Ab Initio Computational Studies of Heterocycloalkynes: Structures, Natural Bond Orders, Ring Strain Energies, and Isomerizations of Cyclic Iminoboranes and Iminoalanes†

Thomas M. Gilbert

Department of Chemistry and Biochemistry, Northern Illinois University, DeKalb, Illinois 60115

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Ab initio calculations of series of cyclic iminoboranes $(\overline{CH_2)_nB{\equiv}N}$ and iminoalanes $(\overline{CH_2)_n\text{-}Al{\equiv}N}$ show that they adopt angularly distorted structures compared to the isoelectronic cycloalkynes. Natural bond order analyses indicate that the larger ring iminoboranes contain BN triple bonds, but the smaller ring iminoboranes and all the iminoalanes contain MN double bonds and a lone pair on the nitrogen atom. Group equivalent calculations confirm that cyclic iminoboranes and iminoalanes contain less ring strain energy than the corresponding cycloalkynes, but the data do not distinguish between doubly and triply bonded systems. Examination of the rearrangements of isomeric azacycloalkane borines to cyclic iminoboranes shows that they are exothermic, with moderate activation barriers. Thus, a way by which the heterocycloalkynes might be synthesized is suggested.

Small-ring cycloalkynes continue to be a source of intense experimental and theoretical study. Experimentally, Gilbert has recently postulated that cycloalkynes (specifically, cyclopentyne) prepared through dehydrohalogenation of a 1-halocycloalkene are actually complexed to the resulting alkali-metal salt.[1] This has ramifications for the kinetics and stereochemistry of cycloadditions employing cycloalkynes prepared this way. In a related vein, Gilbert and Kirschner have published computational work using AM models indicating that cyclobutyne and cyclopentyne are "lumomers": molecules displaying isomer characteristics based on their frontier orbital patterns.[1−3] However, Johnson and Daoust's[4] more sophisticated second-order Moeller−Plesset (MP2) calculations suggest this is an artifact of the AM model. These authors further used their MP2 data to show that cyclobutyne, cyclopentyne, and cyclohexyne exhibit remarkably large ring strain energies compared to those of the corresponding cycloalkenes and cycloalkanes.

My research group has developed a computational effort meant to compare the reaction behavior and energetics of olefins and alkynes with the isoelectronic group III−group V aminoboranes and aminoalanes $R_2M{=}NR_2$ and iminoboranes[5] and iminoalanes $RM{\equiv}NR$ (M = B, Al).[6,7] It seemed worthy to examine cyclic versions of the last two to see whether the results would address the orbital controversy noted above. I report here the predicted structures of eight heterocycloalkynes, of general formula $(\overline{CH_2)_nM{\equiv}N}$ (M = B, Al; n = 2−5). Natural bond order models of these systems indicate that only the largest cyclic iminoboranes contain BN triple bonds; the smaller ring systems and all the iminoalanes contain MN double bonds and a lone pair on the nitrogen atom. The data show that all these molecules exhibit smaller ring strain energies than the corresponding cycloalkynes. For the smallest cyclic iminoborane, $(\overline{CH_2)_2B{\equiv}N}$ (**4BN**), the ring strain energy is small enough that rearrangement of the isomeric azacyclobutane to **4BN** is exothermic, in contrast to the homologous cyclobutyne. This suggests how one might prepare **4BN** and the larger ring compounds.

Computational Methods

All calculations were performed with the GAUSSIAN-92 or -94 code.[8] Each conformation of every molecule was fully optimized without constraints at the HF/6-31G* level. Several different starting geometries for the compounds were chosen to explore a large region of the potential surface and ensure that the lowest energy conformation was selected. The struc-

† This paper is dedicated to Professor John C. Gilbert, University of Texas, Austin, on the occasions of his 60th and 61st birthdays.

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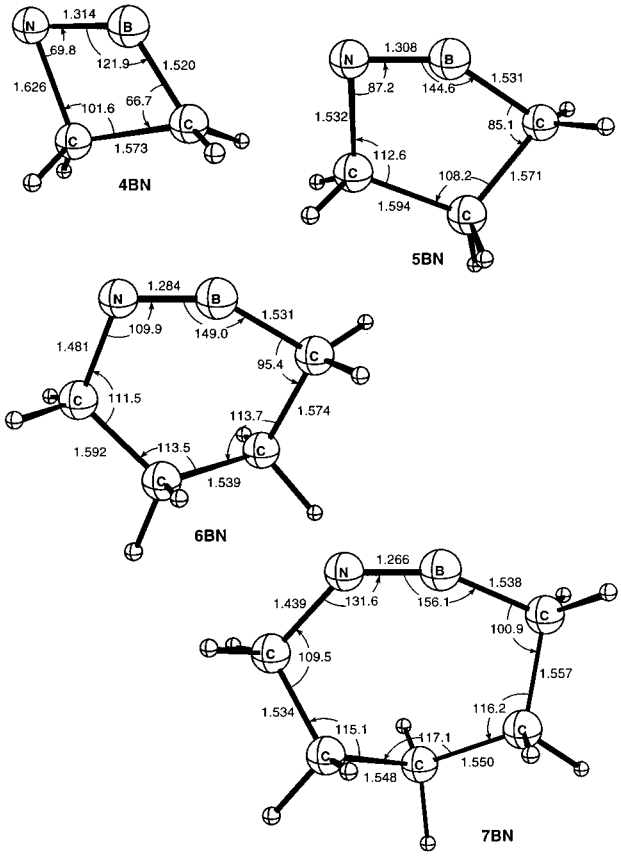

Figure 1. Predicted structures (MP2/6-31G*) of cyclic iminoboranes **4BN**−**7BN**. Distances are in Å and angles in deg.

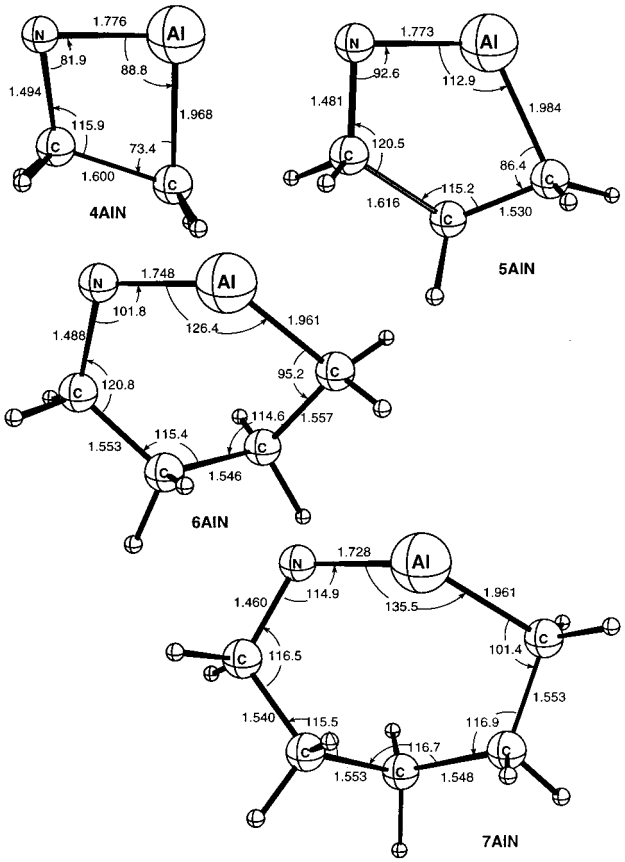

Figure 2. Predicted structures (MP2/6-31G*) of cyclic iminoalanes **4AlN**−**7AlN**. Distances are in Å and angles in deg.

tures were reoptimized at the MP2/6-31G* level; these were used to calculate single-point energies obtained at the MP4(SDTQ)/6-31G* level. The natures of all stationary point structures were assessed by analytical frequency analysis, which also provided zero-point energies (ZPEs). ZPEs were scaled by factors appropriate to the level of the calculational method (0.9135 for HF runs, 0.9670 for MP2 runs).[9,10] Natural bond order analyses were performed at the MP2/6-31G* level using the appropriate keywords in the Gaussian program.[11]

Results and Discussion

Structures of Cyclic Iminoboranes 4BN−7BN and Iminoalanes 4AlN−7AlN. The predicted structures for the 1-bora-2-azacycloalkynes examined appear in Figure 1. The structural parameters follow a pattern consistent with chemical intuition: as ring size increases, the BNC and NBC angles increase, while the BN distance decreases.[12] In contrast to the cycloalkyne analogues, the molecules are highly asymmetric, with the NBC angle being much larger than the BNC angle. This results in unusually long NC distances, particularly for 1-bora-2-azacyclobutyne (**4BN**) (1.626 Å).[12] One sees small BCC angles as well, again most notably in **4BN**, where accommodating the NBC angle of 121° forces the BNC and BCC angles to values less than 70°.

The predicted structures for the 1-alumina-2-azacycloalkynes examined appear in Figure 2. The general structural parameter pattern mimics that of the analogous iminoboranes, but the iminoalanes are more symmetric. This arises because the NAlC angles adopt substantially smaller values than their NBC counterparts. As a result, the other molecular parameters exhibit values more consistent with expectation.

Natural Bond Order Analyses of Cycloalkynes and 4BN−7BN and 4AlN−7AlN. To provide a basis for interpreting the natural bond order (NBO) data for the heterocycles, it is instructive to examine the NBO results for cyclobutyne, cyclopentyne, and cyclohexyne. The analyses provide a useful picture of the triple bond in small-ring cycloalkynes. In each case the model depicts it as consisting of one σ and two π bonds, in accord with chemical intuition. However, owing to the compressed CC≡C angles, the σ orbital and one π bonding orbital are distinctly distorted. Relevant data appear in Table 1. The Δ heading represents the deviation of the bond molecular orbital from the line of the nuclear centers (bond axis). Thus, for a σ bond the ideal value is 0°, while for a π bond the ideal value is 90°. The π_1 bond is that in the pseudo-plane of the ring. In cyclobutyne, the σ component lies 17.3° and the π_1 component 123.5° off the bond axis. This results in sizable mixing of carbon s and p atomic orbitals in formation of the molecular orbitals; the σ MO, ideally an sp hybrid, is characterized as $sp^{1.35}$, corresponding to 42.5% s and 57.3% p character. The π_1 orbital is $sp^{8.04}$, corresponding to 11.0% s character and 88.8% p

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(12) By way of comparison, the predicted values in MeBNMe are BN = 1.252 Å, BC = 1.550 Å, NC = 1.416 Å.

Table 1. Natural Bond Order Data for Cycloalkynes

	bond/ e⁻ pair	Δ	% C_1 s	% C_1 p	% C_2 s	% C_2 p	hybrid
$C_2H_4C{\equiv}C$	σ	17.3	42.5	57.3	42.5	57.3	$sp^{1.35}$
	π_1	123.5	11.0	88.8	11.0	88.8	$sp^{8.04}$
$C_3H_6C{\equiv}C$	σ	12.7	45.1	54.8	45.1	54.8	$sp^{1.21}$
	π_1	116.1	7.2	92.8	7.2	92.8	$sp^{13.0}$
$C_4H_8C{\equiv}C$	σ	7.3	47.5	52.4	47.5	52.4	$sp^{1.10}$
	π_1	108.7	4.7	95.2	4.7	95.2	$sp^{20.4}$

character. The data show that the atomic orbital characteristics and the resulting hybridizations change as expected with ring size. As the CC≡C*C* axis becomes more linear from cyclobutyne to cyclohexyne, the σ bond orbitals approach sp hybridization, and the π bond increases in pure p orbital character. Concomitantly, the deviations of the orbitals from the ideal values decrease.

The NBO results unfortunately provide little insight into the question of orbital inversion in cyclobutyne and cyclopentyne, as suggested by Gilbert and Kirschner.[1] The π_1 orbital certainly deviates from the ideal orientation perpendicular to the bond axis but contains so little atomic s orbital character it is difficult to think of it as unusually hybridized. If the two small cycloalkynes do react in a concerted [2 + 2] fashion, while cyclohexyne does not, the balance of factors causing this is very subtle.

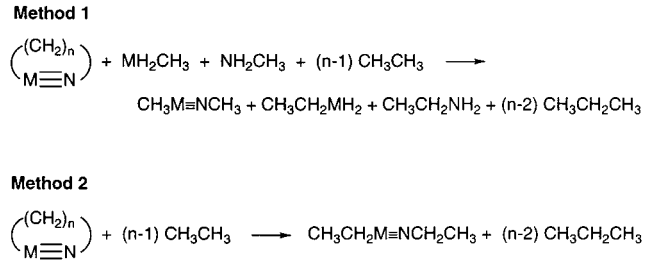
Before looking at the NBO analyses of the cyclic systems, it is useful to examine that for the acyclic MeB≡NMe. The analysis connects the boron and nitrogen atoms in this molecule with a BN triple bond composed of a σ bond and two π bonds. The σ bond comprises a boron $sp^{1.30}$ hybrid (44.5% s and 56.4% p atomic orbital character) and a nitrogen $sp^{0.70}$ hybrid (59% s and 41% p). The π bonds are composed entirely of boron and nitrogen p orbitals and lie at 90° to the B−N axis, just as for a CC triple bond.

NBO analysis of the distorted **4BN** and **5BN** does not reproduce this simple picture (Table 2). The model describes these as containing BN double bonds, with a single π orbital resulting from overlap of boron and nitrogen p orbitals and lying perpendicular to the ring plane. The electrons which previously formed the other π bond become a lone pair localized on the nitrogen atom. One would describe the nitrogen atom as sp^2-hybridized, and the NBO analysis suggests this is reasonable, though approximate. In **4BN**, the σ bond involves an $sp^{1.77}$-hybridized nitrogen atom (36% s, 64% p character); in **5BN**, the nitrogen is $sp^{1.37}$ (42% s, 58% p). However, the lone pair in **4BN** resides in a near-sp-hybrid orbital ($sp^{1.14}$); in **5BN** this orbital contains more p character ($sp^{1.77}$). The σ bond hybrid and the lone pair hybrid should behave complementarily, since they compete for the same orbitals, and they do.

In contrast, the model characterizes the boron atom in both cyclic compounds as little changed electronically from boron in the acyclic system. The σ bond in both involves a boron interpreted as $sp^{1.21}$ hybridized (45% s, 55% p character). This result is in accord with the large NBC angles predicted.

One expects that the geometry around the nitrogen atom, i.e., the relative positions of the lone pair and boron atom, determines whether a second π bond forms between boron and nitrogen. The model indicates that the crossover point occurs at a BNC angle between 87 and 110°, because the NBO analysis characterizes **6BN** and **7BN** as containing BN triple bonds. Interestingly, despite the fact that the C−B−N−C axes are far from linear, the σ bond in each exhibits orbital percentages and hybridizations nearly identical with those of the acyclic molecule. The in-plane π bond in **6BN** contains >97% pure p atomic orbital character (>8.5% in **7BN**), showing that the nitrogen atom can be distinctly nonlinear but still form a triple bond.

Scheme 1



As in the boron analogue above, the NBO analysis of acyclic MeAl≡NMe interprets the wave functions as providing the molecule with a $\sigma/2\pi$ AlN triple bond. The π bonds arise from overlap of exclusively aluminum and nitrogen p orbitals; the σ bond is nearly, but not exactly, an sp hybrid (46% Al s, 54% Al p, $sp^{1.19}$; 53% N s, 47% N p, $sp^{0.90}$).

Despite the higher molecular symmetry, the NBO analysis characterizes **4AlN**−**7AlN** as containing only AlN σ/π double bonds. Thus, the crossover point for the nitrogen lone pair to be donated to the electron-poor aluminum to form the third π bond occurs at an AlNC angle >115°, in stark contrast to the boron system. This presumably arises because of poorer overlap between N 2p and Al 3s/3p orbitals.

The competition between the lone pair and AlN σ molecular orbitals is pronounced in these heterocycles. In **4AlN** and **5AlN**, the σ orbital contains largely N p_x and p_y character (it could almost be called a p^2 hybrid), while the lone pair orbital is ca. 66% N s. In **6AlN**, however, the lone pair is essentially the expected sp hybrid, though the σ orbital still contains excess p character. The balance of the data resembles that for **4BN**/**5BN**, save that as the ring size increases from **4AlN** to **7AlN**, Al s orbital character appears in the Al−N π bond (10% for **7AlN**). This lowers the amount of s character in the Al−N and Al−C σ bonds but does not have a detectable effect on the structural data.

Ring Strain Energies. Ring strain energies provide a way of examining the internal energy of a ring system. We determined the RSEs of the cyclic iminoborane and iminoalane compounds through the use of the group equivalent reactions shown in Scheme 1.[13] Two independent calculations were used to check the self-consistency of the group equivalent method. The results appear in Table 3, along with data for some cycloalkynes.[4] The decrease in RSE resulting from the longer BN and AlN triple bonds as compared to the CC triple bond proves substantial. Of particular note is the 60 kcal difference in RSE between **4AlN** and cyclobu-

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Table 2. Natural Bond Order Data for 4BN−7BN and 4AlN−7AlN (M = B, Al)

	bond/ e⁻ pair	Δ	% M s	% M p	M hybrid	% N s	% N p	N hybrid
$C_2H_4B{\equiv}N$ (**4BN**)	σ	33.3	45.1	54.7	$sp^{1.21}$	36.0	63.7	$sp^{1.77}$
	LP					46.6	53.3	$sp^{1.14}$
$C_3H_6B{\equiv}N$ (**5BN**)	σ	25.2	45.3	54.6	$sp^{1.21}$	42.1	57.5	$sp^{1.37}$
	LP					36.6	63.2	$sp^{1.73}$
$C_4H_8B{\equiv}N$ (**6BN**)	σ	32.5	42.3	57.5	$sp^{1.36}$	55.2	44.5	$sp^{0.81}$
	π_1	127.8	2.5	97.0	$sp^{38.3}$	1.0	98.8	$sp^{98.2}$
$C_5H_{10}B{\equiv}N$ (**7BN**)	σ	19.1	43.7	56.2	$sp^{1.29}$	56.9	42.9	$sp^{0.75}$
	π_1	115.7	0.2	99.5	$sp^{99.5}$	1.4	98.5	$sp^{72.9}$
$C_2H_4Al{\equiv}N$ (**4AlN**)	σ	23.1	53.2	46.0	$sp^{0.87}$	4.3	95.4	$sp^{22.0}$
	LP					67.1	32.8	$sp^{0.49}$
$C_3H_6Al{\equiv}N$ (**5AlN**)	σ	21.2	46.9	52.3	$sp^{1.12}$	7.5	92.2	$sp^{12.2}$
	LP					64.3	35.7	$sp^{0.55}$
$C_4H_8Al{\equiv}N$ (**6AlN**)	σ	18.2	44.9	54.4	$sp^{1.21}$	20.7	79.0	$sp^{3.81}$
	LP					48.5	51.4	$sp^{1.06}$
$C_5H_{10}Al{\equiv}N$ (**7AlN**)	σ	10.9	45.3	54.0	$sp^{1.19}$	23.4	76.3	$sp^{3.26}$
	LP					42.1	57.8	$sp^{1.37}$

Table 3. ZPE-Corrected MP4/6-31G*//MP2/6-31G* Energies (hartree) and Derived Ring Strain Energies (kcal mol^{-1}) for 4BN−7BN and 4AlN−7AlN

	MP4 cor	RSE 1	RSE 2
CH_3CH_3	−79.458 178		
$CH_3CH_2CH_3$	−118.610 856		
BH_2CH_3	−65.625 743		
AlH_2CH_3	−282.831 949		
NH_2CH_3	−95.476 079		
$BH_2CH_2CH_3$	−104.774 774		
$AlH_2CH_2CH_3$	−321.976 531		
$NH_2CH_2CH_3$	−134.633 694		
$CH_3B{\equiv}NCH_3$	−158.851 437		
$CH_3CH_2B{\equiv}NCH_2CH_3$	−237.156 878		
$CH_3Al{\equiv}NCH_3$	−375.991 263		
$CH_3CH_2Al{\equiv}NCH_2CH_3$	−454.296 927		
$C_2H_4C{\equiv}C$			105.7[4]
$C_2H_4B{\equiv}N$ (**4BN**)	−157.600 392	62.5	61.7
$C_2H_4Al{\equiv}N$ (**4AlN**)	−374.766 366	43.3	45.4
$C_3H_6C{\equiv}C$			73.9[4]
$C_3H_6B{\equiv}N$ (**5BN**)	−196.770 126	51.7	51.0
$C_3H_6Al{\equiv}N$ (**5AlN**)	−413.931 407	35.5	37.7
$C_4H_8C{\equiv}C$ (MP2)			41.2[4]
$C_4H_8B{\equiv}N$ (**6BN**)	−235.953 826	32.3	31.5
$C_4H_8Al{\equiv}N$ (**6AlN**)	−453.094 980	28.7	30.8
$C_5H_{10}B{\equiv}N$ (**7BN**)	−275.124 099	21.2	20.5
$C_5H_{10}Al{\equiv}N$ (**7AlN**)	−492.258 768	21.7	23.9

tyne. Also notable is the observation that **6BN** and **6AlN**, and **7BN** and **7AlN**, exhibit similar RSEs despite the fact that the iminoboranes contain triple bonds, while the iminoalanes contain double bonds and a lone pair.

Comments on the Nature of 4BN. A reviewer wondered whether one should view **4BN** as a complex of ethene and BN, which would account for its very long NC distance, rhomboidal structure, maintenance of the nitrogen lone pair, and lowered RSE compared to cyclobutyne. The long NC distance and lowered RSE coincide with prior comparisons between BN and CC systems,[7] but the extent to which the parameters for **4BN** differ from those for cyclobutyne is unusual. Thus, the point is well taken. However, answering it poses difficulties, some of which are semantic (how does one distinguish a covalent bond from a strong dative bond?)[14]

One simple approach to addressing the question involves comparing the energies of ethene and BN with that of **4BN**. These were determined at the MP4/6-311+G**//MP2/6-311+G** level in order to minimize the effect of basis set superposition error but were not corrected for zero point effects. **4BN** lies 74.3 kcal mol^{-1} lower in energy than the summed component molecules. This value represents the gain in energy resulting from the formation of the NC and BC bonds minus the loss in energy resulting from decreasing the CC and BN bond orders, making the carbon atoms more tetrahedral and forming a strained four-membered ring. Using bond energies gleaned from several sources[15−17] and the RSE of **4BN** determined above, one calculates that the value should equal about 92 kcal mol^{-1}. Given the assumptions and approximations made in attaining this result, one should probably not view this as substantively different from the 74.3 kcal mol^{-1} determined theoretically. Therefore, it appears that the BC and NC bonds are covalent rather than dative. However, more reassuring evidence for this view awaits further calculations and experiments.

Rearrangement of Cycloazineborines to Cyclic Iminoboranes. While no cycloalkynes smaller than cyclooctyne are isolable, the RSE data suggest that far smaller cyclic iminoboranes and iminoalanes could be. Stabilizing such compounds will require sterically demanding groups at the 3- and *n*-carbon positions to inhibit polymerization;[5] synthesizing them probably requires a different route than those employed previously to prepare acyclic examples.[5,18] Cycloalkynes are often prepared through rearrangement of a cycloalkylidenecarbene; this process was studied computationally

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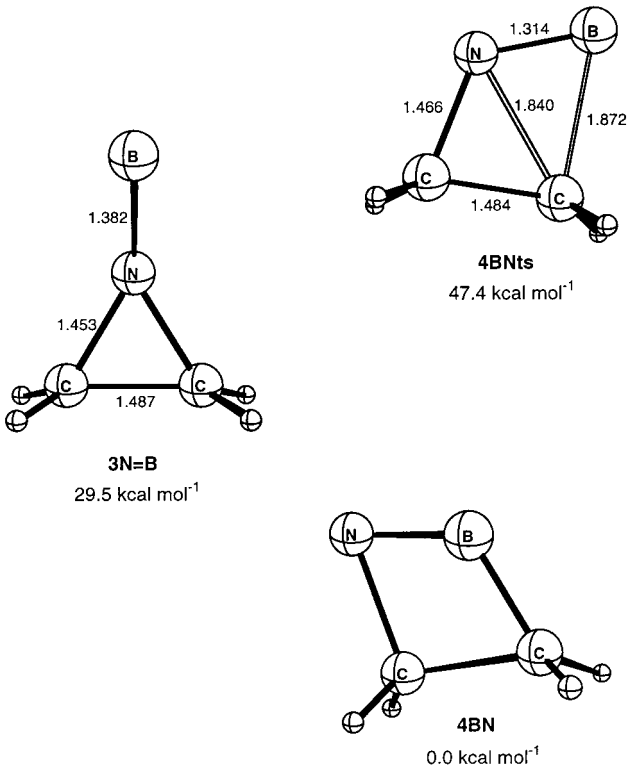

Figure 3. Predicted structures (MP2/6-31G*) and energies (MP4/6-31G*//MP2/6-31G*) for the rearrangement of **3N=B** to **4BN**. Distances are in Å.

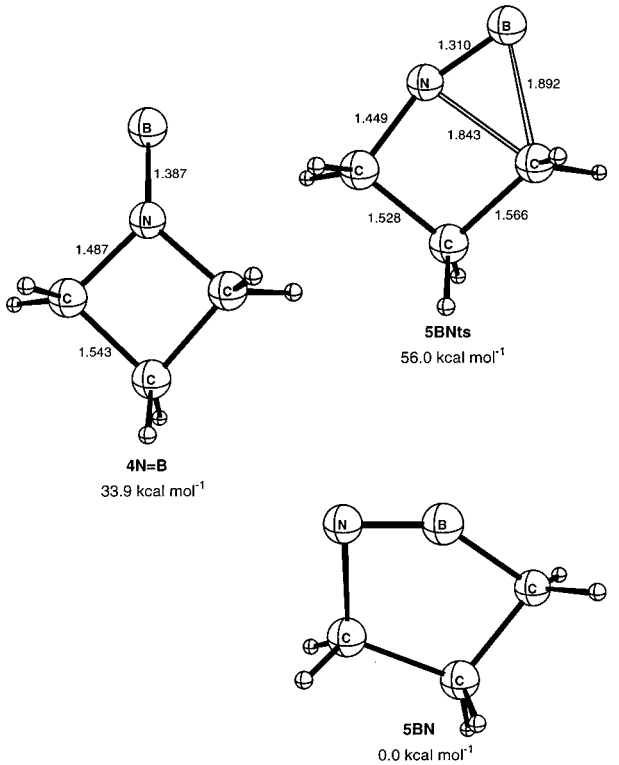

Figure 4. Predicted structures (MP2/6-31G*) and energies (MP4/6-31G*//MP2/6-31G*) for the rearrangement of **4N=B** to **5BN**. Distances are in Å.

by Johnson and Daoust.[4] They showed that the exocyclic carbene cyclopropylidenecarbene is favored over cyclobutyne but that the reverse held for larger systems. It seemed worthy to examine the analogous boron−nitrogen systems to see if the lower strain energy in **4BN** would change this scenario. Furthermore, comparison of the energies for the rearrangement for doubly bonded **5BN** and triply bonded **6BN** might provide or remove support for these NBO characterizations.

The stationary point structures and relative energies for the rearrangement **3N=B** to **4BN** appear in Figure 3. (The cyclic isomer of **3N=B** where boron is endocyclic and nitrogen exocyclic is not a stationary point on the MP2/6-31G* potential surface.) The structures of **3N=B** and the transition state **4BNts** resemble those of the all-carbon analogues. However, their relative energies do not. Cyclopropylidenecarbene is calculated to be about 20 kcal mol^{-1} more stable than cyclobutyne; the two are connected by a transition state only 1−5 kcal mol^{-1} above cyclobutyne. In contrast, **4BN** lies 30 kcal mol^{-1} below the borine **3N=B**, with the transition state 17 kcal mol^{-1} above the borine (and so 47 kcal mol^{-1} above **4BN**). Therefore, a reasonable way to form **4BN** (or some analogue substituted for stability) involves preparing a precursor such as the aminoborane $\overline{CH_2\text{-}CH_2N{=}BHCl}$, α,α-dehydrohalogenating it with strong base to provide the borine, and hoping that the system contains enough energy to scale the activation barrier.

The analogous structures and energies for the larger ring systems appear in Figures 4 and 5. Surprisingly, the energetics of the rearrangements mimic those for **4BN** and apparently do not correlate with whether the BN bond in the cyclic iminoborane is double or triple. Johnson and Daoust found that the rearrangements of cycloalkylidenecarbenes to cycloalkynes show higher activation barriers and become more exothermic as the number of carbons increases.[4] While it appears the former holds for the iminoborane systems, the latter does not.

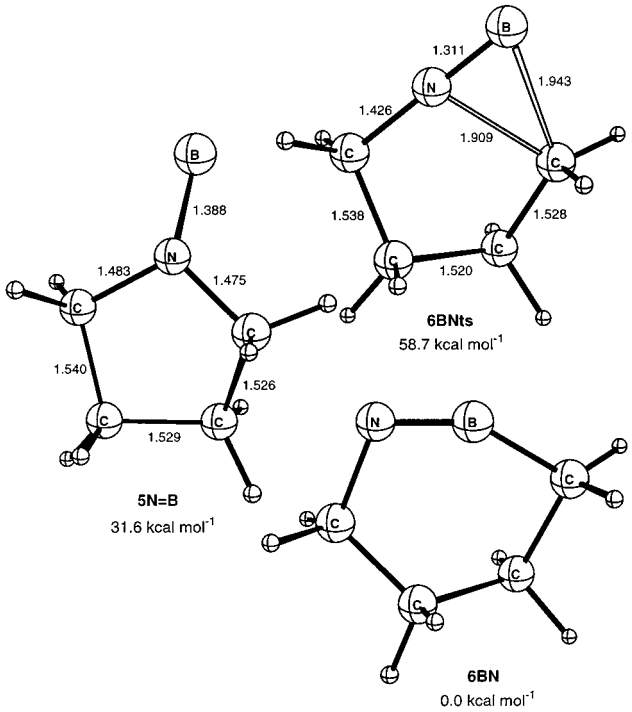

Figure 5. Predicted structures (MP2/6-31G*) and energies (MP4/6-31G*//MP2/6-31G*) for the rearrangement of **5N=B** to **6BN**. Distances are in Å.

Conclusions

The overall message from the computational data is that cyclic iminoboranes and -alanes do not provide good models for cycloalkynes, despite their being isoelectronic. The combination of different atomic sizes and different electronegativities of the heteroatoms allows these systems to adopt structures and electronic configurations unavailable to the cycloalkynes. The positive side is that the small ring strain energies of these systems means they should prove more stable than the small-ring cycloalkynes and, thus, more amenable to study. Nonetheless, their polar multiple bonds and flexible lone pair/π bond electronics should make them fascinating reactants as well.

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