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Research paper

# Synthesis and structures of 1,3,2,4,5-diazatriborolidines

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ABSTRACT

The derivatives of diazatriborolidine are a class of 5-membered heterocyclic compounds containing a ring with two nitrogen atoms and three boron atoms. The 1,3,2,4,5-diazatriborolidine derivatives were synthesized from 1,2-bis(N-lithium-arylamino)diborane(4) and dichloro-dimethylaminoborane with high yield. The structures of these new derivatives were determined using nuclear magnetic resonance (NMR) spectroscopy. The molecular structures of **3a**, **3b**, **3d**, **4b** and **4c** were determined using single-crystal X-ray diffraction. Their structural features were discussed and compared with similar diazatriborolidines. In addition, the enthalpy of formation of B and N atoms containing five membered heterocycles were calculated theoretically for the first time. Also, an easy and efficient synthesis route has been reported for preparation of 1,3,2,4,5-diazatriborolidine derivatives.

## 1. Introduction

Boron-containing heterocyclic compounds have become of significant interest because of their wide range applications such as drug discovery [1], photoelectronic materials [2] and semiconductors [3]. Also, B, N pair containing heterocycles are important in boron heterocycles owing to the fact that B-N unit is isolectronic and isostructural to C=C. This feature of the B-N unit gives an opportunity to prepare B, N atoms containing aromatic and antiaromatic heterocycles [4]. In particular, five membered B, N containing heterocyles such as azoborolidines can be viewed as analogues of cyclopentadiene. Roesler's studies showed that 1,2,3,5-diazadiborolidine derivatives could act as cyclopentadienly ligand with alkali or transition metals [5–7]. Besides, they pointed out 1,2,3,5-diazadiborolidine derivatives in ferrocene and ruthenocene analogs are more electron rich than classic ferrocene and ruthenocene [7]. Diazatriborolidines are another azoborolidine derivative, which include one more boron atom instead of carbon. In the diazadiborolidines, there are only two studies including mono 1,3,2,4,5-diazatriborolidines in the literature. The first mono 1,3,2,4,5-diazatriborolidine derivative was synthesized by the reaction of the bis (N-lithium monoalkylamino)boranes $RB(NR'Li)_2$ with 1,2-bis(dimethylamino)diborane(4) dichloride by Nöth et al. in 1968 [8]. Paetzold and co-workers obtained alkyl substituted mono 1,3,2,4,5-diazatriborolidine from ring expansion of B and N containing three membered ring and characterized by X-ray crystallography [9].

In this study was presented an easy and tunable method for the preparation of 1,3,2,4,5-diazatriborolidines **3** and **4**. Also, the reaction chloride substituted derivatives with aryl lithium was examined and obtained **5d**. All new derivatives were characterized by NMR spectroscopy and the molecular structures of **3a**, **3b**, **3d, 4b** and **4c** were determined using single-crystal X-ray diffraction.

## 2. Results and discussion

The diazatriborolidine derivatives of **3** were prepared from the reaction of N,N′-diarylaminodiborane dilithium salts **2** and dichlorodimethylaminoborane in a mixture of THF/hexane at −78 °C. The chlorinated diazatriborolidine derivatives **4** were obtained from reaction of excess dichloro(dimethylamino)borane or boron trichloride with 2-dimethylamino-diazatriborolidine derivatives **3** in THF/Hexane mixture at 0 °C (Scheme 1).

The structures of the synthesized compounds were determined from one- and two-dimensional $^{1}H$, $^{13}C$ and $^{11}B$ NMR spectra. Also, the structures of **3a**, **3b**, **3d**, **4b** and **4c** were confirmed by X-ray crystallography. The results revealed diazatriborolidines in which $Cl_2BR$ reactants were added to the nitrogen atom pairs in a 1,2-fashion to form the symmetric derivatives of **2** (Scheme 1). The chemical shifts of **3** and **4** derivatives in the NMR spectra are fairly similar to each other. In the $^{11}B$ NMR spectra **3a** and **3b** showed two broad singlets at 36 ppm and 30 ppm, which were assigned the two symmetrical B atoms and 2-

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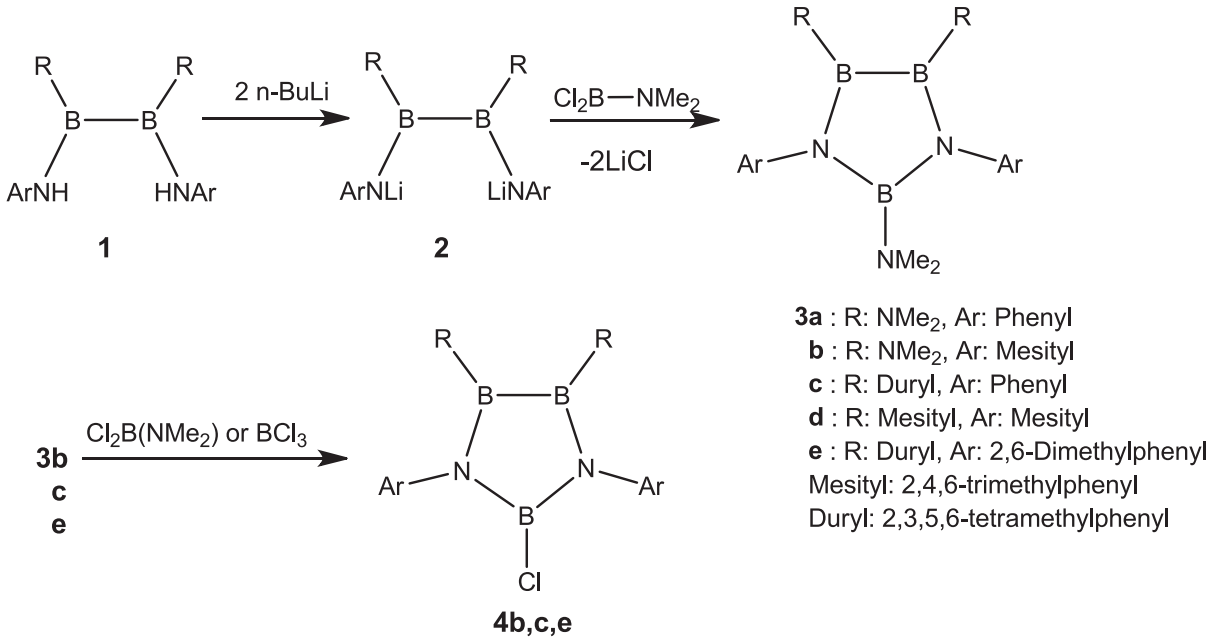



**Scheme 1.** Synthesis of **3** and **4** derivatives.

**Table 1**
$^{11}$B NMR chemical shifts of prepared compounds.

| | 3a | 3b | 3c | 3d | 3e | 4b | 4c | 4e |
|---|---|---|---|---|---|---|---|---|
| $\delta_B{}^{11}$ Exp. | 36; 31 | 36; 30 | 58; 30 | 58; 31 | 58; 31 | 36 | 58; 40 | 60; 41 |
| $\delta_B{}^{11}$ Calc. | 35.3; 30.6 | 35.6; 28.6 | 58.9; 32.3 | 58.3; 31.0 | 58.6; 31.4 | 34.9; 36.8 | 60.2; 41.5 | 60.0; 41.2 |

position B atom, respectively. These values are consistent with the symmetrically substituted tetraaminodiboranes, aminoboranes and similar diazatriborolodines [8–11]. **3c**, **3d** and **4c** gave singlet at 58 ppm for the aryl substituted symmetrical B atoms. Although they shifted downfield from **3a** and **3b**, the obtained chemical shifts chimed in with the reported symmetrically substituted aryl diboranes [12]. The $^{11}$B signals of 2-position B atom of **3c**, **3d** and **4c** were observed at 30, 31 and 40 ppm, respectively. Owing to the fact that **4b** has similar chemical environments around boron atoms, one broad singlet peak was observed at 36 ppm for three boron atoms in the $^{11}$B NMR spectra. $^{11}$B NMR chemical shifts of prepared compounds were calculated with DFT which complied with experimental values (Table 1).

In the $^{1}$H NMR spectra of **3a**, **3b** and **4b**, a broad singlet peak was observed for the boron-bonded $Me_2N$ methyl protons although the B—N bond of dimethylaminoborane species had a high bond rotation barrier (59–84 kJ·mol$^{-1}$) [13]. The B—N bond lengths were ca. 1.408(2) Å, 1.412(3) Å and 1.393(8) Å in **3a**, **3b** and **4b**, respectively. They supported by N-B backbonding (Table 2).

Nucleophilic, anionic boryl compounds have long been sought after but elusive. It has been reported (Nozaki et al.) that reductive cleavage of the boron-bromide bond in diazaborole was performed by lithium naphthalenide [14]. To synthesis the corresponding boryllithium, we have tried the reduction of the boron-chloride bond of **4e** with lithium and potassium graphite. Unfortunately, the target compound or dimerized product could not be detected (Scheme 2).

The calculated enthalpy of formation for the lithium substituted **4u** is 5.5 kcal/mole. The calculation procedure same as the other five membered rings that is described in the Supplementary file. The nucleophilic substitution reaction of **4e** with duryllithium was achieved which leads to compound **5d**. The reaction was not successful when using alkyllithium. This might be evaluated as π-delocalization is effective in the stability of **5d**. The new diazatriborolidine **5d** was characterized by $^{1}$H, $^{11}$B, and $^{13}$C NMR spectroscopy. In the $^{11}$B NMR spectra of **5d**, the one peak was observed at 61 ppm while the precursor **4e** had two signal ($\delta_B$ = 41, 60 ppm). In $^{13}$C NMR spectrum, the i-C atoms of the 2,6-dimethylphenyl groups in **5d** occurred at 141.7 and 141.1 ppm.

To obtain information on the suggested structures and gain more insight into electronic and steric effects of the ligands in the solid state of **3** and **4** rings, the molecular structure of **3a**, **3b**, **3d**, **4b** and **4c** were confirmed by using X-ray diffraction technique. Exocyclic B-N bonds are usually more reactive than endocyclic ones [15,16]. The results of the X-ray analysis reveal that the exocyclic B—N bonds are shorter than those of the endocyclic. Considering the B—N endocyclic bond lengths in **3a**, **3b** and **3d**, the bond lengths of the exocyclic N atoms attached to one of B-B atoms are slightly shorter than those of B1-N bonds. This can infer in that N atoms are preferentially attacked by a Lewis acid and the two boron atoms of the B-B bond are more electrophilic than the third boron atom in the ring, which case can be clearly seen in **4b**. However, with excess dichlorodimethylaminoborane one boron atom which remains in position 2 of the five-membered ring can be chlorinated. Furthermore, the π-bond fraction extended relatively uniformly over all the bonds in the ring system, except for the B—B bond. Considering the asymmetric units of the crystal structures, half of the molecule is present in the asymmetric unit for **3a**, **3b.** However, **3d** and **4c** have one whole molecule, while the asymmetric unit of **4b** contains four molecules. In **3a** and **3b**, the whole molecule possesses two-fold symmetry with the symmetry codes (−x, y, ½−z) and (1−x, y, ½−z), respectively. In Fig. 1, the symmetrically related parts of the whole molecules are indicated by " ' " superscript.

Comparing the B-B bond lengths with the literature, **3a** (1.714(3) Å), **3b** (1.705(5) Å), **3d** (1.728(8) Å), **4b** (1.727(9) Å) and **4c** (1.747(3) Å) are slightly shorter than alkyl substituted diazatriborolidine (1.789 Å) [9], but they consist of single B—B bond lengths of

**Table 2**
Selected bond lengths (Å) and bond angles (°) determined from X-ray studies are as follows.

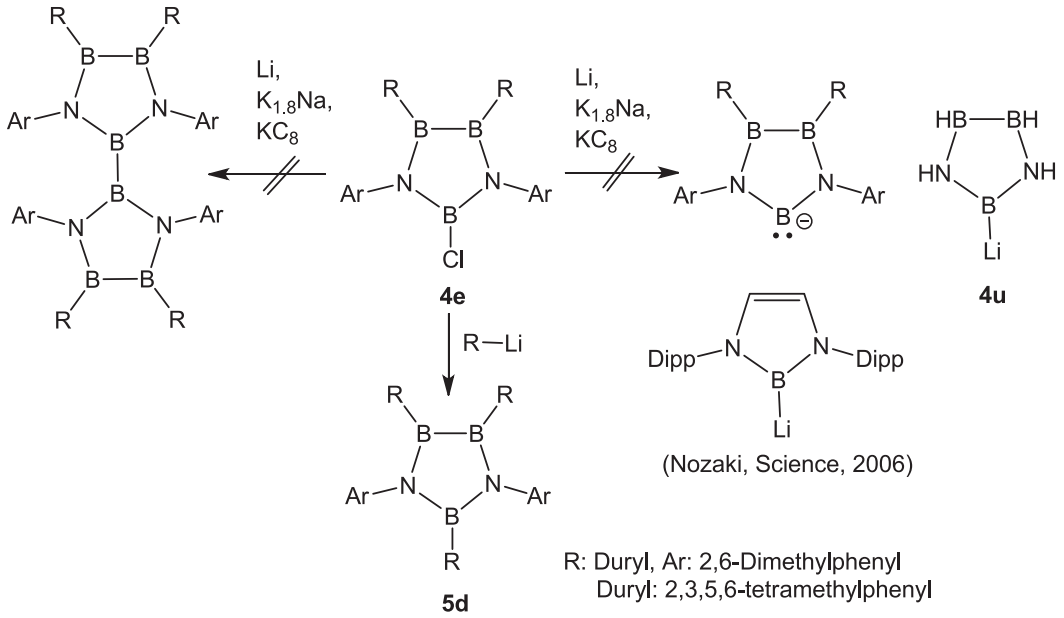
| 3a | | 3b | |
|---|---|---|---|
| B2-B2′ | 1.714(3) | B2-B2′ | 1.705(5) |
| B2-N1 | 1.455(2) | B2-N1 | 1.462(3) |
| B1-N1 | 1.466(2) | B1-N1 | 1.461(2) |
| B2-N3 | 1.408(2) | B2-N3 | 1.412(3) |
| B1-N2 | 1.418(3) | B1-N2 | 1.419(4) |
| N1-C1 | 1.431(2) | N1-C1 | 1.428(3) |
| N1-B1-N1′ | 111.4(2) | N1-B1-N1′ | 111.7(3) |
| B2′-B2-N1 | 103.0(1) | B2′-B2-N1 | 103.3(1) |
| B1-N1-B2 | 109.3(1) | B1-N1-B2 | 109.2(2) |

| **3d** | | **4b** (One of the four molecules in the *asym.* Unit | | **4c** | |
|---|---|---|---|---|---|
| B2-B3 | 1.728(8) | B2-B3 | 1.727(9) | B2-B3 | 1.747(3) |
| B2-N1 | 1.414(8) | B2-N1 | 1.459(8) | B2-N1 | 1.433(3) |
| B1-N1 | 1.494(6) | B1-N1 | 1.416(8) | B1-N1 | 1.444(3) |
| B1-N2 | 1.468(8) | B1-N2 | 1.426(7) | B1-N2 | 1.442(3) |
| B3-N2 | 1.434(8) | B3-N2 | 1.468(8) | B3-N2 | 1.436(3) |
| B1-N3 | 1.388(8) | B1-Cl1 | 1.776(7) | B1-Cl1 | 1.745(3) |
| B2-C21 | 1.585(7) | B2-N3 | 1.393(8) | B2-C21 | 1.573(3) |
| B3-C31 | 1.548(9) | B3-N4 | 1.395(8) | B3-C31 | 1.569(3) |
| N1-C1 | 1.427(7) | N1-C1 | 1.454(6) | N1-C1 | 1.446(3) |
| N2-C11 | 1.449(6) | N2-C11 | 1.426(7) | N2-C11 | 1.444(2) |
| N1-B1-N2 | 109.1(5) | N1-B1-N2 | 116.3(5) | N1-B1-N2 | 113.5(2) |
| B3-B2-N1 | 104.7(5) | B3-B2-N1 | 103.2(5) | B3-B2-N1 | 103.2(2) |
| B2-B3-N2 | 103.1(5) | B2-B3-N2 | 103.0(5) | B2-B3-N2 | 103.6(2) |
| B1-N1-B2 | 111.1(5) | B1-N1-B2 | 108.1(5) | B1-N1-B2 | 110.0(2) |

Xie's dimeric 1,3,2,4,5-diazatriborolidine (1.723(5) Å and 1.718(5) Å) [17]. The exocyclic B—N bond lengths of **3a** (1.408(2) Å, 1.418(3) Å) and **3b** (1.412(3) Å, 1.419(4) Å) are slightly longer than **3d** (1.388(8) Å), **4b** (1.393(8) Å, 1.395(8) Å) due to substitution effect. On the other hand, the average of the endocyclic B—N bond lengths of **3a**, **3b** and **4b** are 1.461 Å, 1.462 Å and 1.469 Å which are close to each other. The endocyclic and exocyclic B-N bond lengths of **3a** and **3b** are approximately 1.460 Å and 1.415 Å respectively. The B1—N1 and B1—N2 bond lengths in **4b** differ from those of other endocyclic B—N bonds by approximately 0.05 Å. Within the dimethylamino-substituted diazatriborolidin series, compounds **3a**, **3b**, **3d** and **4b** show B-$NMe_2$ bond lengths between 1.388(8) Å and 1.419(4) Å. In contrast, endocyclic B-N bond lengths are between 1.455(2) and 1.494(6) Å. Apparently, the exocyclic $Me_2$B-N bonds possess a more pronounced π-component.

The unsubstituted form of the diazatriborolidine ring is planar, but in the studied crystals, the B—B bonds of the 5-membered rings have a twisted geometry, and the rings are in half-chair conformations, except **3d** and **4c**, which are in planar form. The related torsion angle τ5 is in the vicinity of 0° for **3d** and **4c**, and approximately ± 20° for **3a**, **3b** and **4b**. This geometry distortion arises from the $NMe_2$ substitutions to B2 and B3 atoms. $NMe_2$ or Cl substitution to B1 atom is not affect the dihedral angle R2-R3. This value of all molecules is about 50°, except **4c**, which arises from the relatively large duryl ligands substituted to B2 and B3 atoms. For a similar reason, the dihedral angles R1-R2 and R1-R3 of **4c** are slightly different from the others (Fig. 2).

Considering the torsion angles τ3 and τ4, since the mesityl ligands substituted to B2 and B3 atoms, the values of **3d** are approximately 10°




**Scheme 2.** Synthesis of **5** derivatives.

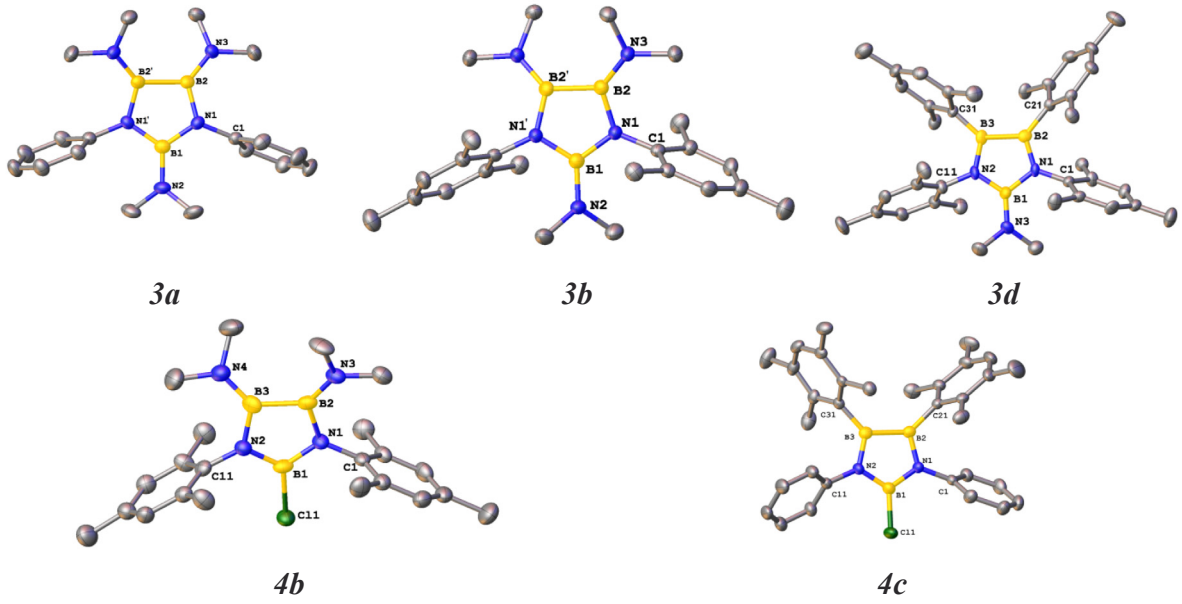


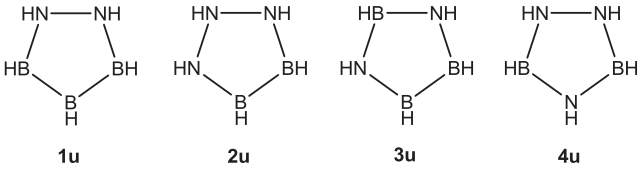

**Fig. 1.** Molecular structure of **3a**, **3b**, **3d, 4b** and **4c**. For the sake of clarity, H atoms were omitted.

larger than **3a**, **3b** and **4b**. Even though the torsion angle τ3 of **3d** is 10° larger than **4c**, the difference of τ4 angle between **3d** and **4c** is approximately 18° due to intra and inter molecular interactions of **4c**.

Comparing the diazatriborolidine ring geometries with those in the previous study by Paetzold et al. [9], B2—B3 (1.789 Å) and B1—N (1.406 Å) bond lengths are slightly shorter, B2—N (1.404 Å) and B3—N (1.491, 1.476 Å) bond lengths are slightly longer in the present study. Endocyclic bond angles are in good agreement with those in the Paetzold study, except for the B—N—B bond angles. The B—N—B bond angles of **3a**, **3b**, **3d**, **4b** and **4c** are larger ca. 10° than in the given literature due to different substituents at B and N atoms [9].

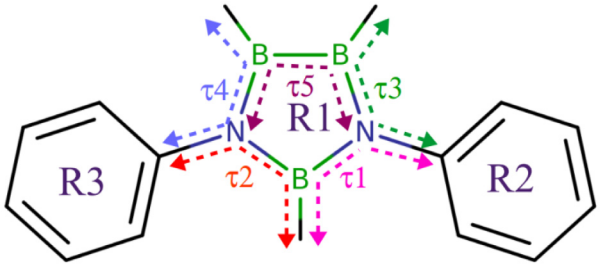
There are two possible structural isomers of triazadiborolidine ring (**2u**, **4u**) Likewise, diazatriborolidine ring has two possible structural isomers (**1u**, **3u**). Derivatives of **3u** [10] and **4u** [18] are known in these selected isomers. According to our calculations, the enthalpy formation of **3u** and **4u** were found as −40.7 and −43.8 kcal/mol respectively (Scheme 3).

The experimental results are consistent with the calculations; better




**Scheme 3.** The selected combinations of $B_{5-x}N_x$ five membered heterocyclic rings.

electronic saturation of the boron atoms can be expected in a ring system consisting of three $sp^2$-hybridized N and two $sp^2$-hybridized B atoms than in a ring containing only two nitrogen atoms to remedy the electron deficiency at three boron atoms. The results of our theoretical calculations are in good agreement with the studies conducted by Nöth and Balaban et al. [8,19]. The enthalpy formation of **1u** and **2u** were calculated as 54.0 and 35.9 kcal/mol, respectively. We believe that the ability of the aryl groups bound to the N atoms to create steric




*Torsion Angles (°)*

| | 3a | 3b | 3d | 4b | 4c |
|---|---|---|---|---|---|
| τ1 | 13.9(2) | -11.4(3) | -5.8(8) | 4.8(2) | -1.4(2) |
| τ2 | 13.9(2) | -11.4(3) | -9.4(9) | 9.5(2) | 4.9(1) |
| τ3 | 0.4(2) | -1.7(5) | 10.4(8) | 3.3(5) | -1.9(2) |
| τ4 | 0.4(2) | -1.7(5) | 10.6(7) | 1.8(3) | -7.5(1) |
| τ5 | -19.7(5) | 18.4(5) | 0.4(5) | -13.6(2) | 3.5(1) |

*Dihedral Angles*

| | 3a | 3b | 3d | 4b | 4c |
|---|---|---|---|---|---|
| R1-R2 | 77.4(5) | 73.6(6) | 71.0(3) | 81.4(1) | 66.4(1) |
| R1-R3 | 77.4(5) | 73.6(2) | 68.5(3) | 89.3(2) | 52.8(1) |
| R2-R3 | 46.7(8) | 58.2(1) | 53.2(2) | 50.2(8) | 75.8(1) |

**Fig. 2.** Selected torsion (τ) angles and dihedral angles. Ring planes are denotes as R.

hindrance and reduce the nucleophilicity of the N atoms may partially inhibit the intramolecular conversion to undesired products.

The new derivatives **3** and **4** were prepared without any restriction in contrast to Nöth and Paetzold studies [8,9]. A thorough investigation of the chemical reactivity of diazatriborolidines was primarily hampered by the lack of functional substituents of the molecules. The new synthetic method is the inverse of the method described by Nöth. It allows the use of more diarylamino diborane containing various substituents. In addition, the importance of 2-chloro diazatriborolidines (**4b** and **4c**) for their high chemical reaction potentials is indicated. The prepared dizatriborolidines were proved to be stable in the air apart from **4b** and **4c**.

## 3. Conclusion

In this study we presented the practical synthesis of novel 1,3,2,4,5-diazatriborolidine derivatives with high yield. Our synthesis pathway offers tunability of diazatriborolidines owing to the diversity of using starting reactants. $NMe_2$ bonded at 2-position B atom of diazatriborolidines were founded to be air stable. The chloride substituted diazatriborolidine derivatives have potential to reach boron containing heterocycle derivatives. **5e** was obtained from the displacement of chloride in **4d** with aryl. The prepared compounds were characterized by using one- and two-dimensional NMR spectroscopy. Also, the structures of **3a**, **3b**, **3d, 4b** and **4c** were confirmed using X-ray crystallography. These structures were investigated as detail and the computed enthalpies of formation of these heterocycles were reported for the first time. Furthermore, the present method removes the synthetic limitation for reach the desired diazatriborolidine derivatives.

## 4. Experimental

### 4.1. Synthesis

*General:* All reactions were performed under an argon atmosphere using standard schlenk techniques. Solvents were dried with suitable methods and saturated with argon. Glassware was dried using a heat gun under high vacuum. NMR spectra were measured on a Varian 400 spectrometer. The chemical shifts are given in ppm, and are referenced against residual solvent signals. Elemental analyses were done on a Leco-932. Dichlorodimethylaminoborane [8], Tetrakis(dimethylamino) diborane(4) [20], 1,2-bis(dimethylamino)diborane(4) dichloride [21], 1,2-bismesityldiborane(4) dichloride [22], 1,2-bisphenylamino-1,2-bis (dimethylamino)diborane(4) [23], 1,2-bismestylamino-1,2-bis(dimethylamino)diborane(4) [12], 1,2-bismestylamino-1,2-bismesityldiborane(4) [24] and 1,2-bisphenylamino-1,2-bisduryldiborane(4) [12] were synthesized according to the literature.

### 4.2. General procedure for synthesis of 2-dimethylamino-1,3,2,4,5-diazatriborolidine derivatives

n-BuLi (7.6 mL, 13 mmol, 1.6 M solution in hexane) was added dropwise onto a THF/Hexane (ca. 1:5) mixture (approx. 50 mL) of 1,2-diarylamino-diborane(4) derivative **1** (6 mmol) at −2 °C. The Mixture was warmed to room temperature and stirred overnight. The resulting suspension of **2** was cooled to −78 °C then $Cl_2BNMe_2$ (0.74 g, 5.8 mmol) was added dropwise. All volatile components were removed in vacuum after the mixture was slowly warmed to room temperature. The residue was extracted into pentane (50 mL). The solution was concentrated to a volume of about 10 mL. The concentrated solution was kept to −35 °C and the crystals were obtained.

### 4.3. 1,3-Diphenyl-2,4,5-tris(dimethylamino)-1,3,2,4,5-diazatriborolidine 3a

Yielding 70%, m.p.: 130 °C (decomposed).

$^1$H NMR (400 MHz, $CDCl_3$, 300 K): $\delta$ = 1.92 (s, 6H, $NMe_2$), 2.48 (br. s, 12H, $NMe_2$), 7.09 (t, 6H, $J_{HH}$ = 8 Hz, Ph), 7.22 (dd, 4H, $J_{HH}$ = 8 Hz, Ph); $^{13}$C NMR (100 MHz, $CDCl_3$, 300 K): $\delta$ = 39.5 (4C, $Me_2N$), 117.3 (2C, *p*-C, Ph), 128.1 (4C, *m*-C, Ph), 129.3 (4C, *o*-C, Ph), 149.0 (2C, *i*-C, Ph); $^{11}$B NMR (128 MHz, $CDCl_3$, 300 K): $\delta$ = 31 (B), 36 (2B) [25].

### 4.4. 1,3-Dimesityl-2,4,5-tris(dimethylamino)-1,3,2,4,5-diazatriborolidine 3b

Yielding 76.0%, m.p.: 159–160 °C (decomposed).

$^1$H NMR (400 MHz, $CDCl_3$, 300 K): $\delta$ = 1.80 (s, 6H, $NMe_2$), 2.14 (s, 12H, *o*-Me, Mes), 2.24 (s, 6H, *p*-Me, Mes), 2.42 (br. s, 12H, $NMe_2$), 6.78 (s, 4H, *m*-H, Mes); $^{13}$C NMR (100 MHz, $CDCl_3$, 300 K): $\delta$ = 19.0 (4C, *o*-Me, Mes), 20.9 (2C, *p*-Me, Mes), 38.3 (6C, $NMe_2$), 127.9 (4C, *m*-C, Mes), 132.6 (4C, *o*-C, Mes), 134.9 (2C, *p*-C, Mes), 144.6 (2C, *i*-C, Mes); $^{11}$B NMR (128 MHz, $CDCl_3$, 300 K): $\delta$ = 30 (B), 36 (2B). Anal. Calcd. for $C_{24}H_{40}B_3N_5$ (431.36): C, 66.87; H, 9.35; N, 16.25. Found: C, 66.67; H, 9.93; N, 15.60 [25].

### 4.5. 1,3-Diphenyl-2-dimethylamino-4,5-diduryl-1,3,2,4,5-diazatriborolidine 3c

Yielding 63.7%, m.p.: 198 °C (decomposed).

$^1$H NMR (400 MHz, $CDCl_3$, 300 K): $\delta$ = 2.04 (s, 12H, *m*-Me, Dur), 2.06 (s, 12H, *o*-Me, Dur), 2,31 (s, 6H, $NMe_2$), 6.64 (s, 2H, *p*-H, Dur), 6.96 (d, 4H, $J_{HH}$ = 8 Hz, *o*-H, Ph), 6.98 (t, 4H, $J_{HH}$ = 8 Hz, *m*-H, Ph), 7.13 (t, 2H, $J_{HH}$ = 8 Hz, *p*-H, Ph); $^{13}$C NMR (100 MHz, $CDCl_3$, 300 K): $\delta$ = 19.1 (4C, *m*-Me, Dur), 19.9 (4C, *o*-Me, Dur), 40.6 (2C, $NMe_2$), 123.7 (2C, *p*-C, Dur), 126.0 (6C, *p*- and *m*-C, Ph), 127.9 (4C, *m*-C, Ph), 129.5 (4C, *m*-C, Dur), 131.9 (4C, *o*-C, Ph), 132.5 (4C, *o*-C, Dur), 141.2 (br., 2C, *i*-C, Dur), 146.7 (2C, *i*-C, Ph); $^{11}$B NMR (128 MHz, $CDCl_3$, 300 K): $\delta$ = 30 (B), 58 (2B). Anal. Calcd. for $C_{34}H_{42}B_3N_3$ (525.37): C, 77.76; H, 8.06; N, 8.00. Found: C, 76.23; H, 8.58; N, 7.61 [25].

### 4.6. 1,3,4,5-Tetramesityl-2-dimethylamino-1,3,2,4,5-diazatriborolidine 3d

Yielding 80.0%, m.p.: > 220 °C (decomposed).

$^1$H NMR (400 MHz, $CDCl_3$, 300 K): $\delta$ = 1.98 (s, 12H, *o*-Me, B-Mes), 2.00 (s, 6H, *p*-Me, B-Mes), 2.11 (s, 12H, *o*-Me, N-Mes), 2.11 (s, 6H, $NMe_2$), 2.21 (s, 6H, *p*-Me, N-Mes), 6.47 (s, 4H, *m*-H, B-Mes), 6.73 (s, 4H, *m*-H, N-Mes); $^{13}$C NMR (100 MHz, $CDCl_3$, 300 K): $\delta$ = 19.0 (4C, *o*-Me, B-Mes), 19.9 (2C, *p*-Me, B-Mes), 21.0 (2C, *p*-Me, N-Mes), 22.4 (4C, *o*-Me, N-Mes), 38.1 (6C, $NMe_2$), 127.0 (4C, *m*-C, N-Mes), 128.9 (4C, *m*-C, B-Mes), 131.3 (br. 2C, i-C, B-Mes), 133.0 (2C, *p*-C, N-Mes), 133.3 (2C, *p*-C, B-Mes), 135.8 (4C, *o*-C, B-Mes), 138.4 (4C, *o*-C, N-Mes), 142.3 (2C, *i*-C, N-Mes); $^{11}$B NMR (128 MHz, $CDCl_3$, 300 K): $\delta$ = 31 (B), 58 (2B).

### 4.7. 1,3-Bis(2,6-dimethyl)phenyl-2-dimethylamino-4,5-diduryl-1,3,2,4,5-diazatriborolidine 3e

Yielding 78%, m.p.: > 220 °C (decomposed).

$^1$H NMR (400 MHz, $CDCl_3$, 300 K): $\delta$ = 1.88 (s, 12H, *m*-Me, Dur), 1.95 (s, 12H, *o*-Me, Dur), 2,00 (s, 6H, $NMe_2$), 2.14 (s, 12H, *o*-Me, Ph), 6.62 (s, 2H, *p*-H, Dur), 6.87 (m, 6H, *m*- und *p*-H, Ph); $^{13}$C NMR (100 MHz, $CDCl_3$, 300 K): $\delta$ = 19.2 (4C, *m*-Me, Dur), 19.3 (4C, *o*-Me, Dur), 20.1 (4C, *o*-Me, Ph), 38.0 (2C, $NMe_2$), 124.1 (2C, *p*-C, Dur), 128.1 (2C, *p*-C, Ph), 130 (4C, *m*-C, Ph), 132.1 (4C, *o*-C, Ph), 133.5 (4C, *m*-C, Dur), 134.0 (4C, *o*-C, Dur), 142.0 (br., 2C, *i*-C, Dur), 144.8 (2C, *i*-C, Ph); $^{11}$B NMR (128 MHz, $CDCl_3$, 300 K): $\delta$ = 32 (B), 59 (2B).

### 4.8. General procedure for synthesis of 2-chloro-1,3,2,4,5-diazatriborolidine derivatives

The suspension of **3** (8 mmol) was cooled to −78 °C in THF/Hexane mixture than $Cl_2BNMe_2$ (1.15 g, 10 mmol) was added dropwise. All volatile components were removed in vacuum after the mixture was

slowly warmed to room temperature. The residue was extracted into pentane (50 mL). The solution was concentrated to a volume of about 10 mL. The concentrated solution was kept to −30 °C and the crystals were obtained.

### 4.9. 2-Chloro-4,5-bis(dimethylamino)-1,3-dimesityl-1,3,2,4,5-diazatriborolidine 4b

Yielding 55%, m.p.: > 210 °C (decomposed).

$^1$H NMR (400 MHz, $CDCl_3$, 300 K): $\delta$ = 2.14 (br. s, 24H, *o*-Me, Mes and $NMe_2$), 2.26 (s, 6H, *p*-Me, Mes), 6.85 (s, 4H, *m*-H, Mes); $^{13}$C NMR (100 MHz, $CDCl_3$, 300 K): $\delta$ = 18.9 (4C, *o*-Me, Mes), 20.9 (2C, *p*-Me, Mes), 44.2 (4C, $NMe_2$), 128.2 (4C, *m*-C, Mes), 133.8 (4C, *o*-C, Mes), 134.3 (2C, *p*-C, Mes), 141.6 (2C, *i*-C, Mes); $^{11}$B NMR (128 MHz, $CDCl_3$, 300 K): $\delta$ = 36 (3B) [25].

### 4.10. 2-Chloro-1,3-diphenyl-4,5-diduryl-1,3,2,4,5-diazatriborolidine 4c

Yielding 57%, m.p.: 200 °C (decomposed).

$^1$H NMR (400 MHz, $CDCl_3$, 300 K): $\delta$ = 1.83 (s, 12H, *m*-Me, Dur), 1.99 (s, 12H, *o*-Me, Dur), 6.64 (s, 2H, *p*-H, Dur), 6.74 (d, 4H, $J_{HH}$ = 8 Hz, *o*-H, Ph), 7.09 (t, 4H, $J_{HH}$ = 8 Hz, *m*-H, Ph), 7.19 (t, 2H, $J_{HH}$ = 8 Hz, *p*-H, Ph); $^{13}$C NMR (100 MHz, $CDCl_3$, 300 K): $\delta$ = 19.1 (4C, *m*-C, Me, Dur), 19.8 (4C, *o*-C, Me, Dur), 124.4 (2C, *p*-C, Dur), 125.5 (2C, *p*-C, Ph), 128.2 (4C, *m*-C, Ph), 130.2 (4C, *m*-C, Dur), 132.2 (4C, *o*-C, Ph), 132.8 (4C, *o*-C, Dur), 141.2 (br., 2C, *i*-C, Dur), 143.2 (2C, *i*-C, Ph); $^{11}$B NMR (128 MHz, $CDCl_3$, 300 K): $\delta$ = 39 (B), 59 (2B). Anal. Calcd. for $C_{32}H_{36}N_2Cl$ (516.28): C, 74.41; H, 7.02; N, 5.42. Found: C, 74.37; H, 8.48; N, 5.74 [25].

### 4.11. 2-Chloro-1,3-bis(2,6-dimethyl)phenyl-4,5-diduryl-1,3,2,4,5-diazatriborolidine 4e

Yielding 64%, m.p.: > 210 °C

$^1$H NMR (400 MHz, $CDCl_3$, 300 K): $\delta$ = 1.94 (s, 12H, *m*-Me, Dur), 1.99 (s, 12H, *o*-Me, Dur), 2.18 (s, 12H, *o*-Me, Ph), 6.69 (s, 2H, *p*-H, Dur), 6.97 (m, 6H, *m*- und *p*-H, Ph); $^{13}$C NMR (100 MHz, $CDCl_3$, 300 K): $\delta$ = 19.1 (4C, *m*-C, Me, Dur), 19.4 (4C, *o*-C, Me, Dur), 19.9 (4C, *o*-C, Ph), 125.2 (2C, *p*-C, Dur), 128.5 (2C, *p*-C, Ph), 130.8 (4C, *m*-C, Dur), 132.5 (4C, *o*-C, Dur), 133.6 (4C, *m*-C, Ph), 134.5 (4C, *o*-C, Ph), 141.1 (br., 2C, *i*-C, Dur), 141.4 (2C, *i*-C, Ph); $^{11}$B NMR (128 MHz, $CDCl_3$, 300 K): $\delta$ = 41 (B), 61 (2B).

### 4.12. 2-Duryl-1,3-bis(2,6-dimethyl)phenyl-4,5-diduryl-1,3,2,4,5-diazatriborolidine 5d

**4e** (3.44 g, 6 mmol) was cooled to 0 °C in THF/Hexane mixture than Dur-Li (7.5 mL, 12 mmol, $Et_2O$) was added dropwise. All volatile components were removed in vacuum after the mixture was slowly warmed to room temperature. The residue was extracted with $CH_2Cl_2$/Hexane (3:1) mixture (approx. 30 mL). After all solutions were removed, the residue was crystallized at −30 °C in THF.

Yielding 76%, mp: > 220 °C

$^1$H NMR (400 MHz, $CDCl_3$, 300 K): $\delta$ = 1.71, 1.74 (each s, je 6H, *m*-, *o*-Me, Dur), 1.75, 1.76 (je s, each 12 H, *m*-, *o*-Me, Dur), 1.96 (s, 12H, *o*-Me, Ph), 6.42 (s, 2H, *p*-H, Dur), 6.48 (s, H, *p*-H, Dur), 6.68–6.72 (m, 6H, *m*- und *p*-H, Ph); $^{13}$C NMR (100 MHz, $CDCl_3$, 300 K): $\delta$ = 18.6, 18.7 (each 4C, *m*-, *o*-C, Me, Dur), 18.7, 19.7 (each 2C, *m*-, *o*-C, Me, Dur), 19.2 (4C, *o*-C, Ph), 124.0 (C, *p*-C, Dur), 124.8 (2C, *p*-C, Dur), 127.6, 127.7 (each C, p-C, Ph), 130.1 (2C, *m*-C, Dur), 131.0 (4C, *p*-C, Dur), 131.7 (2C, *o*-C, Dur), 132.2 (4C, *o*-C, Dur), 132.9, 133.0 (each 2C, m-C, Ph), 133.8, 133.9 (each 2C, o-C, Ph), 141.1, 141.7 (each C, *i*-C, Ph); $^{11}$B NMR (128 MHz, $CDCl_3$, 300 K): $\delta$ = 61 (3B).

### 4.13. Crystal structure determinations

The crystal data on **3a**, **3b**, **3d**, **4b** and **4c** were collected on a Rigaku Oxford Diffraction Xcalibur Eos diffractometer using graphite-monochromated $MoK_\alpha$ radiation ($\lambda$ = 0.71073 Å) in the ω-scan mode. The data collection, cell refinement and data reduction were performed using the CrysAlis$^{Pro}$ program [26]. Analytical numeric absorption correction using a multifaceted crystal model [27] and empirical absorption correction using spherical harmonics based on multiple scans [26] were performed. The structures were solved using Olex2 [28]and the ShelXT [29] structure solution program using Direct Methods and refined with the ShelXL [30] refinement package using Least Squares minimization. All non-hydrogen atoms were refined anisotropically. In **3a**, H atoms were determined from the electron density maps; in the other compounds, the H atoms were located at calculated positions and refined using a riding model. In determining the crystal structure of **4b**, the reflections with Error/esd > 5 were omitted. In **4c**, the crystal structure was refined by using squeeze procedure to complete the structure determination. There are two voids; one is possibly $BCl_3$ with a serious disorder, which is the center of the micelle as shown in Supplementary file, Fig. S5. The other void is possibly the hexane solvent. The crystallographic data and structure refinement summary for the compounds are given in Supplementary data Table S1.

### 4.14. Computational procedures

Geometry optimizations, frequency and NMR calculations were performed using Gaussian09W program suite [31] using B3LYP [32] functional with 6-311G(d,p) [33] basis set. Atomization method, which is one of the *ab initio* calculation method of Enthalpy of Formation ($\Delta H_f^o$) energies, is used to calculate the $\Delta H_f^o$ of **1u**-**4u**. $\Delta H_f^o$ are calculated using G4 method [34] which is one of the high accuracy energy calculation methods. Details of $\Delta H_f^o$ are in Supplementary data.

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## Appendix A. Supplementary data

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