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Green synthesis and structural characterisation of a novel tetraoxadisiladiborocane-bridged thiadiazole oligomer and its transformation into a hydrogen-bonded 1D polymer

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ABSTRACT

This study reports on the synthesis and characterization of novel cyclodiboradisiloxane derivatives. A one-pot 2+2 cyclo-condensation reaction of diphenylsilanediol and phenylboronic acid produced an eight-membered 2,2,4,6,6,8-hexaphenyl-1,3,5,7,2,6,4,8-tetraoxadisiladiborocane ($Ph_6B_2Si_2O_4$) (3). The reaction of compound 3 with 3,5-di-(3-pyridyl)-1,2,4-thiadiazole (L) and phenylboronic acid produced an oligomer (4) and a hydrogen-bonded-induced 1D polymer (5), respectively. Products (4 and 5) have been characterized by melting point, FT-IR spectroscopy, nuclear magnetic resonance, and single-crystal X-ray diffraction. Single-crystal X-ray diffraction revealed triclinic crystal systems with centrosymmetric space group for compounds 4 and 5. On the other hand, the hydrogen-bonded induced 1D polymer $[Ph_6B_2Si_2O_4]\cdot 2L\cdot 2[PhB(OH)_2]$ is colourless blocky cocrystals which also crystallized in the triclinic crystal system with a centrosymmetric space group of *P*-1. These two novel products (4 and 5) exhibit various intermolecular and intramolecular π-π non-covalent interactions and hydrogen bonds in their crystal packing. Compound 4 shows intramolecular non-covalent C-H···π (3.427 Å), C-H···N (2.601 and 2.684 Å), C-H···O (2.360 and 2.684 Å), C-H···S (2.601 Å and 2.701 Å) interactions in its crystal packings. In addition, compound 4 also displays some intermolecular short distance non-covalent interactions in its crystal packing such as π centroid···π centroid (3.805 Å) and C-H17A···π centroid (3.112 Å). On the other hand, the crystal packing of compound 5 also shows intra-molecular non-covalent C-H···π 3.440 Å, C-H···N 2.563 Å, C-H···O 2.654 Å, C-H···S 2.876 Å and H···B 2.939 Å interactions. Furthermore, compound 5 also exhibits short noncovalent intermolecular interactions in its crystal packing such as π···π, (3.362 Å, C14-C3 and 3.243, C11-C37), CH···π (2.587 Å, CH37A···πC38 and 2.452 Å, H7A···O42). The individual molecules of compounds 4 and 5 interact intermolecularly via C-H···N, C-H···O, C-H···S and N-B. Therefore, this study demonstrates the potential for the production of novel materials via the combination of cyclodiboradisiloxane (a Lewis acid) and a nitrogen-, oxygen-, and sulphur-containing ligand (a Lewis bases).

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1. Introduction

Tetra- and tri-coordinated cyclodiboradisiloxanes-based molecules and their derivatives have attracted significant attention in different research areas in recent years as a result of their unique crystal and architectural structures [1,2], π-conjugation [3-5], π-π intermolecular and intramolecular interactions [6], magnetic properties [7], electronic properties [8], optical properties [9], photophysical properties [10,11], and quasi-aromatic character around the eight-membered cyclodiboradisiloxanes [6,12], as well as extended inter-molecular and intramolecular hydrogen bonding [6,13-15]. Cyclodiboradisiloxanes have the ability to form stable covalent bonds between boron and nitrogen atoms enabling the creation of novel materials with tailored properties [16-18]. These materials have shown great promise in various fields, such as conductive polymers [19-22] for advanced energy devices [23], catalysis [24], carbon capture [25], gas separation [26,27] and adsorption [28], lightweight materials [15,29], high-strength materials [16] for spacecraft applications, pharmaceuticals [6,13], and drug delivery [30-32]. On the other hand, 3,5-di-(3-pyridyl)-1,2,4-thiadiazole is a heterocyclic compound that has shown potential in medicinal chemistry [32]. The compound has been found to have anticancer activity, making it a potential candidate for cancer treatment [30,31]. Furthermore, 3,5-di-(3-pyridyl)-1,2,4-thiadiazole as a Lewis base has the ability to form coordination complexes with metal ions (Lewis acids) due to availability of a non-bonded pair of electrons on nitrogen as well as on sulphur atom in its motif [31,33]. As a result, 3,5-di-(3-pyridyl)-1,2,4-thiadiazole can form complexes with metals, which can be used to develop new therapeutic agents [31]. Studies have shown that 3,5-di-(3-pyridyl)-1,2,4-thiadiazole exhibits antimicrobial activity against various bacteria and fungi [23,34]. Furthermore, the pyridyl groups in the compound

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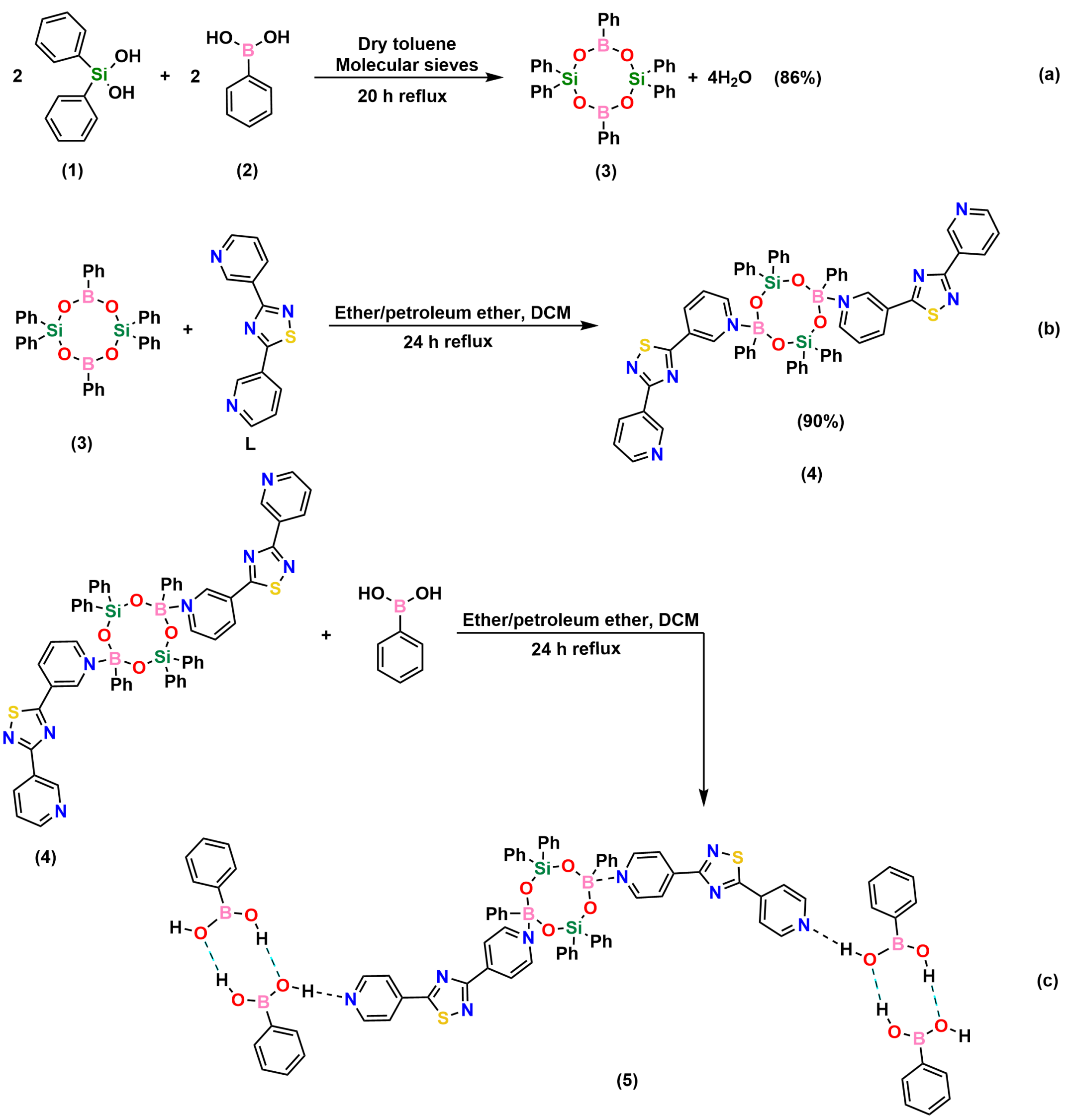

Scheme 1. (a) Synthesis of eight-membered 2,2,4,6,6,8-hexaphenyl-1,3,5,7,2,6,4,8-tetraoxadisiladiborocane (3), (b) Six-membered cyclodiborasiloxane oligomer and (c) hydrogen-bonded macrocyclic siloxane-azo-pyridine.

can interact with biological targets, such as nicotinic acetylcholine receptors, which could lead to neuroprotective effects [32].

The synthesis of 2, 2, 4, 6, 6, 8-hexaphenyl-1, 3, 5, 7, 2, 6, 4, 8-tetraoxadisiladiborocane and its reaction with 3,5-di-(3-pyridyl)-1,2,4-thiadiazole (L) are described in Scheme 1. The resulting oligomer (4) was further reacted with phenylboronic acid to form a new hydrogen-bonded-induced 1D polymer (5). The development of novel materials with unique properties is an active area of research. The incorporation of cyclodiboradisiloxanes and boron-nitrogen adducts and B-H bonds into polymer backbones or side chains offers a promising route to creating materials with enhanced performance and functionality [13]. The importance of 3,5-di-(3-pyridyl)-1,2,4-thiadiazole in medicine highlights its potential as a therapeutic agent [30,31]. More research is needed to explore the full potential of these materials. Therefore, the objective of this study is the synthesis of eight-membered 2, 2, 4, 6, 6, 8-hexaphenyl-1, 3, 5, 7, 2, 6, 4, 8-tetraoxadisiladiborocane, and its reaction with 3, 3, 5-di-(3-pyridyl)-1, 2,4-thiadiazole (L), to give an eight-membered 2, 2, 4, 6, 6, 8-hexaphenyl-1, 3, 5, 7, 2, 6, 4, 8-tetraoxadisiladiborocane-bridge-3, 5-di-(3-pyridyl)-1, 2, 4-thiadiazole (4) oligomer. A further reaction of compound 4 with phenylboronic acid yields a novel hydrogen-bonded-induced 1D polymer (5) as shown in Scheme 1 (a-c), respectively [35].

2. Experimental

2.1. Chemicals and reagents

All chemicals, reagents, and solvents were of analytical grades 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 fourteen days before use. Furthermore, all reactions were performed under an inert atmosphere of dry nitrogen.

2.2. Instrumentation

^{1}H, ^{13}C{^{1}H}, ^{11}B{^{1}H} and ^{29}Si{^{1}H} NMR spectra were recorded on a Bruker Avance III HD 400 MHz or 500 MHz spectrometer in $CDCl_3$ solvent unless otherwise stated. The chemical shifts (δ) for ^{1}H and ^{13}C{^{1}H}, ^{29}Si{^{1}H}, and ^{11}B{^{1}H}, are quoted in ppm with reference to Me_4Si and BF_3OEt_2, respectively. The coupling constants are reported in Hz.

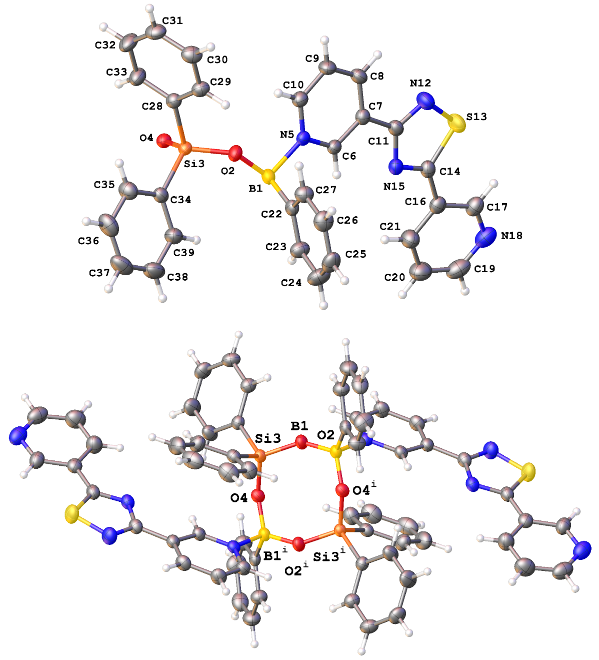

Figure 1. An ORTEP view of compound 4 oligomer with some atom labelling.

Infrared spectra were obtained on a PerkinElmer 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 analyses were performed using a Thermo Quest CE Instruments Model EA/110 CHNS-O elemental analyser. The single-crystal 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) = 1.2Ueq(C). The hydrogen atoms on the nitrogen were located in the difference Fourier map and refined freely using the SHELXL instruction DFIX 0.87 0.01. The MS instrument is the MALDI-TOF matrix-assisted laser desorption/ionization time of flight. MALDI-TOF analysis was performed using a Bruker Daltonics UltrafleXtreme instrument. The matrix used was α-cyano-4-hydroxycinnamic acid, and the instrument was operated in positive ion mode with a laser frequency of 1,000 Hz. The mass range was set to 500-5,000 Da, and 500 shots were accumulated for each sample. Data processing was performed using Bruker FlexAnalysis software.

2.3. Synthesis

2.3.1. Synthesis of $Ph_6B_2Si_2O_4$ (3)

As shown in Scheme 1a, 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 molecular sieves. The mixture was refluxed under N_2 for 20 h. Thereafter, the round bottom flask and its content was cooled to ambient temperature. The cooled reaction 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 using a rotary evaporator, and the solid residue was recrystallized from diethyl ether and petroleum ether (3:1 ratio) to give compound 3.

2, 2, 4, 6, 6, 8-Hexaphenyl-1, 3, 5, 7, 2, 6, 4, 8-tetraoxadisiladiborocane (3): Colour: White. Yield: 86%. M.p.: 162-163 °C. ^{1}H 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{^{1}H} 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 $[Ph_6B_2Si_2O_4]\cdot 2L$ (4)

In a round bottom flask, $[(C_6H_5BO)_2(Ph_2SiO)_2]$ (3), (0.25 g 0.415 mmol) was added to 3,5-di(3-pyridyl)-1,2,4-thiadiazole (0.10 g 0.415 mmol) (L) and a mixture of solvents (diethyl ether 21 mL, petroleum ether 7 mL and dichloromethane 7 mL). The mixture was heated at reflux while stirring for 24 h. The resultant solution was cooled to room temperature. After 48 h, colourless crystals of compound 4 were obtained. Color: White. Yield: 90%. M.p.: 111-112 °C. ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 7.28-7.42 (m, 18H, *m*, *p*-C_6H_5), 7.48-7.52 (m, 4H, *m*-C_5H_4N), 7.70-7.73 (m, 8H, *o*-C_6H_5Si), 8.03-8.07 (m, 4H, *o*-C_6H_5B), 8.34 (dd, *J* = 4.0 Hz, *J'* = 2.0 Hz, 2H, *p*-C_5H_4N), 8.64-8.65 (t, 2H, *m*-C_5H_4N), 8.76 (dd, *J* = 6.8 Hz, *J'* = 1.6 Hz, 2H, *o*-C_5H_4N), 8.80 (dd, *J* = 6.8 Hz, *J'* = 2.0 Hz, 2H, *o*-C_5H_4N), 9.27 (dd, *J* = 2.4 Hz, *J'* = 0.8 Hz, 2H, *o*-C_5H_4N), 9.65 (d, *J* = 2.4 Hz, 2H, *o*-C_5H_4N). ^{13}C NMR (125 MHz, $CDCl_3$, δ, ppm): 185.53, 171.27, 152.67, 150.45, 149.00, 148.31, 135.94, 135.32, 134.31, 134.09, 133.74, 133.00, 131.26, 130.36, 127.91, 127.80, 127.60, 121.16. ^{11}B NMR (160 MHz, $CDCl_3$, δ, ppm): 22.82. ^{29}Si{^{1}H} NMR (99 MHz, $CDCl_3$, δ, ppm): -45.17. MS (70 eV, EI, *m/z*): 1084 (M^+), 604 $(M\text{-}Ph_6Si_2B_2O_4)^+$, 527 $(M\text{-}Ph)^+$, 423 $(M\text{-}Ph\text{-}PhBO)^+$, 406 $(M\text{-}Ph_2SiO)^+$, 240 $(M\text{-}C_{11}SN_5)^+$. FT-IR (ATR, ν, cm^{-1}): 3023 (C-H aromatic), 1550 (C=N and N=N str), 1450 (C=N and C=N str.), 1349 (B-O), 1307 (Si-C str.), 1071 (Si-O str.).

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

Parameter	Value
Empirical formula	$C_{60}H_{46}B_2N_8O_4S_2Si_2$
Formula weight (g/mol)	1084.97
Temperature (K)	173(2)
Crystal system	Triclinic
Space group	*P*-1
a (Å)	9.2619(5)
b (Å)	11.6769(8)
c (Å)	13.9086(9)
α (°)	111.337(6)
β (°)	99.104(5)
γ (°)	102.564(5)
Volume (Å^3)	1320.12(16)
Z	1
ρ_{calc} (g/cm^3)	1.365
μ (mm^{-1})	1.817
F(000)	564.0
Crystal size (mm^3)	0.38 × 0.145 × 0.056
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection (°)	7.068 to 147.268
Index ranges	$-11 \le h \le 9$, $-14 \le k \le 13$, $-17 \le l \le 15$
Reflections collected	7555
Independent reflections	5045 [R_{int} = 0.0378, R_{sigma} = 0.0557]
Data/restraints/parameters	5045/0/352
Goodness-of-fit on F^2	1.044
Final R indexes [I≥2σ (I)]	R_1 = 0.0470, wR_2 = 0.1163
Final R indexes [all data]	R_1 = 0.0637, wR_2 = 0.1320
Largest diff. peak/hole (e.Å^{-3})	0.34/-0.30

Table 2. Bond lengths for compound 4.

Bond	Length (Å)	Bond	Length (Å)
B(1)–O(2)	1.431(3)	B(1)–O(4)#1	1.436(3)
B(1)–C(22)	1.615(3)	B(1)–N(5)	1.699(3)
O(2)–Si(3)	1.6074(16)	Si(3)–O(4)	1.6120(16)
Si(3)–C(28)	1.867(2)	Si(3)–C(34)	1.881(2)
O(4)–B(1)#1	1.436(3)	N(5)–C(10)	1.344(3)
N(5)–C(6)	1.345(3)	C(6)–C(7)	1.386(3)
C(7)–C(8)	1.394(3)	C(7)–C(11)	1.471(3)
C(8)–C(9)	1.380(4)	C(9)–C(10)	1.388(3)
C(11)–N(12)	1.324(3)	C(11)–N(15)	1.370(3)
N(12)–S(13)	1.638(2)	S(13)–C(14)	1.733(2)
C(14)–N(15)	1.313(3)	C(14)–C(16)	1.457(3)
C(16)–C(17)	1.387(4)	C(16)–C(21)	1.399(4)
C(17)–N(18)	1.330(4)	N(18)–C(19)	1.338(4)
C(19)–C(20)	1.397(5)	C(20)–C(21)	1.372(4)
C(22)–C(23)	1.396(3)	C(22)–C(27)	1.399(3)
C(23)–C(24)	1.388(4)	C(24)–C(25)	1.380(4)
C(25)–C(26)	1.378(4)	C(26)–C(27)	1.388(4)
C(28)–C(29)	1.397(3)	C(28)–C(33)	1.396(3)
C(29)–C(30)	1.394(3)	C(30)–C(31)	1.379(4)
C(31)–C(32)	1.380(4)	C(32)–C(33)	1.394(4)
C(34)–C(35)	1.395(3)	C(34)–C(39)	1.399(3)
C(35)–C(36)	1.393(4)	C(36)–C(37)	1.380(5)
C(37)–C(38)	1.381(5)	C(38)–C(39)	1.392(4)

#1 -*x*+1, -*y*+1, -*z*+1.

2.3.3. Synthesis of [$Ph_6B_2Si_2O_4$]·2L·2[$PhB(OH)_2$] (5)

In a round bottom flask, [$Ph_6B_2Si_2O_4$]·2L (4) (0.45 g 0.415 mmol) was added to phenylboronic acid (0.10 g, 0.830 mmol) and a mixture of solvents (diethyl ether 21 mL, petroleum ether 7 mL and dichloromethane 7 mL). The mixture was heated at reflux while stirring for 24 h. The resultant solution was cooled to room temperature. After 72 h, colourless crystals were obtained from the solvent to give compound 5. Colour: White. Yield: 85%. M.p.: 124.0 - 125.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 7.29-7.42 (m, 18H, *m*, *p*-C_6H_5Si/*m*, *p*-C_6H_5B), 7.65-7.74 (m, 8H, *o*-C_6H_5Si), 7.89- 7.92 (m, 8H, *m*-C_5H_4N); 7.99-8.06 (m, 4H, *o*-C_6H_5B); 8.24-8.27 (m, 8H, *o*-C_5H_4N); 8.84-8.87 (m, 10H, C_6H_5). ^{13}C NMR (125 MHz, $CDCl_3$, δ, ppm): 186.69, 171.92, 151.11, 150.02, 139.40, 136.81, 135.35, 134.10, 133.63, 130.39, 127.93, 127.57, 122.30, 121.00. ^{11}B NMR (160 MHz, $CDCl_3$, δ, ppm): 21.53. ^{29}Si{^{1}H} NMR (99 MHz, $CDCl_3$, δ, ppm): -45.17. MS (70 eV, EI, *m/z*): 1627 (M^+), 604 ($M-Ph_6Si_2B_2O_4$)$^+$, 527 (M-Ph)$^+$, 423 (M-Ph-PhBO)$^+$, 406 ($M-Ph_2SiO$)$^+$, 240 ($M-C_{11}SN_5$)$^+$. FT-IR (ATR, ν, cm^{-1}): 3300 (O-H), 3023 (C-H aromatic), 1550 (C=N and N=N str), 1450 (C=N and C=N str.), 1349 (B-O), 1307 (Si-C str.), 1150 (B-C str), 1071 (Si-O str.)

3. Results and discussion

3.1. Compound 4 [$Ph_6B_2Si_2O_4$]·2L

At room temperature, compound 4 was soluble in organic solvents such as dichloromethane, ether, toluene, and acetone. Chemical analysis for C, H, and N reveals compound 4 as a 1:2 adduct. The ^{1}H NMR spectrum of compound 4 showed well-resolved resonances with aromatic proton signals found within the range of δ 7.28-8.87 ppm, while the ^{13}C{^{1}H} NMR spectrum showed signals for aromatic carbons in the range of δ 121.00-186.69 ppm. Additionally, the ^{11}B{^{1}H} NMR of compound 4 showed a singlet at δ 22.82 ppm, and the ^{29}Si{^{1}H} NMR of compound 4 showed a singlet at δ -45.17 ppm. The NMR spectra (^{1}H, ^{13}C{^{1}H}, ^{11}B{^{1}H}, and ^{29}Si{^{1}H}) of compound 4 are consistent with the compound.

Table 3. Bond angles for compound 4.

Angle	Value (°)	Angle	Value (°)
O(2)–B(1)–O(4)#1	116.93(19)	O(2)–B(1)–C(22)	113.12(19)
O(4)#1–B(1)–C(22)	111.63(19)	O(2)–B(1)–N(5)	102.06(17)
O(4)#1–B(1)–N(5)	105.30(17)	C(22)–B(1)–N(5)	106.42(16)
B(1)–O(2)–Si(3)	143.47(15)	O(2)–Si(3)–O(4)	113.53(9)
O(2)–Si(3)–C(28)	107.18(10)	O(4)–Si(3)–C(28)	106.84(9)
O(2)–Si(3)–C(34)	110.35(10)	O(4)–Si(3)–C(34)	110.16(9)
C(28)–Si(3)–C(34)	108.57(10)	B(1)#1–O(4)–Si(3)	142.70(15)
C(10)–N(5)–C(6)	119.38(19)	C(10)–N(5)–B(1)	121.95(18)
C(6)–N(5)–B(1)	118.64(17)	N(5)–C(6)–C(7)	122.0(2)
C(6)–C(7)–C(8)	118.6(2)	C(6)–C(7)–C(11)	119.7(2)
C(8)–C(7)–C(11)	121.7(2)	C(9)–C(8)–C(7)	119.3(2)
C(8)–C(9)–C(10)	119.1(2)	N(5)–C(10)–C(9)	121.7(2)
N(12)–C(11)–N(15)	118.9(2)	N(12)–C(11)–C(7)	120.8(2)
N(15)–C(11)–C(7)	120.2(2)	C(11)–N(12)–S(13)	108.19(18)
N(12)–S(13)–C(14)	92.71(11)	N(15)–C(14)–C(16)	125.3(2)
N(15)–C(14)–S(13)	111.10(18)	C(16)–C(14)–S(13)	123.54(18)
C(14)–N(15)–C(11)	109.1(2)	C(17)–C(16)–C(21)	117.8(3)
C(17)–C(16)–C(14)	120.9(2)	C(21)–C(16)–C(14)	121.4(2)
N(18)–C(17)–C(16)	124.9(3)	C(17)–N(18)–C(19)	116.1(3)
N(18)–C(19)–C(20)	123.9(3)	C(21)–C(20)–C(19)	118.6(3)
C(20)–C(21)–C(16)	118.7(3)	C(23)–C(22)–C(27)	116.5(2)
C(23)–C(22)–B(1)	122.3(2)	C(27)–C(22)–B(1)	121.1(2)
C(24)–C(23)–C(22)	122.0(2)	C(25)–C(24)–C(23)	120.1(3)
C(26)–C(25)–C(24)	119.2(2)	C(25)–C(26)–C(27)	120.7(3)
C(26)–C(27)–C(22)	121.5(2)	C(33)–C(28)–C(29)	117.5(2)
C(33)–C(28)–Si(3)	122.06(18)	C(29)–C(28)–Si(3)	120.43(18)
C(30)–C(29)–C(28)	121.3(2)	C(31)–C(30)–C(29)	120.0(2)
C(30)–C(31)–C(32)	120.0(2)	C(31)–C(32)–C(33)	119.9(2)
C(32)–C(33)–C(28)	121.4(2)	C(35)–C(34)–C(39)	117.5(2)
C(35)–C(34)–Si(3)	121.25(18)	C(39)–C(34)–Si(3)	121.22(19)
C(36)–C(35)–C(34)	121.7(3)	C(37)–C(36)–C(35)	119.5(3)
C(36)–C(37)–C(38)	120.3(3)	C(37)–C(38)–C(39)	119.9(3)
C(38)–C(39)–C(34)	121.1(3)		

#1 -*x*+1, -*y*+1, -*z*+1.

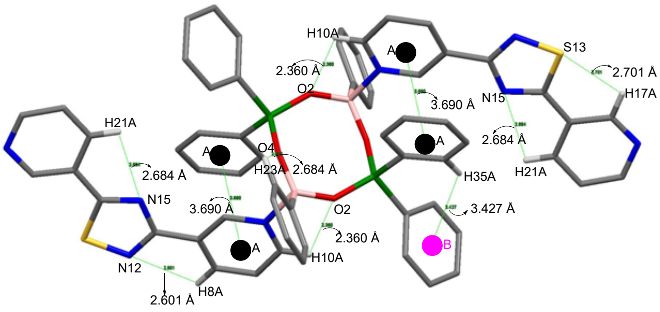

Figure 2. Non-bonded interactions in $[Ph_6B_2Si_2O_4]\cdot 2L$ (4) units with intramolecular C-H···π, C-H···N, C-H···O and π···π interactions. Colour identity; pink = B; green = Si; grey = C; blue = N; red = O; yellow = sulphur; light grey = H. Most H atoms have been omitted for clarity.

Data obtained from single crystal X-ray diffraction studies of compound 4 showed that it is a short chain oligomer consisting of compound 3 and only two linkers (L) connected at the two boron (B1) centres as shown by the ORTEP diagram with atom numbering shown in Figure 1. Crystallographic data of compound 4 are shown in Tables 1-3.

Unlike similar compounds found in the literature [6,13,15], in compound 4 one end of each of the Lewis base linkers is not connected to any other molecule. The two B-O distances in compound 4 are 1.431(3) Å (B1-O2) and 1.436(3) Å (B1-O4), respectively, and are longer than the B-O length for the tri-coordinated B in compound 3 that range from (1.36-1.39 Å) [17,36,37] but similar to those of compounds reported in the literature [6,15]. However, the B-O bond lengths in compound 4 are also similar to other B-O distances for tetrahedrally coordinated B in compounds such as $Ph(OSiR_2R')B\{OCH_2\}_3N$ [38] (R or R′ = Ph or CH_3) and $[Bu^tSi(OPhBO)_3SiBu^t]\cdot NC_5H_5$ [36] where the B is directly bonded to two O atoms, a phenyl group, and the N atom. The observed longer bond length at the tetrahedrally bonded B centres compared to the tri-coordinated B, as for the other compound discussed above, may be connected with the reduction of some B-O π-bonding component on changing from trigonal to tetrahedral coordination geometry at the B centres.

The two Si-O bond lengths in compound 4 are 1.6074(16) (Si3-O2) and 1.6120(16) Å (Si3-O4), respectively. These two Si-O bond lengths are comparable to those found in compounds in the literature [6,15]. However, the literature reports a mean value of 1.645 Å [17,36] for Si-O, for a four-coordinate Si to two O and two C atoms. But similar Si-O bond distances reported here have been observed in the literature [36,38]. The shorter Si-O distances associated with compound 4 suggest an increase in electron density in the Si-O bond, which is consistent with the decrease in the B-O electron density just as in compounds [6,15].

The B-N bond length in compound 4 is 1.699(3) Å (B1-N5), as in compounds in the literature [6,15]. The B-N bond lengths in compound 4 are comparable to those of simple borosiloxane such as $Ph(OSiR_2R')B\{OCH_2\}_3N$ [38] (R or R′ = Ph or CH_3) and $[Bu^tSi(OPhBO)_3SiBu^t]\cdot NC_5H_5$ [36] where the reported B-N distances were 1.639 and 1.655 Å, respectively. The Si-C bond lengths in compound 4 are 1.867(2) Å (Si3-C28) and 1.881(2) Å (Si3-C34) and are as expected and consistent with those of [6,15].

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

Parameter	Value
Empirical formula	$C_{72}H_{60}B_4N_8O_8S_2Si_2$
Formula weight (g/mol)	1328.82
Temperature (K)	173(2)
Crystal system	Triclinic
Space group	*P*-1
a (Å)	11.6316(7)
b (Å)	12.4462(8)
c (Å)	12.9148(8)
α (°)	113.649(6)
β (°)	90.799(5)
γ (°)	103.151(6)
Volume (Å^3)	1656.1(2)
Z	1
ρ_{calc} (g/cm^3)	1.332
μ (mm^{-1})	1.593
F(000)	692.0
Crystal size (mm^3)	0.237 × 0.134 × 0.039
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection (°)	7.526 to 147.45
Index ranges	$-14 \le h \le 13$, $-15 \le k \le 15$, $-10 \le l \le 16$
Reflections collected	9599
Independent reflections	6324 [R_{int} = 0.0325, R_{sigma} = 0.0524]
Data/restraints/parameters	6324/22/450
Goodness-of-fit on F^2	1.019
Final R indexes [I≥2σ (I)]	R_1 = 0.0405, wR_2 = 0.0967
Final R indexes [all data]	R_1 = 0.0606, wR_2 = 0.1096
Largest diff. peak/hole (e.Å^{-3})	0.24/-0.30

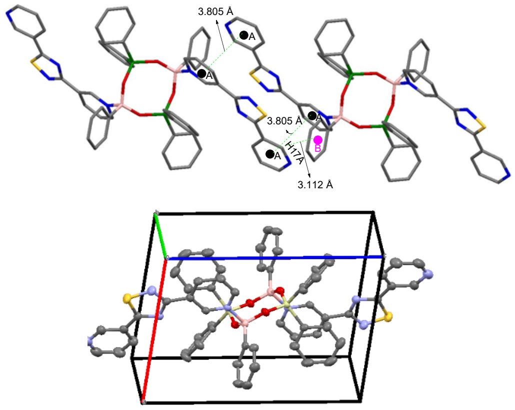

Figure 3. Crystal packing of two individual [$Ph_6B_2Si_2O_4$]·2L (4) connected by intermolecular C-H···π and π···π interactions. Colour identity; pink = B; green = Si; gray = C; blue = N; red = O; yellow = sulfur; light gray = H; solid color circles = centroid. H atoms have been omitted for clarity.

The dihedral angle O2-B1-C22-C23 in compound 4 is 2.85° which is lower than 8.6° reported for compound 3 [39] while the ring angle at the B centre (O2-B1-O4) is 116.93°. Therefore, the ring angles of compound 4 at the two B centres are higher than 109.5° expected for a tetrahedral geometry, but similar to those of compounds [6,15] and those reported in the literature [36]. Similarly, the ring angle of O2-Si3-O4 is 113.53(9)°, which is higher than 109.5° for a tetrahedral silicon. The bond angles at the Si centres as well as the Si-C bond distances in compound 4 are comparable to those of compounds [6,15] as well as other borasiloxane compounds and simple adducts in the literature [17,36,40].

Compound 4, shows non-covalent intramolecular (C-H···π, C-H···N, C-H···O, C-H···S and π···π) interactions in its crystal packings as depicted in Figure 2. In addition, compound 4 also displays some intermolecular short distance interactions in its crystal packing such as black dot A π centroid···π centroid black dot A (3.805 Å) and C-H17A···π centroid pink dot B (3.112 Å), as depicted in Figure 3.

3.2. Compound 5 [$Ph_6B_2Si_2O_4$]·2L·2[PhB(OH)$_2$]

The ^{1}H NMR spectrum of compound 5 shows well-resolved resonances with aromatic proton signals found within the range of δ 7.28-9.66 ppm, while the ^{13}C{^{1}H} NMR spectrum shows signals for aromatic carbons in the range of δ 123.80-185.37 ppm. The ^{11}B{^{1}H} NMR and ^{29}Si{^{1}H} NMR spectra of compound 5 showed singlets at δ 21.53 and -45.17 ppm, respectively.

The compound crystalizes in the triclinic space group *P*-1 and single-crystal XRD analysis showed an interesting 1D polymeric assembly, in which each eight-membered ring is bound to two (L) nitrogen atoms via coordinate covalent bonds (N→B). The other two nitrogen atoms are connected to phenylboronic acid molecules through hydrogen bonding, as shown in Figure 4. The crystallographic data of compound 5 are in Tables 4-6.

As can be seen in Figure 4, only one OH group of each phenylboronic acid (O41H) is connected to the linker (L) (N19) by hydrogen bonding, leaving the other OH group (H42 and O41) available for further H bonding. H42 and O41 are connected to another molecule of phenylboronic acid through hydrogen bonding with oxygen to give an 8-membered ring of phenylboronic acids. The lengths of the hydrogen bonds in compound 5 are 1.909 Å (H41···N19) and 1.925 Å (H42···O41), respectively. Furthermore, as can be seen from Figure 5 below,

Table 5. Bond lengths for compound 5.

Bond	**Length (Å)**	**Bond**	**Length (Å)**
B(1)–O(2)	1.430(2)	B(1)–O(4)#1	1.432(2)
B(1)–C(22)	1.619(3)	B(1)–N(5)	1.714(2)
O(2)–Si(3)	1.6177(14)	Si(3)–O(4)	1.6041(14)
Si(3)–C(34)	1.858(2)	Si(3)–C(28)	1.868(2)
O(4)–B(1)#1	1.432(2)	N(5)–C(6)	1.340(3)
N(5)–C(10)	1.343(2)	C(6)–C(7)	1.385(3)
C(7)–C(8)	1.392(3)	C(8)–C(9)	1.392(3)
C(8)–C(11)	1.471(3)	C(9)–C(10)	1.378(3)
C(11)–N(12)	1.336(4)	C(11)–N(15)	1.361(3)
C(11)–S(12')	1.631(7)	N(12)–S(13)	1.637(4)
S(13)–C(14)	1.718(2)	S(12')–N(13')	1.646(12)
N(13')–C(14)	1.335(11)	C(14)–N(15)	1.323(3)
C(14)–C(16)	1.472(3)	C(16)–C(21)	1.386(3)
C(16)–C(17)	1.387(3)	C(17)–C(18)	1.384(3)
C(18)–N(19)	1.334(3)	N(19)–C(20)	1.330(3)
C(20)–C(21)	1.382(4)	C(22)–C(27)	1.393(3)
C(22)–C(23)	1.397(3)	C(23)–C(24)	1.390(3)
C(24)–C(25)	1.388(4)	C(25)–C(26)	1.374(4)
C(26)–C(27)	1.396(3)	C(28)–C(33)	1.397(3)
C(28)–C(29)	1.399(3)	C(29)–C(30)	1.397(3)
C(30)–C(31)	1.379(3)	C(31)–C(32)	1.389(3)
C(32)–C(33)	1.388(3)	C(34)–C(35)	1.389(3)
C(34)–C(39)	1.408(3)	C(35)–C(36)	1.395(3)
C(36)–C(37)	1.381(4)	C(37)–C(38)	1.379(4)
C(38)–C(39)	1.388(3)	B(40)–O(42)	1.358(3)
B(40)–O(41)	1.364(3)	B(40)–C(43)	1.578(3)
C(43)–C(48)	1.393(3)	C(43)–C(44)	1.397(3)
C(44)–C(45)	1.390(3)	C(45)–C(46)	1.381(4)
C(46)–C(47)	1.381(4)	C(47)–C(48)	1.391(4)

#1 -*x*+1, -*y*+1, -*z*.

Table 6. Bond angles for compound 5.

Angle	**Value (°)**	**Angle**	**Value (°)**
O(2)–B(1)–O(4)#1	116.77(16)	O(2)–B(1)–C(22)	111.34(16)
O(4)#1–B(1)–C(22)	114.01(16)	O(2)–B(1)–N(5)	106.56(15)
O(4)#1–B(1)–N(5)	101.45(14)	C(22)–B(1)–N(5)	105.21(14)
B(1)–O(2)–Si(3)	136.97(12)	O(4)–Si(3)–O(2)	113.97(8)
O(4)–Si(3)–C(34)	111.92(8)	O(2)–Si(3)–C(34)	107.90(8)
O(4)–Si(3)–C(28)	107.05(8)	O(2)–Si(3)–C(28)	106.38(8)
C(34)–Si(3)–C(28)	109.41(9)	B(1)#1–O(4)–Si(3)	149.53(13)
C(6)–N(5)–C(10)	118.40(17)	C(6)–N(5)–B(1)	121.91(15)
C(10)–N(5)–B(1)	119.68(16)	N(5)–C(6)–C(7)	122.72(18)
C(6)–C(7)–C(8)	118.83(19)	C(9)–C(8)–C(7)	118.19(18)
C(9)–C(8)–C(11)	119.52(18)	C(7)–C(8)–C(11)	122.27(19)
C(10)–C(9)–C(8)	119.48(19)	N(5)–C(10)–C(9)	122.36(19)
N(12)–C(11)–N(15)	118.7(2)	N(12)–C(11)–C(8)	121.2(2)
N(15)–C(11)–C(8)	120.01(18)	N(15)–C(11)–S(12′)	111.0(3)
C(8)–C(11)–S(12′)	129.0(3)	C(11)–N(12)–S(13)	108.0(2)
N(12)–S(13)–C(14)	93.00(16)	C(11)–S(12′)–N(13′)	94.8(6)
C(14)–N(13′)–S(12′)	106.3(8)	N(15)–C(14)–N(13′)	118.7(5)
N(15)–C(14)–C(16)	122.41(19)	N(13′)–C(14)–C(16)	118.7(5)
N(15)–C(14)–S(13)	111.35(16)	C(16)–C(14)–S(13)	126.24(16)
C(14)–N(15)–C(11)	108.97(18)	C(21)–C(16)–C(17)	117.9(2)
C(21)–C(16)–C(14)	119.54(19)	C(17)–C(16)–C(14)	122.6(2)
C(18)–C(17)–C(16)	119.2(2)	N(19)–C(18)–C(17)	123.2(2)
C(20)–N(19)–C(18)	117.1(2)	N(19)–C(20)–C(21)	124.0(3)
C(20)–C(21)–C(16)	118.6(2)	C(27)–C(22)–C(23)	116.54(18)
C(27)–C(22)–B(1)	121.08(18)	C(23)–C(22)–B(1)	122.34(17)
C(24)–C(23)–C(22)	122.0(2)	C(25)–C(24)–C(23)	119.9(2)
C(26)–C(25)–C(24)	119.4(2)	C(25)–C(26)–C(27)	120.2(2)
C(22)–C(27)–C(26)	121.9(2)	C(33)–C(28)–C(29)	117.12(18)
C(33)–C(28)–Si(3)	121.04(15)	C(29)–C(28)–Si(3)	121.81(15)
C(30)–C(29)–C(28)	121.5(2)	C(31)–C(30)–C(29)	119.8(2)
C(30)–C(31)–C(32)	120.0(2)	C(33)–C(32)–C(31)	119.6(2)
C(32)–C(33)–C(28)	121.9(2)	C(35)–C(34)–C(39)	117.47(19)
C(35)–C(34)–Si(3)	121.47(16)	C(39)–C(34)–Si(3)	120.67(16)
C(34)–C(35)–C(36)	121.5(2)	C(37)–C(36)–C(35)	119.4(2)
C(38)–C(37)–C(36)	120.7(2)	C(37)–C(38)–C(39)	119.5(2)
C(38)–C(39)–C(34)	121.3(2)	O(42)–B(40)–O(41)	118.1(2)
O(42)–B(40)–C(43)	118.2(2)	O(41)–B(40)–C(43)	123.8(2)
C(48)–C(43)–C(44)	117.3(2)	C(48)–C(43)–B(40)	120.2(2)
C(44)–C(43)–B(40)	122.5(2)	C(45)–C(44)–C(43)	121.3(2)
C(46)–C(45)–C(44)	120.3(2)	C(47)–C(46)–C(45)	119.4(2)
C(46)–C(47)–C(48)	120.2(2)	C(47)–C(48)–C(43)	121.5(2)

#1 -*x*+1, -*y*+1, -*z*.

the other hydrogen atoms in the hydrogen-bonded ring are then connected with the linker (L) via further hydrogen bonding to give a 1D polymeric structure.

An ORTEP plot with atom numbering is shown in Figure 6. As revealed in Figure 6, compound 5 is similar to compound 4 but with extra hydrogen bonding that results in the formation of a 1D polymer. Thus, there are two types of boron atoms (B1

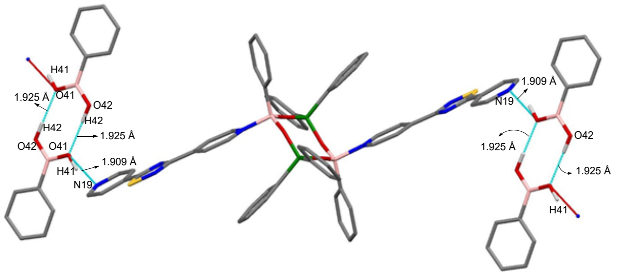

Figure 4. 1D polymeric structure of $[Ph_6B_2Si_2O_4]\cdot 2L\cdot 2[PhB(OH)_2]$ (5) showing hydrogen bonds as pale blue bonds between phenylboronic acids and linkers. Colour identity; pink = B; green = Si; grey = C; blue = N; red = O; yellow = sulphur; light grey = H, Most H atoms are omitted for clarity.

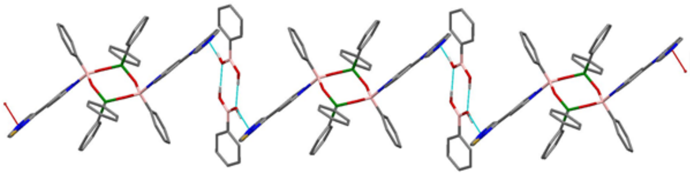

Figure 5. 1D chain structure of $[Ph_6B_2Si_2O_4]\cdot 2L\cdot 2[PhB(OH)_2]$ (**5**), pale blue bonds, hydrogen bonding (H···O) and linker (H···N). Colour identity; pink = B; green = Si; grey = C; blue = N; red = O; yellow = sulphur; light grey = H. Most H atoms have been omitted for clarity

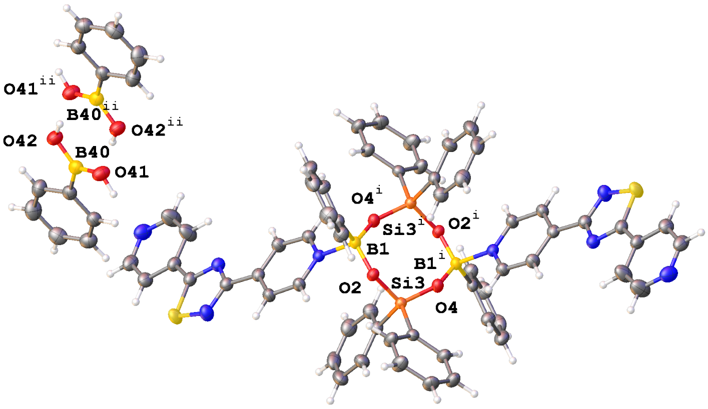

Figure 6. An ellipsoid view of $[Ph_6B_2Si_2O_4]\cdot 2L\cdot 2[PhB(OH)_2]$ (**5**) with some atom labeling.

and B40) in compound 5. The B1 atoms are tetrahedrally coordinated, whereas the B40 atoms are tri-coordinated. The two tetrahedrally coordinated B atoms are bonded to two O atoms (O2 and O4), one C atom (C22) from a phenyl ring and one N (N5) from the linker (L) via a dative bond. Unlike in compound 4, where some of the nitrogen atoms of the linker (L) were not bonded to any other molecule or atom, in compound 5 these N atoms (N19) connect to other phenylboronic acids by hydrogen bonding (H41···N19). Furthermore, two other hydrogen bonds are formed between two phenylboronic acids (H42···O42), and the other H41 from the hydrogen bonds of the phenylboronic acid to another linker (L).

The two B-O distances in compound 5 are 1.430(2) Å (B1-O2) and 1.432(2) Å (B1-O4), respectively, which are longer than the B-O lengths for the tri-coordinated B in compound 3 ring, which range from 1.36-1.39 Å [17,36,37,39], but are similar to those of compounds [6,15]. However, the B-O bond lengths in compound 5 are also similar to other B-O distances for tetrahedrally coordinated B in compounds such as $Ph(OSiR_2R')B\{OCH_2)_3N\}$ [38] (R or R′ = Ph or CH_3) and $[Bu^tSi(OPhBO)_3SiBu^t]\cdot NC_5H_5$ [36] However, the trigonally coordinated boron atoms (B40) in compound 5 have B-O bond lengths of 1.364(3) Å (B40-O41) and 1.358(3) Å (B40-O42). Thus, the four-coordinate B-O bond distances in compound 5 are longer than the tricoordinate B-O lengths. But these are comparable with a tri-coordinated B in $Si_2B_2O_4$ that ranges from 1.36-1.39 Å [17,36,37].

The two Si-O bond lengths in compound 5 are 1.6177(14) (Si3-O2) and 1.6041(14) Å (Si3-O4) respectively. These two Si-O bond lengths are similar to those found in compounds [6,15] but shorter than Si-O for a four-coordinate Si to two O atoms in the literature which have mean value of 1.645 Å [17,34]. However, some similar Si-O bond distances reported here have been observed in the literature [36,38]. The shorter Si-O distances observed in compound 5 suggest an increase in electron density in the Si-O bond, which is also consistent with a decrease in the B-O electron density as in compounds [6,15].

The length of the B1-N5 bond in compound 5 is 1.714(2) Å and is comparable to those of compounds in the literature [6,15]. The Si-C bond lengths in compound 5 are 1.868(2) Å (Si3-C28) and 1.858(2) Å (Si3-C34) and are as expected.

The ring angle of compound 5 at the B centre (O2-B1-O4) is 116.77 Å, which is higher than 109.5° expected for a tetrahedral geometry but similar to compounds [6,15] as well as those reported in the literature [36]. Similarly, the ring angle of O2-Si3-O4 is 113.97(9)°, which is higher than 109.5° for a tetrahedral silicon, but is comparable to the value found for compound 4.

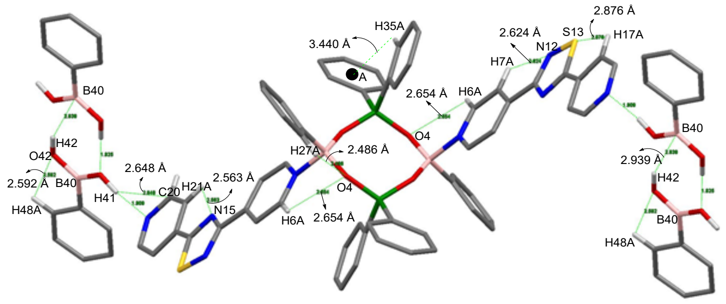

Figure 7. Crystal packing in [$Ph_6B_2Si_2O_4$]·2L·2[$PhB(OH)_2$] (5) with intramolecular C-H···π, C-H···N, C-H···O and H···B interactions. Colour identity; pink = B; green = Si; grey = C; blue = N; red = O; yellow = sulphur; light grey = H.; black dot = centroid. Most H atoms have been omitted for clarity

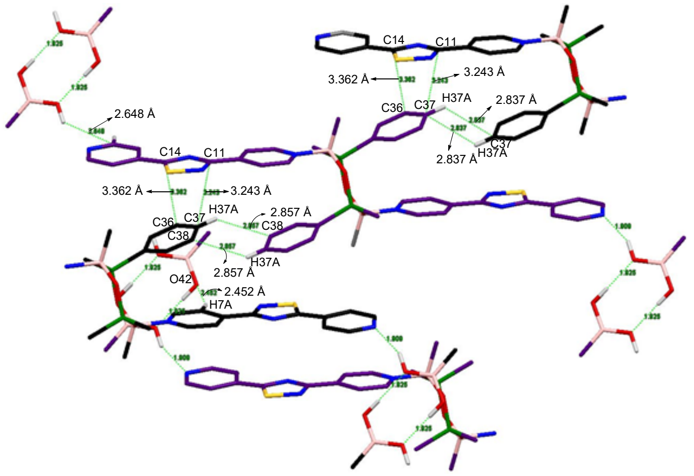

Figure 8. Crystal packing of three individual [$Ph_6B_2Si_2O_4$]·2L·2[$PhB(OH)_2$] (5) chains connected by intermolecular C-H…π and π…π interactions. Colour identity; pink = B; green = Si; grey = C; blue = N; red = O; yellow = sulphur; light grey = H; colour solid circles = centroid. Most H atoms have been omitted for clarity.

The bond angles as well as the Si-C bond lengths in compound 5 are comparable to those of compounds [6,15], as well as other borasiloxane compounds and simple adducts in the literature [17,36,40].

The crystal packing of compound 5 also shows intra-molecular non-covalent (C-H···π, C-H···N, C-H···O, C-H···S and H···B) interactions as depicted in Figure 7. Interestingly, compound 5 also exhibits short non-covalent intermolecular interactions in its crystal packing, such as π···π, (3.362 Å) (C14···C36) and (3.243 Å) (C11···C37), (CH···π) 2.587 Å (CH37A···πC38), and H7A···O42 (2.452 Å) as depicted in Figure 8.

The sum of all these interactions and the stability of compound 4 and 5 as well as the hydrogen bonding are key for the formation of these compounds 4 and 5. The judicial selection of building blocks and stepwise coupling of monomers and oligomers to give the products speak volumes of the novelty of the green synthetic approaches presented in this report.

4. Conclusions

In this study, an eight-membered 2, 2, 4, 6, 6, 8-hexaphenyl-1,3,5,7,2,6,4,8-tetraoxadisiladiborocane (3) Lewis acid has been successfully synthesized at reflux through a 2 + 2 cyclo-condensation reaction of diphenylsilanediol and phenylnoronic acid using molecular sieves as a water sorbent. Subsequently, compound 3 was further reacted with 3, 5-di(3-pyridyl)-1, 2, 4-thiadiazole (a Lewis base) leading to the formation of a novel eight-membered 2, 2, 4, 6, 6, 8-hexaphenyl-1, 3, 5, 7, 2, 6, 4, 8-tetra-oxadisiladiborocane-bridge-3, 5-di-(3-pyridyl)-1, 2, 4-thiadiazole oligomer (4). A further stepwise coupling of compound 4 oligomer with phenylboronic acid yielded another eight-membered 2, 2, 4, 6, 6, 8-hexaphenyl-1, 3, 5, 7, 2, 6, 4, 8-tetraoxadisiladiborocane-bridge-3, 5-di-(3-pyridyl)-1, 2, 4-thiadiazole-phenylboronic acid hydrogen-bonded 1D polymer (5). The crystal structures of these compounds 4 and 5 were determined using single-crystal XRD. The oligomer shows extensive intermolecular and intramolecular π-π interactions. On the other hand, compound 5 shows quite interesting hydrogen bonding. These two novel compounds have promising potential to enhance the performance and functionality of borasiloxane backbone materials. The importance of 3,5-di-(3-pyridyl)-1,2,4-thiadiazole in medicine highlights its potential as a therapeutic agent. For these reasons, more research is needed to explore the full potential of these 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 [41-43].

Acknowledgements

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Supporting information S

CCDC-2495667 and CCDC-2495668 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 author declares that there is no conflict of interest.
Ethical approval: All ethical guidelines have been adhered to.
Sample availability: Samples of the compounds are available from the author.

CRediT authorship contribution statement

Conceptualization: Okpara Sergeant Bull, Ihesinachi Appolonia Kalagbor; Methodology: Okpara Sergeant Bull, Ngozi Jane Maduelosi; Software: Okpara Sergeant Bull; Validation: Okpara; Formal Analysis: Okpara Sergeant Bull; Investigation: Okpara Sergeant Bull, Ngozi Jane Maduelosi; Resources: Okpara Sergeant Bull; Data Curation: Okpara Sergeant Bull, Ngozi Jane Maduelosi; Writing - Original Draft: Okpara Sergeant Bull Writing - Review and Editing: Okpara Sergeant Bull; Visualization: Don- Okpara Sergeant Bull; Funding acquisition Okpara Sergeant Bull; Supervision: Okpara Sergeant Bull; Project Administration: Okpara Sergeant Bull, Ihesinachi Appolonia Kalagbor.

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