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# New air stable diarylamino substituted diborane(4) derivatives: Synthesis and structures

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#### ABSTRACT

In recent years, the rekindled interest in B/N ring systems has led to a plethora of novel compounds with varying substitution patterns. Diaminodiboranes are the starting compounds for the preparation of many boron compounds such as diborane derivatives, used for many addition and insertion reactions into multiple bonds in the literature, however there are few air-stable diborane(4) derivatives. In this study, to synthesize new air-stable B,B'-diaryl and bis(dimethylamino)-B,B'-diarylaminodiboranes(4), the bulky amines were selected. These derivatives were prepared through the reaction of lithium anilide derivatives and 1,2-dichlorodiboranes. The structures of the compounds were characterized by using nuclear magnetic resonance (NMR) spectroscopy. The crystal and molecular structures of 3ae, 3af, 3bb, 3be, 3ce, 3cd and 3cf were determined using the singlecrystal X-ray diffraction technique. X-ray diffraction studies have showed that the diarylamino group in the solid state is nearly orthogonal to the plane due to the boron-bound bulky groups.

#### **KEYWORDS**

Diborane(4); diaminodiboran(4); air-stable; crystal structure; NMR

#### **1. Introduction**

Diarylamino substituted diboranes are an important class of compounds in boron chemistry for use in the synthesis of other boron-containing compounds. Heterocycles consisting of boron, nitrogen and carbon ring systems have led to a plethora of novel compounds with varying substitution patterns, thus leading the way to potential applications. Especially, diarylamino substituted diboranes are the starting compounds for the synthesis of boron heterocycles, such as diazatriborolidines, diazadiborolidines and diazadiborinane derivatives [1–4]. Many researchers have focused on aminodiborane(4) compounds and the reported studies have emphasized that the stability of compounds can be increased with electron releasing and bulky groups [5–7]. Also, the previous studies have reported that aliphatic amines-substituted diaminodiboranes are less stable [8]. We believe that the ability of the aryl group to bind to the N-atom forms a steric hindrance and reduces the efficiency of the nucleophilic N atoms, thus, allowing the stability of molecules. In this study, we present the synthesis, characterization and structural analysis of a variety of diaryl- and a dialkyl amino-substituted diborane(4)

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92 😔 D. B. CELEPCI ET AL.

derivatives. All prepared compounds were found to be stable in air. Furthermore, the study was conducted to exhibit further information for air, thermal stabilities and conformations of such species.

#### 2. Experimental Section

#### 2.1. Syntheses

General considerations: All reactions were carried out under argon, using standard schlenk techniques. Solvents were dried, distilled, and saturated with argon. Glassware was dried using a heat gun under high vacuum. NMR spectra were recorded on a Varian 400 spectrometer. The chemical shifts are given in ppm, and are referenced against external  $Me_4Si$ ,  $BF_3 \cdot OEt_2$ . 1,2-Bis(dimethylamino)diborane(4) dichloride [9], 1,2-bismesityldiborane(4) dichloride [10] and 1,2-bisdiduryldiborane(4) dichloride [11] and were synthesized according to literatures.

## **2.2.** General procedure for synthesis of arylamino substituted diborane(4) derivatives

Arylamine derivative (1, 6 mmol) was dissolved in THF/hexane mixture (1:4, 50 mL) and *n*-BuLi (7.5 mL, 12 mmol, 1.6 M solution in hexane) was added dropwise at 0 °C. The solution was warmed to room temperature and stirred overnight. A hexane solution of  $R^1$ ClB-BCl $R^1$  (0.75 g, 6 mmol) was added dropwise, resulting in a suspension of 2 at -20 °C. The mixture was slowly warmed to room temperature and removed of volatile components in vacuum (Scheme 1). The residue was extracted into hexane/CH<sub>2</sub>Cl<sub>2</sub> mixture (1:2, 50 mL). The concentrated solution was kept to -30 °C and the crystals were obtained.

#### 2.2.1. 1,2-Di(tert-butyl)amino-1,2-bis(dimethylamino)diborane, 3ad

Yielding 88%, a colorless viscous liquid.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, 300 K):  $\delta = 1.18$  (s, 18H, Me, t-Bu), 2.47 (s, 6H, Me, NMe), 2.56 (s, 2H, NH), 2.63 (s, 6H, Me, NMe); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>, 300 K):  $\delta = 33.3$  (6C, Me, t-Bu), 35.3 (2C, Me, NMe), 42.6 (2C, Me, NMe), 49.4 (2C, t-Bu); <sup>11</sup>B-NMR (128.32 MHz, CDCl<sub>3</sub>, 300 K):  $\delta = 33$  (2B).



Scheme 1. Synthesis of diborane(4) 3 derivatives.

#### 2.2.2. 1,2-Bis(2-methoxyphenyl)amino-1,2-bis(dimethylamino)diborane, 3af

Yielding 87%, a colorless crystal, m.p.: 138 °C.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, 300 K):  $\delta$  = 2.76, 2.82 (each s, each 6H, Me<sub>2</sub>N), 3.92 (s, 6H, MeO, Ph), 5.87 (br., s, 2H, NH), 6.76-6.79 (m, 4H, p-, and m-H, Ph), 6.83, 6.85 (m, 2H, o-H, Ph), 7.20-7.23 (m, 2H, m'-H, Ph); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>, 300 K):  $\delta$  = 35.9 (2C, MeN), 41.7 (2C, MeN), 55.6 (2C, MeO-C, Ph), 109.9 (2C, m-C, Ph), 114.9 (2C, p-C, Ph), 118.3 (2C, m-C, Ph), 121.3 (2C, o-C, Ph), 136.4 (2C, o-C, Ph), 147.9 (2C, i-C, Ph); <sup>11</sup>B-NMR (128.32 MHz, CDCl<sub>3</sub>, 300 K):  $\delta$  = 33 (2B).

#### 2.2.3. 1,2-Dimesitylamino-1,2-dimesityldiborane, 3bb

Yielding 91%, a colorless crystal, m.p.: 169°C.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, 300 K):  $\delta = 1.91$  (s, 12H, o-Me, NMes), 2.16 (s, 6H, p-Me, NMes), 2.17 (s, 12H, o-Me, BMes), 2.22 (s, 6H, p-Me, BMes), 6.26 (s, 2H, NH), 6.68 (s, 4H, m-H, MesN), 6.71 (s, 4H, m-H, BMes); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>, 300 K):  $\delta = 18.8$  (4C, o-C, NMes), 20.0 (2C, p-C, NMes), 21.0 (2C, p-C, BMes), 22.2 (4C, o-C, BMes), 127.6 (4C, p-C, NMes), 128.9 (2C, p-C, BMes), 131.2 (4C, m-C, NMes), 133.3 (4C, m-C, BMes), 136.2 (4C, o-C, BMes), 138.6 (4C, o-C, NMes), 139.1 (br. 2C, i-C, BMes), 139.3 (2C, i-C, NMes); <sup>11</sup>B-NMR (128.32 MHz, CDCl<sub>3</sub>, 300 K):  $\delta = 48$  (2B).

#### 2.2.4. 1,2-Bis(2,6-diisopropylphenyl)amino-1,2-dimesityldiborane, 3be

Yielding 87%, a colorless crystal, m.p.: 179 °C

<sup>1</sup>H-NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K):  $\delta = 0.90$  (d, 24H, <sup>3</sup>J<sub>HH</sub> = 8 MHz, i-Pr -Me, Ph), 2.13 (s, 6H, p-Me, Mes), 2.32 (s, 12H, o-Me, Mes), 3.33 (sept., 4H, iPr -CH), 6.72 (s, 4H, m-H, Mes), 6.84 (s, 2H, HN), 7.00 (m, 6H, m- and p-H, Ph); <sup>13</sup>C-NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K):  $\delta = 21.1$  (2C, p-Me, Mes), 22.2 (4C, o-Me, Mes), 23.2 (8C, i-Pr-C), 28.4 (4C, i-Pr-CH), 123.5 (6C, m- und p-C, Ph), 125.8 (4C, m-C, Mes), 136.7 (4C, o-C, Mes), 138.5 (br. 2C, i-C, Mes), 139.2 (4C, o-C, Ph), 139.4 (2C, p-C, Mes), 142.2 (2C, i-C, Ph); <sup>11</sup>B-NMR (128.32 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K):  $\delta = 50$  (2B).

#### 2.2.5. 1,2-Di(tert-butyl)amino-1,2-diduryldiborane, 3cd

Yielding 90%, a colorless crystal, m.p.: >210 °C.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, 300 K):  $\delta = 0.92$  (s, 18H, Me, t-Bu), 2.09 (s, 12H, m-Me), 2.21 (s, 12H, o-Me), 4.68 (br. s, 2H, NH), 6.82 (s, 2H, p-Dur); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>, 300 K):  $\delta = 19.7$  (8C, o-, m-Me, Dur), 31.5 (6C, Me, t-Bu), 51.7 (2C, t-Bu), 128.9 (2C, p-C, Dur), 130.8 (br., 2C, i-C, Dur), 132.4 (4C, m-C, Dur), 132.8(4C, o-C, Dur); <sup>11</sup>B-NMR (128.32 MHz, CDCl<sub>3</sub>, 300 K):  $\delta = 46$  (2B).

#### 2.2.6. 1,2-Bis(2,6-diisopropylphenyl)amino-1,2-diduryldiborane, 3ce

Yielding 89%, a colorless crystal, m.p.: >210 °C.

#### 94 🍝 D. B. CELEPCI ET AL.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, 300 K):  $\delta = 0.78$  (d, 24H, <sup>3</sup>J<sub>HH</sub> = 4 MHz, i-Pr -Me, Ph), 2.06 (s, 12H, m-Me, Dur), 2.12 (s, 12H, o-Me, Dur), 3.08 (sept., 4H, iPr -CH), 6.52 (s, 2H, NH), 6.77 (s, 2H, p-H, Dur), 6.95 (d, 4H, <sup>3</sup>J<sub>HH</sub> = 8 MHz, m-H, Ph), 7.02 (t, 2H, <sup>3</sup>J<sub>HH</sub> = 8 Hz, p-H, Ph); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>, 300 K):  $\delta = 18.8$  (4C, o-C, Dur), 19.6 (2C, p-C, Dur), 22.9 (8C, i-Pr -C), 27.8 (4C, i-Pr -CH), 122.9 (2C, p-C, Ph), 124.8 (2C, p-C, Dur), 130.3 (4C, m-C, Dur), 133.1 (4C, m-C, Ph), 134.0 (4C, o-C, Ph), 138.9 (4C, o-C, Dur), 141.7 (2C, i-C, Dur), 142.2 (2C, i-C, Ph); <sup>11</sup>B-NMR (128.32 MHz, CDCl<sub>3</sub>, 300 K):  $\delta = 52$  (2B).

#### 2.2.7. 1,2-Bis(2-methoxyphenyl)amino-1,2-diduryldiborane, 3cf

Yielding 91%, a colorless crystal, m.p.: >210 °C.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, 300 K):  $\delta = 2.11$  (s, 12H, m-Me, Dur), 2.27 (s, 12H, o-Me, Dur), 3.68 (s, 6H, MeO, Ph), 6.57 (t, 2H, <sup>3</sup>J<sub>HH</sub> = 6 Hz, p-H, Ph), 6.75 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 6 MHz, m-H, Ph), 6.81 (t, 2H, <sup>3</sup>J<sub>HH</sub> = 6 MHz, m'-H, Ph), 6.85 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 6 MHz, o-H, Ph), 6.95 (s, 2H, p-H, Dur), 7.50 (br. s, 2H, NH); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>, 300 K):  $\delta = 18.7$  (4C, o-C, Dur), 19.7 (4C, m-C, Dur), 55.8 (2C, MeO-C, Ph), 110.6 (2C, m-C, Ph), 118.9 (2C, p-C, Ph), 121.1 (2C, m'-C, Ph), 122.3 (2C, o-C, Ph), 129.9 (2C, p-C, Dur), 132.8 (4C, m-C, Dur), 133.0 (4C, o-C, Dur), 134.2 (2C, o'-C, Ph), 143.7 (br., 2C, i-C, Dur), 149.1 (2C, i-C, Ph); <sup>11</sup>B-NMR (128.32 MHz, CDCl<sub>3</sub>, 300 K):  $\delta = 48$  (2B).

#### 2.3. X-ray Crystallography

The crystallographic data collections of the compounds were conducted for 3ae at 100 K, for 3af, 3bb, 3be and 3cf at 150 K and for the rest at 293 K, on a Rigaku Oxford Xcalibur diffractometer with an Eos-CCD detector using graphite-monochromated MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å). Data collections, cell refinements and data reductions along with absorption correction were performed using CrysAlis<sup>Pro</sup> software package [12]. Crystal structures were solved with the SHELXT structure solution program using Intrinsic Phasing method [13] embedded in the Olex2 [14]. Refinement of coordinates and anisotropic thermal parameters of non-hydrogen atoms were carried out by the full-matrix least-squares method in SHELXL [15]. All non-hydrogen atoms were refined anisotropically. In 3ae, two methyl carbon atoms are disordered with a 43:57 (C27a:C27b; C28a:C28b) population distribution in one of the isopropyl groups. All H atoms of 3af, 3be, 3cd and 3ce; H atoms of the disordered groups in 3ae; H atoms except those bound to the nitrogen atoms of 3bb and hydrogen atoms of the methyl groups in 3cf were placed at idealized positions and refined using the riding model. All other hydrogens were found in the difference map and refined freely. The crystal structure of 3cd was determined as a non-merohedral twin with the final ratio of the twin domains being 0.310(2):0.690(2). The summary of crystallographic data, experimental details, and refinement results for the compounds are given in Table 1.

	3ae	3bb	3be	3ce	3cd	3af	3cf
Formula	$C_{28}H_{48}B_2N_4$	$C_{36}H_{46}B_2N_2$	$C_{42}H_{58}B_2N_2$	$C_{44}H_{62}B_2N_2$	$C_{28}H_{46}B_2N_2$	$C_{18}H_{28}B_2N_4O_2\\$	$C_{34}H_{42}B_2N_2O_2$
Formula weight	462.32	528.37	612.52	640.58	432.29	354.06	532.31
Temperature (K)	100.01(15)	150.00(10)	150.02(10)	293(2)	293(2)	150.04(10)	150.01(10)
Crystal system	Triclinic	Monoclinic	Tetragonal	Monoclinic	Triclinic	Monoclinic	Orthorhombic
Space group, Z	P-1, 2	P21/n, 4	P41212, 4	<i>C2/c</i> , 4	<i>P-1</i> , 1	<i>C2/c</i> , 4	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> , 4
a, b, c (Å)	9.8556(7)	11.2786(10)	16.3381(10)	13.4122(10)	7.964(2)	18.397(4)	8.9381(10)
	10.4511(7)	16.8065(14)	16.3381(10)	17.2939(11)	9.881(3)	7.3856(15)	15.8334(19)
	16.4926(12)	17.5921(15)	14.4331(12)	17.1595(10)	10.278(2)	13.999(3)	21.421(3)
α, β, γ (°)	81.397(6)	90	90	90	71.36(2)	90	90
	76.489(6)	104.985(10)	90	92.312(6)	78.47(2)	93.999(17)	90
	62.820(6)	90	90	90	66.59(3)	90	90
Volume (Å <sup>3</sup> )	1467.56(19)	3221.2(5)	3852.7(5)	3976.9(5)	700.7(3)	1897.5(7)	3031.5(6)
$\rho_{calc} \text{ (mg m}^{-3}\text{)}$	1.046	1.089	1.056	1.070	1.024	1.239	1.166
$\mu ({\rm mm^{-1}})$	0.060	0.061	0.059	0.060	0.058	0.080	0.071
F (000)	508	1144	1520	1592	238	760	1144
Reflections collected	7806	10376	7237	6567	4560	3049	11289
Reflections unique/R <sub>int</sub>	5920/0.017	5653/0.048	3656/0.065	3770/0.027	4560/merged	1664/0.046	5689/0.056
Parameters	494	381	219	225	117	121	412
GOF on F <sup>2</sup>	1.025	1.008	1.002	1.047	0.938	1.000	0.990
$R, wR_2$	$R_1 = 0.047$	$R_1 = 0.064$	$R_1 = 0.066$	$R_1 = 0.053$	$R_1 = 0.077$	$R_1 = 0.063$	$R_1 = 0.061$
$[I > 2\sigma(I)]$	$wR_2 = 0.109$	$wR_2 = 0.123$	$wR_2 = 0.130$	$wR_2 = 0.128$	$wR_2 = 0.219$	$wR_2 = 0.143$	$wR_2 = 0.081$

Table 1. Crystallographic data and structure refinement parameters for the compounds.

#### 3. Results and Discussion

The B,B'-diaryl and bis(dimethylamino)-B,B'-diarylaminodiboranes(4) derivatives **3** were prepared from reaction of the lithium anilide salt derivative **2** with 1,2-bis(dimethylamino)diborane(4) dichloride and 1,2-diaryldiborane(4) dichloride in a mixture of THF/ hexane at -20 °C. Then, the suspension was allowed to warm to room temperature (Scheme 1).

The new diaminodiborane(4) compounds were identified by their <sup>1</sup>H-, <sup>11</sup>B- and <sup>13</sup>C-NMR spectra. The NMR spectra of 3 derivatives and their chemical shifts are highly similar to each other. The <sup>11</sup>B NMR spectra of 3bb, 3ce, 3be, 3cf and 3cd showed a characteristic broad singlet for the 2B atoms between 46 and 49 ppm, except for 3ad, this is consistent with a symmetrically substituted aminodiborane [8]. Probably the presence of boron-bound substituents, which have a large volume, showed a slow rotation. **3ad** is liquid at room temperature and its <sup>11</sup>B-signal appears sharp at 32 ppm and the <sup>11</sup>B-signal of **3af** is also 33 ppm. The <sup>11</sup>B-signals of boron atoms in the compounds are shifted upfield as expected for symmetrically substituted tetraaminodiborane compounds, because the boron atoms are more shielded by the amino groups. Also, the difference of chemical shifts of boron atoms might be explained in that, the lone electrons of the nitrogen atom contribute to the aromaticity of the aryl group when an aromatic amine ligand is bound to the boron atoms. A similar situation occurs in the chemical H shifts of arylamino (-NH of 3cf, 3be, 3ce, 3bb, 3af, 3cd) which are at 7.50, 6.84, 6.53, 6.26, 5.78 and 4.68 ppm respectively. In contrast, the chemical H shift of tert-Butylamino of 3ad is at 2.56 ppm. Due to the fact that boron atoms are shielded by four N atoms, NH proton of tetraaminodiborane(4) is shifted upfield. In <sup>13</sup>C NMR spectra of 3ad, 3af, and 3ae [16] a discrete signal is observed at room temperature for



**Figure 1.** View of the molecular structure of **3ae** showing the atom numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Selected bond distances (Å), bond angles and torsion angles (°): B1–B2 1.722(2), B1–N1 1.435(2), B1–N3 1.415(2), B2–N2 1.428(2), B2–N4 1.417(2), N1–C5 1.431(2), N2–C17 1.431(2), N3–C1 1.457(2), N3–C2 1.453(2); N1–B1–B2 119.12(12), N1–B1–N3 118.39(13), B1–B2–N2 113.02(12), B1–B2–N4 123.14(13), N3–B1–B2 122.24(12), B1–N1–C5 126.14(12), B1–N3–C2 124.50(14), B1–N3–C1 123.51(13), B2–N2–N4 123.77(13), B2–N4–C3 122.19(13), B2–N4–C4 128.15(13), B2–N2–C17 133.12(12), C1–N3–C2 111.93(14), C3–N4–C4 109.66(13); N1–B1–B2–N2 55.15(17), N1–B1–B2–N4 -127.75(15), N1–B1–N3–C1 -169.14(17), N1–B1–N3–C2 7.9(3), N2–B2–N4–C3 -178.11(15), N2–B2–N4–C4 1.5(2), N3–B1–B2–N4 58.1(2), C5–N1–B1–B2 14.7(2), C5–N1–B1–N3 -170.85(13), C17–N2–B2–B1 168.95(13), C17–N2–B2–N4 -8.1(2).

each C atom of the NMe<sub>2</sub> ligand due to the hindered rotation. This shows that there is a back bonding between B and N. To obtain information on preferred conformations and further insights into steric and electronic effects of ligands, 1,2-diaryl- and 1,2- (dit-butyl) amino-1,2-diboranes(4) were synthesized. X-ray structure determinations of some representative derivatives were carried out and found that the diarylamino group in the solid state was nearly orthogonal to the plane due to the bulky groups bound to the boron atoms. Also,  $\pi$  bond between N-B atoms was detected with X-ray structural analysis by means of the N-B bond distance values.

#### 4. Structural Determination

The structures of **3ae**, **3af**, **3bb**, **3be**, **3ce**, **3cd** and **3cf** have been determined using single-crystal X-ray diffraction. Their molecular structures are depicted in Fig. 1–7, and packing diagrams are shown in Fig.S1-S7 (see Electronic Supplementary Information). **3ae** had been synthesized by Patton et al. [16]. Its crystal structure has been presented in this study. The compound **3ae** crystallizes in the triclinic crystal system space group P-1. X-ray structural analysis reveals that the molecule features two boron atoms of



**Figure 2.** View of the molecular structure of **3bb** showing the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Selected bond distances (Å), bond angles and torsion angles (°): B1–B2 1.716(5), B1–N1 1.404(4), B1–C1 1.582(4), B2–N2 1.402(4), B2–C28 1.584(4), N1–C10 1.432(3), N2–C19 1.435(3); C1–B1–B2 117.9(2), N1–B1–C1 122.3(3), N1–B1–B2 119.2(3), N2–B2–B1 112.5(2), N2–B2–C28 124.7(3), C28–B2–B1 122.0(2), B1–N1–C10 129.1(2), B2–N2–C19 136.3(3); N1–B1–B2–N2 -170.1(3), N1–B1–B2–C28 0.0(4), C1–B1–B2–C28 171.5(2), C10–N1–B1–B2 161.1(3), C10–N1–B1–C1 -9.9(5), C28–B2–N2–C19 3.4(5).

diborane(4), which connect to the NMe<sub>2</sub> and tert-butylamino moieties (Fig. 1). The B-B bond distance [1.722(2) Å] is slightly longer with respect to those reported previously for mesityl [1.717(15) Å], phenyl [1.714(4) Å and 1.719(2) Å] and pyrrolyl [1.716(2) Å] substituted 1,2-bis(dimethylamino)diborane(4) [17, 18]. On the other hand, this bond length is smaller when comparing with the similar studies reported by Firinci et al. [1.735(6) Å] and Braunschweig et al. [1.731(2) Å] [19, 20]. Boron atoms are close to the trigonal planar geometry except the B1-B2-N2 bond angle of  $113.02(12)^{\circ}$ , while nitrogen atoms have nearly large deviations from the trigonal planarity. There is a strong twist around the B-B bond. The molecule adopts a staggered conformation around this B-B bond considering the torsion angles N1/B1/B2/ N2 at 55.15(14)° and N3/B1/B2/N4 at 58.06(17)°. These values are comparable with the very similar compound studied by Braunschweig and Damme  $[60.4(2)^{\circ}]$  [20]. It's most likely due to the steric repulsion between tert-butylamino groups around the boron atoms. Me<sub>2</sub>N-B bond lengths [1.415(2)-1.417(2) Å] are longer than those in corresponding studies in the literature, and the Me<sub>2</sub>B-N bonds possess better  $\pi$ -bond character [18–21]. The crystal structure is stabilized by intramolecular C-H···N type weak interactions and van der Waals forces. Stacking of the molecules in a head-to-tail and head-to-head fashion in the unit cell are shown in the packing diagram in Fig. S1.



**Figure 3.** View of the molecular structure of **3be** showing the atom numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Selected bond distances (Å), bond angles and torsion angles (°): B1–B1<sup>i</sup> 1.713(8), B1–N1 1.404(5), B1–C1 1.580(5), N1–C10 1.580(5); N1–B1–B1<sup>i</sup> 114.6(4), N1–B1–C1 122.9(3), C1–B1–B1<sup>i</sup> 121.5(4), B1–N1–C10 132.9(3); C10–N1–B1–C1 -13.7(6), C10–N1–B1–B1<sup>i</sup> 155.6(3); symmetry code (i) 1-x, 1-y,  $\frac{1}{2}$ -z.

**3bb** crystallizes in the monoclinic space group *P21/n*. The molecule comprises of dimesityl and dimesitylamino fragments, of which the same groups are in *trans* positions to each other (Fig. 2). At the central point of the B–B bond, a crystallographic inversion center lies, and the  $B_2N_2C_2$  unit is almost planar with the r.m.s. deviation of 0.047 Å. The B–B bond is characteristic of single bond with the bond length of 1.716(5) Å. The C–B–B, N–B–B and N–B–C bond angles around the boron atoms have a range from 112.5(3) to 124.7(3)°. From this point of view, the B1 and B2 atoms have *distorted trigonal planar* geometry. Mesitylamino moieties are tilted around the nitrogen atoms, so N1 and N2 atoms also have *distorted trigonal planar* geometry. The dihedral angles between the ring planes of C1–C6 and C10–C15, C1–C6 and C19–C24, C10–C15 and C28–C33, and C19–C24 and C28–C33 are 61.52(14)°, 82.89(15)°, 74.63(14)° and 78.94(15)°, respectively. Intramolecular C–H…N type weak interactions and van der Waals forces are responsible for the stabilization of the crystal structure. Stacking of the molecules viewed from the *b* axis are shown in the packing diagram in Fig. S2.

The asymmetric unit of the compounds **3be** and **3ce** contain half of the molecule. Molecules are completed with the symmetry operations of <sup>i</sup>1-x, 1-y, 1/2-z and <sup>ii</sup>1-x, y, 3/2-z. **3be** crystallizes in the tetragonal crystal system, *P41212* space group, and **3ce** 



**Figure 4.** View of the molecular structure of **3ce** showing the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Selected bond distances (Å), bond angles and torsion angles (°): B1–B1<sup>ii</sup> 1.732(4), B1–N1 1.408(2), B1–C1 1.591(3), N1–C11 1.445(2); N1–B1–B1<sup>ii</sup> 114.8(2), N1–B1–C1 123.51(15), C1–B1–B1<sup>ii</sup> 121.34(19), B1–N1–C11 133.10(16); C11–N1–B1–C1 -11.7(3), C11–N1–B1–B1 161.57(15); symmetry code (ii) 1-x, y, 3/2-z.

crystallizes in the triclinic *P-1*. Compounds feature 2,6-diisopropylanilide groups connect to the diborane unit in *trans* positions. Also dimesityl and duryl groups in **3be** and **3ce**, bond to the diborane unit in *trans* positions to each other (Fig. 3-4). The B-B bond lengths [1.713(8) Å for **3be**, and 1.732(4) Å for **3ce**] are strictly different when comparing the compounds. This result may be due to the steric repulsion between the duryl and 1,2-diisopropylanilide moieties in the **3ce** molecule. The geometries around the boron atoms adopt *distorted trigonal planar* for both compounds, with the bond angles that span a range from 114.6(4) to  $123.5(15)^{\circ}$ . The dihedral angle of diisopropylanilide fragment with the mesityl is  $57.71(17)^{\circ}$  in **3be**, while its dihedral angle with duryl group is  $72.22(8)^{\circ}$  in **3ce**. Crystal structures of the compounds are stabilized by intramolecular C-H…N type weak interactions and van der Waals forces. Stacking of the molecules viewed from the *c* axis are shown in the packing diagram in Fig. S3-S4.

**3cd** crystallizes in the monoclinic crystal system, C2/c space group. The asymmetric unit has half of the molecule. It is completed by inversion symmetry <sup>iii</sup>1-x, 1-y, 1-z. The B1-B1<sup>iii</sup> bond length is 1.711(7) Å. The compound comprises of tert-butylamino and duryl fragments connect to the boron atoms (Fig. 5). The C-B-B, N-B-B and N-B-C bond angles around the boron atoms have a range from 116.3(3) to 123.5(3)°. This result is proof of the *distorted trigonal planarity* of B1 and B2 atoms. Crystal structure



**Figure 5.** View of the molecular structure of **3cd** showing the atom numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Selected bond distances (Å), bond angles and torsion angles (°): B1–B1<sup>iii</sup> 1.711(7), B1–N1 1.381(4), B1–C1 1.595(5), N1–C11 1.472(4); N1–B1–B1<sup>iii</sup> 116.3(3), N1–B1–C1 123.5(3), C1–B1–B1<sup>iii</sup> 119.9(4), B1–N1–C11 135.7(3); C11–N1–B1–C1 -2.3(6), C11–N1–B1–B1<sup>iii</sup> 178.5(4); symmetry code (iii) 1-x, 1-y, 1-z.

of 3cd is stabilized by van der Waals forces. Stacking molecules viewed from the b axis are shown in the packing diagram in Fig. S5.

**3af** crystallizes in the monoclinic space group *C2/c*. The asymmetric unit comprises one half of the molecule, which is completed with the two-fold rotational symmetry [symmetry code: <sup>iv</sup>1-x, y, 3/2-z]. X-ray structural analysis shows that the molecular structure of the compound features two boron atoms connect to the NMe<sub>2</sub> and methoxyanilide fragments, of which the similar groups are in *cis* conformations (Fig. 6). The B1–B1<sup>iv</sup> bond length is 1.717(6) Å, is comparable to those found in related B<sub>2</sub>N<sub>4</sub> studies [17–20]. B atoms are close to the *trigonal planar* geometry considering the B–B–N and N–B–N bond angles. There is a strong twist around the B–B bond. The molecule adopts a *staggered* conformation around this B–B bond considering the torsion angles N1/B1/ B1<sup>iv</sup>/N1<sup>iv</sup> at 65.34(15)° and N2/B1/B1<sup>iv</sup>/N2<sup>iv</sup> at 65.47(15)°. These values are comparable with **3ae** and the very similar compound studied by Braunschweig and Damme [60.4 (2)°] [20]. Similarly in **3af**, this result may also be due to the steric repulsion between 2-methoxyanilide groups around the boron atoms. The crystal structure is stabilized by intramolecular N–H…O and C–H…N type weak interactions besides the van der Waals



**Figure 6.** View of the molecular structure of **3af** showing the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Selected bond distances (Å), bond angles and torsion angles (°):  $B1-B1^{iv}$  1.720(6), B1-N1 1.441(4), B1-N2 1.410(4), N1-C1 1.389(3), O1-C2 1.374(3), O1-C7 1.426(3);  $N1-B1-B1^{iv}$  119.9(2),  $N2-B1-B1^{iv}$  123.5(2), N1-B1-N2 116.6(2), C1-N1-B1 131.7(2), C2-O1-C7 117.5(2); C1-N1-B1-N2 -159.3(3), C8-N2-B1-N1 9.4(4),  $C8-N2-B1-B1^{iv}$  -170.4(3), C9-N2-B1-N1 -175.7(2),  $C9-N2-B1-B1^{iv}$  4.5(4), C7-O1-C2-C1 -169.7(2); symmetry code (iv) 1-x, y, 3/2-z.

forces. Stacking of the molecules viewed from the c axis are shown in the packing diagram in Fig. S6.

**3cf** crystallizes in the orthorhombic crystal system,  $P2_12_12_1$  space group. Similar to 3ce, the molecule consists of two duryl groups and differently has two 2-methoxyanilide fragments, which are in trans positions to each other (Fig. 7). At the central point of the B-B bond, a crystallographic inversion center lies, and the B2N2C2 unit has almost perfect planarity with the r.m.s. deviation of 0.011 Å. The B-B bond is characteristic of single bond with the bond length of 1.711(7) Å. The C-B-B, N-B-B and N-B-C bond angles around the boron atoms have a range from 114.4(4) to  $126.6(5)^{\circ}$ . From this point of the view, the B1 and B2 atoms have distorted trigonal *planar* geometry. The bond angles of  $118.3(4)^{\circ}$  and  $117.4(4)^{\circ}$  around the O1 and O2 atoms confirm their sp<sup>3</sup> character. N1/B1/N2/B2 plane and the 2-methoxyanilide moieties are together coplanar with the r.m.s. deviation of 0.048 Å. Duryl groups are nearly perpendicular to this plane with the dihedral angles of C1-C6 is 76.01(18)° and C11–C16 is  $75.85(18)^\circ$ . The dihedral angle between the duryl groups is  $7.3(2)^\circ$ , and between the methoxyanilide groups is  $1.8(2)^{\circ}$ . On the other hand, 2-methoxyanilide fragments and duryl groups have dihedral angles between C<sub>28-33</sub> - C<sub>1-6</sub> is  $80.5(2)^{\circ}$ ;  $C_{28-33}$  -  $C_{11-16}$  is  $81.4(2)^{\circ}$ ;  $C_{21-26}$  -  $C_{1-6}$  is  $79.7(2)^{\circ}$ ;  $C_{21-26}$  -  $C_{11-16}$  is 80.4(2)°. The crystal structure is stabilized by intramolecular N-H···O type weak interactions and van der Waals forces. Stacking of the molecules viewed from the a axis are shown in the packing diagram in Fig. S7.



**Figure 7.** View of the molecular structure of **3cf** showing the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Selected bond distances (Å), bond angles and torsion angles (°): B1–B2 1.711(7), B1–N1 1.414(6), B1–C1 1.577(7), B2–N2 1.410(6), B2–C11 1.564(7), N1–C21 1.412(5), N2–C28 1.411(5), O1–C26 1.376(5), O1–C27 1.428(5), O2–C33 1.378(5), O2–C34 1.422(5); N1–B1–B2 114.4(4), N1–B1–C1 125.0(4), C1–B1–B2 120.6(0), B1–N1–C21 135.1(4), N2–B2–B1 114.7(4), N2–B2–C11 126.6(5), C11–B2–B1 118.7(4), B2–N2–C28 134.4(4), C26–O1–C27 118.3(4), C33–O2–C34 117.4(4); C1–B1–B2–N2 -0.4(6), C1–B1–N1–C21 4.4(8), C1–B1–B2–C11 -178.9(4), C11–B2–B1–N1 2.4(6), C11–B2–N2–C28 -5.3(8), B1–N1–C21–C26 -176.8(5), N1–C21–C26–O1 2.3(6), C21–C26–O1–C27 -175.3(4), B2–N2–C28–C33 175.3(5), N2–C28–C33–O2 -3.0(6), C28–C33–O2–C34 174.6(4).

#### 4. Conclusion

In the present study, we have reported the synthesis of new air stable primary arylamido substituted diborane(4) derivatives. The structures of these compounds were characterized by using their one- and two-dimensional NMR spectra. The molecular and crystal structures of the compounds **3ae**, **3af**, **3bb**, **3be**, **3cd**, **3ce and 3cf** were confirmed by single-crystal X-ray diffraction technique. Structural analysis showed that for all complexes the diarylamino group in the solid state is nearly orthogonal to the plane due to the boron-bound aryl groups. Apart from the **3ce**, in all complexes, B–B bond lengths have normal values and compare well with those in diborane(4) compounds. In **3ce**, the B–B bond distance [1.732(4) Å] is relatively large, which may be due to the steric

repulsion between the duryl and 1,2-diisopropylanilide moieties. In the stabilization of the crystal structures, mainly intramolecular C-H…N and N-H…O type weak interactions and van der Waals forces play role. Diarylamino substituted diborane(4) derivatives are used as starting compounds for the synthesis of other air-stable boron compounds, such as diazadiborolidines, diazatriborolidines and diazadiborinane derivatives. Similarly, alkylamino-substituted di- and tri-borolidine heterocycles have already being demonstrated in the literature.

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#### Supplementary data

Crystallographic data as .cif files for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Center with CCDC 1859490, 1859494, 1859493, 1859491, 1859711, 1859492 and 1859495 for **3ae**, **3af**, **3bb**, **3be**, **3cd**, **3ce** and **3cf**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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104 👄 D. B. CELEPCI ET AL.

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