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Structure of and Tetrahedral Character of the Boron Atom in 9-[2-(1-Ethylthiopentyl)phenyl]-9-borabicyclo[3.3.1]nonane

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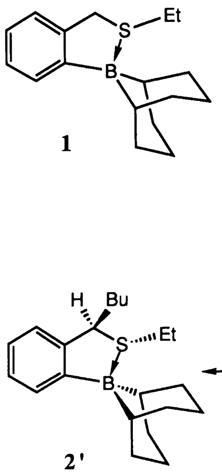
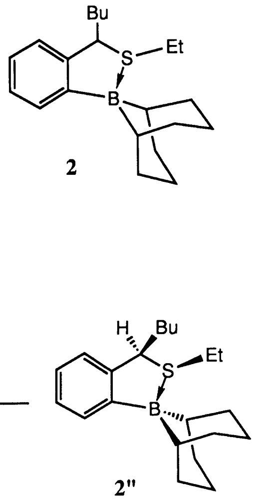
Synopsis. Structure of the title compound was determined by the X-ray analysis. The sulfur atom intramolecularly coordinates to the boron atom with a distance of 2.071 Å and the relation between the butyl group at the benzylic position and the *S*-ethyl group is nearly *anti*. The observed dynamic behavior in the compound is discussed on the basis of the structure and the results of some NMR experiments. Other structural features and the tetrahedral character of the boron atom are also reported.

Determination of rates of dissociation of the intramolecular S–B coordination bond in 9-[2-(ethylthiomethyl)-phenyl]-9-BBN (**1**) (9-BBN: 9-borabicyclo[3.3.1]nonane) as well as a related compound obtained as a by-product in the synthesis of **1** by the dynamic NMR method was reported.[1] The structure of the compound obtained as the by-product was assigned to 9-[2-(1-ethylthiopentyl)-phenyl]-9-BBN (**2**), which has an extra butyl group at the benzylic position with respect to the structure of compound **1**, from NMR and mass spectra. The dynamic process was attributed to the diastereomerization between **2′** and **2″** accompanied with dissociation of the S–B bond. Though we concluded that the major isomer should be an *anti* form **2′** from a general consideration of the steric repulsion between the butyl group at the benzylic position and the ethyl group at the sulfur atom, there still remains ambiguity in the conformation because the steric hindrance seems to be less important in the case of thioethers owing to long C–S bonds as shown by the fact that a *gauche* form is preferred over an *anti* form in ethyl methyl sulfide in the gas phase.[2] In order to get further information on the structure and the conformation of compound **2**, the X-ray analysis and some NMR measurements were carried out.

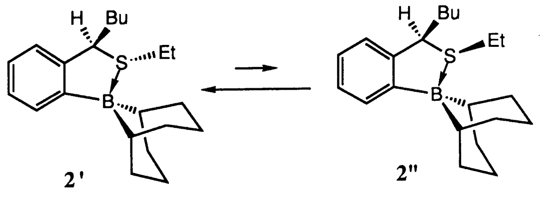
Tetrahedral character (THC) has been proposed for the correlation of the molecular structure to the barrier to dissociation of the N–B coordination bond in boron–amine complexes.[3] We suggested that this parameter would be applicable to boron complexes with other ligands such as sulfides and ethers. The value of THC for **2**, a model compound of trialkylborane-sulfide complexes, is also reported in connection with the strength of the S–B coordination bond.



1



2



2′ **2″**

Results and Discussion

The final atomic coordinates and thermal parameters are listed in Table 1 and an ORTEP drawing is shown in Fig. 1. Selected bond distances, bond angles, and torsion angles are compiled in Table 2.

It is apparent that the compound possesses a butyl group at the benzylic position and this structure is consistent with that determined from spectral data in the previous paper.[1] The sulfur atom coordinates to the boron atom in the same molecule, which takes a tetrahedral geometry, and the S–B bond distance is 2.071(2) Å. Though the structural data of borane-sulfide complexes are limited owing to weak coordina-

Table 1. Atomic Coordinates and Equivalent Isotropic Thermal Parameters of Non-Hydrogen Atoms in Compound **2**[a)]

Atom	x	y	z	B_{eq}[b)]
B	0.1930(1)	0.90552(9)	0.3057(2)	2.94(4)
S	0.17666(2)	0.99797(2)	0.46729(4)	3.059(8)
C(1)	0.1680(1)	0.82594(9)	0.3970(2)	3.51(4)
C(2)	0.0707(1)	0.8308(1)	0.4436(2)	4.54(5)
C(3)	−0.0064(1)	0.8498(1)	0.2913(2)	4.89(6)
C(4)	0.0169(1)	0.9160(1)	0.1750(2)	4.21(5)
C(5)	0.1155(1)	0.91490(9)	0.1336(2)	3.29(4)
C(6)	0.1326(1)	0.8479(1)	0.0120(2)	4.02(5)
C(7)	0.1282(1)	0.7659(2)	0.0874(2)	4.58(5)
C(8)	0.1774(1)	0.7568(1)	0.2753(2)	4.33(5)
C(9)	0.2973(1)	0.92614(8)	0.2823(2)	3.00(4)
C(10)	0.32893(9)	1.00192(9)	0.3239(2)	3.09(3)
C(11)	0.4158(1)	1.0272(1)	0.3024(2)	4.39(5)
C(12)	0.4740(1)	0.9772(1)	0.2362(3)	5.37(6)
C(13)	0.4460(1)	0.9018(1)	0.1955(3)	5.19(6)
C(14)	0.3595(1)	0.8769(1)	0.2174(2)	4.20(5)
C(15)	0.2640(1)	1.05762(9)	0.3910(2)	3.13(4)
C(16)	0.2203(1)	1.11721(9)	0.2554(2)	3.64(4)
C(17)	0.1561(1)	1.17559(9)	0.3179(2)	3.64(4)
C(18)	0.1352(1)	1.2451(1)	0.1982(2)	4.10(5)
C(19)	0.0704(2)	1.3031(1)	0.2594(3)	4.91(6)
C(20)	0.2422(1)	0.9663(1)	0.6737(2)	3.90(5)
C(21)	0.2542(2)	1.0282(1)	0.8104(2)	4.88(6)

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

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

Bond distances (Å)			
B–S	2.071(2)	B–C(1)	1.614(2)
B–C(5)	1.620(2)	B–C(9)	1.618(2)
S–C(15)	1.824(2)	S–C(20)	1.823(2)
C(9)–C(10)	1.401(2)	C(10)–C(15)	1.510(2)
C(15)–C(16)	1.536(2)	C(20)–C(21)	1.500(2)
Bond angles (°)			
S–B–C(9)	96.60(9)	S–B–C(1)	108.4(1)
S–B–C(5)	107.2(1)	C(1)–B–C(5)	105.9(1)
C(1)–B–C(9)	121.9(1)	C(5)–B–C(9)	115.4(1)
B–S–C(15)	93.76(7)	B–S–C(20)	102.53(7)
C(15)–S–C(20)	99.50(7)	B–C(9)–C(10)	117.4(1)
B–C(9)–C(14)	126.9(1)	C(10)–C(9)–C(14)	115.6(1)
C(9)–C(10)–C(11)	122.5(1)	C(9)–C(10)–C(15)	117.6(1)
C(11)–C(10)–C(15)	119.8(1)	S–C(15)–C(10)	106.5(1)
S–C(15)–C(16)	111.5(1)	C(10)–C(15)–C(16)	113.2(1)
S–C(20)–C(21)	113.9(1)		
Torsion angles (°)			
S–B–C(9)–C(10)	−18.2		
B–C(9)–C(10)–C(15)	1.4		
C(9)–C(10)–C(15)–S	19.4		
C(10)–C(15)–S–B	−25.4		
C(15)–S–B–C(9)	24.1		
C(10)–C(15)–S–C(20)	78.0		
C(16)–C(15)–S–C(20)	−158.0		
C(15)–S–C(20)–C(21)	75.1		

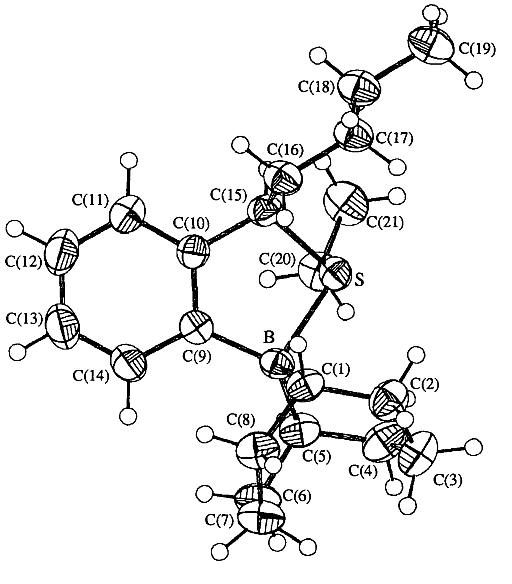


Fig. 1. ORTEP drawing of compound **2** with thermal ellipsoids at 50% probability.

tion of the sulfur ligand to the boron atom,[4] there are two reports on the structure of complexes, as far as we have surveyed, in which the distances are ca. 2.04 Å.[5,6] The long S–B bond length in **2** compared to those in the complexes can be mainly ascribed to bulkiness of the 9-BBN moiety.

Torsion angles about the C(15)–S bond reveal that the relative position between the butyl group at the benzylic position and the *S*-ethyl group is nearly *anti* rather than *gauche* as expected from the steric viewpoint. All of the molecules take the same conformation in crystals if we neglect enantiomers, though the NMR spectra observed at a low temperature in a solution indicated existence of a minor isomer in 4%.

It is well recognized that some compounds take different conformations in a solution from those in a crystal due to effects of solvation or crystal packing. To make the assignment of the diastereomers in a solution more explicitly, some NMR experiments were carried out.

We attempted to observe the isomerization process directly by using a sample solution, in which crystals were dissolved at a low temperature. If we could measure the NMR spectrum before the isomerization, only one isomer which was identical with that in crystals should be observed. However, we failed to detect the process even at −90 °C; the signals assigned to the minor isomer existed in ca. 3% population and the equilibrium of isomerization was already reached within an error limit. This indicates that the diastereomerization takes place very fast relative to the time scale in laboratories at the temperature.

In order to establish the structure of the major isomer, an NOE experiment was performed. This isomer is known, from pieces of evidence of ^{1}H NMR as well as ^{11}B NMR spectra,[1] to exist as a coordinated form shown as **2′** or **2″**. When the benzylic methine proton of the major isomer was irradiated at −52 °C, signals due to the methyl protons and one of the methylene protons in the *S*-ethyl group were enhanced by ca. 3%. This small but unambiguous NOE suggests that the relation between the methine and the *S*-ethyl group is *gauche*, that is, the butyl group and the ethyl group are *anti*. These experimental data indicate that the major isomer is indeed **2′**.

Unfortunately, the scarce population of the minor isomer prevented us from performing the NOE experiment as well as the measurement of ^{11}B NMR spectra. However, from the following discussion the structure of the minor isomer is strongly suggested to be **2″**. Thus we believe that discussion by assuming the equilibrium between **2′** and **2″**, as was done in the previous paper,[1] is still valid.

The minor component in the solution is undoubtedly an isomer of **2′**, because the exchange in the magnetic sites of some protons was observed. There are two possible isomers to be considered: A diastereomer **2″** and an isomer in which the coordination bond is broken. However, the uncoordinated isomer is not likely to exist to an observable extent, because it is less stable than **2′** by more than 12 kcal mol^{-1} (1 cal=4.184 J) as the bond breaking energy suggests. The isomer **2″**, though disfavored by the steric effects, is the much favorable isomer to be considered.

Following structural features also deserve mention. The five membered ring is an envelope with the sulfur atom out of the plane to the opposite direction to the butyl group as observed in the boron-amine complexes. The distance between the sulfur atom and the average plane comprised of the B–C–C–C moiety is 0.57 Å and comparable to the deviation of the nitrogen atoms in the boron-amine complexes (0.51—0.58 Å)[3] in spite of the long S–C and S–B bonds compared with the N–C and N–B bonds. This coincidence can be ascribed to the small puckering angle in the envelope conformation of the five membered ring (27.5°).

The ethyl group extends toward the direction almost perpendicular to the five membered ring. The methyl carbon, C(21), in the ethyl group extends to the opposite direction to the 9-BBN group to diminish the steric repulsion. As a result, the relation between C(15) and C(21) about the S–C(20) bond becomes nearly *gauche*.

The THC value, which could be calculated from bond angles at the boron atom, was proved to be a convenient empirical parameter to estimate the strength of an N–B coordination bond in boron-amine complexes.3) We should like to use THC in the system of borane-sulfide complexes in order to see whether it is possible or not to extend the scope of the parameter.

The THC value of compound **2** was calculated from the equation reported previously3) as 53%, this value being similar to those of boronic acid-amine complexes in the series of boron-amine complexes. The free energy of dissociation of the S–B bond in **2** was estimated to be 12 kcal mol^{-1} by the coalescence method.1) This barrier height is close to that of the N–B bond dissociation in a boronic ester-amine complex, 2-[2-(dimethylaminomethyl)phenyl]-4,4-diphenyl-1,3,2-dioxaborolane (11.5 kcal mol^{-1})7) whose THC value is 51%.3) Hence, the THC value seems to be well correlated to the strength of the boron-ligand coordination bond. Further study is awaited whether the THC value is applicable to other ligands which are attached to a boron atom in a complex.

Experimental

X-Ray Crystallography.8) The compound, 9-[2-(1-ethylthiopentyl)phenyl]-9-BBN, was obtained by the procedure reported previously.1) A Crystal used for the X-ray measurement was grown from hexane solution and its size was 0.35×0.35×0.30 mm^3. X-Ray data were collected 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 $0.90°+0.35°\tan\theta$. The structure was solved by the direct method (MULTAN 78) and refined by the full-matrix least-squares method by using CRYSTAN program. Anisotropic thermal parameters were employed for non-hydrogen atoms and isotropic for hydrogens. No absorption correction was employed. Total number of measured unique reflection was 4924 within the range of $2°<2\theta<55°$ and 3789 reflections within $|F_o|>3\sigma|F_o|$ were used for the structure determination and refinement. The function minimized was $\sum[w(|F_o|^2-|F_c|^2)^2]$, where $w=[(\sigma_c|F_o|)^2+5.3\times10^{-5}|F_o|^2]^{-1}$. Formula $C_{21}H_{33}BS$, F. W. 328.40, Monoclinic, Space group $P2_1/a$, a=14.727(1), b=17.161(3), c=7.858(1) Å, β=99.91(1)°, V=1956.3(6) Å^3, Z=4, D_c=1.12 g cm^{-3}, μ=1.28 cm^{-1}. R 0.041, R_w 0.040.

NMR Measurements. NMR spectra were measured on a JEOL GSX-400 spectrometer operating at 399.8 MHz. Detailed NMR data of compound **2** were reported in the paper.1) A solution of 10 mg of the compound in 0.6 cm^3 of dichloromethane-d_2 was used for NOE experiment and the sample was degassed just before the measurement in an ordinary manner. Spectra were measured at −52 °C and 45° pulse was employed. Irradiation power and irradiation time were IRA=350 and 7 s, respectively. When the benzylic methine proton (δ=3.87) was irradiated, the methyl protons in the *S*-ethyl (δ=1.22), one of the methylene protons in the *S*-ethyl (δ=1.98), and an aromatic signal (δ=7.01—7.09) were enhanced in 3, 3, and 9%, respectively. An attempt at observing a single isomer before the isomerization was carried out as follows. A solvent, ca. 0.6 cm^3 of dichloromethane-d_2, in an NMR sample tube was frozen and 10 mg of crystals of **2** was added to the solvent. The sample was inserted into a precooled probe and NMR spectrum was measured at −90 °C within a minute after the dissolution. The population of the minor isomer was 3% from the intensity of the signals due to the benzylic methine protons.

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8) Tables of coordinates for the hydrogen atoms, anisotropic thermal parameters, and complete thermal F_o-F_c data are deposited as Document No. 9032 at the Office of the Editor of Bull. Chem. Soc. Jpn.