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Synthesis of an eight-membered 2,2,4,6,6,8-hexaphenyl-1,3,5,7,2,6,4,8-tetraoxadisiladiborocane and its reaction with 4,4-azo-pyridine leading to ring contraction to give a dimer and hydrogen bonded macrocyclic siloxane-azo-pyridine

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ABSTRACT

We hereby report the syntheses and characterization of a new dimer of azopyridine connected through the six-membered B-N dative-bonded-adduct $Ph_8B_4Si_2O_6 \cdot L$ (4) and a hydrogen-bond-induced macrocyclic product $4(Ph_2Si(OH)_2) \cdot 3(C_{10}H_8N_4)$ (5). The products were obtained after an eight-membered 2,2,4,6,6,8-hexaphenyl-1,3,5,7,2,6,4,8-tetraoxa disiladiborocane ($Ph_6B_2Si_2O_4$) (3), which is abundant in the literature, was successfully synthesized and characterized by standard analytical and spectroscopic methods such as single-crystal XRD, melting point, nuclear magnetic resonance and Fourier transform infrared spectroscopy. Subsequently, compound 3 and 4,4-azopyridine (L) were reacted in a mixture of diethyl ether and petroleum ether solvents at reflux. This reaction caused a contraction of the eight-membered compound 3 to give two products - a dimer compound 4 ($Ph_8B_4Si_2O_6 \cdot L$), and a macrocyclic product $4(Ph_2Si(OH)_2) \cdot 3(C_{10}H_8N_4)$ (5). These two products have been characterized by single-crystal XRD, nuclear magnetic resonance, Fourier transform infrared spectroscopy, and melting point. Single crystal X-ray diffraction studies reveal that the dimer compound 4 compound crystalized in the monoclinic crystal system with a centrosymmetric space group of $P2_1/c$, a = 11.0879(4) Å, b = 14.3707(4) Å, c = 16.2697(5) Å, β = 98.759(3)°, V = 2562.20(13) Å^3, Z = 2. On the other hand, the macrocyclic product $4(Ph_2Si(OH)_2) \cdot 3(C_{10}H_8N_4)$ (5) is orange blocky needles that crystallized in the triclinic crystal system with a centrosymmetric space group of P-1, a = 12.2352(3) Å, b = 15.3274(6) Å, c = 20.0271(6) Å, α = 89.879(3)°, β = 89.988(2)° γ = 78.298(3)°, V = 3677.7(2) Å^3, Z = 2. Furthermore, compounds 4 and 5 exhibit various noncovalent interactions in crystal packing, such as intermolecular and intramolecular π-π as well as hydrogen bonding. This study demonstrates the potential for making novel materials via the combination of cyclodiboradisiloxane (a Lewis acid) and nitrogen-containing ligand (a Lewis base).

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1. Introduction

For a long time, cyclodiboradisiloxanes, and their derivatives as a class of organoborasilicon compounds, have been the focus of a large number of studies due to their exceptional structural architecture [1,2], magnetic properties [3], electronic properties [4], optical properties [5], quasiaromatic characters [2] as well as their aptitude for the formation of extended π-π intramolecular and intermolecular interactions [6]. These group of compounds consists mainly of alkyl Si-O-B and O-B-O ring systems for which the boron centers (if tricoordinated) are further ligated with Lewis bases such as pyridines, leading to the formation of a B-N dative bond, which imparts remarkable stability and reactivity [2,7]. The presence of silicon and oxygen atoms within cyclodiboradisiloxane bestows the framework unusual high elasticity and plasticity when subjected to sudden and slow stress [2,8]. Boron-nitrogen adducts, such as those formed between cyclodiboradisiloxanes and nitrogen-containing ligands, have shown great promise in various fields, such as conductive polymers for advanced energy devices, catalysis, carbon capture, gas separation and adsorption, lightweight, high-strength materials for application in spacecraft, pharmaceuticals, and drug delivery [9]. The ability to form stable, covalent bonds between boron and nitrogen atoms enables the creation of novel materials with tailored properties. Furthermore, polymers, in particular, have revolutionized modern technology, finding applications in everything from packaging materials to advanced electronics [9-11]. The development of novel polymers with unique properties, such as conductivity [5], luminescence [12], or response to stimulation [13,14], is an active area of research [15]. Incorporation of cyclodiboradisiloxanes and boron-nitrogen adducts into polymer backbones or side chains offers a promising route to create materials with improved performance and functionality [16]. Regardless of the functions and uses of this borasiloxane material, as well as their promising future prospects, only a few

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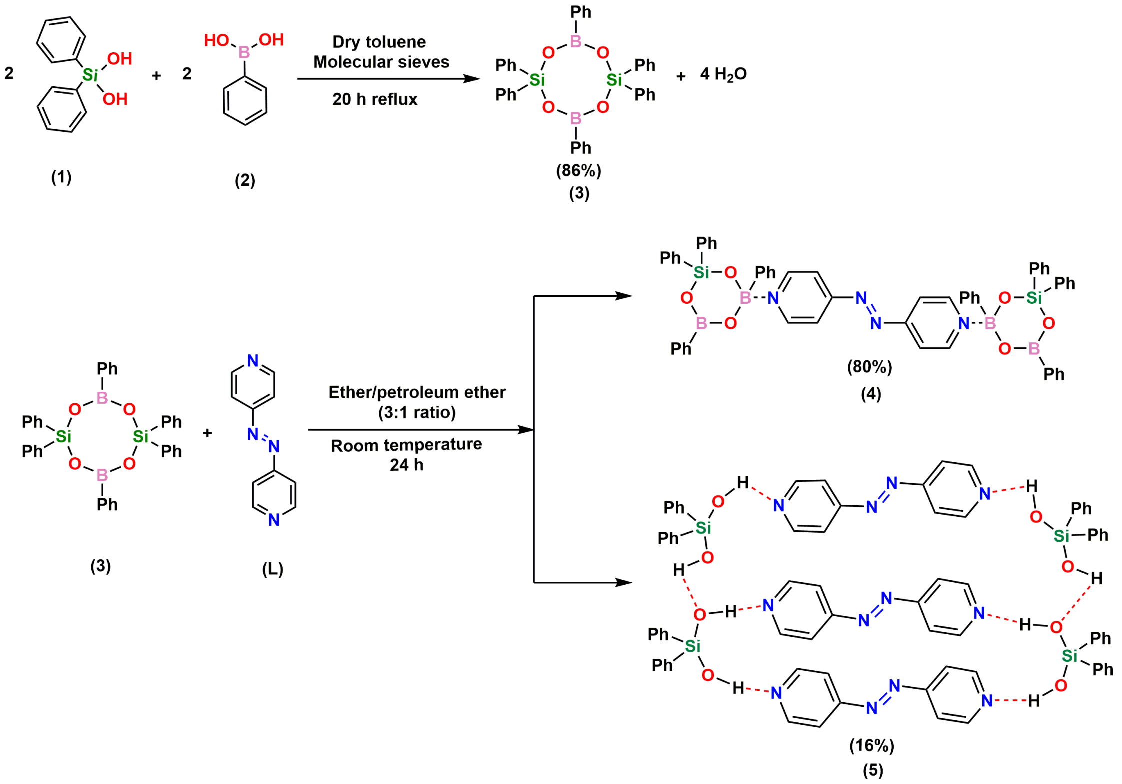


Scheme 1. Synthesis of 2,2,4,6,6,8-hexaphenyl-1,3,5,7,2,6,4,8-tetraoxadisiladiborocane (3), six-membered cyclodiborasiloxane and hydrogen-bonded macrocyclic siloxane-azopyridine.

of these materials are available in the literature [2]. This dearth of literature and materials could be as a result of a handful of commercially available silanols, difficulty in structural modification of available materials as well as problems of stability. The aromatic and potential quasi-aromatic character, and the ability to form extended π-π intramolecular and intermolecular interactions of a ring system are governed by the general formula $B_nSi_mO_{n+m}$ [2,17]. This implies that rings of general formula, $B_nSi_mO_{n+m}$ will have 2(n + m) π-electrons available for delocalization from the oxygen lone pairs [2]. If n + m = 3, the Hückel principle of 6 π-electrons is satisfied, while if n + m = 4, an anti-aromatic 8 π-electron count results [2]. Furthermore, the ring systems (B-O-Si) and (Si-O-Si) have been used as molecular building blocks in the construction of metal-organic frameworks (MOFs) [3-9], covalent organic frameworks (COFs) [3,10,11] and other supramolecular compound such as silsesquioxanes [10]. The methods for the preparation of these materials are discussed in details in the literature [2-4,18-21]. However, the method used in this study is similar to that described in the literature [2,7], for which molecular sieves were used for the removal of water to obtain crude compound 3. Compound 3 (a Lewis acid) was then ligated with 1,2-di (pyridin-4-yl) ethane, resulting in the formation of the aforementioned 1D polymer following a literature procedure [2]. Therefore, the main purpose of the study is the synthesis of 2, 2, 4, 6, 6, 8-hexaphenyl-1, 3, 5, 7, 2, 6, 4, 8-tetraoxadisiladiborocane (3), and its reaction with 4,4-azopyridine (L) leading to a ring contraction to give a dimer and hydrogen-bonded macrocyclic siloxane-azo-pyridine as shown in Scheme 1.

2. Experimental

2.1. Chemicals and reagents

All reactions were carried out under an inert atmosphere of dry nitrogen. All chemicals, reagents, and solvents were purchased from Sigma-Aldrich or Alfa-Aesar and used as received unless otherwise stated. Molecular sieves (1.6 mm rods and 0.4 nm pores) were preheated to dryness in the oven at 120 °C for two weeks prior to use.

2.2. Instrumentation

^1H, $^{13}C\{^1H\}$, $^{11}B\{^1H\}$ and $^{29}Si\{^1H\}$ NMR spectra were recorded on Bruker Avance III HD 400 MHz or 500 MHz spectrometers in $CDCl_3$ solvent unless otherwise stated. The chemical shifts (δ) for ^1H and $^{13}C\{^1H\}$, $^{29}Si\{^1H\}$, and $^{11}B\{^1H\}$, are quoted in ppm with reference to Me_4Si and BF_3OEt_2, respectively. The coupling constants are reported in Hz. Infrared spectra were obtained on a Perkin Elmer Spectrum 100 FTIR Spectrometer operating in ATR mode. The melting points were obtained using the Stanford Research Systems MPA100 (CE LABELED) automatic digital melting point apparatus 03012-90. Elemental analyzes were performed using a Thermo Quest CE Instruments Model EA/110 CHNS-O elemental analyzer. The single crystal diffraction (SC-XRD) measurement was performed on a Bruker D-QUEST diffractometer. The intensity data were collected using graphite monochromated with λ = 0.71073 Å. The structure was solved by the direction method and refined by full matrix least squares against F^2 for all data using SHELXTL-97 program. The carbon and hydrogen atoms were positioned geometrically and constrained to ride on their parent atoms with $U_{iso}(H)$ = $1.2U_{eq}(C)$. The hydrogen atoms on the nitrogen were located in the difference Fourier map and refined freely using SHELXL instruction ′DFIX 0.87 0.01. The MS instrument is the MALDI-TOF (Matrix-Assisted Laser Desorption/ Ionization Time-of-Flight.

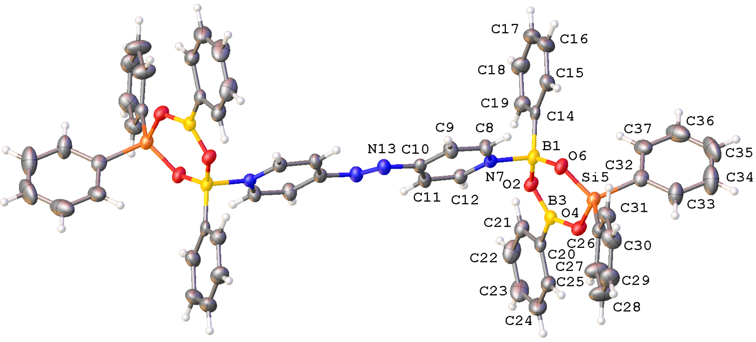


Figure 1. An ORTEP view of compound 4 with atom numbering.

2.3. Synthesis

2.3.1. Synthesis of compound 3 ($Ph_6B_2Si_2O_4$)

In a round bottom flask equipped with a magnetic stirrer bar, diphenylsilanediol (1) 1.082 g, (5.0 mmol) was mixed with 0.609 g (5.0 mmol) of phenylboronic acid (2) in dry toluene (50 mL) and 0.5 g of molecular sieves. The mixture was refluxed under N_2 for 20 h. Thereafter, the round bottom flask and its contents were cooled to room temperature. The mixture was filtered and the filtrate collected. The molecular sieves were washed with dry toluene (3×25 mL). The filtrates were combined and concentrated under reduced pressure, and the solid residue was recrystallized from diethyl ether and petroleum ether (3:1 ratio) to give compound 3 (Scheme 1). *2,2,4,6,6,8-Hexaphenyl-1,3,5,7,2,6,4,8-tetraoxadisiladiborocane* (3): Color: White. Yield: 86%. M.p.: 162-163 °C. ^1H NMR (500 MHz, $CDCl_3$, δ, ppm): 7.31-7.54 (m, 18H, *m,p*-C_6H_5), 7.73-7.75 (m, 8H *o*-C_6H_5Si), 8.08-8.10 (m, 4H, *o*-C_6H_5B). ^{13}C NMR (125 MHz, $CDCl_3$, δ, ppm): 127.93, 128.06, 130.60, 131.74, 133.40, 134.12, 135.65 (C_6H_5Si, C_6H_5B). ^{11}B NMR (160 MHz, $CDCl_3$, δ, ppm): 25.69. $^{29}Si\{^1H\}$ NMR (99 MHz, $CDCl_3$, δ, ppm): -45.00. MS (70 eV, EI, *m/z*): 604 (M^+), 527 $(M\text{-}Ph)^+$, 423 $(M\text{-}Ph\text{-}PhBO)^+$, 406 $(M\text{-}Ph_2SiO)^+$. FT-IR (ATR, ν, cm^{-1}): 3023 (C-H aromatic), 1349 (B-O), 1307 (Si-C str.), 1071 (Si-O str.)

2.3.2. Synthesis of compound 4 [$Ph_8B_4Si_2O_6$]·L

In a round bottom flask, compound 3 (0.25 g, 0.415 mmol) was dissolved in ether (20 mL) and then stirred with a magnetic stirrer bar. In another round bottom flask, 4,4'-azopyridine (L) (0.076 g, 0.415 mmol) was dissolved in ether (20 mL) and stirred. The solution of compound 3 was added to the L solution while stirring. The reaction mixture was stirred for 24 h during which time an orange-brown precipitate formed. The removal of solvents via filtration yielded an orange-brown powder as shown in Scheme 1. Recrystallization of the powder from CH_2Cl_2:ether (1:1, v:v) gave compound 4 as orange crystals after 24 h. *Compound 4*: Color: Orange. Yield: 80%. M.p.: 194-195 °C. ^1H NMR (500 MHz, $CDCl_3$, δ, ppm): 7.27-7.36 (m, 8H, *m*-C_6H_5Si), 7.49-7.55 (m, 4H, *p*-C_6H_5Si), 7.68-7.74 (m, 8H, *o*-C_6H_5Si), 7.76-7.78 (m, 4H, *p*-C_6H_5B), 7.84-7.87 (m, 8H, *m*-C_6H_5B), 8.04-8.10 (m, 8H, *o*-C_6H_5B), 8.11-8.18 (m, 4H, *m*-C_5H_4N), 8.94-8.97 (m, 4H, *o*-C_5H_4N). ^{13}C NMR (125 MHz, $CDCl_3$, δ, ppm): 156.95, 150.13, 135.57, 135.02, 134.37, 134.08, 133.80, 133.40, 131.64, 130.53, 129.98, 128. 06, 128.00, 127.87, 127.62, 116.90. ^{11}B NMR (160 MHz, $CDCl_3$, δ, ppm): 29.52, 22.36. $^{29}Si\{^1H\}$ NMR (99 MHz, $CDCl_3$, δ, ppm): -45.04. FT-IR (KBr, ν, cm^{-1}): 3071 (C-H aromatic), 3004 (C-H), 1624 (C=C), 1436 (B-O), 1340 (C-N aromatic), 1289 (Si-C str.), 1063 (Si-O). Anal. calcd. for $C_{58}H_{48}B_4N_4O_6Si_2$: C, 69.91, H, 4.86, N, 5.62. Found: C, 69.84, H, 4.94; N, 5.70%.

2.3.3. Synthesis of compound 5 [$4(C_{12}H_{12}O_2Si)\cdot 3(C_{10}H_8N_4)$]

In a round bottom flask, compound 3 (0.25 g, 0.415 mmol) was dissolved in ether:petroleum ether (2:1, v:v) (20 mL) and then stirred with a magnetic stirrer bar. In another round bottom flask, 4,4'-azopyridine (L) (0.076 g, 0.415 mmol) was dissolved in ether:petroleum ether (2:1, v:v) (20 mL) and stirred. The solution of compound **3** was added to the 4,4'-azopyridine solution while stirring. The reaction mixture was stirred for 24 h where an orange-brown precipitate formed. The removal of solvents via filtration yielded an orange-brown powder. Recrystallization of the powder from CH_2Cl_2:ether (1:1, v:v) gave compound 5 as orange-brown crystals after 24 h. *Compound 5*: Colour: Orange-brown. Yield: 16%. M.p.: 190-193 °C. FT-IR (KBr, ν, cm^{-1}): 3071 (C-H aromatic), 3004 (C-H), 1624 (C=C), 1436 (B-O), 1340 (C-N aromatic), 1289 (Si-C str.), 1063 (Si-O). Anal. calcd. for $C_{78}H_{72}N_{12}O_8Si_4$: C, 66.08, H, 5.12, N, 11.85. Found: C, 66.47, H, 4.69; N, 11.83%.

3. Results and discussion

3.1. Compound 4 [$Ph_8B_4Si_2O_6$]·L

The $^{11}B\{^1H\}$ NMR spectrum of compound 4 showed two singlets at δ 29.52 and 22.36 ppm, while the $^{29}Si\{^1H\}$ NMR of compound 4 showed a singlet at δ -45.04 ppm. The crystal structure confirms compound 4 as a dimer instead of a 1-D polymer-like compounds in the literature [2,7]. Furthermore, in the reaction leading to the formation of compound 4, the eight-membered ring of compound 3 has contracted to a six-membered ring ($Ph_2B_2Ph_2SiO_3$) together with $Ph_2Si(OH)_2$. The $Ph_2B_2Ph_2SiO_3$ then reacted with the linker (L) to form compound 4, while $Ph_2Si(OH)_2$ interacted with the linker (L) via hydrogen bonding to give compound 5 discussed in detail below. The ORTEP diagram with atom numbering shown in Figure 1 shows that the B1 and B3 atoms are tetracoordinated and tricoordinated, respectively. The linker (L) bridges the two B_2SiO_3 rings via a dative bond on the two B1 atoms.

The B1-O2 and B1-O6 distances at the tetragonal boron atoms (B1) in compound 4 are 1.451(3) and 1.446(3) Å, respectively. The B3-O2 and B3-O4 bond lengths at the trigonal boron atoms (B3) are 1.346(3) and 1.373(3) Å, respectively. Therefore, the lengths of the B-O bonds associated with tetrahedrally coordinated B1 are longer than those of the tricoordinate B3 in compound 4, consistent with stronger $B_\pi \cdots O_\pi$ interactions with O atoms bound to B_{sp^2}-O than B_{sp^3}-O. The trigonally bonded boron in the B-O distance in compound 4 is comparable to the tricoordinated B-O distance of 1.374(7) Å, reported for the $Ph_5Si_2BO_3$ ring [17], as well as to other tricoordinated B-O distances in other $Si_2B_2O_4$ rings, which ranges from 1.36-1.39 Å [21-23]. However, the values reported here are comparable to other B-O distances for tetrahedrally coordinated B in compounds such as $N(CH_2CH_2O)B$ (1.43(1) Å)

Table 1. Crystal data and structure refinement for compound 4.

Empirical formula	$C_{58}H_{48}B_4N_4O_6Si_2$
Formula weight (g/mol)	996.42
Temperature (K)	173(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
a, (Å)	11.0879(4)
b, (Å)	14.3707(4)
c, (Å)	16.2697(5)
α (°)	90
β (°)	98.759(3)
γ (°)	90
Volume (Å^3)	2562.20(13)
Z	2
ρ_{calc} (g/cm^3)	1.292
μ (mm^{-1})	0.126
F(000)	1040.0
Crystal size (mm^3)	0.46 × 0.42 × 0.04
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection (°)	5.066 to 56.49
Index ranges	$-13 \leq h \leq 9$, $-16 \leq k \leq 18$, $-13 \leq l \leq 21$
Reflections collected	8564
Independent reflections	5118 [R_{sigma} = 0.0569]
Data/restraints/parameters	5118/0/334
Goodness-of-fit on F^2	1.049
Final R indexes [I≥2σ (I)]	R_1 = 0.0570, wR_2 = 0.1394
Final R indexes [all data]	R_1 = 0.0789, wR_2 = 0.1559
Largest diff. peak/hole (e.Å^{-3})	0.35/-0.55

Table 2. Selected bond lengths for compound 4 *.

Atom	Atom	Length (Å)	Atom	Atom	Length (Å)
B1	O2	1.451(3)	Si5	C32	1.868(3)
B1	O6	1.446(3)	N7	C8	1.339(3)
B1	N7	1.670(3)	N7	C12	1.338(3)
B1	C14	1.614(4)	C8	C9	1.381(3)
O2	B3	1.346(3)	C9	C10	1.376(3)
B3	O4	1.373(3)	C10	C11	1.387(3)
B3	C20	1.569(3)	C10	N13	1.432(3)
O4	Si5	1.6573(17)	C11	C12	1.371(3)
Si5	O6	1.6116(16)	N13	N13 ^{1}	1.238(4)
Si5	C26	1.845(2)	C14	C15	1.382(3)

* Symmetry code: ^{1} 1-x, -y, -z.

Table 3. Selected bond angles for compound 4 *.

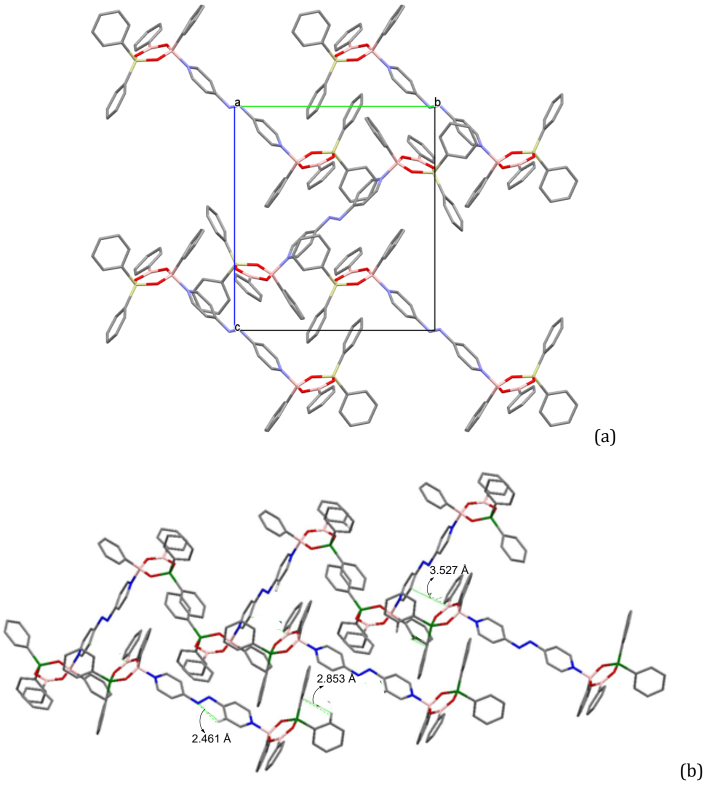
Atom	Atom	Atom	Angle (°)	Atom	Atom	Atom	Angle (°)
O2	B1	N7	103.80(18)	C26	Si5	C32	110.32(11)
O2	B1	C14	111.44(19)	B1	O6	Si5	123.75(15)
O6	B1	O2	115.7(2)	C8	N7	B1	119.67(19)
O6	B1	N7	105.08(17)	C12	N7	B1	121.12(18)
O6	B1	C14	114.5(2)	C12	N7	C8	119.2(2)
C14	B1	N7	104.82(17)	N7	C8	C9	121.7(2)
B3	O2	B1	127.08(19)	C10	C9	C8	118.8(2)
O2	B3	O4	121.7(2)	C9	C10	C11	119.6(2)
O2	B3	C20	118.0(2)	C9	C10	N13	116.9(2)
O4	B3	C20	120.2(2)	C11	C10	N13	123.6(2)
B3	O4	Si5	122.40(15)	C12	C11	C10	118.3(2)
O4	Si5	C26	106.55(10)	N7	C12	C11	122.4(2)
O4	Si5	C32	108.64(10)	N13 ^{1}	N13	C10	112.9(2)
O6	Si5	O4	106.46(9)	C15	C14	B1	122.9(2)
O6	Si5	C26	113.58(10)	C15	C14	C19	117.1(2)
O6	Si5	C32	111.02(10)	C19	C14	B1	119.9(2)

[24], $Ph_2BOCH_2CH_2NH_2$ (1.484(3) Å) [25], and Ph(OSiR$_2$R')B{OCH$_2$)$_3$N} (1.439(4) Å, and 1.461(3) Å) [26], (R or R' = Ph or CH$_3$) and [Bu^{t}Si(OPhBO)$_3$SiBu^t]·NC$_5$H$_5$ (1.457(18) Å, and 1.469(18) Å) [22] where the B is directly bonded to two O atoms, a phenyl group, and the N atom.

The Si-O bond lengths in compound 4 are 1.6573(17) Å (Si5-O4) and 1.6116(16) Å (Si5-O6), which are similar to those found in the literature [2,5,7] and comparable to the bond lengths for Si-O for a four-coordinate Si to two O atoms with a mean value of 1.645 Å [21,22,26]. The shorter Si5-O6 distances associated with compound 4 suggest an increase in electron density in the Si5-O6 bond, which is consistent with the decrease in the B-O electron density.

The B1-N7 bond length of compound 4 is 1.670(3) Å which is similar to those found in references [2,7], but a bit longer than those of simple borosiloxane such as Ph(OSiR$_2$R')B{OCH$_2$)$_3$N} [26] (R or R' = Ph or CH$_3$) and [Bu^{t}Si(OPhBO)$_3$SiBu^t]·NC$_5$H$_5$ [22] where the B-N distances reported were 1.639 and 1.655 Å, respectively. The two Si-C bond lengths in compound 4 are 1.845(2) Å (Si5-C26) and 1.868(3) Å (Si5-C32) and are similar to those found in the literature [2,7].

The ring angles O2-B1-O6 and O2-B3-O4 are 115.7(2)° and 121.7(2)°, respectively. The angle of the internal ring of compound 4 at the tetrahedral coordinated B (B1) is higher than the expected 109.5° for a tetrahedral geometry but similar to the compounds in the literature [2,7] as well as the observations reported in the literature [22]. However, the ring angle O2-B3-O4 for the three coordinate B (B3) is higher than that of the tetracoordinated boron centre but similar to other compounds in the literature [21,22,27,28]. Similarly, the angle



(a)

(b)

Figure 2. (a) Crystal packing and (b) noncovalent interactions of compound 4.

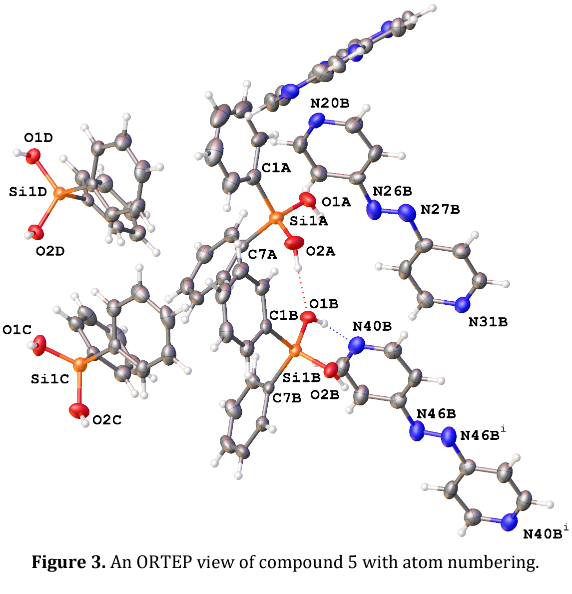


Figure 3. An ORTEP view of compound 5 with atom numbering.

of O4-Si5-O6 is 106.46(9)° which is lower than 109.5° for a tetrahedral silicon but is comparable to the values of the literature [29]. The bond angles at Si as well as the Si-C bonds lengths are comparable to those [2,7] as well as other borasiloxane compounds and simple adducts in the literature [21,22,27]. In addition to the covalent and dative bonds found in compound 4, the crystal packing of the compound also shows noncovalent interactions such as C-H···π (2.853 Å), C-H···N (2.461 Å) and π···B3 (3.527 Å) as shown in Figure 2. The crystallographic data of compound 4 are shown in Tables 1-3.

3.2. Compound 5 [4($C_{12}H_{12}O_2Si$) 3($C_{10}H_8N_4$)]

Compound 5 is a combination of L and the other part of the product [$Ph_2Si(OH_2)$] from the preparation of compound 4, in which compound 3 contracted into a six-membered ring ($Ph_2B_2Ph_2SiO_3$) and $Ph_2Si(OH)_2$ as described above. As the crystals of compounds 4 and 5 have different morphologies and shapes, compound 5 was isolated by hand picking from that of compound 4 but in low yield. The crystal structure of $Ph_2Si(OH)_2$ and the linker (L) that gave compound 5 [4[$Ph_2Si(OH)_2$]·3($C_{10}H_8N_4$)] is shown in Figure 3. The $Ph_2Si(OH)_2$ and the linker (L) interact through hydrogen bonding (H···O and H···N) as shown in Figure 3.

Table 4. Crystal data and structure refinement for compound 5.

Empirical formula	$C_{78}H_{72}N_{12}O_8Si_4$
Formula weight (g/mol)	1417.83
Temperature (K)	173(2)
Crystal system	Triclinic
Space group	P-1
a, (Å)	12.2352(3)
b, (Å)	15.3274(6)
c, (Å)	20.0271(6)
α (°)	89.879(3)
β (°)	89.988(2)
γ (°)	78.298(3)
Volume (Å^3)	3677.7(2)
Z	2
ρ_{calc} (g/cm^3)	1.280
μ (mm^{-1})	0.146
F(000)	1488.0
Crystal size (mm^3)	0.64 × 0.27 × 0.13
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection (°)	4.886 to 56.208
Index ranges	$-12 \le h \le 15$, $-20 \le k \le 18$, $-25 \le l \le 25$
Reflections collected	20569
Independent reflections	20569 [R_{sigma} = 0.0829]
Data/restraints/parameters	20569/649/991
Goodness-of-fit on F^2	0.891
Final R indexes [I≥2σ (I)]	R_1 = 0.0470, wR_2 = 0.1013
Final R indexes [all data]	R_1 = 0.0891, wR_2 = 0.1098
Largest diff. peak/hole (e.Å^{-3})	1.04/-0.50

Table 5. Selected bond lengths for compound 5 *.

Atom	Atom	Length (Å)	Atom	Atom	Length (Å)
Si1A	O1A	1.6176(18)	C23A	N26A	1.452(3)
Si1A	O2A	1.6126(18)	N26A	N27A	1.205(3)
Si1A	C1A	1.862(3)	N27A	C28A	1.465(3)
Si1A	C7A	1.865(3)	C30A	N31A	1.329(3)
Si1B	O1B	1.6314(17)	N31A	C32A	1.338(3)
Si1B	O2B	1.6218(17)	N20B	C21B	1.342(3)
Si1B	C1B	1.864(2)	N20B	C25B	1.323(3)
Si1B	C7B	1.860(3)	C23B	N26B	1.469(3)
Si1C	O1C	1.6183(17)	N26B	N27B	1.201(3)
Si1C	O2C	1.6169(18)	N27B	C28B	1.488(3)
Si1C	C1C	1.861(2)	C30B	N31B	1.328(3)
Si1C	C7C	1.858(3)	N31B	C32B	1.335(3)
Si1D	O1D	1.6308(16)	C43A	N46A	1.515(5)
Si1D	O2D	1.6253(17)	N46A	N47A	1.113(5)
Si1D	C1D	1.867(2)	N47A	C48A	1.423(5)
Si1D	C7D	1.859(3)	N40B	C41B	1.323(3)
N20A	C21A	1.339(3)	N40B	C45B	1.328(3)
N20A	C25A	1.322(3)	N46B	N46B^1	1.219(4)

* Symmetry code: ^{1} 2-*x*, 1-*y*, -*z*.

Table 6. Selected bond angles for compound 5 *.

Atom	Atom	Atom	Angle (°)	Atom	Atom	Atom	Angle (°)
O1A	Si1A	C1A	105.92(11)	C8D	C7D	Si1D	121.81(18)
O1A	Si1A	C7A	109.47(11)	C12D	C7D	Si1D	121.8(2)
O2A	Si1A	O1A	113.68(10)	C25A	N20A	C21A	116.3(2)
O2A	Si1A	C1A	104.10(10)	N20A	C21A	C22A	123.9(3)
O2A	Si1A	C7A	111.02(10)	C22A	C23A	N26A	126.6(2)
C1A	Si1A	C7A	112.50(11)	C24A	C23A	N26A	114.2(3)
C2A	C1A	Si1A	120.6(2)	N20A	C25A	C24A	124.6(3)
C6A	C1A	Si1A	121.9(2)	N27A	N26A	C23A	112.6(2)
C8A	C7A	Si1A	120.5(2)	N26A	N27A	C28A	112.3(2)
C12A	C7A	Si1A	122.7(2)	C29A	C28A	N27A	115.5(3)
O1B	Si1B	C1B	105.81(10)	C33A	C28A	N27A	125.3(2)
O1B	Si1B	C7B	109.57(10)	N31A	C30A	C29A	124.3(3)
O2B	Si1B	O1B	113.39(9)	C30A	N31A	C32A	116.6(2)
O2B	Si1B	C1B	107.31(10)	N31A	C32A	C33A	123.2(3)
O2B	Si1B	C7B	108.40(10)	C25B	N20B	C21B	116.5(2)
C7B	Si1B	C1B	112.39(11)	N20B	C21B	C22B	123.6(3)
C2B	C1B	Si1B	119.63(19)	C22B	C23B	N26B	127.1(2)
C6B	C1B	Si1B	123.32(19)	C24B	C23B	N26B	113.5(2)
C8B	C7B	Si1B	121.72(18)	N20B	C25B	C24B	124.1(3)
C12B	C7B	Si1B	121.98(19)	N27B	N26B	C23B	110.5(2)
O1C	Si1C	C1C	106.48(10)	N26B	N27B	C28B	110.4(2)
O1C	Si1C	C7C	109.19(10)	C29B	C28B	N27B	114.2(3)
O2C	Si1C	O1C	114.25(10)	C33B	C28B	N27B	125.9(3)
O2C	Si1C	C1C	103.97(10)	N31B	C30B	C29B	124.2(3)
O2C	Si1C	C7C	110.80(10)	C30B	N31B	C32B	116.8(2)
C7C	Si1C	C1C	112.03(11)	N31B	C32B	C33B	123.1(3)
C2C	C1C	Si1C	120.50(18)	C42A	C43A	N46A	115.3(3)
C6C	C1C	Si1C	122.57(19)	C44A	C43A	N46A	124.5(3)
C8C	C7C	Si1C	120.93(19)	N47A	N46A	C43A	110.6(4)

Table 6. Continued.

Atom	Atom	Atom	Angle (°)	Atom	Atom	Atom	Angle (°)
C12C	C7C	Si1C	122.5(2)	N46A	N47A	C48A	112.2(6)
O1D	Si1D	C1D	106.43(9)	C49A	C48A	N47A	108.5(4)
O1D	Si1D	C7D	109.26(10)	C53A	C48A	N47A	131.5(4)
O2D	Si1D	O1D	113.39(9)	C41B	N40B	C45B	117.7(2)
O2D	Si1D	C1D	107.22(10)	N40B	C41B	C42B	124.0(3)
O2D	Si1D	C7D	109.66(10)	C42B	C43B	N46B	114.7(2)
C7D	Si1D	C1D	110.83(11)	C44B	C43B	N46B	125.1(2)
C2D	C1D	Si1D	119.53(18)	N40B	C45B	C44B	122.6(3)
C6D	C1D	Si1D	123.70(18)	N46B[1]	N46B	C43B	111.6(3)

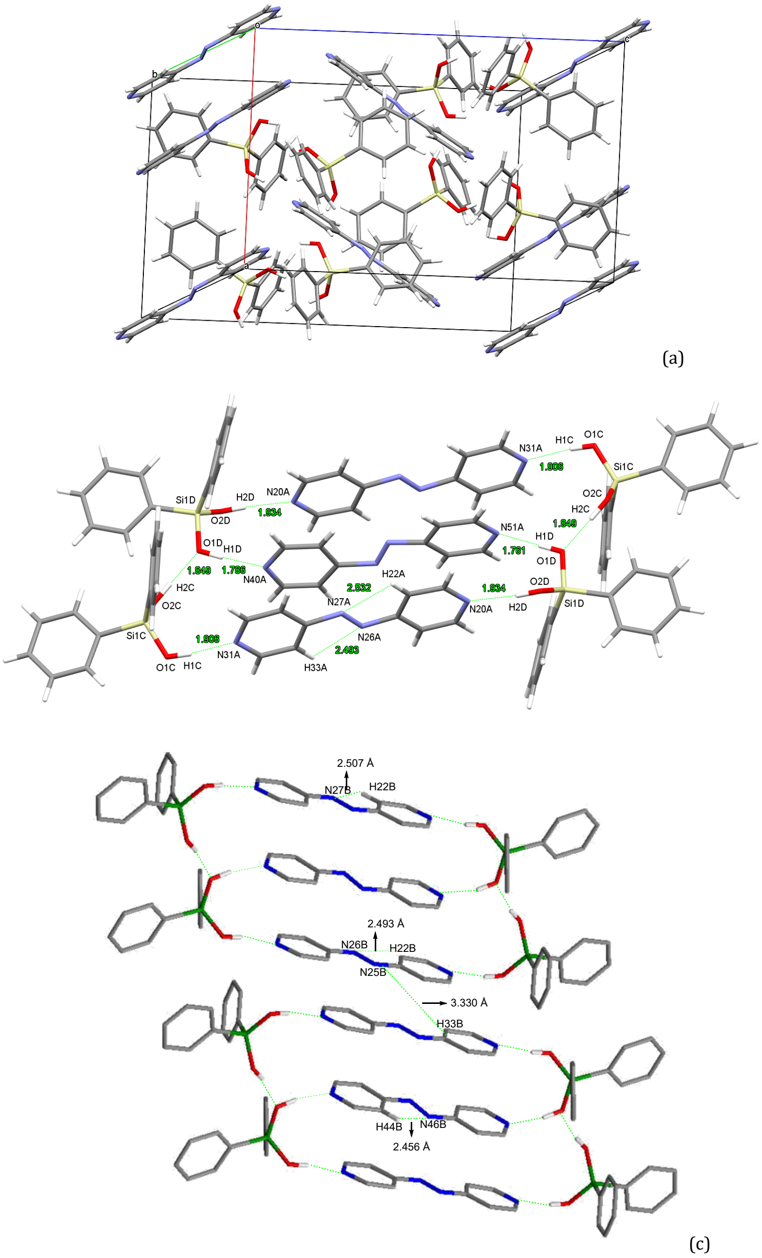


Figure 4. (a) Crystal packing of compound 5 and (b) and (c) intramolecular and intermolecular interactions.

As can be seen in Figure 3, the H atoms that bond with O atoms in the molecule are H2A···O1B (1.815 Å) and H2A···O1A (1.815 Å), while H1A and H2B hydrogen bond with N31B (H1A···N31B) (1.891 Å) and N20B (H2B···N20B) (1.931 Å), respectively. H1B hydrogen bonds with another molecule at N40B (H1B···N40B) (1.773 Å). Therefore, the three-linker L molecules that bond to the four $Ph_2Si(OH)_2$ molecules are parallel to each other. In addition to the hydrogen bonding displayed by compound 5, the crystal packing of the compound also shows other forms of inter- and intra-non-covalent (C-H···N, C-H···O, C-H···π, and π···π) interactions as depicted in Figure 4. The ring angle from O1A-Si1A-O2A and O1B-Si1B-O2B is 113.68° and 113.40°, which are higher than those of compound 4 (106.46(9)°) but comparable to those of the literature [2,7]. Furthermore, individual molecules of compound 5 interact intermolecularly via C-H···N (3.330 Å).

The sum of all these interactions and the stability of products 4 and 5 as well as the basicity of L may be the reason for the contraction of the compound 3 ring to ($Ph_2B_2Ph_2SiO_3$) and $Ph_2Si(OH)_2$, which later reacted with the linker L to give compounds 4 and 5, respectively. Crystallographic data of compound 5 are in Tables 4-6.

4. Conclusions

In this article, we report the successful synthesis of an eight-membered 2, 2, 4, 6, 6, 8-hexaphenyl-1, 3, 5, 7, 2, 6, 4, 8-tetraoxa disiladiborocane ($Ph_6B_2Si_2O_4$) (3) (a Lewis acid) and its reaction with 4,4-azo-pyridine (L) (a Lewis base) leading to the contraction of compound 3 to form a six-membered cyclodiborasiloxane dimer (compound 4) and a hydrogen-bonded connected macrocyclic system. Crystal structures of these compounds 4 and 5 were determined using single crystal X-ray diffraction. The dimer shows extensive channels in its packing occupied by solvent molecules. Furthermore, the structure dimer possesses intermolecular and intramolecular π-π interactions as well as hydrogen bonding. Furthermore, compound 5 showed more extensive hydrogen (inter and intra) bonding than the dimer. These two novel compounds have a promising potential to enhance the performance and functionality of borasiloxane backbone materials. Hence, further work is recommended to explore some functions and uses of these unique compounds in areas such as the heterogeneous catalyst in the conversion of waste cooking oil to biodiesel, the adsorption of heavy metals from waste water, *etc*. [1,3,18,30,31], synthesis of silicon-based dendrimers and cores.

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Supporting information

CCDC-2429585 and -2429589 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

Disclosure statement

Conflict of interest: The authors declare that they have no conflict of interest.
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Sample availability: Samples of the compounds are available from the author.

CRediT authorship contribution statement

Conceptualization: Okpara Sergeant Bull; Methodology: Okpara Sergeant Bull; Software: Okpara Sergeant Bull; Validation: Don-Lawson Chioma, Okpara Sergeant Bull, Ahamefula Anslem Ahuchaogu; Formal Analysis: Ahamefula Anslem Ahuchaogu; Investigation: Okpara Sergeant Bull; Resources: Don-Lawson Chioma; Data Curation: Okpara Sergeant Bull; Writing - Original Draft: Okpara Sergeant Bull Writing - Review and Editing: Okpara Sergeant Bull, Don-Lawson Chioma; Visualization: Don-Lawson Chioma; Funding acquisition: Don-Lawson Chioma, Ahamefula Anslem Ahuchaogu; Supervision: Don-Lawson Chiom; Project Administration: Okpara Sergeant Bull.

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