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Structure of Intramolecular Boron–Amine Complexes and Proposal of Tetrahedral Character for Correlation between Molecular Structure and Barrier to Dissociation of the N–B Bonds

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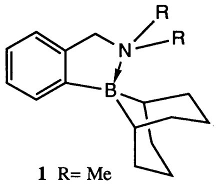
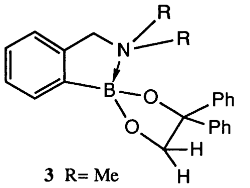
The molecular structures of a set of intramolecular boron–amine complexes, 9-[2-(dialkylaminomethyl)phenyl]-9-borabicyclo[3.3.1]nonanes (alkyl=Me and Et) and 2-[2-(dimethylaminomethyl)phenyl]-4,4-diphenyl-1,3,2-dioxaborolane, were determined by the X-ray analyses. The boron atom has a tetrahedral geometry and the five-membered ring is puckered with the nitrogen atom out of the plane in every complex. The distances of the N–B coordination bonds, which are in the range of 1.74—1.77 Å, are not always correlated to the barrier to dissociation of the N–B bonds. In order to correlate the molecular structures to the strength of the N–B coordination bonds, the tetrahedral character, which is calculated from bond angles at a boron atom, is proposed. The usefulness as well as the limitation of this parameter are discussed.

Determination of the kinetic parameters for dissociation of the N–B coordination bonds in intramolecular boronate-amine (**3**)[1)] and borane–amine (**1** and **2**)[2)] complexes by the dynamic NMR method has been reported. These reports reveal that the barrier height for N–B bond dissociation is affected by various factors including substituents and solvents. The substituents on the nitrogen atom (R) significantly influence the barrier; for example, when the *N*-methyl groups are replaced by two ethyl groups, the barriers are reduced by 4.2 and 1.5 kcal mol^{-1} in the borane and boronate systems, respectively.[1,2)] These reductions in the barrier height were explained by the steric effect or F-strain to the amino-nitrogen atom, thus the bulky substituents weakened basicity of the amine ligands.



1 R= Me
2 R= Et



3 R= Me

The strength of the N–B coordination bond is also affected by Lewis acidity of the boron atom. Acidity of the boron atom in a boronate is known to be weaker than that in a trialkylborane[3)] because attached oxygen atoms donate electron to the boron atom in the boronates. The boron atom in the 9-BBN group (9-BBN: 9-borabicyclo[3.3.1]non-9-yl) is more acidic than those in the boronates, but less acidic than those in general trialkylboranes due to the bulkiness of the 9-BBN moiety.

If these electronic and steric effects operate at the ground state in the dissociation process of the N–B coordination bond, the difference in the barrier heights is supposed to be reflected in the molecular structure of the complexes, e.g. the N–B bond distance and bond angles around the boron atom. These backgrounds tempted us to determine the molecular structures of these intramolecular boron-amine complexes by the X-ray analysis. We report here the molecular structure of 9-[2-(dimethylaminomethyl)phenyl]-9-borabicyclo[3.3.1]nonane (**1**), 9-[2-(diethylaminomethyl)phenyl]-9-borabicyclo[3.3.1]nonane (**2**), and 2-[2-(dimethylaminomethyl)phenyl]-4,4-diphenyl-1,3,2-dioxaborolane (**3**) and discuss the correlation between the molecular structure and the barrier to dissociation of the N–B bond.

Results and Discussion

Structures of Intramolecular Boron–Amine Complexes 1—3. The compounds used for the structure analyses were prepared by the methods reported previously.[1,2)] The final atomic coordinates and thermal parameters obtained from X-ray analyses are listed in Table 1 and their ORTEP drawings are shown in Fig. 1. Selected bond distances, bond angles, and torsion angles are listed in Tables 2—4 for compounds **1**—**3**, respectively.

These molecules have some common features of the structure which follow. It is evident that all compounds form intramolecular coordination bonds as is expected from general considerations. The bond angles in the boron atom are smaller than 120° predicted in a planar geometry, these values showing a distorted tetrahedral geometry of the boron atom. According to the torsion angles in the five-membered ring made by the NCCCB atoms, the ring is puckered and the nitrogen atom is displaced out of the plane. The distance between the nitrogen atom and the average plane made by other four atoms are 0.58, 0.54, and 0.51 Å in **1**—**3**, respectively. Torsion angles about the C(benzyl)–N bonds indicate that substituents at the carbon and the nitrogen atoms are in the nearly staggered forms rather than the eclipsed. The nitrogen atom cannot but move to the direction to avoid an unfavorable eclipsed form since the C–C–C–B moiety is immobilized by the rigid benzene plane. Such a puckered five-membered ring is also observed in other *o*-metallo-*N*,*N*-dimethylbenzylamines.[4)]

Table 1. Atomic Coordinates and Equivalent Isotropic Thermal Parameters in Compounds **1**—**3**[a)]

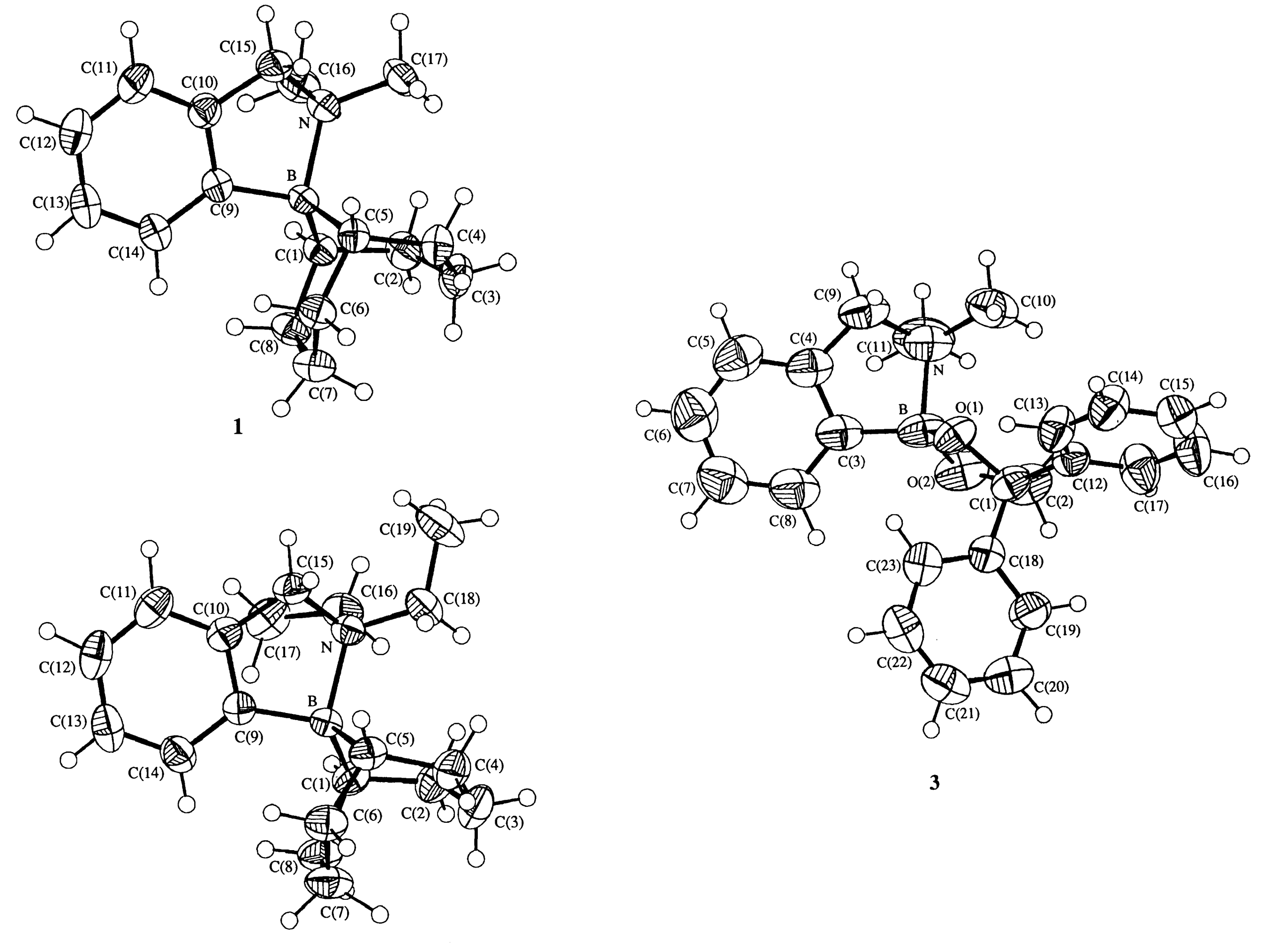
Atom	x	y	z	B_{eq}[b)]
Compound **1**				
B	0.42259(9)	0.1852(1)	0.2769(1)	2.47(4)
N	0.34788(7)	0.0577(1)	0.1997(1)	2.86(3)
C(1)	0.53012(9)	0.1467(1)	0.3051(1)	2.90(4)
C(2)	0.5515(1)	0.1236(2)	0.1677(2)	3.93(4)
C(3)	0.5267(1)	0.2370(2)	0.0636(2)	4.83(5)
C(4)	0.4333(1)	0.3037(2)	0.0457(2)	4.00(4)
C(5)	0.40512(9)	0.3155(1)	0.1799(1)	2.94(4)
C(6)	0.4617(1)	0.4243(1)	0.2759(2)	3.43(4)
C(7)	0.5661(1)	0.3962(2)	0.3375(2)	3.95(4)
C(8)	0.5914(1)	0.2565(2)	0.3913(2)	3.43(4)
C(9)	0.38546(9)	0.1984(1)	0.4116(1)	2.70(3)
C(10)	0.29911(9)	0.1386(1)	0.3864(1)	3.26(4)
C(11)	0.2528(1)	0.1332(2)	0.4844(2)	4.47(5)
C(12)	0.2927(1)	0.1907(2)	0.6140(2)	4.90(5)
C(13)	0.3768(1)	0.2533(2)	0.6425(2)	4.13(5)
C(14)	0.4228(1)	0.2574(1)	0.5427(1)	3.30(4)
C(15)	0.2633(1)	0.0841(2)	0.2413(2)	3.65(4)
C(16)	0.3888(1)	−0.0678(2)	0.2657(2)	4.01(4)
C(17)	0.3170(1)	0.0397(2)	0.0449(2)	3.90(4)
Compound **2**				
B	0.8736(2)	0.2115(2)	0.7714(2)	2.55(5)
N	0.9667(1)	0.1622(1)	0.8928(2)	2.92(4)
C(1)	0.9117(2)	0.2187(2)	0.6004(2)	3.25(5)
C(2)	0.9299(2)	0.1232(2)	0.5298(3)	4.42(7)
C(3)	0.8337(3)	0.0608(2)	0.5276(4)	5.17(8)
C(4)	0.7720(2)	0.0572(2)	0.6741(4)	4.38(7)
C(5)	0.7657(2)	0.1493(2)	0.7641(3)	3.28(6)
C(6)	0.6833(2)	0.2146(2)	0.6955(3)	4.11(7)
C(7)	0.7110(2)	0.2477(2)	0.5385(3)	4.84(8)
C(8)	0.8272(2)	0.2740(2)	0.5130(3)	4.24(7)
C(9)	0.8596(2)	0.3076(2)	0.8649(2)	2.89(5)
C(10)	0.8969(2)	0.2986(2)	1.0097(2)	3.19(5)
C(11)	0.8962(2)	0.3717(2)	1.1117(3)	4.19(7)
C(12)	0.8570(2)	0.4572(2)	1.0691(4)	4.61(8)
C(13)	0.8191(2)	0.4690(2)	0.9278(4)	4.51(8)
C(14)	0.8199(2)	0.3954(2)	0.8272(3)	3.72(6)
C(15)	0.9390(2)	0.2038(2)	1.0402(3)	3.49(6)
C(16)	1.0774(2)	0.1875(2)	0.8503(3)	3.82(6)
C(17)	1.1059(2)	0.2899(2)	0.8522(4)	4.48(7)
C(18)	0.9612(2)	0.0573(2)	0.9062(4)	4.04(7)
C(19)	1.0243(3)	0.0135(3)	1.0301(5)	6.0(1)
Compound **3**				
B	0.6442(1)	0.1987(3)	0.3178(2)	5.4(1)
N	0.62131(9)	0.1248(2)	0.3857(1)	5.87(8)
O(1)	0.60535(6)	0.1360(2)	0.23797(8)	4.92(5)
O(2)	0.71052(7)	0.1678(2)	0.34371(9)	6.09(6)
C(1)	0.64757(9)	0.0761(2)	0.2121(1)	4.39(8)
C(2)	0.7106(1)	0.0591(3)	0.2944(2)	5.7(1)
C(3)	0.6233(1)	0.3430(3)	0.3268(1)	5.37(9)
C(4)	0.5791(1)	0.3438(3)	0.3561(1)	5.7(1)
C(5)	0.5507(1)	0.4587(4)	0.3636(2)	7.2(1)
C(6)	0.5671(2)	0.5774(4)	0.3418(2)	8.1(1)
C(7)	0.6110(2)	0.5802(4)	0.3118(2)	8.0(1)
C(8)	0.6386(1)	0.4641(3)	0.3043(2)	6.9(1)
C(9)	0.5654(1)	0.2074(3)	0.3753(2)	6.4(1)
C(10)	0.6033(2)	−0.0171(3)	0.3690(2)	8.1(1)
C(11)	0.6761(2)	0.1398(4)	0.4728(2)	7.8(1)
C(12)	0.6180(1)	−0.0526(2)	0.1676(1)	4.38(8)
C(13)	0.5524(1)	−0.0595(3)	0.1159(2)	5.7(1)
C(14)	0.5233(1)	−0.1731(3)	0.0724(2)	6.4(1)
C(15)	0.5594(2)	−0.2821(3)	0.0793(2)	6.6(1)
C(16)	0.6247(2)	−0.2759(3)	0.1285(2)	8.0(1)
C(17)	0.6543(1)	−0.1625(3)	0.1726(2)	6.6(1)
C(18)	0.6573(1)	0.1692(2)	0.1538(1)	4.15(8)
C(19)	0.7022(1)	0.1385(3)	0.1284(2)	5.7(1)
C(20)	0.7121(1)	0.2213(3)	0.0756(2)	6.8(1)
C(21)	0.6761(2)	0.3339(3)	0.0455(2)	6.6(1)
C(22)	0.6312(1)	0.3651(3)	0.0695(2)	6.2(1)
C(23)	0.6219(1)	0.2840(3)	0.1238(2)	5.4(1)

a) Values in parentheses are estimated standard deviations. b) $B_{eq}/\text{Å}^2=(8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j$.

The length of the N–B coordination bond is 1.746(3) and 1.764(2) Å for the borane–amine complexes **1** and **2**, respectively. There are a few reports on structures of trialkylborane–trialkylamine complexes to be compared with the results. One of the available data is the N–B length of 1.698 Å in trimethylamine–trimethylborane complex determined by microwave analysis in the gas phase.[5)] The N–B bond distances in the gas phase are larger than the corresponding distances in the solid phase.[6)] Nevertheless the N–B bonds in **1** and **2** are longer than that in the $Me_3N:BMe_3$ complex. These long N–B bond distances in the 9-BBN complexes can be ascribed to the weak acidity of the boron and/or the weak basicity of the amine in the complexes with respect to those in $Me_3N:BMe_3$. Especially the Lewis acidity of the boron atom in the 9-BBN group is weaker than that in other trialkylboranes due to its bulkiness.

In the boronate complex **3**, the N–B length is 1.756(4) Å and comparable to those in the borane complexes **1** and **2**. Several data are available for the N–B bond distance in boronate complexes as references. Structures of tetrahedral and trigonal boronate complexes have been extensively studied by Rettig et al.[7)] They reported that N–B bond distances in those compounds were in the range from 1.666 Å in **9**[8)] to 1.759 Å in **4**,[9)] being dependent on the basicities of amine ligands. When basicity of the nitrogen atom which coordinates to the boron atom is not so strong, the distance is long and is in the range of 1.74—1.76 Å.[9,10)] They concluded that the steric effects were the most important factor in determining the lengths of the N–B bond.[9)] Incidentally the N–B bond distance we obtained in compound **3** is just in this long distance range.

One of the significant differences between the structures of the borane and boronate complexes is the distance of the B–C_{Ph} bond. The bond distances are ca. 1.63 Å in the borane complexes, while the bond is very short in the boronate complex **3**, 1.576 Å, this distance being comparable to the B–C_{Ph} bond in trigonal boron



1

2

3

Fig. 1. ORTEP drawings of compounds **1**—**3** with thermal ellipsoids at 50% probability.

compounds, triphenylborane[11] and phenylboronic acid.[12] The difference in the bond lengths can be explained by hybridization of the boron atom as discussed later.

^{1}H NMR spectra of compounds **1** and **2** showed identical chemical shifts for the two methyl or ethyl protons at the nitrogen atoms, the benzylic methylene protons, and some pairs of protons in the 9-BBN group at a low temperature.[2] These features led us to conclude that the molecule had a σ-plane which passed through the five-membered ring. The molecular structure obtained from X-ray analysis is inconsistent with the feature predicted by the NMR. This can be attributed to the fact that the pseudorotation in the five membered ring takes place much faster than the time scale of NMR in solution.

Torsion angles in the phenyl group bonded to the boron atom are less than 2° in all compounds, these values suggesting that the phenyl group is almost planar. The phenyl group, however, has some unusual bond angles. The C(10)–C(9)–C(14) bond angle is 115.8° in **1** and this value is significantly smaller than a normal angle 120°. In contrast, the bond angles at the neighboring phenyl carbons, C(9)–C(10)–C(11) and C(9)–C(14)–C(13), are larger than 120°. This kind of deformation of a phenyl group, a small bond angle at the *ipso* carbon and large bond angles at the *ortho* carbons, are generally observed in arylboranes whichever structure, trigonal or tetrahedral, the boron takes. For example, the average C(*ortho*)–C(*ipso*)–C(*ortho′*) bond angle in the phenyl carbons attached to boron atom was reported to be 116.8° in triphenylborane by X-ray analysis.[11] Rettig and Trotter explained that this deformation was due to the electron releasing character of the boron atom.[8,13] When an electron-repelling group (X) substitutes at a phenyl carbon, the C–X bond has a larger s-character and the C–C(*ortho*) bonds have a smaller s-character than that in an ordinary sp^2 hybridization (33%). As a result, the bond angle C(*ortho*)–C(*ipso*)–C(*ortho′*) becomes less than 120°.[14]

The bond angles at C(9) and C(10) in the five-membered ring, B–C(9)–C(10) and C(9)–C(10)–C(15), are small (ca. 112°) and the remaining bond angles, B–C(9)–C(14) and C(15)–C(10)–C(11), are large in **1**. In particular, the B–C(9)–C(14) bond angle of 132.5° is much larger than a standard value. This deformation

Table 2. Selected Bond Distances, Bond Angles, and Torsion Angles in Compound **1**

Bond distances (Å)			
B–N	1.746(2)	B–C(1)	1.621(2)
B–C(5)	1.627(2)	B–C(9)	1.634(2)
N–C(15)	1.504(2)	N–C(16)	1.491(2)
N–C(17)	1.489(2)	C(1)–C(2)	1.538(2)
C(2)–C(3)	1.530(2)	C(3)–C(4)	1.539(3)
C(4)–C(5)	1.548(2)	C(5)–C(6)	1.546(2)
C(6)–C(7)	1.540(2)	C(7)–C(8)	1.537(2)
C(1)–C(8)	1.542(2)	C(9)–C(10)	1.401(2)
C(10)–C(11)	1.386(2)	C(11)–C(12)	1.383(2)
C(12)–C(13)	1.380(3)	C(13)–C(14)	1.398(2)
C(9)–C(14)	1.397(2)	C(10)–C(15)	1.495(2)
Bond angles (°)			
N–B–C(9)	94.7(1)	N–B–C(1)	112.0(1)
N–B–C(5)	113.02(8)	C(1)–B–C(5)	105.5(1)
C(1)–B–C(9)	118.4(1)	C(5)–B–C(9)	113.3(1)
B–N–C(15)	103.7(1)	B–N–C(16)	109.17(9)
B–N–C(17)	120.1(1)	C(15)–N–C(16)	107.8(1)
C(15)–N–C(17)	107.6(1)	C(16)–N–C(17)	107.8(1)
B–C(9)–C(10)	111.7(1)	B–C(9)–C(14)	132.5(1)
C(10)–C(9)–C(14)	115.8(1)	C(9)–C(10)–C(11)	123.5(1)
C(9)–C(10)–C(15)	111.7(1)	C(11)–C(10)–C(15)	124.8(1)
C(10)–C(11)–C(12)	118.9(2)	C(11)–C(12)–C(13)	119.6(2)
C(12)–C(13)–C(14)	120.7(1)	C(9)–C(14)–C(13)	121.3(1)
N–C(15)–C(10)	105.2(1)		
Torsion angles (°)			
N–B–C(9)–C(10)	−18.0	C(15)–N–B–C(9)	31.9
B–C(9)–C(10)–C(15)	−2.4	C(10)–C(15)–N–C(16)	79.8
C(9)–C(10)–C(15)–N	25.7	C(10)–C(15)–N–C(17)	−164.1
C(10)–C(15)–N–B	−35.9		

Table 3. Selected Bond Distances, Bond Angles, and Torsion Angles in Compound **2**

Bond distances (Å)			
B–N	1.746(3)	B–C(1)	1.620(3)
B–C(5)	1.642(3)	B–C(9)	1.625(3)
N–C(15)	1.499(3)	N–C(16)	1.509(3)
N–C(18)	1.509(3)	C(1)–C(2)	1.528(4)
C(2)–C(3)	1.520(4)	C(3)–C(4)	1.539(4)
C(4)–C(5)	1.552(4)	C(5)–C(6)	1.538(4)
C(6)–C(7)	1.535(4)	C(7)–C(8)	1.549(4)
C(1)–C(8)	1.552(4)	C(9)–C(10)	1.396(3)
C(10)–C(11)	1.394(4)	C(11)–C(12)	1.377(4)
C(12)–C(13)	1.374(5)	C(13)–C(14)	1.391(4)
C(9)–C(14)	1.398(3)	C(10)–C(15)	1.487(3)
C(16)–C(17)	1.511(4)	C(18)–C(19)	1.514(4)
Bond angles (°)			
N–B–C(9)	95.2(1)	N–B–C(1)	114.4(2)
N–B–C(5)	111.9(2)	C(1)–B–C(5)	104.4(2)
C(1)–B–C(9)	118.2(2)	C(5)–B–C(9)	112.8(2)
B–N–C(15)	103.4(2)	B–N–C(16)	112.2(2)
B–N–C(18)	114.6(2)	C(15)–N–C(16)	110.6(2)
C(15)–N–C(18)	108.2(2)	C(16)–N–C(18)	107.7(2)
B–C(9)–C(10)	111.7(2)	B–C(9)–C(14)	132.5(2)
C(10)–C(9)–C(14)	115.8(2)	C(9)–C(10)–C(11)	123.0(2)
C(9)–C(10)–C(15)	112.4(2)	C(11)–C(10)–C(15)	124.6(2)
C(10)–C(11)–C(12)	119.1(2)	C(11)–C(12)–C(13)	119.7(3)
C(12)–C(13)–C(14)	120.6(2)	C(9)–C(14)–C(13)	121.7(3)
C(10)–C(15)–N	106.5(2)	N–C(16)–C(17)	117.1(2)
N–C(18)–C(19)	116.6(2)		

Table 3. (Continued)

Torsion angles (°)			
N–B–C(9)–C(10)	−17.7	C(10)–C(15)–N–C(18)	−154.1
B–C(9)–C(10)–C(15)	−0.2	C(15)–N–C(16)–C(17)	−53.2
C(9)–C(10)–C(15)–N	22.3	C(15)–N–C(18)–C(19)	−53.6
C(10)–C(15)–N–B	−32.1	C(18)–N–C(16)–C(17)	−171.3
C(15)–N–B–C(9)	29.4	C(16)–N–C(18)–C(19)	65.9
C(10)–C(15)–N–C(16)	88.2		

Table 4. Selected Bond Distances, Bond Angles, and Torsion Angles in Compound **3**

Bond distances (Å)			
B–N	1.754(4)	B–O(1)	1.450(3)
B–O(2)	1.437(3)	B–C(3)	1.577(4)
O(1)–C(1)	1.433(3)	O(2)–C(2)	1.428(4)
C(1)–C(2)	1.538(3)	N–C(9)	1.498(4)
N–C(10)	1.488(4)	N–C(11)	1.504(3)
C(3)–C(4)	1.391(4)	C(4)–C(5)	1.383(5)
C(5)–C(6)	1.380(5)	C(6)–C(7)	1.394(7)
C(7)–C(8)	1.384(5)	C(3)–C(8)	1.396(4)
Bond angles (°)			
N–B–O(1)	105.9(2)	N–B–O(2)	109.6(2)
N–B–C(3)	95.7(2)	O(1)–B–O(2)	107.2(2)
O(1)–B–C(3)	115.8(2)	O(2)–B–C(3)	120.9(2)
B–N–C(9)	103.2(2)	B–N–C(10)	114.9(2)
B–N–C(11)	108.3(2)	C(9)–N–C(10)	111.5(2)
C(9)–N–C(11)	109.4(2)	C(10)–N–C(11)	109.3(2)
B–C(3)–C(4)	112.3(2)	B–C(3)–C(8)	130.0(3)
C(4)–C(3)–C(8)	117.5(3)	C(3)–C(4)–C(5)	122.4(3)
C(3)–C(4)–C(9)	112.0(3)	C(5)–C(4)–C(9)	125.5(3)
C(4)–C(5)–C(6)	119.1(4)	C(5)–C(6)–C(7)	120.1(4)
C(6)–C(7)–C(8)	120.0(4)	C(3)–C(8)–C(7)	120.9(4)
C(4)–C(9)–N	105.4(3)		
Torsion angles (°)			
N–B–C(3)–C(4)	−20.4	B–O(1)–C(1)–C(2)	21.9
B–C(3)–C(4)–C(9)	2.8	O(1)–C(1)–C(2)–O(2)	−31.6
C(3)–C(4)–C(9)–N	20.3	C(1)–C(2)–O(2)–B	29.8
C(4)–C(9)–N–B	−31.6	C(2)–O(2)–B–O(1)	−16.7
C(9)–N–B–C(3)	31.1	O(2)–B–O(1)–C(1)	−4.5
C(4)–C(9)–N–C(10)	−155.5	C(4)–C(9)–N–C(11)	83.5

can be mainly attributed to the coordination between the boron and the nitrogen which attracts the aminomethyl group and the boron group with each other. Similar features of the bond angles in the phenyl carbons are observed in **2** and **3** as well.

The structure of the 9-BBN group in **1** and **2** is similar to those in uncoordinated compounds[15] and a tetrahedral compound[16] as a whole. The carbons at 3,7-positions are directed opposite to the boron atom in the chair form of the six-membered rings made by B–C(1)–C(2)–C(3)–C(4)–C(5) and B–C(5)–C(6)–C(7)–C(8)–C(1). There are, however, some differences between structures of 9-BBN groups in uncoordinated and coordinated compounds. In compounds **1** and **2**, the B–C(1) and B–C(5) bonds are longer and the C(1)–B–C(5) bond angle is smaller than those in the 9-BBN groups of uncoordinated compounds, in which the averages of corresponding bond distances and angles are 1.57 Å and 111.8°, respectively.[15] These features are consistent with the change in hybridization of the boron atom as discussed later. The bond angles of C(9)–B–C(1) and C(9)–B–C(5) indicate that the 9-BBN group is twisted to the opposite side of the CCCB plane to the nitrogen which is also displaced from the plane in **1** and **2**. Furthermore the bond distances of B–C(1) and B–C(5) are significantly different in the diethyl compound **2** from each other. The 9-BBN group may be deformed to minimize the steric hindrance between the two ethyl groups and the 9-BBN group.

The orientation of the methyls in the two ethyl groups in **2** deserves mention. One of the methyl groups, C(19), extends upward in the ORTEP view (Fig. 1), namely opposite to the 9-BBN group, and another, C(17), extends above the five membered ring. Focusing our attention on the N–C(16 or 18) bond, we can see that the positions of C(17) and C(18) are *anti* and those of C(16) and C(19) *gauche* with each other. The both methyl groups were first assumed to be directed away from the 9-BBN group to avoid steric hindrance, thus taking ±*gauche* conformations. This orientation is, however, less stable than the observed one because the steric interactions between the methyl groups in the ethyl groups of the conformation are large.

The 1,3,2-dioxaborolane ring in **3** is a distorted envelope form and the carbon at the 5-position, C(2), is out of the plane made by other four atoms. This carbon is bent up to the plane in the ORTEP view. Although we cannot explain why this conformation is stable from available information, the steric effects of the two phenyl groups at the 4-position in the 1,3,2-dioxaborolane ring should play an important role in favoring this structure.

Correlation between Structure and Barrier to Dissociation of N–B Bond. The distance of the N–B bond in the diethyl compound **2** is slightly but significantly larger by 0.18 Å than that in the dimethyl compound **1**. It seems that the difference in the bond distance reflects the barrier heights to dissociation of the N–B bond ($\Delta G^{\neq}_{323}$ **1**: 18.4 kcal mol^{-1}, **2**: 14.4 kcal mol^{-1}).[2] Compound **3** has a comparable N–B bond distance to the borane complexes nevertheless it gave the lowest barrier ($\Delta G^{\neq}_{233}$ 11.3 kcal mol^{-1})[1] in the three compounds. Though the distance of the N–B bond may be used as a clue of the strength of the bond in the borane system, the correlation—the longer the N–B bond distances, the easier the bond dissociates—is not always held in these intramolecular boron–amine complexes. A similar finding is reported in the relation between the N–B bond distances and the heat of reaction in pyridine–boron trihalide complexes. The bond distance is longer in the trichloro complex than the trifluoro complex, though the heat of reaction is larger in the trichloro complex.[17] We must correlate the bond length with the stability with great care.

One of the reasons for the ambiguity of the correlation is the steric effects of the boron moiety. The amino-nitrogen atom cannot approach the boron atom closely enough to optimize the N–B interaction due to the bulkiness of the 9-BBN group, this reason being reflected in the deformation of the five membered ring. The difference in the B–C_{Ph} bond distance can influence the N–B bond distances as well. It is assumed that the long B–C_{Ph} bond in the borane complexes brings important influence on the deformation of the five membered ring.

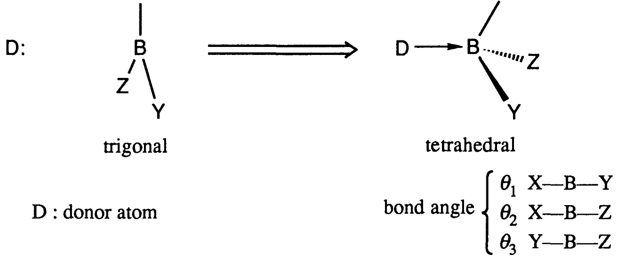
In order to get further insights into the correlation between the structure and the barrier height to dissociation of the N–B bond, we wish to use another set of parameters. In the literature, there are at least two attempts to correlate the molecular interactions with the deformation in molecular structures. One is the attempt of Dunitz et al.,[18] which is successfully utilized to the carbonyl-amine interactions, and uses the quantity (pyramidality) of pyramidal deformation of the carbonyl moiety; the stronger the interaction, the more pyramidal the structure of the carbonyl moiety. The other is that of Tamao et al.[19] which succeeds in correlating the molecular structures with the Si–F interactions; the trigonal-bipyramidal character of a hypervalent silicon atom was correlated with the bond angles involving the silicon atom.

The correlation of the strength of the molecular interactions between amines and boranes with pyramidality of the structure about the boron atom seems to have some shortcomings. Firstly, the bond lengths of the B–X involved in the borane complexes, RBX_2, in which we are interested, are in a wide range, with respect to the ketones, R_2CO, which were studied by Dunitz and coworkers[18] and had two C–C bonds of almost the same lengths. The bond lengths will affect the pyramidality, even if the molecular interactions are of the same strength. In addition, the method may succeed if the amine moiety approaches the boron in the bisecting plane of the borane, RBX_2, with the lone pair of electrons of the amine in the same plane, as is the case of approach of a base to a carbonyl group. However, the cases here clearly show that the geometry of approach of the amine to the boron moiety is not ideal for the use of the pyramidality: The direction of approach of the lone pair electrons is not in the bisecting plane of the RBX_2 moiety. Therefore, we decided to modify the Tamao's method to correlate the strength of the amine–borane bond with the structure.

When a boron atom is trigonal, that is in the case where an amine ligand locates infinitely far from the boron, the bond angles at the boron should be 120°. The closer a donor comes to the boron, the more the boron atom changes its hybridization from trigonal (sp^2) to tetrahedral (sp^3) by the coordination. Then we consider a parameter calculated from three bond angles at the boron atom as follows:

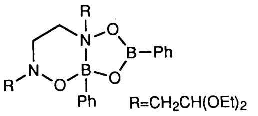
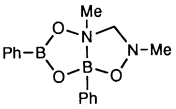
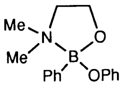
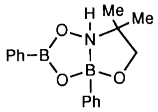
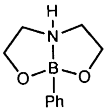
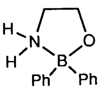
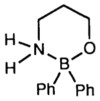
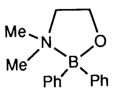
$$\mathrm{THC}/\% = \frac{120^\circ - (\theta_1 + \theta_2 + \theta_3)^\circ/3}{120^\circ - 109.5^\circ} \times 100 \qquad (1)$$

The θ_n (n=1,2,3) represents the bond angles of substituent–B–substituent shown in Scheme 1. When the boron atom is planar or trigonal, the summation of bond angles is 360° and the value is 0%. On the other hand this value is 100% in the tetrahedral form. If the structure of the boron atom is in intermediate of the two states, the values change from 0 to 100% according to the bond angles; the value can exceed 100%. Therefore we call this parameter "tetrahedral character" (THC).



Scheme 1.

Table 5. N–B and B–C$_{\mathrm{Ph}}$ Bond Distances and Tetrahedral Character (THC) of Various Boron–Amine Complexes[a]

Compound	Structure	N–B/Å	B–C$_{\mathrm{Ph}}$/Å	THC/%
1		1.746	1.634	78
2		1.764	1.625	72
3		1.754	1.576	51
4[9]		1.759	1.579 1.557[b]	52 0[b]
5[10]		1.740	1.586 1.551[b]	54 0[b]
6[20]		1.682	1.613	54
7[21]		1.692	1.599 1.557[b]	60 0[b]
8[22]	$(PhBO)_3$–Amine[c]	1.663	1.620	63
9[8]		1.666	1.613	65
10[23]		1.653	1.611	74
11[24]		1.634	1.623	79
12[24]		1.691	1.625	80
13[25]	BF_3–py	1.602	—	82
14[17]	BBr_3–py	1.59	—	87
15[5]	BMe_3–NMe_3[d]	1.698	—	89
16[26]	BCl_3–py	1.592	—	94
17[27]	BCl_3–NMe_3	1.575	—	102
18[28]	BF_3–NMe_3	1.585	—	124
19[12]	$PhB(OH)_2$	—	1.565	0
20[11]	BPh_3	—	1.577	0

a) Structures are determined by X-ray analysis in crystals unless otherwise mentioned. b) Values for uncoordinated boron atom. c) 2:3 Adduct triphenylboroxin and *p*-phenylenediamine. d) Determined by microwave analysis in the gas phase.

We calculated THC's of compounds **1**—**3** as well as various boron–amine complexes of which structures were reported previously, shown in Table 5. The THC values for **1**—**3** are 78, 72, and 51%, respectively. The larger the value, the higher the barrier to the dissociation of the N–B bond. The magnitude of the tetrahedral character of the boron atom is well correlated with the strength of the N–B bond as far as the compounds reported here concern.

The THC values of various complexes in Table 5 show those of complexes of boronic esters are 52—54% when the nitrogen has no hydrogen substituents, **4**—**6**, and 60—65% when the nitrogen has hydrogens, **7**—**9**. Complexes of borinic esters, **10**—**12**, give the value in the range of 74—80% and complexes of trialkyl- or trihaloboranes, **13**—**18**, give more than 82%. This order of THC's corresponds to the following order of Lewis acidity of boron atoms; trihaloborane>trialkylborane>borinic acid>boronic acid.[3] Though we have no information on the barrier to dissociation of the N–B bond in other complexes, the barrier must be correlated to the strength of the N–B bonds which are affected both by the Lewis acidities of boron atoms and the basicities of amines. The THC values of uncoordinated boron atoms are 0% as a matter of course.

The THC of compound **3** is normal and similar to those of the corresponding compounds, the boronic ester–amine complexes without hydrogen substituents at the amine-nitrogen atom. For complexes **1** and **2** which carry the 9-BBN group, the values are smaller by more than 10% than those of trimethylamine–borane complexes. This finding can be again attributed to the steric effects of the 9-BBN group. When one compares the N–B bond distance with the THC's in Table 5, one can find the correlation as follows; the larger the THC value, the shorter the N–B bond distance. Of course some irregularities exist in the correlation, compounds **12** and **15** as well as **1** and **2**. The common feature of these compounds is that the steric effects are rather large in the complex formation. We may use the N–B bond distance as an indication of the barrier to dissociation in a given series of compounds, if the steric hindrance is not so severe.

So far the THC values, which afford better correlation of the stability of amine–borane complexes than the N–B bond distances, are found to be one of the convenient empirical parameters to estimate the strength of the coordination bonds. There are, however, some limitations in using this parameter. Firstly, the most of the boron compounds of which we calculated THC's are intramolecular complexes. Then the bond angles at the boron atom should be influenced not only by the coordination but by the restriction caused on ring formation though the effects of cyclic structures may be canceled to some extent because of the use of the three bond angles at the boron atom. Secondly, the steric effects at the back side of the boron atom, B-strain, must be important in tetrahedral forms in determining the bond angles as well as F-strain when the boron atom has large substituents. If the steric effects are severe, the deformation of the structure of the boron compound from a trigonal form to a tetrahedral form requires additional energy and the THC value tends to be small. If the substituents at the boron atom are small, the deformation is easy and the THC may exceed 100% in certain circumstances, such as the case of complexes with very bulky amines. We must take these into considerations in using the THC values at present. When more structures and kinetic data of boron complexes, specially intermolecular complexes, are available, the situation will become clearer.

In this report, we use the THC only in borane–amine complexes. This parameter can be applied to other boron complexes, for example complexes with sulfides, ethers, and phosphines.

Finally we wish to discuss the distances of the B–C_{Ph} bond in connection with the strength of the N–B coordination bonds. The standard length of B–C_{Ph} bond is ca. 1.57 Å in uncoordinated arylboranes.[3] The bond distances in various complexes range from 1.551 to 1.634 Å shown in Table 5. The B–C_{Ph} bond distance tends to be long as the THC value is large or coordination of the N–B bond is strong. These phenomena can be correlated to the changes in the hybridization of the boron atom from sp^2 to sp^3. The borane complexes **1** and **2** belong to the group in which the B–C_{Ph} bond is long. In particular, the bond distance in **1** is the longest in all compounds in Table 5. This feature is partly attributed to the strong coordination in the borane complexes, but the steric hindrance between the 9-BBN group and the phenyl moiety must be important in determining the B–C_{Ph} bond distance.

The same tendency in bond distances is recognized in the B–O bonds in **3** as well as in the B–C(9-BBN) bonds in **1** and **2** mentioned above. The average B–O bond distance of 1.444 Å in **3** is longer than that in phenylboronic acid (1.371 Å).

Experimental

9-[2-(Dimethylaminomethyl)phenyl]-9-borabicyclo[3.3.1]-nonane (**1**), 9-[2-(diethylaminomethyl)-phenyl]-9-borabicyclo[3.3.1]nonane (**2**), 2-[2-(diethylaminomethyl)phenyl]-4,4-diphenyl-1,3,2-dioxaborolane (**3**) were prepared by the known method.[1,2] Crystals used for the X-ray measurements were grown from ether for **1** and **2** and from hexane–dichloromethane for **3**.

X-Ray Crystallography.[29] X-Ray data were obtained on a MAC Science MXC18 four circle diffractometer with Mo $K\alpha$ radiation (λ=0.71073 Å). The scan mode was the 2θ method in the range of $2\theta<30°$ and the ω-2θ method in $2\theta>30°$. The scan rate was 4° min^{-1} and the scan range was calculated by $0.82°+0.35° \tan\theta$ in **1** and **2** and by $0.97°+0.35° \tan\theta$ in **3**. The structures were solved by the direct method (MULTAN) and refined by the full-matrix least-squares method by using

Table 6. Crystal and Structure Analysis Data of Compounds **1**—**3**

Compound	**1**	**2**	**3**
Formula	$C_{17}H_{26}BN$	$C_{19}H_{30}BN$	$C_{23}H_{24}BNO_2$
F. W.	255.21	283.26	357.26
Crystal size/mm^3	0.45×0.40×0.30	0.40×0.35×0.30	0.30×0.30×0.25
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/n$	$P2_12_12_1$	$C2/c$
a/Å	15.252(4)	12.772(2)	23.670(5)
b/Å	10.264(2)	14.327(3)	10.130(2)
c/Å	10.069(2)	9.020(2)	18.428(4)
β/°	108.68(2)	90	118.96(1)
V/Å^3	1493.3(6)	1650.5(5)	3866(1)
Z	4	4	8
D_c/g cm^{-3}	1.13	1.14	0.95
μ/cm^{-1}	0.32	0.32	0.42
2θrange/°	2—60	2—60	2—55
No. of data	4360	2830	4526
No. of data used	3370	2200	2502
R	0.058	0.056	0.068
R_w	0.058	0.055	0.046
g	4.0×10^{-4}	4.0×10^{-4}	1.3×10^{-4}

CRYSTAN program on an NSSUN work-station. Anisotropic thermal parameters were employed for non-hydrogen atoms and isotropic for hydrogens. No absorption correction was employed. The reflections with $|F_o|>3\sigma|F_o|$ were used for the structure determination and refinement and the function minimized was $\sum[w(|F_o|^2-|F_c|^2)^2]$, in which $w=[(\sigma_c|F_o|)^2+g|F_o|^2]^{-1}$. Additional experimental data are given in Table 6.

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29) Tables of coordinates for the hydrogen atoms, anisotropic thermal parameters, and complete thermal F_o-F_c data are deposited as Document No. 9012 at the Office of the Editor of Bull. Chem. Soc. Jpn.