# Complexation of Arylboronates with Nitrogen-containing Bases

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Complex formation between a number of arylboronates and nitrogenous bases has been studied using different physical techniques. The results of quantitative measurements obtained from $^1H$ and $^{13}C$ n.m.r. spectroscopy, calorimetry, and polarimetry have been compared, and are in close agreement with each other. In all cases, two unknown variables have been determined by carrying out the experiments with varying concentrations of the esters and bases and treatment of the data thus generated by iterative procedures.

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Phenylboronic acid-based materials have found wide applications in recent years as stationary phases for the chromatographic separation of diols in aqueous media.[1] However, owing to a slower rate of equilibration and broadening of the peaks during chromatography, organic solvents are less commonly used for this purpose.[2]

During our previous investigations we have observed a marked enhancement in the rate of esterification between phenylboronic acid and diols in the presence of a catalytic amount of piperidine. In contrast, the effect of triethylamine as the base was insignificant.[3] The marked difference in the behaviour of these two bases has been attributed to the co-ordination of the nitrogen atom of piperidine with the boron centre which is inhibited due to the sterically crowded environment of triethylamine. Using suitably modified arylboronic acids with relatively non-bulky substituents on the nitrogen atom, a strong intramolecular B–N interaction along with high reactivity was observed.[4,5] It should be emphasized at this point that the B–N co-ordination on its own is not responsible for the rate enhancement of boronic acid and diol esterification. Instead, the nitrogen base can be regarded as a proton transfer agent held in closer proximity to the boron nucleus by the B–N interaction.

If this assumption is correct, the rate of the reaction of boronic acids with diols should be accelerated in the presence of those bases which are capable of entering into effective co-ordination with the boron atom. Certainly, it was considered worthwhile to carry out an in-depth study to verify this hypothesis. This paper thus presents the results of our systematic investigations on the complex formation of cyclic esters of some arylboronic acids with different amines in chloroform as the solvent medium.

## Experimental

*Materials.*—All the esters except (**1c**) were prepared following previously reported procedures,[6] while the latter was prepared according to reference 4. Nitrogen bases (AR grade) were obtained commercially and were used as received since it was found that rigorously dried and purified bases gave identical results.

*N.m.r. Studies.*—$^1H$ N.m.r. measurements were carried out with a Varian EM-390 spectrometer (90 MHz) coupled with an EM-3940 temperature-control unit. Temperature calibration was carried out using methanol or ethylene glycol following the manufacturer's specifications. $^1H$ N.m.r. chemical shift data of the ester units are as follows: δ (**1a**) 1.41 (3 H, d, $J$ 6 Hz, $CH_3$), 3.87* (1 H, m, H at 5), 4.43 (1 H, m, H at 5), and 4.7 (1 H, m, H at 4); δ (**1b**) 4.37* (4 H, s, H at 4 and 5); δ (**1c**) 1.07 (6 H, s, $CH_3$) and 3.82* (4 H, s, H at 4 and 6); δ (**1d**) 2.05 (2 H, t, $J$ 5.5 Hz) and 4.15* (4 H, t, $J$ 5.5 Hz); δ (**1e**) 1.45 (3 H, d, $J$ 7 Hz, $CH_3$), 3.92* (1 H, m, H at 5), 4.47 (1 H, m, H at 5), and 4.73 (1 H, m, H at 4).

The signals marked * were used for measuring the chemical shift differences. $^{13}C$ N.m.r. spectra were recorded on a Varian XL-100 n.m.r. spectrometer (25.2 MHz).

*Optical Rotations.*—Optical rotations of the samples were measured with a Perkin-Elmer 241 polarimeter using $CHCl_3$ as the solvent. The measurements were carried out at 365 nm and a temperature of 0 °C was maintained by circulation with a thermostatted bath.

*Calorimetry.*—The calorimetric studies were done in the batch cell of the calorimeter [LKB-Microcalorimeter 2107 (Sweden)]. A two-cell apparatus with two compartments per cell was used. Typically, the boronate (2 ml) and the nitrogen base (2 ml) dissolved in a known amount of the solvent were placed in the first cell, while the reference cell was loaded with base + solvent and pure solvent. The heat difference between the two cells upon mixing was measured and calibrated using the procedure recommended by the manufacturing company. In order to exclude dilution effects of the boronate, a second experiment with a boronate–solvent couple *versus* solvent–solvent was performed. This value, typically about 5—10% of the amount of heat in the first experiment, was deducted from the first value to give the heat of interaction between the nitrogen base and boron acceptor.

No attempt was made to attribute the measured heat of interaction to effects other than complexation effects. Additional effects like B-O and H-N binding are likely to be even weaker than the N-H and H-N binding effects considered.

When we used pyridine or triethylamine, both experimental values for the dilution couples base–boronate *vs.* base–solvent and boronate–solvent *vs.* solvent–solvent nearly cancelled each other. With respect to the usual heat of dilution, the observed effects were too small to justify calculation of complexation effects.

*Calculations.*—A program[7] was used for the iterative procedure of data treatment for calculation.

## Results and Discussion

The generalized interaction of cyclic boronates (**1**) with amines is given in equation (1). Though intermolecular boron complexes of general formula ($BX_3$–$NR_3$; X = halogen, hydrogen,

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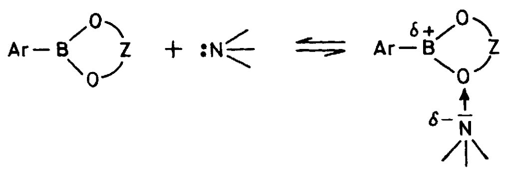

(1)

(1) (2) (3)

| | Ar | Z | | |
|---|---|---|---|---|
| (1) **a**; | Ph | $-CH_2-CHMe-$ | (2) **A**; | Piperidine |
| **b**; | Ph | $-CH_2-CH_2-$ | **B**; | 1,4-Ethanopiperidine |
| **c**; | Ph | $-CH_2-CMe_2-CH_2-$ | **C**; | Triethylamine |
| **d**; | Ph | $-CH_2-CH_2-CH_2-$ | **D**; | Pyridine |
| **e**; | $o$-$MeC_6H_4$ | $-CH_2-CHMe-$ | | |

alkyl) have been widely studied in the past,[8] literature on intermolecular adducts of the type $ArB(OR)_2 \cdot NR_3$ is relatively scarce.[9] Few of these adducts have been isolated since they undergo rapid dissociation on dissolution. Their instability has usually been explained as being due the reduced Lewis-acidity of boron as a result of π-back-donation from oxygen.[10] More precise quantitative data on this type of complexation phenomena have so far not appeared.

Our initial attempts to study the complex formation between 2-phenyl-4-methylborolane (**1a**) with piperidine (**2A**) in chloroform with the aid of vapour pressure osmometry[11] did not meet with much success. Although a slight indication of the formation of the complex was obtained, the effects were too negligible to allow any quantitative studies to determine the complexation constant $K$.

In the past, $^1H$ n.m.r. spectroscopic experiments have often been used for the study of weak complexation equilibria,[12–14] and this prompted us to use this technique for our purpose. The $^1H$ n.m.r. spectrum of (**1a**) was recorded in the presence of varying amounts of piperidine. Interestingly, increasing the piperidine concentration shifted the doublet of doublets of the alcohol moiety centred at 3.87 p.p.m. (A part of $CH_2O$) as well as the multiplets initially at 4.43 p.p.m. (B part of $CH_2O$) and 4.70 p.p.m. (CHO) slowly upfield. The chemical shifts of aromatic and methyl protons were also affected albeit to a lesser extent. When similar experiments were performed with triethylamine or pyridine, presumably non-complexing bases, no striking change in the chemical shift was observed. These observations can therefore not be attributed to a simple medium effect and hence can be interpreted as the consequence of the formation of a fast and reversible complex between piperidine and the phenylboronic ester (**1a**). For a more precise evaluation of the complexation constant $K$, the chemical shift differences relative to methylene dichloride as an internal standard were measured at different concentrations of (**1a**) and (**2A**), as shown in Table 1.

Closer examination of the data presented in Table 1 indicates the impracticability of separating the two unknown quantities, the complexation constant $K$ and the shift difference $\Delta\delta$ [between (**1a**) and (**3aA**)], from these data alone owing to the partial covering of the saturation curve.[15,16] Further increase in the concentration of piperidine would undesirably induce significant solvent effects,[5] and lowering the boronic ester concentration was not permissible due to the sensitivity limit of the n.m.r. spectrometer. At this juncture, an attempt was made to resolve the signals due to the complexed ester[17] by carrying out n.m.r. measurements at a lower temperature (−54 °C). These experiments did not enable us to resolve the above mentioned peaks; however, fortunately a large increase in the $\Delta\delta$ values (see Table 2) was observed. Assuming the δ values of both the complex (**3**) and the free ester to be temperature independent, a large increase in complexation at lower temperature is evident. Indeed, the temperature-dependent chemical shift differences of the pure ester were found to be less than 2 Hz in the temperature range under investigation. Owing to the formation of higher amounts of the complex at lower temperature, it was therefore possible to cover a larger portion of the saturation index as indicated by the data in Table 3.

Processing of the obtained data by iterative procedures[7] gave rise to a complexation constant $K = 2.7$ ($mol^{-1}$) at −11 °C and a value of 42 Hz (0.47 p.p.m.) for the shift difference of (**1a**) and the pure complex (**3aA**). This result is in reasonably good agreement with the data obtained at −54 °C, where nearly complete complexation is likely to occur. The $\Delta\delta$ value was subsequently used for calculating the complexation constant at 30 °C, which was found to be 0.30 ($mol^{-1}$). Similarly, the

**Table 1.** Chemical shift differences[a] in $^1H$ n.m.r. spectroscopy on addition of (**2A**) to (**1a**) at 30 °C

| (**1a**)/mol $l^{-1}$ | (**2A**)/mol $l^{-1}$ | $-\Delta$/Hz |
|---|---|---|
| 0.088 | 0.476 | 5.0 |
| 0.084 | 0.909 | 9.1 |
| 0.141 | 0.566 | 5.5 |
| 0.138 | 0.741 | 7.4 |
| 0.136 | 0.909 | 9.1 |
| 0.275 | 0.291 | 3.0 |
| 0.270 | 0.385 | 3.9 |
| 0.267 | 0.476 | 4.8 |
| 0.263 | 0.566 | 5.5 |
| 0.260 | 0.741 | 7.3 |

[a] The observed shift difference in the $^1H$ n.m.r. spectrum for the proton at C-4 of the borolane ring of (**1a**) on addition of (**2A**). In the absence of base it resonates at $\delta(CDCl_3)$ 3.87 at 30 °C. Given is the shift difference (in Hz) relative to the signal of methylene dichloride.

**Table 2.** Temperature dependence of shift differences[a]

| $T$/°C | $-\Delta$/Hz |
|---|---|
| 43 | 4.8 |
| 23 | 8.1 |
| 6 | 17.4 |
| −11 | 24.6 |
| −24 | 33.0 |
| −32 | 37.2 |
| −40 | 40.8 |
| −54 | 45.6 |

[a] The observed shift differences in the $^1H$ n.m.r. spectrum for the proton at C-4 of the borolane ring of (**1a**) at different temperatures. [(**1a**)] = 0.353 mol $l^{-1}$, [(**2A**)] = 0.741 mol $l^{-1}$ in $CDCl_3$.

**Table 3.** Chemical shift differences[a] in the $^1H$ n.m.r. spectrum of (**1a**) on addition of (**2A**) at −11 °C

| (**1a**)/mol $l^{-1}$ | (**2A**)/mol $l^{-1}$ | $-\Delta$/Hz |
|---|---|---|
| 0.120 | 0.099 | 7.3 |
| 0.120 | 0.147 | 10.2 |
| 0.119 | 0.196 | 13.0 |
| 0.118 | 0.291 | 17.3 |
| 0.116 | 0.385 | 21.5 |
| 0.114 | 0.566 | 26.0 |
| 0.374 | 0.196 | 8.9 |
| 0.370 | 0.291 | 12.3 |
| 0.366 | 0.385 | 15.8 |
| 0.359 | 0.566 | 21.6 |
| 0.353 | 0.741 | 25.8 |

[a] For the details see Table 1.

enthalpic and entropic terms for complex formation were deduced using the variable-temperature n.m.r. data and are presented in Table 7. The authenticity of the results obtained by this method was verified by comparison with the results from other independent experiments.

The availability of the optically active boronic ester (**1a**) suggested the use of polarimetric techniques, with the presumption that complexation with amines would bring about adequate change in the specific rotation of the resulting complex compared with the pure ester. To our knowledge, determination of complexation constants with the aid of polarimetric measurements has not been reported. This method is analogous to the n.m.r. spectroscopic technique since the chemical shift terms have merely been replaced by the optical rotation values.

Polarimetric measurements of mixtures of (**1a**) and (**2A**) showed a pronounced difference in optical rotation compared with that of pure (**1a**). As expected, control experiments in the presence of triethylamine and pyridine did not bring about any significant change in the optical rotation. The results are thus indicative of measurable changes in optical rotations of the pure ester (**1a**) and its piperidine complex (**3aA**). The data on polarimetric study performed at 0 °C are summarized in Table 4. Although the molar rotation of (**1a**) in chloroform is known to be concentration dependent, this problem was overcome by keeping the ester concentration constant in both the presence and absence of piperidine, while measuring the optical rotations. Using these data, the optical rotation of the complex (**3aA**) and the complexation constant $K$ were calculated, and were found to be $[M]^0_{365} = +228° \pm 20°$ ($c$ 1.0, $CHCl_3$) and $K = 1.3$ ($mol^{-1}$) respectively. The results obtained in this case are in good agreement with those from low-temperature $^1H$ n.m.r. studies.

**Table 4.** Differences in molar optical rotation[a] on addition of (**2A**) to (**1a**) at 0 °C

| (**1a**)/mol $l^{-1}$ | (**2A**)/mol $l^{-1}$ | $\Delta[M]_D$/° |
|---|---|---|
| 0.30 | 0.30 | +29.3 |
| 0.40 | 0.40 | +36.1 |
| 0.50 | 0.50 | +42.9 |
| 0.60 | 0.60 | +46.5 |
| 0.70 | 0.70 | +48.2 |
| 0.80 | 0.80 | +49.0 |
| 0.90 | 0.90 | +53.9 |
| 1.00 | 1.00 | +56.2 |

[a] Solvent: $CHCl_3$, optical rotation measured at 365 nm. Pure (**1a**) showed $[M]^0_{365} = +96.0°$ ($c$ 1.0, $CHCl_3$).

**Table 5.** Reaction enthalpies[a] on addition of (**2A**) to (**1a**) at 30 °C

| (**1a**)/mol $l^{-1}$ | (**2A**)/mol $l^{-1}$ | $-Q$/kJ $mol^{-1}$ |
|---|---|---|
| 0.339 | 0.167 | 0.489 |
| 0.339 | 0.339 | 0.903 |
| 1.003 | 1.003 | 6.604 |
| 0.669 | 0.669 | 3.252 |
| 0.447 | 0.447 | 1.496 |
| 0.226 | 0.226 | 0.435 |
| 0.500 | 0.500 | 1.940 |
| 0.503 | 0.995 | 3.386 |
| 0.800 | 0.800 | 4.318 |

[a] Measurement of reaction enthalpies was performed with a batch calorimeter (LKB 2107 Microcalorimetry System). Given is the heat evolved per mole (**1a**) used in the experiment.

Besides $^1H$ n.m.r. spectroscopy and polarimetry, calorimetric techniques can also be used for the study of the formation of molecular complexes.[18] Measuring the heat generated during the mixing of varying concentrations of (**1a**) and (**2A**) (Table 5) and subsequent treatment of the data in a manner similar to the one discussed above led to $K = 0.25$ ($mol^{-1}$) at 30 °C, which is in excellent agreement with the $^1H$ n.m.r. results. The enthalpy of the formation of (**3aA**) was found to be 36.8 kJ $mol^{-1}$.

N.m.r. studies of non-hydrogen nuclei have also been found to be helpful in deriving information about the formation of molecular complexes.[14,19,20] In our previous studies, we have observed the sensitivity of $^{11}B$-nuclei to complex formation, but only at a qualitative level.[3] Since the chemical shifts of aromatic carbon atoms of phenylboranes, especially the *para* carbon atom, are known to be sensitive to the electronic environment of boron,[21] $^{13}C$ n.m.r. spectroscopy could be considered as an alternative tool for the quantitative study of this phenomenon of complex formation. Indeed, addition of quinuclidine (**2B**) to a solution of (**1b**) caused the *para* carbon atom to resonate at higher field (128.40 p.p.m.) compared with 131.28 p.p.m. in the case of the pure ester. The shift differences for the *ortho* and *meta* carbons though observable were smaller (0.6 p.p.m.) and the *ipso* carbon resonance was usually not visible.[21] The control experiments using triethylamine in place of quinuclidine produced a negligibly small shift difference (0.04 p.p.m.). The data obtained are summarized in Table 6 and application of the usual iterative method yielded a value of 1.1 ($mol^{-1}$) at 30 °C for $K$ and the chemical shift value for the *para* carbon atom of the complex (**3aB**) was found to be 125.6 p.p.m. (131.28—5.63).

## Conclusions

The results of this study on complexation of cyclic boronic esters with amines using various techniques are summarized in Table 7. The salient features of this investigation can be summarized as follows.

(*a*) While cyclic phenyl boronates form weak molecular complexes with piperidine and quinuclidine, they fail to do so in the presence of pyridine and triethylamine. Quinuclidine-based complexes have a relatively higher stability than those obtained

**Table 6.** Chemical shift differences[a] in $^{13}C$ n.m.r. spectra on addition of (**2B**) to (**1b**) at 30 °C

| (**1b**)/mol $l^{-1}$ | (**2B**)/mol $l^{-1}$ | $\delta_C$(*ortho*) | $\delta_C$(*para*) | $\delta_C$(*meta*) | $-\Delta_p$/p.p.m. |
|---|---|---|---|---|---|
| 0.5 | | 134.67 | 131.27 | 127.67 | ≡0 |
| 0.5 | 1.0 $Et_3N$ | 134.71 | 131.28 | 127.66 | ~0 |
| 0.5 | 1.0 | 134.05 | 128.73 | 127.12 | 2.54 |
| 0.1 | 0.1 | 134.52 | 130.77 | 127.55 | 0.50 |
| 0.1 | 0.3 | 134.34 | 129.99 | 127.39 | 1.28 |
| 0.1 | 0.6 | 134.16 | 129.17 | 127.22 | 2.10 |
| 0.1 | 1.1 | 133.97 | 128.40 | 127.03 | 2.87 |
| 0.5 | 1.0 | 134.05 | 128.76 | 127.12 | 2.51 |
| 1.0 | 1.0 | 134.12 | 129.03 | 127.17 | 2.24 |
| 0.2 | 1.0 | 134.02 | 128.57 | 127.10 | 2.70 |

[a] Differences are given for the *para* carbon in the phenyl ring of (**1b**). Solvent: $CDCl_3$.

**Table** 7. Summary of the results from several complexing equilibria obtained by different methods

| Entry | Ester | Base | Method | $T$/°C | $K$ | $\Delta^a$/p.p.m. | $-\Delta H$/kJ mol$^{-1}$ | $-\Delta S$/J mol$^{-1}$ K | $R^{2\,b}$ |
|---|---|---|---|---|---|---|---|---|---|
| 1 | **(1a)** | **(2A)** | $^1$H N.m.r. | 30 | ~0.30$^c$ | | | | |
| 2 | **(1a)** | **(2A)** | $^1$H N.m.r. | −11 | 2.7 | 0.47 | 34.7 | 125 | 0.995 |
| 3 | **(1a)** | **(2A)** | Polarimetry | 0 | 1.3 | 132°$^d$ | 39.3 | 142 | 0.999 |
| 4 | **(1a)** | **(2A)** | Calorimetry | 30 | 0.25 | | 36.8 | 134 | |
| 5 | **(1a)** | **(2B)** | $^1$H N.m.r. | 30 | 0.8 | 0.50 | 33.0 | 113 | 0.993 |
| 6 | **(1b)** | **(2A)** | $^1$H N.m.r. | 30 | 0.57 | 0.55 | 35.1 | 121 | 0.993 |
| 7 | **(1b)** | **(2B)** | $^1$H N.m.r. | 30 | 1.3 | 0.64 | 38.0 | 121 | 0.991 |
| 8 | **(1b)** | **(2B)** | $^{13}$C N.m.r. | 30 | 1.1 | 5.6 | | | |
| 9 | **(1b)** | **(2B)** | Calorimetry | 30 | 1.5 | | 38.0 | 121 | |
| 10 | **(1e)** | **(2A)** | $^1$H N.m.r. | −45 | 1.6 | 0.51 | 30.5 | 130 | 0.998 |
| 11 | **(1d)** | **(2A)** | $^1$H N.m.r. | −50 | 1.3 | 0.70 | | | |
| 12 | **(1c)** | **(2A)** | $^1$H N.m.r. | −55 | 1.9 | 0.58 | | | |
| 13 | **(1c)** | **(2B)** | $^1$H N.m.r. | −65 | 8 | 0.55 | | | |

[a] Δ = difference of chemical shift between **(1)** and **(3)** obtained by an iterative method. Observed nuclei: **(1a)** 4-H of the borolane ring; **(1b)** 4-,5-H of the borolane ring; **(1c)** 4-,6-H of the borinane ring; **(1d)** 4-,6-H of the borinane ring; **(1e)** 4-H of the borolane ring; **(1b)** *p*-carbon of the phenyl ring. [b] $R$ = correlation coefficient. [c] Δδ Used from experiment at −11 °C. [d] Difference in molar optical rotation of **(1a)** and **(3aA)** at 365 nm in $CHCl_3$.

with piperidine (compare entries 4,5; 6,7; 12,13). (*b*) The formation and dissociation of the complexes is quite rapid on the n.m.r. time scale even at lower temperature. (*c*) The difficulties associated with the study of these types of weaker complexes at room temperature can be overcome by lowering the experimental temperature. Lower temperatures shift the equilibrium of equation (1) sufficiently to the right hand side to be determined. (*d*) The determination of the complexation constant using different experimental techniques ($^1$H and $^{13}$C n.m.r. spectroscopy polarimetry and calorimetry) gave rise to consistent values, illustrating the accuracy of our measurements. Thus a combination of these techniques would give a highly reliable $K$ value. (*e*) The stability of these complexes is highly sensitive to their steric environment. The steric hindrance imposed either by *ortho* substituents (entries 2 and 10) in the phenyl ring or due to the alcohol moiety (entries 4 and 6) considerably decrease the stability of the complexes; (*f*) Complexes formed by the five-membered-ring esters (borolanes) have relatively higher stability over those of six-membered-ring esters (borinanes) (entries 2 and 12; 2 and 11).

## Acknowledgements

Thanks are due to the Minister für Wissenschaft und Forschung des Landes Nordrhein-Westfalen and the Fonds der Chemischen Industrie for financial support.

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*Received* 19*th May* 1986; *Paper* 6/956