

# An Intramolecular Boron Nitrogen Lewis Acid Base Pair on a Rigid Naphthyl Backbone

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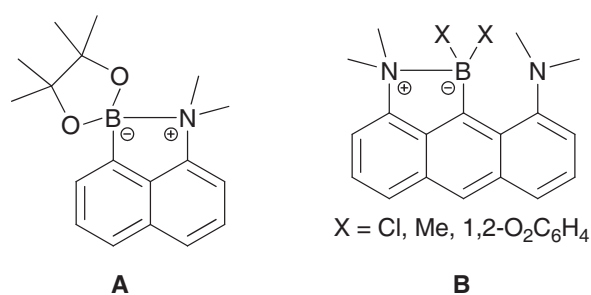
Dedicated to Professor Wolfgang Beck on the occasion of his 80<sup>th</sup> birthday

The reaction of  $(\text{C}_6\text{F}_5)_2\text{BCl}$  with 8-lithio-*N,N*-dimethyl-1-naphthylamine (**1**) afforded the five-membered ring system 8-bis(pentafluorophenyl)boryl-*N,N*-dimethyl-1-naphthylamine (**2**) with an intramolecular dative B–N bond. The compound was characterised by elemental analysis, NMR spectroscopy and single-crystal X-ray diffraction.

**Key words:** Lewis Acid, Boron, Nitrogen, Heterocycle, Naphthalene Derivate

## Introduction

In the field of polyfunctional Lewis acids [1] the pre-organisation of the Lewis acidic sites can be achieved employing rigid backbones. *Ortho*-substituted benzenes [2], *peri*-substituted naphthalene [3–6] and 1,8-substituted anthracene [7, 8] offer promising applications as such backbones in the field of host-guest chemistry [9]. Furthermore, these frameworks can induce unusual interactions between different functionalities. The combination of Lewis acid and base functions fixed to rigid backbones leads to the formation of dative bonds in constrained systems. Examples for such systems include boron nitrogen interactions in 1,8-substituted naphthalenes (**A**) [10] and 1,8,9-substituted



Scheme 1.

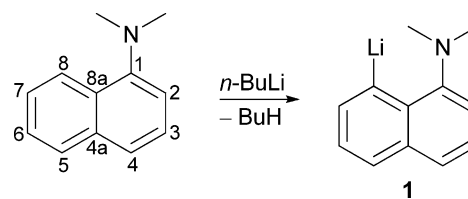
anthracenes (**B**) (Scheme 1) [11] with bond lengths of the dative B–N bonds of 1.89 and 1.67–1.81 Å, respectively.

In this contribution we present an 8-(dimethylamino)-1-naphthyl derivate with strongly electron-withdrawing pentafluorophenyl substituents at the boron atom.

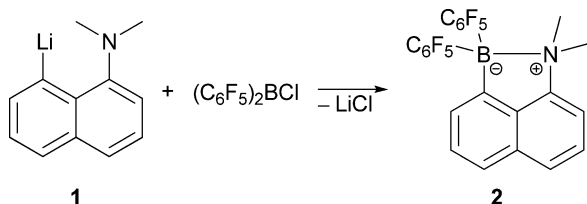
## Results and Discussion

The reaction of *N,N*-dimethyl-1-naphthylamine with *n*-butyllithium in Et<sub>2</sub>O leads to the regioselective lithiation in the 8-position (Scheme 2) [12]. In our experiments this product **1** could be isolated as a yellow solid in 70% yield.

Subsequent reaction of **1** with  $(\text{C}_6\text{F}_5)_2\text{BCl}$  [13] at –30 °C in toluene afforded the pentafluorophenyl-



Scheme 2. Reaction of *N,N*-dimethyl-1-naphthylamine with *n*-BuLi.



Scheme 3. Reaction of 8-lithio-*N,N*-dimethyl-1-naphthylamine (**1**) with  $(\text{C}_6\text{F}_5)_2\text{BCl}$ .

substituted borane **2** as a colourless solid in 87% yield (Scheme 3).

Compound **2** was characterised by elemental analysis and by NMR spectroscopy ( $^1\text{H}$ ,  $^{11}\text{B}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$ ). The  $^1\text{H}$  NMR spectrum shows signals for the protons of the naphthalene ring between  $\delta = 7.60$  and 6.52 ppm. The singlet for the methyl group is detected at  $\delta = 2.17$  ppm. The corresponding signals of the naphthalene ring in the  $^{13}\text{C}$  NMR spectrum are observed between  $\delta = 152.2$  and 111.3 ppm. A broad resonance for the carbon atom in 8-position at  $\delta = 145.7$  ppm indicates the formation of a B–C bond. In the  $^{11}\text{B}$  NMR spectrum a single resonance at  $\delta = 4.8$  ppm ( $\nu_{1/2} = 180$  Hz) is observed. The  $^{19}\text{F}$  NMR signals of the  $\text{C}_6\text{F}_5$  groups are detected at  $\delta = -162.7$  (*m*- $\text{C}_6\text{F}_5$ ),  $-156.1$  (*p*- $\text{C}_6\text{F}_5$ ) and  $-127.7$  ppm (*o*- $\text{C}_6\text{F}_5$ ). The small separation of the *p*- and *m*- $\text{C}_6\text{F}_5$   $^{19}\text{F}$  resonances indicates the presence of a tetra-coordinate boron atom [14–16].

The NMR spectroscopic data are consistent with the formation of an intramolecular coordination of the

dimethylamino group to the boron atom which leads to a five-membered ring structure. This was subsequently confirmed by X-ray diffraction. Single crystals of **2** were obtained from a concentrated toluene solution at  $-30^\circ\text{C}$ . Compound **2** crystallises in the orthorhombic space group *Pbca*; its structure is displayed in Fig. 1; selected structural parameters are listed in Table 1.

The structure of **2** features a five-membered ring system. Due to the rigid naphthalene backbone the B/N ring does not exhibit a typical envelope conformation as it is observed in the related five-membered ring system with a dative B–N bond,  $(\text{C}_6\text{F}_5)_2\text{B}(\text{CH}_2)_3\text{NMe}_2$  [17]. By contrast, compound **2** shows only a small deviation from planarity. The torsion angles  $\text{B}(1)\text{--C}(13)\text{--C}(22)\text{--C}(21)$  and  $\text{N}(1)\text{--C}(21)\text{--C}(22)\text{--C}(13)$  have values of  $6.4(2)^\circ$  and  $5.9(2)^\circ$ , respectively. The length of the bond created by the strongly Lewis acidic boron atom and the nitrogen atom is  $1.742(2)$  Å (Table 1). This is remarkably longer than the B–N bond length in  $(\text{C}_6\text{F}_5)_2\text{B}(\text{CH}_2)_3\text{NMe}_2$  [ $1.672(2)$  Å] and is a consequence of the ring strain established by the rigid naphthyl backbone which prevents a shorter B–N contact. According to the higher electronegativity of the boron substituents, the B–N bond in **2** is clearly shorter than that in the related pinacol-substituted species,  $(\text{Me}_2\text{N})\text{C}_{10}\text{H}_6\text{B}(\text{Pin})$  (**A**, Scheme 1) ( $1.89$  Å) [10]. A comparison with the derivatives of 1,8-bis(dimethylamino)-9-borylanthracene (**B**, Scheme 1) reveals values for the B–N bond of  $1.809(2)$ ,  $1.739(2)$  and  $1.664(3)$  Å

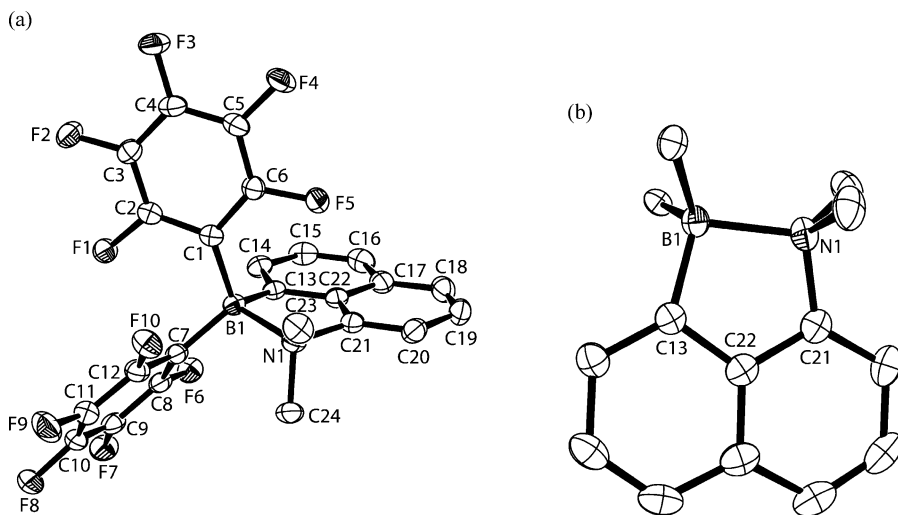


Fig. 1. (a) Molecular structure of **2** in the crystal. Hydrogen atoms are omitted for clarity; (b) illustration of the B–C<sub>3</sub>–N ring geometry of **2**.

|                  |          |                   |          |
|------------------|----------|-------------------|----------|
| N(1)–C(21)       | 1.488(2) | C(13)–B(1)–C(7)   | 119.3(1) |
| N(1)–C(23)       | 1.506(2) | C(13)–B(1)–C(1)   | 106.6(1) |
| N(1)–C(24)       | 1.508(2) | C(7)–B(1)–C(1)    | 112.1(1) |
| N(1)–B(1)        | 1.742(2) | C(13)–B(1)–N(1)   | 97.7(1)  |
| B(1)–C(13)       | 1.609(2) | C(7)–B(1)–N(1)    | 107.2(1) |
| B(1)–C(7)        | 1.633(2) | C(1)–B(1)–N(1)    | 113.4(1) |
| B(1)–C(1)        | 1.650(2) | C(22)–C(13)–B(1)  | 109.6(1) |
| C(21)–N(1)–C(23) | 112.1(1) | C(14)–C(13)–B(1)  | 133.1(1) |
| C(21)–N(1)–C(24) | 105.3(1) | C(22)–C(21)–N(1)  | 110.6(1) |
| C(23)–N(1)–C(24) | 106.9(1) | C(20)–C(21)–N(1)  | 127.5(1) |
| C(21)–N(1)–B(1)  | 104.4(1) | C(21)–C(22)–C(13) | 114.9(1) |
| C(23)–N(1)–B(1)  | 117.4(1) | C(14)–C(13)–C(22) | 116.7(1) |
| C(24)–N(1)–B(1)  | 110.3(1) | C(20)–C(21)–C(22) | 121.9(1) |

Table 1. Selected bond lengths (Å) and angles (deg) for **2** with estimated standard deviations in parentheses.

for 1,2-O<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, Me and Cl substituents at boron, respectively.

As a consequence of the formation of the dative B–N bond the bond angles about C(13) and C(21) feature distorted geometries. The bond angles C(22)–C(13)–B(1) and C(22)–C(21)–N(1) within the five-membered ring system have small values of 109.6(1) and 110.6(1)°, respectively. Consequently, the angles C(14)–C(13)–B(1) and C(20)–C(21)–N(1) adopt larger values with 133.1(1) and 127.5(1)°. Furthermore, the formation of the five-membered ring leads to a distortion of the naphthalene backbone. The intramolecular C···C distance between C(13) and C(21) has a value of 2.37 Å and is thus distinctly shorter than in unsubstituted naphthalene with a value of 2.48 Å [18]. Both, the C(14)–C(13)–C(22) [116.7(1)°] and the C(20)–C(21)–C(22) angle [121.9(1)°] show a distortion in comparison to unsubstituted naphthalene, in which this angle is 119.8° [18]. Deformations of the molecular geometry are also observed in many substituted aryl derivatives [19] and can be explained by the VSEPR model. The electronegative nitrogen atom requires less space, the electropositive boron atom more space than a hydrogen atom at the C atoms which leads to an increase and decrease of these bond angles, respectively.

The geometries about the boron and the nitrogen atom in **2** are distorted tetrahedral. The smallest bond angle at the boron and the nitrogen atom is observed within the five-membered ring system with values of 97.7(1) [C(13)–B(1)–N(1)] and 104.4(1)° [C(21)–N(1)–B(1)], respectively. All other bond angles about the boron and nitrogen atom exhibit larger values which range up to 119.3(1) [C(13)–B(1)–C(7)] and 117.4(1)° [C(23)–N(1)–B(1)], respectively.

The endocyclic B–C bond [C(13)–B(1)] has a length of 1.609(2) Å and is thus shorter than the B–C bond

in (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>B(CH<sub>2</sub>)<sub>3</sub>NMe<sub>2</sub> [1.637(2) Å]. The two N–C bonds of the NMe<sub>2</sub> fragment have values of 1.506(2) and 1.508(2) Å for N(1)–C(23) and N(1)–C(24), respectively. This is slightly longer than the endocyclic N(1)–C(21) bond at 1.488(2) Å.

## Conclusion

The reaction of the chloroborane (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>BCl with 8-lithio-*N,N*-dimethyl-1-naphthylamine (**1**) affords a five-membered B/N ring system with a rigid naphthalene backbone (**2**). Single-crystal X-ray diffraction has revealed a strained ring system with an intramolecular dative B–N bond length of 1.742(2) Å. A comparison with data for other substitution patterns at boron suggests that this B–N distance is largely determined by the substituent electronegativity.

## Experimental Section

All manipulations were performed under a rigorously dried inert atmosphere of argon using standard Schlenk and glove-box techniques. Toluene was dried with potassium before being employed in reactions. C<sub>6</sub>D<sub>6</sub> was dried with Na/K alloy and degassed. (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>BCl was synthesised according to a literature procedure [13]. *N,N*-Dimethyl-1-naphthylamine was purchased from ABCR and degassed prior to use. NMR measurements were undertaken with Bruker DRX 500 and Avance 500 instruments. NMR chemical shifts were referenced to the residual peaks of the protons of the used solvents (<sup>1</sup>H, <sup>13</sup>C) or externally (<sup>11</sup>B, BF<sub>3</sub>·OEt<sub>2</sub>; <sup>19</sup>F, CFC<sub>l</sub><sub>3</sub>). Elemental analysis was performed by using a CHNS elemental analyser HEKAtech EURO EA.

### 8-Lithio-*N,N*-dimethyl-1-naphthylamine (**1**)

According to a literature procedure [12], *n*-BuLi (34 mL, 54 mmol, 4.5 eq, 1.6 M) was added to a solution of *N,N*-dimethyl-1-naphthylamine (2.0 g, 12 mmol) in 25 mL Et<sub>2</sub>O

at ambient temperature. The reaction mixture was stirred for 48 h, and the resulting solid was filtered off, washed with 3 mL Et<sub>2</sub>O and dried in a vacuum. The product was obtained as a yellow solid and used without further characterisation. Yield: 1.5 g (70%).

*8-Bis(pentafluorophenyl)boryl-N,N-dimethyl-1-naphthylamine (2)*

To a solution of 8-lithio-*N,N*-dimethyl-1-naphthylamine (**1**) (74 mg, 0.4 mmol) in 4 mL toluene was added a solution of (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>BCl (150 mg, 0.4 mmol) in 4 mL toluene at –30 °C. After warming to ambient temperature the reaction mixture was stirred over night and filtered. The solvent was removed in a vacuum to leave a colourless solid. Crystals suitable for X-ray diffraction were obtained from a concentrated toluene solution at –30 °C. Yield: 173 mg (87%). –<sup>1</sup>H NMR (500.1 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ = 7.60 (d, *J* = 6.8 Hz, 1H, H-7), 7.52 (d, *J* = 8.3 Hz, 1H, H-4), 7.48 (d, *J* = 8.0 Hz, 1H, H-5), 7.40 (dd, *J* = 6.8 Hz, *J* = 8.0 Hz, 1H, H-6), 7.14 (m, 1H, H-3), 6.52 (d, *J* = 7.4 Hz, 1H, H-2), 2.17 ppm (s, 6H, CH<sub>3</sub>). –<sup>11</sup>B{<sup>1</sup>H} NMR (160.4 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ = 4.8 ppm (*v*<sub>1/2</sub> = 180 Hz). –<sup>13</sup>C{<sup>1</sup>H} NMR (125.7 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ = 152.2 (C-1), 148.5 (dm, <sup>1</sup>*J*<sub>CF</sub> = 241.1 Hz, C<sub>6</sub>F<sub>5</sub>), 145.7 (br, C-8), 140.3 (dm, <sup>1</sup>*J*<sub>CF</sub> = 251.3 Hz, C<sub>6</sub>F<sub>5</sub>), 137.7 (dm, <sup>1</sup>*J*<sub>CF</sub> = 249.9 Hz, C<sub>6</sub>F<sub>5</sub>), 132.9 (C-4a), 132.3 (C-8a), 129.9 (C-6), 128.5 (C-7), 126.5 (C-4), 125.6 (C-3), 123.8 (C-5), 118.0 (br, *i*-C<sub>6</sub>F<sub>5</sub>), 111.3 (C-2), 51.2 ppm (CH<sub>3</sub>). –<sup>19</sup>F NMR (470.5 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ = –162.7 (m, 4F, *m*-C<sub>6</sub>F<sub>5</sub>), –156.1 (t, <sup>3</sup>*J*<sub>FF</sub> = 20.8 Hz, 2F, *p*-C<sub>6</sub>F<sub>5</sub>), –127.7 ppm (m, 2F, *o*-C<sub>6</sub>F<sub>5</sub>). – C<sub>24</sub>H<sub>12</sub>BF<sub>10</sub>N (515.15): calcd. C 55.96, H 2.35, N 2.72; found C 53.03, H 2.36, N 3.04.

*X-Ray crystallographic structure determination*

A single crystal suitable for X-ray diffraction measurement was picked inside a glove-box, suspended in a paratone-N/paraffin oil mixture, mounted on a glass fibre and transferred onto the goniometer of the Bruker Nonius Kappa CCD

Table 2. Crystal structure data for **2**.

|   |  |
|---|--|
| Formula   | C <sub>24</sub> H <sub>12</sub> BF <sub>10</sub> N |
| <i>M<sub>r</sub></i>  | 515.16   |
| Crystal size, mm <sup>3</sup>   | 0.72 × 0.72 × 0.60                                 |
| Crystal system  | orthorhombic                                       |
| Space group   | <i>Pbca</i>  |
| <i>a</i> , Å  | 7.6624(2)  |
| <i>b</i> , Å  | 21.7295(5)   |
| <i>c</i> , Å  | 24.5402(6)   |
| <i>V</i> , Å <sup>3</sup>   | 4085.95(17)  |
| <i>Z</i>  | 8  |
| <i>D</i> <sub>calcd.</sub> , g cm <sup>–3</sup>                         | 1.68   |
| <i>μ</i> (MoK <sub>α</sub> ), cm <sup>–1</sup>                          | 0.2  |
| <i>F</i> (000), e   | 2064   |
| <i>hkl</i> range  | ±10, ±30, ±34                                      |
| ((sin θ)/λ) <sub>max</sub> , Å <sup>–1</sup>                            | 0.703  |
| Refl. measured / unique / <i>R</i> <sub>int</sub>                       | 66732 / 5950 / 0.063                               |
| Param. refined  | 327  |
| <i>R</i> ( <i>F</i> ) / <i>wR</i> ( <i>F</i> <sup>2</sup> ) (all refs.) | 0.0666 / 0.0968                                    |
| GoF ( <i>F</i> <sup>2</sup> )   | 1.063  |
| Δρ <sub>fin</sub> (max / min), e Å <sup>–3</sup>                        | 0.27 / –0.24                                       |

diffractometer. The measurement was carried out with MoK<sub>α</sub> radiation (λ = 0.71073 Å). The structure was solved by Direct Methods and refined by full-matrix least-squares cycles (program SHELXS/L-97 [20]). Further details of the crystal structure data are given in Table 2.

CCDC 873670 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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