Dynamic NMR as a Nondestructive Method for the Determination of Rates of Dissociation. XVIII. Factors Affecting the Rates of Dissociation of N–B Bond in the Coordinated Form of 9-[2-(Dialkylaminomethyl)-phenyl]-9-borabicyclo[3.3.1]nonanes[1)]

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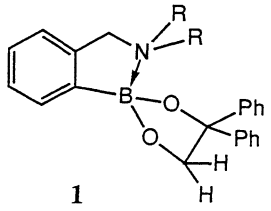
NMR spectra of the title compounds reveal that they exist in the intramolecularly N–B coordinated form. The NMR signals exhibited dynamic behaviors accompanied with the dissociation of the N–B bond and total line shape analyses of the exchanging nuclei afforded kinetic parameters for the topomerization. Entropies of activation are large and positive, typical for the dissociation of coordination bonds. Examination with the multiple probes shows that the nitrogen inversion requires additional energy after the N–B bond dissociation. The barrier for the topomerization is affected by *N*-alkyl groups due to their F-strain. The barrier height is reduced in nonpolar solvents and not influenced by nucleophilicity of solvents. These solvent effects are discussed in connection with polarity of the N–B bond and steric hindrance of the boron atom.

The dynamic NMR method is a convenient technique for observation of dynamic processes of ligands in various coordination compounds,[2-4)] of which uniqueness is that rates of bond dissociation can be determined in the absence of foreign materials in organic solvents. An amine ligand is one of the well investigated examples. The dissociative processes of lignads were observed by NMR for tin–amine,[5)] silicon–amine,[6)] boron–amine,[7,8)] and other complexes.[9)] From the ease of dissociation, the kinetic basicity of an amine ligand or the kinetic Lewis acidity of a metal center can be estimated.

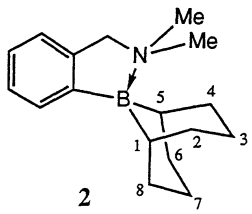
Recently, the kinetic parameters for the N–B bond dissociation in an intramolecular boronate–amine complexes (**1**) were determined by the total line shape analysis.[1)] The low barrier of the dissociation (**1a** $\Delta G^{\neq}_{233}$ 11.5 kcal mol^{-1}) was ascribed to the weak Lewis acidity of the boron atom which accepts electron from two attached oxgen atoms by p_π–p_π interactions. Trialkylborane–amine complexes should exhibit higher barriers to the N–B bond dissociation, since in these compounds the carbon atoms attached to the boron do not bear lone-pair electrons that suppress the acidity of the boron, and indeed trialkylboranes are known to be better electron acceptors than boronates.[10)]

In 1984, Kalbarczyk and Pasynkiewicz reported the synthesis of this type of compound, 9-[2-(dimethylaminomethyl)phenyl]-9-borabicyclo[3.3.1]nonane (**2**), which was stable in the air.[11)] They proposed the intramolecularly coordinated form with a four-coordinated center of boron from the chemical shift data in ^{1}H NMR spectrum. It seemed convincing on one hand, but on the other their ^{13}C NMR data were not in conformity with the expected structure. They reported that the *N*-methyl groups were diastereotopic and the carbon atoms in the positions 2(4) and 6(8) in the borabicyclononane skeleton (2(4)-C and 6(8)-C) and those in the positions 3 and 7 (3-C and 7-C) were isochronous. Since the molecule has a σ plane, passing N, B, 3-C, and 7-C, the *N*-methyl groups should be enantiotopic in the coordinated form. On the other hand, the 2-C/8-C pair as well as the pairs of 4-C/6-C and 3-C/7-C should not be equivalent in the coordinated form. From our experience, however, we were convinced that compounds **2** should exist as a coordinated form in solution and were prompted to reexamine this compound as a model for the trialkylborane-amine complexes. Evidence for the structure, the coordinated form, will be presented in this paper.



1

a : R= Me
b : R= Et



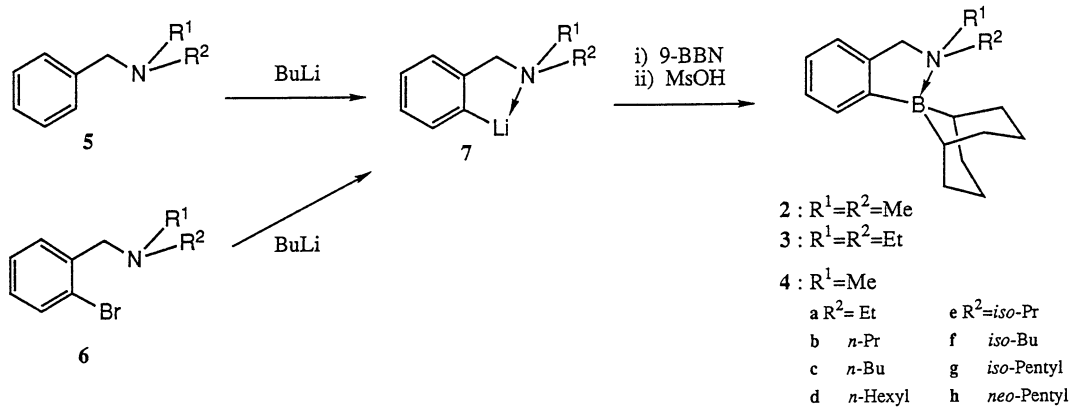
2

The strength of the N–B bond is affected by steric hindrance and solvents in addition to the basicity of the nitrogen atom and the acidity of the boron atom.[1)] Since the barrier to the dissociation in **1b** was lower than that in **1a** due to the steric effect (F-strain), the steric effect is expected to become more important, when the electron acceptor is bulky, as is the case of the 9-borabicyclo[3.3.1]-9-nonyl (9-BBN) group. Polarity and nucleophilicity of the solvent affected the rates of the N–B bond dissociation in **1** by affecting the ground state stability and by assisting the leaving of the amino moiety, respecively. These effects are expected to be affected by the bulkiness of the borane as well. It should be of interest to compare the strength of coordination in the 9-BBN system bearing various *N*-alkyl groups in various solvents because the data can assist us to get further insight into the acid-base properties of the amine-borane complexes in solution.

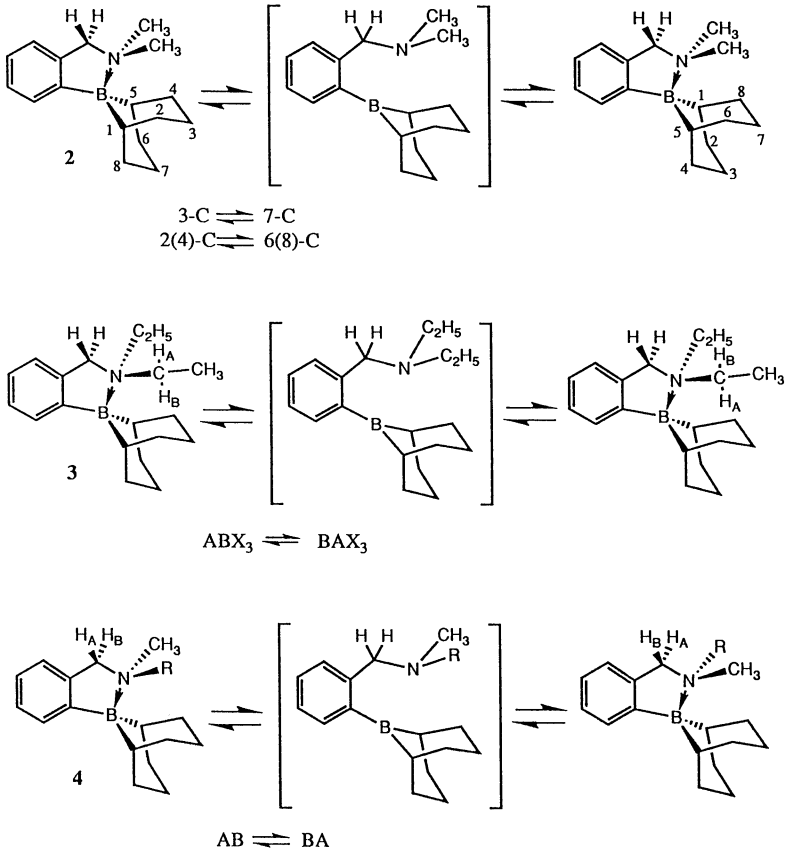
Results and Discussion

Since compound **2** possesses no convenient diastereotopic proton pairs for the NMR line shape analysis, the topomerization process in this compound must be observed by ^{13}C NMR spectra. To make this system amenable to ^{1}H NMR dynamic study, we designed **3** and **4**; instead of two methyl groups in **2**, **3** carries two ethyl groups and **4** a methyl group and an alkyl group.

These compounds were synthesized according to a known method shown in Scheme 1. The treatment of *o*-lithio-*N*,*N*-dialkylbenzylamines (**7**) with 9-BBN afforded the desired compounds. The point which deserves mention here is the steric effect in the preparation of the lithio compounds. The *o*-lithiation of *N*,*N*-diethylbenzylamine with butyllithium requires several days[12] although that of *N*,*N*-dialkylbenzylamine (**5**) proceeds smoothly during a day or so,[13] when one of the alkyl groups is a methyl and another in an alkyl group which has no branch at α- or β-position. For the syntheses of **3**, **4e**, **4f**, and **4h**, the corresponding lithio compounds



Scheme 1.



Scheme 2. Idealized topomerization processes in **2**, **3**, and **4**.

were prepared from *o*-bromo-*N*,*N*-dialkylbenzylamines (**6**) and butyllithium by the halogen–lithium exchange method,[14] because the corresponding benzylamines were too slowly lithiated under ordinary conditions.

Both ^{1}H NMR and ^{13}C NMR spectra were in conformity with the expected structure of compounds **2**, **3**, and **4**. The two methyl groups were equivalent, whereas 2(4)-C and 6(8)-C were not equivalent in **2**. Nonequivalent signals of ring carbons were reported in intermolecular 9-BBN complexes with pyridine.[15] The methylene protons in the ethyl groups were nonequivalent in **3**. Compound **4** showed nonequivalent benzylic methylene protons and other similar characteristics with those mentioned for **2**. These are in accord with the coordinated forms of these compounds.

The methylene protons in the ethyl groups in **3**, which are diastereotopic unless the dissociation of the N–B bond is too rapid on the NMR time scale, exchange their sites after the dissociation of the N–B bond followed by the nitrogen inversion and recoordination. Similarly, the benzylic methylene protons in compound **4** satisfy the requirement as a probe. Idealized topomerization processes in these compounds are shown in Scheme 2.

^{11}B NMR signals of these compounds were observed at 9.5 ppm (**2**), 10.5 ppm (**3**), and 9.3 ppm (**4a**) with reference to BF_3:OEt_2, these shifts being in accord with those in other trialkylborane–amine complexes[15,16] and being at higher fields by ca. 70 ppm relative to the nitrogen-free borane (cf. 9-phenyl-9-BBN; 80.35 ppm).[17] Such a high field shift of a coordinated tetrahedral boron compared with a trivalent one was reported in similar compounds.[8,17]

Kinetic Parameters for Topomerization in 2 and 3. The methylene protons of the ethyl group in compound **3** showed broad signals at room temperature and they became sharp (AB part of the ABX_3 system) at −20 °C. ^{13}C NMR signals due to the carbons at 2(4)-C/6(8)-C exhibited line broadening at room temperature as well. The total line shape analyses of these spectra afforded kinetic parameters for the topomerization shown in Table 1. We could also obtain the kinetic parameters for **2** by taking advantage of the diastereotopic carbon pairs, carbons at 3-C/7-C and 2(4)-C/6(8)-C. The data are also compiled in Table 1.

Several points of interest can be mentioned here. Firstly, both compounds **2** and **3** give much higher barriers to the topomerization than **1**. As expected, the N–B coordination in borane–amine complexes is stronger than that in boronate–amine complexes, although the steric effects could reverse the situation. The result can be well explained by the enhanced Lewis acidity of the boron atom. Secondly, the entropy of activation is large, positive in every case. This value is typical, when the ground state possesses the ionic character which is reduced at the transition state, and is often observed in the dissociation of coordination bonds. The dissociation in borane–amine complexes is no exceptions. Thirdly, there is no concentration effect on the kinetic parameters for the topometrization. Therefore we can compare the parameters obtained in different concentrations directly.

Mechanism of Topometization in 3. The free energies of activation for the topomerization obtained from the proton and the carbon probes in **3** are significantly different, the proton probe giving a 1.2 kcal mol^{-1} higher barrier than the carbon probe (Table 1). We wish to explain the result in the following way.

The site exchange of the methylene protons takes place after dissociation of the N–B bond followed by inversion of the nitrogen atom (and then rotation about an N–C bond) and recombination to form the N–B bond. Thus the difference in barriers obtained by the two probes suggests that the nitrogen inversion requires additional energy after the N–B bond dissociation and that the rate-limiting step is the nitrogen inverstion rather than the N–B bond dissociation.

Nitrogen inversion in *N*,*N*-dialkylbenzylamine complexes was reported to be much faster than the N–M bond scission in boronate–amine complex (**1**)[1] and tertiary amine hydrogen chlorides.[18] Barriers to nitrogen inversion in *N*,*N*-dialkylamines are relatively high (ca. 11 kcal mol^{-1}), although inversion in open-chain amines generally requires lower activation energy than this value.[19] Therefore, unless otherwise affected, nitrogen inversion in general should exhibit lower barriers than the N–B bond dissociation.

However, the nitrogen inversion in compound **3** is specifically affected by the steric effects. The nitrogen inversion is effected by either displacing one of the ethyl groups to the position where the lone pair electrons has occupied before inversion, or by true inverstion of the nitrogen. The latter seems too much energy-requiring because the two ethyl groups which change their posi-

Table 1. Kinetic Parameters for the Topomerization in **2** and **3** in Toluene-d_8[a]

Compound	Probe	$\Delta H^{\neq}$/kcal mol^{-1}	$\Delta S^{\neq}$/cal mol^{-1} K^{-1}	$\Delta G^{\neq}_{323}$/kcal mol^{-1}	r[b]
2	^{13}C	23.7±0.5	16.6±1.4	18.3	0.9996
3	^{13}C	18.9±0.5	14.9±1.6	14.1	0.9997
3	^{1}H	22.8±1.7	23.1±5.6	15.3	0.9991
3	^{1}H[c]	23.0±1.1	24.0±3.4	15.3	0.9992

a) 1 cal=4.184 J. Concentration ca. 200 mmol dm^{-3} unless otherwise mentioned. b) Correlation coefficient. c) Concentration 31 mmol dm^{-3}.

tions will strongly interact with the 9-BBN moiety. Even the former, however, suffers from the steric hindrance of the 9-BBN group because one of the ethyl groups must come very close to the 9-BBN during the site exchange. It may be argued that the nitrogen inversion can take palce after rotation about the benzyl carbon-to-nitrogen bond. This process, however, also requires much energy because the two ethyl groups interfere strongly with the 9-BBN group during the rotation, if nitrogen inversion does not take place.

On the other hand, the site-exchange of the ring carbons is caused by rotation of the C_{Ph}–B bond after the N–B bond dissociation. If the rotation about the bond in question is much faster than the dissociation, the rate-limiting step should be the latter process and the rates of topomerization should be equal to half of the rates of the N–B bond dissociation. Although it is difficult to conclude which is faster by the data presented in this paper, the following paper[20] provides a clue for the diagnosis.

In the paper, dissociation of an S–B bond and sulfur-inversion in a similar complex are discussed. The sulfur-inversion is a faster process than the rotation about the C_{Ph}–B bond. The free energy of activation for the rotation is ca. 12.5 kcal mol^{-1}. Because of the similar steric situations in both compound **3** and the sulfur compoud, in which a lone-pair electron lobe directs toward the 9-BBN group, we may take the activation energy for the sulfur compound as an approximate value for the rotation of the 9-BBN group in **3**. Since this value is well below the activation energy for the topomerization obtained with the carbon probe, we may now conclude that the activation energy obtained with the carbon probe is indeed that of the N–B bond scission.

It is tempting to consider that the entropy of activation observed by the carbon probes are larger, positive than that observed by the proton probe because freedom increases in the transition state for the nitrogen inversion. Although it is difficult to justify or to exclude the possibility that the transition state structure for the nitrogen inversion is such that rotation about the benzylic carbon-to-nitrogen bond takes place to some extent with simultaneous partial exchange of the positions of the ethyl group and the N-lone pair electrons, the results clearly show that nitrogen inversion is a slower process than the N–B bond dissociation.

We conclude that the proton probes and the carbon ones give information on different processes in this molecule: the carbon probes give information on the N–B bond dissociation and the proton probe that on nitrogen inversion. Unfortunately, the information on the nitrogen inversion cannot be quantitative becaues the process is influenced by the N–B bond dissocaiton. This is clear from the entropy of activation for the nitrogen inversion which is large positive. Independent nitrogen inversion is known to show near-zero entropy of activation.[19]

Steric Effects on Rates of Topomerization. The free energy of activation in the dimethyl compound (**2**) was ca. 4 kcal mol^{-1} higher than that in the diethyl compound (**3**), as is revealed by comparison of kinetic parameters obtained by the carbon probes (Table 1). The reduction of the barrier height in **3** is attributed to the steric effect (F-strain).[21] This phenomenon was also observed in the boronate–amine system **1** and the difference in the free energies of activation between the dimethyl and the diethyl compounds was 1.5 kcal mol^{-1}.[1] The more bulky the borane in borane–amine complexes, the more important the F-strain. The result presented here is in accord with this generalization because 9-BBN is a very bulky group.[22]

To get further insight into the steric effects of *N*-alkyl groups on the topomerization, the kinetic parameters for compound **4** were similarly determined. The bezylic methylene protons were used as a probe in unsymmetrical compounds **4**, the carbon probe (3-C/7-C) being also used for **4a** for comparison. The kinetic data thus obtained are listed in Table 2.

Compounds **4a–d**, which possess a methyl group and a straight chain alkyl group, give almost the same barriers to the topomerization. This is reasonable becasue the steric effects on the stability of the ground state is given by the first methylene group which is attached to the nitrogen and those methylene groups in β- and farther positions will direct away from the boron to minimize the steric effects. In addition, the basicity of

Table 2. Kinetic Parameters for the Topomerization of Benzylic Methylene Protons in **4** in Toluene-d_8

Compound	$\Delta H^{\neq}$/kcal mol^{-1}	$\Delta S^{\neq}$/cal mol^{-1} K^{-1}	$\Delta G^{\neq}_{323}$/kcal mol^{-1}	k_{323}/s^{-1}	r
4a	24.5±0.5	18.9±1.2	18.4	2.4	0.9997
4a[a]	20.1±1.1	10.8±3.2	16.6	38	0.9993
4b	25.1±0.4	21.8±1.1	18.0	4.3	0.9998
4c	24.7±0.3	21.0±0.9	18.2	3.4	0.9999
4d	25.0±0.4	21.0±1.0	18.2	3.3	0.9998
4e	20.4±0.3	19.3±1.1	14.1	1900	0.9998
4f	23.4±0.4	22.7±1.2	16.1	86	0.9998
4g	24.8±0.6	20.3±1.7	18.2	3.1	0.9996
4h	19.8±0.5	20.4±1.8	13.2	8000	0.9995

a) Obtained from carbon probes in the 9-BBN group.

the amines is not affected appreciably by the chain-length of the alkyl group. Although this situation should affect the entropy of the ground state and consequently the entropy of activation in principle, it does not increase the entropy of activation to a significant extent as is seen in Table 2.

Comparison of free energies of activation for compounds **2**, **3**, and **4a**, obtained with the proton and carbon probes provides other points of interest. On one hand, compound **4a** shows medium barrier height among the compunds, when they are determined with carbon probes. This means the steric effects of the alkyl groups on the amino-nitrogen is significant. On the other hand, if the barrier is determined with proton probes, **4a** gives a higher barrier than that obtained with the carbon probes. This will mean that the steric effects given by a methyl group on inversion of the amine after the N–B bond dissociation is strong enough to make the barrier significantly higher than that for the N–B bond dissociation.

In **4e–g** bearing an isoalkyl group, the free energy of activation decreases in the order **4g**>**4f**>**4e**. Apparently branching at the α-position of the alkyl group which is attached to the nitrogen has a very large effect which lowers the barrier hight. Branching at the β-position has a small effect but that at farther positions inserts little effect on the N–B bond scission. In order to see the effect of further branching at the β-position of the alkyl group, we introduced a neopentyl group. As is seen in Table 2, compound **4h** shows the lowest barrier to the N–B bond dissociation among the compounds examined. This type of steric effects are known as γ-effect in ^{13}C NMR spectroscopy[23] and this is the manifestation of the similar effect in kinetics. The series of compounds **4e**—**4h** together with **4a**—**4d** constitute clear examples which show that destabilization of the ground state without affecting the transition state significantly indeed lowers the barrier to dissociation.

Solvent Effects on Topomerization in 3 and 4a. Kinetic parametrs for the topomeization in **3** and **4a**, determined for solutions of various solvents, are listed in Tables 3 and 4, respectively. Solvents are arranged in the order of their dielectric constants in these tables.

There are unambiguous solvent effects on the rates of topomerization; the more polar the solvent, the larger the free energy of activation at 323 K. The free energy of activation obtained in cyclohexanes, typical nonpolar solvents, are ca. 2 kcal mol^{-1} smaller than those obtained

Table 3. Solvent Effect on Kinetic Parameters for the Topomerization of the Methylene Protons in the Ethyl Groups in **3**

Solvent	$\Delta H^{\neq}$/kcal mol^{-1}	$\Delta S^{\neq}$/cal mol^{-1}K^{-1}	$\Delta G^{\neq}_{323}$/kcal mol^{-1}	k_{323}/s^{-1}	r
$C_6D_{11}CD_3$[a]	22.4±0.7	24.7±2.3	14.4	1280	0.9995
$C_6D_5CD_3$	23.0±1.1	24.0±3.4	15.3	320	0.9992
$(C_2D_5)_2O$	23.9±0.6	28.3±1.9	14.8	680	0.9997
$CDCl_3$	24.1±0.4	27.6±1.2	15.2	360	0.9998
C_6D_5Cl	25.7±0.8	31.8±2.5	15.5	230	0.9996
THF-d_8	22.9±0.3	22.1±0.7	15.7	155	0.9999
$C_2D_2Cl_4$[b]	21.7±0.6	18.2±1.7	15.8	145	0.9997
CD_2Cl_2	22.5±0.7	21.4±2.1	15.6	185	0.9997
$(CD_3)_2CO$	22.0±0.4	18.6±1.3	16.0	105	0.9998
CD_3NO_2	24.4±0.8	24.6±2.4	16.5	47	0.9995
CD_3CN	27.1±0.8	33.5±2.4	16.3	67	0.9997
DMF-d_7	22.1±0.6	17.9±1.9	16.3	59	0.9997

a) Methylcyclohexane-d_{14}. b) 1,1,2,2-Tetrachloroethane-d_2.

Table 4. Solvent Effect on Kinetic Parameters for the Topomerization of the Benzylic Methylene Protons in **4a**

Solvent	$\Delta H^{\neq}$/kcal mol^{-1}	$\Delta S^{\neq}$/cal mol^{-1} K^{-1}	$\Delta G^{\neq}_{323}$/kcal mol^{-1}	k_{323}/s^{-1}	r
C_6D_{12}[a]	23.0±0.3	16.9±0.8	17.6	8.5	0.9999
$C_6D_{11}CD_3$[b]	22.7±0.4	15.8±1.0	17.6	8.5	0.9998
C_6D_6	24.7±0.7	19.3±2.0	18.5	2.1	0.9997
$C_6D_5CD_3$	24.5±0.4	18.9±1.2	18.4	2.4	0.9997
$CDBr_3$	24.9±0.5	19.0±1.2	18.7	1.5	0.9998
C_6D_5Cl	25.0±0.3	19.8±0.8	18.6	1.7	0.9999
$C_2D_2Cl_4$[c]	25.5±0.2	20.9±0.6	18.8	1.3	0.9999
Pyridine-d_5	23.4±0.4	14.3±1.2	18.7	1.5	0.9998
$C_6D_5NO_2$	26.6±0.3	22.1±0.8	19.4	0.48	0.9999
CD_3NO_2	26.7±0.9	21.9±2.3	19.6	0.38	0.9996
CD_3CN	28.0±0.6	26.2±1.6	19.5	0.42	0.9998
DMF-d_7	24.2±0.8	15.3±1.4	19.2	0.65	0.9997
DMSO-d_6	25.5±0.5	18.0±1.2	19.7	0.35	0.9998

a) Cyclohexane-d_{12}. b) Methylcyclohexane-d_{14}. c) 1,1,2,2-Tetrachloroethane-d_2.

in polar solvents. Though the proton probes afford the barrier to nitrogen inverstion, it is not separated from the barrier to the bond dissociation and thus the solvent affects the activation parameters. We attribute the results to the stabilization of the ground state in polar solvents. Since the N–B coordination bond is polar, the ground state is more polar than the transition state in the topomerization process. A polar solvent stabilizes the ground state better than the transition state by solvation: Consequently, the barrier to the topomerization is enhanced in the polar solvent.

Similar solvent effects were observed in the boronate–amine complexes (**1a**).[1] Some irregularities, however, existed in rates of dissociation in **1a**. Oxygen-contatining solvents, especially ethers, gave larger rate constants than that expected from their polarity. We postulated that the dissociation of the N–B bond was assisted by solvent molecules in these solvents (S_N2 type dissociation). Such irregularities are insignficant in **3** and **4a**. This difference can be ascribed to the steric environments of the boron atoms. Back-side approach of the solvent molecules to the boron atom is unfavorable in **3** and **4a** because of the bulkiness of the substituents on the boron atom in the 9-BBN group: They resemble the *t*-alkyl case in S_N2 reactions.

The kinetic parameters in **4a** could be obtained even in pyridine-d_5, which is well known to be a good donor, and the rates are normal on the stand point of expectation from its polarity. This result also suggests that solvent polarity rather than nucleophilicity of solvent molecules plays important role in the dissociation processes. Although methanol-d_4 and acetic acid-d_4 were used for a solvent, these solvent were unsuitable for a solvent because of reaction with the complexes.

Experimental

Melting points are uncorrected. Elemental analyses were performed on a Perkin–Elmer 240C analyzer. High resolution mass spectra were measured with a JEOL JMS-DX303 spectrometer. Silica gel used for column chromatography was Wako-gel C-200. *N,N*-Dimethylbenzylamine (Tokyo Kasei Co.) and a THF solution of 9-BBN (Aldrich Chemical Co.) were commercially available. *N*-Alkyl-*N*-methylbenzylamines[24] and *o*-bromo-*N*-alkyl-*N*-methylbenzylamines[14] were prepared according to known methods and these amines were distilled before use. Deuterated solvents for NMR measurements were purchased from Aldrich Chemical Co., E. Merck, or MSD ISOTOPES.

General Procedure for the Syntheses of Compound 2,3, and 4. For the preparation of an *o*-lithio-*N,N*-dialkylbenzylamine solution in ether, *N,N*-dialkylbenzylamines were used for the case of **2**, **4a**—**d**, and **4g** (Method A) and *o*-bromo-*N,N*-dialkylbenzylamines were used for others (Method B).

Method A. To a solution of an *N,N*-dialkylbenzylamine (20 mmol) in 30 ml of dry ether was added 13 ml (20 mmol) of a 1.5 mol dm^{-3} hexane solution of butyllithium at −78 °C under a nitrogen atmosphere. The mixture was allowed to stand until the temperature became ambient and stirred for another 12 h at the temperature. The mixture was slowly transferred to 40 ml of a 0.50 mol dm^{-3} THF solution of 9-BBN and stirred for 10 min at room temperature. To the reaction mixture cooled to 0 °C, 1.3 ml (20 mmol) of methanesulfonic acid was added. Then white precipitate was formed with evolution of hydrogen gas. After the gas evolution ceased, the reaction mixture was stirred for 1 h at room temperature and filtered with a glass filter. The filtrate was evaporated under reduced pressure and the residue was extracted with 30 ml of ether for three times. The combined extracts were evaporated and the crude material was purified by recrystallization from hexane–ether and/or chromatography on silica gel (eluent: hexane).

Method B. To a solution of an *o*-bromo-*N,N*-dialkylbenzylamine (20 mmol) in 40 ml of dry ether was added 13 ml (20 mmol) of 1.5 mol dm^{-3} hexane solution of butyllithium at −78 °C under a nitrogen atmosphere. The mixture was allowed to stand until the temperature became ambient and stirred for another hour at the temperature. The solution was slowly transferred to 40 ml of a 0.50 mol dm^{-3} THF solution of 9-BBN. The following procedures are the same as in Method A.

9-[2-(Dimethylaminomethyl)phenyl]-9-borabicyclo[3.3.1]nonane (2). **2** was obtained in 45% yield. Mp 124.5—126.0 °C. Found: C, 80.10; H, 10.41; N, 5.45%. Calcd for $C_{17}H_{26}NB$: C, 80.01; H, 10.27; N, 5.49%. ^{1}H NMR ($CDCl_3$) δ=0.90 (2H, m), 1.60—1.76 (6H, m,) 1.89—2.30 (6H, m), 2.70 (6H, s), 3.96 (2H, s), 7.02 (1H, m), 7.09 (1H, dt, *J*=1.3 and 7.4 Hz), 7.18 (1H, m), 7.68 (1H, d, *J*=7.4 Hz). ^{13}C NMR ($CDCl_3$)[25] δ=21.9 (br), 23.7 and 23.9 (3-C/7-C), 30.4 and 33.6(2(4)-C/6(8)-C), 49.1, 69.7, 121.2, 124.6, 126.2, 133.3, 138.0. ^{11}B NMR ($CDCl_3$) δ=9.5.

9-[2-(Diethylaminomethyl)phenyl]-9-borabicyclo[3.3.1]nonane (3). **3** was obtained in 17% yield. Mp 122.0—125.0 °C (with decomp). Found: C, 80.34; H, 10.84; N, 4.95%. Calcd for $C_{19}H_{30}NB$: C, 80.56; H, 10.68; N, 4.95%. ^{1}H NMR ($CDCl_3$) δ=0.93 (2H, br s), 1.12 (6H, t, *J*=7.2 Hz), 1.5—2.4 (12H, br m), 3.08—3.27 (4H, br m), 4.01 (2H, s), 7.01 (1H, d, *J*=7.5 Hz), 7.07 (1H, dt, *J*=1.0 and 7.4 Hz), 7.16 (1H, dt, *J*=1.0 and 7.4 Hz), 7.66 (1H, d, *J*=7.5 Hz). ^{13}C NMR ($CDCl_3$)[25] δ=10.9, 22.7 (br), 23.7, 31.1 and 34.0 (br, 2(4)-C/6(8)-C), 51.6, 61.5, 120.6, 124.5, 125.9, 132.7, 138.8. ^{11}B NMR ($CDCl_3$) δ=10.5.

9-[2-(Ethylmethylaminomethyl)phenyl]-9-borabicyclo[3.3.1]-nonane (4a). **4a** was obtained in 17% yield. Mp 144.5—147.0 °C (with decomp). Found: C, 80.27; H, 10.61; N, 5.18%. Calcd for $C_{18}H_{28}NB$: C, 80.30; H, 10.48; N, 5.20%. ^{1}H NMR ($CDCl_3$) δ=0.90 (1H, br s), 0.96 (1H, br s), 1.19 (3H, t, *J*=7.3 Hz), 1.57—1.73 (6H, m), 1.89—2.37 (6H, m), 2.60 (3H, s), 3.20 (2H, q, *J*=7.3 Hz), 3.87 and 4.04 (2H, ABq, *J*=13.3 Hz), 7.03 (1H, d, *J*=7.5 Hz), 7.09 (1H, dt, *J*=1.0 and 7.2 Hz), 7.18 (1H, t, *J*=7.2 Hz), 7.69 (1H, d, *J*=7.2Hz). ^{13}C NMR ($CDCl_3$)[25] δ=8.0, 22(br), 23.6 and 23.9 (3-C/7-C), 30.4, 30.7, 33.6, 34.1, 42.9, 52.5, 63.4, 121.3, 124.6, 126.2, 133.4, 138.0. ^{11}B NMR ($CDCl_3$) δ=9.3.

9-[2-(Methylpropylaminomethyl)phenyl]-9-borabicyclo[3.3.1]-nonane (4b). **4b** was obtained in 23% yield. Mp 111.0—113.0 °C (with decomp). Found: C, 80.79; H, 10.97; N, 4.94%. Calcd for $C_{19}H_{30}NB$: C, 80.56; H, 10.68; N, 4.95%. ^{1}H NMR ($CDCl_3$) δ=0.93 (3H, t, *J*=7.2 Hz), 0.95 (2H, br m), 1.50—1.77 (8H, m), 1.89—2.38 (6H, m), 2.63 (3H, s), 3.03 (2H, m), 3.90 and 4.07 (2H, ABq, *J*=13.4 Hz), 7.01 (1H, d,

Table 5. Temperature Dependence of the Chemical Shift Difference, Coupling Constant, and T_2 of Methylene Protons in Ethyl Groups in Compound **3**

Solvent	Correlation[a]		Coupling constant/Hz			T_2/s
	$\Delta\nu_{AB}$/Hz	$\Delta\nu_{AX}$/Hz	J_{AX}	J_{BX}	J_{AB}	
$C_6D_{11}CD_3$[b]	$-0.148t+25.9$	$-0.145t+846.2$	7.2	7.5	−13.3	0.15
$C_6D_5CD_3$	$-0.145t+21.0$	$+0.167t+845.0$	7.2	7.4	−13.4	0.20
$C_6D_5CD_3$[c]	$-0.123t+21.4$	$+0.155t+844.8$	7.2	7.4	−13.4	0.18
$(C_2D_5)_2O$	$-0.210t+32.2$	$-0.146t+844.0$	7.2	7.3	−13.3	0.19
$CDCl_3$	$-0.162t+32.6$	$-0.135t+834.9$	7.2	7.4	−13.4	0.21
C_6D_5Cl	$-0.142t+24.8$	$-0.090t+838.3$	7.2	7.4	−13.3	0.16
THF-d_8	$-0.203t+39.1$	$-0.214t+854.7$	7.2	7.4	−13.2	0.23
$C_2D_2Cl_4$[d]	$-0.184t+35.9$	$-0.145t+832.2$	7.1	7.3	−13.5	0.16
CD_2Cl_2	$-0.155t+33.2$	$-0.180t+842.8$	7.3	7.3	−13.3	0.21
$(CD_3)_2CO$	$-0.155t+41.5$	$-0.244t+857.2$	7.2	7.4	−13.2	0.25
CD_3NO_2	$-0.151t+40.8$	$-0.228t+862.5$	7.2	7.3	−13.3	0.19
CD_3CN	$-0.139t+38.1$	$-0.235t+859.6$	7.2	7.4	−13.3	0.16
DMF-d_7	$-0.124t+41.5$	$-0.201t+853.3$	7.2	7.4	−13.3	0.20

a) $\Delta\nu$/Hz$=xt/°C+y$. Spin A in the ABX_3 system represents the methylene signals in lower magnetic field. b) Methylcyclohexane-d_{14}. c) Concentration 200 mmol dm^{-3}. d) 1,1,2,2-Tetrachloroethane-d_2.

J=7.2 Hz), 7.08 (1H, dt, J=1.1 and 7.4 Hz), 7.18 (1H, t, J=7.0 Hz), 7.69 (1H, d, J=7.5 Hz).

9-[2-(Butylmethylaminomethyl)phenyl]-9-borabicyclo[3.3.1]-nonane (4c). **4c** was obtained in 15% yield. Mp 113.5—117.0 °C (with decomp). Found: C, 80.63; H, 11.04; N, 4.70%. Calcd for $C_{20}H_{32}NB$: C, 80.80; H, 10.85; N, 4.71%. ^{1}H NMR ($CDCl_3$) δ=0.90 (1H, br s), 0.96 (3H, t, J=7.4 Hz), 1.0 (1H, br s), 1.32 (2H, sextet, J=7.4 Hz), 1.48—1.73 (8H, m), 1.90—2.38 (6H, m), 2.62 (3H, s), 3.08 (2H, m), 3.89 and 4.07 (2H, ABq, J=13.7 Hz), 7.02 (1H, d, J=7.5 Hz), 7.08 (1H, dt, J=1.0 and 7.5 Hz), 7.18 (1H, t, J=7.5 Hz), 7.69 (1H, d, J=7.5 Hz).

9-[2-(Hexylmethylaminomethyl)phenyl]-9-borabicyclo[3.3.1]-nonane (4d). **4d** was obtained in 14% yield. Mp 78.0—79.5 °C. Found: C, 81.40; H, 11.42; N, 4.35%. Calcd for $C_{22}H_{36}NB$: C, 81.22; H, 11.15; N, 4.31%. ^{1}H NMR ($CDCl_3$) δ=0.83—0.98 (5H, m), 1.22—1.38 (6H, m), 1.46—1.75 (8H, m), 1.89—2.38 (4H, m), 2.61 (3H, s), 3.07 (2H, m), 3.88 and 4.07 (2H, ABq, J=13.4 Hz), 7.02 (1H, d, J=7.2 Hz), 7.08 (1H, dt, J=1.0 and 7.4 Hz), 7.18 (1H, dt, J=1.0 and 7.4 Hz), 7.69 (1H, d, J=7.2 Hz).

9-[2-(Isopropylmethylaminomethyl)phenyl]-9-borabicyclo-[3.3.1]nonane (4e). **4e** was obtained in 13% yield. Mp 114.0—119.0 °C (with decomp). Found: C, 80.40; H, 10.94; N, 5.17%. Calcd for $C_{19}H_{30}NB$: C, 80.56; H, 10.68; N, 4.95%. ^{1}H NMR ($CDCl_3$, r.t.) δ=0.7—2.6 (20H, br m), 2.76 (3H, s), 3.58 (1H, septet, J=6.5 Hz), 3.8—4.2 (2H, br), 6.96 (1H, d, J=7.5 Hz), 7.05 (1H, dt, J=1.4 and 7.4 Hz), 7.14 (1H, t, J=7.4 Hz), 7.59 (1H, d, J=7.4 Hz). ($CDCl_3$, −20 °C) δ=0.78 (1H, br s), 0.86 (3H, d, J=6.5 Hz), 1.09 (1H, br s), 1.24 (3H, d, J=6.5 Hz), 1.50—2.18 (10H, m), 2.48—2.62 (2H, m), 2.78 (3H, s), 3.59 (1H, septet, J=6.5 Hz), 3.91 and 4.12 (2H, ABq, J=14.5 Hz), 7.00 (1H, d, J=7.5 Hz), 7.08 (1H, dt, J=1.0 and 7.5 Hz), 7.17 (1H, t, J=7.5 Hz), 7.60 (1H, d, J=7.5 Hz).

9-[2-(Isobutylmethylaminomethyl)phenyl]-9-borabicyclo[3.3.1]-nonane (4f). **4f** was obtained in 8% yield. Mp 118.0—121.0 °C (with decomp). Found: C, 80.99; H, 11.10; N, 4.70%. Calcd for $C_{20}H_{32}NB$: C, 80.80; H, 10.85; N, 4.71%. ^{1}H NMR ($CDCl_3$) δ=0.92 (2H, br s), 0.99 (3H, d, J=6.8 Hz), 1.07 (3H, d, J=6.8 Hz), 1.45—2.40 (13H, br m), 2.67 (3H, s), 2.94 and 3.01 (2H, AB part of ABX system, J_{AB}=14.1 Hz, J_{AX}=J_{BX}=4.8 Hz), 3.96 and 4.08 (2H, ABq, J=13.3 Hz), 7.01 (1H, d, J=7.5 Hz), 7.08 (1H, dt, J=1.0 and 7.2 Hz), 7.18 (1H, dt, J=0.7 and 7.4 Hz), 7.68 (1H, d, J=7.2 Hz).

Table 6. Temperature Dependence of the Chemical Shift Difference, Coupling Constant, and T_2 of Benzylic Methylene Protons in Compound **4**

Compound	Solvent	$\Delta\nu_{AB}$/Hz[a]	J_{AB}/Hz	T_2/s
4a	C_6D_{12}[b]	$-0.243t+71.7$	−13.0	0.19
4a	$C_6D_{11}CD_3$[c]	$-0.252t+72.3$	−13.0	0.20
4a	C_6D_6	$-0.337t+82.9$	−13.5	0.19
4a	$C_6D_5CD_3$	$-0.272t+73.8$	−13.3	0.21
4a	$CDBr_3$	$-0.153t+67.3$	−13.4	0.18
4a	C_6D_5Cl	$-0.233t+72.2$	−13.4	0.19
4a	$C_2D_2Cl_4$[d]	$-0.165t+73.1$	−13.6	0.18
4a	Pyridine-d_5	$-0.179t+68.7$	−13.7	0.22
4a	$C_6D_5NO_2$	$-0.129t+65.1$	−13.8	0.17
4a	CD_3NO_2	$-0.118t+68.6$	−13.9	0.20
4a	CD_3CN	$-0.129t+66.1$	−13.9	0.18
4a	DMF-d_7	$-0.121t+63.0$	−13.9	0.20
4a	DMSO-d_6	$-0.132t+62.4$	−13.9	0.18
4b	$C_6D_5CD_3$	$-0.203t+74.4$	−13.4	0.19
4c	$C_6D_5CD_3$	$-0.272t+91.4$	−13.3	0.20
4d	$C_6D_5CD_3$	$-0.239t+84.4$	−13.5	0.18
4e	$C_6D_5CD_3$	$-0.041t+39.5$	−14.5	0.18
4f	$C_6D_5CD_3$	$+0.142t+39.0$	−13.5	0.18
4g	$C_6D_5CD_3$	$-0.333t+105.4$	−13.4	0.18
4h	$C_6D_5CD_3$	$+0.175t+107.3$	−13.4	0.14

a) Chemical shift differences between AB signals: $\Delta\nu_{AB}$/Hz$=xt/°C+y$. b) Cyclohexane-d_{12}. c) Methylcyclohexane-d_{14}. d) 1,1,2,2-Tetrachloroethane-d_2.

9-[2-(Isopentylmethylaminomethyl)phenyl]-9-borabicyclo-[3.3.1]nonane (4g). **4g** was obtained in 35% yield. Mp 103.0—105.0 °C. Found: C, 81.09; H, 11.12; N, 4.71%. Calcd for $C_{21}H_{34}NB$: C, 81.02; H, 11.01; N, 4.50%. ^{1}H NMR ($CDCl_3$) δ=0.90 (1H, br s), 0.93 (3H, d, J=6.2 Hz), 0.94 (3H, d, J=6.2 Hz), 0.97 (1H, br s), 1.40—1.78 (9H, m), 1.90—2.23 (5H, m), 2.30—2.42 (1H, m), 2.59 (3H, s), 3.13 (2H, m), 3.86 and 4.07 (2H, ABq, J=13.5 Hz), 7.02 (1H, d, J=7.2 Hz), 7.08

(1H, dt, J=1.0 and 7.2 Hz), 7.18 (1H, t, J=7.2 Hz), 7.69 (1H, d, J=7.2 Hz).

9-[2-(Methylneopentylaminomethyl)phenyl]-9-borabicyclo-[3.3.1]nonane (4h). **4h** was obtained in 2% yield. Mp 106.0—111.0 °C (with decomp). Found: M^+ 311.2820. Calcd for $C_{21}H_{34}N^{11}B$: M^+ 311.2785. ^1H NMR ($CDCl_3$, r.t.) δ=0.94 (2H, br s), 1.18 (9H, s), 1.35—2.40 (12H, br m), 2.71 (3H, s), 2.8—3.5 (2H, br), 3.9—4.5 (2H, br), 7.01 (1H, d, J=7.2 Hz), 7.09 (1H, dt, J=0.7 and 7.2 Hz), 7.18 (1H, t, J=7.2 Hz), 7.68 (1H, d, J=7.2 Hz). ($CDCl_3$, −20 °C) δ=0.85 (1H, br s), 1.04 (1H, br s), 1.19 (9H, s), 1.50—2.22 (10H, m), 2.35—2.52 (2H, m), 2.70 (3H, s), 2.96 and 3.36 (2H, ABq, J=14.4 Hz), 4.11 and 4.33 (2H, ABq, J=13.7 Hz), 7.06 (1H, d, J=7.2 Hz), 7.13 (1H, dt, J=1.0 and 7.2 Hz), 7.21 (1H, t, J=7.2 Hz), 7.70 (1H, d, J=7.2 Hz).

NMR Measurement and Line Shape Analysis. ^1H and proton-decoupled ^{13}C NMR spectra were measured on a JEOL GSX-400 spectrometer operating at 399.8 MHz and 100.5 MHz, respectively. Temperature were calibrated using the chemical shift differences of methanol and ethylene glycol. Unless otherwise mentioned the concentration of the solution was ca. 30 and 200 mmol dm^{-3} for ^1H and ^{13}C NMR measurement, respectively. The FID data were accumulated more than 8 times for ^1H and more the 100 times for ^{13}C. The line

Table 7. Rate Constants of Topomerization Obtained from Proton Probes in Compounds **3** and **4**

Compound	Solvent	k/s^{-1} (temperature/°C)
3	$C_6D_{11}CD_3$[a]	6.0(8.0), 11.2(12.0), 19.8(16.0), 33.5(20.0), 54(24.0), 88(28.0), 155(32.0), 265(36.0)
3	$C_6D_5CD_3$	7.4(19.9), 12.5(23.8), 20.5(27.8), 34(32.0), 58(36.0), 78(38.0), 102(40.0)
3	$C_6D_5CD_3$[b]	7.7(20.0), 14.2(26.5), 26.5(30.0), 51(35.0), 98(40.0)
3	$(C_2D_5)_2O$	6.7(15.0), 9.5(17.6), 13.5(20.0), 18.8(22.5), 27.5(25.0), 39(27.5), 56(30.0), 80(33.0)
3	$CDCl_3$	3.9(16.1), 7.2(20.0), 13.0(24.1), 22.0(28.0), 38(32.0), 63(36.0), 100(40.0), 172(44.0), 290(48.0), 410(50.8)
3	C_6D_5Cl	6.5(24.0), 11.6(28.0), 20.0(32.0), 34.5(36.0), 60(40.0), 102(43.5), 160(47.0)
3	THF-d_8	3.6(19.9), 6.3(23.9), 10.8(28.1), 18.0(32.0), 29.2(36.0), 47(39.9), 76(44.0), 125(48.0), 195(52.0)
3	$C_2D_2Cl_4$[c]	7.2(24.0), 11.5(28.0), 17.8(32.0), 29.5(36.0), 47(39.9), 74(44.0), 115(47.9), 160(50.7)
3	CD_2Cl_2	4.7(19.9), 7.8(24.0), 12.8(28.0), 21.6(32.0), 31.5(35.0), 47(38.1), 66(40.9)
3	$(CD_3)_2CO$	4.7(24.0), 8.0(28.0), 12.8(32.0), 21.0(36.0), 34.5(40.0), 53(44.0), 82(48.0)
3	CD_3NO_2	4.7(32.0), 8.5(36.0), 12.6(40.0), 22.5(43.9), 37.0(48.1), 60(52.0), 98(56.0), 150(59.9)
3	CD_3CN	5.2(31.9), 9.8(36.1), 16.2(40.0), 31.0(44.1), 54(48.1), 88(52.0), 145(56.0)
3	DMF-d_7	4.4(28.0), 7.3(32.0), 12.4(36.0), 18.8(40.0), 29.5(43.9), 46(47.9), 75(52.0)
4a	C_6D_{12}[d]	8.5(50.1), 13.5(54.0), 20.8(58.0), 31(62.0), 48(66.0), 74(70.0), 110(74.0), 160(78.0), 235(82.0)
4a	$C_6D_{11}CD_3$[a]	8.8(50.0), 13.2(54.0), 20.2(58.0), 31(62.0), 46.5(66.0), 70(70.0), 106(74.0), 155(78.0), 230(82.0)
4a	C_6D_6	4.0(55.1), 6.7(60.0), 10.6(64.0), 17.2(68.0), 26.5(72.0), 39.5(76.0), 58(79.5)
4a	$C_6D_5CD_3$	7.8(60.3), 11.9(64.1), 19.2(68.1), 29.8(72.2), 47(76.2), 68(80.2), 102(84.0), 148(88.1), 220(92.1), 310(96.2)
4a	$CDBr_3$	8.8(65.0), 14.4(69.5), 23.6(74.0), 34.5(78.0), 54(81.9), 82(85.9), 120(90.0), 175(94.0)
4a	C_6D_5Cl	8.8(64.0), 13.6(68.0), 21.2(72.0), 33.5(76.0), 50(80.0), 75(83.9), 115(88.0), 168(92.0), 240(96.0)
4a	$C_2D_2Cl_4$[c]	8.0(65.0), 13.8(69.5), 22.4(74.0), 34.5(78.0), 53(82.0), 80(86.0), 118(90.0), 175(93.9), 260(97.9)
4a	Pyridine-d_5	7.1(64.0), 10.4(68.0), 15.6(72.0), 23.4(76.0), 31.5(78.9), 42.0(82.0), 63(85.9), 170(97.0)
4a	$C_6D_5NO_2$	5.6(70.0), 9.8(74.9), 16.6(79.5), 27.6(84.0), 41.5(88.0), 64(91.9), 95(96.0), 140(100.0), 205(104.0)
4a	CD_3NO_2	4.7(69.9), 7.7(74.9), 13.8(80.0), 23.8(85.0), 42.0(90.0), 62(93.9), 94(97.9)
4a	CD_3CN	5.0(69.0), 7.4(72.0), 10.2(74.9), 14.6(77.9), 18.4(79.9), 24.2(82.3), 31(84.3)
4a	DMF-d_7	6.4(70.0), 9.5(74.0), 14.0(78.0), 21.2(82.0), 30.2(86.0), 45.5(90.0), 69(94.0), 98(97.9), 140(101.9)
4a	DMSO-d_6	6.3(75.0), 10.4(79.5), 16.8(84.0), 25.6(88.0), 37.5(91.9), 55(95.9), 82(100.0), 115(104.0)
4b	$C_6D_5CD_3$	7.7(55.0), 14.6(60.0), 22.4(63.9), 35(67.9), 54(71.9), 86(75.9), 128(80.0), 190(84.0), 295(88.0)
4c	$C_6D_5CD_3$	5.9(55.0), 11.0(60.0), 17.5(63.9), 27.2(67.9), 41(71.9), 64(75.9), 95(79.9), 150(84.5), 235(89.0), 370(93.8)
4d	$C_6D_5CD_3$	6.0(55.1), 11.2(60.0), 17.8(64.0), 28.0(68.0), 42.5(72.0), 66(76.0), 102(80.0), 145(84.0), 220(88.0), 330(91.9)
4e	$C_6D_5CD_3$	6.1(1.8), 11.0(6.0), 19.5(10.0), 32(14.0), 52.5(18.1), 83(22.0), 135(26.0), 215(29.9), 350(33.9)
4f	$C_6D_5CD_3$	7.4(30.0), 12.1(33.9), 19.5(38.0), 33.0(42.0), 55(46.0), 86(50.0), 135(53.9), 210(57.9)
4g	$C_6D_5CD_3$	8.8(59.0), 14.3(63.0), 23.4(67.0), 36.5(71.0), 56(75.0), 83(79.0), 124(82.9), 180(87.0), 290(91.9)
4h	$C_6D_5CD_3$	5.6(−10.1), 9.6(−6.0), 18.5(−2.0), 32(1.9), 57(6.0), 95(10.0), 155(14.0), 230(17.9), 380(22.0), 610(26.0)

a) Methylcyclohexane-d_{14}. b) Concentration 200 mmol dm^{-3}. c) 1,1,2,2-Tetrachloroethane-d_2. d) Cyclohexane-d_{12}.

shape analysis was performed using DNMR3K program.[36] The coupling constants and chemical shift differences of exchanging nuclei were checked at several points where the exchange was negligibly slow. The coupling constants were constant throughout the temperature ranges. The chemical shift differences were linearly correlated with temperature. T_2 values were estimated from the line width of exchanging signals at the slow exchange limit. For the simulation of methylene protons of ethyl groups in **3**, the calculations were performed only for the AB part in the $ABX_3 \rightleftarrows BAX_3$ system. The benzylic methylene protons in **4** were simulated as the $AB \rightleftarrows BA$ system. These parameters are listed in Tables 5 and 6. The rate contants are compiled in Table 7.

The line shape analyses for compound **2** were performed by using ^{13}C NMR signals due to 3-C/7-C and 2(4)-C/6(8)-C as the $A \rightleftarrows X$ exchange. Input parameters and rate constants follow: 3-C/7-C: $\Delta\nu$=0.037 t+24.5 Hz, T_2 0.30, 030 s. 2(4)-C/6(8)-C: $\Delta\nu$=−0.071 t+329.1 Hz, T_2 0.36, 0.38 s. Rate constant k/s^{-1} (temperature/°C): 5.0(55.0), 8.5(60.0), 15.6 (65.0), 25(69.9), 40(75.0), 64(79.9), 110(84.9), 190(89.9), 300(95.0), 450(99.9), 1000(109.8) in toluene-d_8.

The carbon signals in **3** and **4a** observed in toluene-d_8 were similarly analyzed. **3** 2(4)-C/6(8)-C: $\Delta\nu$=0.135 t+285.5 Hz; T_2 0.19, 0.20 s; k/s^{-1} (temperature/°C): 49(14.9), 90(20.0), 165(25.0), 280(30.0), 470(35.0), 740(40.0), 1950(49.6). **4a** 3-C/7-C: $\Delta\nu$=29.2 Hz (constant); T_2 0.20, 0.21 s; k/s^{-1} (temperature/°C): 13.5(39.8), 22.5(45.0), 37(50.1), 50(52.9), 65(55.1), 100(60.0).

^{11}B NMR spectra were measured on the same spectrometer operating at 128.2 MHz at room temperature. The chemical shifts were recorded relative to BF_3:OEt_2 used as an external reference.

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