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Quantum Chemical Investigation of Initial Reactions between the Molecular Precursor TADB and Ammonia. 1. Gas-Phase Reactions

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$Cl_3Si(NH)BCl_2$, i.e., [(trichlorosilyl)amino]dichloroborane or TADB, may act as a molecular precursor in syntheses to high-demand Si/B/N ceramics. To build a ceramic such as $Si_3B_3N_7$, one may use liquid ammonia as the network forming agent. The actual processes which lead to such amorphous material are not yet fully understood. With this work, we aim at a quantification of product formation probabilities during initial reactions of TADB with NH_3. For this reason, we have investigated the less complicated case of various *gas-phase* reactions with perturbation theory, and the situation in the liquid phase will be published separately. In more detail, the reactions comprise (a) the first and second *ammonolysis* of TADB, (b) the decomposition of *adducts* ($H_3N \rightarrow \mathbf{Si}Cl_3NHBCl_2$ and $H_3N \rightarrow \mathbf{B}Cl_2NHSiCl_3$), (c) the *dimerization* of TADB, and finally (d) a continuing reaction of TADB with the most probable product of the first ammonolysis of TADB (which we term TACBA, trichlorosilylaminochloroboryl amine). Besides these initial steps, and because of the significance of their products, reactions of TACBA with other TACBA molecules and formations of borazine derivates have also been looked into. Our results confirm qualitative chemical intuition: The major primary process in the gas phase is a substitution at the boron center of TADB to yield TACBA. Also, it can be seen that the dissociation of the $H_3N \rightarrow \mathbf{B}Cl_2NHSiCl_3$ adduct into BCl_2NH_2 and $SiCl_3NH_2$ is a side reaction. Albeit, in the continuing stage, the trimerization of TACBA under formation of a borazane six-membered ring releases much more energy than competing processes and is therewith important. As further reactions to be taken into consideration, we find a branching of the molecular backbone accompanied by a break-up of the Si−N−B unit in TADB and a second ammonolysis at the boron side of TACBA. Linking monomer units becomes energetically less and less probable as the ammonolyses of Si−Cl and B−Cl bonds proceed.

1. Introduction

High performance Si/B/N ceramics exhibit high-temperature stability, as well as physical and chemical resistance.[1,2] Often, the preparation of such materials formally proceeds in two steps via the so-called *polymer route*.[3−9] The first step in this process consists of the reaction of a molecular precursor with a network building agent to form a polymer. In a second step, the polymer is pyrolytically transformed (solid-state pyrolysis, SST) into the ceramic. The polymer route is an elegant approach to the synthesis of multinary ceramics, because, therewith, an optimal distribution (and ratio) of elements in the ceramic can be achieved. In addition, phase separations can often be avoided. One of the representatives, a high-performance ceramic of approximate stoichiometry $Si_3B_3N_7$ was prepared in the 1990 by dropping the molecular precursor [(trichlorosilyl)amino]-dichloroborane (TADB, Figure 1) into liquid ammonia and subsequent pyrolysis of the rinsed solid polymer.[3,4] Besides SST there is at least one alternative approach: For example, silane/diborane/ammonia mixtures have been utilized to create borosilazane nitride films by chemical vapor deposition (CVD).[10,11]

The lack of translational symmetry in $Si_3B_3N_7$ renders it difficult to determine the structure of the Si−B−N network solely by means of diffraction experiments. NMR spectroscopy provides clues concerning the short-range order of the ceramic: Boron exhibits a trigonal planar nitrogen coordination environment, and silicon is 4-fold coordinated by nitrogen (distorted tetrahedral).[17,18] So far, no indications for tetracyclic $(Si−N)_2$ units have experimentally been found. Nitrogen appears to prefer a 3-fold coordination to either boron or silicon. Four different possibilities are conceivable in this case: NB_3, NB_2Si,

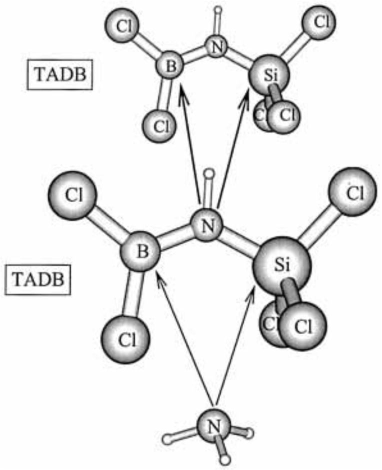

Figure 1. [(Trichlorosilyl)amino]]dichloroborane, a multifunctional molecule.

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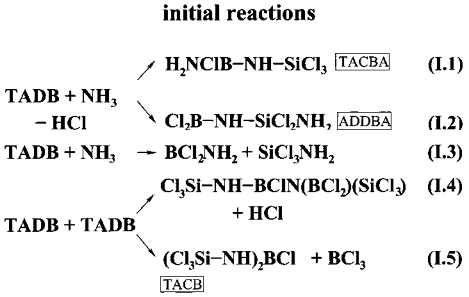


Figure 2. Overview over all initial reactions.

$NBSi_2$, and NSi_3. Unfortunately, signals corresponding to these four environments cannot be resolved in ^{15}N-MAS NMR experiments.[18] However, enrichment of ^{15}N in $Si_3B_3N_7$ through either $^{15}NH_3$, $Cl_3Si-{}^{15}NH-BCl_2$, or both yields differently shaped signals indicating that the Si−N−B bridge of TADB is at least partially retained during the manufacturing process. Very recent ^{11}B-{^{29}Si}-REDOR NMR studies have revealed that boron and silicon are not uniformly distributed on a short-range scale.[19] Instead, B is supposed to have only 1.4 ± 0.1 second nearest Si neighbors on the average. Assuming a purely statistical distribution of Si and B atoms, one would expect a mean value of 3.43 second nearest Si neighbors. The findings of the REDOR study can be interpreted in different ways: The nonuniform distribution could be due to a breaking of the Si−N−B unit of TADB followed by a partial segregation into BN- and Si_3N_4-rich areas, or there may be a preferred primary linkage of TADB units via their boron centers because of the higher Lewis acidity of the latter compared to $SiCl_3$. To find out which processes can lead to a nonuniform distribution of boron and silicon in the final ceramic, a quantum chemical investigation of the reactions during the cross-linking of TADB with NH_3 appears to be helpful.

In the past, quantum chemical investigations of gas-phase reactions have supplied us with a deeper understanding of CVD processes.[20−24] In this work, we present theoretical studies on the initial reactions of TADB with ammonia in the gas phase.[26] In a second paper of this series, we will give an estimation of *solvent effects* for all initial reactions in the system TADB/NH_3.[28] Matters quickly become very complicated to survey, because TADB (Figure 1) is a multifunctional molecule. In fact, it incorporates both a Lewis base (N) and Lewis acids (Si and B). A reaction with another Lewis base such as ammonia is consequently possible at the silicon and boron sites of the molecule. Furthermore, TADB is expected to react with another TADB molecule by attack of its central amino group at the boron or silicon centers of the partner. After a first ammonolysis, the newly formed amino group may act as a Lewis base. Hence, many follow-up reactions are possible which have to be taken into consideration.

Some words on the organization of this paper: In the *first* section of this publication, we study the initial reactions in the system TADB/NH_3. An overview is provided in Figure 2. All reactions carry numbers, and these initial steps are denoted with a Roman I. A primary focus is put on the substitution of a chlorine atom for an amino group at the boron or silicon sites of TADB (reactions I.1 and I.2). Although it can be assumed that ammonia preferably attacks the boron atom, this knowledge does not supply a *quantitative* understanding of matters. Therefore, we have investigated the energetics and mechanisms of all possible first substitution reactions. In this context, we have also studied in how far a decomposition of the Si−N−B unit can be expected (reaction I.3). Dimerization of TADB under HCl elimination is a further possible initial reaction (reaction I.4). Experimentally, a formation of $(Cl_3Si-NH)_2BCl$ under loss of BCl_3 was observed when TADB was heated to 110 °C (reaction I.5).[27] The *second* section is concerned with follow-up reactions, summarized in Figure 3. Throughout, these reactions are categorized under II and III. Next, we have investigated the products of second substitutions (with respect to TADB) of chlorine for NH_2 (reactions II.1−II.4). Then came the reactions of TADB with TACBA (see Figure 3), a product of the first ammonolysis of TADB. For TACBA/TADB-reactions, we distinguish between three possibilities: (a) the attack of the terminal amino group of TACBA at the boron side of TADB, i.e., an elongation of the molecular backbone via boron (in other words, an extension of the backbone under formation of a B−N−B linkage, reaction II.5), (b) the attack of the terminal amino group of TACBA at the silicon side of TADB (i.e., an extension of the molecular backbone via silicon, Si−N−B linkage, reaction II.6), and (c) the attack of the central amino group of TACBA at the boron side of TADB. Elimination of HCl from the latter transition state leads to a *branching* of the molecular backbone (reaction II.7). If BCl_2NH_2 is eliminated instead of HCl, reaction II.8 occurs. As with II.7, this reaction is also termed a "branching" reaction, because the molecular connectivity graph bifurcates. Finally, two TACBA molecules can react with one another (II.9−II.13). We have investigated (a) the attack of the terminal NH_2 group at the B/Si centers of another TACBA (reactions II.9 and II.10), (b) the attack of the central NH group at the boron side of TACBA with subsequent BCl_2NH_2/HCl elimination (reactions II.11 and II.12), and (c) the formation of a four-membered borazane ring (reaction II.13).

Before we started these investigations, we had preexamined the much simpler case of a reaction of BCl_3 with NH_3. There, six-membered borazane rings were found to be very stable.[20] Hence, we have looked into the trimerizations of TACBA and trichlorosilyldiaminoboryl amine (TDABA; reactions II.14 and III.3 in Figure 3). As a last substitution reaction, we were interested in how far the reactivity of the $SiCl_3$ groups would be influenced by the formation of a six-membered borazane: Our test case was the substitution of one chlorine atom from the $SiCl_3$ group of the TACBA trimer (upper right in (25), reaction III.1 in Figure 3). Finally, the elimination of three hydrogen chloride molecules from $[TACBA]_3$ to yield a borazine derivate has been studied (reaction III.2).

2. Computational Details

Throughout, a valence-triple-ζ basis set with a polarization function was employed (TZVP).[29] Auxiliary basis sets for the RI approximation of two-electron integrals were taken from the work of Eichkorn et al. and Weigend et al. in all cases.[30,31] (RI is an acronym for *resolution of identity* known from the closure relation in Hilbert space theory. It stands for an approximation of computationally expensive four-index integrals by three-index integrals and proceeds by utilizing an auxiliary basis set, which is inserted as an approximated identity. The RI approximation leads to an enormous speed-up and so enabled us to get reliable data also for larger systems.) Minima on the potential hypersurface were determined with the TURBOMOLE 4.6 program package,[32,33] making use of quasi-Newton−Raphson optimizations. Transition states were localized by means of an *eigenvector following* program that is interfaced to TURBOMOLE.[34] By means of this procedure, we can ensure that the transition state connects reactants with the desired products.

For most of the structures, we carried out energy optimizations in two steps. First, structures were preoptimized at the RI-DFT level.[35] For these calculations, we employed a local

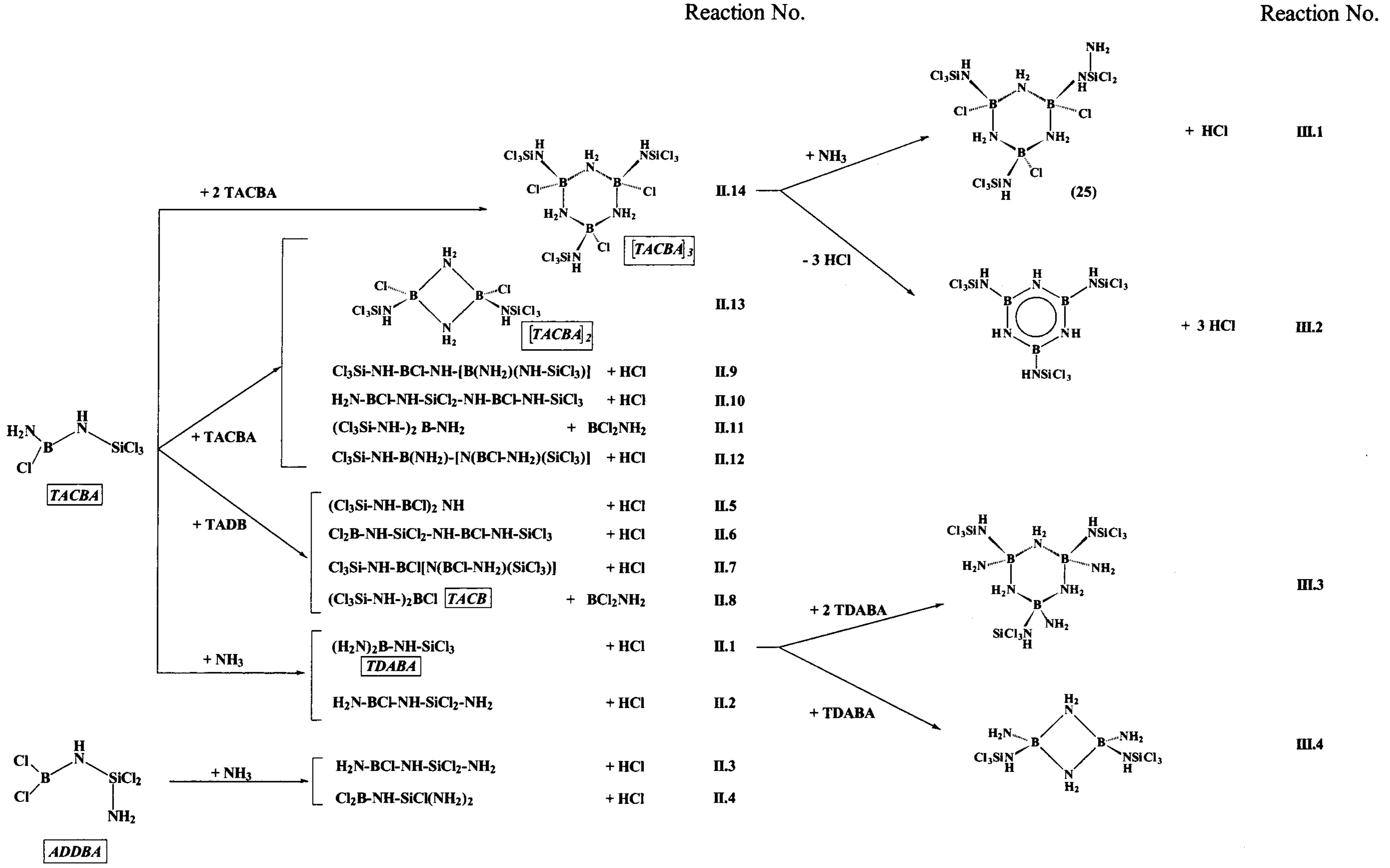


Figure 3. Survey of the investigated continuing reactions.

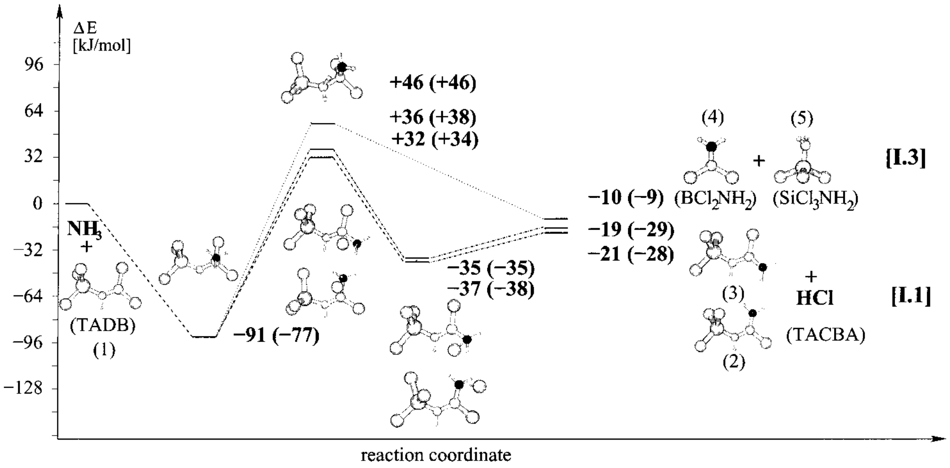


Figure 4. Energetic courses of the reactions of TADB with ammonia at the boron side.

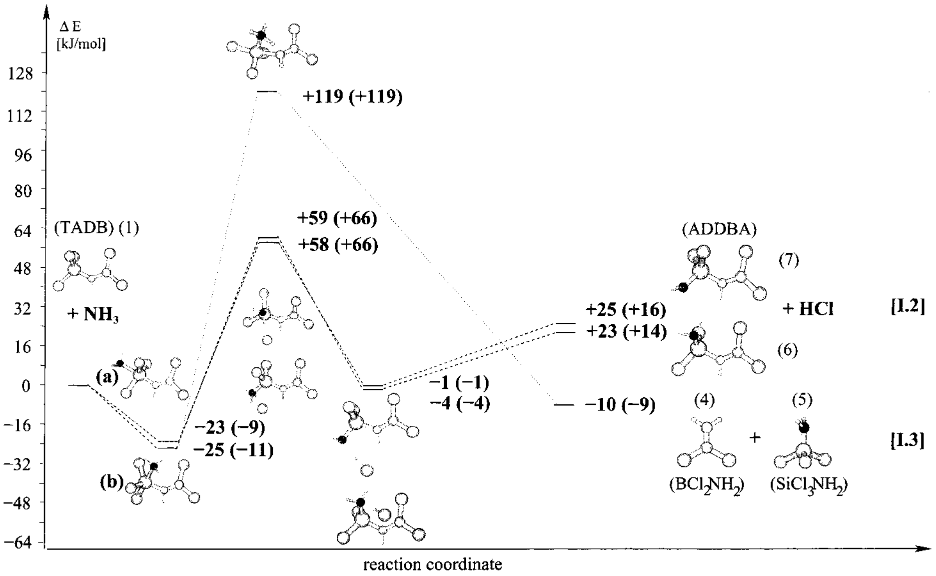


Figure 5. Energetic courses of the reactions of TADB with ammonia at the silicon side.

density functional (Becke88 exchange,Vosko−Wilk−Nusair correlation) and the Perdew gradient correction for the correlation functional (BP).[36−38] The choice of this functional was motivated by its satisfactory performance in geometry optimizations for molecules of this substance class.[25,39] Further, the BP expression does not contain parts of the Hartree−Fock exchange interaction that would prevent its usage in the RI routine of TURBOMOLE. Because reaction barriers are usually underestimated by density functional methods,[40,41] the structures which resulted from RI-DFT calculations were refined at the level of an RI-approximated second-order Møller−Plesset perturbation theory (RI-MP2).[42,43] We have tested the applicability of the RI-MP2 method by means of single-point energy calculations at the MP2 level of theory for ammonia and hydrogen chloride. Energy differences were found to be negligible, e.g., RI-MP2 yields −460.244 613 81 E_H for HCl which is 0.1 kcal/mol above the full MP2 treatment; the same applies to NH_3 [−56.416 004 74 E_H (RI-MP2)/−56.415 885 95 E_H (MP2)].

A structure refinement at the RI-MP2 level of theory has not been performed for larger molecules (reactions II.12, II.13, and III.1−III.4). Because structures at minima of the potential energy surface (PES) are reproduced well at the RI-DFT level, only single-point calculations were performed at the RI-MP2 level of theory.

3. Results

3.1. Initial Gas-Phase Reactions. *3.1.1. First Ammonolyses of TADB.* The substitution of a chlorine atom at the *boron side* of TADB (reaction I.1) proceeds in three steps (Figure 4). Ammonia readily forms an adduct with the boron atom of TADB. This adduct formation involves no transition state and is exothermic by 91 kJ mol^{-1}, or 77 kJ mol^{-1} if the zero-point vibrational energy (ZPVE) correction is taken into account. (In the following, values corrected for ZPVE are given in parentheses.) The HCl elimination reaction path bifurcates in its subsequent course: Either the chlorine atom in the transoid or the one in the cisoid position with respect to the central amino group can be exchanged. The saddle point for the elimination of hydrogen chloride in the transoid position is energetically slightly preferred. Note that the $SiCl_3$ group has rotated through 60° about the SiN axis. The energy gain of this torsion is moderate, 8 kJ mol^{-1} (5 kJ mol^{-1}) with respect to the original conformation. The barrier for the substitution of the cisoid chlorine is slightly higher, but in this case, a rotation of the $SiCl_3$ group is not required. Subsequently, the eliminated HCl forms a stable hydrogen-bonded complex with the product. The overall reaction to TACBA is exothermic, yielding approximately equal heats of reaction for the cisoid or transoid substitutions. It can be supposed that rates of both reactions

TABLE 1: Energy Differences (kJ mol^{-1}) between Reactants and Intermediates and Products of Primary Processes[a]

	reactants	(lowest) intermediate	(highest) TS	heat of reaction	products		reaction no.
1	TADB + NH_3	−91 (−77)	+32 (+34)	−21 (−28)	2	*trans*-TACBA +HCl	
		−91 (−77)	+36 (+38)	−19 (−29)	3	*cis*-TACBA +HCl	I.1
		−91 (−77)	+46 (+46)	−10 (−9)	4 + 5	BCl_2NH_2 + $SiCl_3NH_2$	I.3
		−25 (−11)	+119 (+119)				
		−25 (−11)	+59 (+66)	+23 (+14)	6	*trans*-ADDBA +HCl	
		−23 (−9)	+58 (+66)	+25 (+16)	7	*cis*-ADDBA +HCl	I.2
1	TADB + TADB		+128	+18	8	$Cl_3Si{-}NH{-}BClN(BCl_2)(SiCl_3)$ + HCl	I.4
		−17	+33	+19	9	TACB + BCl_3	I.5

[a] Values in parentheses have been corrected for zero-point vibrational energies.

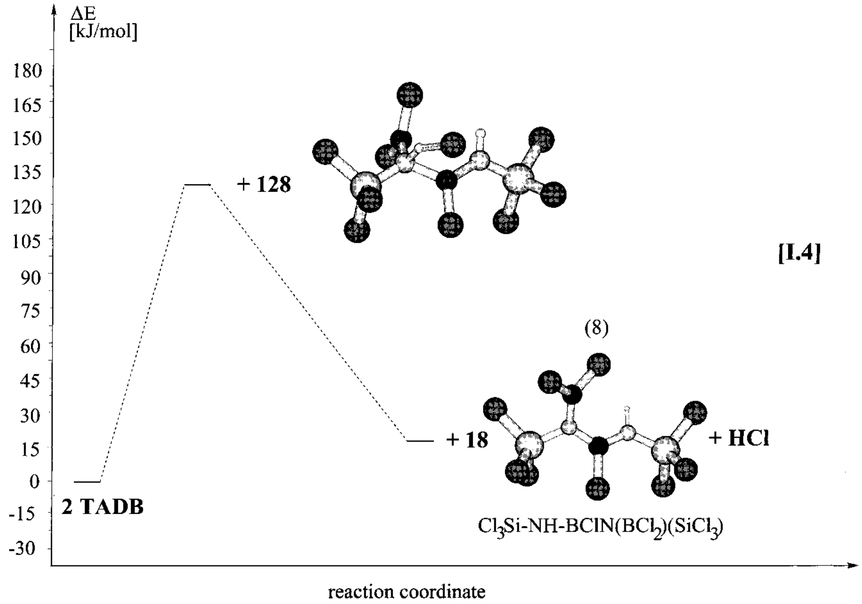


Figure 6. Reactions between two TADB molecules under elimination of HCl.

are equivalent. The substitution of a chlorine atom for an amino group at the *silicon* site (reaction I.2) is also a three-step reaction: an unhindered formation of an adduct and the subsequent elimination of hydrogen chloride via an H-bonded complex (Figure 5). In the adduct, silicon has a trigonal bipyramidal coordination environment. We have investigated two conformers of this adduct: (a) $NH{-}BCl_2$ and NH_3 in the axial positions or (b) Cl and NH_3 in the axial positions. A look at Figure 5 shows that adduct b is slightly favored. From these adducts, HCl is eliminated to form the product aminodichlorosilyldichloroboryl amine (ADDBA, Figure 2). The heights of the respective reaction barriers are equal. Starting from adduct a, the cisoid chlorine is exchanged. A total of 25 kJ mol^{-1} (16 kJ mol^{-1}) is needed, when this conformer is built. The formation of the transoid product is somewhat less endothermic. In either case, a stable H-bonded complex is located between the transition state and the product side. It is noteworthy that the $Cl{-}H{\cdots}NH_2{-}SiCl_2{-}$ hydrogen bonds are more stable than the corresponding H bridges at the boron side. Because the rotation about the Si−N bond occurs in an almost unhindered way in TADB,[25] it can be assumed that the conformers of the aminated molecule are also separated by small barriers and therefore easily convert into one another.

Instead of eliminating a chlorine ion from the 4-fold coordinated boron center of the ammonia adduct of TADB, the B−N bond of the central Si−N−B unit could be broken in order to restore the 3-fold coordination of boron. A similar scenario is possible for the Si−N bond of the 5-fold coordinated silicon center of adduct b in Figure 5. In either case, the breaking of the nitrogen bond is accompanied by migration of a hydrogen atom of the adduct ammonia to the central amino group, and thus, Cl_3SiNH_2 and Cl_2BNH_2 are formed. This reaction is exothermic by 10 kJ mol^{-1}. The transition state following the $H_3N \rightarrow BCl_2NHSiCl_3$ adduct formation is located at 46 kJ mol^{-1} (Figure 4). Certainly, a considerably higher barrier (119 kJ mol^{-1}) has to be overcome for the dissociation of $H_3N \rightarrow SiCl_3NHBCl_2$. An overview over the location of all stationary points in the course of primary reactions is given in Table 1.

3.1.2. Reaction of Two TADB Molecules. Because a first attack of a Lewis base is favored at the boron side of TADB, we may assume that the most probable case of a dimerization of TADB is the attack of the central amino group of one TADB (1) at the boron side of another TADB (2). Because of the considerable computational expense, we have refrained from computing vibrational frequencies although second derivatives were necessary for the verification of minima and saddle points. Following the trends observed in the previous sections, we can assume, however, that ZPVE corrections will favor the product side of HCl eliminations.

In analogy to the dimerization of BCl_2NH_2,[20] we had expected the first step during the dimerization of TADB to be the formation of an adduct $(BCl_2)(SiCl_3)HN \rightarrow BCl_2NHSiCl_3$. However, such an adduct does not correspond to a minimum on the PES, probably because of the bulky substituents (Figure 6). Although the dimerization of TADB with subsequent elimination of hydrogen chloride (reaction I.4) is only slightly endothermic, the reaction will probably not take place in the gas phase because of the high barrier (128 kJ mol^{-1}).

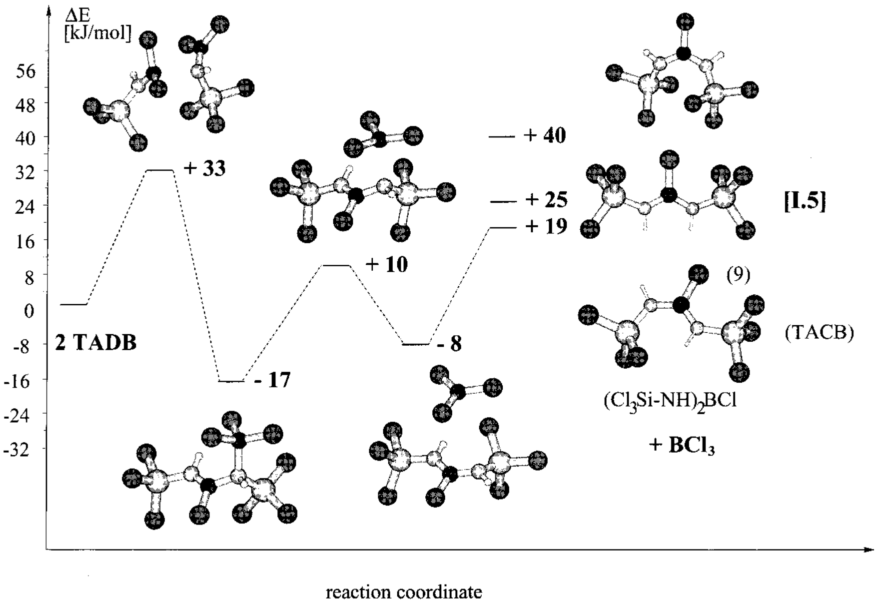


Figure 7. Reactions between two TADB molecules under elimination of BCl3.

TABLE 2: Energy Differences (kJ mol^{-1}) between Reactants and Intermediates and Products of Reactions between TACBA and ADDBA with Ammonia[a]

reactants		(lowest) intermediate	(highest) TS	(lowest) intermediate	products		reaction no.
2	*trans*-TACBA	−34	<+32[b]	+12 (+1)	10	TDABA + HCl	II.1
	+ NH_3	≈−25[b]	≈+60[b]	+12 (0)	11	*trans,trans*-$(SiCl_2NH_2)NH(BClNH_2)$+HCl	II.2
		≈−25[b]	≈+60[b]	+19 (+8)	12	*cis,trans*-$(SiCl_2NH_2)NH(BClNH_2)$+HCl	
3	*cis*-TACBA	≈−34[b]	<+32[b]	+10 (+1)	10	TDABA + HCl	II.1
	+ NH_3	≈−25[b]	≈+60[b]	+26 (+14)	13	*trans,cis*-$(SiCl_2NH_2)NH(BClNH_2)$+HCl	II.2
		≈−25[b]	≈+60[b]	+32 (+26)	14	*cis,cis*-$(SiCl_2NH_2)NH(BClNH_2)$+HCl	
6	*trans*-ADDBA	≈−90[b]	≈+30[b]	−32 (−42)	11	*trans,trans*-$(SiCl_2NH_2)NH(BClNH_2)$+HCl	II.3
	+ NH_3	≈−90[b]	≈+30[b]	−16 (−29)	13	*trans,cis*-$(SiCl_2NH_2)NH(BClNH_2)$+HCl	
		>−25[b]	<+60[b]	+24 (+10)	15	$Cl(NH_2)_2Si{-}NH{-}BCl_2$+HCl	II.4
7	*cis*-ADDBA	≈−90[b]	≈+30[b]	−27 (−36)	12	*cis,trans*-$(SiCl_2NH_2)NH(BClNH_2)$+HCl	II.3
	+ NH_3	≈−90[b]	≈+30[b]	−12 (−19)	14	*cis,cis*-$(SiCl_2NH_2)NH(BClNH_2)$+HCl	
		>−25[b]	<+60[b]	+22 (+8)	15	$Cl(NH_2)_2Si{-}NH{-}BCl_2$+HCl	II.4

[a] Values in parentheses have been corrected for zero-point vibrational energies. [b] Estimated by comparison to the stationary points of first ammonolysis reactions at the boron and silicon sides of TADB, respectively.

However, reducing the distance between the N atom of TADB and the B atom of another TADB molecule to an approximate single bond length, we observed the migration of one chlorine atom (Figure 7). The resulting BCl_3 substituent should be easily removable, yielding a $(Cl_3SiNH)_2BCl$ molecule (TACB). The reaction path leading to the most stable, C_s-symmetric $(Cl_3SiNH)_2BCl$ conformer (reaction I.5) proceeds via two intermediates and two shallow barriers. Please note that this path corresponds to a constrained minimum energy path. Further, we have not computed second derivatives, so that saddle points are not properly characterized as such. The overall reaction is only slightly endothermic and may therefore proceed at elevated temperatures. Indeed, $(Cl_3SiNH)_2BCl$ can be observed in experiment, if TADB is heated to 110 °C under inert gas atmosphere. It has been identified by means of NMR and IR spectroscopy as well as mass spectrometry.[27]

3.2. Continuing Gas-Phase Reactions. *3.2.1. Second Ammonolyses of TADB.* Having studied various reactions of TADB with one ammonia molecule further above, we now turn to a second substitution of a chlorine atom for an amino group (reactions II.1−II.4 in Figure 3). We will confine the analysis to a comparison of the product energies. From our previous study of the BCl_3 ammonolysis, we have learned that the heats of formation for the ammonia adducts and the barrier heights for the HCl eliminations diminish with progressing amination.[20] A theoretical investigation of the reaction of mono-silane with ammonia reveals similar trends.[44] On these grounds, we have assumed that adduct formation energies and barrier heights for the sequential ammonolysis of TADB behave likewise and are not decisive for the course of the reaction. Notice that in all HCl elimination reactions considered ZPVE corrections are considerably large.

First, let us focus on the case in which the primary reaction has taken place at the boron side of TADB to yield TACBA. A second amination will be possible at either the boron or the silicon sides. The formation of TDABA (Figure 3) is nearly energy neutral if ZPVE corrections are taken into account (Table 2). These results are in accord with the energetics of the boron trichloride ammonolysis, where the substitution of the last chlorine atom is slightly endothermic.[20] For a second substitution at the silicon side, four possibilities emerge: Each of the terminal amino substituents can be located either in transoid or in cisoid position with respect to the central amino group. All of these substitutions are endothermic, some however only very slightly or even energy neutral when ZPVE corrections are taken into account (Table 2). Concerning the energetic order of the conformers, we find the following general trends: Decisive is the position of the amino substituent at boron with respect to the central amino group. ADDBA molecules with a transoid arrangement of these groups are energetically favored over those

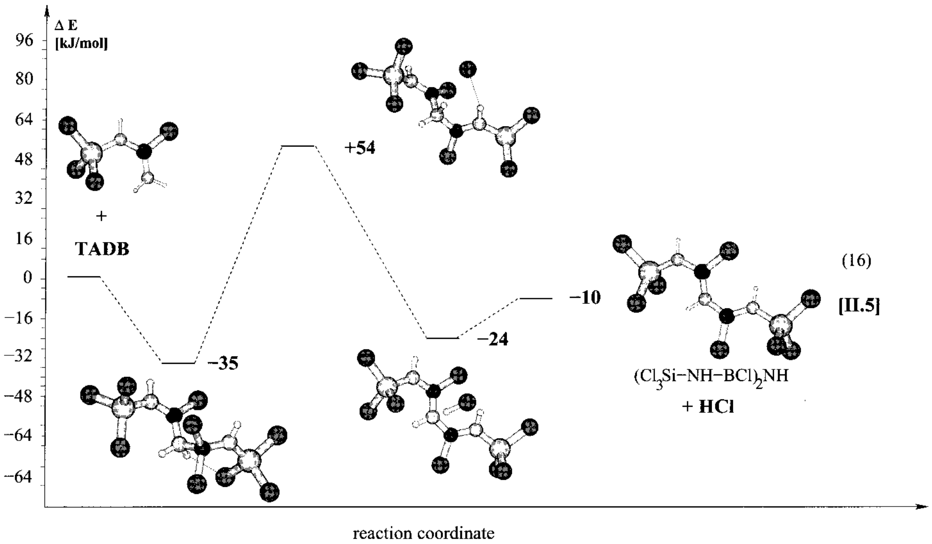


Figure 8. Elongation of the molecular backbone: the reaction of TACBA with TADB via boron.

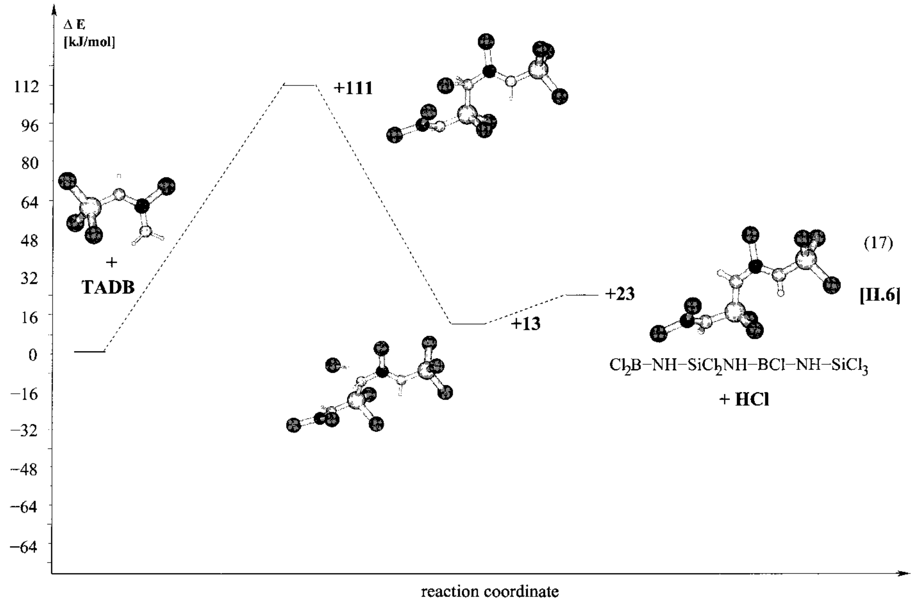


Figure 9. Elongation of the molecular backbone: the reaction of TACBA with TADB via silicon.

with a cisoid position. A similar, but less pronounced, influence of the position on the energy can be made out for amino groups at the silicon side.

If the first reaction between TADB and NH_3 has taken place at the silicon site, a second substitution can be expected either at the boron or the silicon sides. Of course, the exchange of a chlorine at the boron center of ADDBA yields the same reaction products as the amination of the silicon center of TACBA. With respect to the reactants ADDBA and NH_3, all aminations at B are exothermic. A second substitution at the silicon site is endothermic by 22 (8) and 24 kJ mol^{-1} (10 kJ mol^{-1}) for the two stable conformers of ADDBA, respectively (see Table 2 in which we have denoted the ZPVE-corrected values in parentheses).

In summary, the substitution of two chlorine atoms of TADB for NH_2 groups is exothermic, unless both amino groups are connected to the silicon site. With respect to TACBA, the most favorable second substitution products are either isoenergetic or somewhat less stable. Surprisingly, chlorine substitution at the silicon site of transoid TACBA will need only 12 (0) and 19 kJ mol^{-1} (8 kJ mol^{-1}), respectively. This is less than is needed for the analogous reaction with TADB. It can therefore be assumed that a substitution of the transoid chlorine in the BCl_2 group of TADB for an amino group *activates* the silicon atom for an attack by a nucleophilic partner.

3.2.2. Reactions of TACBA and TADB. After the first exchange of chlorine by an amino group, this new amino group can act as a Lewis base and attack the boron or silicon sites of another TADB molecule. These reactions lead to an elongation of the molecular backbone. Because the first ammonolysis of TADB yields four varying products which can again react with a TADB molecule in four different ways, many different products are possible. To obtain an idea whether this reaction path is favored, we have investigated the attack of the most stable first substitution product, *trans*-TACBA, at the boron and silicon atoms of another TADB molecule as sample reactions (reactions II.5 and II.6).

Figures 8 and 9 give a survey of calculated stationary points on the PES. Analogous to the reaction of TADB with ammonia at the boron center, the B−N−B linkage proceeds in three steps. The first step is the formation of an adduct which is exothermic by 35 kJ mol^{-1}. The subsequent elimination of hydrogen

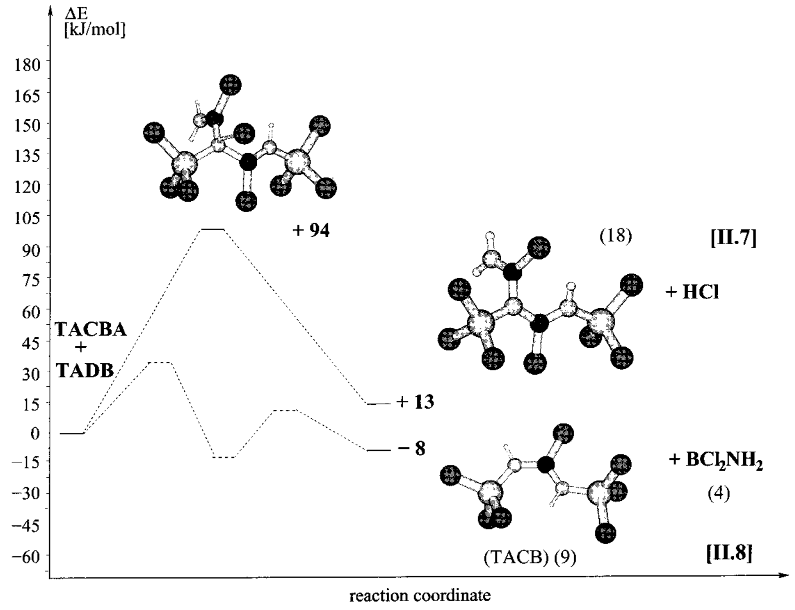


Figure 10. Branching of the molecular backbone: the reaction of TACBA with TADB under elimination of HCl.

TABLE 3: Energy Differences (kJ mol^{-1}) between Reactants and Intermediates and Products of Reactions between TACBA and TADB or TACBA[a]

reactants		(lowest) intermediate	(highest) TS	heat of reaction	products		reaction no.
2 + 1	*trans*-TACBA + TADB	−35	+54	−10	16	$(Cl_3SiNHBCl)_2NH + HCl$	II.5
			+111	+23	17	$Cl_2B{-}NH{-}SiCl_2NH{-}BCl{-}NH{-}SiCl_3 + HCl$	II.6
			+94	+13	18	$Cl_3Si{-}NH{-}BCl[N](BClNH_2)(SiCl_3) + HCl$	II.7
		≈−17[b]	≈+33[b]	−8	9 + 4	$TACB + BCl_2NH_2$	II.8
2	*trans*-TACBA + *trans*-TACBA	≈−24[c]	≈+12[c]	−50	19	TACBA dimer tetracyclic	II.13
		>−35[b] (No.(20))	<+54[d]	+16	21	$Cl_3Si{-}NH{-}BCl{-}NH{-}B(NH_2){-}NH{-}SiCl_3 + HCl$	II.9
			≈+111[d]	+25	22	$ClNH_2B{-}NH{-}SiCl_2{-}NH{-}BCl{-}SiCl_3 + HCl$	II.10
		>−17[b]	<+33[b]	+10	23	$(Cl_3Si{-}NH{-}B)_2NH + BCl_2NH_2$	II.11
			<+94[d]	+21	24	$Cl_3Si{-}NH{-}BNH_2[N](BClNH_2)(SiCl_3) + HCl$	II.12

[a] Values in parentheses have been corrected for zero-point vibrational energies. [b] Estimated by comparison to similar reactions between TADB and TADB (reaction II.5) or TADB and TACBA (reactions II.9−II.12). [c] Estimated by comparison to the stationary points during the dimerization of diaminochloroborane in ref 20. [d] Supposed to be lower than the barrier height of the corresponding reaction between TADB and TACBA (II.5−II.7).

chloride proceeds via a transition state and a hydrogen-bonded complex between HCl and the products. The barrier height amounts to 54 kJ mol^{-1}, and the overall reaction releases 10 kJ mol^{-1}. For the chain elongation of the molecular backbone via silicon, a formation of an adduct is expected as a first step, too. However, such an adduct does not correspond to a minimum on the PES. The Si−N−B linkage is a two-step reaction and involves a considerable barrier. Moreover, the overall reaction is endothermic.

Also, the central amino group of TACBA may attack the boron side of a TADB molecule (branching of the molecular backbone). The energy profiles of the hydrogen chloride or BCl_2NH_2 elimination reactions (reactions II.7 and II.8 in Figure 10) closely resemble the aforementioned dimerization of TADB (section 3.1.2). A high barrier has to be surmounted in the course of the HCl elimination (94 kJ mol^{-1}). In comparison to the corresponding TADB dimerization reaction I.4, reaction II.7 is enhanced, however. The same trend is observed for the cleavage of the B−N bond (reactions I.5 and II.8). The reaction of TACBA with TADB under elimination of BCl_2NH_2 yielding the C_s-symmetric $(Cl_3SiNH)_2BCl$ conformer (reaction II.8) becomes even slightly exothermic (−8 kJ mol^{-1}). These findings indicate that the central amino group of TACBA should be a stronger Lewis base than the central amino group of TADB. We have refrained from calculating the other stationary points of this reaction because the reaction path is supposed to be similar to the dimerization of TADB under BCl_3 elimination (reaction I.5).

3.2.3. Reactions of Two TACBA Molecules. The nucleophilic attack of the terminal amino group of TACBA is also possible at the boron and silicon centers of another TACBA molecule (reactions II.9−II.13). In TACBA, boron has two direct nitrogen neighbors, carries only one chlorine substituent, and is thus a weaker Lewis acid than the corresponding boron center of TADB. On the basis of the discussion in section 3.2.1, it can be assumed that the adduct formation at the boron center yields less energy and that the barrier is somewhat lower than during the reaction between TACBA and TADB. The B−N−B linkage under HCl elimination (reaction II.9) has been calculated to be endothermic by +16 kJ mol^{-1}, ZPVE corrections not taken into account. The products of this reaction (21 in Table 3) contain a strongly nucleophilic terminal amino group that can attack another monomeric TACBA, and so on, to yield a polymer of the composition $Cl_3Si{-}NH{-}BCl{-}NH{-}[BX{-}NH{-}]_n{-}BX{-}NH_2$ where X denotes an $-NH{-}SiCl_3$ substituent perpendicular to the $(BN)_n$ zigzag chain. Because of the high nucleophilicity of the terminal NH_2 group, the chain elongation is expected to be less endothermic than the first linkage reaction II.9 or even to release energy. Considering the formation of a B−N−Si link, the energetic locations of the intermediate and the transition

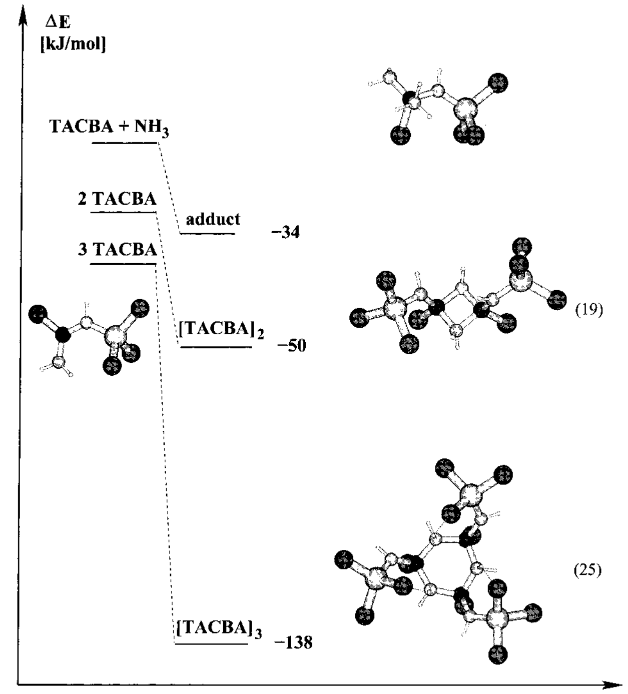


Figure 11. Oligomerizations of TACBA.

state should be similar to those of the chain elongation at the silicon center of TADB. Although the silicon side of TACBA is activated by the amino substituent at the boron center (analogous to a second ammonolysis at Si), the formation of the products requires +25 kJ mol^{-1}. In both substitution reactions, the product sides are assumed to be considerably stabilized by ZPVE corrections.

As expected, the attack of the central amino group of TACBA at the boron side of another TACBA molecule with subsequent BCl_2NH_2/HCl elimination (reactions II.11 and II.12) have less favorable energy balances than similar reactions between TACBA and TADB: the BCl_2NH_2 elimination is endothermic by +10 kJ mol^{-1} and the HCl elimination requires +21 kJ mol^{-1}.

3.2.4. Oligomerizations of TACBA. Because TACBA and TDABA contain both a Lewis base and a Lewis acid, an adduct formation between several of these molecules is possible. In these oligomerizations, no hydrogen chloride is eliminated, but 4-fold coordinated boron and nitrogen atoms are formed.

Borazane-like structures were postulated to occur as intermediates in the production of tris[trimethylsilyl]borazine from diborane and hexamethyldisilazane,[45] as well as in the formation of a borosilazane polymer from the molecular precursors $H_3B{\cdot}Si(CH_3)_3$ and $(CH_3SiHNH)_3$.[46] On these grounds, we investigated the dimerization and trimerization of TACBA (reactions II.13 and II.14). Among the conformers of [TACBA]$_2$ and [TACBA]$_3$, we optimized only those corresponding to the most stable forms of $[(NH_2)BCl]_n$.[20]

An overview of the product energies is given in Figure 11. The dimerization energy for the conformer of [TACBA]$_2$ with both $Cl_3Si{-}NH$ groups placed above the plane of the four-centered $(BN)_2$ ring amounts to 50 kJ mol^{-1}. The conformer of [TACBA]$_3$ which is expected to be the most favorable one exhibits all $-NH-SiCl_3$ groups in equatorial positions. We find that the formation of this conformer releases 138 kJ mol^{-1} (i.e., about 46 kJ mol^{-1} per newly formed BN bond). This is considerably more than in [TACBA]$_2$ where only 25 kJ mol^{-1} are gained per new BN bond. The larger energy gain is plausible because the ring strain of a six-membered cycle should be much smaller than those typical for four-membered rings. As for $[(NH_2)BCl]_2$, the trimer is also more stable than three ammonia adducts. It can be assumed that the stability of this [TACBA]$_3$ conformer is induced by three intramolecular hydrogen bonds, each between a chlorine atom of a $SiCl_3$ group and a hydrogen atom of a ring amino group.

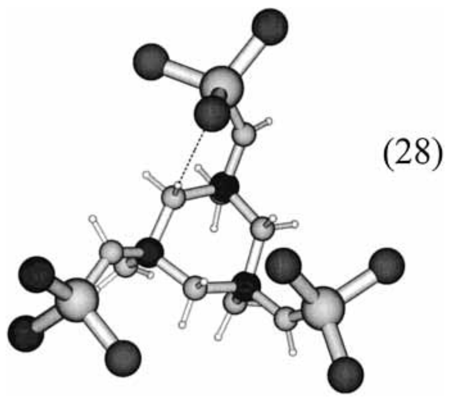


Figure 12. TDABA trimer.

3.2.5. Further Oligomerization Reactions. In comparison to TACBA, the formation of [TDABA]$_3$ (reaction III.3 in Figure 3) releases less energy, only slightly more than 20 kJ mol^{-1} per newly formed BN bond. Nevertheless, the trimerization shifts the equilibrium of the previous reaction, the second ammonolysis of TADB, to its product side. The formation of [TDABA]$_2$ is even endothermic (reaction III.4). This is plausible because the Lewis basicity of boron diminishes with a decreasing number of chlorine substituents.

In addition to pure BN rings, we have investigated the heat of reaction of six-membered rings containing varying amounts of silicon atoms (not shown). As SiN eight-membered rings are typical structural units in crystalline modifications of Si_3N_4, also the tetramerization of ADDBA has been considered. The building of trimers consisting of (a) 1 ADDBA/2 TACBA, (b) 2 ADDBA/1 TACBA, or (c) 3 ADDBA, with one, two, or three silicon atoms in the ring, releases less energy than the complexation of the reactants with ammonia or are even endothermic [(a) −68, (b) −28, and (c) +43 kJ mol^{-1}]. Also the reaction of four ADDBA molecules to form an SiN eight-membered ring is endothermic by 128 kJ mol^{-1}.

3.3. Reactions of the TACBA Trimer. As the trimerization of TACBA to form a BN six ring is considerably exothermic, it would be interesting to know the energetic course of a substitution reaction at the boron or the silicon sites of the trimer. For an ammonolysis of [TACBA]$_3$ at the boron centers yielding [TDABA]$_3$ (Figure 12), the energy balance is +113 kJ mol^{-1} (i.e., +38 kJ mol^{-1} per amino group in comparison to +12 kJ mol^{-1} for monomeric TACBA). The trimerization therefore passivates the further ammonolysis of the BCl bonds which one would probably not have anticipated. The elimination of three HCl molecules from [TACBA]$_3$ yielding a borazine derivate might also be a possible reaction path (Figure 13). However, with respect to the trimer, 174 kJ mol^{-1} are needed to form the planar BN six ring; with respect to three monomeric TACBA molecules, this process is endothermic by 36 kJ mol^{-1}.

In analogy to the substitution of a first chlorine atom of TADB at the silicon side, the ammonolysis of an $SiCl_3$ group of [TACBA]$_3$ proceeds in three steps. The formation of an ammonia adduct yields 16 kJ mol^{-1}, somewhat less than for monomeric TADB (25 kJ mol^{-1}). The subsequent elimination of HCl to form the product proceeds via a transition state and a hydrogen-bonded complex. The barrier height of this process

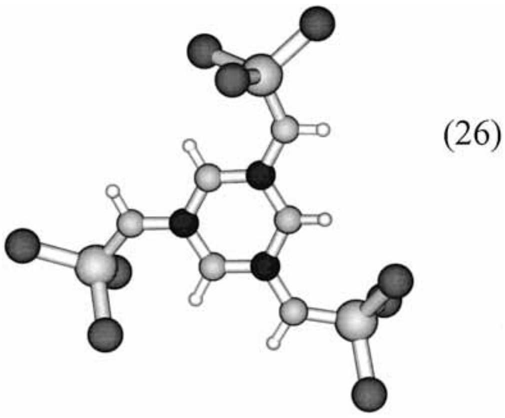

(26)

Figure 13. Borazine derivate.

has not been computed but should be similar to the one of the first ammonolysis. Overall, the ammonolysis of the Si−Cl bond of $[TACBA]_3$ requires 18 kJ mol^{-1} with respect to the reactants. Again, we expect the inclusion of ZPVE corrections to be in favor of the product side. If the energy required to substitute one chloride at each of the Si centers is assumed to be additive, an energy balance of + 54 kJ mol^{-1} results for the formation of 27.

4. Discussion

With several reactions having been investigated in detail, it has to be made clear which processes dominate a polymerization in the gas phase. Thereto, barrier heights and heats of reaction are compared.

Table 1 offers a survey of the positions of stationary points of the primary processes. It can be noticed that the substitution of a chlorine atom at the boron center (reaction I.1) has the lowest transition state and is the most exothermic primary reaction. The dissociation of $H_3N \rightarrow BCl_2NHSiCl_3$ adduct into BCl_2NH_2 and $SiCl_3NH_2$ (reaction I.3) is exothermic, too, and exhibits a moderate reaction barrier. All other primary processes are endothermic in the gas phase. Accordingly, the formation of TACBA is the main reaction, and the break-up of the Si−N−B bridge may occur as a side reaction. The barrier of the TADB dimerization under BCl_3 elimination (reaction I.5) is found to be low, and the reaction is only slightly endothermic. We conclude, therefore, that this reaction may take place in the absence of ammonia and at elevated temperatures, in agreement with experimental observations.[27] The corresponding dimerization reaction under HCl elimination (reaction I.4) is kinetically hindered by a high reaction barrier. Because of their high-lying transition states and their endothermicities, substitutions at the silicon side of TADB (reactions I.2) do not play a role in the initial stage of the gas-phase reaction.

Because all secondary processes are bimolecular reactions, their rates will depend on the relative concentrations of NH_3, TACBA, and TADB. In addition, the temperature is assumed to influence the further course of reactions. A look at Tables 2 and 3 reveals that there are two processes starting from TACBA (II.13 and II.8) which are exothermic and exhibit a low barrier; these two should therefore be very probable.

The second ammonolysis at the boron side of TACBA (reaction II.1) has a low-lying transition state, too, but products and reactants are isoenergetic. This process is therefore only slightly at a disadvantage to reaction II.8. Also an ammonolysis at the silicon side of TACBA (reaction II.2) is energy neutral but the barrier height is larger in this case. It should be kept in mind that ZPVE corrections will stabilize the products of HCl elimination reactions. Furthermore, the energy released in the TACBA formation makes many of the slightly endothermic follow-up reactions thermodynamically accessible if the transition state can be overcome.

Endothermic reactions with a low-lying transition state or exothermic reactions with a high barrier are less probable than the reactions mentioned in the last paragraph. Their occurrence can be controlled by the reaction temperature. At lower temperatures, the reaction of two TACBA molecules under branching of the molecular backbone with subsequent BCl_2NH_2 elimination (reaction II.11) might be accessible because of its low barrier. At slightly elevated temperatures, reactions II.5 and II.9 (extension of the molecular backbone) should easily proceed, too.

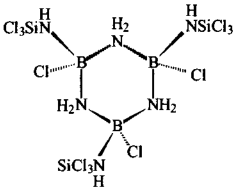
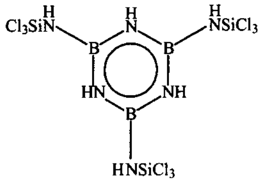
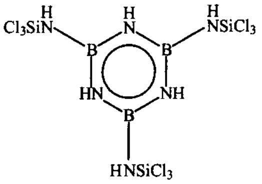
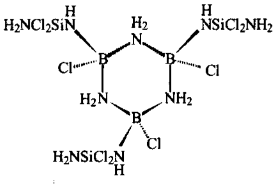
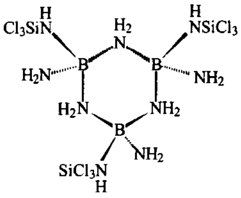
Most of the continuing reactions investigated are endothermic and exhibit a high barrier and are thus rather improbable in the gas phase. Among these are the branching reactions with subsequent HCl elimination (reactions II.7 and II.12) and the elongations of the molecular chain via the silicon side (reactions II.6 and II.10). It is noticeable that a link of two TACBA molecules via the boron side is only slightly less endothermic than via the silicon center, but the latter reaction is kinetically hindered because of its high transition state.

A comparison between Tables 2−4 shows that the trimerization of TACBA (reaction II.14) is much more exothermic than all other secondary processes investigated; it releases 138 kJ mol^{-1}.

Because of the high energy gain, the formation of trimers with a BN six-membered ring is assumed to be the main secondary process. A reaction path starting from the four-cyclic dimer (19) has not been found. However, the trimerization may proceed by adding a third TACBA molecule to a chainlike adduct of two TACBA molecules (20) and a subsequent ring-closure (Table 4). Because 4-fold coordinated boron and nitrogen atoms are formed in this reaction, it competes with the formation of three TACBA ammonia adducts, yielding 102 kJ mol^{-1} if ammonia attaches to boron and even less if it forms a dative bond to silicon. On the other hand, the attack of an ammonia molecule at the boron or silicon sides of TACBA proceeds without a transition state, whereas the trimerization requires the surmounting of a barrier, in analogy to $[BCl_2NH_2]_3$.[20] Thus, the formation of ammonia adducts is kinetically preferred. It has to be taken into account, however, that the HCl eliminations at the boron and silicon sides of TACBA do not release energy.

The formation of six-membered rings containing one or two silicon atoms is exothermic but releases less energy than the ammonia adduct formation. Six-membered rings including three silicon atoms or an SiN eight-membered ring are less stable than the reactants they are made of, and their formation is therefore improbable. $[TACBA]_3$ itself can react in several ways (Table 4). Whereas an ammonolysis at the silicon center is endothermic by 18 kJ mol^{-1}, a substitution at the boron site requires already 38 kJ mol^{-1}. Therefore, a cross-link at the silicon side is preferred and may proceed under mild heating. Because the elimination of three HCl molecules from $[TACBA]_3$ to form a borazine derivate requires 174 kJ mol^{-1}, the transformation into 3-fold coordinated boron and nitrogen may occur in the gas phase only during pyrolysis. Also, the formation of a borazine derivate via two chain elongation reactions between three TACBA molecules via intermediate 20 and a subsequent ring-closure cannot be expected in the gas phase because of the endothermicity of each step (Table 4).

TABLE 4: Energy Differences (kJ mol^{-1}) between Reactants and Products of Oligomerizations where n.d. Stands for Not Determined

reactants		(lowest) intermediate	heat of reaction	product(s)	reaction no.
(2)	3 TACBA	n.d.	−138	 (25)	II.14
(21)+(2)	[Cl_3Si-NH-(B-NH_2)]$_2$NH + TACBA	n.d.	≈+17[a]	 + 2 HCl (26)	
(25)	[TACBA]$_3$	n.d.	+174 [b]	 + 3 HCl (26)	III.2
(25)	[TACBA]$_3$ + 3NH$_3$	3·(−16)	3·(+18)	 + 3 HCl (27)	
(25)	[TACBA]$_3$ + 3NH$_3$	n.d.	+113	 + 3 HCl (28)	

[a] Estimated. [b] Corresponds to +36 compared to 3 × TACBA.

5. Conclusions

In this work, we studied *gas phase* reactions between molecular precursors which may form silicon boron nitrides. In the case of TADB (the molecule we considered as the starting compound in this paper), the main primary reaction occurs between TADB and NH_3 and is a first substitution of a chlorine atom for an amino group at the boron center, with the major product being TACBA (reaction I.1). The further course of reaction is dominated by the oligomerization of TACBA to form very stable trimers with 4-fold coordinated B and N (reaction II.14).

Elongation and branching of the Si−N−B backbone occur preferably after a single ammonolysis of a B−Cl or Si−Cl bond of the molecular precursor because the Lewis acidity of boron and silicon diminishes with an increasing number of amino substituents. For the same reasons, the continuing substitution of a chlorine atom for an amino group becomes more and more endothermic. It can therefore be concluded that a completely aminated TADB molecule will not be formed in the gas phase.

Probable side reactions are a second ammonolysis at the boron center of TACBA and processes during which the predesigned Si−N−B unit of the precursor opens up. Among the latter is the dissociation of the $H_3N \rightarrow BCl_2NHSiCl_3$ adduct to yield BCl_2NH_2 and $SiCl_3NH_2$ (reaction I.3) and the attack of the central amino group of TACBA at the boron center of another TADB (reaction II.8) in which TACB and BCl_3 are formed. For these reasons, TADB is not suited as a molecular precursor for the chemical vapor deposition of homogeneous borosilazane ceramic coatings.

Experimentally, the polymerization of TADB is conducted in liquid ammonia. Presumably, the presence of additional ammonia molecules shows a differential effect on the energetic course of different types of reactions and will thus influence the structure of the polymer. This topic will be assessed in the second part of this series.[28]

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