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Conformations of 1,3,3,5,7,7-Hexamethyl-1,5-diazacyclooctane and Its Bis-BH_3 Adduct. Mono- and Bis-BH_3 Adducts of Di-Tertiary Amines

P. Livant,* A. W. Majors,[1] and T. R. Webb

Department of Chemistry, Auburn University, Auburn, Alabama 36849-5312

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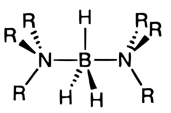
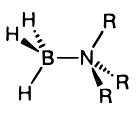
A variable-temperature ^{1}H- and ^{13}C-NMR study revealed a conformational equilibrium for 1,3,3,5,7,7-hexamethyl-1,5-diazacyclooctane (**4**) having $\Delta G^\ddagger = 8.8 \pm 0.6$ kcal/mol at 184 K. This activation barrier connects a major and a minor form of **4**. Molecular mechanics calculations on **4** led to the conclusion that the major form is a set of twist-chair-chairs interconverting rapidly via the chair-chair and that the minor form is most likely a set of twist-boat-boats interconverting rapidly via the boat-boat. The proximity of the two nitrogen lone pairs in the major form of **4** made plausible the expectation that **4**, as well as a related diamine with apposed nitrogens, 3,7-dimethyl-3,7-diazabicyclo[3.3.1]nonane (**3**), might bind a Lewis acid, namely BH_3, using both lone pairs simultaneously and equally. This proved not to be the case: for **3** only the bis-BH_3 adduct was found and for **4** the mono-BH_3 adduct utilized only one nitrogen lone pair. The structure of the bis-BH_3 adduct of **4** (**12**) was determined by X-ray crystallography to be a twist-boat-boat with BH_3s *cis*. Molecular mechanics calculations on **12** were consistent with the solid state conformation found.

A BH_3 involved simultaneously and symmetrically with bonding to two amine donors constitutes an example of a pentacovalent, pentacoordinate—*viz.* hypervalent—boron species. Such a species, *e.g.* **1**, would be an example of a 10-B-5 system.[2] Examples of 10-B-5 and even 12-B-6 (hexacovalent boron) systems have been reported.[3] Compound **1** could dissociate to give **2** + NR_3. Thus in the degenerate reaction shown in eq 1, **1** might be a transition state or possibly an intermediate. We wanted to design a system which would make **1** an observable, if not isolable, intermediate. An obvious strategy would be to use a diamine in which structural features constrain the two donor nitrogens to occupy positions favorable to the bis-chelation of one BH_3. 3,7-Dimethyl-3,7-diazabicyclo[3.3.1]nonane (**3**) and 1,3,3,5,7,7-hexamethyl-1,5-diazacyclooctane (**4**) have been shown by photoelectron spectroscopy to exist with the two nitrogens in close proximity.[4,5] They are also fairly easy to synthesize.



1
10-B-5



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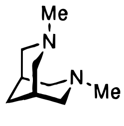
8-B-4



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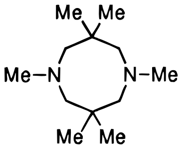
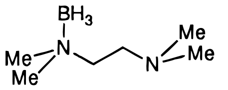


4

$$\underset{\mathbf{2}}{R_3N\text{–}BH_3} + NR_3 \rightleftharpoons \underset{\mathbf{1}\text{ or }\mathbf{1}^\ddagger\text{ ?}}{\left[R_3N\text{–}BH_3\text{—}NR_3\right]} \rightleftharpoons R_3N + \underset{\mathbf{2}}{BH_3\text{–}NR_3} \qquad (1)$$

Thus, these diamines were chosen as initial candidates for investigation of their ability to bind one BH_3 symmetrically.

It has been reported[6−8] that tetramethylethylenediamine (TMEDA), *N,N′*-dimethylpiperazine (DMP), and 1,4-diazabicyclo[2.2.2]octane (DABCO) each form a monoborane adduct which may be isolated and characterized. The monoborane adduct of TMEDA, **5**, and the monoborane adduct of DMP, **6**, are each unsymmetrical as evidenced by ^{1}H NMR. The monoborane adduct of DABCO, **7**, must of necessity be unsymmetrical. Likewise, the disposition of the nitrogens in **8**[9] make bis-chelation unreasonable. In **9**,[10] bis-chelation is possible in principle, but in fact BH_3 bonds to phosphorus only. Therefore the sort of symmetrical bis-chelation represented by **1** has not been observed to date.[11]



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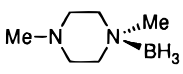

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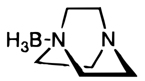

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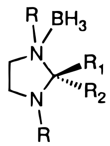

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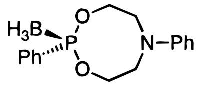

9

The ability of **4** to function in the desired manner is contingent on the nature of its conformation in solution.

[⊗] Abstract published in *Advance ACS Abstracts*, April 15, 1996.

(1) Present address: Cleveland Clinic Foundation, L1-443, 9500 Euclid Avenue, Cleveland, OH 44106.

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(11) It should be noted that symmetrical bis-chelation of transition metals by 1,5-diazacyclooctane and related mesocyclic diamines is well-known (Musker, W. K. *Coord. Chem. Rev.* **1992**, *117*, 133−157).

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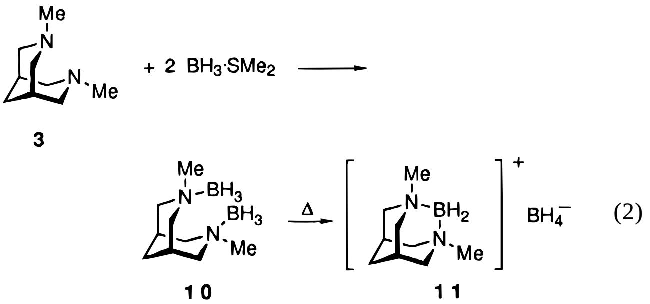
Since details of its conformation in solution were hitherto unknown, a variable-temperature NMR study of **4** was performed. After a brief discussion of the adduct chemistry of **3** and **4**, the results of the conformational analysis of **4** will be presented. The bis-BH_3 adduct of **4** became available to us in crystalline form in the course of our work, and the X-ray structure of this highly congested heterocycle is also reported herein.

Results and Discussion

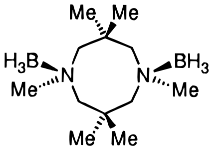
Diamine **3** reacted completely with 2 equiv of $BH_3 \cdot SMe_2$ to give a high-melting solid, **10**, whose ^1H-NMR spectrum indicated that the symmetry of the diamine ligand was preserved. Heating the product at 100 °C for 20 h in the solid state led to a new material, **11**, whose ^1H-NMR spectrum showed, in addition to the peaks ascribable to the diamine ligand, a 1:1:1:1 quartet ($J = 81$ Hz) and a smaller 1:1:1:1:1:1:1 septet ($J = 27$ Hz), both centered at −0.06 ppm. These multiplets are the ^1H-NMR signature of the borohydride anion. We propose that the reaction occurred as shown in eq 2. All attempts to limit the addition to one BH_3 unit failed.



(2)

The cation of salt **11** (an 8-B-4 species) is a member of a class of boron-containing cations of the type $BH_2L_2^+$ (L = donor) first examined by Miller and Muetterties.[12] Numerous borane cations of this type have since been reported,[13] with Keller and Rund[14] having paid particular attention to bidentate ligands. Indeed, the cation of **11** has been reported by Douglass *et al.*, but paired with a ClO_4^- counterion.[15] These authors refluxed $\mathbf{3}H^+ClO_4^-$ with Pyr·BH_3 in diglyme. Two aspects of our synthesis of **11** which are novel in comparison to reported reactions of BH_3 with diamines are that **10** is isolable and that the isomerization of **10** to **11** occurs in the solid state.

Reaction of **4** with Me_2S-BH_3 produced a colorless air-stable solid, the elemental analysis of which was consistent with its being the bis-BH_3 adduct of **4**. Nonequivalent geminal methyl signals in the ^1H-NMR spectrum seemed to indicate that a *trans* diadduct could be ruled out, leaving **12** as the probable structure of the diadduct. The 90 MHz ^1H-NMR spectrum of this solid, however, exhibited *no* peaks corresponding to the methylene protons! The possibility that B-H protons and CH_2 protons were involved in some sort of exchange was ruled out by the observation that $\mathbf{4}\cdot 2BD_3$ did not incorporate deuterium at the methylene (or methyl) positions.



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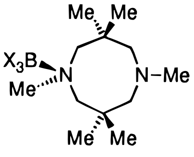
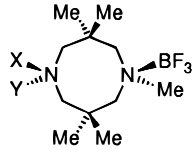


13a; X = D
b; X = H



14a; X =BF3, Y=Me
b; X =Me, Y=BF3

In performing this deuterium (non-)incorporation experiment, we found evidence bearing on the structure of the mono-BH_3 adduct of **4**, which was one of the original goals of this research. As $\mathbf{4}\cdot 2BD_3$ reacts with excess pyridine to regenerate free **4** + 2 pyridine·BD_3, a ^1H-NMR spectrum ascribable to $\mathbf{4}\cdot BD_3$ could be easily discerned. In $\mathbf{4}\cdot BD_3$, only *one* of the two nitrogen donors interacts with the BD_3; *i.e.*, it has the structure **13a**. Two AB quartets were observed at 2.85 and 2.20 ppm, assigned to CH_2 neighboring tetracoordinate nitrogen and CH_2 neighboring tricoordinate nitrogen, respectively, and two singlets were observed at 2.60 and 2.30 ppm, assigned to methyl on tetracoordinate nitrogen and methyl on tricoordinate nitrogen, respectively. Oddly, the *gem*-dimethyls appeared as a singlet (0.90 ppm). The mono-BH_3 adduct of **4**, **13b**, could also be clearly observed when the reaction of **4** with Me_2S-BH_3 was followed by ^1H NMR. Also, in the synthesis of **12**, the purification of crude **12** by vacuum sublimation of volatile byproducts (0.5 Torr, 100 °C, 3 h) produced a hard plate of solid on the cold finger which exhibited the ^1H-NMR spectrum of **13b**.

The problem of the "missing" CH_2 signal in the 90 MHz ^1H-NMR spectrum of **12** was solved when a 400 MHz ^1H-NMR spectrum of **12** was obtained. This spectrum revealed the CH_2 signal as a series of four doublets at 2.56, 2.65, 3.12, and 4.00 ppm. The explanation for the difference between the 90 and 400 MHz spectra is that the ring is not completely conformationally averaged at room temperature. When the conformational equilibrium at an NMR frequency of 90 MHz is observed, the exchange rate is such as to fortuitously produce coalescence at room temperature, and the CH_2 signals broaden into the base line and are not observed. However, this same room temperature conformational exchange rate appears sufficiently slow at an observation frequency of 400 MHz that individual multiplets may be seen. Since **12** was soluble in methylene chloride only, and very sparingly so, it was impossible to perform a variable-temperature NMR study.

The behavior of **12** prompted us to prepare the bis-BF_3 adduct of **4**, **14**, for purposes of comparison. In this case, it is found that the ring is pseudorotating rapidly enough to give a "normal" ^1H-NMR spectrum—AB quartet at 3.00 ppm (CH_2), singlet at 2.63 ppm ($N-CH_3$), and singlets at 1.16 and 0.76 ppm (geminal CH_3s), consistent with the *cis*-diadduct, **14a**. Interestingly, adding 3 mol % of **4** to a solution of **14a** caused the CH_2 quartet to be replaced by a broad singlet and the *gem*-dimethyl pair of singlets to be replaced by a broad singlet. Evidently, **4** catalyzes an equilibrium between **14a** and **14b**, most likely via small amounts of **13b**. When the catalyst is removed under vacuum, the spectrum reverts to that of **14a**, indicating that **14a** is both the kinetic and thermodynamic product of the reaction of **4** with $BF_3 \cdot OEt_2$.

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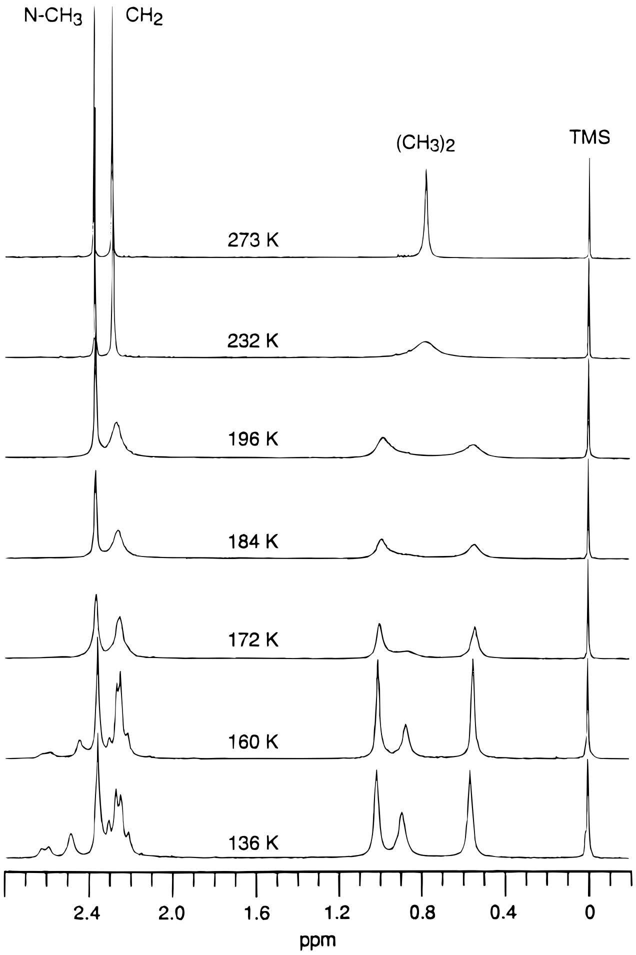

Figure 1. ^{1}H-NMR spectra of **4** at various temperatures.

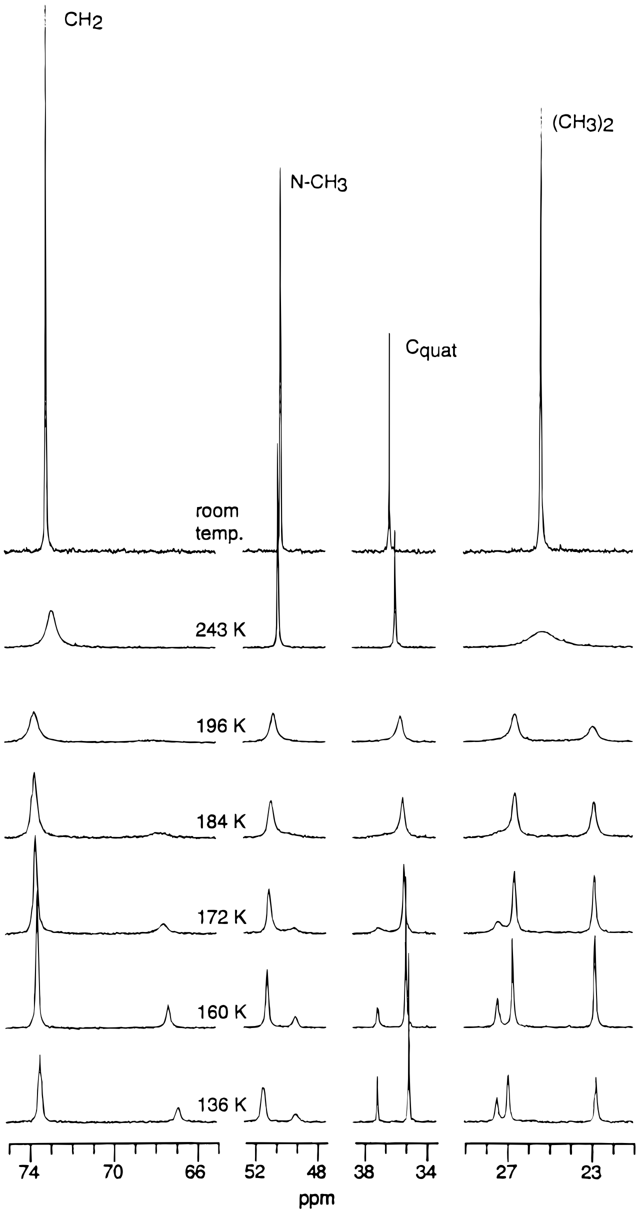

Figure 2. ^{13}C-NMR spectra of **4** at various temperatures.

In summary, we were unable to find an example of the symmetrical bis-chelation depicted in **1.** Ligand **3** bound two BH$_3$s. Ligand **4** could be made to bind one BH$_3$, but it did so *via* one nitrogen only, forming a structure analogous to **5** or **6**.

Conformational Analysis of 4

Temperature-dependent ^{1}H- and ^{13}C-NMR spectra of **4** are shown in Figures 1 and 2, respectively. In Figure 2, all singlets at room temperature become two singlets of unequal intensity at low temperature, with the exception of the 25.67 ppm singlet (due to the geminal methyls) which gives rise to three peaks at low temperature. In Figure 1, the geminal methyl singlet (0.71 ppm), already noticeably broad at room temperature, gives rise to three peaks at low temperature. Clearly, a conformational equilibrium between what we shall call a "major form" and a "minor form" has been delineated in these spectra.

Line-shape analysis was performed using the geminal methyl proton signals, the geminal methyl carbon signals, and the methylene carbon signals. Fitting of the TMS peak was done at each temperature to account for effects of changing field homogeneity and solvent viscosity on line width. Nonlinear least-squares fitting ($\ln(k/T)$ vs $1/T$) led to similar activation parameters from the carbon data and the proton data. Using the spread between these two sets of figures to represent the uncertainty, we find $\Delta H^\ddagger = 5.1 \pm 0.1$ kcal/mol, $\Delta S^\ddagger = -18.7 \pm 0.4$ cal/mol·K. Anet and Anet[16a] view experimental $\Delta S^\ddagger$ values outside the range of ±10 eu as meaningless in conformational processes. Our value is certainly too large. Using the quaternary carbon signal (*ca.* 37 ppm), which would be most free of quadrupolar coupling to ^{14}N, a $\Delta G^\ddagger$ of 8.8 ± 0.6 kcal/mol for major form going to minor form at 184 K was derived graphically.[16b,17]

To try to understand the conformational equilibri(um/a) evident in Figures 1 and 2, an extensive series of molecular mechanics calculations was undertaken. Minimizations using the MM2 force field were carried out first and these structures were reoptimized using the MM3 force field as implemented in the SPARTAN suite of programs.[18] The results are summarized in Table 1. The nomenclature and numbering convention adopted are those of Anet[19] for cyclooctane conformations. Prefixed numbers indicate the locations of the nitrogens in the

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[16] (a) Anet, F. A. L.; Anet, R. In *Dynamic Nuclear Magnetic Resonance Sepctroscopy*; Jackman, L. M., Cotton, F. A., Eds.; Academic: New York, 1975; p 575. (b) Binsch, G., ref 16a, p 77.

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[19] Anet, F. A. L. *Top. Curr. Chem.* **1974**, *45*, 169–220.

Table 1. Results of Molecular Mechanics (MM3) Calculations on 4[a]

		torsion angle[c]							
E_{rel}[b]	ω_1	ω_2	ω_3	ω_4	ω_5	ω_6	ω_7	ω_8	
3,7 twist- chair-chair	0.00	52.9	−91.9	122.6	−75.3	52.9	−91.9	122.6	−75.3
	[0.00]	56.2	−85.4	114.6	−85.4	*56.2*	*−85.4*	*114.6*	*−85.4*
3,7 chair-chair	0.87	−65.9	109.9	−109.9	65.9	−65.9	109.9	−109.9	65.9
		−66.0	*105.2*	*−105.2*	*66.0*	*−66.0*	*105.2*	*−105.2*	*66.0*
3,7 boat-chair	1.72	42.2	65.6	−114.5	54.7	−54.8	114.4	−65.1	−42.6
	[0.28]	*65.0*	*44.7*	*−102.2*	*65.0*	*−65.0*	*102.2*	*−44.7*	*−65.0*
3,7 twist- boat-chair	2.26	55.6	39.3	−124.2	65.8	31.0	−80.6	97.2	−106.1
	[1.91]	*51.9*	*44.8*	*−115.6*	*44.8*	*51.9*	*−93.2*	*88.0*	*−93.2*
2,6 boat-chair	2.70	66.0	39.2	−117.2	79.1	−54.2	86.5	−50.6	−58.8
	[0.93]	*65.0*	*44.7*	*−102.2*	*65.0*	*−65.0*	*102.2*	*−44.7*	*−65.0*
1,5 twist- boat-chair	8.71	74.4	24.2	−99.8	48.3	47.6	−76.1	79.9	−112.5
	[7.09]	*51.9*	*44.8*	*−115.6*	*44.8*	*51.9*	*−93.2*	*88.0*	*−93.2*
1,5 boat-chair[d]	24.34	63.6	37.9	−91.3	78.2	−78.0	89.8	−36.4	−66.4
		65.0	*44.7*	*−102.2*	*65.0*	*−65.0*	*102.2*	*−44.7*	*−65.0*
1,5 twist-boat	4.50	−45.1	60.4	42.4	−58.8	−45.1	60.4	42.4	−58.8
	[1.49]	*−37.6*	*64.9*	*37.6*	*−64.9*	*−37.6*	*64.9*	*37.6*	*−64.9*
2,6 boat-boat	5.02	48.4	55.9	−52.8	−53.8	53.7	50.2	−50.6	−52.6
	[1.80]	*52.5*	*52.5*	*−52.5*	*−52.5*	*52.5*	*52.5*	*−52.5*	*−52.5*
boat[d]	24.69	−1.1	73.4	0.7	−73.5	1.1	73.4	0.7	−73.5
		0.0	*73.5*	*0.0*	*−73.5*	*0.0*	*73.5*	*0.0*	*−73.5*
2,6 twist- boat[d]	29.07	67.1	33.8	−61.3	−37.6	68.4	34.1	−61.4	−35.8
		64.9	*37.6*	*−64.9*	*−37.6*	*64.9*	*37.6*	*−64.9*	*−37.6*
1,5 boat-boat[d]	33.27	47.2	47.7	−47.7	−47.3	47.2	47.7	−47.7	−47.3
		52.5	*52.5*	*−52.5*	*−52.5*	*52.5*	*52.5*	*−52.5*	*−52.5*
3,7 chair	5.37	−11.5	90.0	−127.9	68.3	11.5	−90.0	127.9	−68.3
		0.0	*76.2*	*−119.9*	*76.2*	*0.0*	*−76.2*	*119.9*	*−76.2*
3,7 twist- chair	6.44	36.8	−115.2	116.1	−37.9	−36.3	115.4	−116.0	37.2
	[9.37]	*37.3*	*−109.3*	*109.3*	*−37.3*	*−37.3*	*109.3*	*−109.3*	*37.3*
2,6 twist-chair[d]	13.09	37.7	−110.1	105.7	−37.7	−37.9	110.2	−105.3	37.5
		37.3	*−109.3*	*109.3*	*−37.3*	*−37.3*	*109.3*	*−109.3*	*37.3*
1,5 twist- chair	19.40	26.8	−83.4	96.4	−52.0	−26.8	83.4	−96.4	52.0
		37.3	*−109.3*	*109.3*	*−37.3*	*−37.3*	*109.3*	*−109.3*	*37.3*
1,5 chair[d]	26.26	−21.0	86.4	−119.8	76.3	2.2	−76.1	100.1	−52.9
		0.0	*76.2*	*−119.9*	*76.2*	*0.0*	*−76.2*	*119.9*	*−76.2*

[a] Notation follows that of Anet (ref 19). [b] kcal/mol. Numbers in brackets are the results of MM2 calculations. Steric energy of 3,7 twist-chair-chair = 43.8014 kcal/mol (MM3); 41.78 kcal/mol (MM2). [c] Numbers in italics are for cyclooctane (ref 19). [d] Torsion angles constrained during calculation.

ring following Anet's numbering scheme. Sketches of the conformations are given in Figure 3. It will be noted that in some cases ring positions are equivalent and the choice of numbers to designate the placing of the N-CH_3s is arbitrary. For example 1,5 boat-boat is the same as 3,7 boat-boat. For the sake of simplicity, we will choose, arbitrarily, the lower numbers for our notation. In Table 1, only those conformations having optimal *N*-methyl inversion geometry are listed; higher-energy nitrogen invertomers are omitted. Inasmuch as was possible no symmetry constraints were introduced into the calculations. However, some artifice was required to obtain several of the higher-energy conformations, and these are noted in the table.[20]

The major form may be a single conformation or a set of rapidly equilibrating conformations. Single conformations with the proper symmetry to account for the ^{13}C-NMR spectrum are 3,7 chair-chair (3,7CC), 1,5 twist-chair (1,5TC), 2,6 twist-boat (2,6TB), boat, and 1,5 boat-boat (1,5BB). Of these, the latter three have very high calculated strain energies, and required artificial constraints on some torsion angles in order to do the calculation at all. The 1,5TC required no torsion constraints but gave a high strain energy. Therefore the only relatively unstrained static conformation consistent with the ^{13}C-NMR spectrum of the major form is 3,7CC with a calculated strain energy 0.87 kcal/mol higher than the conformation calculated to have the lowest strain energy—the 3,7 twist-chair-chair (3,7TCC). For the remainder of the discussion, strain energies are given relative to the 3,7TCC conformation.

A set of rapidly equilibrating conformers may be consistent with the ^{13}C NMR of the major form. Indeed, the "static" conformation just mentioned - 3,7CC - is a transition structure connecting mirror image 3,7TCC conformations. The barrier to this 3,7TCC-to-3,7TCC′ (the prime indicating the mirror image) interconversion (Figure 4A) is calculated to be only 0.87 kcal/mol and is therefore consistent with rapid equilibration even at 136 K, the lowest temperature at which an NMR spectrum was obtained.

Pseudorotation itineraries within other conformer families are unsatisfactory. The boat family has the highly strained 1,5BB, 2,6TB, and B forms. This leaves accessible the 1,5TB $\rightleftarrows$ 2,6BB $\rightleftarrows$ 3,7TB equilibrium shown in Figure 4B. This would give one methylene carbon signal and one geminal methyl carbon signal, which is inconsistent with the major form. (It is consistent with the minor form, however.) In the boat-chair family, a complete pseudorotation itinerary, which would

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[20] It is important to be aware of a hidden problem in SPARTAN's dihedral constraint method. The calculated energy of a structure which had been geometry-optimized with one or more torsion angles constrained was routinely 3−4 kcal/mol *lower* than that calculated for the identical structure with the constraints removed and with no optimization, *i.e.*, a single-point calculation with the constraints lifted. The result is energies of structures optimized with torsion constraints cannot be compared with those of structures optimized without constraints. This is not pointed out in the documentation. All calculations noted in Table 1 as having had constrained torsion angles refer to a single-point calculation with constraints removed on the geometry found by optimizing with constraints in force.

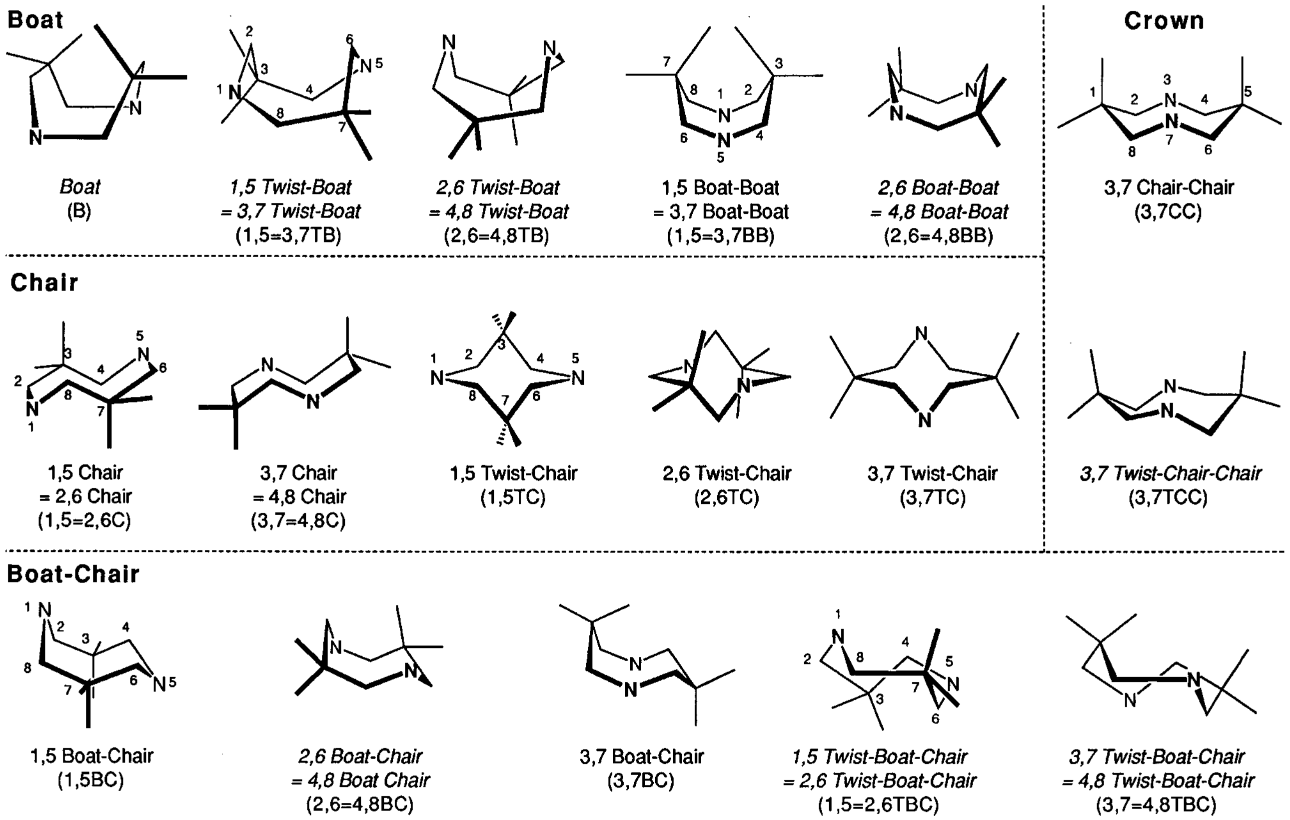


Figure 3. Concordance to Table 1. "N" indicates the position of an N$-$CH$_3$ entity.

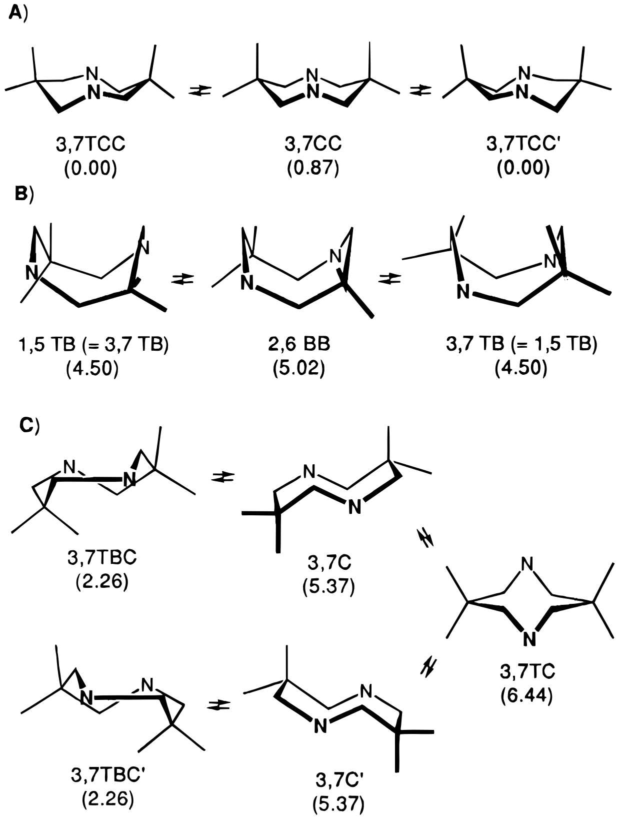


Figure 4. Interconversions of conformers of **4**. "N" indicates the position of an N$-$CH$_3$ entity. Numbers in parentheses are MM3 strain energies (kcal/mol) relative to 3,7TCC.

lead, correctly, to two geminal methyl carbons and one methylene carbon, is precluded by the very high strain of the 1,5BC (24.34 kcal/mol), through which the system would have to pass twice to achieve the required averaging. This leaves 3,7TBC $\rightleftarrows$ 2,6BC $\rightleftarrows$ 1,5TBC $\rightleftarrows$ 3,7BC $\rightleftarrows$ 1,5TBC′ $\rightleftarrows$ 2,6BC′ $\rightleftarrows$ 3,7TBC′, which is the complete pseudorotation path with the 1,5BC excised. The 1,5TBC (8.71 kcal/mol) is 6.99 kcal/mol more strained than the 3,7BC (1.72 kcal/mol), and it seems unlikely that this equilibrium is not frozen out at 136 K. Further, even if this incomplete boat-chair pseudorotation were rapid, it would lead to four geminal methyl ^{13}C resonances rather than the observed two and two methylene ^{13}C resonances rather than the observed one. Within the chair family, only the 3,7C and 3,7TC are not highly strained, so a 3,7C $\rightleftarrows$ 3,7TC $\rightleftarrows$ 3,7C′ equilibrium is possible. This would be part of a slightly larger equilibrium depicted in Figure 4C, so this equilibrium actually crosses family lines. The overall barrier, 4.18 kcal/mol, seems reasonable, but the process leads to one CH$_2$ carbon signal and one geminal CH$_3$ carbon signal, which is not consistent with the major form. It is consistent with the minor form.

Other itineraries crossing family lines which seem reasonable to fingers working a molecular model become unreasonable when the energies of the forms are calculated. For example, a 2,6BC $\rightleftarrows$ 2,6TC $\rightleftarrows$ 2,6BC′ process seems likely, but is calculated to involve a 10.39 kcal/mol barrier. Further, it predicts two geminal methyl carbon signals and two methylene carbon signals, contrary to fact.

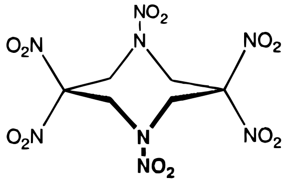
Having exhausted the reasonable possibilities, it seems most satisfactory, then, to take the major form to be rapidly equilibrating twist-chair-chairs. Another fact lends credence to this: the UV photoelectron spectrum of **4** shows a nitrogen$-$nitrogen lone pair splitting of 0.70 eV, which indicates that the two nitrogens are in close proximity in the radical cation of **4**.[5] If one assumes little geometry change accompanying ionization, one may infer that the two nitrogens in **4** itself are in close proximity too. The nitrogen–nitrogen distances calculated for the 3,7TCC and 3,7CC conformers proposed for the major form are 2.96 and 2.92 Å respectively, which may be compared with the sum of van der Waals radii for nitrogen, 3.10 Å.[21]

The minor form shows one ^{13}C signal for each type of carbon and may be either a static conformer of high symmetry or a set of equilibrating conformers. The only conformers of proper symmetry to account for the ^{13}C-NMR spectrum of the minor form are 2,6BB and 3,7TC. The 3,7TC, however, is calculated to have a strain energy of 6.44 kcal/mol. With regard to equilibria, those depicted in Figures 4B and 4C have already been noted and, not coincidentally, involve the two high-symmetry "static" conformations just mentioned. These constitute two good suggestions for the identity of the minor form. The lower calculated barrier for the 1,5TB ⇄ 2,6BB ⇄ 3,7TB process (0.52 kcal/mol *vs* 4.18 kcal/mol for the process shown in Figure 4C) makes this process slightly more attractive than the process shown in Figure 4C.

The picture which emerges from these considerations is that of the major form as a rapidly equilibrating set of 3,7TCC conformers (Figure 4A) and the minor form as a rapidly equilibrating set of 1,5TB conformers (Figure 4B), or a set of conformers engaged in the equilibrium shown in Figure 4C.

By iterative fitting of the lines in the 136 K ^{13}C-NMR spectrum to Lorentzian shapes, the ratio of the major to minor forms is found to be 2.7 ± 0.1. This means that the major and minor forms differ in free energy by roughly 0.3 kcal/mol. The assignment of Figure 4B as the minor form and 4A as the major form corresponds to a calculated enthalpy difference of 4.5 kcal/mol, and the assignment of Figure 4C as the minor form and 4A as the major form corresponds to a calculated enthalpy difference of 2.3 kcal/mol. Neither of these is close to 0.3 kcal/mol. Indeed, Table 1 shows that MM3 tends to calculate bigger energy differences between conformers than does MM2. The MM2 energy differences just referred to are 1.5 and 1.9 kcal/mol, which, while not 0.3 kcal/mol, are at least smaller.

Allinger has rightly pointed out that ΔG and ΔH are not the same thing,[22] and, in the case of cyclooctane, at least, estimating ΔS is not straightforward.[23] Further, the difference between the ways MM2 and MM3 handle amines is fundamental in that the nitrogen lone pair is thrown out in MM3.[24] The lone pair is accounted for, more or less, in the MM3 parameters used to describe torsions involving nitrogen. These in turn were derived from a small sample of experimental data and, in some cases, ab initio calculations. So, while it is natural to assume a method labeled 3 (*viz.* MM3) is "better" than a method labeled 2, and indeed it probably is when averaged over all types of compounds it handles, in the small world of heavily methylated cyclic aliphatic eight-membered ring diamines, *viz.* **4**, we suggest MM2 may give more realistic results than MM3, at least for relative energies of conformers. In contrast to the general trend of lower strain energies with MM2 than with MM3 (relative to the global minimum), of particular importance is the fact that MM2 puts 3,7TC 2.93 kcal/mol *higher* in strain energy than does MM3. This suggests that MM3's treatment of the 3,7TC conformer produced an anomalously low strain energy. In this conformer MM3 has the nitrogens 2.87 Å apart. The lack of an explicit lone pair on nitrogen in MM3 is not penalizing this propinquity properly, perhaps. If that is the case, the MM2-calculated barrier for the process in Figure 4C—7.46 kcal/mol—is to be preferred to the MM3 barrier, and the equilibrium in Figure 4C would then appear much less likely to account for the minor form than the equilibrium in Figure 4B, which has a barrier calculated by MM2 to be 0.31 kcal/mol. That being stated, it must be noted that the X-ray structure of **15**, which is simply **4** with nitro groups in place of methyl groups, has been reported.[25,26] The eight-membered ring of **15** adopts the 3,7TC form, with a transannular N···N distance of 2.707(2) Å. Notwithstanding the example of **15**, we tend to favor the boat-boat equilibrium (Figure 4B) as the minor form.



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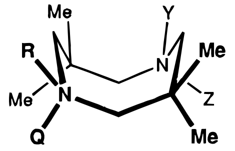

16a; Q=Z=CH$_3$, R=Y=BH$_3$
b; Q=Y=CH$_3$, R=Z=BH$_3$
c; Q=R=Y=Z=CH$_3$

With perhaps unwarranted optimism, we decided to try MM3 at calculating various transitions between the major and minor forms. The Spartan program will calculate a structure intermediate between two structures by assuming the geometrical parameters change linearly from one structure to the other. This assumption is, of course, debatable, but it allows one to make rough estimates of barriers, which in many cases is better than no estimate at all. The procedure we adopted was to calculate structures 40%, 45%, 50%, 55%, and 60% of the way along the "linear transit". In each structure, atoms involved most significantly in the transition were frozen and the remainder of the molecule was allowed to optimize. The constraints were then lifted, and a single-point energy calculation provided the energy of that structure. With constraints lifted a geometry optimization was carried out to see whether the structure fell back to the starting conformation (0% along the linear transit) or ahead to the ending conformation (100%). The final step was to throw out most of the "significant" figures in the energy reported by the program and view the remaining figures with skepticism. The results are presented in Figure 5.

The most direct way from 3,7TCC (the major form) to 1,5TB (the minor form) is illustrated in Figure 5A. In this pathway, two carbons simultaneously pass through the "plane" of the ring, with an understandably high calculated barrier of over 30 kcal/mol. In Figure 5B, the same process occurs sequentially, one carbon at a time,

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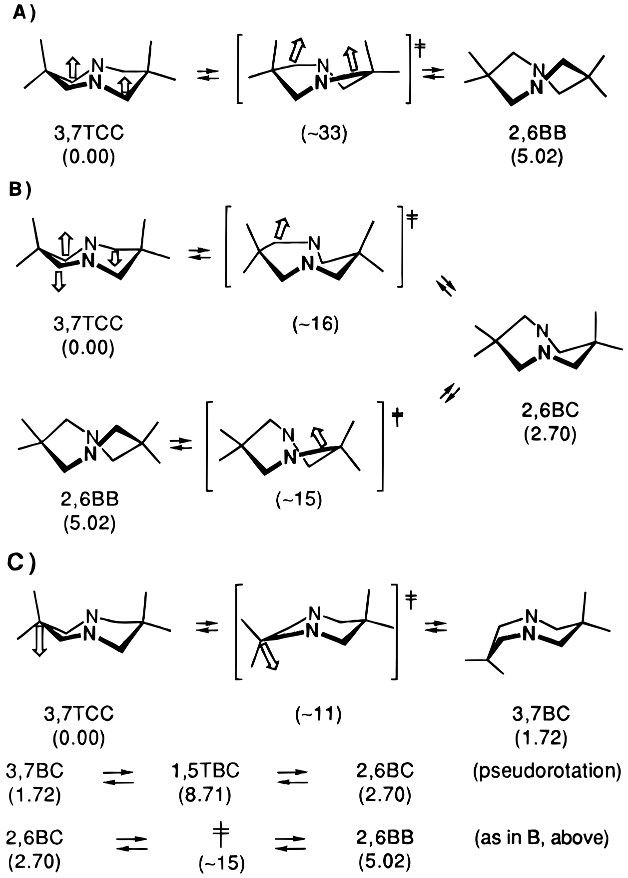

Figure 5. Several 3,7TCC-to-2,6BB interconversions. MM3 energies (kcal/mol) relative to 3,7TCC are indicated in parentheses below each species.

to give first the 2,6BC over a 16 kcal/mol barrier and then the 2,6BB over a 12 kcal/mol barrier. Figure 5C is the same as Figure 5B except the first step of Figure 5B (3,TCC → 2,6BC over a 16 kcal/mol barrier) is replaced by 3,7TCC → 3,7BC → 1,5TBC → 2,6BC with an overall 11 kcal/mol barrier so that the overall barrier for the complete 3,7TCC → 2,6BB path given in Figure 5C is 15 kcal/mol.

The conformations preferred by heteroatom-substituted eight-membered rings are quite varied,[27] but nitrogen-substituted eight-membered rings seem to prefer the chair-chair. For example, 3,7-diphenyl-3,7-diaza-1,5-dithiacyclooctane exists mainly as a chair-chair in solution.[28,29] The close analogue 3,7-dimethyl-3,7-diaza-1,5-dithiacyclooctane is also a chair-chair, with methyls axial, in the solid state.[30] Choi *et al.*[31] found by X-ray crystallography a distorted chair-chair for 1,3,5,7-tetraacetyl-1,3,5,7-tetraazacyclooctane. A chair-chair is adopted by 1,3,5,7-tetraphenyl-1,5-diaza-3,7-diphosphacyclooctane,[32] 1,5-dibenzyl-3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctane *P*,*P*-disulfide,[33] and *cis*-3,7-dihydroxy-1,5-ditosyl-1,5-diazacyclooctane.[34] An exception, the twist-chair **15**, has been noted above. The quaternary ammonium salt 2,6,6-trimethyl-2-oxo-1,3-dioxa-6-azonia-2-phosphacyclooctane iodide adopts a boat-chair conformation.[35]

Before leaving our discussion of **4**, we note the ^{13}C chemical shift of the methylene carbon in this molecule (73.04 ppm) struck us as surprisingly lowfield. Indeed, consultation of several compilations of ^{13}C chemical shifts of amines in particular (790 entries)[36,37] as well as a general listing (500 entries)[38] revealed no CH_2 adjacent to nitrogen further downfield than 67.1 ppm.[39] Even amines which seemed to be good models of the steric environment of the methylene of **4** (*e.g. tert*-butylneopentylisobutylamine) absorbed no further downfield than 64.4 ppm.[40] Thus, it would appear that **4** can claim the distinction of being the amine with the world's lowest-field α-CH_2 ^{13}C NMR absorption, unassisted by double bonds or other heteroatoms.

Conformation of 12

The ^1H-NMR spectrum of **12** exhibits four broad doublets at 2.56, 2.64, 3.12, and 3.96 ppm, each integrating for two hydrogens, for the CH_2s, a singlet at 2.78 ppm for the N−CH_3, and two singlets at 1.33 and 1.12 ppm for the geminal CH_3s. The ^{13}C-NMR spectrum shows two broad singlets at 66.6 and 64.9 ppm for the methylene carbons, a singlet at 57.3 ppm for the N−CH_3s, a singlet at 36.3 ppm for the quaternary carbon, and two singlets at 31.3 and 29.0 ppm for the geminal methyls. Since the NMR spectra indicate incomplete conformational averaging, one may not assume that observation of two geminal methyl signals rules out the *trans* isomer.

The consideration of the preferred conformation of **12** is, mercifully, simplified by two factors. One is Hendrickson's recipe for geminal disubstitution in medium rings: the geminal substituents should be placed on "carbon[s] bounded by bonds of the same dihedral angle sign" [41] (in our case two "carbons" are nitrogens). Another way to think of this is that the bulky substituents should occupy isoclinal positions if possible. The other factor is the requirement that such positions must be nonadjacent around the ring (*i.e.* 1, 3, 5, and 7). Taken together, these factors lead inescapably to the boat-boat and the twist-boat conformers only. Indeed, MM2 calculations on several other conformations as well as the 2,6BB, **16c**, reveal **16c** to be at least 8 kcal/mol more stable than the next higher-energy conformer, confirming the Hendrickson recipe. The *N*,*N*,*N*′,*N*′-tetramethyl struc-

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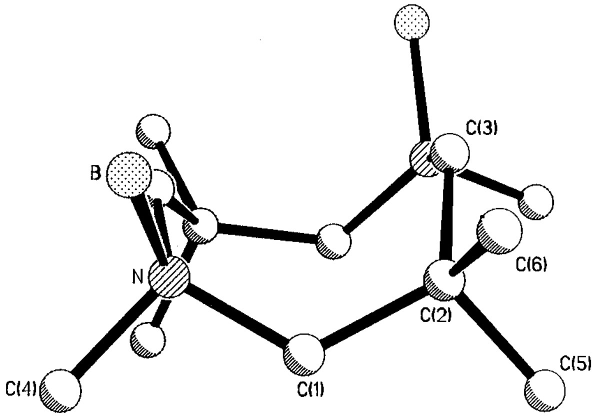

Figure 6. Ball and stick drawing of **12**, using parameters determined by X-ray crystallography. Spheres are drawn at the 50% level. Hydrogens are omitted for the sake of clarity.

Table 2. Geometric Parameters for 12

N1−C1	1.503(5)	N1−C4	1.502(5)
N1−B1	1.626(6)	N1−C3A	1.503(5)
C1−C2	1.539(5)	C2−C3	1.522(6)
C2−C5	1.531(5)	C2−C6	1.531(5)
C3−N1A	1.503(5)		
C1−N1−C4	104.2(3)	C1−N1−B1	115.0(3)
C4−N1−B1	105.3(3)	C1−N1−C3A	115.3(3)
C4−N1−C3A	110.2(3)	B1−N1−C3A	106.3(3)
N1−C1−C2	122.4(3)	C1−C2−C3	116.7(3)
C1−C2−C5	104.6(3)	C3−C2−C5	113.4(3)
C1−C2−C6	111.9(3)	C3−C2−C6	104.2(3)
C5−C2−C6	105.8(3)	C2−C3−N1A	124.1(3)

ture **16c** was used to model the bis-BH$_3$ adduct **12** because suitable molecular mechanics parameters for B−N coordination compounds were unavailable. Therefore, instead of a passel of seven relatively unstrained conformers within a few kcal/mol of each other, as in the case of **4**, the only conformers of **12** which need to be considered are (i) the 2,6 boat-boat (**16**) and (ii) the 1,5-(= 3,7) twist-boat conformers one obtains by twisting **16**, which are 1.82 kcal/mol more stable than the boat-boat, from calculations performed on **16c**. This is simply the equilibrium depicted in Figure 4B except that each nitrogen has two substituents instead of one and the 2,6BB is 1.82 kcal/mol higher in energy than the twist-boat forms. That established, the one remaining point is whether **12** is **16a**, the *cis* diadduct, or **16b**, the *trans* diadduct. The answer hinges on the ^{13}C-NMR quaternary carbon signal: **16a** predicts one signal, **16b** predicts two. Therefore, since one signal is observed, the diadduct **12** is *cis*.

We were able to grow crystals of **12** suitable for X-ray crystallography and therefore submitted **12** to X-ray diffraction analysis. The results are shown in Figure 6 and Tables 2 and 3. A C_2 axis passes through the center of the ring; atoms whose label has an "A" appended are related by this symmetry element to atoms with the same label *sans* "A". In the solid state, **12**, which the X-ray results establish incontrovertably as *cis*, adopts precisely the twist-boat conformation deduced from the NMR spectra and supported by molecular mechanics calculations. Table 4 compares ring torsion angles for an ideal twist-boat, those calculated for **16c**, and those found for **12**. The agreement is remarkable. The most striking aspect of the structure is the quite substantial expansion of various endocyclic angles, namely (average of angles from crystal structure followed in parentheses by corresponding average calculated for **16c** by MM2) N−C−C (average of both types) 123.3° (120.8°), C−C−C 116.7° (117.4°), and C−N−C 115.3° (116.1°). In fact, the bending term in the molecular mechanics calculation of **16c** contributes 41% of the strain energy, whereas for calculations on all conformers of **4** which were done without torsion constraints this term averaged 21% (range 9−37%).

Table 3. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for 12[a]

	x	y	z	U(eq)
N	653(2)	1622(5)	6657(2)	41(1)
C1	972(2)	3064(6)	7453(2)	40(1)
C2	1038(2)	2289(6)	8403(2)	40(1)
C3	288(3)	876(6)	8524(2)	42(1)
C4	767(3)	2963(7)	5896(3)	57(2)
C5	1167(3)	4364(6)	8959(3)	57(2)
C6	1866(3)	926(7)	8783(3)	58(2)
B	1241(3)	−541(8)	6660(4)	63(2)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4. Torsion Angles for the Twist-Boat Conformation

	ω_1	ω_2	ω_3	ω_4	ω_5	ω_6	ω_7	ω_8
ideal[a]	−37.6	64.9	37.6	−64.9	−37.6	64.9	37.6	−64.9
MM2 (**16c**)	−39.7	64.3	40.1	−62.8	−39.5	64.1	40.1	−62.6
X-ray (**12**)	−40.5	63.5	38.4	−63.4	−40.5	63.5	38.4	−63.4

[a] For cyclooctane; taken from ref 19.

Experimental Section

3,7-Dimethyl-3,7-diazabicyclo[3.3.1]nonane (3) was prepared by the method of Douglass and Ratliff.[42]

1,3,3,5,7,7-Hexamethyl-1,5-diazacyclooctane (4) was prepared following the method of Williams.[43]

3,7-Dimethyl-3,7-diazabicyclo[3.3.1]nonane·2BH$_3$ (10). All manipulations were performed under N$_2$. To an ice-cold solution of 0.50 mL (0.46 g, 3.0 mmol) of **3** in 3.0 mL dry ether was added slowly by syringe 0.6 mL (6 mmol) of a 10 M BH$_3$·SMe$_2$ solution. The reaction mixture became milky white over 5 min. Stirring at 0 °C was continued for 0.5 h and then at room temperature for 1 h. The precipitate was allowed to settle, and the supernatant was carefully removed from the serum-capped tube by syringe. Fresh ether was added, the mixture swirled, the precipitate allowed to settle, and the solvent again removed by syringe. The solid product was dried on the vacuum line. ^{1}H NMR (90 MHz): 3.35 (AB quartet, J_{AB} = 11.5 Hz, $\Delta\nu$ = 44 Hz), 2.63 (s), 2.50 (br m), 2.10 (br t).

1,5-Dimethyl-9-bora-1,5-diazatricyclo[3.3.1.1^{3,7}]decane Borohydride (11). Solid adduct **10** was heated *in vacuo* at 100 °C for 20 h, giving a colorless solid which decomposed at ca. 300 °C. ^{1}H NMR (90 MHz): 3.37 (AB quartet, J_{AB} = 10.5 Hz, $\Delta\nu$ = 33 Hz), 2.7 (s), 2.61 (br m), 2.19 (br t), −0.06 (1:1:1:1 quartet, J_{BH} = 81 Hz and 1:1:1:1:1:1:1 septet, J_{BH} = 27 Hz). Addition of NaBH$_4$ and 18-crown-6 increased the intensity of the multiplets centered at −0.06 ppm. IR (CDCl$_3$): 3423 (br), 2952 (m), 2465 (m), 2445 (m), 2378 (m), 2293 (m), 2218 (s), 1466 (s), 1365 (m), 1300 (m), 1293 (m), 1250 (m), 1202 (m), 1172 (s), 1143 (m), 1131 (s), 1080 (s), 1015 (s) cm^{-1}.

1,3,3,5,7,7-Hexamethyl-1,5-diazacyclooctane·2BH$_3$ (12). In a flame-dried 15 mL round-bottom flask a stirred solution of 0.91 g (4.6 mmol) diamine **4** in 5 mL dry ether at 0 °C under N$_2$ was treated dropwise by syringe with 0.92 mL of a 10 M solution of BH$_3$·SMe$_2$ in CH$_2$Cl$_2$ (9.2 mmol). A white precipitate formed immediately. Stirring was continued 0.5 h at 0 °C, and the reaction was allowed to warm to room temperature and stirred for 0.5 h at room temperature. The product was collected by filtration and dried under vacuum overnight. The

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solid was sublimed at 100 °C for 1 h at 0.05 Torr. The solid which collected on the cold finger was characterized as **13b**, the mono-BH_3 adduct (see below). The solid which did not sublime was the bis-BH_3 adduct **12**, 0.82 g (77% yield). Anal. Calcd for $C_{12}H_{32}B_2N_2$: C, 63.72; H, 14.04; N, 12.42. Found: C, 63.77; H, 14.27; N, 12.39. ^1H NMR (400 MHz, CD_2Cl_2): 3.96 (br d, 2H), 3.12 (br d, 2H), 2.74 (s, 6H), 2.64 (br d, 2H), 2.56 (br d, 2H), 1.33 (s, 6H), 1.12 (s, 6H) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): 66.6 (br), 64.9 (br), 57.3, 36.3, 31.3, 29.0 ppm.

Crystal Structure of 12.[44] Slow evaporation of a CH_2Cl_2 solution of **12** yielded a colorless needle, 0.20 × 0.25 × 0.50 mm. The diffractometer used was a Siemens R3m/V, Mo Kα (λ = 0.710 73 Å). Monoclinic, $C2/c$, a = 15.761(5) Å, b = 6.176(2) Å, c = 15.662(4) Å, β = 105.83(2)°, V = 1466.8(7) Å^3, $Z = 4$. $F(000) = 512$ e^{-1}. Cell parameters were based on 22 reflections $10.6 \leq 2\theta \leq 26.3°$. Two standard reflections were measured every 50 reflections. A total of 1125 reflections (970 independent) were collected of which 652 were considered observed ($F > 4\sigma(F)$), $0 \leq h \leq 16$, $0 \leq k \leq 6$, $-16 \leq l \leq 16$; $3.0 \leq 2\theta \leq 45.0°$. The structure was solved using direct methods, refined by full matrix least squares on F using SHELXTL-PLUS. Data-to-parameter ratio 8.9:1. Hydrogens were treated according to a fixed isotropic riding model. R(obs data) = 0.0626; wR(obs data) = 0.0911, R(all data) = 0.0968, wR(all data) = 0.1129, goodness of fit 1.07. Largest difference peak 0.21 e Å^{-3}. Largest difference hole −0.16 e Å^{-3}.

1,3,3,5,7,7-Hexamethyl-1,5-diazacyclooctane·BH_3 (13b). As described above, the synthesis of **12** afforded a small amount of **13b** which could be sublimed away from **12** at 100 °C and 0.05 Torr. Yields were typically less than 10%. In the solid state **13b** disproportionated to **12** and **4** over a few days. ^1H NMR (90 MHz, CH_2Cl_2): 2.99 (AB quartet, J_{AB} = 14.4 Hz, $\Delta\nu$ = 18.9 Hz, 4H), 2.72 (s, 3H), 2.45 (s, 3H), 2.35 (AB quartet, J_{AB} = 13.5 Hz, $\Delta\nu$ = 16.5 Hz, 4H), 1.05 (s, 12H).

1,3,3,5,7,7-Hexamethyl-3,7-diazacyclooctane·2BF_3 (14a). To an ice-cold stirred solution of 0.91 g (4.6 mmol) of **4** in 5 mL of anhydrous ether was added slowly, *via* syringe, 1.1 mL (1.3 g, 9.2 mmol) of freshly-distilled BF_3 etherate. Stirring at 0 °C was continued for 15 min and then continued at room temperature for 0.5 h. The white precipitate was filtered, washed with ether, and dried on the vacuum line, to afford 1.2 g (78%) **14a**. The diadduct could be recrystallized from ethanol. ^1H NMR (90 MHz, D_2O): 3.00 (8H, AB quartet, J_{AB} = 14.5 Hz, $\Delta\nu$ = 31.5 Hz), 2.63 (6H, s), 1.16 (6H, s), 0.76 (6H, s). IR (KBr): 3400 (br), 2960 (s), 2880 (s), 2828 (m), 2720 (br), 1810 (br, w), 1485 (br, s) 1455 (s), 1400 (s), 1380 (s), 1335 (s), 1280 (m), 1235 (m), 1185(m), 1080 (br, vs), 950 (s), 870 (m), 845 (s) cm^{-1}.

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(44) The author has deposited atomic coordinates for structure **12** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.