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Ab Initio Studies of Pericyclic Reactions of Aminoboranes. [2 + 2] Dimerization and [4 + 2] Diels−Alder Reactions of H_2BNH_2, Me_2BNMe_2, and $(F_3C)_2BNMe_2$

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Examination of the dimerizations and Diels−Alder reactions of the aminoboranes H_2BNH_2, **1**; Me_2BNMe_2, **2**; and $(F_3C)_2BNMe_2$, **3**, employing the B3LYP/6-31G* model and basis set, provides a reasonable picture of the experimental results. Dimerization of **1** requires less activation energy and is more exothermic than its Diels−Alder reaction. Both the Diels−Alder and dimerization reactions of **2** have high barriers and are endothermic. Thus one expects that **1** will dimerize rather than react with a diene, while **2** should prove unreactive toward dienes or itself. Both expectations match experiment. By contrast, the Diels−Alder reaction of **3** exhibits a lower activation barrier and is more exothermic than dimerization. The activation energy required for the former reaction is sufficiently small that the reaction should occur at room temperature, which it does. In broad terms, these observations are explained by a combination of steric and electronic considerations. Dimerization of **2** and **3** is inhibited by the bulky substituents, but dominates for unsubstituted **1**. The Lewis acidity of the bis(trifluoromethyl)borane moiety in **3** enhances its reactivity toward a diene, while the lowered Lewis acidity of the dimethylborane moiety in **2** renders this compound inert.

Aminoboranes R_2BNR_2 exhibit several types of chemical reactions analogous to those seen for isoelectronic alkenes R_2CCR_2, such as hydrogenation, hydrohalogenation, and oxidation.[1−3] However, aminoboranes undergo pericyclic processes unknown for alkenes, such as thermal [2 + 2] dimerization, while generally not undergoing [4 + 2] processes such as the Diels−Alder reaction, the ene reaction, and the Cope rearrangement. These distinctions are typically attributed to the electronic differences between the nonpolar C=C bond in alkenes and the polar B=N bond in aminoboranes.

Over the past few years, Bürger and co-workers have demonstrated the capacity of the aminoborane $(F_3C)_2BNMe_2$ to participate in a range of pericyclic reactions.[4−7] Unlike its simpler homologue H_2BNH_2, this compound resists oligomerization, and unlike other substituted aminoboranes it undergoes [2 + 2] cyclizations and Diels−Alder-like [4 + 2] reactions with a variety of enophiles. In contrast to all-carbon Diels−Alder reactions, which typically require elevated temperatures, $(F_3C)_2BNMe_2$ forms a 1-azonia-2-boratacyclohexene upon treatment with 2,3-dimethylbutadiene at 0 °C![7] Furthermore the range of enophiles with which it reacts includes many heteroatom systems, such as vinyl sulfoxides, providing promise for the synthesis of an impressive range of new heterocycles.

I have been performing computational studies of multiply bonded main-group compounds and their reactions and felt the novel reactivity of $(F_3C)_2BNMe_2$ merited detailed computational examination. I report here ab initio studies of the dimerization and Diels−Alder reactions of H_2BNH_2, **1**, its tetramethyl-substituted analogue Me_2BNMe_2, **2**, and the bis(trifluoromethyl)-substituted $(F_3C)_2BNMe_2$, **3**. The experimental trends are reproduced well by the computational models; in particular the B3LYP model predicts low-temperature Diels−Alder chemistry for **3**.

Computational Methods

All computations were perfomed using the Gaussian suite of programs.[8] Calculations involving H_2BNH_2 and its derivatives were performed at the MP4/6-31G*//MP2/6-31G* level and then at the B3LYP/6-31G* level for comparison. The comparison showed that the two methods predicted essentially identical structures for reactants, intermediates, and products, but slightly different energetics (Table 1). Since the trends were maintained, only the B3LYP/6-31G* energy values are discussed in the text below. Because of their size, Me_2BNMe_2, $(F_3C)_2BNMe_2$, and their derivatives were optimized at the

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Table 1. Computed Energies of Aminoboranes and Derivatives (Molecular Energies in hartrees, Energy Differences Δ in kcal mol^{-1})

	MP4/6-31G*//MP2/6-31G*	Δ	B3LYP/6-31G*	Δ
cis-$H_2C{=}CHCH{=}CH_2$	−155.396 736 4		−155.902 826 8	
H_2BNH_2, **1**	−81.713 080 6		−81.992 219 5	
$H_2BNH_2BH_2NH_2$, **1dts** (transition state)	−163.412 628 7	8.49	−163.967 395 9	10.69
$H_2BNH_2BH_2NH_2$, **1d**	−163.456 949 7	−19.32	−164.004 710 5	−12.72
$H_2BNH_2CH_2CH{=}CHCH_2$, **1cts** (transition state)	−237.071 599 7	23.98	−237.858 145 8	23.16
$H_2BNH_2CH_2CH{=}CHCH_2$, **1c**	−237.122 639 5	−8.05	−237.898 979 8	−2.47
Me_2BNMe_2, **2**			−239.150 192 2	
$Me_2BNMe_2BMe_2NMe_2$, **2dts** (transition state)			−478.261 901 8	24.15
$Me_2BNMe_2BMe_2NMe_2$, **2d**			−478.286 202 2	8.90
$Me_2BNMe_2CH_2CH{=}CHCH_2$, **2cts** (transition state)			−395.000 264 9	33.10
$Me_2BNMe_2CH_2CH{=}CHCH_2$, **2c**			−395.044 063 3	5.62
$(F_3C)_2BNMe_2$, **3**			−834.619 686 2	
$(F_3C)_2BNMe_2B(CF_3)_2NMe_2$, **3dts** (transition state)			−1669.203 593 9	22.45
$(F_3C)_2BNMe_2B(CF_3)_2NMe_2$, **3d**			−1669.250 616 7	−7.06
$(F_3C)_2BNMe_2CH_2CH{=}CHCH_2$, **3cts** (transition state)			−990.498 683 9	14.95
$(F_3C)_2BNMe_2CH_2CH{=}CHCH_2$, **3c**			−990.543 894 9	−13.42

B3LYP/6-31G* level only. Optimized structures were confirmed as ground or transition states through frequency calculations. Transition-state structures were confirmed as those linking the desired reactants and products by intrinsic reaction coordinate calculations. Energies were corrected for zero-point vibrational energy.

Results

H_2BNH_2, Its Dimer, and Its Diels−Alder Product. The structure of the parent aminoborane H_2BNH_2, **1**, has been determined by microwave spectroscopy.[9] The compound exhibits planar geometries around both core atoms and a BN bond length of 1.391(2) Å. The data have been interpreted as evidence for the presence of BN π bonding in this compound. **1** and its cyclic dimer $H_2BNH_2BH_2NH_2$ (cyclodiborazane, **1d**) have been computationally examined several times previously.[10,11] The additional calculations performed here at the B3LYP/6-31G* level are entirely consistent with those prior. The model predicts for **1** a short BN bond distance (1.393 Å) and the planar core geometry, in excellent agreement with experiment (Figure 1). Cyclodiborazane **1d** adopts a planar, nearly square geometry, with the NBN angle only 1.9° more obtuse than the ideal 90° and the BNB angle 1.9° more acute. The computed BN distance in the ring (1.612 Å) is short for a BN single bond supported by hydrogen atoms (for example, the experimental value in $H_3B{-}NH_3$ is 1.658(2) Å,[12] and the predicted value for $MeH_2B{-}NH_2Me$ is 1.654 Å[13]); this presumably reflects the increased p orbital character in the BN bonds resulting from the nearly right angle bonding motif.

The transition state **1dts** between **1** and **1d** has not been examined before. **1dts** is predicted to adopt a planar parallelogram geometry. The two molecules of **1** attack each other at a slant 8° from the perpendicular, with the BNB angle < 90°. This is precisely what one would expect if one envisions each monomeric aminoborane as containing an N lone pair → B empty p orbital dative π bond. As the two approach each other, the lone pair localizes toward the nitrogen, but is still pointed toward the bonded boron. The slant represents the position of this reorienting lone pair as it is attacked by the Lewis-acidic boron of the other molecule. If there were no π bonding and the nitrogen atom purely sp^3 hybridized, the lone pair would point away from the bound boron and the attack slant would require the BNB angle to be >90°.

The activation barrier between two aminoboranes **1** and the cyclic dimer **1d** is only 10.7 kcal mol^{-1}, and the dimerization reaction is exothermic by 12.7 kcal mol^{-1} (Table 1). It is thus unsurprising that monomeric **1** is difficult to isolate.

The Diels−Alder reaction between aminoborane **1** and butadiene superficially resembles the concerted all-carbon ethene + butadiene analogue (Figure 2).[14] The diene and aminoborane approach at an angle of ca. 100°

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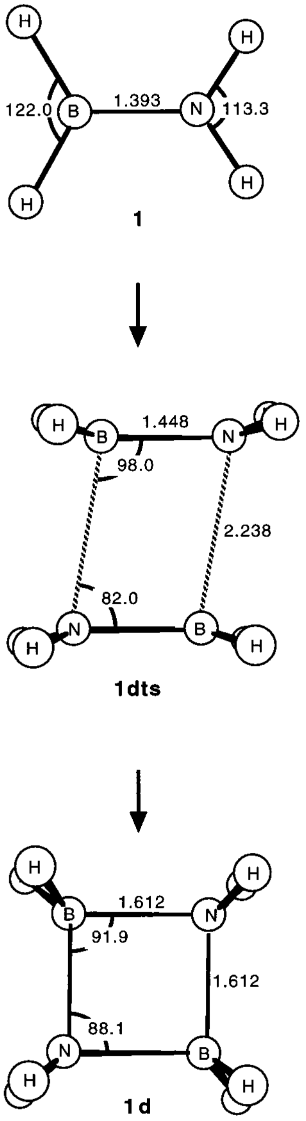

Figure 1. B3LYP/6-31G*-optimized structures of H_2BNH_2, **1**; the transition state for its dimerization **1dts**; and its dimer, **1d**.

in reaching the transition state **1cts**, as the BN bond lengthens about 7% (1.393 Å to 1.500 Å). However, the detailed structure of **1cts** differs distinctly from that of the all-carbon transition state. The ethene–butadiene transition state exhibits mirror symmetry; in **1cts**, the boron is much closer to its butadiene carbon than the nitrogen is to its butadiene carbon (1.901 vs 2.269 Å). The carbon–nitrogen distance is what one would expect given that the carbon–carbon distance in the ethene–butadiene transition state is predicted to be ca. 2.20–2.30 Å,[14] so clearly the boron–carbon distance is unusually short. One can justify this observation by theorizing that as the aminoborane and butadiene molecules approach each other, the dative lone pair in the former localizes toward the nitrogen. This enhances the Lewis acidity of the three-coordinate boron atom, strengthening the attraction between it and the electron-rich carbon–carbon π orbital. The nitrogen atom, with its increased electron density, experiences repulsion from the other filled carbon–carbon π orbital, but attraction to the empty carbon–carbon π^* orbital. When the transition state is attained, these interactions manifest themselves in a relatively short boron–carbon distance and an unexceptional nitrogen–carbon distance. In keeping with this hypothesis, the carbon–carbon bonds in the butadiene fragment of **1cts** do not alternate in length as they do in ethene–butadiene. Instead, the CC bond near the boron is long, indicating loss of much of the π bond, while the CC bond near the nitrogen is short, indicating that much of the π density is intact.

Further support of a sort is provided by the natural charge data derived from natural population analysis.[15] In **1**, the natural charges of the boron and nitrogen are 0.409 and −1.05, respectively. The hypothesis predicts that as the aminoborane and butadiene approach, the boron should become more positive and the nitrogen more negative. However, as the two molecules get closer to the transition state **1cts**, the flow of electrons from the carbon–carbon π orbital to the boron will lessen its positive charge, while the flow from nitrogen to the other carbon–carbon π^* orbital will decrease its negative charge. It is thus unpredictable how the charges on boron and nitrogen in the transition state **1cts** will differ from those in **1**. In fact, both values decrease in magnitude; the natural charge on boron in **1cts** is 0.154; that on nitrogen is −0.961. One recognizes this reflects the incipient loss of the polar BN π bond and the formation of new, more covalent BC and NC bonds. The key is the size of the change. The boron has become considerably less positive, while the nitrogen has become only slightly less negative. One concludes the boron becomes so electron-poor as the aminoborane approaches the transition state that it must coordinate closely to the carbon to which it will bond to allow adequate electron flow from the carbon–carbon π orbital. Thus the B–C distance is relatively short. The electron-rich nitrogen experiences attractions to and repulsions from its carbon as the transition state approaches and so ends up a normal distance away.

The 1-azonia-2-boratacyclohexene product **1c** exhibits no unusual structural features, with all bond distances and angles adopting expected values. The ring adopts a half-chair conformation, with boron and nitrogen on opposite faces of the four-carbon plane.

The computational data predict the experimental result that **1** dimerizes rather than undergoing a Diels–Alder reaction. The aminoborane–butadiene Diels–Alder reaction (Table 1) exhibits a greater activation energy (23.2 kcal mol^{-1}) than does the dimerization reaction and is exothermic only by 2.5 kcal mol^{-1}, much less so than dimerization is. Once formed, 1-azonia-2-boratacyclohexene **1c** lies 26 kcal mol^{-1} below the transition state and thus is unlikely to undergo a retro-Diels–Alder to reform the reactants, but the 14–15 kcal mol^{-1} difference between the transition-state energies dictates that in a mixture of butadiene and **1**, dimerization of the latter to the cyclodiborazane **1d** predominates. Little if any six-membered ring product **1c** will form.

Me_2BNMe_2, Its Dimer, and Its Diels–Alder Product. Tetramethylaminoborane Me_2BNMe_2, **2**, has been examined by single-crystal X-ray diffraction at 110 K.[16]

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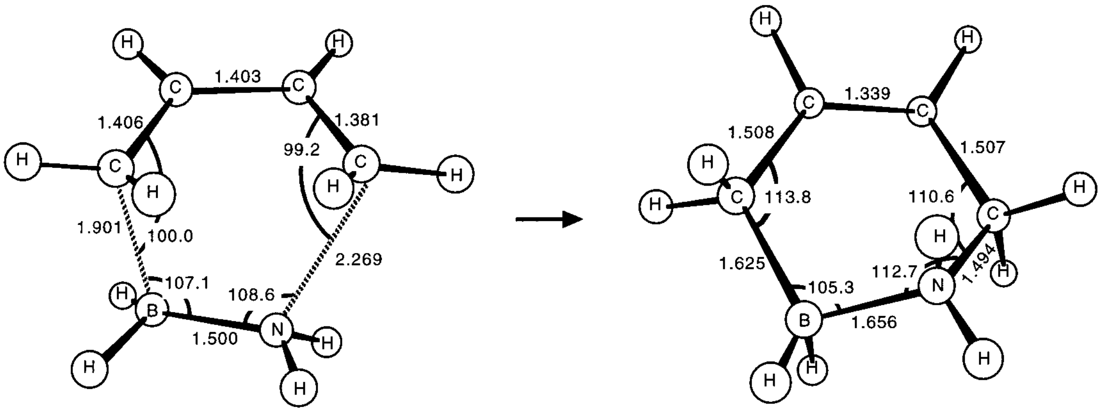


1cts **1c**

Figure 2. B3LYP/6-31G*-optimized structures of the transition state for the Diels–Alder reaction between **1** and butadiene, **1cts**; and the 1-azonia-2-boratacyclohexene product, **1c**.

Table 2. Computed (B3LYP/6-31G*) and Experimental Structural Parameters of Me_2BNMe_2, 2, and $(F_3C)_2BNMe_2$, 3 (Distances in Å, Angles in deg)

	Me_2BNMe_2, **2**		$(F_3C)_2BNMe_2$, **3**	
	calc	expt[16]	calc	expt[17]
BN	1.414	1.403(1)	1.383	1.43(2)
BC	1.598	1.584(2)	1.617	1.623(4)
NC	1.457	1.457(1)	1.469	1.453(7)
CF			1.360	1.343(2)
CH	1.097		1.093	1.079(9)
CBC	120.1	117.9(1)	113.5	122(2)
CNC	111.5	110.8(1)	110.6	111(4)
FCF			106.4	106.5(2)
HCH	111.6		108.7	109(1)

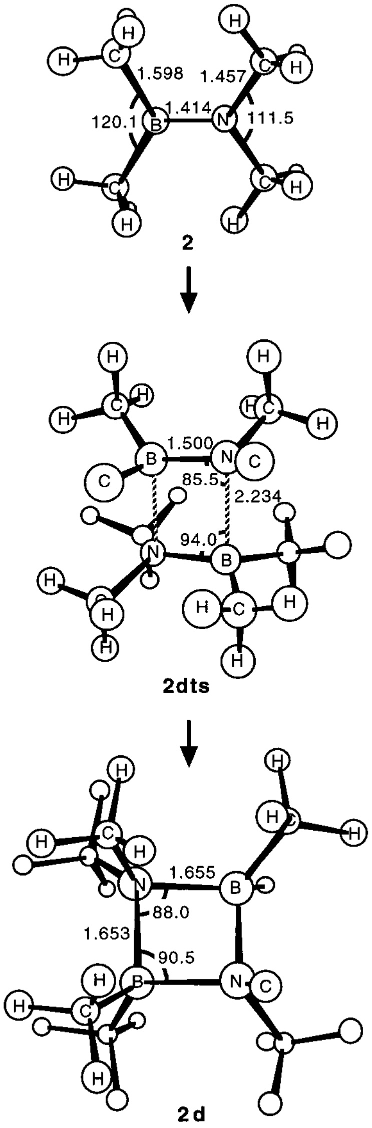
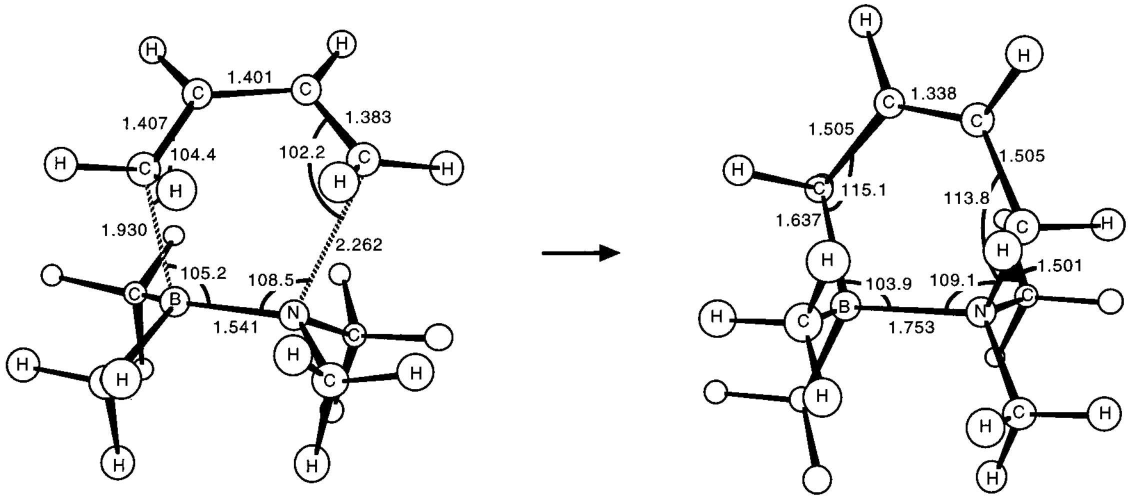


Figure 3. B3LYP/6-31G*-optimized structures of Me_2BNMe_2, **2**; the transition state for its dimerization **2dts**; and its dimer, **2d**. Some of the hydrogen atoms of **2dts** and **2d** were removed for clarity.

Its structure is as expected: the boron and nitrogen atoms are planar and the BN distance is short, at 1.403(1) Å. The computationally optimized geometry of the molecule models the experimental data well (Table 2 and Figure 3), exhibiting planar boron and nitrogen atoms and a predicted BN bond length of 1.414 Å. That these distances are ca. 0.02 Å longer than those determined and predicted for **1** arises from a combination of steric repulsions between opposing methyl groups on boron and nitrogen and of the electron-donor characteristics of the methyl groups. The bond length increases both to lessen the former and because the latter decreases the bond order by lessening the need for boron to gain electron density from the nitrogen (through either σ or π bonding). The increased Lewis basicity of the methyl-substituted nitrogen atom in **2** is inadequate to overcome these combined effects.

The dimer of **2**, octamethylcyclodiborazane **2d**, is unknown, and no experimental data have suggested that the dimerization process occurs under any conditions. Unlike **1d**, **2d** is predicted to adopt a puckered conformation reminiscent of, but flatter than, that of cyclobutane (Figure 3). The ring torsion angle is 12.8°, while that in cyclobutane is ca. 25°. The BN distances are slightly longer than one would expect from a comparison of the BN distances in parent aminoborane **1** and dimer **1d**, presumably a result of the puckering. Interestingly, the ring angles in **2d** are nearly identical to those in **1d**.

The transition state for dimerization, **2dts**, is also nonplanar, displaying a torsion angle between the core atoms forming the ring of 13.4°. Surprisingly, the attack angles between the two molecules of **2** are closer to 90° than those calculated for the dimerization of **1**. Equally surprising is the BN contact distance between the molecules, which is essentially identical to that in



2cts **2c**

Figure 4. B3LYP/6-31G*-optimized structures of the transition state for the Diels–Alder reaction between **2** and butadiene, **2cts**; and the 1-azonia-2-boratacyclohexene product, **2c**.

1dts (2.234 vs 2.238 Å). One might expect that steric repulsions between the methyl groups of the approaching molecules of **2** would dictate more extreme attack angles and a longer BN contact distance in **2dts**, but evidently their canting with respect to each other moderates this. This view is supported by the observation that the contact distance and attack angles observed for planar **3dts** (2.327 Å, 99.6° and 80.1°; see below) are closer to those of **1dts** than of **2dts** despite the fact that **3** is structurally closer to **2** than to **1**. The boron and nitrogen atoms in **2dts** are only slightly distorted from their initial trigonal planar geometries: the CBN and CNB angles vary from 118.3° to 119.8°, indicating that the core atoms rehybridize little in attaining the transition state.

The model predicts the experimental result that dimerization of **2** is unlikely: the barrier to the transition state is sizable (24.2 kcal mol^{-1}), and the overall reaction is endothermic by 8.2 kcal mol^{-1} (Table 1).

The Diels–Alder reaction between **2** and butadiene (Figure 4, Table 1) mimics the parent reaction in most respects. The transition state **2cts** exhibits an attack angle of slightly more than 100°, and the attack is asymmetric. Of note is the fact that, although the NC contact distances in the parent **1cts** and in **2cts** are essentially identical, the BC contact distance in **2cts** is 0.030 Å longer than in the parent. This probably does not arise from steric repulsions (if it did, one would expect the NC contact distance to lengthen too), but must reflect the decreased Lewis acidity of the boron atom in **2** as compared to that in **1**.

The product 1-dimethylazonia-2-dimethylboratacyclohexene **2c** exhibits one unexpected feature: the BN distance is extremely long at 1.753 Å, 0.1 Å longer than that for **1c**. Since the molecule adopts a conformation with staggered methyl groups (thus minimizing steric repulsions), it seems reasonable to attribute this expansion to electronic effects: the trialkyl boron moiety is a poor Lewis acid and is poorly coordinated to the very Lewis basic trialkyl nitrogen. This long interaction has the expected impact on the ring bond angles, but little effect on the other ring bond distances.

Like the dimerization reaction, the Diels–Alder reaction exhibits a considerable activation energy (33.1 kcal mol^{-1}) and is endothermic by 5.6 kcal mol^{-1}. The computational model predicts correctly that tetramethylaminoborane **2** will not participate in these two pericyclic reactions. It is interesting to see that the inertness arises from both kinetic and thermodynamic constraints.

$(F_3C)_2BNMe_2$, Its Dimer, and Its Diels–Alder Product. The structure of the substituted aminoborane $(F_3C)_2BNMe_2$, **3**, has been determined by gas-phase electron diffraction methods.[17] Experimentally, the gross features of **3** mimic those of **2**, with sizable differences appearing only for the BN distance [1.43(2) vs 1.403(1) Å] and the BC distance [1.623(4) vs 1.584(2) Å]. The latter is straightforward to explain: the fluorine atoms draw electron density from the BC bonds, decrease their order, and cause them to lengthen. The former, however, is difficult to rationalize. In the absence of other data, one can argue that the steric repulsions between opposing F_3C and H_3C groups in **3** are greater than those between opposing H_3C groups in **2**, and so the BN bond lengthens. This is at odds with the expectation that the greater Lewis acidity of the $(F_3C)_2B$ moiety in **3** as compared to the $(H_3C)_2B$ moiety in **2** should shorten the BN bond distance.

Computational examination of **3** suggests that the diffraction experiment is in error. To ensure that the computationally predicted structure was the global minimum, a number of different geometries were used as starting points for the optimization; all of these collapsed to the structure shown in Figure 5. The agreement between experimental and computed structural parameters is quite good (Table 2), save that the model predicts a BN bond distance of 1.383 Å. This is much shorter than the experimental value but more in line with what one intuitively expects from the Lewis acidity argument above. Since, one, the experimental BN distance of 1.43(2) Å shows a sizable esd, suggesting that the data refinement is insensitive to this parameter, and two, the authors noted that the BN and NC distances were highly correlated, it seems likely the experimental BN bond length is artifactually long.

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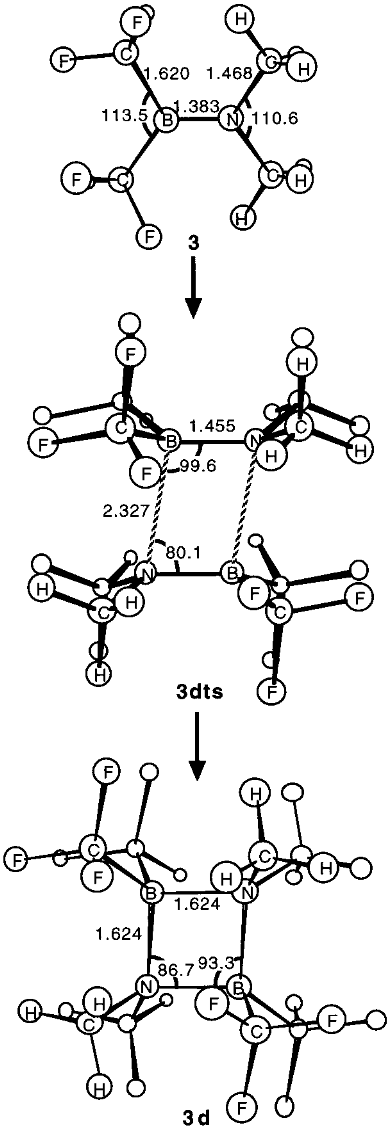


Figure 5. B3LYP/6-31G*-optimized structures of $(F_3C)_2$-$BNMe_2$, **3**; the transition state for its dimerization **3dts**; and its dimer, **3d**.

It is interesting to note that the model predicts the BN bond length in **3** to be slightly shorter than that in **1**; thus the electronic needs of the core atoms overcome the steric repulsions of their substituents. This implies that the electronic needs are substantial, and this is borne out by the natural charge values: that of boron is 0.644 (0.23 greater than that of the boron in **1**), while that of nitrogen is −0.648 (0.4 smaller than that in **1**). Attaching electron-withdrawing fluorines dramatically increases the positive charge, and thereby the Lewis acidity, of the boron; attaching electron-donating methyl groups to the nitrogen lowers its charge and increases its Lewis basicity.

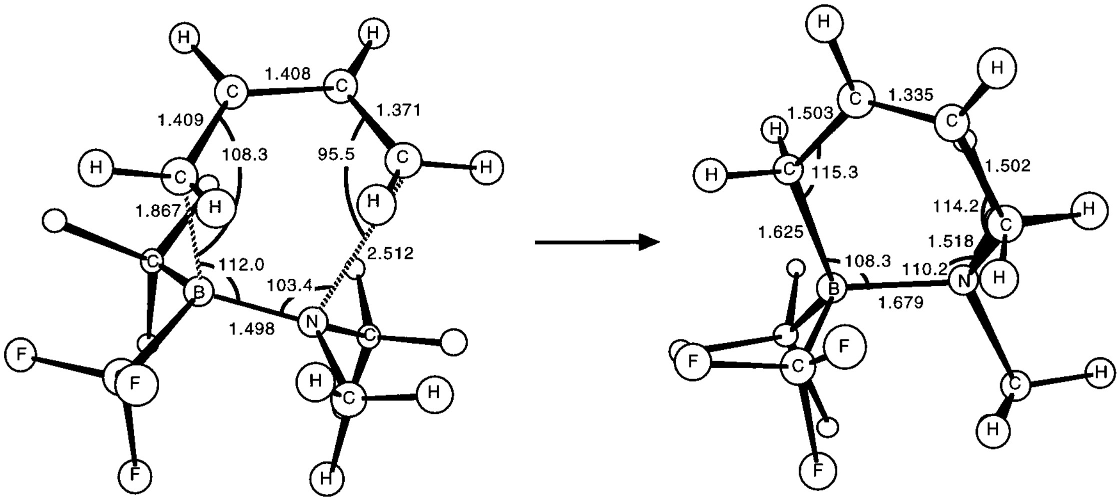
The dimerization process for trifluoromethyl-substituted **3** resembles that of unsubstituted **1** rather than that of **2** (Figure 5). The transition state for dimerization, **3dts**, is planar. The attack angles between the two monomers are more extreme than those for **1**, reflecting steric repulsions between methyl and trifluoromethyl groups on opposite molecules. For the same reason, the BN contact distance is longer than that in **1** or **2**. It is notable that steric considerations override electronic ones here; one might have anticipated that the combination of the extreme Lewis acidity of the bis(trifluoromethyl)borane moiety and the Lewis basicity of the dimethylamine moiety would result in a transition state displaying a very short BN contact distance.

As was true for the unsubstituted dimer, the tetrakis(trifluoromethyl)tetramethylcyclodiborazane **3d** is planar and nearly square, although the rhombic distortion is slightly greater. The BN bond distances are slightly larger than those in **1d**, but shorter than those in **2d**. This nicely illustrates the interplay between electronic and steric considerations: the presence of bulky substituents forces the boron and nitrogen atoms apart, while the contrasting donor and acceptor properties of the dimethylamine and bis(trifluoromethyl)borane moieties pull them together. The electronic issues dominate, since the bond distance is much closer to that in **1d** than that in **2d**. The molecule adopts C_{2h} symmetry, such that the methyl and CF_3 groups on a particular atom are eclipsed. Evidently this conformation is chosen to allow the methyls and CF_3 groups to stagger with respect to each other.

In contrast to the dimerization of **2**, dimerization of **3** is exothermic by 7.1 kcal mol^{-1} (Table 1). This assuredly reflects the electronic needs of the bis(trifluoromethyl)borane moiety. However, the model predicts a considerable barrier of 22.5 kcal mol^{-1} to the transition state, confirming the experimental result that **3** does not dimerize under known conditions. It would be interesting to determine whether one could force it to do so through thermolysis; however, the similarity of the barrier to decomposition of the dimer (29.6 kcal mol^{-1}) to the barrier to its composition severely limits the range of temperatures at which **3d** would be stable. Possibly a high-pressure reaction would allow its formation.

The Diels−Alder reaction between **3** and butadiene (Figure 6, Table 1) presents a distinct contrast to the analogues above. It exhibits a fairly small activation energy (15.0 kcal mol^{-1}) and is exothermic by 13.4 kcal mol^{-1}, 6.3 kcal mol^{-1} more so than dimerization is. One thus expects that six-membered ring formation would predominate significantly over aminoborane dimerization in a mixture of **3** and butadiene, which is the experimental result. That the reaction occurs at surprisingly low temperatures is confirmed by the fact that the activation barrier is only a few kcal mol^{-1} higher than that for the experimentally facile dimerization of **1**.

The transition state **3cts** of the process is similar to those of the other Diels−Alder reactions. Here, however, the asymmetry in the transition state is considerably more pronounced. The boron, made more electron-poor by the coordination of two CF_3 groups, sits only 1.867 Å from the carbon to which it will bond, 0.034 Å closer than in **1cts** and 0.066 Å closer than in **2cts**. This is despite the fact that the boron in **3cts** carries the largest substituents of any case examined. The nitrogen−carbon contact distance is extremely long at 2.512 Å, some 0.25 Å farther away than in the other cases. As a result, the attack angles are more skewed than in the previous systems: the BCC angle is the most obtuse at 108.3°, while the NCC angle is the most acute at 95.5°. The data further support the Lewis acid−base



3cts **3c**

Figure 6. B3LYP/6-31G*-optimized structures of the transition state for the Diels–Alder reaction between **3** and butadiene, **3cts**; and the 1-azonia-2-boratacyclohexene product, **3c**.

model of the system: as the boron becomes more Lewis-acidic, it coordinates more to the carbon π system in the transition state. The nitrogen, with its localizing lone pair, is repelled by the carbon π system, and this is exacerbated when it has large donor substituents. The natural charge data, as they did for the Diels–Alder reaction of **1**, support this view. The charge on the boron decreases substantially, from 0.644 in **3** to 0.479 in **3cts**, while the charge on nitrogen changes only slightly, from −0.648 in **3** to −0.612 in **3cts**.

The 1-(dimethylazonia)-2-bis(trifluoromethyl)borata-cyclohexene product **3c** adopts a structure much like those above, despite the presence of the bulkier substituents. The bond distances and angles associated with the boron and nitrogen atoms change to accommodate the need for space, but the changes are slight. Notably, the BN bond is much shorter than that in **2c**, demonstrating that the remarkably long value there arises nearly entirely from electronic considerations; the steric repulsions in **2c** and **3c** should be similar (or even more pronounced for **3c**). The Lewis acidity of the boron must be lowered substantially when it has two methyl substituents. By way of comparison, the similar BN distances in **1c** and **3c** suggest that the steric repulsions proffered by the substituents in **3c** are countered almost entirely by the increased bonding between its more Lewis acidic boron and more basic nitrogen.

No experimental data for **3c** exist, but the structure of the closely related 1-(dimethylazonia)-2-bis(trifluoromethyl)borata-4,5-dimethylcyclohexene, formed from **3** and 2,3-dimethylbutadiene, was determined by single-crystal X-ray diffraction.[7] Data appear in Table 3. Agreement between experimental values and those computed for **3c** is generally good, although all the predicted ring bond distances are longer than the experimental ones. A notably large discrepancy exists for the BN distance. It is unclear whether this reflects a flaw in the computational model or an experimental artifact. It is possible that the ring is compressed by packing forces in the solid state. It is known that low-energy, dative bonds such as $R_3B{-}NR_3$ BN bonds are particularly subject to such condensed-phase compressions.[18]

Table 3. Comparison of Parameters Computed (B3LYP/6-31G*) for 3c and Those Determined by Single-Crystal X-ray Diffraction for $(F_3C)_2BNMe_2CH_2CMe{=}CMeCH_2$ (Distances in Å, Angles in deg)

	3c calc	$(F_3C)_2BNMe_2CH_2CMe{=}CMeCH_2$ expt[7]
BN (ring)	1.679	1.621(3)
BC (ring)	1.625	1.599(3)
CC (ring)	1.503	1.502(3)
C=C (ring)	1.335	1.317(3)
CC (ring)	1.502	1.501(3)
NC (ring)	1.518	1.509(3)
BC (CF_3) (av)	1.643	1.638(3)
NC (Me) (av)	1.502	1.501(3)
NBC (ring)	108.3	107.4(2)
BCC (ring)	115.3	116.9(2)
CC=C (ring)	124.2	121.8(2)
C=CC (ring)	124.2	123.7(2)
CCN (ring)	114.2	115.4(2)
CNB (ring)	110.2	109.5(1)
$F_3C{-}B{-}CF_3$	107.5	106.3(2)
$F_3C{-}B{-}N$ (av)	110.2	111.4(2)
$F_3C{-}B{-}C$ (ring) (av)	110.4	110.2(2)

Discussion

The results here suggest that one can visualize the Diels–Alder reaction of an aminoborane in much the same way one views the analogous all-carbon reaction. The aminoborane approaches the diene at an angle that allows the diene π cloud to act as a Lewis base toward the "ene" atoms, and the electrons flow correspondingly. The aminoborane connects asymmetrically to the diene in the transition state because one end of it is more Lewis-acidic than the other, but the transition-state structure is still that of a six-membered ring. Furthermore, the activation barrier for the reaction of **1** with butadiene is comparable to that for the ethene/butadiene reaction (experimental value 27.5 kcal mol^{-1}),[14] and the others vary in the expected way: when the dienophile is electron-rich (contains donating substituents), as in **2**, it is repelled by the diene π cloud and the

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activation energy increases; when it is electron-poor (contains withdrawing substituents), as in **3**, it is attracted to the diene π cloud and the activation energy decreases. Our calculations are incapable of allowing meaningful examination of steric contributions to the activation energy, but they are presumably small for **1**−**3**, since **3** exhibits a lower activation energy than the smaller **1**. To simple order, then, an aminoborane behaves like an alkene in a Diels−Alder reaction.

What distinguishes an aminoborane from an alkene is its ability to dimerize. The computational data suggest that steric considerations dictate the viability of this pathway almost entirely. When the aminoborane substituents are small, as in **1**, the activation energy for dimer formation is also small. When the substituents are larger, as in **2** and **3**, the activation energy is 10−15 kcal mol^{-1} larger, so that even when dimerization is exothermic, as for **3**, it does not occur experimentally. There appears to be little of an electronic component to the activation energy: the activation energies for the dimerization of **2** and of **3** are approximately identical, which makes sense since the steric constraints of the processes are nearly the same, but is at odds with the Lewis acid−base characteristics of the boron atom in the two.

Thus, the key to finding an aminoborane that will preferentially undergo the Diels−Alder reaction, as Bürger et al. found, is to design one that is relatively electron-poor, containing substituents sufficiently large to inhibit dimerization, but not so large as to inhibit the pericyclic process itself. **3** and its analogue $(F_3C)_2BNEt_2$ may well be the only preparable aminoboranes for which this will hold. It appears that related molecules containing larger substituents will prove inert; it has already been observed that the diethylaminoborane reacts more slowly and with fewer dienes than does **3**. This suggests that steric repulsions become an acute problem in the Diels−Alder transition state rather quickly. One method of attacking this problem, suggested by a reviewer, involves cyclizing the borane and amine moieties; e.g., preparing molecules such as $F_2CCH_2CF_2BNCH_2CH_2CH_2$. This might expand the compound set a little, but one suspects that the ring size will be limited to four or five members.

One other area where aminoboranes and alkenes differ in their Diels−Alder reactivities is in the stability of the cyclic product. The Diels−Alder reactions of **1**−**3** are substantially less exothermic than the ethene/butadiene reaction (experimental exothermicity 36.3 kcal mol^{-1}), meaning the 1-azonia-2-boratacyclohexenes are less stable than their all-carbon analogues. This appears almost entirely a consequence of the extraordinary weakness of the dative $B \leftarrow N$ bond (20−30 kcal mol^{-1})[18a,19] as compared to a hypothetical BN single bond (90 kcal mol^{-1})[19] or a BN double bond (107 kcal mol^{-1}).[19] The energetic disparities suggest that aminoboranes capable of eliminating H_2 or HX from the 1-azonia-2-boratacyclohexenes to give 1-azo-2-boracyclohexenes might be capable of preferentially undergoing Diels−Alder reactions. Since aminoborane dimerization would represent a competitive pathway, the compounds would need bulky groups, containing the appropriate electron-donating and -withdrawing characteristics. One plausible, but unknown, example of such a molecule is $(C_6F_5)(H)BN(i\text{-}Pr)(H)$. I plan to examine such models computationally and will be interested to see if they are investigated experimentally.

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