Through-bond Modulation of N→B Ring Formation shown by NMR and X-Ray Diffraction Studies of Borate Derivatives of Pyridyl Alcohols

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The preparation of diphenyl(2-pyridylmethoxy-O,N)borane (2a), diphenyl[1-(2-pyridyl)ethoxy-O,N]-borane (2b), diphenyl[α-(2-pyridylbenzyloxy-O,N)]borane (2c), diphenyl[2-(2-pyridyl)ethoxy-O,N]-borane (4), benzene-1,2-diyldioxy(2-pyridylmethoxy-O,N)borane (5) and benzene-1,2-diyldioxy[2-(2-pyridyl)ethoxy-O,N]borane (6) is reported. The cyclic structures 2a and 4 were established by X-ray diffraction studies, the N→B bond distances being 1.642 Å for 2a and 1.685 Å for 4. Complete assignment of the ^{1}H and ^{13}C NMR spectra of 2a–c and 4 was achieved from two dimensional HETCOR data. Additional evidence for the strength of the five- and six-membered rings in boron esters was obtained from variable-temperature measurements which show partial ring opening for the six-membered ring compounds at 180 °C. The observation that five-membered rings are more stable than six-membered ones is attributed to sigma-assistance by through-bond interactions.

In recent years we have been interested in the synthesis of boron esters derived from 2-pyridyl alcohol derivatives,[1] as well as in studying intramolecular N→B coordination.[2,3] It has been found that the formation of five-membered N–B rings is preferred over that of six-membered rings by $\Delta\Delta H \simeq 28$ kJ mol^{-1}, this enthalpy difference being attributed to increased ring stability.[1]

It has also been reported that diarylboron chelates rearrange upon heating, thus undergoing an intramolecular redox reaction in which the N-oxide is deoxygenated and the diarylborinic acid component is oxidized to monoarylboronic acid.[4–7] During this thermally induced rearrangement, the six-membered chelate 7 is transformed into the five-membered ring compound 8, which has an intramolecular N→B coordination (Scheme 3, see later). The ring contraction from 7 to 8 is an exothermic reaction (ΔH ca. -200 kJ mol^{-1}) which shows that five-membered ring boron esters are more stable than six-membered ones since in addition to more favourable steric conditions, the number of electron-rich non-carbon donating ligands at the boron atom is increased.[6]

In addition, it has been reported that six-membered ring borinates derived from amino alcohols are less stable than five-membered ones, and an equilibrium mixture of the simple ester and the chelate is favoured, this being attributed to the greater steric difficulties associated with the formation of the ring.[8]

The aim of the study is to determine the existence of modulation of N–B ring formation by through-bond interactions (TBI).[9–14]

Results and Discussion

In continuation of our studies of the factors that allow the synthesis of boron esters by internal coordination,[1] we report herein the preparation and characterization of six pyridylborinic esters.

The preparation of diphenyl(2-pyridylmethoxy-O,N)borane (2a), diphenyl[1-(2-pyridyl)ethoxy-O,N]borane (2b), diphenyl-[α-(2-pyridyl)benzyloxy-O,N]borane (2c) and diphenyl[2-(2-pyridyl)ethoxy-O,N]borane (4) was achieved by reaction of the corresponding 2-pyridyl alcohols with diphenylborinic acid or diphenylborinic acid 2-aminoethanol (Scheme 1), whilst

1a; R = H
b; R = CH₃
c; R = Ph

2a; R = H
b; R = CH₃
c; R = Ph
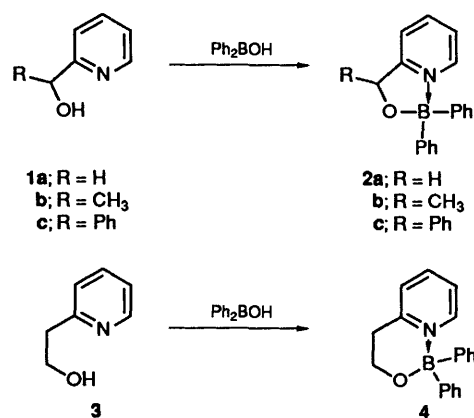
Scheme 1

benzene-1,2-diyldioxy(2-pyridylmethoxy-O,N)borane (5) and benzene-1,2-diyldioxy[2-(2-pyridyl)ethoxy-O,N]borane (6) were prepared by reaction of 1,2-dihydroxybenzene, borane–tetrahydrofuran (THF) and the corresponding 2-pyridyl alcohol (Scheme 2). The structures of compounds 2a–c and 5
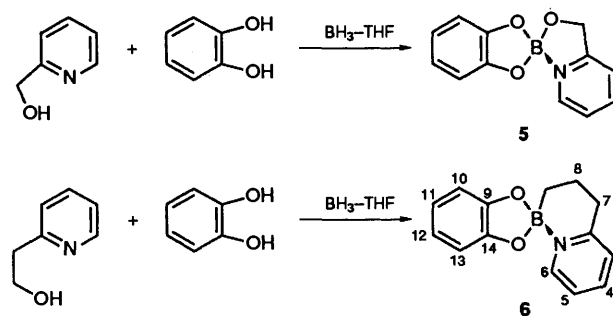
Scheme 2
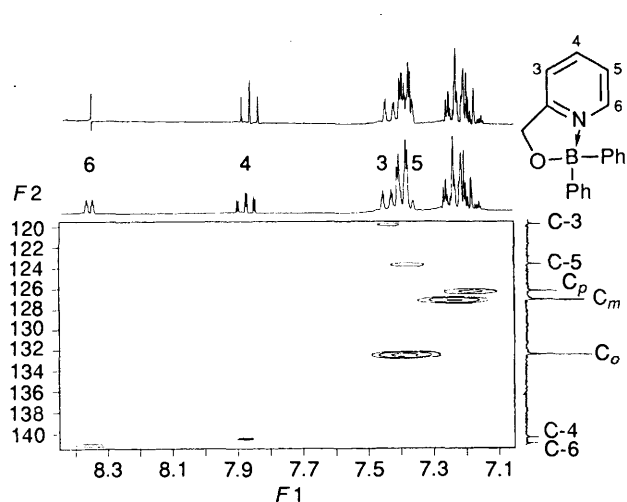
contain a five-membered ring, whilst 4 and 6 have a six-membered ring.

Formation of the cyclic structures can easily be demonstrated by spectroscopic methods since the $\delta(^{11}B)$ values (Table 1)

Table 1 ^{13}C and ^{11}B NMR chemical shifts (ppm) in CDCl₃

Compound	[11]B	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-i	C-o	C-m	C-p
1a		160.2	120.8	136.9	122.2	148.4	64.4	—				
1b		163.6	118.8	136.0	121.1	147.1	68.7	23.3				
1c		161.3	120.9	136.6	122.0	147.6	75.0	—	143.0	126.7	128.2	127.3
3		160.3	123.6	136.6	121.4	148.7	39.7	61.7				
2a	10.8	159.5	120.0	140.6	123.8	141.1	68.9	—	149.0	132.6	127.3	126.4
2b	9.0	162.9	119.9	140.8	123.8	140.9	74.1	21.7	148.6	132.2	127.2	126.6
									148.6	132.1	127.2	126.1
2c[a]	8.4	161.5	121.3	140.8	123.9	140.7	80.8	—	148.4	133.5	127.2	126.1
									148.4	132.1	127.3	126.8
4	6.2	157.7	126.8	139.8	122.0	145.4	32.4	57.7	151.0	133.1	127.2	126.1

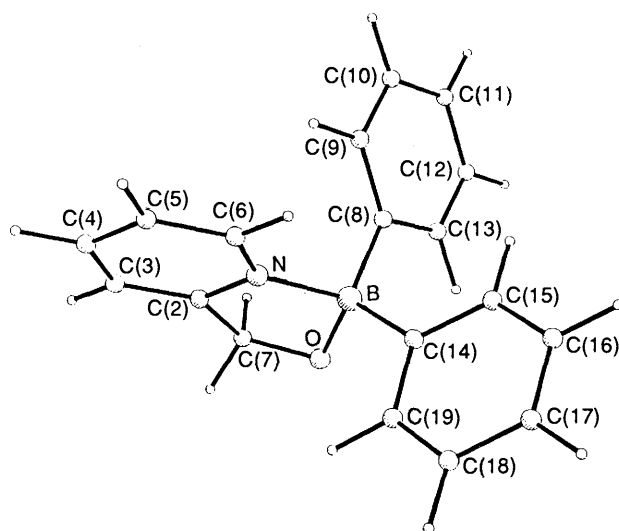|									C(9)	C(10)	C(11)	
5	13.5	157.3	120.4	139.3	124.3	142.3	65.6	—	150.4	108.9	118.9	
6	8.1	156.7	124.6	139.9	122.2	144.0	35.9	59.4	150.1	108.1	118.5	

[a] R = C₆H₅: δ = i, 141.0; o, 127.7; m, 128.8; p, 128.5.

Fig. 1 Two-dimensional [13]C–[1]H HETCOR contour plot of **2a**

Fig. 2 Molecular perspective of **2a** (the atom labelling differs from the chemical nomenclature of **2a**)

Scheme 3

lie in the range corresponding to N→B coordination compounds [3,15-17] (13.5–6.2 ppm).

Comparison of the ^{13}C NMR data for pyridyl alcohols (**1a–c** and **3**) with those of the boron esters (**2a–c, 4, 5** and **6**) shows that C-6 is shifted to higher magnetic fields in the five-membered ring compounds (**2a–c**) owing to steric interactions of the phenyl group on C-6. As a result of this shifting, the chemical shifts of C-4 and C-6 lie very close. Thus, unequivocal assignment of these carbon signals was achieved by 2D carbon–proton correlated experiments with the aid of [1]H[^{1}H] decoupling experiments. This allowed us to establish that the chemical shift assignments for C-3 and C-5 in compound **3** are reversed in the literature.[18] The chemical shift assignments of compounds **2a–c, 4, 5** and **6** are listed in Table 1, while Fig. 1 shows the HETCOR contour plot for compound **2a**. This two-dimensional experiment provides secure chemical shift assignments for the pyridine ring carbons, since in the ^{1}H NMR spectrum 6-H is trivial to assign, whence C-6 follows. In addition, homonuclear irradiation of 6-H provides the unequivocal distinction of 4-H and 5-H, and thus the assignments of C-4 and C-5 follow directly from the HETCOR contour plot.

The differences in bond length and bond energy between the five- and six-membered rings are rationalized in terms of through-bond interactions. If an odd number of bonds are involved between the nitrogen and boron atoms, the antisymmetrical combination of the AO on nitrogen and boron gives the lower molecular orbital (MO) energy and forms the HOMO before ring closure. In order to form the ring by a N→B bond both electrons of the antisymmetrical HOMO have to be
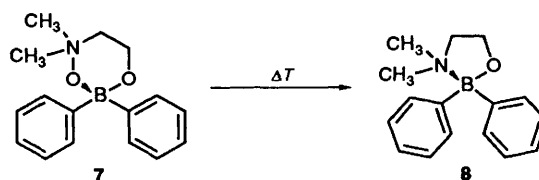
promoted to the LUMO and therefore the bond energy will be correspondingly smaller, as we find experimentally.

In the case of the bis(2-pyridylmethoxy)(2-pyridylmethoxy-O,N)borane (**9**) and bis[2-(2-pyridyl)ethoxy][2-(2-pyridyl)-ethoxy-O,N]borane (**10**) we found that the five-membered N→B ring is favoured over the six-membered one by ca. 28 kJ mol⁻¹.[1]
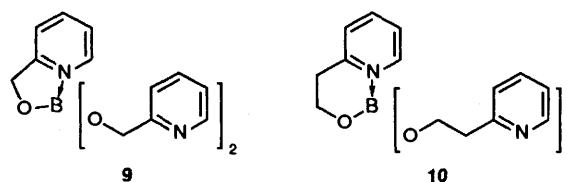
The cyclic structures of **2a** and **4** were also established by X-ray diffraction studies (Figs. 2 and 3). The N→B bond distances are 1.642 Å for **2a** and 1.685 Å in **4**. This is evidence

**Table 2** Selected bond lengths (Å) for substituted diphenylboranes

	2a	4[a]	11[b]	12[c]
B–O	1.487	1.452	1.476	1.481
N→B	1.642	1.685	1.655	1.643
Ph–B	1.628	1.624	1.620	1.620
	1.613	1.626	1.613	1.626

[a] Average values from the two molecules in the asymmetric unit of the crystal cell. [b] Ref. 20. [c] Ref. 19.

Table 3 Selected bond angles (deg) for the boron-containing ring of substituted diphenylboranes

	2a	4[a]	11	12
N–B–Ph[1]	108.3	106.8	109.8	108.0
N–B–Ph[2]	109.3	107.2	109.6	108.6
N–B–O	97.4	105.9	98.4	104.9
O–B–Ph[1]	112.0	108.1	112.2	113.9
O–B–Ph[2]	112.6	113.8	112.1	108.3
Ph[1]–B–Ph[2]	115.6	114.6	113.6	112.7
B–O–C	109.0	114.1	107.7	117.0
O–C–C	105.6	110.2	106.0	110.5
C–C–C	—	113.5	—	110.8
N–C–C	108.5	118.8	105.2	108.7
B–N–C	108.4	122.3	105.5	113.3

[a] Average values from the two molecules in the asymmetric unit of the crystal cell. [b] Ref. 20. [c] Ref. 19.
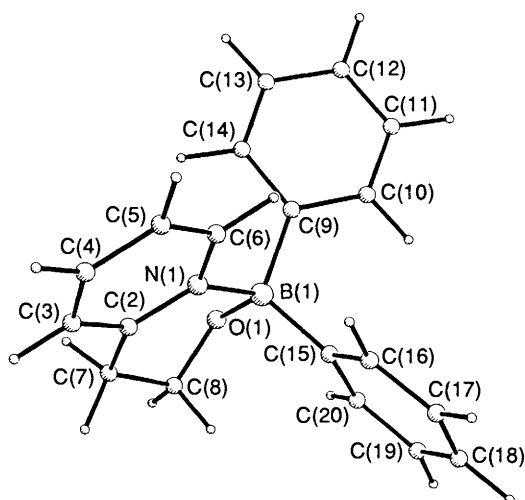
Fig. 3 Molecular perspective of **4** (the atom labelling differs from the chemical nomenclature of **4**)

for a stronger N→B bond in the five-membered ring compound and and will be discussed below. Comparison of bond distances (Table 2) and bond angles (Table 3) with literature data for related compounds (**11** and **12**)[19,20] shows that the co-ordination bond in **11** and **12** is stronger than that in **4**, but has almost the same strength as in **2a** as evidenced by the smaller B–N bond length values.
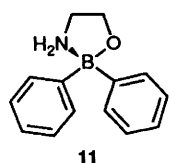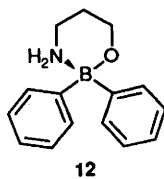
The five-membered heterocyclic ring in **2a** has an envelope

conformation, the oxygen atom being displaced from the plane of the other four ring atoms [torsion angles B–N–C(2)–C(7) 3.3°, B–O–C(7)–C(2) −32.8° and O–C(7)–C(2)–N 17.3°]. The B–N– C(2)–C(7) portion of the six-membered heterocyclic ring in **4** is nearly planar (average torsion angle 6.2°), the oxygen and C(8) atoms being displaced out of the plane. Bond angles and distances for both molecules are normal for five- and six-membered rings having unsaturation, as evaluated by comparison with calculated values obtained using an MMX program.[21]

We now concentrate on discussing three of our experiments allowing comparison of the N→B bond strengths in five- and six-membered rings.

(a) Variable temperature NMR experiments have been performed on compounds **2a–c**, **4**, **5**, **6**, **11** and **12** in [²H₆]dimethyl sulfoxide (DMSO). No differences can be detected in the ¹H and ¹¹B NMR spectra of **2a–c**, **5a** and **11** between 25 and 180 °C, indicating that the N–B bond does not break under these experimental conditions. On the other hand, the spectra of **4**, **6** and **12** are indicative of an initial breaking of the N→B bond, as evidenced by the changes in ¹¹B NMR chemical shifts: for **4** from 25 °C (6.6 ppm) to 180 °C (7.4 ppm), for **6** from 25 °C (8.1 ppm) to 180 °C (10.8 ppm) and for **12** from 25 °C (1.6 ppm) to 180 °C (2.5 ppm). The data indicates that the N→B bond is weaker in the six-membered ring compounds **4**, **6** and **12** than in the five-membered ones (**2a–c**, **5** and **11**).

(b) It has been found that Δδ of C-4 is an appropriate descriptor for the strength of the coordination bond in pyridine adducts.[22] Similarly, we have observed: Δδ(C-4) 3.7 (**2a**), 4.8 (**2b**), 4.2 (**2c**) and 3.2 (**4**) (Table 1). We conclude that the N→B bond strengths decrease in the order **2b** > **2c** > **2a** > **4**.

(c) The N→B bond lengths in the cyclic structures of **2a** and **4** (Figs. 2 and 3) have already been mentioned as 1.642 Å (**2a**) and 1.685 Å (**4**). The shorter bond in **2a** is a further evidence for a stronger N→B bond in the five-membered ring and plays an important role in the following interpretation of our results.

Earlier evidence for the reduced stability of six-membered borinates has been attributed to steric effects.[1,4–8] Such effects should be satisfactorily modelled by molecular-mechanics calculations. The MMX method is known to correctly account for the steric hindrance in normal sized rings.[21] However, MMX calculations come up with the reversed ordering of the N→B bond. From the failure of the MMX model to account for our results we conclude that: (a) steric factors are unlikely to be the reason for the preference of the five-membered ring formation; and (b) an electronic effect not included in the MMX model is responsible for our observations (a)–(c).

We propose that the differences in bond length and bond energy between the five- and six-membered ring systems are due to TBI.[9–14] The interaction between two atomic orbitals is said to be through-n-bonds, if delocalization takes place via n intervening bonds, with each bond orbital having a significant overlap with the next.[13] TBI is not included in MMX and similar molecular-mechanics models, which assume complete localization of the bond orbitals.[21] TBI over n bonds has been qualitatively discussed in terms of second-order perturbation theory.[9,10] Quantitative studies require either (n + 1)-order perturbation theory for the delocalization corrections of strictly localized bond orbitals,[13] or a delocalized MO model, such as Sándorfy's C-approximation,[9,11,12,23,24] with a novel first-order perturbational MO (PMO) formulation of TBI using frontier orbitals.[14]

The formation of a five-membered ring is sigma-assisted by TBI as evidenced in many biradicaloid systems.[11,12] Sigma-resistance by TBI is found in the formation of even-membered rings. Frontier-orbital correlation diagrams indicate that an energy barrier has to be overcome in the formation of an even-membered ring, whereas no barrier is encountered during the

closure of odd-membered rings.[11,12,14] This picture was shown to reproduce *ab initio* results for the cyclization of biradicaloid polymethylene chains.[11] In addition to transition-state effects in their formation, the ground states of odd-membered rings are stabilized by sigma-aromaticity and predicted to be more stable than their next higher even-membered, sigma-antiaromatic homologues.[11,25,26] A modulation of the pyridylborinic ester ring formation by TBI has not yet been considered, as far as we know. The difference to the biradicaloid case is that the interacting orbitals are no longer degenerate. While the sign and character of the TBI remain the same, the amount of interaction is affected by the electronegativity difference between the lone pair of nitrogen and the empty AO on boron. Quantitative calculations involving a self-consistent version of the Sándorfy C-method[27,28] are under way.

In conclusion, this study provides further evidence for the fact that six-membered ring borinates derived from amino alcohols are less stable than their five-membered ring analogues. In contrast with earlier rationalizations by steric effects, we explain the results as being due to through-bond modulations, which assists the sigma-aromatic five-membered ring formation, but resists the formation of a sigma-antiaromatic six-membered ring.

Experimental

The ^1H, ^{11}B and ^{13}C NMR spectra were recorded using Varian EM-390, Varian XL300 GS, JEOL FX 90Q and JEOL GSX 270 spectrometers. Chemical shifts (ppm) are relative to $BF_3 \cdot Et_2O$ and $(CH_3)_4Si$. Coupling constants are quoted in Hz. The HETCOR standard pulse sequence, which incorporates quadrature detection in both domains, was used. The spectral windows for HETCOR experiments were adjusted to perform optimum measurements for the aromatic region. The X-ray studies were performed in a Nicolet R3m four circle diffractometer. Mass spectra were obtained with a Hewlett-Packard 5985-A spectrometer and infrared spectra with a Nicolet MX-1 spectrophotometer.

2-(Hydroxymethyl)pyridine(**1a**)*and2-(2-Hydroxyethyl)pyridine* (**3**).—These compounds are commercially available.

2-(1-Hydroxyethyl)pyridine (**1b**).—A solution containing 0.78 g (20.6 mmol) of $NaBH_4$ in 50 cm³ of THF was treated with 5 g (41.2 mmol) of 2-acetylpyridine and refluxed for 3 h under anhydrous conditions. The solvent was evaporated and the solid residue was dissolved in H_2O followed by neutralization with aqueous sodium hydroxide. The organic phase was extracted with $CHCl_3$ and evaporated to yield 3.8 g (75%) of a viscous yellow liquid characterized as **1b**; δ_H(300 MHz, $CDCl_3$) 1.48 (3 H, d, *J* 6.5, CH_3), 4.93 (1 H, q, *J* 6.5, C*H*CH₃), 5.76 (1 H, s, OH), 7.10 (1 H, ddd, *J* 7, 4, 1, 5-H), 7.44 (1 H, d, *J* 7, 3-H), 7.62 (1 H, dd, *J* 7, 1, 4-H) and 8.40 (1 H, dt, *J* 1, 4, 6-H).

2-(α-Hydroxybenzyl)pyridine (**1c**).—This compound was prepared as in the case of **1b** from 0.516 g (13.6 mmol) of $NaBH_4$ and 5 g (27.3 mmol) of 2-benzylpyridine. This gave 10.1 g (65% yield) of **1c**, as crystals, m.p. 67–69 °C; δ_H(300 MHz, $CDCl_3$) 5.73 (1 H, s, OH), 5.75 (1 H, s, C*H*–C₆H₅), 7.01 (1 H, ddd, *J* 7, 5, 1, 5-H), 7.16 (1 H, dt, *J* 7, 1, 3-H), 7.17–7.29 (3 H, m, *m*-H and *p*-H), 7.35 (2 H, dt, *J* 6, 1, *o*-H), 7.46 (1 H, td, *J* 7, 1, 4-H) and 8.38 (1 H, dd, *J* 5, 1, 6-H).

Diphenyl(2-pyridylmethoxy-O,N)borane (**2a**).—A solution of 2-(hydroxymethyl)pyridine (0.48 g, 4 mmol) in 30 cm³ of dry toluene was placed into a 100 cm³ flask equipped with a stirrer and a Dean–Stark trap. Diphenylborinic acid–2-aminoethanol complex (1 g, 4.4 mmol) was added and the mixture was kept under reflux for 10 h. After removal of the solvents *in vacuo*, the

product was recrystallized from chloroform–hexane to give 0.42 g (35%) **2a**, m.p. 150–152 °C; δ_H(300 MHz, $CDCl_3$) 5.26 (2 H, s, CH₂), 7.15–7.28 (6 H, m, *m*-H and *p*-H), 7.35–7.43 (5 H, m, 5-H, *o*-H), 7.44 (1 H, dt, *J* 8, 1, 3-H), 7.87 (1 H, dt, *J* 8, 1 4-H) and 8.35 (1 H, dt, *J* 6, 1, 6-H); ν_{max}/cm⁻¹(KBr) 1618, 1478, 1193, 1078 (N→B), 953, 778, 754, 742 and 706; *m/z*, 274 (M⁺ + 1, 10.2), 273 (M⁺, 0.8%), 272 (1.6), 195 (25), 196 (100) and 92 (40).

Diphenyl[1-(2-pyridyl)ethoxy-O,N]*borane* (**2b**).—A solution of 3.6 g (16.3 mmol) diphenylborinic acid–2-aminoethanol was hydrolysed as described in the literature.[29] Diphenylborinic acid in ether was treated with 2.0 g (16 mmol) 2-(1-hydroxyethyl)pyridine and allowed to stand overnight with stirring. The precipitate formed was filtered and washed with ether to yield a white solid, m.p. 198–200 °C in 10% yield (0.55 g); δ_H(300 MHz, $CDCl_3$) 1.72 (3 H, d, *J* 7, CH₃), 5.35 (1 H, q, *J* 7, CH), 7.17–7.28 (6 H, m, *m*-H and *p*-H), 7.40 (4 H, dd, *J* 8, 2, *o*-H), 7.40–7.50 (2 H, m, 3-H and 5-H), 7.96 (1 H, dd, *J* 5.6, 1.4, 4-H) and 8.34 (1 H, dt, *J* 5.6, 2.3, 6-H); ν_{max}/cm⁻¹(KBr) 3064 and 1111; *m/z* 288 (M⁺ + 1, 0.1), 287 (M⁺, 1%), 211 (10), 210 (60), 209 (12), 106 (100), 78 (30), 77 (18) and 51 (15).

Diphenyl[α-(2-pyridylbenzyloxy-O,N)]*borane* (**2c**).—This compound was prepared using the procedure described for **2a** from 2.4 g (10.9 mmol) of diphenylborinic acid and 2.0 g (10.9 mmol) of 2-(hydroxybenzyl)pyridine. Compound **2c** was obtained as crystals, m.p. 164–165 °C in 30% yield (1.1 g); δ_H(300 MHz, $CDCl_3$) 6.09 (1 H, s, C*H*C₆H₅), 7.17–7.32 [7 H, m, 3-H and BC₆H₅ (*p*-H and *m*-H)], 7.34–7.44 [6 H, m, 5-H, CHC₆H₅ (*p*-H and *m*-H), BC₆H₅ (*o*-H)] and 7.50–7.60 [4 H, m, CH–C₆H₅ (*o*-H) and BC₆H₅ (*o*-H)]; ν_{max}/cm⁻¹(KBr) 3063, 3042, 3004, 742 and 734; *m/z*, 350 (M⁺ + 1, 0.5), 349 (M⁺, 1) 273 (18), 272 (83), 271 (20), 168 (88), 167 (100), 77 (30) and 51 (32).

Diphenyl[2-(2-pyridyl)ethoxy-O,N]*borane* (**4**).—This compound was prepared from 2-(2-hydroxyethyl)pyridine (0.54 g, 4.4 mmol) using the procedure described for **2a**. The residue was crystallized from dichloromethane–hexane to give 670 mg (53%) of **4**, m.p. 162–169 °C. δ_H(300 MHz, $CDCl_3$) 3.14 (2 H, t, *J* 6, CH₂), 4.05 (2 H, t, *J* 6, CH₂–O), 7.15–7.30 (11 H, m, 5-H and C₆H₅), 7.35 (1 H, d, *J* 8, 3-H), 7.81 (1 H, dt, *J* 8, 2, 4-H) and 8.16 (1 H, d, *J* 5, 6-H); ν_{max}/cm⁻¹(KBr) 3869, 3752, 1500 and 705; *m/z*, 288 (M⁺ + 1, 0.2), 287 (M⁺, 0.7), 211 (10), 210 (95), 209 (20), 106 (100), 78 (51) and 51 (25).

Benzene-1,2-diyldioxy(2-pyridylmethoxy-O,N)borane (**5**).—In a dry 200 cm³ round-bottom flask equipped with a magnetic stirrer under nitrogen atmosphere were placed 0.5 g (4.5 mmol) of catechol and 100 cm³ of dry THF. To this solution 1.9 cm³ (4.5 mmol) of a 2.4 mol dm⁻³ solution of borane–THF were added and the solution was stirred for 0.5 h, followed by addition of 0.49 g (4.5 mmol) of 2-pyridylmethanol with stirring at 60 °C for 4 h. Removal of THF *in vacuo* afforded 1 g of **5** as a viscous liquid; δ_H(90 MHz, $CDCl_3$) 5.00 (2 H, s, CH₂), 6.40–6.80 (4 H, m, 10-H to 13-H), 7.40–7.70 (2 H, m, 3-H and 5-H), 8.00 (1 H, t, *J* 7, 4-H) and 8.25 (1 H, d, *J* 6, 6-H); *m/z*, 228 (M⁺ + 1, 20), 227 (M⁺, 100%), 226 (33), 198 (83), 197 (26), 92 (38), 78 (22), 65 (39), 63 (23), 53 (20) and 51 (21).

Benzene-1,2-diyldioxy[2-(2-pyridyl)ethoxy-O,N]*borane*(**6**).—Compound **6** was prepared by the procedure described for **5** from catechol (0.5 g, 4.5 mmol), 1.9 cm³ (4.5 mmol) of borane–THF (2.4 mol dm⁻³) and 55 g (4.5 mmol) of 2-(2-hydroxyethyl)pyridine to give 1.0 g of **6** as a viscous liquid; δ_H(90 MHz, $CDCl_3$) 3.20 (2 H, t, *J* 6, 7-H), 4.25 (2 H, t, *J* 6, 8-H), 6.60–7.2 (4 H, m, 10-H and 13-H), 7.30–7.60 (2 H, m, 3-H and 5-H), 8.00 (1 H, td, *J* 6, 1, 4-H) and 8.45 (1 H, d; *J* 6, 6-H); *m/z*, 242 (M⁺ +

Table 4 Summary of crystallographic data

	Compound	
	2a	**4**
Crystal data		
Crystal size/mm	0.4 × 0.5 × 0.6	0.3 × 0.5 × 0.3
Stoichiometry	$C_{18}H_{16}BNO$	$C_{19}H_{18}BNO$
Molecular weight	273.15	287.17
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
$a/Å$	14.176(5)	14.400(5)
$b/Å$	9.844(2)	10.381(2)
$c/Å$	10.637(3)	21.029(7)
$\beta/°$	96.09(2)	95.01(3)
$V/Å^3$	1476.0(7)	3131(1)
Crystal colour	White	White
Z	4	8
T/K	298	298
$D_x/g\ cm^{-3}$	1.22	1.22
$F(000)$	576	1216
$\mu(Cu\ K\alpha, 1.541\ 78\ Å)/cm^{-1}$	5.9	5.8
Data collection		
Mode	$\theta:2\theta$	$\theta:2\theta$
2θ limits/°	3–110	3–110
Scan width, below $k\alpha1/°$	0.9	0.9
Scan width, above $k\alpha2/°$	1.2	1.1
Scan speed (variable)/deg min⁻¹	4.0–29.3	4.0–29.3
Exposure time/h	43.8	91.6
Total reflections collected	2083	4346
Unique reflections $[I \geq 3\sigma(I)^2]$	1696	2311
Structure refinement		
Reflections for final refinement	1608	1810
Parameters refined	195	408
$R(F)\ (\%)$	4.68	6.22
$R(W)\ (\%)$	5.30	6.71
Goodness of fit for last cycle	1.131	1.065
Final G	0.003 01	0.002 84
Residual electron density/ e Å⁻³	0.21	0.24

Table 5 Final atomic coordinates for compound **2a**

Atom	x	y	z
N	8 238(1)	1 917(2)	1 205(1)
B	7 134(1)	2 063(2)	573(2)
O	7 149(1)	952(1)	−358(1)
C(2)	8 545(1)	659(2)	962(2)
C(3)	9 448(1)	243(2)	1 435(2)
C(4)	10 029(1)	1 152(2)	2 138(2)
C(5)	9 707(1)	2 448(2)	2 364(2)
C(6)	8 797(1)	2 811(1)	1 887(2)
C(7)	7 772(2)	−69(2)	148(2)
C(8)	6 439(1)	1 722(2)	1 655(2)
C(9)	6 685(1)	1 791(2)	2 962(2)
C(10)	6 040(1)	1 493(2)	3 821(2)
C(11)	5 121(1)	1 126(2)	3 399(2)
C(12)	4 857(1)	1 036(2)	2 115(2)
C(13)	5 506(1)	1 330(2)	1 266(2)
C(14)	6 986(1)	3 534(2)	−86(1)
C(15)	6 376(1)	4 518(2)	307(2)
C(16)	6 288(1)	5 796(2)	−264(2)
C(17)	6 821(1)	6 113(2)	−1 239(2)
C(18)	7 432(1)	5 159(2)	−1 655(2)
C(19)	7 506(1)	3 889(2)	−1 092(2)

1, 10%), 241 (M⁺, 56), 136 (100), 135 (30), 106 (67), 79 (30) and 78 (28).

Table 6 Final atomic coordinates for compound **4**

Atom	x	y	z
N(1)A	5749(3)	1043(5)	1816(2)
B(1)A	4605(4)	967(7)	1570(3)
O(1)A	4484(3)	−160(4)	1161(2)
C(2)A	6343(4)	48(6)	1765(3)
C(3)A	7261(4)	119(7)	2031(3)
C(4)A	7582(5)	1218(8)	2341(3)
C(5)A	6978(4)	2285(7)	2383(3)
C(6)A	6068(4)	2139(6)	2105(3)
C(7)A	5974(5)	−1150(6)	1419(3)
C(8)A	4915(5)	−1283(6)	1420(3)
C(9)A	4361(4)	2230(6)	1138(3)
C(10)A	3933(4)	3345(6)	1359(3)
C(11)A	3740(4)	4406(6)	976(3)
C(12)A	3966(4)	4388(7)	342(4)
C(13)A	4385(5)	3309(7)	110(3)
C(14)A	4590(4)	2254(6)	501(3)
C(15)A	4063(4)	861(5)	2219(3)
C(16)A	4475(4)	563(5)	2834(3)
C(17)A	3940(5)	389(6)	3355(3)
C(18)A	2981(5)	597(6)	3271(3)
C(19)A	2564(5)	926(7)	2679(3)
C(20)A	3084(4)	1028(6)	2160(3)
N(2)B	−389(3)	7796(5)	681(2)
B(2)B	688(5)	7370(7)	986(3)
O(2)B	931(3)	8281(4)	1497(2)
C(22)B	−706(4)	9015(7)	738(3)
C(23)B	−1575(5)	9363(8)	450(3)
C(24)B	−2135(5)	8489(9)	110(4)
C(25)B	−1808(5)	7241(8)	72(3)
C(26)B	−932(4)	6902(7)	357(3)
C(27)B	−134(5)	9978(7)	1144(4)
C(28)B	858(5)	9602(6)	1299(3)
C(29)B	591(4)	5950(6)	1306(3)
C(30)B	1189(5)	4948(7)	1190(3)
C(31)B	1151(5)	3752(7)	1493(3)
C(32)B	470(5)	3512(7)	1909(3)
C(33)B	−144(5)	4502(8)	2035(3)
C(34)B	−80(5)	5688(7)	1739(3)
C(35)B	1379(4)	7407(5)	420(3)
C(36)B	1143(4)	6985(6)	−210(3)
C(37)B	1797(5)	6961(6)	−666(3)
C(38)B	2704(5)	7379(7)	−504(3)
C(39)B	2957(5)	7812(7)	111(3)
C(40)B	2299(4)	7799(6)	563(3)

Crystal Structure Determination of Compounds **2a** *and* **4**.—
The X-ray data collections, structure resolutions and refinements were performed using a Nicolet R3m four circle automatic diffractometer at room temperature using Cu-Kα graphite-monochromated radiation ($\lambda = 1.541\ 78$ Å) which was operated in the $\theta:2\theta$ scanning mode. The cell parameters were established by least-squares adjustment of the setting angles of 25 machine centred strong reflections. The crystal data and the details of the data collections and structure analyses are summarized in Table 4. During the data collections two standard reflections were measured after measurement of 46 reflections as check reflections to monitor crystal deterioration and/or misalignment. The measured data were corrected for background, Lorentz and polarization effects, but not for absorption. The structures were solved by use of the direct methods package included in the software provided by the diffractometer manufacturer. After several cycles of anisotropic refinement of the non-hydrogen atoms, the hydrogen atoms were located in difference Fourier maps, placed at idealized geometries, at distances of 1.09 Å, as in previous studies,[2,3] and included in the structure factor calculation with their isotropic contribution [$\mu_{iso} = 0.08$ Å²]. The least-squares weighting scheme used is $w = 1/[\sigma^2(F_o) + G(F_o)^2]$, where σ is the standard deviation of observed amplitudes based on counting

statistics, and G is a variable adjusted after each cycle to minimize the function $\Sigma w(\Delta F)^2$. Some reflections were removed to improve the final fit. The final G value and other relevant refinement values are summarized in Table 4. The fractional atomic coordinates for all non-hydrogen atoms in **2a** and in **4** are given in Tables 5 and 6, respectively, whilst the relevant bond distances and bond angles for both compounds are given in Tables 2 and 3, respectively.*

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* Lists of hydrogen parameters, bond distances and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. For details of the CCDC scheme see 'Instructions for Authors,' *J. Chem. Soc., Perkin Trans. 2,* 1992, issue 1.

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