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Structural and Stereochemical Studies of Tris[2-(trifluoromethyl)phenyl]borane: Spontaneous Resolution, Stereodynamics, and Intramolecular C–F···B Interactions

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The structure and stereochemistry of the title organoboron compound, prepared from the corresponding organolithium compound and BCl_3, were studied by spectroscopic methods and molecular orbital calculations. The X-ray crystal structure analysis shows that molecules take a propeller-shaped structure of nearly C_3 symmetry, in which three CF_3 groups lie at the same side of the boron sp^2 plane. This compound crystallizes as conglomerates to give single crystals consisting of one or the other enantiomeric forms, both of which are CD active in the solid state. In solutions, molecules exist as a mixture of two conformational isomers, the C_3 and C_1 symmetric forms. Interconversion between the two isomers was observed by the variable temperature ^{19}F NMR, the barriers to isomerization being 8 and 6 kcal mol^{-1} for two independent processes in the two ring flip mechanism. The presence of C–F···B interactions was supported by the short F···B contacts (ca. 2.80 Å) in the X-ray structure and by the chemical shift of ^{19}F NMR in solutions.

A large number of triarylboranes have been studied from structural and stereochemical aspects, their features being the propeller-shaped conformations and stereodynamics via the flip of aryl rings.[1,2] When a boron atom carries bulky aryl groups such as *o*-substituted phenyl and 1-naphthyl groups, the stereodynamic processes are often observable by the dynamic NMR method.[3,4] As an example of this class of molecules, we studied tris[2-(trifluoromethyl)phenyl]borane (**1**)[5] to measure the effect of *o*-CF_3 groups on the conformational behavior as well as the molecular structure and properties.

Several papers pointed out that CF_3 groups are able to coordinate to various kinds of metal atoms at the *ortho* position in organometallic compounds carrying 2-CF_3 or 2,6-$(CF_3)_2$ phenyl groups, on the basis of X-ray structures and NMR spectra.[6—10] Because little is known about the interaction of C–F units with boron atoms in phenylborane derivatives, the spectroscopic data of **1** were closely analyzed to explore the presence of the C–F···B interactions. It is also meaningful to compare the X-ray structure and kinetic data of **1** with those of *o*-(substituted methyl)phenylborane derivatives carrying a N, O, or S ligand at the benzylic position, which we reported in the series of studies to determine the kinetic basicity of coordinating ligands.[11]

In the course of the study, we found from the X-ray analysis that this compound crystallized as conglomerates. The chiroptical properties of these crystals were determined by CD spectroscopy in the solid state. An interesting phenomenon, spontaneous resolution of propeller-shaped triarylboranes, is also described in this paper.

Results and Discussion

Synthesis and General Properties. Compound **1** was synthesized by the reaction of 2-(trifluoromethyl)phenyllithium, prepared from the corresponding bromide and BuLi, with BCl_3 in the 3 : 1 molar ratio in 61% yield. Recrystallization from hexane afforded colorless plates, which were stable under ordinary conditions, as expected for boranes carrying sterically crowded aryl groups. The ^{11}B NMR chemical shift of $\delta = 71$ ($BF_3 : OEt_2$ at $\delta = 0$) is within the typical range for tricoordinated boron atoms with three aryl substituents.[12]

While ordinary triarylboranes, for example BPh_3 and $B(C_6F_5)_3$, form stable complexes with Lewis bases,[13,14] we failed to isolate an adduct of **1** in a stable form by the treatment with various Lewis bases. The NMR signals of **1** were hardly influenced at all by the addition of a large amount of NEt_3 or CH_3CN into the sample solution. These observations indicate that the Lewis acidity of **1** is much weaker than those of other triarylboranes because of steric hindrance.

Molecular Structure. The structure in the solid state was analyzed by X-ray crystallography. An ORTEP diagram is shown in Fig. 1 together with some selected structural parameters in the figure legend.

A molecule takes a propeller-shaped conformation, in which all the three CF_3 groups lie at the same side of the boron atom, being of nearly C_3 symmetry. The three phenyl groups are twisted by 45.6, 49.3, and 52.9° toward the same direction from the reference plane, which is defined by the average plane made by the three carbons bonded to the boron atom, C(1), C(8), and C(15). These angles are larger than those observed in triphenylborane (28.3°),[15] and comparable to those in mesitylboranes (40—60°),[4a] reflecting the

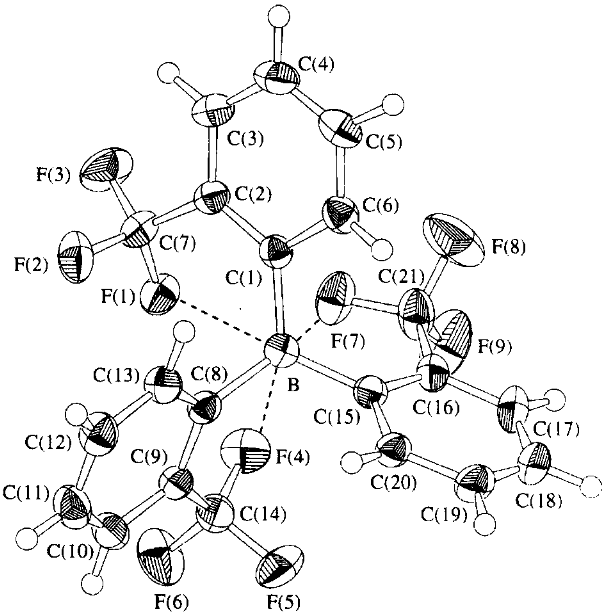


Fig. 1. An ORTEP diagram of **1** with thermal ellipsoids at 50% probabilities. Selected structural parameteres: B–C(1) 1.582(4), B–C(8) 1.576(4), B–C(15) 1.571(4), C–F 1.326—1.347, B···F(1) 2.845(3), B···F(4) 2.816(4), B···F(7) 2.763(3) Å. C(1)–B–C(8) 119.7(2), C(1)–B–C(15) 118.6(2), C(8)–B–C(15) 119.3(2), C(2)–C(1)–B 127.5(2), C(9)–C(8)–B 127.5(2), C(16)–C(15)–B 127.8°.

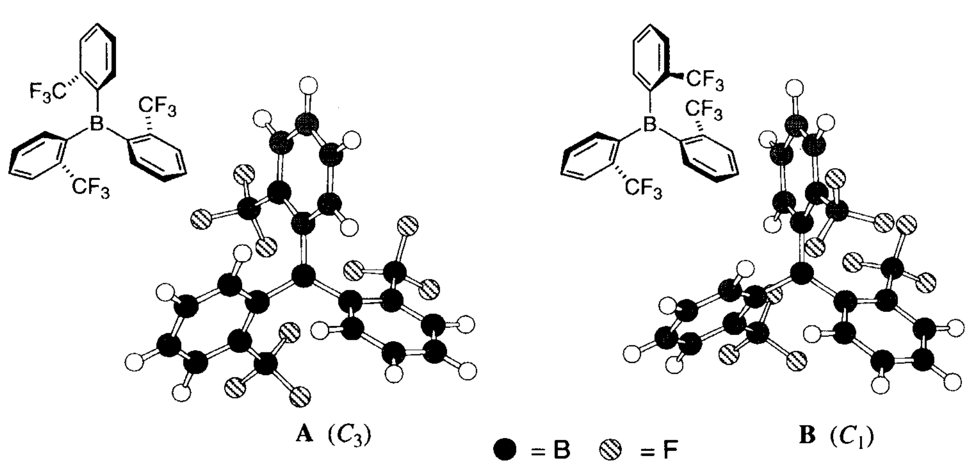
steric size of the *ortho* substituents. The sum of the three C–B–C bond angles, 357.6° (8% in the tetrahedral character),[11e] means that the boron atom is just slightly pyramidized toward the less hindered side. The short B···F contacts are observed at F(1), F(4), and F(7) with the interatomic distance of ca. 2.80 Å. This value is smaller than the sum of van der Waals radii of B (ca. 1.70 Å)[16] and F (1.47 Å) atoms. Another structural feature is the bond angles at C(1), C(8), and C(15): a significant bending deformation, for example C(2)–C(1)–B 127.5(2)° and C(6)–C(1)–B 115.5(2)° at C(1), results from the avoidance of the steric interactions between B and CF_3 moieties.

To gain more structural information, MO calculations were carried out by the AM1 Hamiltonian. The structural optimization gave two types of propeller-shaped conformations, **A** (C_3) and **B** (C_1), except for their enantiomers: the former is almost the same as the X-ray structure and the latter is a structure where one CF_3 group is *anti* from the others (Fig. 2). The calculation suggests that **A** is less stable by 3.4 kcal mol^{-1} than **B**, reflecting the steric congestion of the three CF_3 groups in the former. As mentioned later, the two conformers exist in a comparable ratio in solutions. The presence of a significant amount of **A** is attributable to its highly polar character, as indicated by the calculated dipole moments: 7.6 and 3.7 Debye (1 Debye$\approx 3.33564\times10^{-30}$ C m) for **A** and **B**, respectively. The polar structure **A** is stabilized more than **B** by solvation in solutions and by crystal packing in crystals.

Spontaneous Enantiomeric Resolution. Further analysis of the X-ray data of **1** reveals that all molecules possess the same stereochemistry about propeller helicity in a crystal belonging to the chiral space group of $P2_1$. Namely, the compound crystallizes as conglomerates, the spontaneous resolution taking place.

The CD spectra in the solid state were measured in Nujol® for five single crystals grown from a hexane solution. These are all CD active: four of them gave spectra as shown in Fig. 3 and the remaining one gave that of the identical curve of opposite signs.[17] The crystals did not show enantiomorphorism as far as we could visually observe the crystal shapes. The CD spectrum in Fig. 3 exhibits complex bands around 280—330 nm in the positive region and relatively sharp negative troughs at 245 and 230 nm, these being assignable to the interactions between aromatic chromophores (π-π*). The CD activity was lost on dissolution in organic solvents because racemization took place rapidly on the laboratory timescale in solutions. It was impossible to establish the absolute stereochemistry by the Bijvoet method because of the lack of heavy atoms.

Relatively few examples of optically active triarylboranes have been known up to date. In 1991, Okada et al. reported the first isolation of enantiomerically pure triarylboranes by introducing ethano-bridges across the aryl rings to enhance



A (C_3) **B** (C_1)

Fig. 2. Calculated structures of two conformational isomers of **1** by the AM1 method.

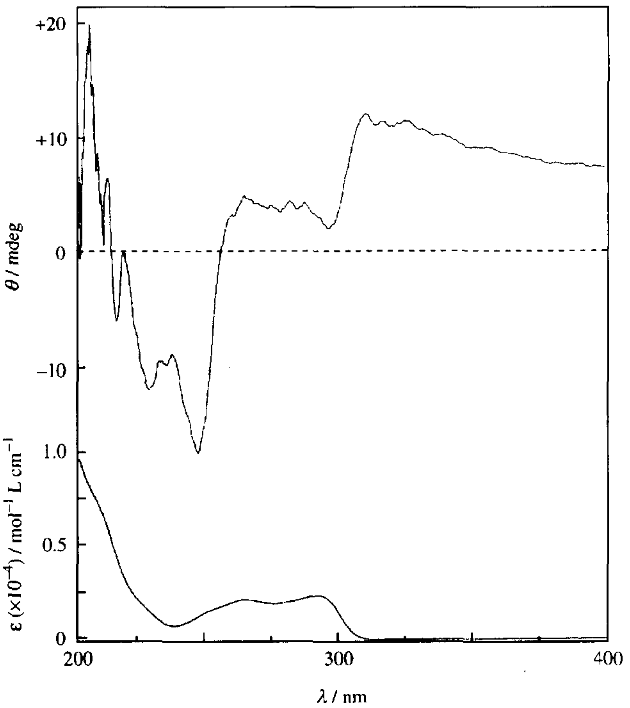


Fig. 3. CD (Top: in Nujol®) and UV (Bottom: in hexane) spectra of **1**.

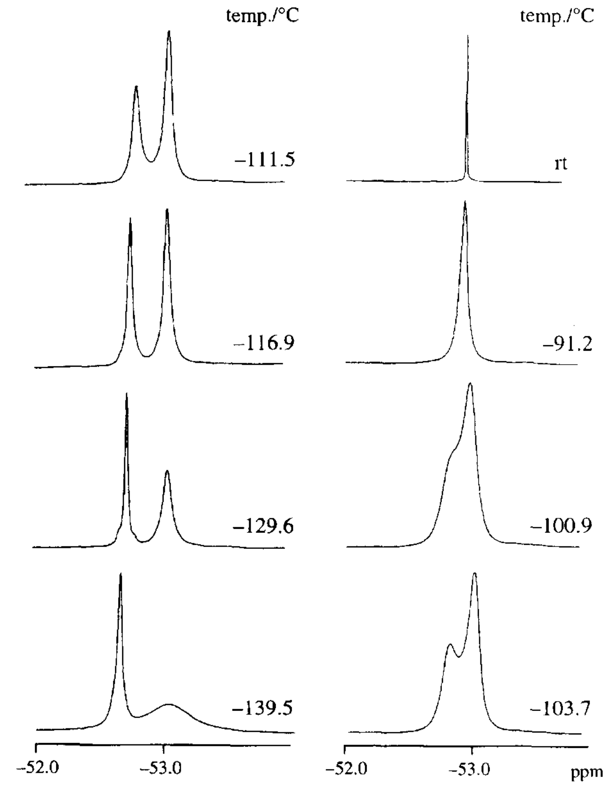


Fig. 4. Variable temperature ^{19}F NMR of **1** in CD_2Cl_2 (C_6F_6 at $\delta = -162.9$).

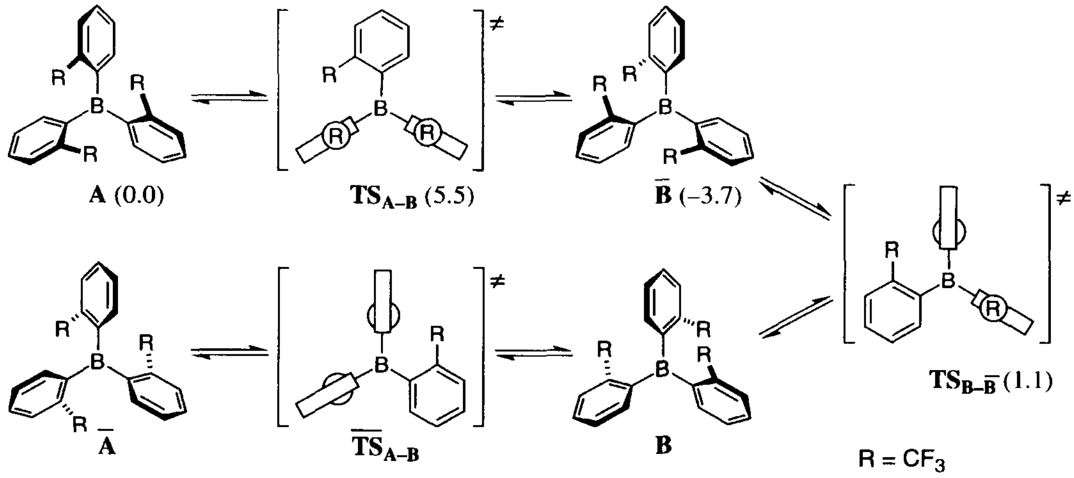
the barrier to racemization.[18] As for simple triarylboranes, the only example is the spontaneous resolution of tri(1-naphthyl)borane, which was confirmed only by the space group of single crystals.[19,20] The spontaneous resolution itself is not an unusual phenomenon, as pointed out by Jacques et al.: 5—10% of chiral organic molecules do crystallize as conglomerates.[21] Therefore, there must be a large number of compounds that crystallize as conglomerates among hundreds of crystalline triarylboranes so far prepared. We anticipate that CD spectra in the solid state are another powerful tool to study the chiroptical properties of these propeller-shaped molecules.

Stereodynamics. The stereodynamic processes were observed as the lineshape changes in the ^{1}H, ^{13}C, and ^{19}F NMR at low temperatures. The analysis was carried out by use of the ^{19}F NMR due to its simple signal pattern. The observed signals at various temperatures are shown in Fig. 4. A sharp singlet observed at room temperature was decoalesced at −100 °C, and separated into two singlets at $\delta = -52.7$ and −53.0 in the ratio of 0.70 : 1 at −117 °C (process I). The minor and major signals are assignable to **A** and **B**, respectively. At lower temperatures, only the signal due to **B** was broadened, although it did not reach decoalescence even at the lowest attainable temperature (process II). The total lineshape analysis afforded the following kinetic parameters of process I: $\Delta H^{\neq}$ 6.7±0.1 kcal mol^{-1}, $\Delta S^{\neq}$ −8.2±0.4 cal mol^{-1} K^{-1}, $\Delta G^{\neq}$ 8.2 kcal mol^{-1} at 190 K (1 cal = 4.184 J). The barrier height of the process II is roughly estimated to be 6 kcal mol^{-1}.

The dynamic behavior is readily explained by Mislow's ring flip mechanism.[1,4,22] On steric grounds, the two ring flip is a preferred pathway for the conformational interconversions in ordinary triarylboranes, where two rings rotate through planes perpendicular to the reference plane (Scheme 1). Process I is attributed to the exchange between **A** and **B** via the transition state $\mathbf{TS_{A-B}}$ (diastereomerization), and process II to the exchange between **B** and its enantiomer $\overline{\mathbf{B}}$, via the transition state $\mathbf{TS_{B-\overline{B}}}$ (enantiomerization). At about −120 °C, only process I is virtually frozen on the NMR timescale to give the signals due to **A** and **B** separately, where the magnetic environments of three CF_3 groups are still averaged in the unsymmetrical structure of **B** due to facile enantiomerization. The broadening of the signal due to **B** at lower temperatures results from the hindered ring flip via process II. If this process could have been completely frozen, the broad signal should have been separated into three signals. According to the proposed mechanism, the barriers to isomerization were calculated by the AM1 method to be 5.5 and 4.8 kcal mol^{-1} for processes I and II, respectively (Scheme 1). Although the effect of solvation is ignored, the calculation can approximately reproduce the barrier heights of the two processes, where the barrier to process I is significantly higher than that to process II.

These dynamic processes are similar to those observed in tris(2-methyl-1-naphthyl)borane (**2**), whose barriers are 15.9 and 14.6 kcal mol^{-1} for processes I and II, respectively.[4a] The ease of stereointerconversion in **1** relative to **2** is understood by the steric size of aryl groups.

C–F···B Interaction. The significant F···B contacts in the X-ray structure provide evidence of the C–F···B in-



Scheme 1. A part of the network of stereointerconversion between stereoisomers **A** and **B** via the two ring flip mechanism and calculated relative energies of each structure by the AM1 method in parentheses (bars denote enantiomeric relationships).

teraction in the crystals, as discussed above. The nature of this interaction is further explored with the aid of the MO calculation and multinuclear NMR.

It is known that C–F units in organic fluorine compounds are able to work as ligands toward metal atoms[5,6] and as hydrogen bond acceptors,[23,24] even though the interactions are weak. To confirm whether the C–F···B type interaction is likely or not, MO calculations were carried out for a simple model reaction. In the following process,

$$CHF_3 + BH_3 \rightarrow CHF_3 : BH_3 \qquad (1)$$

the energy optimization gave a complexed structure as a global minimum, in which one of the F atoms in trifluoromethane was apparently close to the B atom. At the MP2/6-31G* level, the F···B interatomic distance and the complexation energy are 2.41 Å and 3.6 kcal mol^{-1}, respectively.[25]

The interaction in solutions is discussed from the ^{19}F and ^{11}B NMR data. The ^{19}F NMR chemical shift of **1** ($\delta = -52.8$) is unambiguously at lower field than those of ordinary (trifluoromethyl)benzenes (ca. $\delta = -64$).[26] The NMR data of various organometallic compounds carrying *o*-(trifluoromethyl)phenyl groups reveal that the coordination of CF_3 groups brings about a downfield shift by ca. 10 ppm.[8] Therefore, we consider that the C–F···B interaction is one of the important factors in the deshielding effect observed in **1**.

It is not straightforward to estimate the effect of coordination from the chemical shift of ^{11}B NMR. Although boron signals are generally shifted upfield by the structural change from trigonal to tetrahedral by coordination, the chemical shift of **1** ($\delta = 71$) is apparently at higher field than that of the CF_3-free compound, triphenylborane, at $\delta = 60$.[12] This finding is explained by the conformation of aryl groups. Namely, the phenyl rings in **1** are twisted from the reference plane so much that the electron donation from the phenyl π system to the boron empty orbital through conjugation is decreased. This trend was reasonably reproduced by the GIAO calculations of triphenylborane molecules with various twist angles.[27] The effect of coordination on the chemical shift seems to be much smaller than the conformational effect.

These experimental and theoretical findings support the presence of the C–F···B interaction in **1**, although it is much weaker than the interactions with N, S, and O ligands in other related compounds.[11,28,29] From the above discussion, we consider that the strength will be within a few kcal mol^{-1}. However, the C–F···B interactions can play a significant role in influencing molecular structure and properties, especially when the interacting groups are appropriately arranged, as other types of weak interactions are important in the molecular recognition and crystal engineering.

Experimental

^{1}H NMR spectra were measured on a Bruker ARX-400 spectrometer at 400 MHz. ^{13}C, ^{11}B, and ^{19}F NMR spectra were measured on the same instrument at 100, 128, and 375 MHz, respectively, under the complete irradiation of proton signals. The chemical shifts of the ^{11}B and ^{19}F NMR were referred to the signals due to $BF_3 : OEt_2$ ($\delta = 0$) and C_6F_6 ($\delta = -162.9$) as external references, respectively. Melting points are uncorrected. CD spectra were measured on a JASCO J-720 spectropolarimeter, and samples were prepared by spreading a Nujol® mull of ground powders between two quartz plates. UV and IR spectra were measured with HITACHI U-2000 and I-2000 spectrometers, respectively.

Tris[2-(trifluoromethyl)phenyl]borane (1). To a solution of 500 mg (2.22 mmol) of 1-bromo-2-(trifluoromethyl)benzene in 5 mL of dry ether was added 1.4 mL (2.3 mmol) of a 15% butyllithium solution in hexane at −78 °C under nitrogen atmosphere. The solution was allowed to warm up to room temperature and then stirred for 24 h. To the solution was added 0.63 mL (0.63 mmol) of a 1.0 mol L^{-1} BCl_3 solution in hexane at −78 °C. The whole was allowed to warm up to room temperature and then stirred overnight. The mixture was treated with ca. 10 mL of water, and extracted with 20 mL of ether three times. The organic solution was dried over $MgSO_4$, and the solvent was evaporated. The crude material was chromatographed on silica gel with hexane eluent. Recrystallization from hexane gave 600 mg (61%) of the pure compound as colorless plates. Mp 114—115 °C (for racemic powders). Mp 111—112 °C (for nonracemic powders). Found: C, 56.84; H, 2.79%. Calcd for $C_{21}H_{12}BF_9$: C, 56.54; H, 2.71%. ^{1}H NMR ($CDCl_3$) $\delta = 7.23$ (3H, d, $J = 7.1$ Hz), 7.48 (3H, dt, $J = 1.3$, 7.4 Hz), 7.56 (3H, dt,

$J = 1.5, 7.5$ Hz), 7.71 (3H, d, $J = 7.3$ Hz). ^{1}H NMR (CD_2Cl_2, −128 °C) $\delta = 6.96$ ($3H_A$, d, $J = 7.0$ Hz), 7.26 ($3H_B$, d, $J = 6.2$ Hz), 7.46 ($3H_A$, t, $J = 6.8$ Hz), 7.51 ($3H_B$, t, $J = 7.1$ Hz), 7.58 ($3H_B$, d, $J = 7.3$ Hz), 7.62 ($3H_A$, t, $J = 7.3$ Hz), 7.67 ($3H_B$ d, $J = 7.6$ Hz), 7.72 ($3H_A$, d, $J = 7.5$ Hz). The isomer ratio, **A** : **B**, was 0.77 : 1 at the temperature. ^{13}C NMR ($CDCl_3$) $\delta = 124.3$ (q, $^{1}J_{C-F} = 272.9$ Hz), 125.8, 130.1, 130.5, 133.0 (q, $^{2}J_{C-F} = 32.3$ Hz), 134.9, 141.7 (br). ^{11}B NMR ($CDCl_3$, rt) $\delta = 71.0$ (half-band width 719 Hz). ^{19}F NMR (CD_2Cl_2) $\delta = -52.8$. ^{19}F NMR (CD_2Cl_2, −128 °C) $\delta = -52.7$ (**A**), −53.0 (**B**). UV (hexane) 208 (sh, ε 3.85), 262 (3.30), 291 nm (3.36). IR (KBr) 3069, 1598, 1571, 1485, 1439, 1316, 1258, 1217, 1164, 1129, 1062, 1034, 999, 961, 899, 887, 772, 701, 669, 617, 596 cm^{-1}. CD (Nujol®) : $[\theta]_{217}$ −5.45, $[\theta]_{227}$ −11.3, $[\theta]_{235}$ −8.5, $[\theta]_{247}$ −16.7, $[\theta]_{263}$ +5.0, $[\theta]_{295}$ +4.8, $[\theta]_{308}$ +12.2.

Dynamic NMR Measurement. During the variable temperature measurements, the temperatures of the sample were read from a thermocouple after the calibration with chemical shift differences of the methanol signals. The total lineshape analysis was performed by the DNMR3K program.[30] The lineshapes were analyzed as an exchange between two unequally populated sites. Chemical shift differences and isomer populations were measured at several temperatures, where the exchange rate was negligibly small. The chemical shift differences (Δv) were assumed to be correlated with the temperature (t/°C) linearly as $\Delta\nu = 1.37t + 60.7$ Hz. The isomer population was put into the van't Hoff equation under the consideration of the statistical contribution, the thermodynamic parameters from **A** to **B** being $\Delta H^\circ = 0.4 \pm 0.1$ kcal mol^{-1}, $\Delta S^\circ = 1.1 \pm 0.1$ cal mol^{-1} K^{-1}, and $\Delta G^\circ_{190} = 0.19$ kcal mol^{-1}. Spin-spin relaxation times (T_2's) were estimated from the lineshapes at the slow exchange limit to be 0.03 s. The total lineshape analysis gave the following rate constants of isomerization from **A** to **B** (process I) at each temperature indicated in parentheses, k/s^{-1} (t/°C): 14.0 (−119.3), 20 (−116.9), 30 (−114.0), 36.5 (−112.7), 43 (−111.5), 54 (−109.8), 70 (−107.6), 115 (−103.7). The free energy of activation for the process II was estimated by assuming that the rate constant was in the order of 10^3 s^{-1} at the lowest attainable temperature (−139 °C).

X-ray Analysis.[31] Each crystal used for the measurement was grown from a hexane solution. The diffraction data were collected on a Rigaku RAXIS-IV imaging plate diffractometer with Mo $K\alpha$ radiation ($\lambda = 0.71070$ Å) to a maximum 2θ value of 55.1° at −80 °C. A total of 13 × 6.00° oscillation images were collected, each being exposed for 20.0 min. The reflection data were corrected for the Lorentz-polarization effects and secondary extinction. The crystal-to-detector distance was 100.0 mm with the detector at the zero swing position. The readout was performed in the 0.100 mm pixel mode. The structure was solved by the direct method and refined by the full-matrix least-squares method by using a teXan program (ver. 1.9) on a comtec O2 workstation. Anisotropic thermal parameters were employed for nonhydrogen atoms and isotropic ones for hydrogen atoms. Among 2135 observed reflections, 2049 unique reflections ($I > 0.0\ \sigma(I)$) were used for the refinement of 326 variable parameters. The function minimized was $\sum[w(|F_o| - |F_c|)^2]$, where $w = [\sigma_c^2|F_o| + (p^2/4)|F_o|^2]^{-1}$. Formula $C_{21}H_{12}BF_9$, F. W. 446.12, Monoclinic, Space group $P2_1$, $a = 9.326(1)$, $b = 10.620(2)$, $c = 10.618(2)$ Å, $\beta = 110.80(2)^\circ$, $V = 983.1(4)$ Å^3, $Z = 2$, $D_c = 1.507$ g cm^{-3}, R 0.043, R_w 0.046.

MO calculation. The AM1 calculations were carried out by the MacSpartan Plus program[32] with a Macintosh computer. The ab initio calculations were carried out by the Gaussian 94 program[33] with a Tempest-3 workstation. The ^{11}B NMR shift was calculated by the GIAO method with the Gaussian program.

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28 A referee pointed out that the comparison of the structure and dynamic behavior of **1** with those of a reference molecule such as tri-*o*-tolylborane (**3**) should be instructive to understand the C–F···B interactions in the former compound. Although the X-ray structure is not available, the AM1 calculation suggests that the closest H···B contact is ca. 2.7 Å in the global minimum structure of **3** (C_3). The following paper reports that the ^1H NMR signals of **3** did not show any lineshape changes by the VT measurements: T. J. Weismann and J. C. Schug, *J. Chem. Phys.*, **40**, 956 (1964).

29 The strengths of N–B, S–B, and O–B coordination bonds in 9-[*o*-(XCH_2)phenyl]-9-borabicylco[3.3.1]nonanes ($X = NMe_2$, SEt, OEt) are 18.4, 11.6, and < 9 kcal mol^{-1}, respectively.[11c,11d]

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31 Tables of positional and thermal parameters and bond lengths and angles for nonhydrogen atoms have been deposited as Document No. 73060 at the Office of the Editor of the Bull. Chem. Soc. Jpn. Crystallographic data have been also deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number CCDC 147479.

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