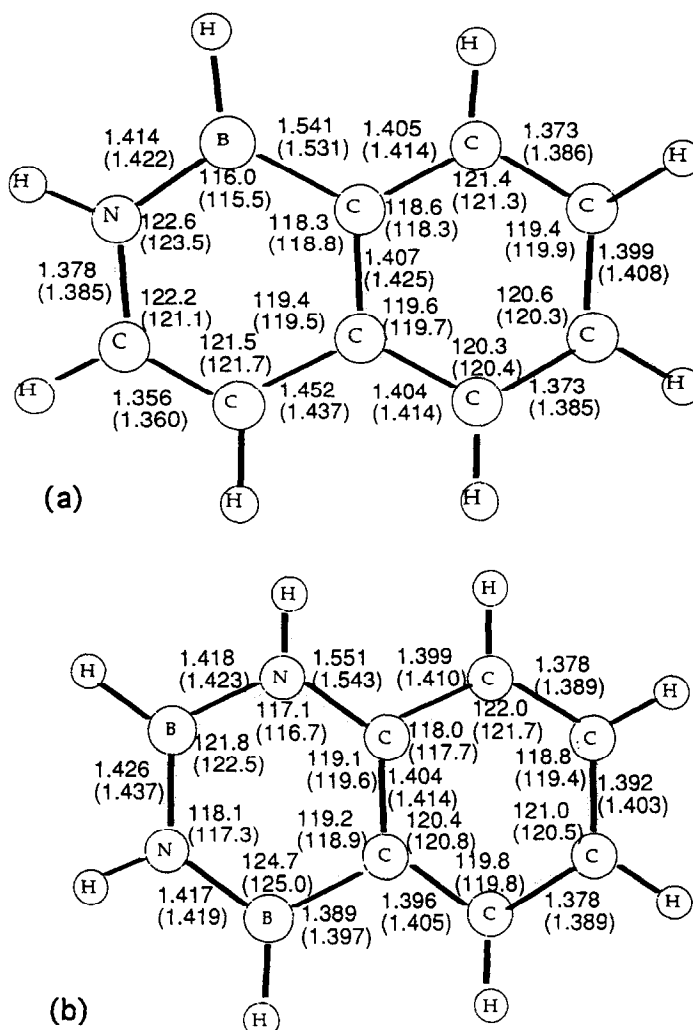


Fig. 4. HF/6-31G\* (MP2/6-31G\*) geometries (in Ångströms and degrees) of the most stable isomer of: (a) 1-BN-naphthalene; (b) 2-BN-naphthalene.

fused-ring site by a B atom is preferred, as in **16** and **17** which lie about 20 kcal mol<sup>-1</sup> higher in energy. **19** and **20**, characterized by a nitrogen at a single fused-ring site, are 8–22 kcal mol<sup>-1</sup> higher still. The other three 3-BN-naphthalenes studied occupy both fused-ring sites by a B–N pair. **21** and **22** are far higher in energy than **18**, a distinction which may be associated with the carbon arrangement. The carbon atoms occur in even-numbered consecutive sets in **15**–**20**, i.e. in groups of two or four. In contrast, the carbon atoms are isolated in odd-numbered sets of one and three in both **21** and **22**.

Six isomers of tetraazatetraboranaphthalene or 4-BN-naphthalene were considered. The three most stable, **23**–**25**, within 3 kcal mol<sup>-1</sup> of one another, all contain a fully substituted ring. Of these three, **25** is the least stable, which may be associated with the fact that the B and N atoms in the partially substituted ring are not adjacent to one another, as they are in **23** and **24**. With regard to the latter two isomers, application of MP2 suggests that **24** is more stable than **23** by 4.5 kcal mol<sup>-1</sup>. The other three 4-BN-naphthalenes carry over a pattern mentioned above for the less-substituted molecules. There is a

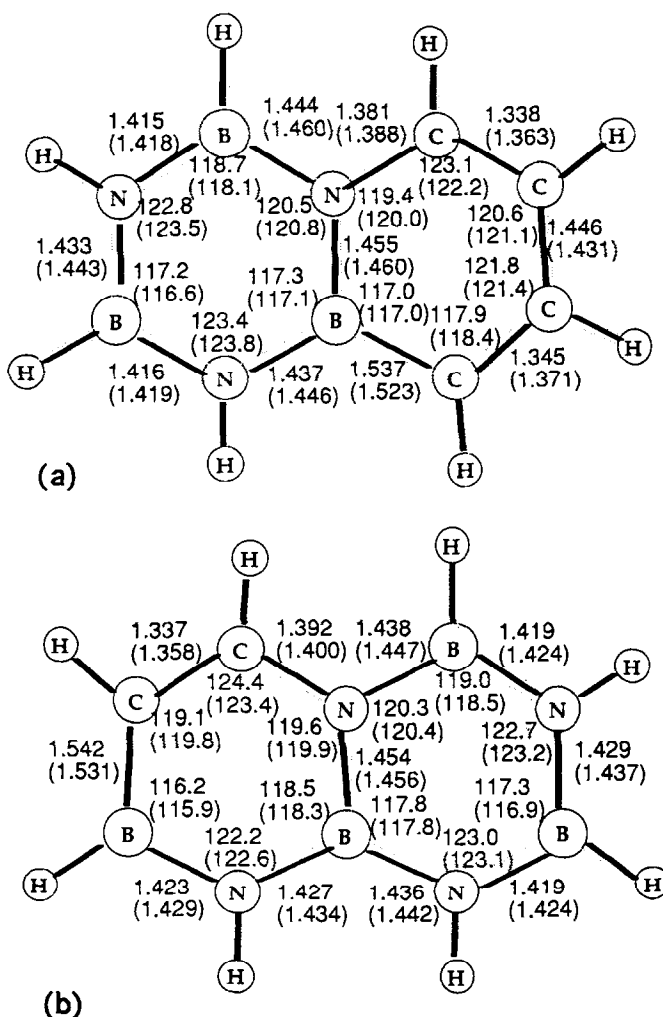


Fig. 5. HF/6-31G\* (MP2/6-31G\*) geometries (in Ångströms and degrees) of the most stable isomer of: (a) 3-BN-naphthalene; (b) 4-BN-naphthalene.



preference for a single substituted fused-ring position to be occupied by B (**26**) over N (**27**). **28** is highest in energy, perhaps because it breaks up the consecutive nature of the eight heteroatoms into two groups of four.

As noted above, replacement of each CC pair by BN decreases the covalent character of the system. In fact, a nearly linear correlation (Fig. 3) is observed between  $V_M$  and the number of such BN groups. Electron pairs become more localized (around N atoms) in the BN-naphthalene series and hence pentaazapenta-

boranaphthalene or 5-BN-naphthalene (**29**) is harder than its organic counterpart, naphthalene (**1**). This finding is directly reflected in the  $\eta$  value.  $\eta$  increases as more and more CC pairs are replaced by BN (see Fig. 3) and is highest for fully substituted BN-naphthalene. It is interesting to note that this plot is far from linear and shows evidence of a sharp rise as the number of BN pairs increases beyond three.

The geometric parameters obtained at the SCF/6-31G\* and MP2/6-31G\* levels of the most stable isomers of the BN-substituted naphthalenes are

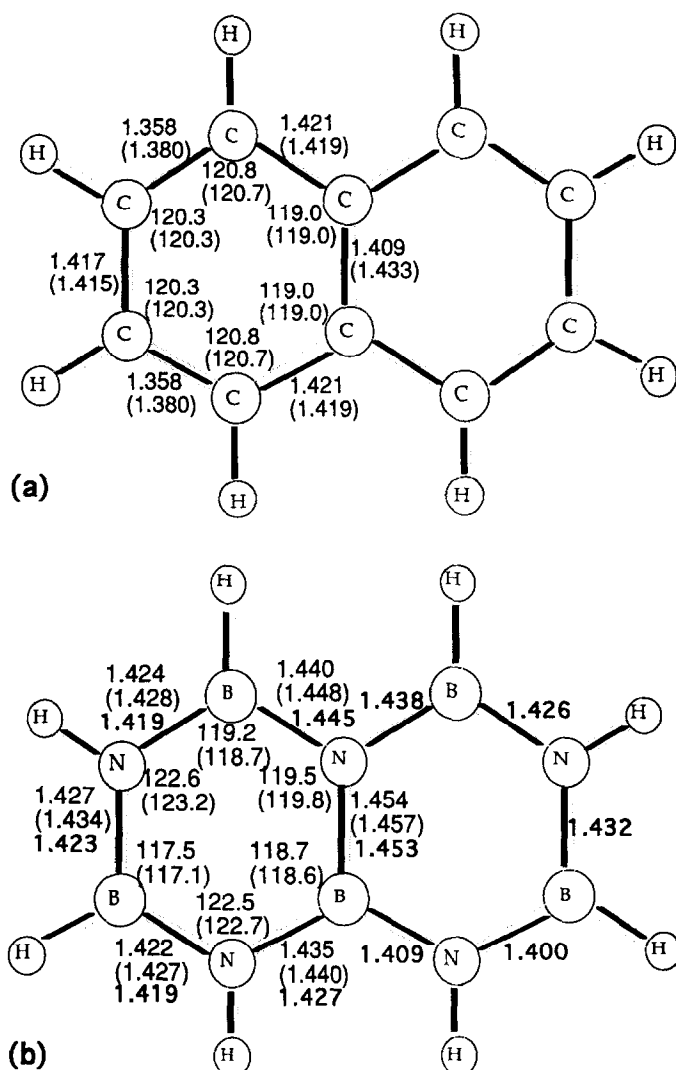


Fig. 6. HF/6-31G\* (MP2/6-31G\*) experimental geometries (in Ångströms and degrees) of: (a) naphthalene; (b) BN-naphthalene. The two rings in the experimental structure are not equivalent as they are in the two computed geometries.

illustrated in Figs. 4–6. The BN bond lengths cover a range between 1.418 and 1.460 Å at the MP2/6-31G<sup>\*</sup> level, which may be compared with the 1.425–1.433 Å range for the most stable benzene isomer analogues, where one, two or all three C–C pairs are replaced by B–N. The experimental bond lengths of BN-naphthalene [6] are given in Fig. 6. It can be seen that the HF/6-31G<sup>\*</sup> values are in good agreement with the corresponding experimental values. MP2 values are slightly higher than the experimental values. It is worthwhile to mention that several attempts of optimization at both HF and MP2 levels of the unsymmetric form of BN-naphthalene as reported by Sneddon and co-workers [6] led to a symmetric structure.

#### 4. Conclusions

Replacement of CC pairs of aromatic rings like benzene and naphthalene by the isoelectronic BN combination is most favourable when the B and N atoms are kept adjacent to one another. Moreover, when replacing multiple pairs of CC atoms, the BN pairs prefer to be consecutive with one another, as in 1,3,2,4-diazadiborine. In the case of a pair of fused rings as in naphthalene, a single BN pair is most favourably disposed on the  $\alpha$  and  $\beta$  positions, avoiding the fused-ring locations.

Even keeping the BN pairs consecutive leads to a large number of possible isomers for multiple substitutions in naphthalene. Two such pairs will prefer to occupy the two  $\alpha$  and two  $\beta$  positions of a single ring, leaving the fused-ring positions occupied by C. Distributing the BN pairs such that they spread over both rings is a particularly unstable arrangement. This trend is especially evident with three pairs where the most stable isomer has all six heteroatoms on a single ring. It appears that another factor to be considered is the number of C atoms that are adjacent to one another. Odd-numbered sets of carbons, e.g. one and three, lead to much higher energies than do even-numbered sets like two and four.

Molecular valency  $V_M$  is lowered and hardness  $\eta$  rises with each progressive substitution of CC by BN.

In fact, one can observe a nearly linear correlation between the number of such substitutions and  $V_M$ . On the other hand, these parameters are fairly insensitive to the particular positions of the BN atoms within the various isomers, so would not serve as good indicators of their relative energies.

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