

## The Structure of Diethyl(3-pyridyl)borane

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Single-crystal X-ray crystallographic study together with spectroscopic data and vapour pressure osmometry reveal that diethyl(3-pyridyl)borane constitutes a cyclic tetramer both in solid state and in solution.

Synthesis of diethyl(3-pyridyl)borane **1** was initially reported by Terashima *et al.*,<sup>1</sup> who then developed a coupling reaction using **1** as the starting material.<sup>2</sup> Compound **1**, 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 nucleophilicity of the nitrogen and electrophilicity of a boryl group, caused by the interaction of the vacant p-orbital of the boron and the  $\pi$ -electron system in the pyridine ring. However, since pyridine **2** is known to be highly deactivated towards electrophilic substitution, the pyridine ring in **1** should not act effectively as a  $\pi$  donor. Furthermore the boron is electropositive and thus delocalization of the  $\pi$  electron onto this atom would not cause significant stabilization. This would suggest that the boron and the nitrogen in **1** should act as Lewis acid and Lewis base,<sup>3</sup> respectively, to form intermolecular boron–nitrogen coordination.

As already reported,<sup>1</sup> only one set of the signals as a monomer was observed both in <sup>1</sup>H and <sup>13</sup>C NMR spectra. The <sup>1</sup>H NMR spectrum of **1** was essentially independent of both temperature ranging from  $-90$  to  $80^\circ\text{C}$  and concentration ranging from  $6 \times 10^{-3}$  to  $3 \times 10^{-1}$  mol dm<sup>-3</sup>. Listed in Table 1 are chemical shifts of protons and carbons of a pyridine ring in **1** together with those of some related compounds at room temperature. As is generally known, the protons and carbons of the *ortho* and *para* positions of the electron-accepting group, such as a cyano group in **5**, appear downfield as compared with pyridine **2**. However, both the protons and carbons at the same positions in **1** do not show such a simple trend. The data indicate that the boryl group does not behave merely as an electron-withdrawing group in **1**.

Like the triethylborane–pyridine adduct **6**,<sup>4</sup> the boron of **1** is found to resonate at a far higher position than that of species **3**<sup>3</sup> and **10**,<sup>5</sup> which possess strong  $\pi$ -electron donating thiophene and dimethylamino moieties, respectively. Since the marked shielding of the boron in **6** as well as that in trimethylborane–pyridine adduct **7** and triethylborane–trimethylamine adduct **8**<sup>4,6</sup> has been established to be due to the coordination bond between the trivalent boron and the nitrogen of amines, the upfield shift of the boron in **1** suggests

that molecule **1** forms the oligomer by a head–tail coordination bond. The chemical shift of the nitrogen atom in **1** ( $-133$  ppm, half width:  $1.2 \times 10^3$  Hz) also supports our consideration. Thus, while the value of pyridine **2**<sup>7</sup> is  $-59$  ppm, nitrogens in **1**, **6** and **7** are shielded by over  $-40$  ppm. Furthermore, it should be pointed out that the comparable chemical shifts of the boron and the nitrogen in **1** with those of **6** and **7** clarify that the equilibrium between the oligomer and the species free from the coordination bond is to the side of the former.

The same conclusion can be derived from the NOE. Namely, upon irradiation of the signals due to the methyl groups in **1**, the differential NOE spectrum exhibited distinct and comparable enhancement of the signals due to 2-H, 4-H and 6-H.

In the spectra of EIMS (30 eV), in addition to the M<sup>+</sup> – Et peak (118, 100%) and parent peak as a monomer (M<sup>+</sup>, 147, 45%), peaks of 2 × M<sup>+</sup> – Et (265, 47%), 3 × M<sup>+</sup> – Et (412, 67%), 4 × M<sup>+</sup> – Et (559, 39%) were observed. FABMS displayed the same peaks at intensities of 14, 19, 100, 41 and 2%, respectively, together with the new peaks of 2 × M<sup>+</sup> (293, 7%) and 3 × M<sup>+</sup> (441, 1%).

Furthermore, upon standing the 1 : 1 mixture of **1** and bases **2**, piperidine **4** or quinuclidine **11** in dichloromethane at room temp. for several days, the spectra remained unchanged, indicating that these bases did not trap any fragment of the oligomer.

Vapour pressure osmometry by Knauer Digital Vapor Pressure Osmometer with benzil as a standard indicated that **1** existed as a tetramer in solution. Namely, with various concentrations of **1** in benzene (from  $3.78 \times 10^{-3}$  to  $2.96 \times 10^{-1}$  mol dm<sup>-3</sup>) at  $60^\circ\text{C}$ , the value 3.73 was considered to be

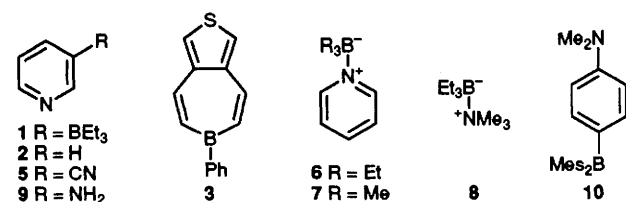


Table 1  $\delta$  <sup>1</sup>H ( $\delta$  <sup>13</sup>C) of **1** and related compounds

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

<sup>a</sup> Chemical shift in CDCl<sub>3</sub>. <sup>b</sup> Ref. 1. <sup>c</sup> This work.

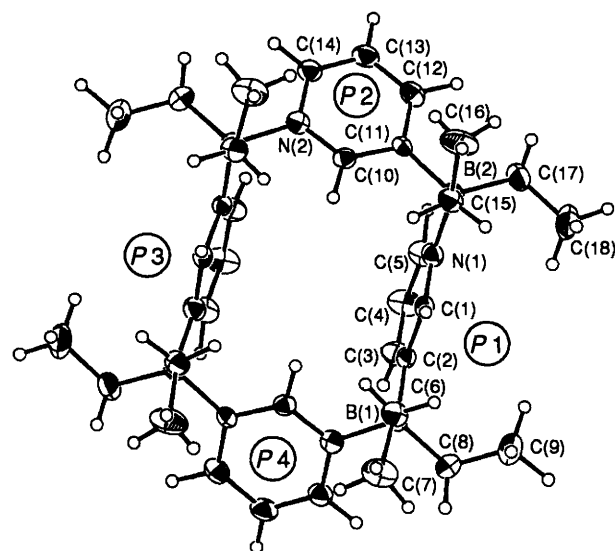


Fig. 1 Computer-generated thermal ellipsoid of **1**. Some important bond distances (Å) and angles ( $^\circ$ ) not given in the text are as follows: N(1)–B(2) 1.636(4), B(2)–C(11) 1.641(5), B(2)–C(15) 1.622(6), B(2)–C(17) 1.620(5), N(1)–B(2)–C(11) 103.6(3), N(1)–B(2)–C(15) 111.3(3), C(11)–B(2)–C(15) 107.8(3), C(11)–B(2)–C(17) 111.9(3), C(15)–B(2)–C(17) 113.7(3). Dihedral angles of B(2)–N(1)–C(5)–C(4) and B(2)–N(1)–C(1)–C(2) are 178.8(4) and 177.8(3) $^\circ$ , respectively.

Table 2  $\delta^{11}\text{B}$  and  $\delta^{14}\text{N}$  of **1** and related compounds

	1 <sup>a,b,c</sup>	3 <sup>a,d</sup>	6 <sup>a,e</sup>	7 <sup>a,e</sup>	8 <sup>a,g</sup>	10 <sup>a,c,f</sup>	2 <sup>a,h</sup>	5 <sup>a,h</sup>
<sup>11</sup> B <sup>i</sup>	-0.35	50.8	-2.2	0.0	0.0	71.5	—	—
<sup>14</sup> N <sup>j</sup>	-133	—	-108	-108	—	—	-59	-60

<sup>a</sup> Chemical shifts in  $\text{CDCl}_3$ . <sup>b</sup> Ref. 1. <sup>c</sup> This work. <sup>d</sup> Ref. 3. <sup>e</sup> Ref. 4. <sup>f</sup> Ref. 5. <sup>g</sup> Ref. 6. <sup>h</sup> Ref. 7. <sup>i</sup>  $\text{BF}_3\text{OEt}_2$  as standard. <sup>j</sup>  $\text{NaNO}_3$  (aq.) as standard.

the average number of constituent molecules. With chloroform (from  $6.39 \times 10^{-3}$  to  $9.98 \times 10^{-2}$  mol  $\text{dm}^{-3}$ ) at 40 °C and tetrahydrofuran (from  $1.17 \times 10^{-2}$  to  $1.82 \times 10^{-1}$  mol  $\text{dm}^{-3}$ ) at 45 °C, values of 3.92 and 3.91 were obtained, respectively.

Compound **1** could be recrystallized from benzene. A single-crystal X-ray crystallographic study revealed that **1** forms a cyclic tetramer with a  $C_2$  symmetry as illustrated in Fig. 1.<sup>8†</sup> Of the structural features, outstanding is the distance between the boron and the nitrogen [B(1)–N(2)\*, 1.639(5) Å]. The length of this coordination bond is comparable with that of the B(1)–C(2)  $\sigma$  bond [1.630(4) Å], symmetrizing the framework of the tetramer. The bond angles constituted by the boron and three substituents are 113.9(3)° [C(2)–B(1)–C(6)], 107.2(3)° [C(2)–B(1)–C(8)], and 113.7(3)° [C(6)–B(1)–C(8)], respectively. Furthermore the coordination bond [N(2)\*–B(1)] forms the angles of 104.1(3)° [N(2)\*–B(1)–C(2)], 106.9(3)° [N(2)\*–B(1)–C(6)], and 110.5(3)° [N(2)\*–B(1)–C(8)] with these substituents, clearly showing the pyramidal structure of the boron [B(1)]. The coordination bond [N(2)\*–B(1)] lie in the plane of the pyridine ring (P1) with a deviation of only 1.6–3.0°. Furthermore, the angles between C(10)\*–N(2)\*–B(1) and C(14)\*–B(2)\*–B(1) are 117.9(2) and 125.1(3)°, respectively, indicating that the coordination bond almost lies on the extension of the line which binds N(2)\* and C(12)\*. A similar situation is found around the B(2)–N(1) coordination bond. Of the four pyridine rings two rings (P1 and P3) are confronted 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 of C(1)–C(1)\* is 5.119(4) Å and that of C(4)–C(4)\* is 4.228(7) Å. The other set of the pyridine rings (P2 and P4) fairly lies on this plane (dihedral angle between least-squares planes of pyridine rings: 125.65°) and the distance of C(10)–C(10)\* is 5.797(4) Å.

The B(1)–C(2) bond is much longer than the corresponding boron–carbon bond in triphenylborane **12** (1.577 Å),<sup>9</sup> indicating the low double bond character of this bond in **1**. As regard to the length of the coordination bond, an early X-ray crystallographic study revealed an N–B bond distance of  $1.56 \pm 0.05$  Å<sup>10</sup> 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 a gas phase.<sup>11</sup> For the B–N bond of the alkylated adduct  $\text{Me}_3\text{NBMe}_3$ , an elongated distance of  $1.70 \pm 0.01$  Å was revealed by means of the microwave spectroscopy.<sup>12</sup> 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 aryldiethylborane. Eventually **1** is found to constitute the firm cyclic-tetramer with a void through the strainless coordination bond.

In conclusion, the formation of the coordination bond between the boron and the nitrogen atoms seems to be responsible for the stability of **1**, which would be useful in the design of tractable synthetic reagents that contain the trivalent boron. It should likewise be worthy to note that in spite of the

direct conjugation between the Lewis acidic and Lewis basic sites the pyridylborane constitutes the stable and strainless supramolecule through self-assembly, whose microstructure is predictable from the firm skeleton of the component molecule.

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## Footnote

† Crystal data for **1**:  $\text{C}_{36}\text{H}_{56}\text{B}_4\text{N}_4$ , colourless, prismatic crystals ( $0.30 \times 0.30 \times 0.15$  mm), orthorhombic, *Fdd2* (No. 43),  $a = 22.700(3)$ ,  $b = 45.297(4)$ ,  $c = 7.289(4)$  Å,  $V = 7494(3)$  Å<sup>3</sup>,  $Z = 8$ , 1358 reflections with  $I > 3\sigma(I)$ ,  $R = 0.043$  ( $T = 300$  K) were measured on a Rigaku AFC5R diffractometer with graphite monochromated Cu-K $\alpha$  radiation ( $\lambda = 1.54178$  Å) and a 12 kW rotating anode generator.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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