N-Methyl-anilinoborane: Monomer, Dimers, Molecular Structure, and Rearrangement into μ-(N-Methyl-anilino)diborane(6). A Convenient Route to μ-(Amino)diboranes(6)

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Abstract. *N*-Methyl-anilinoborane exists as a dimer in the solid state, shown by X-ray structural analysis, whereas in solution, a monomerdimer equilibrium is present (¹H, ¹¹B and ¹³C NMR spectroscopy). The phenyl groups are in *trans* positions in the crystalline dimer. In solution, both possible isomers of the dimer exist in a *trans/cis* ratio of 3:2, in agreement with the energies for calculated optimized geometries

Introduction

Aminoboranes of the general formula R^1R^2N –BH₂ (monomers or dimers) are well known and readily available by various standard procedures.^[1–3] It was shown that they can also be obtained by transition metal catalyzed dehydrocoupling starting from the corresponding amine borane adducts R^1R^2NH –BH₃.^[4,5] Potential applications of aminoboranes focus on the presence of B–H bonds, which invite to studies of aminoboranes as precursors of BN ceramic materials.^[6] Recently, some aspects of the synthetic potential of aminoboranes have been investigated,^[7,8] of which the Pd-catalyzed C–B bond formation with aryl halides is particularly attractive.^[7]

The present knowledge on thermally induced reactions of secondary amines R^1R^2 NH with Et₃N–BH₃ is summarized in Scheme 1. In principle, this method appears to be the most convenient route towards monomeric aminoboranes R^1R^2 N–BH₂ in bulk quantities (Scheme 1a), if the groups R^1 and R^2 are secondary alkyl groups.^[2] Sterically less demanding substituents lead to dimers (Scheme 1b). Problems are encountered if the rate of the reaction of R^1R^2 N–BH₂ with Et₃N–BH₃ is comparable to that of the starting amine R^1R^2 NH with Et₃N–BH₃, typical if one or both groups R^1 , R^2 are aryl groups (Scheme 1c).^[2] Although appropriate changes in the experimental procedure (e.g. a large excess of Et₃N–BH₃) help to suppress the competitive formation of $(R^1R^2N)_2$ BH, the desired

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[B3LYP/6-311+G(d,p) level of theory]. In solution, the monomer is rather reactive and disproportionates completely after several days to give a 1:1 mixture of bis(*N*-methyl-anilino)borane and μ -(N-methylanilino)diborane(6). This observation led to a convenient high yield synthesis of μ -(amino)diborane(6) derivatives, starting from bis(amino)boranes and borane/THF.

products R^1R^2N -BH₂ (e.g. R^1 or R^2 = Ph), monomers or dimers (Scheme 1b), are difficult to obtain in pure state,^[2] and therefore, their properties in solution and in the solid state are not well studied.^[2,3a] However, such aminoboranes deserve interest, since dimers, if present, can readily dissociate because of the reduced basicity of the nitrogen atoms. The monomers thus formed may be more reactive than dialkylaminoboranes owing to reduced B–N(pp) π interactions, considering the aryl group as a π acceptor competing successfully with the three-coordinate boron atom for the lone pair of electrons at the nitrogen atom. In this work, we report the molecular structure of *N*methyl-anilinoborane dimer (**1**₂) and its behavior in solution. The latter part of this study prompted us to develop a new route to μ -(amino)diborane(6) derivatives.

$$R^{1} = \text{Me}; R^{2} = \text{Ph}$$

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$$R^{1}R^{2}\text{NH} + \text{Et}_{3}\text{N-BH}_{3} \xrightarrow{\frac{>100 \ ^{\circ}\text{C}}{-H_{2}}} R^{1}_{2} + \frac{(\text{C})}{R^{2}} + \frac{(\text{C})}{R^{2}} + \frac{(\text{C})}{R^{2}} + \frac{(\text{Me})}{R^{2}} + \frac{(\text{Me})}{R^$$

Scheme 1. Thermally induced reaction of secondary amines with Et_3N –BH₃ to give aminoboranes, which may be monomers or dimers. In the case of R^1 = Me, R^2 = Ph, the reaction may proceed to give the bis(N-methyl-anilino)borane.

Results and Discussion

N-Methyl-anilinoborane, Structure and Properties

N-Methyl-anilinoborane (1_2) was obtained as described,^[2] and colorless crystals, grown from hexane, were studied by

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X-ray diffraction. The molecular structure (Figure 1) shows a dimer, in which the phenyl groups are in trans positions. Intermolecular interactions appear to be negligible. All bond lengths and angles are in the expected ranges, similar as in other known molecular structures of aminoborane dimers.^[3a,9] The four-membered ring is planar within the experimental error. Interestingly, the optimized calculated [B3LYP/6-311+G(d,p) level of theory]^[10] geometry of 1_2 reveals a nonplanar ring (folding angle 15.1°), where all bond lengths and angles are in well agreement with the experimental data. Similarly, the four-membered ring in the dimer of dimethylaminoborane [Me₂N–BH₂]₂ is planar in the solid state,^[9] whereas the calculated gas-phase geometry was found to be a minimum in energy with a non-planar four-membered ring (folding angle of 5°). In the parent aminoborane dimer [H₂N-BH₂]₂, the calculated gas phase geometry reveals a planar ring. Although packing forces in the crystal lattice may account for differences between calculated and experimental structures, the driving forces for non-planar four-membered rings are not readily apparent.



Figure 1. Molecular structure of 1_2 (ORTEP, 40 % probability, hydrogen atoms were omitted, except for the hydrogen atoms linked to boron). Selected bond lengths /Å and angles /°: N1–C1 1.4642(16), N1–C7 1.4924(17), N1–B1 1.6155(18), C1–N1–C7 107.59(10), C1–N1–B1 117.71(10), C7–N1–B1 113.30(11), C1–N1–B1 118.17(11), C7–N1–B1 112.55(10), B1–N1–B1 86.56(10), N1–B1–N1 93.44(10).

When crystalline material of pure $\mathbf{1}_2$ was dissolved in [D₈]toluene, ¹H-, ¹¹B-, and ¹³C NMR spectra showed more signals than expected. In the ¹H NMR spectrum (Figure 2), recorded immediately after dissolution, selective ¹¹B decoupling at $\delta^{11}B = 40$ (for the monomer 1) led to sharpening of two ¹H(BH) NMR signals, as expected for the two different ¹H(BH) nuclei. These signals are significantly broadened owing to slow rotation of the amino group about the B-N axis. The energy of activation ΔG^{\neq} for this process can be estimated^[11] to $\Delta G^{\neq}_{(310 \text{ K})} = 61 \pm 1 \text{ kJ} \cdot \text{mol}^{-1}$, which is rather low.^[12] Thus, for the parent aminoborane H₂N–BH₂ this rotational energy barrier was calculated as $\Delta G^{\neq} \approx 117-$ 143 kJ·mol⁻¹, using different theoretical methods.^[12a] The analogous selective ¹H{¹¹B} experiment for $\delta^{11}B = 3$ (for the dimer 1_2) caused sharpening of three ¹H(BH) NMR signals, of which two are in a 1:1 ratio [doublets with ${}^{2}J({}^{1}HB^{1}H) = 3.8$ Hz (calcd. -3.9 Hz)] and belong to the isomer cis-1'₂ as indicated. The dimers trans-1₂ and cis-1'₂ are present in a ratio of \approx 3:2.

From the calculations of the optimized geometries, it follows that trans- 1_2 is slightly more stable than cis- $1'_2$, and the energy of two molecules of 1 is slightly higher than that of 1_2 . This reflects approximately the situation in solution, although the differences in energy are small (< $4 \text{ kJ} \cdot \text{mol}^{-1}$). After several hours, new signals can be detected, which arise from rearrangement into bis(N-methyanilno)borane 2 and μ -(N-methylanilino)borane(6) **3** (vide infra). The ${}^{1}H{}^{11}B{}$ NMR spectrum of **3** shows three ¹H(BH) NMR signals in a ratio of 2:2:1, with the resonance for the unique bridging ¹H nucleus at lowest frequency (see Exp. Sect.). This signal is split into a quintet with ${}^{2}J({}^{1}H(\mu)B^{1}H) = 8.5$ Hz, in agreement with the calculated values (-8.3 Hz and -8.7 Hz). Both ¹H NMR signals for the terminal B⁻¹H nuclei appear as doublets $(^{2}J(^{1}H(u)B^{1}H) =$ 8.5 Hz) without further fine structure. This is surprising at first sight, since one would expect further splitting owing to two bond coupling between the different terminal B-1H nuclei. However, according to calculations this coupling constant is predicted to be small (-0.1 Hz), and therefore, the splitting would not be resolved experimentally.



Figure 2. 399.8 MHz ¹H NMR spectra of freshly dissolved 1_2 (in [D₆]toluene, 23 °C), showing the region of ¹H(BH) NMR signals.

The ¹¹B NMR spectra (Figure 3), measured within less than 10 min after dissolving crystals of 1_2 , indicated the presence of the dimer 1_2 and the monomer 1, and there were already fairly weak signals, assigned to bis(*N*-methyl-anilino)borane 2, and to μ -(*N*-methyl-anilino)diborane(6) 3. All NMR spectroscopic assignments are in full agreement with literature data,^[13] and all chemical shifts agree well with those calculated



on the basis of optimized geometries.^[14] The liquid compounds 2 and 3 were definitely not present in the solid 1_2 , which had a sharp melting point (65–66 °C, as reported^[2]). The signals for 2 and 3 were growing at the expense of those for dimers and the monomer, and finally after several days, conversion of 1 (or its dimers) into a 1:1 mixture of 2 and 3 was almost complete (> 95 %) (Scheme 2).



Figure 3. 128.4 MHz ¹H coupled ¹¹B NMR spectrum of the dimer 1_2 (in [D₈]toluene, 23 °C), measured less than 10 min after dissolution, showing a triplet signal for 1, a doublet signal for 2, a poorly resolved triplet for 1_2 , and the typical doublet signals of a triplet for 3. A quartet signal (unlabeled) may arise from an amine borane adduct (Me(Ph)NH–BH₃) because of traces of hydrolysis.



Scheme 2. Rearrangement of *N*-methyl-anilinoborane 1 into μ -*N*-methyl-anilino-diborane.

The inspection of ¹³C NMR spectra (Figure 4) gave analogous information, which confirms the evidence from ¹H NMR spectra (Figure 2) that 1_2 in solution is accompanied by the isomer $1'_2$, in which the phenyl groups occupy *cis* positions.

μ-(Amino)diborane(6) Derivatives

Apparently, aminoboranes of type 1 and 2, provide an easy access to μ -(amino)diborane(6) derivatives, for which various synthetic methods have been proposed, most of them tedious and rather inefficient,^[15] involving e.g. the handling of gaseous diborane(6). There is a renewed interest in µ-(amino)diboranes(6) in the context of H₃N-BH₃ as a potential hydrogen storage material^[16] as well as μ -(amino)diborates(1⁻) as useful ligands, an alternative to [BH4], in transition metal complexes.^[17] Thus, recently a straightforward synthesis of the parent μ -(NH₂)B₂H₅ from H₃N–BH₃ and BH₃ in THF has been reported.^[18] Since bis(amino)boranes of type 2 are readily accessible.^[1-3] fairly unreactive, and stable for prolonged periods of time at ambient temperature, we performed preliminary experiments in order to convert these compounds into the respective µ-(amino)diboranes(6), as shown here for bis(diethylamino)- (4a) and dipyrrolidinoborane (4b) (Scheme 3).



Scheme 3. μ-(Diethylamino)- and μ-(pyrrolidino)diborane(6) from the reactions of bis(amino)boranes or aminoborane dimers with BH₃/THF.

The fast reaction of **4a**,**b** with BH₃/THF under mild conditions suggests that the first step involves exchange to give $R^{1}_{2}N$ -BH₂ as a short lived monomer, which is trapped immediately by BH₃ to give μ -(amino)diboranes(6) **6a**,**b**. Even without optimizing the reaction conditions, only minor quantities



Figure 4. 100.4 MHz ${}^{13}C{}^{1}H$ NMR spectrum of a solution of 1_2 in [D₈]toluene, 23 °C), showing the regions of the ${}^{13}C(Ph-ipso)$ and the ${}^{13}C(NMe)$ resonances, 10 min (bottom traces) and 12 h after dissolution (top traces). Spurious signals (unlabeled) appear after several hours.

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(< 5 %) of the aminoborane dimers 5a,b were formed, according to the ¹¹B NMR spectra. In contrast, starting from the dimers **5a**,**b**, also readily available, [1-3] the analogous conversion into **6a,b** proceeded slowly (up to 24 h), even upon heating. Under these conditions, the reactions were accompanied by formation of (BuO)₂BH and B(OBu)₃ due to THF-cleavage. The proposed intermediacy of R^{1} ₂N–BH₂ as a monomer is further supported by the observation that sBu₂N-BH₂ 7, which has no tendency for dimerization,^[2] reacts smoothly at room temperature, in spite of the bulky sBu groups, with BH₃/THF to afford μ -(sBu₂N)B₂H₅ 8 in essentially quantitative yield after several hours (Scheme 4). It should be noted that 7 survives in a toluene solution heating at 110 °C for several days, without any trace of disproportionation. The same is true for the dimers 5a,b. Therefore, it can be safely assumed that the N-methyl-anilino group in 1 favors disproportionation into 2 and **3**. In previous work^[2] (see also Scheme 1), formation of μ -(*N*-methylanilino)diborane(6) **3** was not observed owing to the presence of Et₃N which, in the absence of a stronger base like $R^1 R^2$ NH, traps all "free" BH₃. In comparison with Et₃N, THF is a weaker base towards BH₃ and releases BH₃ for reactions with amino- and bis(amino)boranes.



Scheme 4. Quantitative conversion of the strictly monomeric aminoborane 7 into μ -(amino)diborane(6) (8).

Conclusions

The title compound is a dimer in the solid state, whereas in solution a monomer–dimer equilibrium is present. Reduced BN(pp) π bonding in the *N*-methyl-anilinoborane monomer apparently gives rise to disproportionation. In the absence of another base, borane BH₃ is trapped by bis(*N*-methyl-anilino)borane and *N*-methyl-anilinoborane to give finally μ -(*N*-methylanilino)diborane(6). Using BH₃/THF as the source for borane, it proved possible to convert readily available, otherwise fairly unreactive and stable bis(amino)boranes into the respective reactive μ -(amino)diborane(6) derivatives.

Experimental Section

Starting Materials, Measurements, and Calculations

N-methyl-anilinoborane (1), bis(*N*-methyl-anilino)borane (2), bis(diethylamino)borane (4a), dipyrrolidinoborane (4b), diethylaminoborane dimer (5a), pyrrolidinoborane dimer (5b), and bis(sec-butyl)aminoborane (7) were prepared as described,^[2] and a THF solution of BH₃/ THF (1 M) (Aldrich) was used as received. The 1:1 mixture containing 2 and μ -(*N*-methyl-anilino)diborane(6) (3) was obtained as a colorless oil by dissolving crystals of 1₂ in toluene, keeping the solution at r. t. for 8 d, and removing all readily volatile materials in vacuo (10⁻¹ Torr). Samples of μ -(diethylamino)- (6a) and μ -(pyrrolidino)diborane(6) (6b) were prepared by adding three equivalents of BH₃/THF to the respective bis(amino)borane at -78 °C, and warming the mixture to room temp. The reactions were essentially complete after 1 h at room temp. NMR spectra (¹H, ¹¹B, and ¹³C NMR) were measured from solutions in [D8]toluene with samples in 5 mm tubes at 23 \pm 1 °C, using Bruker ARX-250 and AMX-500, and Varian Inova 400 spectrometers. Chemical shifts (ppm) are given with respect to Me₄Si $[\delta^{1}H (C_{6}D_{5}CD_{2} H) = 2.08; \delta^{13}C (C_{6}D_{5}CD_{3}) = 20.4],$ external BF₃-OEt₂ [$\delta^{11}B = 0$ for $\Xi(^{11}B) = 32.083971$ MHz]; chemical shifts $\delta^{1}H$ are given to \pm 0.03, δ^{13} C to \pm 0.1; and δ^{11} B to \pm 0.3. The melting points (uncorrected) were determined using a Büchi 510 melting point apparatus. Calculations were carried out using the Gaussian 03 (Revision.B02) program package^[10] by optimizing geometries at the B3LYP/6-311+G(d,p) level of theory. The structures correspond to minima in energy as indicated by the absence of imaginary frequencies by computing force constants and vibrational frequencies. Chemical shifts (GIAO^[19]) and coupling constants^[20] were calculated at the same level of theory.

12: m.p. 65–66 °C, ¹H NMR (399.8 MHz): δ = 2.51 (s, 6 H, NMe), 3.69 (s, 4 H, BH₂) 7.5–6.80 (m, NPh, overlap with signals from monomer and other dimer). ¹³C NMR (125.8 MHz): δ = 56.2 (NMe), 154.5 (NPh-*i*), 124.7 (NPh-*o*), 129.0 (NPh-*m*), 124.3 (NPh-*p*). ¹¹B NMR (128.4 MHz): δ = 4.3 (t, ¹J(¹¹B, ¹H) = 117 Hz).

1'₂: ¹**H NMR** (399.8 MHz): $\delta = 2.78$ (s, 6 H, NMe), 3.81, 3.48 [d, d, 4 H, ${}^{2}J({}^{1}\text{HB}{}^{1}\text{H}) = 3.8$ Hz, BH₂], 7.5–6.80 (m, NPh, overlap with signals from monomer and other dimer). ¹³C **NMR** (125.8 MHz): $\delta = 56.3$ (NMe), 155.9 (NPh-*i*), 125.8 (NPh-*o*), 128.9 (NPh-*m*), 124.6 (NPh-*p*). ¹¹B **NMR** (128.4 MHz): $\delta = 4.3$.

1: ¹H NMR (399.8 MHz): $\delta = 2.50$ (s, 3 H, NMe), 4.68, 4.84 (s, s, br, 2 H, BH₂), 7.5–6.80 (m, NPh, overlap with signals from dimers). ¹³C NMR (125.8 MHz): $\delta = 43.4$ (NMe), 149.5 (NPh-*i*), 121.5 (NPh*o*), 128.8 (NPh-*m*), 125.5 (NPh-*p*). ¹¹B NMR (128.4 MHz): $\delta = 40.0$ (t, ¹*J*(¹¹B,¹H) = 134 Hz).

2: ¹H NMR (399.8 MHz): δ = 2.70 (s, 6 H, NMe), 3.71 (s, 1 H, BH), 6.73–7.10 (m, 10 H, NPh). ¹³C NMR (125.8 MHz): δ = 39.0 (NMe), 149.9 (NPh-*i*), 122.7 (NPh-*o*), 128.8 (NPh-*m*), 125.8 (NPh-*p*). ¹¹B NMR (d 128.4 MHz): δ = 29.6 (¹J(¹¹B, ¹H) = 122 Hz).

3: ¹H NMR (399.8 MHz): $\delta = 0.80$ (quintet, 1 H, ²*J*(¹HB¹H) = 8.5 Hz μ -HB₂), 1.92, 2.05 (d, d, 4 H, ²*J*(¹HB¹H) = 8.5 Hz BH₂), 2.55 (s, 3 H, NMe), 6.70–7.00 (m, 5 H, NPh). ¹³C NMR (125.8 MHz): $\delta = 56.4$ (NMe), 152.5 (NPh-*i*), 122.7 (NPh-*o*), 128.8 (NPh-*m*), 125.8 (NPh-*p*). ¹¹B NMR (128.4 MHz): $\delta = -17.0$ (t, d, ¹*J*(¹¹B, ¹H) = 131 Hz, 29 Hz).

6a: ¹**H NMR** (399.8 MHz): $\delta = 0.07$ (m, 1 H, μ -HB₂), 1.30 (m, 4 H, BH₂), 2.56, 0.89 (q, t, 4 H, 6 H, NEt₂). ¹³**C NMR** (125.8 MHz): $\delta = 51.6, 10.5$ (NEt₂). ¹¹**B NMR** (89.3 MHz): $\delta = -18.7$ (t, d, ¹*J*(¹¹B, ¹H) = 128.6 Hz, 31.3 Hz).

6b: ¹³**C NMR** (125.8 MHz): $\delta = 61.3$, 24.7 (pyrrolidine). ¹¹**B NMR** (89.3 MHz): $\delta = -18.3$ (t, d, ${}^{1}J({}^{11}\text{B},{}^{1}\text{H}) = 131$ Hz, 29 Hz).

8: ¹**H** NMR (399.8 MHz): $\delta = 0.28$ (m, 1 H, μ -HB₂), 1.49 (m, 4 H, H₂B; overlap with signals from sec-butyl groups). ¹³C NMR (125.8 MHz): $\delta = 65.7$ 29.6, 18,9, 12.2, 12.1 (N-*s*Bu; some signals are broadened, preventing the resolution of all signals for the two diastereomers). ¹¹B NMR (89.3 MHz): $\delta = -20.1$ (t, d, ¹*J*(¹¹B, ¹H) = 128 Hz, 33 Hz).

X-ray Structural Analysis of 12

The X-ray crystal structural analysis of $1_2^{[21]}$ was carried out for a single crystal (selected in perfluorinated oil^[22] at room temperature) at

133(2) K using a STOE IPDS II system equipped with an Oxford Cryostream low-temperature unit; wavelength: $\lambda = 0.71069$ Å. Formula weight: 360.15. Crystal system: monoclinic; space group: $P2_1/n$. Unit cell dimensions: a = 5.8260(8) Å, b = 15.8580(16) Å, c = 7.80.10(8) Å, $a = 90^\circ$, $\beta = 110.161^\circ(8)$, $\gamma = 90^\circ$. Volume V = 676.56(13) Å³. Z = 2. Absorption coefficient $\mu = 0.067$ mm⁻¹. F(000): 256. Crystal size: $0.42 \times 0.39 \times 0.34$ mm. Theta range for data collection: 1.28 to 26.145°. Index ranges: $-7 \le h \le 7$, $-19 \le k \le 19$, $-9 \le l \le 9$; reflections collected: 8869, independent reflections: 989 [R(int) = 0.0544]. Completeness to $\theta = 25.65^\circ$: 99.4 %. Data/restraints/parameters: 1271/0/96; goodness-of-fit on F^2 : 1.028. Final R indices [$I > 2\sigma$ (I)] R1 = 0.0415, wR2 = 0.1118; R indices (all data): R1 = 0.0544, wR2 = 0.1072. Largest difference peak and hole: 0.142 and -0.188 e·Å^{-3}. Structure solution and refinement were accomplished using SIR97,^[23] SHELXL-97,^[24] and WinGX^[25].

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