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Dimerization of Diboradiazacyclobutadienes To Form Tetraboratetraazacyclooctatetraenes: Computational Study of Boron−Nitrogen Ring Formation and Ring Opening

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Computational studies of the dimerization of the diboradiazacyclobutadienes $(HBNH)_2$ and $(MeBNMe)_2$ to form the tetraboratetraazacyclooctatetraenes $(RBNR)_4$ suggest that the preferred pathway involves "face-to-face" dimerization of the four-membered ring, followed by asynchronous, one-step scission of the two transannular BN bonds to form the eight-membered monocyclic product. Detection of the proposed intermediates in either system is unlikely, as they lie in shallow potential energy wells. That in certain situations the four- and eight-membered rings establish equilibria is consistent with the comparatively small energy difference between $(MeBNMe)_2$ and $(MeBNMe)_4$.

Iminoboranes $RB{\equiv}NR'$ prefer to oligomerize rather than react with other molecules.[1−3] Paetzold[4] and coworkers, among others,[5] have examined in detail the relationship between the size of R/R′ and the degree of oligomerization, finding in broad terms an inverse correlation, as one would expect. However, inexplicable subtleties exist, and these are readily seen in the behavior of the iminoborane tetramers,[6] here termed tetraboratetraazacyclooctatetraenes.[7] For example, NMR studies show that equilibria between the iminoborane dimers (diboradiazacyclobutadienes) and the tetramers can occur at or somewhat above room temperature for $R = Me$, $R' = tBu$[8] and for $R = R' = iPr$[9] but not for $R = nPr$, $R' = iPr$, $R = R' = iBu$, or several other combinations.[10]

The mechanism by which the equilibria are established remains lightly studied. Paetzold proposed the mechanism shown in Scheme 1.[4] The diboradiazacyclobutadiene **1** dimerizes to the tricyclic "Dewar cyclooctatetraene" analogue **2**. This undergoes sequential breakage of the internal transannular BN bonds to form first fused bicyclic **3** and then the product tetraboratetraazacyclooctatetraene **4**. All steps proceed reversibly, so that equilibria between the four species can occur. Experimentally, however, only the end points **1** and **4** were observed, suggesting that **2** and **3**, if they are intermediates, lie in very shallow potential energy wells.

Close inspection of the mechanism suggests several issues meriting computational examination. First, does the diboradiazacyclobutadiene dimerization occur "edge-to-edge", to give a staircase-like tricycle, or "face-to-face", to give a tub-like tricycle? Can these tricycles equilibrate, possibly through decomposition back to the four-membered rings and then recombination? Second, need the internal bond breaking occur stepwise, or can it occur synchronously (or nearly so)? Third, given that rather strong bonds (ca. 88−90 kcal mol^{-1})[11,12] must break to convert the tricyclic intermediate to the bicyclic intermediate and monocyclic product, why are the proposed intermediates **2** and **3** so difficult to observe? Are the wells they lie in really so shallow?

We report here an examination of these questions through calculations of the structures and energetics of the parent perhydrogen and permethyl homologues represented in Scheme 1 and the transition states connecting them. We find that the model favors a process by which "face-to-face" dimerization is followed by a one-step asynchronous scission of the internal B−N bonds. Equilibria between species appear unlikely for

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[1] Greenwood, N. N.; Thomas, B. S. In *Comprehensive Inorganic Chemistry*; Trotman-Dickenson, A. F., Ed.; Pergamon: Oxford, England, 1973; Vol. 1.

[2] Niedenzu, K.; Dawson, J. W. In *The Chemistry of Boron and Its Compounds*; Muetterties, E. L., Ed.; Wiley: New York, 1967.

[3] Dawson, J. W.; Niedenzu, K. *Boron−Nitrogen Compounds*; Academic Press: New York, 1965.

[4] Paetzold, P. *Adv. Inorg. Chem.* **1987**, *31*, 123−170.

[5] Franz, T.; Hanecker, E.; Nöth, H.; Stöcker, W.; Storch, W.; Winter, G. *Chem. Ber.* **1986**, *119*, 900−916.

[6] Turner, H. S.; Warne, R. J. In *Boron−Nitrogen Compounds*; Gould, R. F., Ed.; Advances in Chemistry 42; American Chemical Society: Washington, DC, 1964; pp 290−300.

[7] At least three methods exist for naming the compounds in this paper. In the Hantzsch−Widman system, the four-membered rings are diazadiboretanes and the eight-membered monocycle is a tetraazatetraborocine. We suspect few inorganic/organometallic chemists are familiar with this approach and so have chosen to use the replacement nomenclature method. Here one begins with the appropriate name for the all-carbon molecule and replaces carbons with specifically labeled heteroatoms. For further information on this topic, see: (a) Block, B. P.; Powell, W. H.; Fernelius, W. C. *Inorganic Chemical Nomenclature: Principles and Practice*; American Chemical Society: Washington, DC, 1990. (b) Cahn, R. S.; Dermer, O. C. *Introduction to Chemical Nomenclature*, 5th ed.; Butterworth: London, 1979.

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[9] Paetzold, P.; Delpy, K.; Boese, R. *Z. Naturforsch., B* **1988**, *43*, 839−845.

[10] Thiele, B.; Schreyer, P.; Englert, U.; Paetzold, P.; Boese, R.; Wrackmeyer, B. *Chem. Ber.* **1991**, *124*, 2209−2216.

[11] Haaland, A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 992−1007.

[12] Leroy, G.; Sana, M.; Wilante, C. *Theor. Chim. Acta* **1993**, *85*, 155−166.

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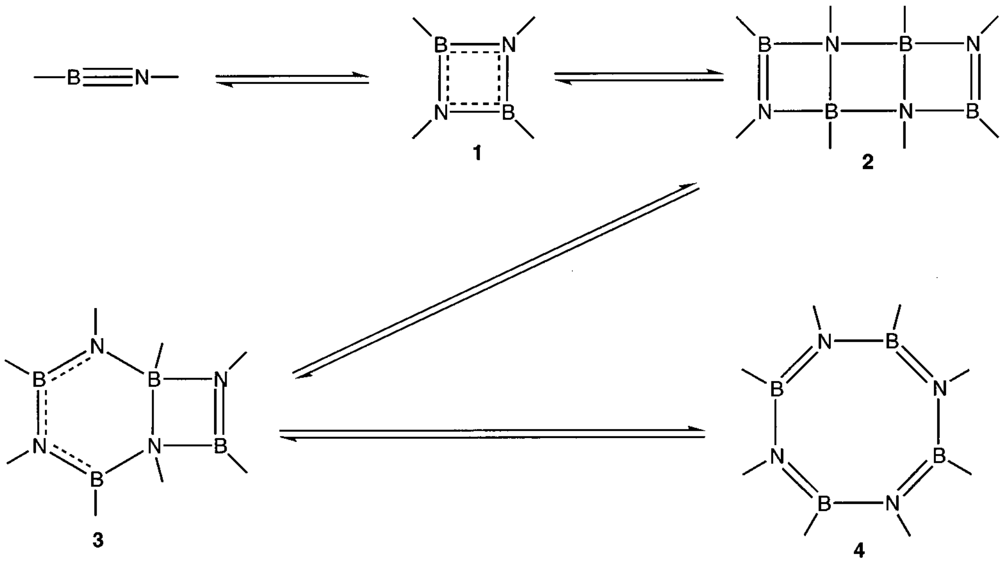
Publication on Web 09/26/2001

Scheme 1



the parent system but are energetically plausible for the end points in the permethyl system. However, in both cases the intermediates lie in shallow potential energy wells, making their observation unlikely under solution NMR conditions. This agrees with the experimental facts.

Computational Methods

All computations were performed using the Gaussian suite of programs.[13] Every molecule was fully optimized without constraints at the HF/6-31+G* level. Though one usually employs diffuse functions solely in the description of anions, and none were examined here, our experience suggests BN multiple bonds are better described with diffuse functions included. This probably arises from their lone-pair origin. The natures of all stationary point structures were assessed by analytical frequency analysis at this level, which also provided zero-point energies (ZPEs). ZPEs were scaled by a factor of 0.9153[14] when used to correct the electronic energies. The structures of $(HBNH)_2$ and its oligomers were reoptimized at the MP2/6-31+G* level and then at the B3LYP/6-31+G* level for comparison. The two models predicted essentially identical structures for reactants, intermediates, and products and only slightly different energetics (see Figures 1−5). Because of their size, oligomers of $(MeBNMe)_2$ were reoptimized at the B3LYP/6-31+G* level only. Transition state structures were confirmed as those linking the desired reactants and products by intrinsic reaction coordinate calculations. Natural bond order (NBO) analyses were performed at the B3LYP/6-31G* level using the appropriate keywords in the Gaussian program.[15]

Results and Discussion

The Parent System Based on $(HBNH)_2$. As calculated previously,[12] diboradiazacyclobutadiene $(HBNH)_2$ (**1**) adopts a slightly nonplanar butterfly structure, with a B−N−B−N torsion of ca. 20°. The dimerization of **1** appears barrierless, as assessed by scans of the potential energy surface, leading nearly isoenergetically either to the edge-to-edge tricyclic **2e** or the face-to-face tricyclic **2f** (Figure 1). To a very small extent, the latter is favored over the former. The values lie so close that one might predict that attaining equilibrium between the two should prove easy. However, the sizable energy gap between **2e**/**2f** and two molecules of monomer **1** suggests that a dissociation/recombination equilibrium should prove difficult to achieve at temperatures similar to those employed in Paetzold's NMR experiments. Potential energy surface scans further indicate **2e** and **2f** cannot interconvert easily by a path involving inversion at transannular boron and nitrogen atoms, as this requires these atoms to adopt nearly square-planar conformations. Approaching this state forces scission of the internal B−N bond, giving the bicycle **3e** (see below). We believe, therefore, that for this system **2e** and **2f** do not equilibrate in the early steps of the process, and so the two pathways resulting from them do not interconnect.

The tricycles differ only slightly in bond lengths, in accord with the presence of BN double bonds at the ends and BN single bonds elsewhere. The single bonds fall into three groups: short, 1.52−1.53 Å, between three-coordinate and four-coordinate atoms; medium, ca. 1.59 Å, between peripheral four-coordinate atoms; long, 1.63−1.65 Å, the internal (transannular) BN bonds. Presumably the last allow release of some ring strain in the peripheral rings; the amount of ring strain in the central ring, composed of four four-coordinate atoms, is probably relatively small.

It is somewhat surprising that **2f** is more stable than **2e**, since the former contains two eclipsing N−B−N−B torsions (and two H−B−N−H torsions within the central ring as well) not present in the latter. Possibly this is countered by decreased ring strain in **2f** arising from its longer internal BN bond.

As suggested by Paetzold, formation of the tetraboratetraazacyclooctatetraene **4** from **2e** occurs in two discrete steps involving scission of the internal BN

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(13) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, revision B.2; Gaussian, Inc.: Pittsburgh, PA, 1995.

(14) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502−16513.

(15) (a) Glendenning, E. D.; Badenhoop, J. K.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. NBO 3.1; Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, 1993. (b) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

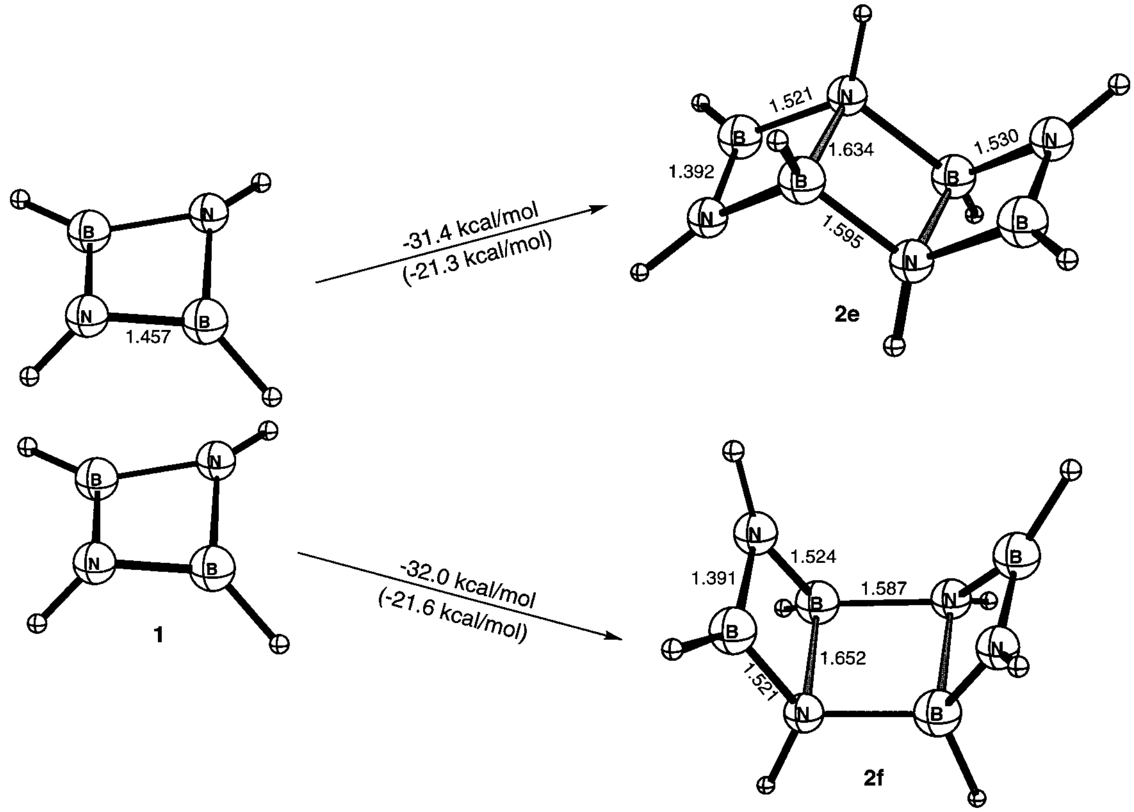

Figure 1. Predicted structures and energies (MP2/6-31+G* unbracketed; B3LYP/6-31+G* in parentheses) for the dimerization of **1** to tricyclics **2e** and **2f**. Distances are given in Å.

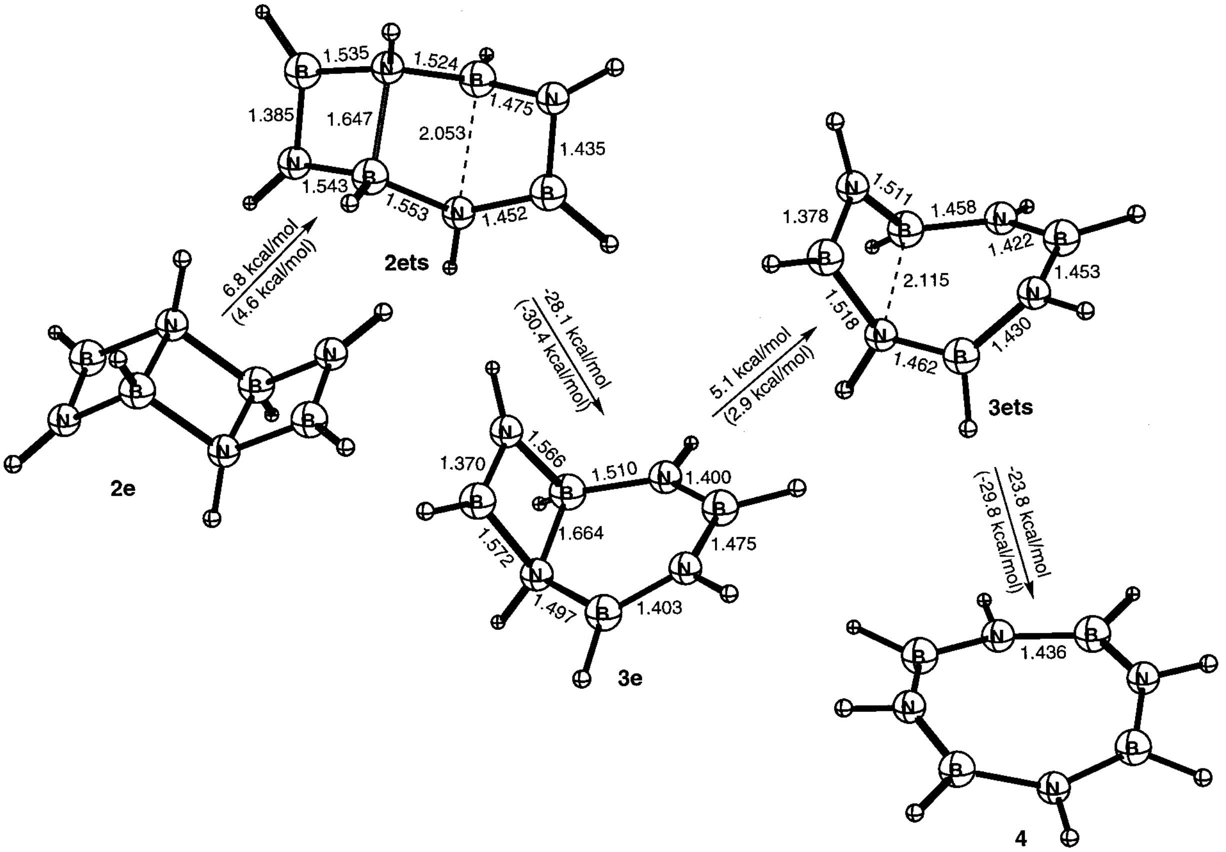

Figure 2. Predicted structures and energies (MP2/6-31+G* unbracketed; B3LYP/6-31+G* in parentheses) for the formation of monocycle **4** in a two-step process from “edge-to-edge” tricyclic **2e**. Distances are given in Å.

bonds (Figure 2). The first scission passes through the transition state **2ets**, with an energy drain of about 6 kcal mol^{-1}, and continues to the fused bicyclic **3e**. In keeping with the low barrier, the transition state lies

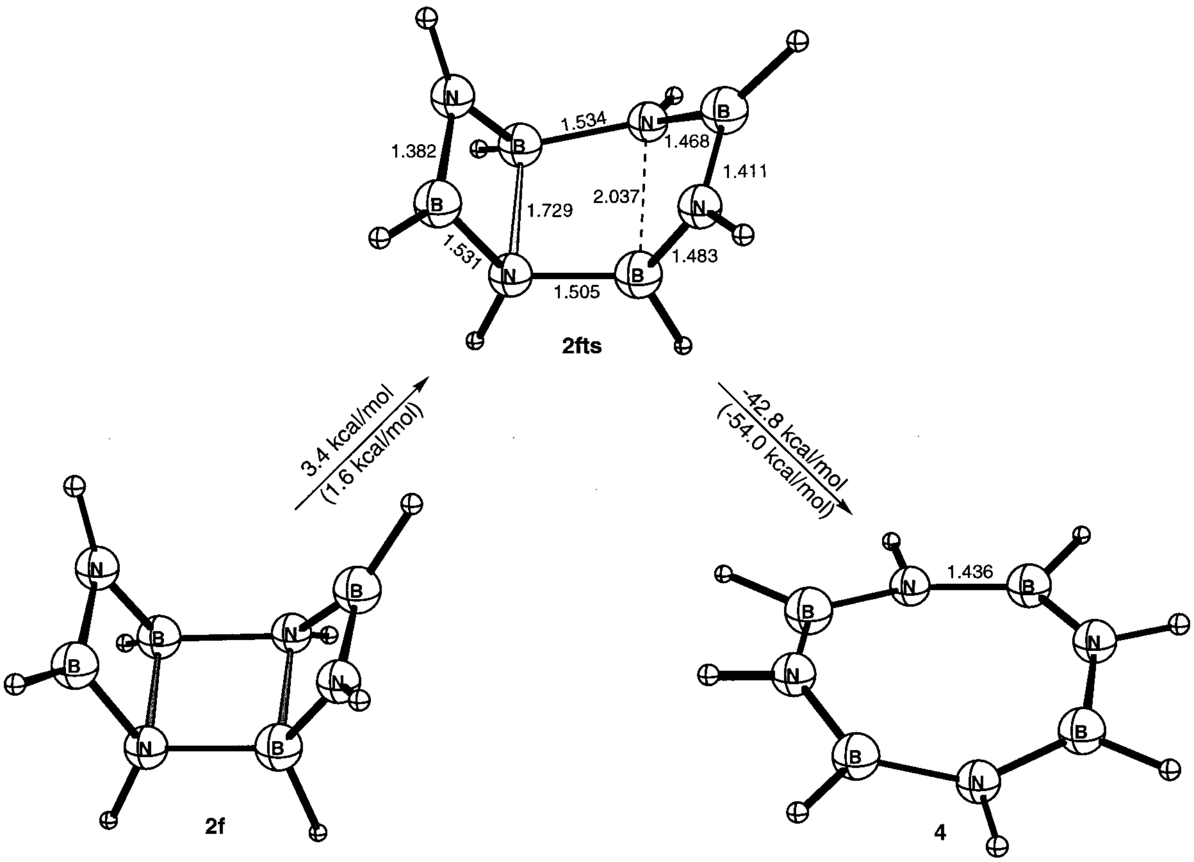

Figure 3. Predicted structures and energies (MP2/6-31+G* unbracketed; B3LYP/6-31+G* in parentheses) for the formation of monocycle **4** in a one-step, asynchronous process from "face-to-face" tricyclic **2f**. Distances are given in Å.

early on the pathway, with the breaking BN bond lengthening from 1.634 Å in **2e** to 2.053 Å in **2ets**. Although this 0.4 Å change seems substantial, in the product **3e** the corresponding nonbonded BN distance is 2.938 Å. Thus, 0.4 Å represents only about one-third of the total distance reached between the two atoms. Bicyclic **3e** lies nearly 30 kcal mol^{-1} below **2ets** in energy, making reversibility of this step (and thus equilibrium between **2e** and **3e**) unlikely. The bicycle structure shows no unexpected features, save that the bond length pattern in the heterocyclohexadiene ring is more consistent with the presence of localized single and double bonds than a delocalized system (see **3** in Scheme 1). Scission of the internal BN bond of **3e** requires 3−5 kcal mol^{-1} to allow passage through the transition state **3ets** and ultimate formation of **4**. As above, the transition state is early, as gauged by the BN distance in the starting points, transition state, and product (1.664, 2.118, and 3.437 Å, respectively), consistent with the small energy needed to attain it.

In contrast, formation of monocycle **4** from **2f** seems to be a one-step process, although the internal BN bonds break asynchronously (Figure 3). The model locates the transition state **2fts** 2−3 kcal mol^{-1} above **2f**. **2fts** resembles **2ets** in that the distance between the boron and nitrogen of the breaking bond is 2.037 Å. However, the other internal BN bond lengthens to 1.729 Å, some 0.08 Å longer than its counterpart in **2ets**. As the molecule passes through the transition state, this bond lengthens further and ultimately breaks without a detectable barrier and without formation of an intermediate similar to **3e**. Thus, since the face-to-face pathway forms **4** with lower activation barriers and fewer steps, it appears to be the preferred mechanism for formation of the monocycle. An energy profile comparing the two pathways appears in Figure 4.

Regardless of which path the reaction takes, the energy wells in which **2e**/**2f** and **3e** lie are surprisingly shallow. The energy transferred to the surrounding environment just by dimerization of **1** will under normal circumstances be sufficient to push these intermediates over their activation barriers to form monocyclic **4**. Since breaking the transannular bonds should require some 88−90 kcal mol^{-1},[11,12] we find this result quite surprising. Presumably relief of ring strain, particularly in the four-membered peripheral rings, counters this energy demand to give the small barriers observed. We will explore this issue in future work; we note for the moment that the ring strain energies in cyclobutane (the analogue to the central ring) and cyclobutene (the analogue to a peripheral ring) are ca. 26 and 30 kcal mol^{-1}, respectively.[16] Thus, one crudely predicts that breaking the transannular bond in **2e**/**2f** should provide only ca. 56 kcal mol^{-1} of ring strain relief, not enough to explain the low barriers found here. In any event, the combination of the kinetic instability of **2e**/**2f** and **3e** and the sizable exothermicity of the reaction (−71 to −74 kcal mol^{-1}) strongly suggest that, if one cleanly generated **1**, it would form **4** quickly and completely, without forming observable intermediates.

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(16) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; HarperCollins: New York, 1987; pp 159−177.

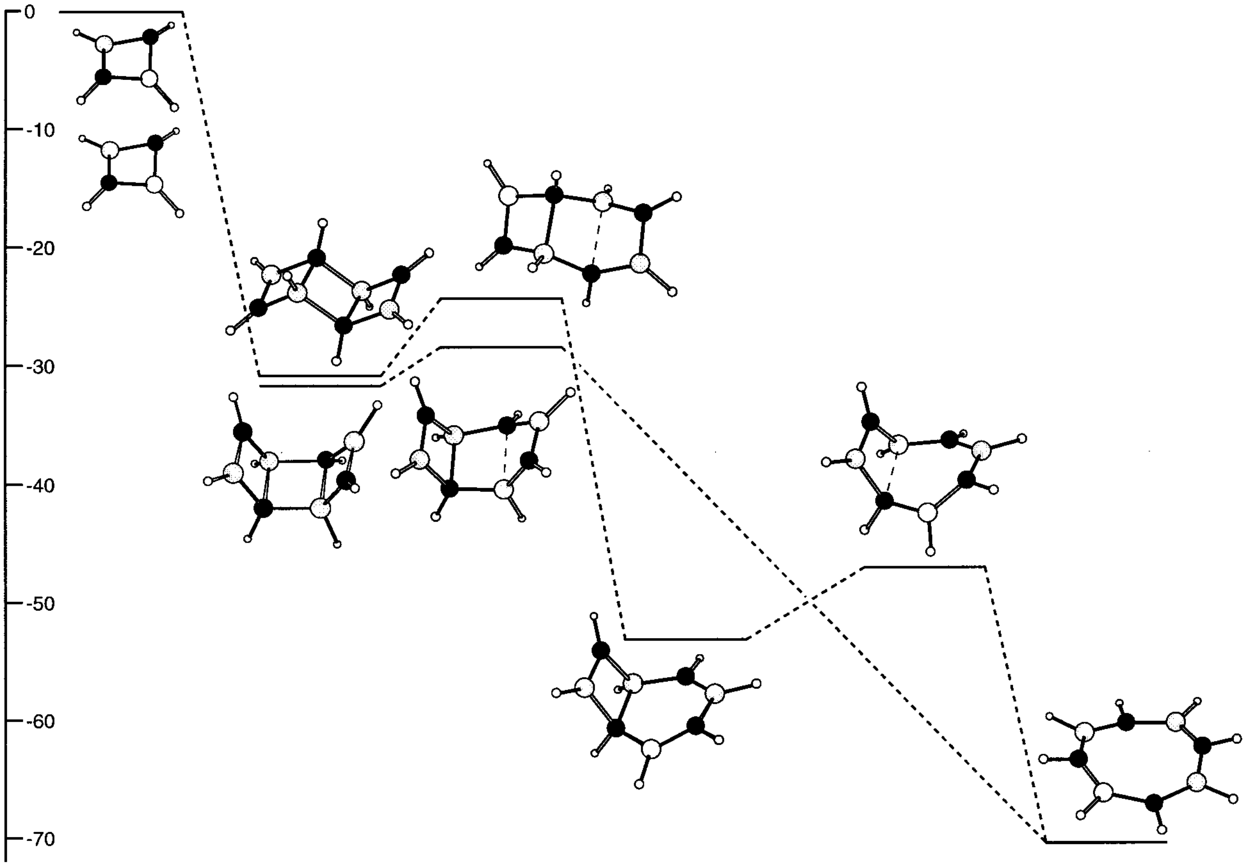

Figure 4. Overall energy profile for the reaction 2(HBNH)$_2$ → (HBNH)$_4$. The MP2/6-31+G* energies on the abscissa are given in kcal mol^{-1}.

Surprisingly, tetraboratetraazacyclooctatetraene **4** adopts an essentially planar conformation, in contrast to the tub conformation of cyclooctatetraene. The B−N−B−N torsion angle in the ring is only ca. 16° (MP2 model; 0° with the B3LYP model), far less than the 60° value for a tub. Correspondingly, rather than exhibiting alternating long and short BN bonds, analogous to those in cyclooctatetraene, **4** displays bonds of equal length intermediate between BN single and double bonds (1.436 Å). This value is essentially identical with that observed and calculated for borazine,[17] suggesting that this 8-π-electron system is as delocalized as the related 6-π-electron system. Such a phenomenon draws a dramatic distinction between BN systems and their organic analogues, where Hückel's rule of aromaticity dictate that planar 8-π-electron ring systems, being 4*n* antiaromatic rather than 4*n* + 2 aromatic, are highly destabilized with respect to nonplanar conformers.

To probe the bonding interactions present, we performed NBO calculations[15] on **4**. The model gives the π-bond occupation as 1.83 e, similar to that in borazine (1.82 e) and rather larger than that in benzene (1.66 e). For comparison, in ethene and aminoborane, each containing a single, localized π bond, the values are 1.997 and 1.999 e, respectively. Thus, the model suggests that **4** and borazine contain similarly delocalized π systems that are less so than the aromatic π system in benzene. The extent to which one can describe borazine as delocalized or aromatic is controversial, although the most recent arguments favor a "cyclohexatriene" analogy rather than a benzene one.[18] Regardless, that **4** prefers a planar structure supports the concept that Huckel's rules do not apply well to extremely polar conjugated π bonds.

The Permethylated System (MeBNMe)$_2$. To assess the generality of our calculations on the parent system and also to model the sterically larger groups on the periphery of the experimental molecules more accurately, we optimized the permethyl analogues of all species calculated above. In general, these molecules conform to the features noted above, with the minor exception that the edge-to-edge dimer **6e** is slightly more stable than the face-to-face dimer **6f**. However, the transition state **6ets** is less stable than **6fts**. The edge-to-edge pathway exhibits two detectable BN bond-breaking steps between dimer formation and monocycle formation, while the face-to-face pathway exhibits only one distinct step, wherein the internal BN bonds break asynchronously. As in the parent, the permethylated transition state **6fts** contains an internal BN bond much longer than that of **6ets** (1.764 vs 1.672 Å), which probably accounts for the lack of a second distinct bond scission step in the former. The latter pathway displays lower barriers along with fewer steps and so appears preferred (Figure 5). The structures of **5**−**8** are available as Supporting Information.

Two notable features distinguish the permethylated system from the parent. First, although the compounds

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[17] For a recent example, see: Parker, J. K.; Davis, S. R. *J. Phys. Chem. A* **1997**, *107*, 9410−9414.

[18] (a) Jemmis, E. D.; Kiran, B. *Inorg. Chem.* **1998**, *37*, 2110−2116. (b) Schleyer, P. v. R.; Jiao, H.; van Eikema Hommes, N. J. R.; Malkin, V.; Malkina, O. L. *J. Am. Chem. Soc.* **1997**, *119*, 12669−12670.

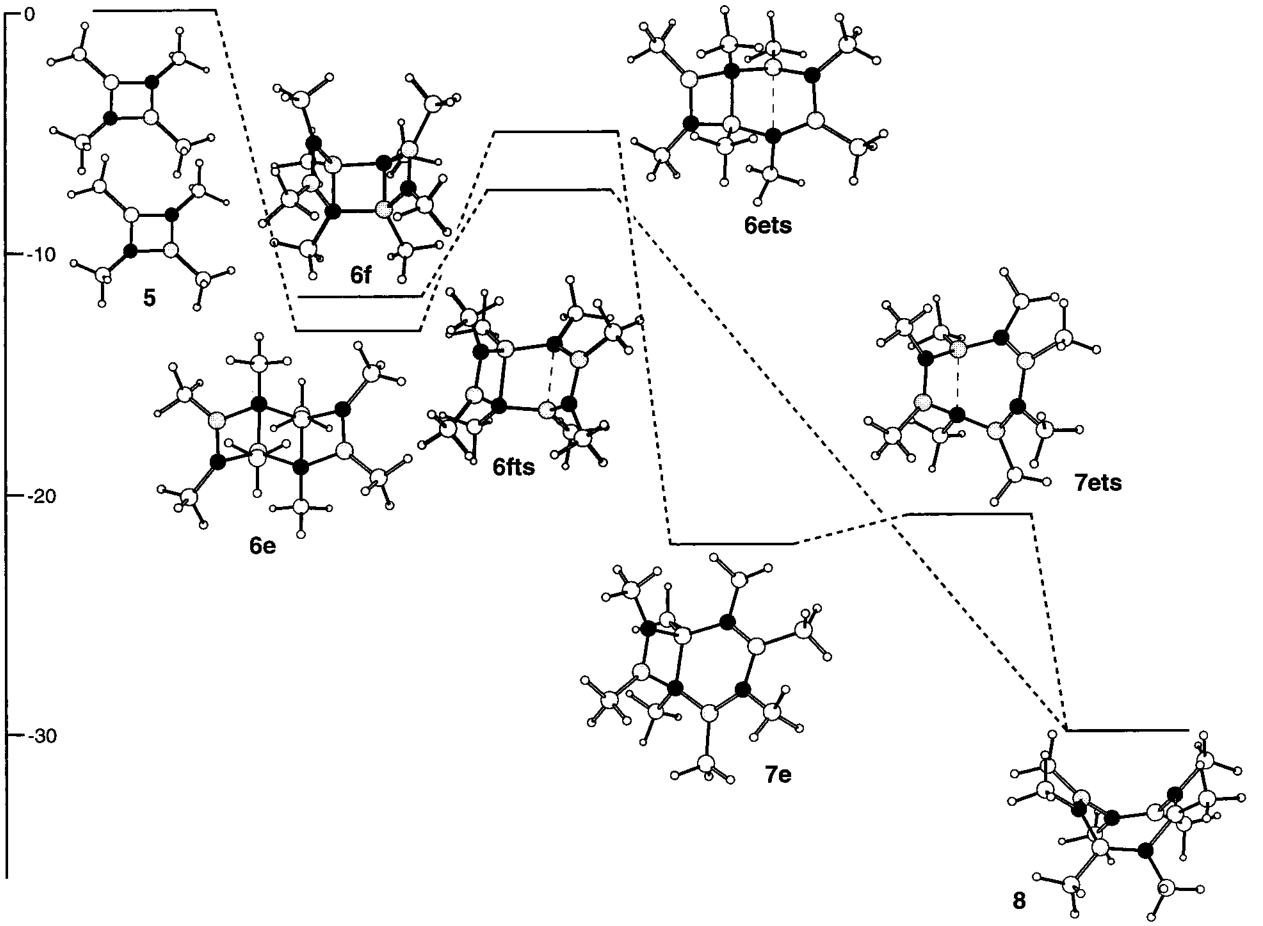

Figure 5. Overall energy profile for the reaction $2(\mathrm{MeBNMe})_2 \rightarrow (\mathrm{MeBNMe})_4$. The B3LYP/6-31+G* energies on the abscissa are given in kcal mol^{-1}.

5−**7ets** display structures nearly identical to **1**−**3ets**, the permethylated monocycle **8** adopts the expected tub structure, rather than being planar like **4**. The B−N−B−N dihedral angles vary between 65 and 70°, similar to those in cyclooctatetraene. Presumably the molecule adopts this conformer to lessen methyl−methyl steric interactions. This argues that any extra stability engendered by delocalization of the π bonds in the eight-membered rings **4** and **8** is less than the methyl−methyl interaction energies. Thus, this stabilization, if it exists, cannot be large, which seems inconsistent with the concept of aromatic stabilization. As one would expect for a tetraene in a tub conformation, **8** exhibits alternating BN bond lengths, with short (1.415 Å) double bonds and longer (1.483 Å) single bonds. These values agree reasonably with those determined by single-crystal X-ray diffraction for 1,3,5,7-tetramethyl-2,4,6,8-tetra-*tert*-butyl-1,3,5,7-tetrabora-2,4,6,8-tetraazacyclooctatetraene (1.404 Å (4, 7, 4))[19] and 1.516 Å (4, 2, 4))[5] and 1,3,5,7-tetraisopropyl-2,4,6,8-tetrabenzyl-1,3,5,7-tetrabora-2,4,6,8-tetraazacyclooctatetraene (1.405 Å (2, 6, 4) and 1.497 Å (2, 5, 4)).[10]

Second, the overall reaction **5** → **8** is less than half as exothermic as **1** → **4** (−31 vs −74 kcal mol^{-1}; for consistency, we compare only B3LYP/6-31+G* energies hereafter). When we examine the individual steps, we see similar behavior. For example, **6e/6f** lie only 12−13 kcal mol^{-1} below **5**, while **2e/2f** lie 21 kcal mol^{-1} below **1**. As a result, a dissociation/recombination equilibrium between **6e** and **6f** through **5** becomes plausible and accessible only slightly above room temperature. However, the energy gap between **6e/6f** and **8** is ca. 18 kcal mol^{-1}, and the activation barriers between the intermediates remain small (1.6−8.2 kcal mol^{-1}). Therefore, pure **5** will probably form **8** irreversibly at room temperature without forming detectable quantities of intermediates, but heating should allow establishment of equilibrium between **8** and **5**.

The sizable energy difference between the parent reaction and the permethyl homologue presumably arises from two factors. Electronically, the increased Lewis basicity of the dimethylnitrogen fragment as compared with its parent does not compensate for the substantially decreased Lewis acidity of the dimethylboron fragment as compared with its parent. Haaland[11] provides theoretical and experimental support for this view, comparing for example calculated bond energies for $\mathrm{H_3BNH_3}$, $\mathrm{H_3BNMe_3}$, $\mathrm{Me_3BNH_3}$, and $\mathrm{Me_3BNMe_3}$. The data indicate that two methyl groups on boron destabilize bonding of a borane fragment by 17−21 kcal mol^{-1}, while two methyl groups on nitrogen stabilize bonding of an amine fragment by only 3−4 kcal mol^{-1}. Sterically, the increased size of the methyl periphery compared to the hydrogen periphery inhibits dimerization of the diboradiazacyclobutadiene **5**, and the presence of steric contacts between adjacent methyl groups

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[19] Esds of averaged values are given in the form (*a*, *b*, *c*), where *a* is the average esd, *b* is the standard deviation of the individual values from the average, and *c* is the number of values averaged.

in the dimer and all subsequent species destabilizes them.

The effect of methyl substitution explains why one can observe equilibria between, for example, the perisopropyl homologues of **5** and **8** without observing **6** and **7**. Putting electron-donating groups on the molecular periphery destabilizes the eight-membered ring electronically with respect to the four-membered ring; sterically bulky groups destabilize the larger ring even more. The point at which the four-membered ring becomes sufficiently energetically similar to the eight-membered ring to allow equilibration between the two evidently occurs when R = R′ = isopropyl. Even with these bulky groups, the intermediates **6** and **7** lie in shallow energy wells, and so are not observable. Why the combinations R = R′ = isopropyl and R = Me, R′ = *tert*-butyl specifically allow observation of equilibria remains undetermined, but why the intermediates have not been observed is explicable.

Conclusion

The computational model generally supports Paetzold's mechanistic proposal. While it appears that the second step of the reaction, wherein **6** converts to **8**, does not require the existence of a stable intermediate **7**, the overall concept of formation of a "BN Dewar cyclooctatetraene" in which the transannular bonds break asynchronously seems sound. The data suggest that observation of **6** will require a fortuitous combination of peripheral groups R and R′, ones that raise the barrier height between **6** and **8** without creating a barrier between **5** and **6**. The experimental and theoretical data do not suggest a choice at this moment. However, the fact that donor groups destabilize the eight-membered ring with respect to the four-membered ring suggests that interesting oligomerization chemistry might be observed in systems such as [(strong donor)BNR]$_2$. In this regard, we note the interesting recent syntheses by Meller and co-workers of [(RO)BNR]$_2$[20] and those by Nöth and co-workers of [(R$_2$N)BNR]$_2$.[21]

The reviewers of this paper noted correctly that the work above neglects the common experimental result that iminoboranes, particularly those with small peripheral groups such as H or Me, prefer to form borazines rather than tetraboratetraazacyclooctatetraenes. They wondered about a quantitative relationship between the formation of differently sized rings and the size of the peripheral groups. As noted above, Paetzold and co-workers' efforts have built a qualitative picture in this regard, but quantitative results are as yet incomplete. Experimentally, we recognize that both kinetics and thermodynamics play critical roles. For example, early experimental work showed that the tetraboratetraazacyclooctatetraene (PhBNtBu)$_4$ and the borazine (PhBNtBu)$_3$ form when (tBuNH$_3$)$^+$(PhBCl$_3$)$^-$ is dehydrochlorinated; the former converts to the latter at 200 °C.[22] Similarly, the reaction between tBuLi and fluoroborazine (FBNiPr)$_3$ gives the Dewar borazine (tBuBNiPr)$_3$, which contracts to the diboradiazacyclobutadiene (tBuBNiPr)$_3$ at 200 °C.[23] Though the mechanisms for forming these ring systems remain unknown, clearly kinetic barriers play as important a role as thermodynamic stabilities in determining which products are observed. We have a continuing interest in the detailed mechanistic steps linking all BN ring systems and will report computational studies of the interconversions between four-, six-, and eight-membered rings in future publications.

Supporting Information Available: Tables giving B3LYP/6-31+G*-optimized Cartesian coordinates for **5**, **6e**, **6ets**, **7e**, **7ets**, **6f**, **6fts**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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