

# Synthesis and structure of 2,4,6-tris[tris(dimethylamino)silylamino]borazine: $\{[(\text{CH}_3)_2\text{N}]_3\text{SiNH}\}_3\text{B}_3\text{N}_3\text{H}_3$

F. Cheng, B. Toury, S.J. Archibald, John S. Bradley\*

Department of Chemistry, University of Hull, Cottingham Road, Hull HU6 7RX, UK

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## Abstract

A novel compound 2,4,6-tris[tris(dimethylamino)silylamino]borazine  $\{[(\text{CH}_3)_2\text{N}]_3\text{SiNH}\}_3\text{B}_3\text{N}_3\text{H}_3$  (**1**) was prepared by reaction between lithium tris(dimethylamino)silylamide  $[(\text{CH}_3)_2\text{N}]_3\text{SiNHLi}$  and 2,4,6-trichloroborazine  $\text{Cl}_3\text{B}_3\text{N}_3\text{H}_3$ . The molecular structure of **1** was discussed on the basis of its FTIR, NMR and X-ray crystallographic analysis. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Dimethylamino; Silylamino; Borazine; Synthesis; Structure

## 1. Introduction

Synthesis of novel organometallic compounds possessing B–N–Si backbones as a potential source of precursor molecules for the chemical synthesis of silicon boron nitride composites has been extensively studied in the recent years [1–4]. We recently reported for the first time the preparation of tris(dimethylamino)silylamine,  $[(\text{CH}_3)_2\text{N}]_3\text{SiNH}_2$  (TDSA), by ammonolysis of tris(dimethylamino)chlorosilane  $[(\text{CH}_3)_2\text{N}]_3\text{SiCl}$ , an intermediate prepared from the reaction of silicon tetrachloride with dimethylamine [5]. From TDSA a high surface area silicon diimide gel, which is a precursor for high purity silicon nitride [6], was prepared via non-aqueous ammonolytic sol–gel method [5]. We are now actively seeking to prepare novel ternary Si–B–N precursor molecules, using tris(dimethylamino)silylamine as a starting material. The synthetic strategy we have adopted is to use tris(dimethylamino)silylamine or its lithium salt  $[(\text{CH}_3)_2\text{N}]_3\text{SiNHLi}$  (**2**) as reagents to assemble precursor molecular containing, in addition to  $\text{Si}(\text{NMe}_2)_3$  groups,  $\text{B}(\text{NHSiN}_3)_n$  backbones. These

precursor materials are expected to be converted into high surface area silicon boron diimide gels by a similar sol–gel process, and hence to Si–B–N ceramics.

In this paper, we report the preparation of a novel Si–B–N precursor molecular 2,4,6-tris[tris(dimethylamino)silylamino]borazine  $\{[(\text{CH}_3)_2\text{N}]_3\text{SiNH}\}_3\text{B}_3\text{N}_3\text{H}_3$  (**1**) by reaction between **2** with 2,4,6-trichloroborazine  $\text{Cl}_3\text{B}_3\text{N}_3\text{H}_3$  (TCB). TCB was chosen as a starting material not only because of the obvious reactivity of the B–Cl functionality, but also because of its borazinic ring  $\text{B}_3\text{N}_3$  structure, which is the basic structural unit of hexagonal boron nitride. The molecular structure of **1** was determined on the basis of its FTIR, NMR and X-ray crystallographic analysis. The sol–gel processing of **1** will be discussed separately.

## 2. Results and discussion

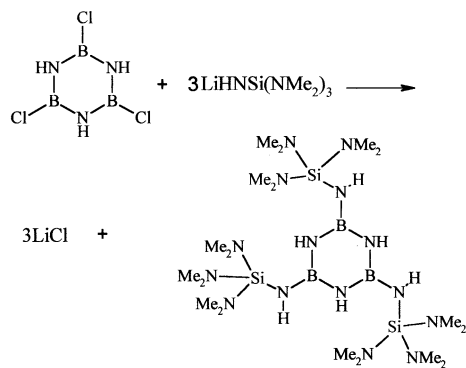
Compound **1** was prepared by reaction between 2,4,6-trichloroborazine  $\text{Cl}_3\text{B}_3\text{N}_3\text{H}_3$  (TCB) and lithium tris(dimethylamino)silylamide  $[(\text{CH}_3)_2\text{N}]_3\text{SiNHLi}$  (**2**) in a 1:3 molar ratio in pentane (Scheme 1). The white solid obtained after removal of LiCl and pentane can be sublimed at 160 °C under reduced pressure without detectable decomposition, showing its relatively high thermal stability towards self-condensation. The  $^1\text{H}$ -

\* Corresponding author. Tel.: +44-1482-466-408; fax: +44-1482-466-410

E-mail address: j.s.bradley@hull.ac.uk (J.S. Bradley).

Table 1  
Crystal data for compound **1**

Compound	<b>1</b>
Formula	C <sub>18</sub> H <sub>60</sub> B <sub>3</sub> N <sub>15</sub> Si <sub>3</sub>
Formula weight	603.51
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
<i>a</i> (Å)	9.030(4)
<i>b</i> (Å)	13.965(6)
<i>c</i> (Å)	14.819(5)
$\alpha$ (°)	83.65(3)
$\beta$ (°)	75.12(3)
$\gamma$ (°)	79.42(4)
<i>V</i> (Å <sup>3</sup> )	1771.2(12)
<i>Z</i>	2
Crystal size (mm)	0.15 × 0.15 × 0.20
Temperature (K)	150(2)
$\lambda$ (Å)	0.71073
$\theta$ Range (°)	2.58–33.68
Index ranges	–11 ≤ <i>h</i> ≤ 13, –21 ≤ <i>k</i> ≤ 21, –22 ≤ <i>l</i> ≤ 22
Reflections collected	39 619
Independent reflections	13 591 [ <i>R</i> <sub>int</sub> = 0.0801]
Observed reflections	5849
Data/restraints/parameters	13 591/0/353
GOF	0.866
<i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0779, <i>wR</i> <sub>2</sub> = 0.2027
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.1617, <i>wR</i> <sub>2</sub> = 0.2432
Largest difference peak and hole (e Å <sup>–3</sup> )	0.576 and –0.765



Scheme 1. Synthesis of compound **1**.

NMR spectrum shows three signals; the most intense at 2.60 ppm is attributed to the protons of dialkylamino substituents. Two other signals at 3.60 and 1.50 ppm are respectively assigned to B–NH–B and B–NH–Si protons. The <sup>11</sup>B-NMR displays a single resonance at 27.70 ppm for boron atoms linked to nitrogen atoms, indicating that no B–Cl (at 30 ppm in TCB) groups are present in **1**. <sup>13</sup>C-NMR and <sup>29</sup>Si-NMR spectra also show expected singlets at 37.8 and –35.0 ppm, respectively. The FTIR data supported the conservation of the borazinic cycle since the spectrum displays bands assigned to the BN ring and bending regions at 1491 and 710 cm<sup>–1</sup> [7]. An absorption at 3390 cm<sup>–1</sup> was assigned to the ν(NH) of BNHSi group. The two others

signals in the NH region at 3414 and 3438 cm<sup>–1</sup>, which were also observed on TCB spectrum, can be ascribed to the symmetric and asymmetric vibration bands of NH in the ring [8]. These spectral features combined with the mass spectra (*m/z*: 603) and elemental analysis indicated that 2,4,6-tris[tris(dimethylamino)silylamino]borazine {[ (CH<sub>3</sub>)<sub>2</sub>N]<sub>3</sub>SiNH}<sub>3</sub>B<sub>3</sub>N<sub>3</sub>H<sub>3</sub> (**1**) had been obtained.

The molecular structure of compound **1** was determined by single-crystal X-ray diffraction analysis (Table 1). A view of the molecule is shown in Fig. 1 and selected bond lengths and angles are collected in Table 2. As expected, the B<sub>3</sub>N<sub>3</sub> ring is planar and the [(CH<sub>3</sub>)<sub>2</sub>N]<sub>3</sub>SiNH groups occupy three *exo*-positions bonded to borons. The average length of the B–N (ring) bonds, 1.438(4) Å [range 1.430(4)–1.442(4) Å] is close to the average values in: (HNBH)<sub>3</sub>, 1.436 Å [9] and (Me<sub>2</sub>NBNH)<sub>3</sub>, 1.433 Å; [10] but longer than the average B–N (ring) distances in (<sup>*t*</sup>Pr<sub>2</sub>NBNH)<sub>3</sub> [11] and parent compound (ClBNH)<sub>3</sub> [12], 1.413 Å because <sup>*t*</sup>Pr<sub>2</sub>N and Cl substitutions have stronger electron-donating effect which can favour the double bond character in the borazine ring and shorten the B–N distance [11,13]. The average *exo*-B–N distance of **1** is 1.442 Å and the position of *exo* nitrogen atoms deviate slightly from the mean least-squares plane calculated for the borazine ring.

### 3. Experimental

#### 3.1. General

All procedures were performed under a protective nitrogen atmosphere using standard Schlenk techniques or in a nitrogen filled glove box. The solvents, *n*-pentane and THF, were freshly distilled from sodium/benzophenone prior to use. Tris(dimethylamino)silylamine (Me<sub>2</sub>N)<sub>3</sub>SiNH<sub>2</sub> (TDSA) and 2,4,6-trichloroborazine Cl<sub>3</sub>B<sub>3</sub>N<sub>3</sub>H<sub>3</sub> (TCB) was prepared according to previous

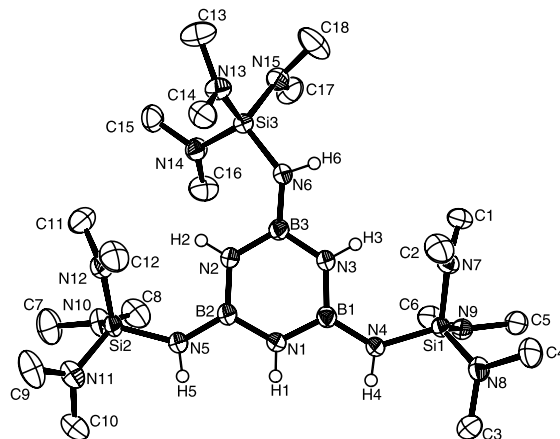


Fig. 1. ORTEP [18] plot of the molecular structure of compound **1**. Hydrogen atoms in the dimethylamino groups are omitted for clarity.

Table 2  
Selected bond distances (Å) and angles (°) for compound **1**

Bond distances		Bond angles	
B(1)–N(1)	1.434(4)	N(1)–B(1)–N(3)	115.8(2)
B(1)–N(3)	1.430(4)	N(1)–B(2)–N(2)	116.9(2)
B(2)–N(1)	1.440(4)	N(2)–B(3)–N(3)	116.2(3)
B(2)–N(2)	1.441(4)	B(1)–N(1)–B(2)	123.7(3)
B(3)–N(2)	1.442(4)	B(2)–N(2)–B(3)	122.7(2)
B(3)–N(3)	1.440(4)	B(1)–N(3)–B(3)	124.5(2)
B(1)–N(4)	1.445(4)	N(3)–B(1)–N(4)	122.4(2)
B(2)–N(5)	1.442(4)	N(1)–B(1)–N(4)	121.7(3)
B(3)–N(6)	1.439(4)	N(2)–B(2)–N(5)	122.7(3)
Si(1)–N(4)	1.727(2)	N(1)–B(2)–N(5)	120.4(3)
Si(2)–N(5)	1.719(3)	N(2)–B(3)–N(6)	123.7(3)
Si(3)–N(6)	1.727(3)	N(3)–B(3)–N(6)	120.1(2)
		B(1)–N(4)–Si(1)	131.5(2)
		B(2)–N(5)–Si(2)	135.3(2)
		B(3)–N(6)–Si(3)	138.8(2)

reports [5,14]. NMR spectra were obtained on a JEOL JNM-LA400FT NMR spectrometer using  $C_6D_6$  as solvent. IR spectrum was recorded on a Nicolet Magna-500 FTIR spectrometer. MS spectra were recorded on a SHIMADZU GC MS–QP 5050 spectrometer. Single crystal X-ray diffraction data were collected on STOE IPDS II system.

### 3.2. Preparation of lithium

#### *tris(dimethylamino)silylamide (TDSA–Li)*

Preparation of TDSA–Li was modified from a previous report [15]. To a rapidly stirred solution of TDSA (31.08 g, 176.3 mmol) in pentane solution (150 ml) at 0 °C was added *n*-butyllithium (110 ml, 1.6 M in hexane, 176 mmol). After stirring at 0 °C for 30 min the reaction mixture was allowed to warm to room temperature (r.t.) and stirred for 1 h, then cooled to –80 °C for 10 h. A white crystalline solid (23.08 g, 71.9% yield) was obtained after being isolated from the solution and washed with cold pentane.  $^1H$ -NMR:  $\delta = -2.65$  (s, 18H,  $N(CH_3)_2$ ),  $-1.46$  (s, 1H,  $SiNH$ );  $^{13}C$ -NMR:  $\delta = 39.08$  (s,  $N(CH_3)_2$ );  $^{29}Si$ -NMR:  $\delta = 25.6$  (s,  $Si[(N(CH_3)_2)_3]$ ); IR (Nujol film,  $cm^{-1}$ ): 3351 (w,  $\nu(NH)$ ).

### 3.3. Preparation of 2,4,6-

#### *tris[tris(dimethylamino)silylamino]borazine (1)*

TCB (1.56 g, 8.5 mmol) was allowed to react with TDSA–Li (4.64 g, 25.5 mmol) in pentane at r.t. overnight. The resulting lithium chloride was removed by filtration, and the filtrate concentrated under reduced pressure to give a gummy solid. Extraction into pentane (20 ml) and cooling to –80 °C for 18 h gave a white solid (4.53 g, yield: 85%). Anal. Calc.: C 35.8, H 10.0, N 34.8. Found: C 35.5, H 10.0, N 34.9%;  $^1H$ -NMR:  $\delta =$

2.60 (s, 18H,  $NCH_3$ ), 3.60 (s, 1H,  $BNHB$ ), 1.50 (s, 1H,  $BNHSi$ );  $^{13}C$ -NMR:  $\delta = 37.8$  (s,  $Si[(N(CH_3)_2)_3]$ );  $^{11}B$ -NMR:  $\delta = 27.70$  (s,  $(NBNH)_3$ );  $^{29}Si$ -NMR:  $\delta = -35.0$  (s,  $Si[(N(CH_3)_2)_3]$ ); MS ( $m/z$ , EI) 603[1]+.

Crystals of **1** suitable for X-ray diffraction experiment were prepared as follows. A solution of **1** (0.5 g) in toluene (1 ml) at r.t. was cooled to 4 °C for 2 days. A crystal suitable for X-ray diffraction was coated with a perfluoropolyether oil and frozen in a stream of  $N_2$  at 150 K during data collection on a Stöe IPDSII diffractometer. The structure was solved by direct methods (SHELXS-86) [16] and refined against  $F^2$  (SHELXL-97) [17]. H-atoms were placed in idealised positions.

## 4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC reference number 181877 for compound **1**. Copies of the information may be obtained from The Director, CCDC, 12, Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

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