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Structure of Diethyl(2-pyridyl)boranes: Rigid Cyclic Dimers

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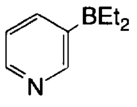
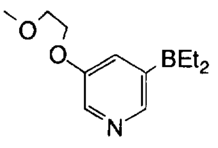
Abstract: Diethyl(2-pyridyl)boranes (**2a**, **2b**) comprise cyclic dimers via intermolecular boron–nitrogen coordination bonds. The boron atoms of diethyl[2-(5-methylpyridyl)]borane (**2b**) show clear pyramidalization. The high tetrahedral character of these boron atoms in **2b** indicates that the dimer is far rigid compared with the tetramer composed of diethyl(3-pyridyl)borane (**1a**).

Introduction

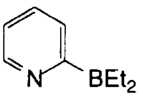
Despite the little steric hindrance, diethylpyridylboranes (**1a**, **2a**, **3**) have been known to be stable compounds under ambient conditions.[1,2,3] We have previously described that compound **1a** constitutes a cyclic tetramer via intermolecular boron–nitrogen coordination bonds both in the solution and solid states.[4,5] The tetramer possesses a highly symmetrical and rigid structure with a void. Such the structure is considered not only to affect the reactivity of **1a** as a versatile building block[3,6,7,8] of arylpyridines but also to be suggestive in construction of skeletons with novel functionality. With respect to the isomers, at the beginning, a dimeric structure of diethyl(2-pyridyl)borane (**2a**) was presented by the authors based on an EI-MS spectroscopy.[2] Only low solubility and a high melting point (> 300 °C) of diethyl(4-pyridyl)borane (**3**)[3] suggests the formation of a higher oligomer or packing of high symmetry in crystalline state. To date, however, the X-ray structure analyses of both isomers have not been succeeded. Herein we disclose the X-ray structure analysis of the dimeric structure of diethyl[2-(5-methylpyridyl)]borane (**2b**) and describe outstanding properties relevant to the strength of the boron–nitrogen coordination bonds in **2a** and **2b**.



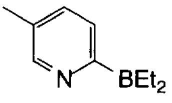
1a



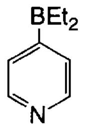
1b



2a



2b



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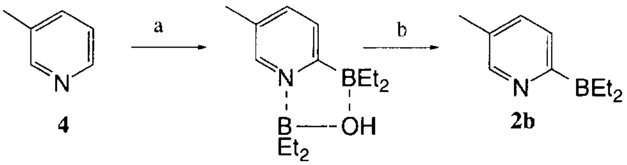
Synthesis

Though 2-lithiopyridines are available via a low-temperature halogen–metal exchange, Martin and his coworkers[9] have demonstrated that direct 2-lithiation of pyridines takes place effectively with sterically hindered base in the presence of reagents having the ability to coordinate with the nitrogen atom of pyridines. In order to introduce a boryl group at the 6 position of 3-methylpyridine (**4**) we applied the similar method, that is, lithiation with lithium diisopropylamide at –78 °C in ether in the presence of diethylmethoxyborane. Usual workup yielded a viscous oil, whose ^{1}H NMR spectrum showed both signals due to four ethyl groups and a pyridine skeleton in the ratio of 20 : 3. Heating of the material at 180 °C under 20 mmHg gave **2b**.[2]



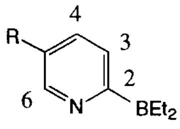
Scheme 1. a, LDA (1.0 equiv), Et_2BOMe (2.0 equiv), ether, from –78 °C to r.t., 3 h; b, 180 °C, 20 mmHg, 30 min.

Nuclear Magnetic Resonance Spectroscopy

As in ^{1}H NMR spectra,[2] only one set of the signals as a monomer was observed in each spectrum of ^{13}C, ^{11}B, and ^{14}N NMR spectroscopies for **2a**. The boron and nitrogen signals appeared at –2.3 and –136 ppm, respectively. The values are similar to those of **1a** and are in the range of signals due to these atoms when forming the mutual coordination bond.[10,11] The same structural features are derived from chemical shifts of atoms that constitute **2b**. In particular, the proton and carbon signals (8.39 and 141.9 for **2a**; 8.19 and 141.3 for **2b**, respectively) appear upfield when compared with those of pyridine (8.60 and 149.8, respectively): the shielding of both these proton and carbon atoms is the reliable indication of the formation of the coordination bond.

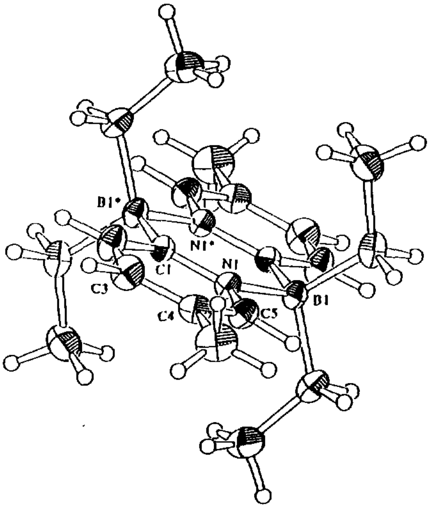
Table 1. Chemical shifts (ppm) of skeletal atoms of **2a** and **2b** in $CDCl_3$. TMS, $BF_3{\bullet}OEt_2$, and $NaNO_3$ aq. as standards, respectively.

	C2	C3	C4	C5	C6	B	N
2a (R = H)	181.6	129.6	135.5	120.2	141.9	-2.3	-136
2b (R = Me)	177.8	129.2	136.9	129.5	141.3	-2.35	-137.2



Structure in crystalline state

A single-crystal X-ray crystallographic study revealed the planar dimeric structure of **2b** as shown in the figure. Thus, dihedral angles of C(2)–C(1)–N(1)–B(1) and C(4)–C(5)–N(1)–B(1) are −177.8(2)° and 178.0(2)°, respectively. A slightly shortened distance by 0.05 Å is found between the boron and the nitrogen atoms [B(1)–N(2), 1.611(2)Å] compared with **1a**,[4] and furthermore the boron atom shows the clear pyramidalization. The angles of [C(1)–B(1)–C(7)], [C(1)–B(1)–C(9)], and [C(7)–B(1)–C(9)] are 109.9(2)°, 110.7(2)°, and 109.1(2)°, respectively, which are far close to those of the tetrahedral structure.



According to the criterion proposed by S. Toyota and M. Ōki,[12] the tetrahedral character (THC) of a boron atom correlates well to the the barrier of dissociation rather than the length of the coordination bond. The THC value of the boron atom is estimated to be 96.9 %. The values for **1a** are 79.7 (B1) and 84.2 (B2) %, respectively.[4,5] Hence, we conclude that the coordination bond of the dimer is stronger than that of the tetramer of **1a**.

Structure in Solution

In line with the results in the MS and NMR spectroscopies, vapor pressure osmometry by Knauer Digital Vapor Pressure Osmometer with benzil as a standard gave the value 2.0 with various concentrations of **2a** in benzene (from 2.1×10^{-2} to 5.5×10^{-2} mol dm^{-3}) at 60 °C, indicating the formation of the dimer.

Though the coupling reactions using **1a** or **3** were reported, the one with **2a** has not been known. A plausible explanation might be that low-temperature halogen-metal exchange readily gives 2-lithiopyridines as the starting species to give arylpyridines.[13] Another possibility would be that the stronger coordination in **2b**, verified by the X-ray structure analysis, prevents dissociation to a monomer which is considered to be more labile in these reactions than the dimer due to the steric hindrance. Hence, we carried out the coupling reactions using **1a** and **2a** with bromotoluene in refluxing tetrahydrofuran. Compound **1a** was completely consumed giving the coupling product in 60 % yield, whereas **2a** remained intact.

A scrambling experiment of the component molecules gave a further support relevant to the marked stability of the dimer. Heating at 100 °C for 24 h is known to effect the complete scrambling of **1a** and **1b** in deuteriotoluene.[5] In contrast, each dimer composed of **2a** or **2b** remained unchanged even when equimolar amounts of these dimers in *p*-xylene-d_{10} were heated at 130 °C for 24 h. The attempt to form the new oligomers composed of **1a** and **2a** by the thermal scrambling resulted in failure giving the starting tetramer and dimer. These results indicate diethyl(2-pyridyl)boranes retain the dimeric structure in solution.

Experimental

General. ^{1}H NMR and ^{13}C NMR spectra were recorded with JEOL LA500 spectrometer. ^{11}B NMR and ^{14}N NMR spectra were recorded with JEOL GSX400 and JEOL GX500 spectrometers, respectively. The proton and carbon signals were assigned by NOESY and C–H COSY spectroscopies.

***Diethyl[2-(5-methylpyridyl)]borane* 2b**. To a solution of diisopropylamine (506 mg, 5 mmol) in ether (10 ml) was added BuLi in hexane (3.13 ml, 5 mmol) with ice-cooling. The solution was stirred for 10 min and was added dropwise to a mixture of 3-methylpyridine (465.6 mg, 5 mmol) and a THF solution of diethylmethoxyborane (10 ml, 10 mmol) in ether (10 ml) at −78 °C. The mixture was allowed to warm to room temperature during 3 h and the reaction was quenched with brine (50 ml). The organic layer was extracted with ethyl acetate (3 × 50 ml). The combined extracts were dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The residue was column chromatographed over silica gel with a mixture of hexane–ethyl acetate (4 : 1 v/v) to give a viscous oil. Heating of the oil at 180 °C under 20 mmHg for 30 min gave a solid, which was crystallized from a mixture of hexane–CH_2Cl_2 (5 : 1 v/v) to give **2b** as colorless crystals (250 mg, 27 %): mp 200–202 °C; ^{1}H NMR δ 0.40 (6H, t, J = 7.9 Hz), 0.72 (4H, q, J = 7.9 Hz), 2.34 (3H, s), 7.48 (1H, dd, J = 7.9 and 1.8 Hz), 7.57 (1H, d, J = 7.9 Hz), 8.19 (1H, d, J = 1.8 Hz); ^{13}C NMR δ 10.5, 18.4, 21.9 (br), 129.2, 129.5, 136.9, 141.3, 177.8 (br); ^{11}B NMR δ −2.35; ^{14}N NMR δ −137.2.

Coupling Reaction of Diethyl(3-pyridyl)borane 1a and Diethyl(2-pyridyl)borane 2a . To a stirred mixture of *p*-bromotoluene (73.5 mg, 0.430 mmol) and $Pd(PPh_3)_4$ (20.2 mg, 0.0173 mmol) in THF (1.7 ml) under Ar atmosphere at room temperature, Bu_4NBr (11.0 mg, 0.0341 mmol), powdered KOH (57.2 mg, 1.02 mmol) and **1a** (50.2 mg, 0.341 mmol) were added. After heating under reflux for 3h, the mixture was diluted with AcOEt, washed with brine and dried over $MgSO_4$. Removal of the solvent and chromatography over silica gel with a mixture of hexane and AcOEt (2 : 1 v/v) gave 3-(*p*-tolyl)pyridine (42.2 mg, 0.249 mmol, 73 %). The mixture of **2a** (50.0 mg, 0.340 mmol), *p*-bromotoluene (72.7 mg, 0.425 mmol), $Pd(PPh_3)_4$ (19.7 mg, 0.0170 mmol), KOH (57.0 mg, 1.02 mg) in THF (1.7 ml) was treated in a similar manner. The starting material was recovered unchanged (43 mg, 86 %).

***X-ray Crystallography*. 2b**: a colorless prismatic crystal of $C_{20}H_{32}B_2N_2$ having a approximate dimensions of 0.30 × 0.40 × 0.50 mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC5R diffractmeter with graphite monochromated Cu-Kα radiation and a 12 kW rotaing 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 reflection in the range $28.59 < 2\theta < 29.98°$ corresponded to an F-centered orthorhombic cell. The structure was solved by direct methods (SHELXS86)[14] and expanded using Fourier techniques (DIRDIF94).[15] The final cycle of full-matrix least-squares refinement was based on 1581 observed reflections ($I > 3.00\sigma(I)$) and 174 variable parameters. Fourier map corresponded to 0.19 and −0.14 $e^{-}/Å$, respectively. Neutral atom scattering factors were taken from Cromer and Waber.[16] Anomalous dispersion effects were included in Fcalc; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[17]

The values for the mass attenuation coefficients are those of Creagh and Hubbel.[18] All caluculations were performed using the teXsan[19] crystallographic software package of Molecular Structure Corportion.

Table 2. Fractional Atomic Coordinates and Thermal Parameters

Atom	x	y	z	Beq
N(1)	1.0809(2)	0.3308(2)	-0.0896(2)	2.89(3)
N(1*)	0.9191(2)	0.6692(2)	0.0896(2)	2.89(3)
C(1)	1.1703(2)	0.4299(2)	-0.0532(2)	2.89(4)
C(1*)	0.8297(2)	0.5701(2)	0.0532(2)	2.89(4)
C(2)	1.3325(3)	0.3639(3)	-0.1053(3)	4.15(5)
C(2*)	0.6675(3)	0.6361(3)	0.1053(3)	4.15(5)
C(3)	1.3985(3)	0.2079(3)	-0.1877(3)	4.42(5)
C(3*)	0.6015(3)	0.7921(3)	0.1877(3)	4.42(5)
C(4)	1.3052(2)	0.1085(2)	-0.2227(2)	3.68(5)
C(4*)	0.6948(2)	0.8915(2)	0.2227(2)	3.68(5)
C(5)	1.1485(2)	0.1750(2)	-0.1713(3)	3.61(5)
C(5*)	0.8515(2)	0.8250(2)	0.1713(3)	3.61(5)
C(6)	1.3695(4)	-0.0646(3)	-0.3142(5)	5.48(7)
C(6*)	0.6305(4)	1.0646(3)	0.3142(5)	5.48(7)
C(7)	0.7529(3)	0.3871(3)	-0.2474(3)	4.19(5)
C(7*)	1.2471(3)	0.6129(3)	0.2474(3)	4.19(5)
C(8)	0.7375(3)	0.4952(4)	-0.4013(4)	5.44(7)
C(8*)	1.2625(3)	0.5048(4)	0.4013(4)	5.44(7)
C(9)	0.8986(3)	0.2489(3)	0.0870(3)	4.07(5)
C(9*)	1.1014(3)	0.7511(3)	-0.0870(3)	4.07(5)
C(10)	1.0452(4)	0.1991(4)	0.2627(4)	5.73(8)
C(10*)	0.9548(4)	0.8009(4)	-0.2627(4)	5.73(8)
B(1)	0.8904(3)	0.3858(2)	-0.0473(3)	3.07(5)
B(1*)	1.1096(3)	0.6142(2)	0.0473(3)	3.07(5)

Table 3. Selected Geometrical Properties[a]

Distances (Å)	
B(1) - N(2)	1.611(2)
B(1) - C(2)	1.615(3)
B(1) - C(7)	1.628(3)
B(1) - C(9)	1.632(3)
Bond Angles (deg)	
N(1) - B(1) - C(1)	110.1(1)
N(1) - B(1) - C(7)	108.0(1)
N(1) - B(1) - C(9)	109.1(1)
C(1) - B(1) - C(7)	109.9(2)
C(1) - B(1) - C(9)	110.7(2)
C(7) - B(1) - C(9)	109.1(2)
B(1) - N(1) - C(1)	123.9(1)
B(1) - N(1) - C(5)	115.7(1)
C(1) - N(1) - C(5)	120.4(1)
Dihedral angles (deg)	
C(2) - C(1) - N(1) - B(1)	-177.8(2)
C(4) - C(5) - N(1) - B(1)	178.0(2)

[a] Numerals in parentheses are estimated standard deviations.

Table 4. Crystallographic Data

molecular form	$C_{20}H_{32}B_2N_2$	α, deg	98.09(4)
molecular weight	322.11	β, deg	105.22(2)
crystal size (mm)	0.30 × 0.40 × 0.50	γ, deg	65.22(3)
crystal shape, color	prismatic, colorless	V, Å^3	489.6(4)
radiation (graphite	Cu-Kα	Z	1
monochromated)	($\lambda = 0.71069$ Å)	$2\theta_{max}$	55.0 °
crystal system	triclinic	no. of reflections collected	2405
space group	P1 (#2)	no. of reflections refined	1581
a, Å	8.631(3)	no. of variables	174
b, Å	8.812(4)	R	0.046
c, Å	7.353(2)	wR	0.033

Vapor pressure Osmometry. **2a**: Vapor pressure osmometry was carried out by means of Knauer Digital Vapor Pressure Osmometer with benzil as standard: 2.0 in benzene at 60 °C [benzil (0, 26.1, 101.7, and 193.9 for 0, 0.0148, 0.054, and 0.1036 mol/l, **2a** (0, 19.8, and 52.4 for 0, 0.0219, and 0.0554 mol/l, respectively).

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