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Dynamic NMR as a Nondestructive Method for the Determination of Rates of Dissociation. XVII. Dissociation of the N–B Bond in the Coordinated Form of 2-[2-(Dimethylaminomethyl)phenyl]-4,4-diphenyl-1,3,2-dioxaborolane and Related Compounds[1)]

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The rates of dissociation of the N-B bonds in the title compounds were reexamined by the dynamic NMR technique to get further insight into the mechanism of dissociation. Entropies of activation were fairly large positive to suggest that the dissociation of a bond of ionic characters is the rate-limiting step. The rates of dissociation were generally larger in nonpolar solvents than in polar solvents, suggesting that the stabilization of the ground state by solvation was important in determining the activation energy for dissociation. Diethyl ether, tetrahydrofuran, and acetone gave larger rate constants of dissociation than those expected from their polarity. Participation of solvent molecules in the dissociation is discussed on the basis of these results. Introduction of various substituents indicated that steric effects as well as electronic effects affect the N–B bond energy.

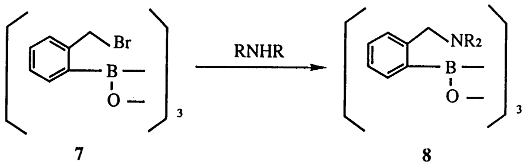
While we have been investigating dissociation of various coordination compounds by the dynamic NMR technique, it has become clear that dissociation of the ligand in coordination compounds is the process which gives a large positive entropy of activation.[2)] This was attributed to the ionic character that is decreased in the transition state for dissociation, the change causing the increase in the freedom of the solvent molecules as well as the ligand.

In view of these findings, it will be interesting to examine the cases of metals (or metalloids) of which d-orbitals are of high energy, since the examples of the metals were confined to transition metals in the past.[3)] Literature search revealed that there were some papers which reported the dissociation of the N–B bond in amine-borane complexes. The oldest literature has obtained the enthalpy and entropy of activation by classical line shape method for trimethylamine-trimethylborane complex.[4)] However, the classical method is known to often give erroneous entropy of activation.[5)] Other two reported the rate constant of the N–B bond dissociation only at one temperature.[6,7)] Though there is another paper which mentions the formation and dissociation of intramolecular amine-borane complexes, mention has not been made on the energy of dissociation.[8)] Since the entropy of activation carries important information in our experience, we decided to reexamine the cases by the total line shape analysis.

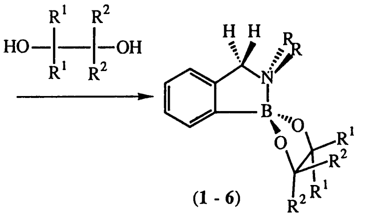
Compounds and Their Syntheses

We chose 2-[2-(dimethylaminomethyl)phenyl]-4,4-diphenyl-1,3,2-dioxaborolane (**1**), which was prepared as reported previously,[7)] for the following two reasons. Firstly the compound possesses 4 probes which exchange sites on dissociation of the N–B bond followed by rotation of the C_{Ph}–B bond: the reliability of the data can be checked by comparing the kinetic data produced by various probes. Secondly we have had ample experiences of similar studies on similar types of organometallic compounds:[3)] if irregularities arise, detailed discussions will be possible.

After the kinetic parameters for the dissociation of compound **1** were determined, we were interested in the effects of various substituents on the activation energy for the dissociation. Thus, compounds with other substituents than those in **1** both on the amino-nitrogen and on the dioxaborolane ring were synthesized. 2,4,6-Tris[2-(bromoethyl)phenyl]boroxin(**7**)[9,10)] was treated with a dialkylamine to produce 2,4,6-tris[2-(dialkylaminomethyl)phenyl]boroxin (**8**) which was treated with appropriate 1,2-diols to produce substituted 2-[2-(aminomethyl)phenyl]-1,3,2-dioxaborolane (**1**—**6**). Compound **8** could also be prepared by treating *N*,*N*-dimethylbenzylamine with butyllithium followed by trimethyl borate.[11)]



7 **8**



(1 - 6)

	R1	R2	R
1	C_6H_5	H	CH_3
2	CH_3	H	CH_3
3	H	H	CH_3
4	CH_3	CH_3	CH_3
5	C_6H_5	C_6H_5	CH_3
6	C_6H_5	H	C_2H_5

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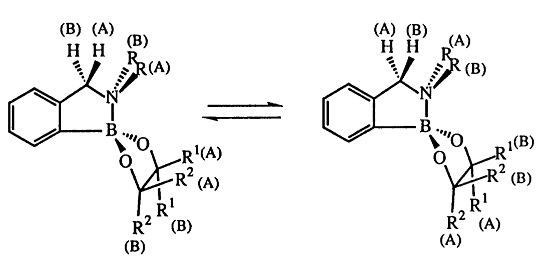
Kinetic Data Obtained by Various Probes in 1

The process of exchange of the magnetic sites of various probes, *N*-methyl groups, benzylic methylene protons, methylene protons in the dioxaborolane, and the phenyl groups (only the ortho protons used), is shown in the following scheme. It will be reasonable to assume that the rate-limiting step in the process is the N–B bond scission, because the rotation about the C_{ph}–B bond in this type of compounds should be fast.[12] It is indeed proved to be so, as is shown later, by observing the same activation parameters for dissociation by various probes. If the rotation of the dioxaborolane were slower than the N–B bond dissociation, the kinetic parameters obtained by the *N*-methyl probe should have been different from those obtained with the probes on the dioxaborolane ring.



The kinetic data of the N–B bond dissociation in compound **1** in dichloromethane-d_2 are compiled in Table 1. The agreement among the data obtained with the use of various probes was excellent. Therefore, we may use any probe available for the dynamic NMR study of this type of compounds. Close examination of the data revealed, however, that the errors in enthalpy and entropy of activation obtained by the *N*-methyl probe are rather large. This is due to the simplicity of the signal patterns concerned, as pointed out earlier.[13,14] Thanks to the large chemical shift differences and the complex patterns, the benzylic and the ring-methylene protons gave large temperature ranges where the change in the line shapes was observed (see Experimental section). We believe therefore that the preferred probes are those which give complex signals with a large chemical shift difference between the exchanging nuclei.

Entropies of activation are large positive, as are expected for the dissociative reactions of coordination compounds.[2] For the dissociation of the amine-borane complexes, the S_N2 type reaction mechanisms may be assumed, when the decrease in the entropy is expected.[15] This point will be discussed with the solvent effects on the dissociation.

Solvent Effects on Dissociation in 1

In order to get further into insight, we have carried out the rate measurements in various solvents. The results are summarized in Table 2. There is a small but distinct solvent effect on the rates of dissociation of the N–B bond. The less polar the solvent, the larger the rate constants or smaller the free energy of activation at a given temperature.

The difference is more sensitive in the rate constants than in free energy of activation. These rate constants are listed in Table 3 with some solvent parameters.[16,17] It is evident that, although there is a general tendency of the increase in the rate constant as the polarity of the solvent decreases, some irregularities do exist. The general tendency may be interpreted as a result of better stabilization of the polar ground state

Table 1. Kinetic Parameters for Dissociation of the N–B Bond in Compound **1** in Dichloromethane-d_2[a)]

Probe	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal mol^{-1} K^{-1}	$\Delta G^{\ddagger}_{233}$/kcal mol^{-1}[b)]	r[c)]
N-CH_3	15.1±1.8	15.2±6.1	11.6	0.9992
N-CH_2[d)]	15.2±0.3	15.6±1.1	11.5	0.9998
5-H[e)]	15.1±0.2	15.3±0.8	11.5	0.9998
o-H[f)]	15.3±0.3	16.3±1.1	11.5	0.9998

a) 1 cal=4.184 J. b) Free energy of ativation at 233 K. c) Correlation factor of the statistical treatment. d) Benzylic protons. e) Methylene protons of the 1,3,2-dioxaborolane. f) *o*-Protons in the phenyl groups at 4 position of the dioxaborolane.

Table 2. Solvent Effects on the Kinetic Parameters for Dissociation of the N–B Bond in Compound **1**[a)]

Solvent	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal mol^{-1} K^{-1}	$\Delta G^{\ddagger}_{233}$/kcal mol^{-1}	r
C_7D_8[b)]	14.4±0.3	14.6±1.0	11.0	0.9998
$(C_2D_5)_2O$	13.6±0.3	12.4±1.3	10.7	0.9997
$CDCl_3$	15.2±0.4	16.1±1.9	11.5	0.9996
C_4D_8O[c)]	14.1±0.3	13.4±1.3	11.0	0.9998
CD_2Cl_2	15.1±0.2	15.3±0.8	11.5	0.9998
$(CD_3)_2CO$	14.5±0.2	13.3±0.8	11.4	0.9998
C_2D_5CN	15.3±0.2	15.8±0.9	11.6	0.9999
$DCON(CD_3)_2$	15.1±0.2	13.9±0.8	11.8	0.9998

a) The probes were the methylene protons at the 4-position of the dioxaborolane ring. b) Toluene-d_8. c) Tetrahydrofuran-d_8.

Table 3. Solvent Parameters and Rate Constants of the N-B Bond Dissociation in Compound **1**

Solvent	ε[a)]	E_T[a)]	DN[a)]	k_{233}/s^{-1}
Toluene	2.38	33.9	—[b)]	232
Diethyl ether	4.34	34.6	19.2	422
$CHCl_3$	4.81	39.1	—[c)]	81.7
Tetrahydrofuran	7.58	37.4	20.0	241
CH_2Cl_2	8.93	41.1	—[c)]	74.2
Acetone	20.7	42.2	17.0	107
Propionitrile	27.2	43.7	16.1	59.7
$HCON(CH_3)_2$	37.0	43.8	26.6	40.1

a) Dielectric constants (ε), $E_T(30)$-values, and donicity numbers (DN). Taken from Refs. 16 and 17. b) DN of benzene is 0.1. c) DN of halogenated hydrocarbons is generally zero.

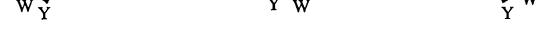
due to solvation in more polar solvents than in less polar solvents: since the transition state is less polar than the ground state, the stability in the ground state is reflected in the free energy of activation.

The irregularities are that ethers, diethyl ether and tetrahydrofuran, give abnormally high rates of dissociation and so does acetone. These irregularities cannot be explained by mere consideration of the dielectric constants (ε) or the E_T values of the solvents. We wish to attribute the irregularities to the solvent assistance in the dissociation of the N-B bond, because ether-oxygen atoms have fairly strong affinity toward boron.[18)]

For the more quantitative discussion, we may use Gutmann's donicity numbers (DN). Since they are derived from the molecular interaction between antimony pentachloride and an electron donor,[17)] they will be good estimates of the affinity of various heteroatoms to the boron atom, which is also a Lewis acid. Although DN for toluene is not available, that for benzene is 0.1. DN of neither chloroform nor dichloromethane is available. However, those for other halogenated aliphatic hydrocarbons have been reported to be zero. Therefore, we assume that the DN values of these solvents are negligibly small.

Strong affinities of oxygen atoms in various molecules toward boron are reflected in donicity numbers. The irregularities of diethyl ether, tetrahydrofuran, and acetone can be understood if one takes into account the followings: if a molecule contains an oxygen atom, that assists the dissociation of the N-B bond by approaching from the backside of the leaving nitrogen. Namely, we postulate that an $\mathrm{S_N2}$ type reactions are taking place in the dissociation of the N-B bond as shown below, if a solvent contains an oxygen atom.

Of course, this type of interaction is possible for the nitrogen in propionitrile. But the donicity number of the nitrile-nitrogen is not so large as those of ethers and ketones. This must be the reason why we do not observe irregularity in the case of propionitrile. Probably, solvent assistance is also great in *N,N*-dimethylformamide , because its DN is very large. We believe that the rate constant of the N-B bond dissociation in DMF is the consequence of the stabilization of the ground state due to its polarity and the assistance provided by the amide oxygen atom.



It may be argued that the entropy of activation should be large negative, if the $\mathrm{S_N2}$ type reaction should occur, whereas the observed entropies of activation for the oxygen-bearing solvents are the same with those obtained with other solvents within the limit of experimental error. However, in the case of stoichiometric involvement of the solvent,[19)] it is known that entropy of activation can be less negative.[12)] The present case will be another type of these examples.

It also deserves mention that the proposed mechanism of the N-B bond breakage in this paper is different from that reported for the trimethylamine-trimethylborane complex,[4)] in which the rate of exchange was not affected by the concentration of trimethylamine in the system. We believe this is because of the steric effects in approaching for a trimethylamine molecule from the backside. It may be understood as an analogy of switching from $\mathrm{S_N2}$ reaction in primary alkyl halides to $\mathrm{S_N1}$ reaction in tertiary alkyl halides.

We should like to summarize the discussion by pointing out that, in examining the rate constant of the N-B bond in compound **1**, considerations have to be given to both the ground state stability and the solvent assistance. The latter factor may be operative in various dissociation reactions.

Substituent Effects on Kinetic Parameters for Dissociation

The kinetic parameters for the dissociation of the N-B bond in compound **2** in dichloromethane-d_2 were obtained as follows with r=0.9998: $\Delta H^{\neq}=13.7\pm0.3$ kcal mol^{-1}, $\Delta S^{\neq}=20.4\pm1.1$ cal mol^{-1} K^{-1}, $\Delta G^{\ddagger}_{233}=9.0$ kcal mol^{-1}. Compound **3** in dichloromethane-d_2 did not show the change in line shapes even at −100 °C at 400 MHz but that in toluene-d_8 exhibited two signals at −100 °C at 400 MHz for the ring protons which in principle should show AA′BB′ signals. The free energy of activation at the coalescence temperature (−62.0 °C) was roughly obtained as 9.6 kcal mol^{-1}. Compound **4** showed the line-broadening of the signal due to the ring methyl protons at −100 °C in dichloromethane-d_2. Although kinetic parameters were not obtained for this compound, it is apparent that this compound has the lowest activation energy for the N-B bond cleavage among the compounds examined. Compound **5** exhibited the line-broadening of the signals due to *o*-protons of the phenyl groups attached to the dioxaborolane ring at −70 °C at 400 MHz in dichloromethane-d_2. However, due to overlapping of the signals with those due to other aromatic protons, it is not possible to obtain kinetic parameters. Compound **6** afforded the following kinetic parameters with r=0.9994: $\Delta H^{\ddagger}=14.2\pm0.6$ kcal mol^{-1}, $\Delta S^{\ddagger}=18.2\pm2.5$ cal mol^{-1} K^{-1}, $\Delta G^{\ddagger}_{233}=10.0$ kcal mol^{-1}.

These data speak importance of two factors in determining the barrier height for the dissociation of the N–B bond. One is the degree of electron defficiency of the boron atom and the other is the steric effects that are known as F-strain.[21] On one hand, high electron-deficiency on the boron atom strengthens the acidity of the boron atom thus enhancing the N–B bond energy. Strong F-strain on the other will reduce the N–B bond energy.

In compound **1**, the two phenyl groups withdraw electrons compared to the two methyl groups in **2**, thus making the free energy of activation for the scission of the N–B bond in the former higher than that in the latter, though the steric size of the former is greater than the latter. The least N–B bond energy shown by compound **4** among the compounds examined is the consequence of weakening the N–B bond both by electronic effects of the methyl groups and the F-strain. The tetraphenyl compound (**5**) shows the barrier lower than that in compound **1** but higher than compound **4**. This is again attributed to the electronic effects and the steric effects of the phenyl group. In this respect, it is interesting to note that compound **3** shows a barrier which is ca. 2 kcal mol^{-1} smaller than that of **1** and is higher than other compounds. The small steric size of hydrogen contributes to enhance the barrier relative to the tetraphenyl compound (**5**). Lowering the barrier to dissociation in compound **6**, which carries two ethyl groups on the amino- nitrogen in place of the methyls in compound **1** is attributed to the F-strain.

Experimental

General Procedure for the Syntheses of Compounds. A solution of 322 mg (0.667 mmol) of 2,4,6-tris[2-(dimethylaminomethyl)phenyl]boroxin[7,9–11] and 2.00 mmol of an appropriate diol in 20 mL of toluene was heated under reflux, the formed water being removed by a Dean-Stark apparatus for 2 h. The solvent was removed and the residue was recrystallized from dichloromethane–hexane or distilled. The yields were almost quantitative.

1,1-Diphenyl-1,2-ethanediol[22] and 2-methyl-1,2-propanediol[23] were prepared following the procedures in the literature. Other diols were commercially available.

2-[2-(Dimethylaminomethyl)phenyl]-4,4-diphenyl-1,3,2-dioxaborolane (1), mp 128—129 °C. Found: C, 77.53; H, 6.68; N, 4.04%. Calcd for $C_{23}H_{24}BNO_2$: C, 77.33; H, 6.77; N, 3.92%. ^{1}H NMR ($CDCl_3$) δ=2.51 (6H, s), 3.92 (2H, s), 4.60 (2H, s), 7.03 (1H, d, J=7.2 Hz), 7.09—7.25 (5H, m), 7.32 (4H, t, J=7.5 Hz), 7.54 (4H, dd, J=7.5 and 1.7 Hz).

2-[2-(Dimethylaminomethyl)phenyl]-4,4-dimethyl-1,3,2-dioxaborolane (2), bp 109—111 °C/3 mmHg (1 mmHg=133.322 Pa). High-resolution mass spectrum: M$^+$ 232.1613. Calcd for $C_{13}H_{20}BNO_2$:M$^+$ 232.1623. ^{1}H NMR ($CDCl_3$) δ=1.46 (6H, s), 2.55 (6H, s), 3.75 (2H, s), 3.86 (2H, s), 7.01 (1H, m), 7.15—7.26 (2H, m), 7.51 (1H, m).

2-[2-(Dimethylaminomethyl)phenyl]-1,3,2-dioxaborolane (3), mp 100—102 °C. Found: C, 64.20; H, 7.84; N, 6.85%. Calcd for $C_{11}H_{16}BNO_2$: C, 64.43; H, 7.86; N, 6.83%. ^{1}H NMR ($CDCl_3$) δ=2.43 (6H, s), 3.88 (2H, s), 4.08 (4H, s), 7.03 (1H, m), 7.18—7.26 (2H, m), 7.50 (1H, m).

2-[2-(Dimethylaminomethyl)phenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4), mp 82—83 °C. Found: C, 69.02; H, 9.35; N, 5.39%. Calcd for $C_{15}H_{24}BNO_2$: C, 68.98; H, 9.26; N, 5.36%. ^{1}H NMR ($CDCl_3$) δ=1.31 (12H, s), 2.55 (6H, s), 3.84 (2H, s), 6.99 (1H, m), 7.13—7.21 (2H, m), 7.54 (1H, m).

2-[2-(Dimethylaminomethyl)phenyl]-4,4,5,5-tetraphenyl-1,3,2-dioxaborolane (5), mp 156—158 °C. Found: C, 82.66; H, 6.59; N, 2.47%. Calcd for $C_{35}H_{32}BNO_2$: C, 82.52; H, 6.33; N, 2.75%. ^{1}H NMR ($CDCl_3$) δ=2.11 (6H, s), 3.96 (2H, s), 7.03—7.37 (24H, m).

2-[2-(Diethylaminomethyl)phenyl]-4,4-diphenyl-1,3,2-dioxaborolane (6), mp 131—132 °C. Found: C, 78.02; H, 7.49; N, 3.69%. Calcd for $C_{25}H_{28}BNO_2$: C, 77.93; H, 7.33; N, 3.64%. ^{1}H NMR ($CDCl_3$) δ=1.06 (6H, t, J=7.3 Hz), 2.94 (4H, q, J=7.3 Hz), 3.90 (2H, s), 4.61 (2H, s), 6.94 (1H, d, J=7.2 Hz), 7.01 (1H, d, J=7.5 Hz), 7.09 (1H, t, J=7.5 Hz), 7.17 (1H, m), 7.20 (2H, m), 7.30 (4H, t, J=7.5 Hz).

NMR Measurement and Line Shape Analysis. ^{1}H NMR spectra were mainly measured on a JEOL GX-270 spectrometer which is installed at The University of Tokyo and operates at 270 MHz. After moving to Okayama University of Science, we obtained the spectra on a JEOL GSX-400 which is installed at the Analytical Center at the University and operates at 400 MHz. Agreement of the kinetic data obtained on the two machines was found satisfactory by running the analysis on compound **1** in dichloromethane-d_2. The data obtained with the GSX-400 machine are those of compounds **3—6** and those of compound **1** in diethyl-d_{10} ether. The temperatures were calibrated with the use of chemical shift differences of methanol and 1,2-ethanediol. The concentration of the solution was ca. 80 mmol L^{-1} and

Table 4. Temperature Dependence of the Chemical Shift Difference and Coupling Constants of Methylene Protons at 4-Position of the Dioxaborolane Ring in Compound 1 and Spin-Spin Relaxation Times

Solvent	Correlation[a]	J_{AB}/Hz	T_2/s
C_7D_8[b]	−0.1292 t+132.2	8.8	0.10
$(C_2D_5)_2O$	−0.7015 t+ 90.0	8.4	0.14
$CDCl_3$	−0.8552 t+115.6	8.8	0.13
C_4D_8O[c]	−0.3347 t+ 83.1	8.4	0.10
CD_2Cl_2	−0.3158 t+120.0	8.8	0.14
CD_2Cl_2[d]	−0.1163 t+ 37.0	14.1	0.12
$(CD_3)_2CO$	−0.5211 t+100.8	8.6	0.14
C_2D_5CN	−0.1885 t+117.1	8.8	0.14
$DCON(CD_3)_2$	−0.5718 t+117.7	8.8	0.10

a) $\Delta\nu$/Hz=At/°C+B. b) Toluene-d_8. c) Tetrahydrofuran-d_8. d) Data for N-CH_2 protons.

Table 5. Rates of Dissociation of the N-B Bond in Compound **1** in Various Solvents[a)]

Solvent	*k*/s^{-1} (temperature/°C)
C_7D_8[b)]	21.0 (−56.2), 36.0 (−53.2), 52.8 (−50.0), 85.0 (−47.0), 128 (−44.2), 204 (−40.9), 300 (−37.9), 528 (−34.0), 1260 (−27.0), 3000 (−20.0)
$(C_2D_5)_2O$	17.0 (−62.0), 33.2 (−58.0), 56.0 (−55.0), 79.0 (−52.4), 136.0 (−48.1), 252 (−44.0), 428 (−40.0), 1390 (−30.0), 4800 (−20.0)
$CDCl_3$	16.8 (−50.1), 33.2 (−46.0), 64.0 (−41.9), 132 (−37.1), 248 (−32.0), 560 (−26.0), 1160 (−20.0)
C_4D_8O[c)]	17.0 (−57.9), 39.0 (−53.2), 92.0 (−46.9), 162 (−42.8), 280 (−38.9), 468 (−34.9), 850 (−30.0), 3000 (−20.0)
CD_2Cl_2	13.2 (−51.0), 22.8 (−48.0), 35.8 (−45.0), 58.8 (−41.9), 89.0 (−38.9), 134.0 (−35.9), 200 (−33.0), 296 (−30.0), 560 (−25.0), 1080 (−20.0), 1840 (−15.0), 3300 (−10.0), 10800 (0.0)
CD_2Cl_2[d)]	8.7 (−54.0), 13.4 (−51.0), 22.0 (−48.0), 36.0 (−45.0), 57.6 (−41.9), 87.2 (−38.9), 133.0 (−35.9), 196 (−33.0), 292 (−30.0)
CD_2Cl_2[e)]	8.6 (−54.0), 13.2 (−51.0), 21.8 (−48.0), 34.8 (−45.0)
CD_2Cl_2[f)]	13.8 (−51.0), 23.0 (−48.0), 36.4 (−45.0), 59.2 (−41.9), 90.0 (−38.9), 138 (−35.9), 208 (−33.0), 304 (−30.0)
$(CD_3)_2CO$	9.8 (−55.9), 16.4 (−53.1), 20.8 (−51.0), 33.6 (−48.0), 54.8 (−44.8), 84.0 (−41.8), 148 (−37.9), 252 (−34.0), 412 (−29.9), 750 (−25.0), 1340 (−20.0), 4100 (−10.1)
C_2D_5CN	17.8 (−48.0), 28.6 (−44.9), 44.4 (−42.0), 78.0 (−38.0), 144 (−34.0), 248 (−30.0), 408 (−26.0), 860 (−20.1)
$DCON(CD_3)_2$	21.8 (−43.9), 40.4 (−40.1), 74.0 (−35.8), 106.0 (−33.0), 164 (−30.0), 300 (−25.1), 570 (−19.9), 1780 (−10.0), 5600 (0.0)

a) The data obtained by analysis of line shapes due to *gem*-protons in the dioxaborolane ring unless otherwise mentioned. b) Toluene-d_8. c) Tetrahydrofuran-d_8. d) With the use of benzylic methylene protons. e) With the use of *N*-methyl protons. f) With the use of *o*-protons in the phenyl groups attached to the dioxaborolane ring.

integration was carried out more than 8 times.

The line shape analysis was performed with the use of the DNMR3 program.[24] Whereas the coupling constants were constant at wide ranges of temperatures in the slow exchange limit, the chemical shift differences drifted as the temperature was varied. The latters at temperatures where line shapes changed were assumed to be linearly correlated with temperature, which was true in the slow exchange limit, and were obtained by extrapolation.

The correlation functions for signals due to 4-methylene protons in compound **1** are given in Table 4, together with T_2 values which were obtained from the line widths of nonexchanging and exchanging proton signals at the slow exchange limit. For the *N*-methyl protons, the following values were used: $\Delta\nu=0.1340t+19.9$ Hz, $T_2=0.11$ s. For the *o*-phenyl protons, the calculation was performed by approximation of an $[ABC]_a \leftrightarrows [ABC]_b$ exchange for an actual $[AA'BB'C]_a \leftrightarrows [AA'BB'C]_b$ system and only the line shapes due to *o*-protons were simulated. Internal chemical shift differences within a given phenyl group were constant and the chemical shift difference of the exchanging phenyl groups was linearly correlated with temperature: $\Delta\nu=-0.0627t+17.9$ Hz. T_2 was 0.14 s for the *o*-proton. In addition the following data were used for the simulation: $\Delta\nu_{AB}=64.0$ Hz, $\Delta\nu_{AC}=94.0$ Hz, $J_{AB}=7.4$ Hz, $J_{AC}=1.0$ Hz, $J_{BC}=7.5$ Hz. The rate constants thus obtained for compound **1** are shown in Table 5.

The rate constants of dissociation of compound **2** were obtained by using the following data: $\Delta\nu=-0.2714t+44.0$ Hz, $J=14.1$ Hz, and T_2 0.095 s for the benzylic protons. The following rate constants (s^{-1}) were obtained [temperatures (°C) given in parentheses]: 20.0 (−83.0), 52.8 (−78.1), 109 (−74.1), 216 (−70.0), 410 (−66.0), 790 (−62.0), 1500 (−58.0), 2500 (−55.0), 5200 (−50.0).

The rates for **6** were obtained by using the line shapes due to *gem*-protons at position 4 of the dioxaborolane ring. The following data were used: $\Delta\nu=-0.897t+246.8$ Hz, $J=8.9$ Hz, $T_2=0.12$ s. The following rate constants (s^{-1}) were obtained [temperature (°C) given in parentheses]: 18.0 (−70.0), 46.0 (−65.0), 104 (−60.4), 200 (−56.4), 370 (−52.4), 1020 (−44.9), 2000 (−39.9).

For the estimation of the barrier to the N-B bond scission in compound **3**, the approximation for the uncoupled AB spin system was used.[25] The constants used were T_c −62.0 °C and $\Delta\nu$ 104.5 Hz. The rate constant thus obtained was 460 s^{-1}.

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