

Structure and Properties of 3-(Diethylboryl)pyridines¹

Yoshikazu Sugihara,^{*,†} Katsuto Takakura,^{*,‡} Toshihiro Murafuji,[†] Ryuta Miyatake,[‡]
Kazuhiro Nakasuji,[‡] Masako Kato,[§] and Shigenobu Yano[§]

Department of Chemistry, Faculty of Science, Yamaguchi University, Yamaguchi City 753, Japan,
Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan, and
Department of Chemistry, Faculty of Science, Nara Women's University, Narashi, Nara 630, Japan

Received May 6, 1996[®]

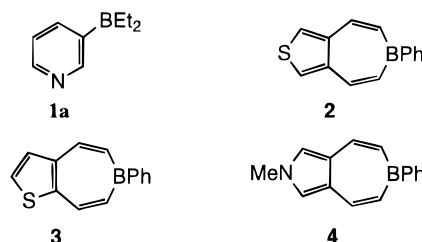
3-(Diethylboryl)pyridine (**1a**), a versatile starting material for the preparation of arylpyridines, is notable for its stability under ambient conditions, in spite of little steric hindrance on the boron atom. ¹H and ¹³C spectra of **1a** indicated that the boryl group does not act as a mere π -acceptor and that the boron atom is shielded by ca. 50 ppm even when compared with trivalent boron atoms conjugated with the π -donor. A single-crystal X-ray crystallographic study for **1a** revealed formation of a cyclic-tetramer with a void via the intermolecular boron–nitrogen coordination bond. Vapor pressure osmometry in various solvents suggested that **1a** comprises the tetramer in these solutions. In order to know the actual structure, synthesis of 3-(2-methoxyethoxy)-5-(diethylboryl)pyridine (**1b**) and its scrambling experiment with **1a** were carried out. Heating at 100 °C for 24 h was required to attain the equilibrium of the scrambling of the component molecules in the tetramers. This means that 3-(diethylboryl)pyridines **1a** and **1b** comprise the rigid cyclic-tetramer in solution at ambient temperature. Compound **1b** is stable in aerated tetrahydrofuran containing up to 33 % water.

Introduction

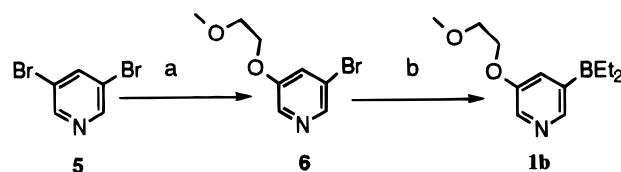
Synthesis of 3-(diethylboryl)pyridine (**1a**) was initially reported by Terashima *et al.*,² who then developed a coupling reaction using **1a** as the starting material.³ Compound **1a**, now commercially available from Aldrich Chemical Co., is notable for its stability under ambient conditions, in spite of little steric hindrance on boron. The authors ascribed the stability to the depression of both the nucleophilicity of the nitrogen atom and the electrophilicity of the boryl group, caused by the donation of π electrons in the pyridine ring to the vacant p-orbital of the boron atom. However, since pyridine is known to be highly deactivated toward electrophilic substitution, the pyridine ring in **1a** (Chart 1) would not act effectively as a π donor. Furthermore the boron is electropositive, and thus, significant stabilization would not arise from delocalization of the π electron onto this atom. Our studies⁴ support this consideration: the boron atom in 6-phenylborepino[4,5-*c*]thiophene (**2**), 6-phenylborepino[4,5-*b*]thiophene (**3**), or 2-methyl-6-phenylborepino[4,5-*c*]pyrrole (**4**) forms the coordination bond with the nitrogen atom of various amines in spite of formal conjugation with strong π -electron donors, such as heteroles.

Hence, it would be suggested that the boron and nitrogen atoms in **1a** should act as a Lewis acid and Lewis base, respectively, to form the intermolecular

Chart 1



Scheme 1^a



^a Reagents (a) NaOCH₂CH₂OCH₃ (1.5 equiv), DMF, 65 °C, overnight; (b) *n*-BuLi (1.2 equiv) then Et₂BOMe (2.1 equiv), ether, 35% in two steps.

boron–nitrogen coordination bond. This paper describes the structure of 3-(diethylboryl)pyridines in both solution and solid state.

Results and Discussion

Synthesis. 3-(2-Methoxyethoxy)-5-(diethylboryl)pyridine (**1b**) was prepared by nucleophilic substitution of 3,5-dibromopyridine (**5**)⁵ with 1.5 equiv of sodium 2-methoxyethoxide in dimethylformamide at 65 °C overnight,⁶ followed by treatment of the resulting crystalline 3-bromo-5-(2-methoxyethoxy)pyridine (**6**) with *n*-butyllithium and with 2.1 equiv of diethylmethoxyborane in ether in 35% yield (Scheme 1).

Nuclear Magnetic Resonance Spectroscopy. As already reported,² only one set of the signals as a

[†] Yamaguchi University.

[‡] Osaka University.

[§] Nara Women's University.

[®] Abstract published in *Advance ACS Abstracts*, August 15, 1996.

(1) A preliminary communication has appeared: Sugihara, Y.; Miyatake, R.; Takakura, K.; Yano, S. *J. Chem. Soc. Chem. Commun.* **1994**, 1925.

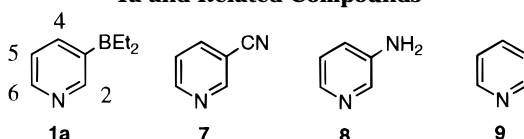
(2) Terashima, M.; Kakimi, H.; Ishikura, M.; Kamada, M.; *Chem. Pharm. Bull.* **1983**, *31*, 4573.

(3) Ishikura, M.; Kamada, M.; Terashima, M. *Heterocycles* **1984**, *22*, 265; *Idem. Synthesis* **1984**, 936. Ishikura, M.; Kamada, M.; Ohta, T.; Terashima, M. *Heterocycles* **1984**, *22*, 2475.

(4) For the Lewis acidity of the trivalent boron conjugated to the electron-rich aromatic ring, see: Sugihara, Y.; Yagi, T.; Murata, I.; Imamura, A. *J. Am. Chem. Soc.* **1992**, *114*, 1479. Sugihara, Y.; Miyatake, R.; Yagi, T.; Murata, I.; Jinguji, M.; Nakazawa, T.; Imamura, A. *Tetrahedron* **1994**, *50*, 6495. Sugihara, Y.; Miyatake, R.; Murata, I.; Imamura, A. *J. Chem. Soc., Chem. Commun.* **1995**, 1249.

(5) Garcia, E. E.; Greco, C. V.; Hunsberger, I. M. *J. Am. Chem. Soc.* **1960**, *82*, 4430.

(6) Comins, D. L.; Killpack, M. O. *J. Org. Chem.* **1990**, *55*, 69.

Table 1. ¹H and ¹³C (in Parentheses) Chemical Shifts of **1a** and Related Compounds


¹ H ^a (¹³ C ^a)	1a ^{b,c}	7 ^c	8 ^c	9 ^c
H ₂ (C ₂)	7.58 (149.2)	8.91 (152.5)	8.04 (137.2)	8.60 (149.8)
H ₄ (C ₄)	7.72 (143.8)	8.00 (139.3)	6.91 (121.4)	7.64 (135.7)
H ₅ (C ₅)	7.23 (123.4)	7.47 (123.7)	6.99 (123.9)	7.25 (123.6)
H ₆ (C ₆)	8.01 (140.9)	8.84 (153.0)	7.95 (139.2)	8.60 (149.8)

^a Chemical shifts in CDCl₃ are given in δ an ppm. ^b Reference 2. ^c This work.

monomer is observed both in ¹H and ¹³C NMR spectra of **1a**. The ¹H NMR spectrum is essentially independent of both temperature ranging from -90 to 80 °C and concentration ranging from 6×10^{-3} to 3×10^{-1} M. As shown in Table 1, the well-known downfield or upfield shift, such as in 3-cyanopyridine (**7**) or in 3-aminopyridine (**8**), when compared with pyridine (**9**), is not seen in signals due to both the proton and carbon at the ortho and para positions of the boryl group in **1a**. Shielding of α -carbons of the nitrogen atom, therefore, implies the formation of a coordination bond at the nitrogen atom rather than the consideration that the boryl group behaves as a mere electron-withdrawing group in **1a**. Thus, the decrease in π bond order of the C₂–N bond results from the formation of the coordination bond, which causes the upfield shift of C₂ and C₆ like the case of pyridinium ions.⁷

The ¹¹B spectrum of **1a** displays a signal at -0.35 ppm (Table 2). This is a farther upfield than the signals of compounds **2**, **3**, and **4** and 1-(dimesitylboryl)-4-(dimethylamino)benzene (**10**),⁸ each possessing the strong π -electron-donating heterole ring or dimethylamino moieties, respectively. Though the chemical shift of the boron atom is believed to correlate well with π -electron density,⁹ the value of **1a** is beyond the criterion. Hence, the marked shielding of this atom, comparable to that of amine adducts of triethylborane or trimethylborane (**11**–**13**),^{10,11} should be ascribed to the formation of the oligomer via a head–tail coordination bond. The chemical shift of the nitrogen atom in **1a** also supports our consideration.¹² Thus, while the value of pyridine (**9**) is -59 ppm, the nitrogen atom in the trialkylborane–amine adducts (**11**, **12**) is shielded by over -40 ppm. It should, furthermore, be pointed out that the chemical shifts of the boron and nitrogen atoms in **1a**, similar to those of the adducts, clarify that the equilibrium is to the side of oligomers.

The same conclusion is derived from the nuclear Overhauser effect. Namely, upon irradiation of the signals due to the methyl groups in **1a**, the differential NOE spectrum exhibited the distinct and comparable enhancement of the signals due to H₂, H₄, and H₆.

(7) Pugmirc, R. J.; Grant, D. M. *J. Am. Chem. Soc.* **1968**, *90*, 699. Jones, A. J.; Grant, D. M.; Russell, J. G.; Fraenkel, G. *J. Phys. Chem.* **1969**, *73*, 1624.

(8) Doty, J. C.; Babb, B.; Grisdale, P. J.; Glogowski, M.; Williams, J. L. R. *J. Organomet. Chem.* **1972**, *38*, 229.

(9) Nöth, H.; Wrackmeyer, B. *Chem. Ber.* **1974**, *107*, 3089. Spielvogel, W. R. Nutt, R. Izydore, R. A. *J. Am. Chem. Soc.* **1975**, *97*, 1609. Nöth, H.; Wrackmeyer, B. *Nuclear Magnetic Resonance Spectroscopy of Boron Compounds*; Springer-Verlag, New York, 1978.

(10) Nöth, H.; Wrackmeyer, B. *Chem. Ber.* **1974**, *107*, 3070.

(11) Nöth, H.; Vahrenkamp, H. *Chem. Ber.* **1966**, *99*, 1049.

(12) Levy, G. C.; Lichter, R. L. *Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy*; John Wiley & Sons, Inc.: New York, 1979.

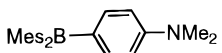
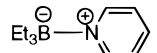
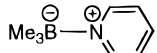
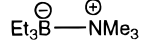
The same trends are shown with respect to the chemical shifts of all the atoms of **1b** and the distinct nuclear Overhauser effect.

Mass Spectroscopy and Vapor Pressure Osmometry. In the spectrum of EIMS (30 eV), in addition to the M⁺ – Et peak (118, 100) and parent peak as a monomer (M⁺, 147, 45), peaks of 2 × M⁺ – Et (265, 47), 3 × M⁺ – Et (412, 67), and 4 × M⁺ – Et (559, 39) are observed. FABMS displays the same peaks at intensities of 14, 19, 100, 41, and 2%, respectively, together with the new peaks of 2 × M⁺ (293, 7) and 3 × M⁺ (441, 1). A FABMS spectrum of **1b** only displays a peak of 3 × M⁺ – Et (634, 31) as a heaviest ion. The strength of the coordination bonds in **1a** and **1b** is indicated to be close to the scope of mass spectroscopy.

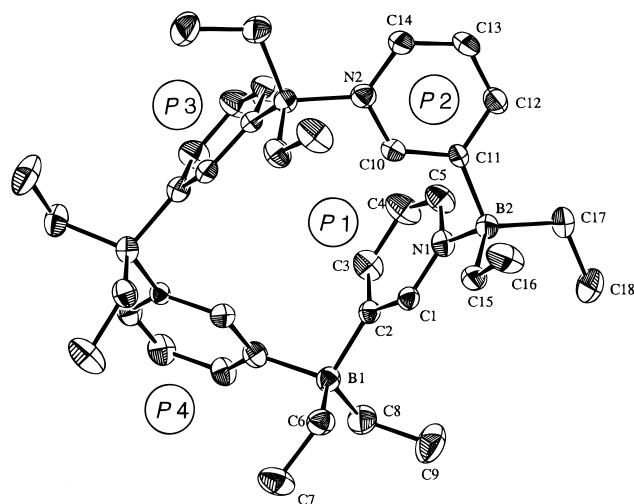
Vapor pressure osmometry by Knauer digital vapor pressure osmometer with benzil as a standard gives 3.73, 3.92 and 3.91 with various concentrations of **1a** in benzene (from 3.78×10^{-3} to 2.96×10^{-1} M) at 60 °C, chloroform (from 6.39×10^{-3} to 9.98×10^{-2} M) at 40 °C, and tetrahydrofuran (from 1.17×10^{-2} to 1.82×10^{-1} M) at 45 °C, respectively. Osmometry values of **1b** in benzene (from 2.0×10^{-3} to 1.1×10^{-1} mol dm⁻³) at 60 °C and in tetrahydrofuran (from 5.0×10^{-3} to 9.4×10^{-2} mol dm⁻³) at 45 °C are 3.6 and 4.1, respectively. In each experiment a clear linear relationship is found between the concentration and the reading. Thus, these estimated values and the clear linear relationship suggest that each compound **1a** or **1b** forms a tetramer in these solvents. Independence of the values on solvent, even in tetrahydrofuran of high affinity with the trivalent boron atom, shows that this atom in **1a** and **1b** is protected from the coordination of an oxygen atom of the solvent by the head–tail mutual intermolecular interaction.

Structure in the Crystalline State. A single-crystal X-ray crystallographic study reveals that **1a** forms a cyclic tetramer with a C₂ symmetry, as illustrated in Figure 1 and outlined in Table 3 and 5. The framework of one side is almost superimposable on the other. An outstanding structural feature is the short distance between the boron and nitrogen atoms (B1–N2*, 1.639(5) Å). The short length of this coordination bond is comparable to that of the B1–C2 σ bond (1.630(4) Å), symmetrizing the framework of the tetramer. The bond angles constituted by the boron atom and three substituent carbons are 113.9(3)° (C2–B1–C6), 107.2(3)° (C2–B1–C8), and 113.7(3)° (C6–B1–C8), respectively. Furthermore, the coordination bond (N2*–B1) forms angles of 104.1(3)° (N2*–B1–C2), 106.9(3)° (N2*–B1–C6), and 110.5(3)° (N2*–B1–C8) with these substituents, clearly showing the pyramidal structure of the boron atom (B1). The coordination bond (N2*–B1) lies in the plane of the pyridine ring with a deviation of only 1.6–3.0°. Furthermore, the angles between C10*–N2*–B1 and C14*–N2*–B1 are 117.9(2)° and 125.1(3)°, respectively, indicating that the coordination bond is almost an extension of the line which binds N2* and C12*. A similar situation is found around the B2–N1 coordination bond. Of the four pyridine rings two rings (P1 and P3) face each other and are perpendicular to the plane of the tetramer (dihedral angle between least-squares planes of the pyridine rings, 18.96°). The distance C1–C1* is 5.119(4) Å and C4–C4* is 4.228(7) Å. The other set of the pyridine rings (P2 and P4) virtually lies on this plane

Table 2. ^{11}B and ^{14}N Chemical Shifts of **1a,b** and Related Compounds

									
	10	11	12	13					
	1a^{a-c}	1b^{a,c}	2^{a,d}	10^{a,c,e}	11^{a,f}	12^{a,f}	13^{a,g}	7^{a,h}	9^{a,h}
$^{11}\text{B}^j$	-0.35	-0.50	50.8	71.5	-2.2	0.0	0.0		
$^{14}\text{N}^j$	-133	-156			-108	-108		-60	-59

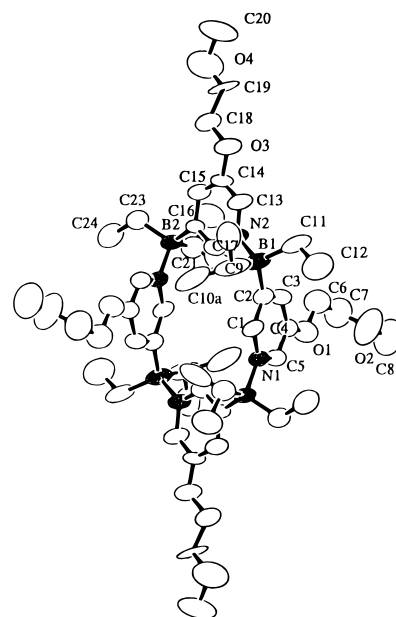
^a Chemical shifts in CDCl_3 are given in δ and ppm. ^b Reference 1. ^c This work. ^d Reference 4. ^e Reference 8. ^f Reference 10. ^g Reference 11. ^h Reference 12. ⁱ $\text{BF}_3 \cdot \text{OEt}_2$ as standard. ^j Aqueous NaNO_3 as standard.

**Figure 1.** Computer-generated thermal ellipsoid of the tetramer of **1a**.

(dihedral angle between least-squares planes of pyridine rings, 125.65°) and the distance $\text{C10}-\text{C10}^*$ is $5.797(4)$ Å.

The $\text{B1}-\text{C2}$ bond is much longer than the corresponding boron-carbon bond in triphenylborane (1.577 Å),¹³ indicating the low double bond character of this bond in **1a**. As regards the length of the coordination bond, an early X-ray crystallographic study revealed an $\text{N}-\text{B}$ bond distance of 1.56 ± 0.05 Å¹⁴ for the prototype adduct $\text{H}_3\text{-NBH}_3$ in a solid state, and microwave spectroscopy revealed the longer length of $1.658(2)$ Å for this bond in the gas phase.¹⁵ For the $\text{B}-\text{N}$ bond of the alkylated adduct Me_3NBMe_3 , an elongated distance of 1.70 ± 0.01 Å was revealed by means of microwave spectroscopy.¹⁶ Accordingly, the distance between the boron and the nitrogen in the tetramer is considered appropriate for the formation of the head-tail coordination bond of the (diethylboryl)pyridine.

Though, due to the disorder around the ethyl groups, the R value is not lowered, the single-crystal X-ray crystallographic study of **1b** confirms formation of a cyclic tetramer with a center of symmetry (Figure 2 and Table 4). In contrast to a cone conformation of **1a**, the tetramer occupies a 1,2-alternate conformation.¹⁷ A distance slightly elongated by 0.024 Å is found between the boron and the nitrogen atoms [$\text{B}(1)-\text{N}(2)^*$, $1.66(1)$ Å] compared with **1a**. Furthermore, this coordination bond makes

**Figure 2.** Crystal structure of the tetramer of **1b**.

angles of $105.6(7)^\circ$ [$\text{N}(2)^*-\text{B}(1)-\text{C}(2)$], $108.3(9)^\circ$ [$\text{N}(2)^*-\text{B}(1)-\text{C}(11)$], and $105.3(9)^\circ$ [$\text{N}(2)^*-\text{B}(1)-\text{C}(9)$].

According to the criterion proposed by Toyota and Ōki,¹⁸ the tetrahedral character (THC) of a boron atom correlates well to the barrier of dissociation rather than the length of the coordination bond. The THC values for **1a** are estimated to be 79.7% (B1) and 84.2% (B2) and those for the two boron atoms in the tetramer **1b** are 72.4% (B1) and 77.6% (B2), respectively. When the weak basicity of pyridine **8** is taken into account, these values indicate that each tetramer is formed via strainless coordination bonds. This will be helpful in prediction of the structure of the cyclic oligomer comprised by the isomer of 3-(diethylboryl)pyridines.

Scrambling and Mixing Behavior in Solution.

Both spectroscopic and vapor pressure osmometric data for **1a** and **1b** suggest that each equilibrium is exclusively to the side of the cyclic oligomer. A scrambling experiment using **1a** and **1b** gives further information concerning the structures in solution. Thus, when a mixture of equimolar amounts of **1a** and **1b** in deuteriotoluene was allowed to stand at 60°C for 10 h, the ^1H NMR spectrum did not show any change. However, upon heating the mixture to 100°C for 24 h, the component molecules were scrambled into tetramers. Isolation of the newly formed tetramers, followed by spectroscopic analysis, showed that the least- and most-polar tetramers (Mp $121-122^\circ\text{C}$, 25%, and Mp $131-133^\circ\text{C}$, 17%, respectively) consist of **1a** and **1b** in 3:1 and 1:3 ratio, respectively. Though

(13) Zettler, F.; Hausen, H. D.; Hess, H. *J. Organomet. Chem.* **1974**, *72*, 157.

(14) Hughes, E. W. *J. Am. Chem. Soc.* **1956**, *78*, 502.

(15) Thorne, L. R.; Suenram, R. D.; Lovas, F. J. *J. Chem. Phys.* **1983**, *78*, 167.

(16) Kuznesof, P. M.; Kuczowski, R. L. *Inorg. Chem.* **1978**, *17*, 2308.

(17) Stewart, D. R.; Krawiec, M.; Kashyap, R. P.; Watson, W. H.; Gutsche, C. D. *J. Am. Chem. Soc.* **1995**, *117*, 586.

(18) Toyota, S.; Ōki, M. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1832.

Table 3. Selected Geometrical Properties of the Tetramer of 1a^a

distances (Å)		bond angles (deg)	
B(1)–N(2)	1.639(5)	N(2)–B(1)–C(2)	104.1(3)
B(1)–C(2)	1.630(4)	N(2)–B(1)–C(6)	106.9(3)
B(1)–C(6)	1.608(6)	N(2)–B(1)–C(8)	110.5(3)
B(1)–C(8)	1.626(5)	C(2)–B(1)–C(6)	113.9(3)
B(2)–N(1)	1.636(4)	C(2)–B(1)–C(8)	107.2(3)
B(2)–C(11)	1.641(5)	C(6)–B(1)–C(8)	113.7(3)
B(2)–C(15)	1.622(6)	B(1)–N(2)–C(10)	117.9(2)
B(2)–C(17)	1.620(5)	B(1)–N(2)–C(14)	125.1(3)
dihedral angles (deg)		C(10)–N(2)–C(14)	117.0(3)
C(11)–C(10)–N(2)–B(1)	–177.0(3)	N(1)–B(2)–C(11)	103.6(3)
C(13)–C(14)–N(2)–B(1)	178.4(4)	N(1)–B(2)–C(15)	111.3(3)
C(2)–C(1)–N(1)–B(2)	177.8(3)	N(1)–B(2)–C(17)	108.1(3)
C(4)–C(5)–N(1)–B(2)	–178.8(4)	C(11)–B(2)–C(15)	107.8(3)
		C(11)–B(2)–C(17)	111.9(3)
		C(15)–B(2)–C(17)	113.7(3)
		B(2)–N(1)–C(1)	124.7(3)
		B(2)–N(1)–C(5)	118.2(3)
		C(1)–N(1)–C(5)	117.1(3)

^a Numerals in parentheses are estimated standard deviations.

Table 4. Selected Geometrical Properties of the Tetramer of 1b^a

distances (Å)		bond angles (deg)	
B(1)–N(2)	1.66(1)	N(2)–B(1)–C(2)	105.6(7)
B(1)–C(2)	1.63(1)	N(2)–B(1)–C(9)	105.3(9)
B(1)–C(9)	1.61(2)	N(2)–B(1)–C(11)	108.3(9)
B(1)–C(11)	1.67(2)	C(2)–B(1)–C(9)	112.3(9)
B(2)–N(1)	1.66(1)	C(2)–B(1)–C(11)	107.7(9)
B(2)–C(16)	1.63(1)	C(9)–B(1)–C(11)	117.0(10)
B(2)–C(21)	1.61(1)	B(1)–N(2)–C(13)	118.5(8)
B(2)–C(23)	1.62(1)	B(1)–N(2)–C(17)	123.3(7)
dihedral angles (deg)		C(13)–N(2)–C(17)	117.9(7)
C(14)–C(13)–N(2)–B(1)	–174(1)	N(1)–B(2)–C(16)	104.6(7)
C(16)–C(17)–N(2)–B(1)	173.6(1)	N(1)–B(2)–C(21)	111.0(8)
C(2)–C(1)–N(1)–B(2)	–178.0(8)	N(1)–B(2)–C(23)	105.5(8)
C(4)–C(5)–N(1)–B(2)	179.6(9)	C(16)–B(2)–C(21)	110.3(9)
		C(16)–B(2)–C(23)	111.5(8)
		C(21)–B(2)–C(23)	113.5(8)
		B(2)–N(1)–C(1)	123.4(9)
		B(2)–N(1)–C(5)	119.1(8)
		C(1)–N(1)–C(5)	117.5(8)

^a Numerals in parentheses are estimated standard deviations.

Table 5. Crystallographic Data for the Tetramers of 1a and 1b

	1a	1b
molecular formula	C ₃₆ H ₅₆ B ₄ N ₄	C ₄₈ H ₈₀ O ₈ B ₄ N ₄
molecular weight	588.11	884.42
crystal size (mm)	0.30 × 0.30 × 0.15	0.22 × 0.16 × 0.08
crystal shape, color	prismatic, colorless	prismatic, colorless
radiation (graphite monochromated)	Cu Kα (λ = 1.54178 Å)	Cu Kα (λ = 0.71069 Å)
crystal system	orthorhombic	triclinic
space group	<i>Fdd2</i> (#43)	<i>P1</i> (#2)
<i>a</i> , Å	22.700(3)	11.815(2)
<i>b</i> , Å	45.297(4)	12.024(2)
<i>c</i> , Å	7.289(4)	11.046(2)
α, deg		107.42(2)
β, deg		102.43(2)
γ, deg		64.12(1)
<i>V</i> , Å ³	7494(3)	1340.6(5)
<i>Z</i>	8	1
2θ _{max} , deg	120.1	60.0
no. of reflections collected	1598	5261
no. of reflections refined	1358	1373
no. of variables	198	308
<i>R</i>	0.043	0.078
<i>wR</i>	0.065	0.082

the other two tetramers could not be separated (51%), the ¹H NMR spectrum was indicative of the tetramers involving **1a** and **1b** in a ratio of 1:1 with divergent sequences. The ratio of the tetramer with a sequence of **1a**, **1a**, **1b**, and **1b** and the one with a sequence of **1a**, **1b**, **1a**, and **1b** was 2:1. The marked thermal stability

of the coordination bonds shows the reliability of vapor pressure osmometry for determination of the actual structure of 3-(diethylboryl)pyridines in solution, though the method generally displays only average values of aggregated molecules.

The ¹H NMR spectra of the mixture of **1a** and bases such as pyridine (**9**) (as solvent), piperidine (**14**) (in deuteriodichloromethane), or quinuclidine (**15**) (in deuteriodichloromethane) left standing at room temperature for several days, remained unchanged. The fact shows that the concentration of the open-chain oligomer, which has a boron atom free from the coordination, is quite low, since the basicity of the nitrogen atom in pyridine (**9**) should be comparable to that of **1a**. The spectrum of the mixture of equimolar amounts of **1a** and *N,N*-dimethylaminopyridine (**16**) displayed proton signals due to the tetramer of **1a** and some sharp doublets having the same coupling constants as that of **16** at higher positions, indicating that some molecules of **16** are coordinated with the boron atom and, namely, several open-chain oligomers of **1a** involving the coordination bond with the pyridine are formed. Integration of the signal showed that 17.5% of the tetramer of **1a** had not decomposed. Interestingly, upon heating, only the signals due to open-chain oligomers were broadened at 90 °C and signals due to the tetramer of **1a** remained unchanged. The mixture of **1b** and **16** exhibited similar behavior. At room temperature 33.3% of the tetramer of **1b** remained intact

and broadening of signals due to open-chain oligomers involving **16** occurred at 90 °C. Though signals due to open-chain oligomers partly started to coalesce at 100 °C, the signals of both tetramers of **1a** and **1b** remained unchanged.

Column chromatography over activated silica gel gave these cyclic tetramers in the ratio that was shown by means of thin-layer chromatography (TLC) or NMR spectroscopy. However, the same chromatography of the mixture containing the open-chain oligomers involving **16**, formation of which was observable by TLC or NMR spectroscopy, gave only the cyclic tetramer and **16**. Since the nitrogen atom of **16** would form a stronger dative bond¹⁹ than that of the pyridine rings in **1a** and **1b**, the stability of these tetramers should be ascribable to facile rebonding of the partly cleaved tetramer.

The tetramer of **1b** was soluble and quite stable in aerated tetrahydrofuran containing water up to 33% at ambient temperature. With the change of water content in deuteriotetrahydrofuran, the signal of ¹¹B did not show any essential shift: only by δ 1.1 ppm, up to 33% water content.

In conclusion, 3-(diethylboryl)pyridines comprise the cyclic tetramer via the coordination bonds, the coordination bond of which is stable at ambient temperature and in aerated organic solvents with high water content. The marked thermal stability and the intriguing structure should be of use both in consideration of the reactivity of **1a** and in construction of the artificial self-assembly systems with novel functionality.²⁰

Experimental Section

3-Bromo-5-(2-methoxyethoxy)pyridine (6). Sodium (0.365 g, 1.59 mmol) was dissolved in 2-methoxyethanol (distilled from sodium, 1.37 mL) under a nitrogen atmosphere. After the excess of the alcohol was removed in vacuo, DMF (distilled from CaH₂, 1 mL) and dibromide **5** (0.250 g, 1.46 mmol) were added. The solution stood at 65 °C overnight and, after cooling, was extracted with ether. Product **6** was obtained by chromatography over silica gel with ether and recrystallized from hexane to yield 0.171 g (0.74 mmol, 50.5%). Mp: 30–33 °C. ¹H NMR (400 Mz, CDCl₃): δ 3.45 (3H, s), 3.75 (2H, m), 4.15 (2H, m), 7.40 (1H, dd, $J = 2.57$ and 1.95 Hz), 8.27 (1H, d, $J = 2.57$ Hz, 1.95 Hz), 8.29 (1H, d, $J = 1.95$ Hz). ¹³C NMR (100 MHz, CDCl₃): δ 59.3, 68.1, 70.7, 120.3, 124.2, 136.6, 143.2, 155.4. Anal. Calcd for C₈H₁₀BrNO₂: C, 41.40; H, 4.34; N, 6.04. Found: C, 41.35; H, 4.28; N, 6.05.

3-(2-Methoxyethoxy)-5-(diethylboryl)pyridine (1b). To a solution of **6** (0.10 g, 0.43 mmol) in dry ether (4.0 mL) was added *n*-butyllithium (0.27 mL, 1.6 M) dropwise at –78 °C. After stirring for 15 min, diethylmethoxyborane (0.12 mL, 1.76 mmol, 1.0 M) was added dropwise. The solution was warmed to room temperature, stood overnight with stirring, and was extracted with ether. Chromatography over silica gel with ether and recrystallization from benzene gave **1b** (0.051 g, 0.23 mmol, 53.5%). Mp: 139–140 °C. ¹H NMR (400 Mz, CDCl₃): δ 0.45 (6H, m), 0.62 (4H, m), 3.45 (3H, s), 3.74 (2H, m), 4.10 (2H, m), 7.20 (1H, dd, $J = 2.31$ Hz), 7.32 (1H, d, $J = 1.98$ Hz), 7.66 (1H, d, $J = 1.98$ Hz). ¹³C NMR (100 MHz, CDCl₃): δ 9.2, 14.6, 59.3, 67.9, 70.8, 128.6, 129.7, 142.2, 155.2, 156.1. ¹¹B NMR (128 Hz, CDCl₃, BF₃·OEt₂ as standard) δ –0.5. ¹⁴N NMR (361 MHz, CDCl₃, aqueous NaNO₃ as standard) δ –156. Anal. Calcd for C₁₂H₂₀BNO₂: C, 65.19; H, 9.12; N, 6.33. Found: C, 64.94; H, 9.11; N, 6.40.

Vapor Pressure Osmometry Results. **1a**: 3.7 in benzene at 60 °C [benzil (2.0, 26.1, 101.7, 193.9 for 0.000 085 6, 0.0148, 0.0540, 0.1036 mol/L, respectively), **1a** (0.9, 20.8, 55.2, 147.3

for 0.00378, 0.0473, 0.122, 0.296 mol/L, respectively)]; 3.92 in chloroform [benzil (15.2, 24.5, 102.5, 193.0 for 0.000 11, 0.0133, 0.0525, 0.103 mol/L, respectively), **1a** (1.5, 6.9, 17.2, 43.3 for 0.006 39, 0.0163, 0.0395, 0.0998 mol/L, respectively)]; 3.91 in tetrahydrofuran at 45 °C [benzil (3.1, 25.0, 86.7, 177.8 for 0.000 131, 0.0163, 0.0514, 0.106 mol/L, respectively), **1a** (3.3, 13.9, 26.8, 76.8 for 0.000 117, 0.0314, 0.0755, 0.182, respectively)]. **1b**: 4.0 in benzene at 60 °C [benzil (0, 3.2, 28.9, 115.8, 193.6 for 0, 0.0022, 0.0164, 0.1075 mol/L, respectively)]; **1b**: 4.1 in tetrahydrofuran at 45 °C [benzil (0, 15.2, 24.5, 102.5, 193.0 for 0, 0.0052, 0.0111, 0.0521, 0.0943 mol/L, respectively), **1b** (0, 11.5, 22.2, 33.3, 52.1 for 0, 0.0211, 0.0423, 0.0634, 0.1057 mol/L, respectively)].

Scrambling Experiment. Compounds **1a** (0.121 g, 0.823 mmol) and **1b** (0.182 g, 0.824 mmol) were dissolved in toluene and heated at 100 °C for 24 h. Chromatography over silica gel with ether gave (**1a**)₃(**1b**)₁, (**1a**)₁(**1b**)₁^A, (**1a**)₁(**1b**)₁^B, and (**1a**)₁(**1b**)₃, together with the starting tetramers (**1a**)₄, (0.004 84 g, 0.0329 mmol) and (**1b**)₄ (0.0145 g, 0.0656 mmol). (**1a**)₃(**1b**)₁ (0.068 g, 0.103 mmol, 25%). Mp: 121–123 °C. ¹H NMR (400 Mz, CDCl₃): δ 0.77 (24H, m), 0.92 (16H, m), 3.05 (3H, s), 3.19 (2H, m), 3.19 (2H, m), 6.65 (2H, m), 6.88 (1H, dd, $J = 7.42$ and 5.86 Hz), 7.21 (1H, dd, $J = 2.47$ and 1.65 Hz), 7.61 (1H, d, $J = 2.47$ Hz), 7.43 (1H, dd, $J = 7.42$ and 1.44 Hz), 7.53 (2H, m), 7.63 (2H, s), 7.67 (1H, d, $J = 1.65$ Hz), 7.70 (1H, dd, $J = 5.86$ and 1.44 Hz), 7.75 (1H, d, $J = 5.77$ Hz), 7.77 (1H, d, $J = 5.77$ Hz), 7.91 (1H, s). (**1a**)₁(**1b**)₁^A [0.154 g (estimated), 34%]. ¹H NMR (400 Mz, CDCl₃): δ 0.82 (24H, m), 0.95 (16H, m), 3.09 (6H, s), 3.28 (4H, m), 3.70 (4H, m), 6.59 (2H, dd, $J = 7.35$ and 5.84 Hz), 7.26 (2H, s), 7.41 (2H, d, $J = 7.35$ Hz), 7.49 (2H, d, $J = 2.43$ Hz), 7.68 (2H, d, $J = 5.84$ Hz), 7.92 (2H, d, $J = 2.34$ Hz), 7.96 (2H, s). (**1a**)₁(**1b**)₁^B [0.0567 g (estimated), 17%]. ¹H NMR (400 Mz, CDCl₃): δ 0.82 (24H, m), 0.95 (16H, m), 3.07 (6H, s), 3.22 (4H, m), 3.54 (4H, m), 6.87 (1H, dd, $J = 7.08$ and 6.04 Hz), 6.87 (1H, dd, $J = 7.08$ and 5.95 Hz), 7.52 (2H, d, $J = 7.08$ Hz), 7.52 (2H, s), 7.74 (1H, d, $J = 6.04$ or 5.95 Hz), 7.76 (1H, d, $J = 5.95$ or 6.04 Hz), 7.77 (1H, d, $J = 2.20$ Hz), 7.77 (1H, d, $J = 2.06$ Hz), 7.29 (1H, d, $J = 2.20$ or 2.06 Hz), 7.32 (1H, d, $J = 2.06$ or 2.20 Hz), 7.82 (2H, s). (**1a**)₁(**1b**)₃ [0.0567 g, 0.070 mmol, 17%]. Mp: 131–133 °C. ¹H NMR (400 Mz, CDCl₃): δ 0.83 (24H, m), 0.97 (16H, m), 3.05 (3H, s), 3.18 (2H, m), 3.47 (2H, m), 3.10 (6H, s), 3.29 (4H, m), 3.72 (4H, m), 6.93 (1H, dd, $J = 7.49$ and 5.77 Hz), 7.20 (1H, d, $J = 2.20$ Hz), 7.23 (2H, s), 7.42 (1H, d, $J = 7.49$ Hz), 7.55 (1H, d, $J = 2.06$ Hz), 7.57 (1H, d, $J = 2.19$ Hz), 7.67 (1H, d, $J = 2.20$ Hz), 7.71 (1H, d, $J = 5.77$ Hz), 7.89 (1H, s), 7.92 (1H, d, $J = 2.19$ Hz), 8.00 (1H, d, $J = 2.04$ Hz).

X-ray Crystallography. **1a**: a colorless prismatic crystal of C₃₆H₅₆B₄N₄, having the approximate dimensions of 0.30 × 0.30 × 0.15 mm, was mounted on a glass fiber. All measurements were made on a Rigaku AFC5R diffractometer with graphite monochromated Cu K α radiation and a 12 kW rotating anode generator. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range 76.51° < 2 θ < 79.79° corresponding to an *F*-centered orthorhombic cell. The structure was solved by direct methods (MULTAN88)²¹ and expanded using Fourier techniques (DIRDIF92).²² The final cycle of full-matrix least-squares refinement was based on 1358 observed reflections ($I > 3.00\sigma(I)$) and 198 variable parameters. The Fourier map corresponded to 0.16 and –0.13 e[–]/Å, respectively.

1b: a colorless prismatic crystal of C₄₈H₈₀O₈B₄N₄, having approximate dimensions of 0.22 × 0.16 × 0.08 mm, was mounted on a glass fiber. Cell constants and an orientation matrix for data collection were obtained from a least-squares

(21) Debaerdemaeker, T.; Germain, G.; Main, P.; Refaat, L. S.; Tate, C.; Woolfson, M. M. *Computer programs for the automatic solution of crystal structures from X-ray diffraction data*; University of New York, U.K., 1988.

(22) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. *The DIRDIF program system, Technical Report of the Crystallography Laboratory*; University of Nijmegen: The Netherlands 1992.

(23) Gilmore, C. J. *MITHRIL—an integrated direct methods computer program*; University of Glasgow, Scotland, 1990.

(19) Haaland, A. *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 992.

(20) Fujita, M.; Ogura, K. *J. Synth. Org. Chem. Jpn.* **1994**, *52*, 839. Hunter, C. A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1079.

refinement using the setting angles of 21 carefully centered reflections in the range $20.61^\circ < 2\theta < 25.66^\circ$ corresponding to a primitive triclinic cell. The structure was solved by direct methods (MTHRIL90)²³ and expanded using Fourier techniques (DIRDIF92).²² The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not re-

(24) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*, The Kynoch Press: Birmingham, England, 1974; Vol IV, Table 2.2 A.

(25) Creagh, D. C.; McAuley, W. L. *International Tables for Crystallography*, Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Boston, 1992; Vol. C, Table 4.2.6.8, pp 219–222.

(26) Creagh, D. C.; Hubbell, J. H. *International Tables for Crystallography*, Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Boston, 1992; Vol. C, Table 4.2.4.3, pp 200–206.

(27) Cystal Structure Analysis Package, Molecular Structure Corporation, 1985 and 1992.

(28) The author has deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 4E2, UK.

fined. The final cycle of full-matrix least-squares refinement was based on 1373 observed reflections ($I > 3.00\sigma(I)$) and 308 variable parameters.

Neutral atom scattering factors were taken from Cromer and Waber.²⁴ Anomalous dispersion effects were included in F_{calc} ; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.²⁵ The values for the mass attenuation coefficients are those of Creagh and Hubbel.²⁶ All calculations were performed using the teXsan²⁷ crystallographic software package of Molecular Structure Corp.

Acknowledgment. This work was supported by Grants-in-Aid for Scientific Research on Priority Area of Reactive Organometallics No. 05236102 and for Developmental Scientific Research (B) (No. 06554027) from the Ministry of Education, Science and Culture, Japan.

JO960825K