



# Synthesis and crystal structure of 2-(anthracen-9-yl)-1-(*tert*-butyldimethylsilyl)-3,6-dihydro-1 $\lambda^4$ ,2 $\lambda^4$ -azaborinine

Philipp J. Gliese,<sup>a,b</sup> Yannik Appiarius,<sup>a,b</sup> Tarek Scheele,<sup>c</sup> Enno Lork,<sup>d</sup> Tim Neudecker<sup>b,c,e</sup> and Anne Staubitz<sup>a,b\*</sup>

Received 18 August 2023

Accepted 23 September 2023

Edited by L. Van Meervelt, Katholieke Universiteit Leuven, Belgium

**Keywords:** crystal structure; 1,2-azaborinine; boron–nitrogen bond; boron–nitrogen heterocycle; ring-closing metathesis; BN cyclohexene.

**CCDC reference:** 2297014

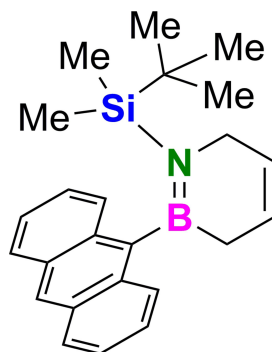
**Supporting information:** this article has supporting information at journals.iucr.org/e

<sup>a</sup>University of Bremen, Institute for Organic and Analytical Chemistry, 28359 Bremen, Germany, <sup>b</sup>University of Bremen, MAPEX Center for Materials and Processes, 28359 Bremen, Germany, <sup>c</sup>University of Bremen, Institute for Physical and Theoretical Chemistry, 28359 Bremen, Germany, <sup>d</sup>University of Bremen, Institute for Inorganic Chemistry and Crystallography, 28359 Bremen, Germany, and <sup>e</sup>Bremen Center for Computational Materials Science, 28359 Bremen, Germany. \*Correspondence e-mail: [staubitz@uni-bremen.de](mailto:staubitz@uni-bremen.de)

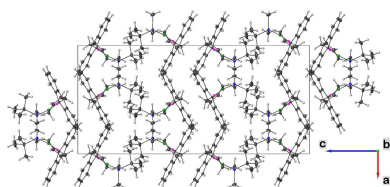
The title compound, C<sub>24</sub>H<sub>30</sub>BNSi (**I**), is an asymmetric 1,2,3,6-tetrahydro-1,2-azaborinine consisting of a BN-substituted cyclohexadiene analog with a *B*-anthracenyl substituent. A ring-closing metathesis with subsequent substitution of the obtained BCl 1,2-azaborinine using anthracenyl lithium yielded the title compound **I**. The asymmetric unit ( $Z = 8$ ) belongs to the orthorhombic space group *Pbca* and shows an elongated N–C bond compared to previously reported BN-1,4-cyclohexadiene [Abbey *et al.* (2008) *J. Am. Chem. Soc.* **130**, 7250–7252]. The primarily contributing surface interactions are H $\cdots$ H and C $\cdots$ H/H $\cdots$ C (as elucidated by Hirshfeld surface analysis) which are dominated by van der Waals forces. Moreover, the non-aromatic BN heterocycle and the protecting group exhibit intra- and intermolecular C–H $\cdots$  $\pi$  interactions, respectively, with the anthracenyl substituent.

## 1. Chemical context

The formal replacement of a C–C bond with a B–N motif (BN isosterism) in six-membered rings changes their reactivity, as well as the dipole moments and electronic and optical properties (Bélanger-Chabot *et al.*, 2017; Campbell *et al.*, 2012; Appiarius *et al.*, 2023). This allows for potential applications in functionalized polymers (Thiedemann *et al.*, 2017), hydrogen-storage materials (Campbell *et al.*, 2010), pharmacology (Boknevitc *et al.*, 2019) or optoelectronics (Appiarius *et al.*, 2021; Hoffmann *et al.*, 2021a,b).



Being the formal BN analogs of 1,4-cyclohexadiene, 1,2,3,6-tetrahydro-1,2-azaborinines were reported to be intermediates for the synthesis of aromatic 1,2-azaborinines (Ashe & Fang, 2000; Marwitz *et al.*, 2009). A B-Cl 1,2,3,6-tetrahydro-1,2-azaborinine was aromatized under inert conditions,



followed by subsequent substitution of the boron atom to obtain an air-stable derivative. The approach of this work presents an alternative: initial replacement of the highly reactive BCl bond by substitution with polycyclic anthracenyl lithium yields an air-stable product early on. Therefore, the respective *B*-anthracenyl heterocycle (**I**) was synthesized giving access to the 1,2,3,6-tetrahydro-1,2-azaborinines with lower oxidation state of the C<sub>4</sub> backbone.

## 2. Structural commentary

The title compound **I** is an example of a 1,2,3,6-tetrahydro-1,2-azaborinine with substituted boron and nitrogen atoms, crystallizing in the centrosymmetric orthorhombic space group, *Pbca* (Fig. 1). Its asymmetric unit ( $Z = 8$  with  $Z' = 1$ ) consists of one molecule. In contrast to the planar ring of the parent 1,4-cyclohexadienes (Jeffrey *et al.*, 1988), the BN-containing ring resembles a flat boat conformer. The C1–B1–N1–C4 unit is not perfectly planar [torsion angle = 10.55 (17)°] and the dihedral angle between the double-bond analog B1–N1 and the C2–C3 bond is 5.04 (11)°. Moreover, the almost perpendicular dihedral twist angle between the planar anthracenyl rings [plane of carbons C11–C24] and the B1–N1 unit is 97.96 (13)° [anthracenyl plane to B1–N1 bond angle].

According to an investigation of the B–N bond lengths in BNC<sub>4</sub> rings ranging from benzene to cyclohexane analogs of B–NPh<sub>2</sub>, *N*-*tert*-butyl 1,2,3,6-tetrahydro-1,2-azaborinines (Abbey *et al.*, 2008), the comparison of the closely related title compound **I** with the reported 1,4-cyclohexadiene analog showed comparable heterocyclic bond lengths. In the title

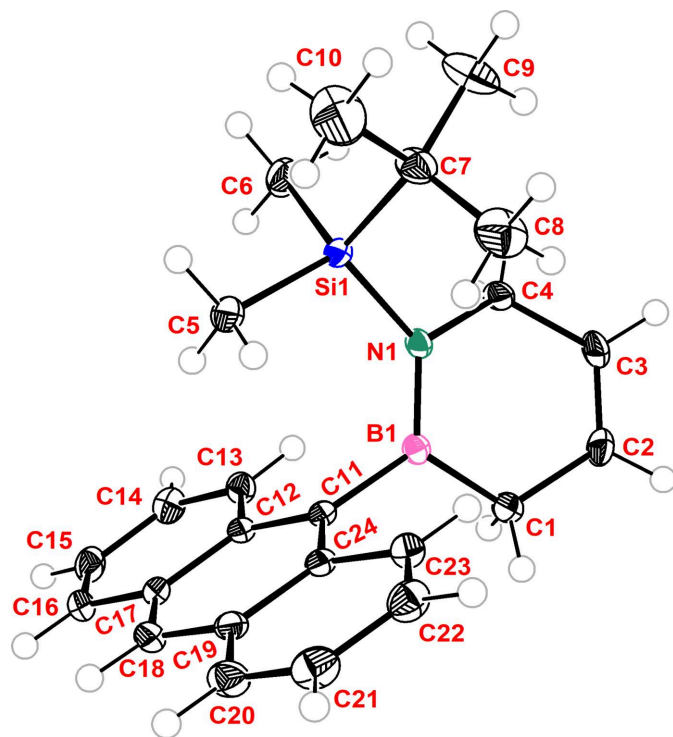


Figure 1

Crystal structure of the title compound **I** with atom labeling with displacement ellipsoids drawn at the 60% probability level.

Table 1

Geometry of C–H... $\pi$  interactions ( $\text{\AA}$ , °).

C<sub>g</sub>2, C<sub>g</sub>5, C<sub>g</sub>7 and C<sub>g</sub>3 are the centroids of rings C11–C12/C17–C19/C24, C11–C18, C11–C24 and C12–C17, respectively.

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
C5–H5A...C <sub>g</sub> 2	0.98	2.86	3.4529 (15)	120
C5–H5A...C <sub>g</sub> 5	0.98	2.91	3.7305 (15)	142
C5–H5A...C <sub>g</sub> 7	0.98	2.88	3.4772 (15)	120
C2–H2...C <sub>g</sub> 3 <sup>i</sup>	0.95	2.92	3.6380 (15)	133
C4–H4B...C <sub>g</sub> 3 <sup>ii</sup>	0.99	2.97	3.9373 (15)	167

Symmetry codes: (i)  $-x + 1, -y + 1, -z + 1$ ; (ii)  $-x + \frac{3}{2}, y - \frac{1}{2}, z$ .

compound **I**, the C2–C3 bond length [1.3276 (19) Å] resembles the bond in 1,4-cyclohexadienes [1.318 (2) Å] and their 1,2-azaborinine analog [1.319 (2) Å] more closely than that in the benzene analog (Jeffrey *et al.*, 1988). Comparison of the title compound **I** with the benzene analog and three additional 1,2-azaborinine examples (Rudebusch *et al.*, 2013; Liu *et al.*, 2021; Pan *et al.*, 2008) showed shorter B1–N1 [1.4052 (17)] and C2–C3 [1.3276 (19) Å] bond lengths. As a result of weaker bond-length compensation effects, the remaining bonds within the ring are elongated by between 0.11 and 0.15 Å.

## 3. Supramolecular features and computational analysis

Analysis of the crystal packing exhibits zigzag layers of the title compound **I** in the *c*-axis direction (Fig. 2). The *tert*-butyl moieties of the protecting groups are paired in groups of two along the *ac* plane (Fig. 2*a*). The anthracenyl substituents are aligned in a zigzag manner [plane normal to plane normal

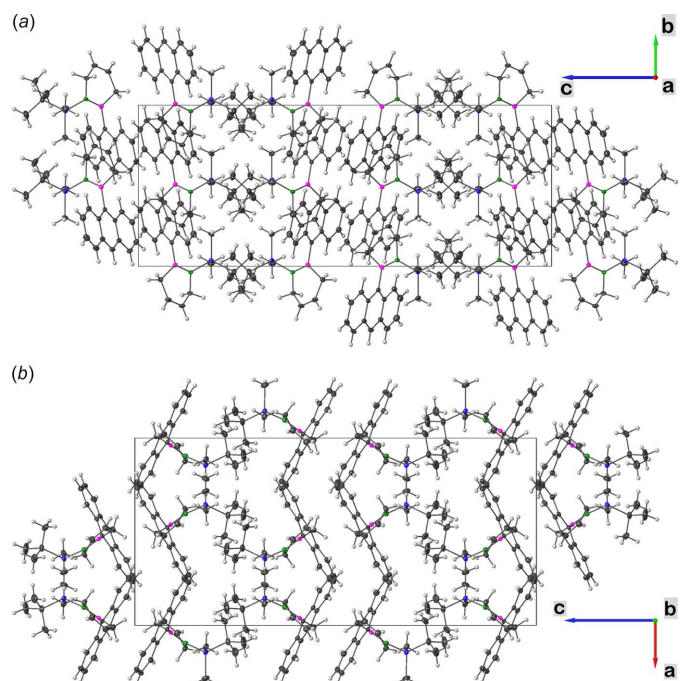
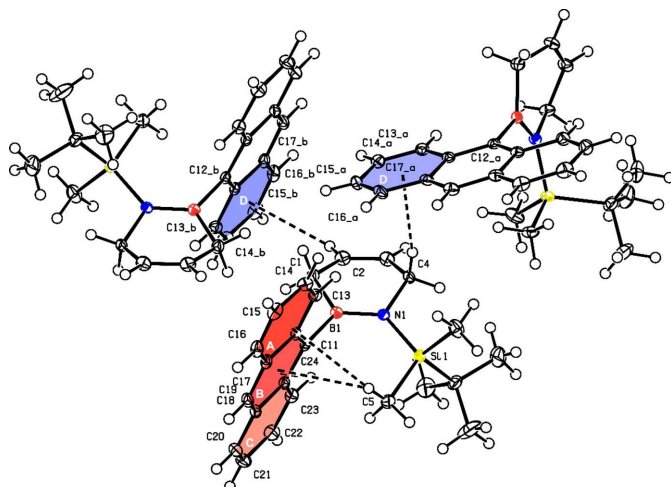


Figure 2

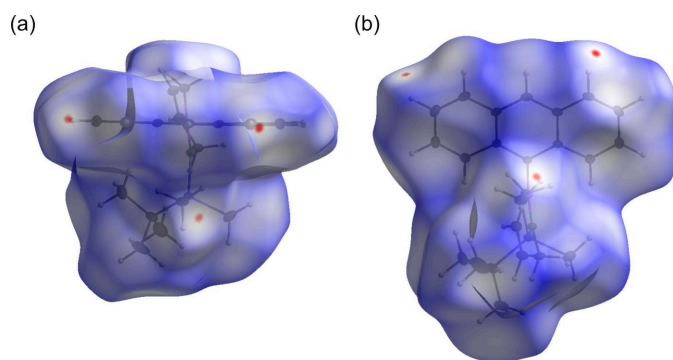
The crystal packing of the title compound **I** viewed along the *a*- (a) and *b*-axes (b). The unit cell is outlined in black.



**Figure 3**  
Inter- and intramolecular C–H... $\pi$  interactions in the title compound **I** with atom labeling between the respective centers of gravity (labels A–D).

angle of  $52.936(18)^\circ$ ], leading to a centroid–centroid distance for the anthracenyl substituents of  $6.4604(8)$  Å for in-plane orientation and  $8.7850(6)$  Å within the pattern (Fig. 2*b*). Therefore, no  $\pi$ -stacking is evident, given the positioning of the anthracenyl substituents in an antiplanar arrangement.

The C5–H5A group exhibits intramolecular C–H... $\pi$  interactions with the anthracene ring [see Fig. 3 (labels A–C) and Table 1 for details; Spek, 2020). Moreover, interactions of the C2–H2 and the C4–H4B groups with the C12–C17 ring [Fig. 3 (label D), Table 1] are observed. Additional theoretical analysis (Becke, 1993; Epifanovsky *et al.*, 2021; Francl *et al.*, 1982; Glendening *et al.*, 2001; Hariharan & Pople, 1973; Hehre *et al.*, 1972; Stephens *et al.*, 1994) matching the obtained crystal bond lengths revealed no aromatic character of the BN heterocycle of the title compound **I**. Instead, the free electron pair of nitrogen shows a significant donation to boron, and the C2–C3 bond exhibits no significant interactions with surrounding atoms (see supporting information). In particular, the C1–B1–N1–C4 motif shows a significant electron deficiency through low bond orders. While the B1–N1 and N1–C4 bonds have bond orders of 0.73 and 0.77, respectively, a value of 0.67 is obtained for the elongated B1–C1 bond.



**Figure 4**  
Two views of the three-dimensional Hirshfeld surface mapped over  $d_{\text{norm}}$ .

**Table 2**

Interatomic contacts with the title molecule **I** as percentage contributions to the Hirshfeld surface.

Entry	Contact	Percentage contribution
1	all...all	100
2	H...H	77
3	C...C	0.1
4	C...H/H...C	22.8
5	B...all/all...B	0
6	N...all/all...N	0
7	Si...all/all...Si	0

#### 4. Hirshfeld analysis

For the analysis of the intermolecular interactions, Hirshfeld surface (HS) calculations (Spackman & Jayatilaka, 2009) were performed and plotted over the  $d_{\text{norm}}$  in the range between  $-1.0432$  and  $+2.0960$  a.u. using *CrystalExplorer 21.5* (Spackman *et al.*, 2021) (Fig. 4).

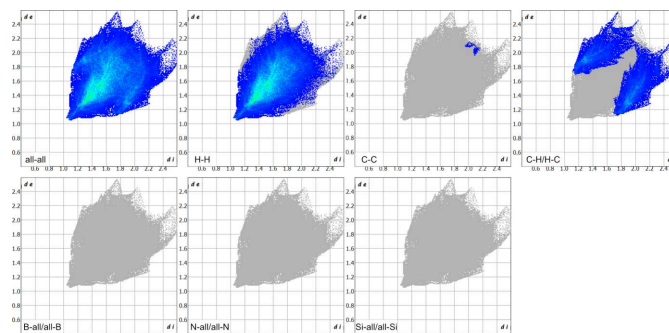
Minor interactions were found for C14–H14, C16–H16, C21–H21, and C23–H23, as well as the two silyl methyl groups (C5 and C6).

The generation of 2D fingerprint plots (McKinnon *et al.*, 2007) was performed using *CrystalExplorer 21.5*, investigating all specific intermolecular contacts (Fig. 5).

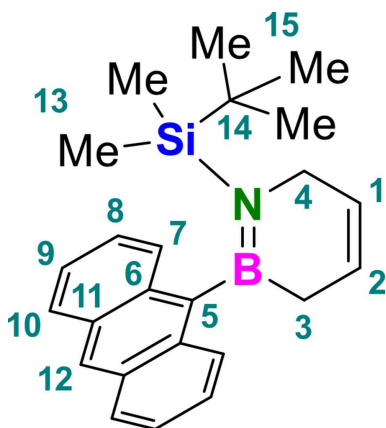
In the crystal packing, the H...H interactions are predominating and contribute to 77.0% of the overall close atom contacts (Entry 1, Table 2). C...C interactions contribute 0.1% (Entry 2, Table 2), while C...H/H...C contacts account for 22.8% (Entry 3, Table 2), indicating no additional interactions involving the heteroatoms.

#### 5. Database Survey

A search of the Cambridge Structural Database (WebCSD version 1.9.32; update 27.06.2023; Groom *et al.*, 2016) revealed no reports of BN-containing 1,4-cyclohexadiene structures with B-anthracenyl substituents. However, a search for the substructure of 1,2,3,6-tetrahydro-1,2-azaborinines produced nine results with the B-NPh<sub>2</sub>, *N-tert*-butyl 1,2,3,6-tetrahydro-



**Figure 5**  
Two-dimensional fingerprint plots of title compound **I** with the respective H...H, C...C, C...H/H...C, B...all/all...B, N...all/all...N, and Si...all/all...Si interactions ( $d_i$  and  $d_e$  are the closest internal and external distances in Å on the Hirshfeld surface).



**Figure 6**  
Numbering scheme of the title compound **I** used for interpretation of spectroscopic data.

1,2-azaborinine derivative (CSD refcode: EFUPIF; Abbey *et al.*, 2008) as the only monocyclic example. Of the 13 substructures with N–Si substitutions, eight examples with a similar protection group were found, but none of these examples had the C<sub>4</sub> oxidation state of the title compound **I**.

## 6. Synthesis and Crystallization

The precursor, 2-chloro-1-methyl-1,2,3,6-tetrahydro-1,2-azaborine, was synthesized according to the literature (Appiaris *et al.*, 2021).

Under a nitrogen atmosphere, 9-bromoanthracene (4.68 g, 18.2 mmol) was dissolved in *n*-pentane (20 mL) and cooled to 273 K. A solution of *n*-butyllithium (1.1 eq., 8.0 mL, 20 mmol, 2.5 M in hexanes) was added over the course of 5 min. The solution was allowed to warm to 292 K and was stirred for 19 h. The mixture was then kept at 269 K for 48 h for subsequent precipitation. In a nitrogen-filled glovebox, the solution was filtered through a frit (pore size 3), and the solid was washed with *n*-pentane (50 mL) until no color was observed in the filtrate. It was then transferred to a flask and dried *in vacuo* (200 mbar). The product was obtained as a yellow powder (3.32 g, 18.0 mmol, 99%, purity: 70%). The purity was determined after a literature-reported procedure (Lin & Paquette, 1994).

Under a nitrogen atmosphere, the B-Cl 1,2-azaborinine (101 mg, 436  $\mu$ mol) was dissolved in THF (5 mL) and cooled to 195 K. The lithium reagent (1.10 eq., 126 mg, 479  $\mu$ mol, purity 70%) was dissolved in THF (5 mL) and added while maintaining the temperature at 195 K. The solution was allowed to warm to 292 K while it was stirred for 2 h. The reaction mixture was quenched with water (2 mL) and extracted with chloroform (3  $\times$  20 mL). The combined organic layers were washed with brine (2  $\times$  20 mL) and dried over MgSO<sub>4</sub>. Subsequently to filtration, the solvent was removed *in vacuo* (200 mbar) to obtain the crude product. Purification by column chromatography (*n*-pentane, *R<sub>f</sub>* = 0.60) gave the title compound **I** as colorless crystals (129 mg, 350  $\mu$ mol, 80%). The title compound was crystallized from a *n*-pentane/acetonitrile mixture by slow evaporation at 273 K. It was stored

**Table 3**  
Experimental details.

Crystal data	
Chemical formula	C <sub>24</sub> H <sub>30</sub> BNSi
<i>M<sub>r</sub></i>	371.39
Crystal system, space group	Orthorhombic, <i>Pbca</i>
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	13.3292 (6), 11.1365 (5), 28.5973 (12)
<i>V</i> (Å <sup>3</sup> )	4245.0 (3)
<i>Z</i>	8
Radiation type	Mo <i>K</i> α
$\mu$ (mm <sup>-1</sup> )	0.12
Crystal size (mm)	0.28 $\times$ 0.22 $\times$ 0.2
Data collection	
Diffractometer	Bruker Photon 100
Absorption correction	Multi-scan ( <i>SADABS</i> ; Krause <i>et al.</i> , 2015)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.707, 0.746
No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections	67479, 5264, 4416
<i>R<sub>int</sub></i>	0.049
(sin $\theta/\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.667
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.042, 0.103, 1.07
No. of reflections	5264
No. of parameters	249
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$ , $\Delta\rho_{min}$ (e Å <sup>-3</sup> )	0.37, -0.29

Computer programs: *PHOTON* and *SAINT* (Bruker, 2019), *SHELXT2014/5* (Sheldrick, 2015a), *SHELXL* (Sheldrick, 2015b), *OLEX2* (Dolomanov *et al.*, 2009), *ORTEP-3 for Windows* (Farrugia, 2012), and *publCIF* (Westrip, 2010).

under non-inert conditions for at least 4–6 weeks (stored at 265 K) without decomposition. The numbering scheme for interpretation of spectroscopic data is given in Fig. 6.

<sup>1</sup>H NMR [600 MHz, CDCl<sub>3</sub>, δ (ppm)]: 8.30 (*s*, 1H, *H*-12), 7.96 (*ddd*, <sup>3</sup>*J* = 8.4 Hz, <sup>4</sup>*J* = 1.4, 0.7 Hz, 2H, *H*-10), 7.80 (*dd*, <sup>3</sup>*J* = 8.5 Hz, <sup>4</sup>*J* = 1.3, 0.7 Hz, 2H, *H*-7), 7.41 (*ddd*, <sup>3</sup>*J* = 8.4, 6.5 Hz, <sup>4</sup>*J* = 1.3 Hz, 2H, *H*-9), 7.36 (*ddd*, <sup>3</sup>*J* = 8.5, 6.5 Hz, <sup>4</sup>*J* = 1.4 Hz, 2H, *H*-8), 6.13–6.07 (*m*, 1H, *H*-2), 6.03–5.97 (*m*, 1H, *H*-1), 4.00–3.95 (*m*, 2H, *H*-4), 1.92–1.86 (*m*, 2H, *H*-3), 0.84 (*s*, 9H, *H*-15), -0.57 (*s*, 6H, *H*-13).

<sup>13</sup>C{<sup>1</sup>H} NMR [151 MHz, CDCl<sub>3</sub>, δ (ppm)]: 132.2 (*C*-6), 131.2 (*C*-11), 129.3 (*C*-7), 128.7 (*C*-10), 127.8 (*C*-2), 126.1 (*C*-1), 125.2 (*C*-12), 124.8 (*C*-9), 124.2 (*C*-8), 45.6 (*C*-4), 28.0 (*C*-15), 19.2 (*C*-14), 3.8 (*C*-13).

<sup>11</sup>B{<sup>1</sup>H} NMR [160 MHz, CDCl<sub>3</sub>, δ (ppm)]: 50.6.

<sup>29</sup>Si{<sup>1</sup>H} NMR [119 MHz, CDCl<sub>3</sub>, δ (ppm)]: 15.9.

IR [ATR, ν (cm<sup>-1</sup>)]: 3048 (*w*), 3024 (*w*), 2925 (*m*), 2854 (*m*), 2359 (*w*), 1621 (*w*), 1463 (*w*), 1442 (*m*), 1414 (*m*), 1378 (*m*), 1295 (*m*), 1272 (*m*), 1251 (*m*), 1123 (*m*), 1079 (*m*), 1044 (*m*), 961 (*m*), 947 (*w*), 829 (*m*), 842 (*s*), 776 (*s*), 731 (*s*), 679 (*s*).

HRMS (ESI positive, *m/z*): calculated for C<sub>24</sub>H<sub>31</sub><sup>11</sup>BN<sup>28</sup>Si 372.23133 [*M* + *H*]<sup>+</sup>; found 372.23167 [*M* + *H*]<sup>+</sup>.

*M.p.* [DSC, Onset, (K)]: 374.

## 7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. Using a riding model with bond

lengths of 0.95 Å (CH), 0.99 Å (CH<sub>2</sub>) and 0.98 Å (CH<sub>3</sub>), the hydrogen atoms were positioned geometrically. Isotropic displacement parameters ( $U_{\text{iso}}$ ) of these H atoms were fixed to 1.2 (CH and CH<sub>2</sub>) or 1.5 (CH<sub>3</sub>) times the values of the parent carbon atoms. The idealized methyl groups were refined as rotating groups.

### Funding information

Funding for this research was provided by: Deutsche Forschungsgemeinschaft (grant No. STA1195/2-1 to A. Staubitz); Deutsche Forschungsgemeinschaft (grant No. STA1526/3-1 to T. Neudecker).

### References

- Abbey, E. R., Zakharov, L. N. & Liu, S.-Y. (2008). *J. Am. Chem. Soc.* **130**, 7250–7252.
- Appiarius, Y. & Staubitz, A. (2023). *Chem. Unserer Zeit*, **57**, 180–190.
- Appiarius, Y., Stauch, T., Lork, E., Rusch, P., Bigall, N. C. & Staubitz, A. (2021). *Org. Chem. Front.* **8**, 10–17.
- Ashe, A. J. & Fang, X. (2000). *Org. Lett.* **2**, 2089–2091.
- Becke, A. D. (1993). *J. Chem. Phys.* **98**, 5648–5652.
- Bélanger-Chabot, G., Braunschweig, H. & Roy, D. K. (2017). *Eur. J. Inorg. Chem.* pp. 4353–4368.
- Boknevit, K., Italia, J. S., Li, B., Chatterjee, A. & Liu, S.-Y. (2019). *Chem. Sci.* **10**, 4994–4998.
- Bruker (2019). *PHOTON* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Campbell, P. G., Marwitz, A. J. & Liu, S. Y. (2012). *Angew. Chem. Int. Ed.* **51**, 6074–6092.
- Campbell, P. G., Zakharov, L. N., Grant, D. J., Dixon, D. A. & Liu, S.-Y. (2010). *J. Am. Chem. Soc.* **132**, 3289–3291.
- Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
- Epifanovsky, E., Gilbert, A. T. B., Feng, X., Lee, J., Mao, Y., Mardirossian, N., *et al.* (2021). *J. Chem. Phys.* **155**, 084801.
- Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
- Francl, M. M., Pietro, W. J., Hehre, W. J., Binkley, J. S., Gordon, M. S., DeFrees, D. J. & Pople, J. A. (1982). *J. Chem. Phys.* **77**, 3654–3665.
- Glendening, E. D., Badenhoop, J. K., Reed, A. E., Carpenter, J. E., Bohmann, J. A., Morales, C. M. & Weinhold, F. (2001). *NBO 5.0*. Theoretical Chemistry Institute, University of Wisconsin, Madison, Wisconsin, USA.
- Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
- Hariharan, P. C. & Pople, J. A. (1973). *Theor. Chim. Acta*, **28**, 213–222.
- Hehre, W. J., Ditchfield, R. & Pople, J. A. (1972). *J. Chem. Phys.* **56**, 2257–2261.
- Hoffmann, J., Geffroy, B., Jaques, E., Hissler, M. & Staubitz, A. (2021a). *J. Mater. Chem. C* **9**, 14720–14729.
- Hoffmann, J., Jacquemin, D., Hissler, M. & Staubitz, A. (2021b). *J. Mater. Chem. C* **9**, 13926–13934.
- Jeffrey, G. A., Buschmann, J., Lehmann, C. W. & Luger, P. (1988). *J. Am. Chem. Soc.* **110**, 7218–7219.
- Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). *J. Appl. Cryst.* **48**, 3–10.
- Lin, H.-S. & Paquette, L. A. (1994). *Synth. Commun.* **24**, 2503–2506.
- Liu, Y., Puig de la Bellacasa, R., Li, B., Cuenca, A. B. & Liu, S.-Y. (2021). *J. Am. Chem. Soc.* **143**, 14059–14064.
- Marwitz, A. J., Matus, M. H., Zakharov, L. N., Dixon, D. A. & Liu, S.-Y. (2009). *Angew. Chem. Int. Ed.* **48**, 973–977.
- McKinnon, J. J., Jayatilaka, D. & Spackman, M. A. (2007). *Chem. Commun.* pp. 3814–3816.
- Pan, J., Kampf, J. W. & Ashe, A. J. (2008). *Organometallics*, **27**, 1345–1347.
- Rudebusch, G. E., Zakharov, L. N. & Liu, S.-Y. (2013). *Angew. Chem. Int. Ed.* **52**, 9316–9319.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
- Spackman, M. A. & Jayatilaka, D. (2009). *CrystEngComm*, **11**, 19–32.
- Spackman, P. R., Turner, M. J., McKinnon, J. J., Wolff, S. K., Grimwood, D. J., Jayatilaka, D. & Spackman, M. A. (2021). *J. Appl. Cryst.* **54**, 1006–1011.
- Spek, A. L. (2020). *Acta Cryst.* **E76**, 1–11.
- Stephens, P. J., Devlin, F. J., Chabalowski, C. F. & Frisch, M. J. (1994). *J. Phys. Chem.* **98**, 11623–11627.
- Thiedemann, B., Gliese, P. J., Hoffmann, J., Lawrence, P. G., Sönnichsen, F. D. & Staubitz, A. (2017). *Chem. Commun.* **53**, 7258–7261.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

## supporting information

*Acta Cryst.* (2023). E79, 1012-1016 [https://doi.org/10.1107/S2056989023008381]

## Synthesis and crystal structure of 2-(anthracen-9-yl)-1-(*tert*-butyldimethylsilyl)-3,6-dihydro-1 $\lambda^4$ ,2 $\lambda^4$ -azaborinine

**Philipp J. Gliese, Yannik Appiarius, Tarek Scheele, Enno Lork, Tim Neudecker and Anne Staubitz**

### Computing details

Data collection: *PHOTON* (Bruker, 2019); cell refinement: *SAINTE* V8.40A (Bruker, 2019); data reduction: *SAINTE* V8.40A (Bruker, 2019); program(s) used to solve structure: *SHELXT2014/5* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL* Sheldrick, 2015b); molecular graphics: Olex2 1.5 (Dolomanov *et al.*, 2009) *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: Olex2 1.5 (Dolomanov *et al.*, 2009), *publCIF* (Westrip, 2010).

### 2-(Anthracen-9-yl)-1-(*tert*-butyldimethylsilyl)-3,6-dihydro-1 $\lambda^4$ ,2 $\lambda^4$ -azaborinine

#### Crystal data

C<sub>24</sub>H<sub>30</sub>BNSi

$M_r = 371.39$

Orthorhombic, *Pbca*

$a = 13.3292$  (6) Å

$b = 11.1365$  (5) Å

$c = 28.5973$  (12) Å

$V = 4245.0$  (3) Å<sup>3</sup>

$Z = 8$

$F(000) = 1600$

$D_x = 1.162$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 9845 reflections

$\theta = 2.5$ – $30.5^\circ$

$\mu = 0.12$  mm<sup>-1</sup>

$T = 100$  K

Block, colourless

$0.28 \times 0.22 \times 0.2$  mm

#### Data collection

Bruker Photon 100

diffractometer

Radiation source: microfocus sealed X-ray tube,

Incoatec  $\lambda\mu$ s

Mirror optics monochromator

Detector resolution: 7.9 pixels mm<sup>-1</sup>

$\omega$  and  $\varphi$  scans

Absorption correction: multi-scan  
(SADABS; Krause *et al.*, 2015)

$T_{\min} = 0.707$ ,  $T_{\max} = 0.746$

67479 measured reflections

5264 independent reflections

4416 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.049$

$\theta_{\max} = 28.3^\circ$ ,  $\theta_{\min} = 2.5^\circ$

$h = -17 \rightarrow 17$

$k = -14 \rightarrow 14$

$l = -38 \rightarrow 38$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.042$

$wR(F^2) = 0.103$

$S = 1.07$

5264 reflections

249 parameters

0 restraints

Primary atom site location: dual

Hydrogen site location: inferred from  
neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0421P)^2 + 2.6379P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$

$$\Delta\rho_{\max} = 0.37 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.28 \text{ e } \text{\AA}^{-3}$$

*Special details*

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Si1	0.64414 (3)	0.53526 (3)	0.67676 (2)	0.01305 (9)
N1	0.59622 (8)	0.46229 (9)	0.62665 (4)	0.0121 (2)
C11	0.52126 (9)	0.64751 (11)	0.58088 (4)	0.0119 (2)
C19	0.41726 (10)	0.83144 (12)	0.58633 (5)	0.0149 (3)
C12	0.59392 (9)	0.71475 (11)	0.55610 (4)	0.0126 (2)
C24	0.43227 (9)	0.70565 (11)	0.59506 (4)	0.0130 (2)
C17	0.57825 (10)	0.84029 (12)	0.54660 (5)	0.0146 (3)
C18	0.49112 (10)	0.89607 (12)	0.56257 (5)	0.0168 (3)
H18	0.481850	0.979511	0.557198	0.020*
C13	0.68530 (10)	0.66195 (12)	0.53987 (4)	0.0153 (3)
H13	0.698476	0.579903	0.546572	0.018*
C16	0.65239 (10)	0.90463 (12)	0.52065 (5)	0.0180 (3)
H16	0.642415	0.987500	0.514292	0.022*
C23	0.35484 (10)	0.64256 (12)	0.61956 (5)	0.0166 (3)
H23	0.363308	0.559548	0.626116	0.020*
C14	0.75406 (10)	0.72648 (12)	0.51500 (5)	0.0182 (3)
H14	0.813807	0.688816	0.504372	0.022*
C2	0.48012 (10)	0.29143 (12)	0.57271 (5)	0.0184 (3)
H2	0.429913	0.239109	0.560836	0.022*
C1	0.48884 (10)	0.41613 (12)	0.55382 (5)	0.0164 (3)
H1A	0.421131	0.445468	0.545345	0.020*
H1B	0.529719	0.414180	0.524923	0.020*
C3	0.54188 (11)	0.25311 (12)	0.60593 (5)	0.0186 (3)
H3	0.534485	0.173818	0.617685	0.022*
C15	0.73675 (11)	0.84979 (13)	0.50489 (5)	0.0195 (3)
H15	0.784345	0.893832	0.487081	0.023*
C20	0.32658 (11)	0.88722 (13)	0.60194 (5)	0.0200 (3)
H20	0.316206	0.970332	0.596236	0.024*
C7	0.58707 (11)	0.46528 (13)	0.73184 (5)	0.0208 (3)
C5	0.61517 (11)	0.69869 (12)	0.67683 (5)	0.0194 (3)
H5A	0.639979	0.735062	0.647849	0.029*
H5B	0.647856	0.736898	0.703685	0.029*
H5C	0.542432	0.710205	0.679006	0.029*
C4	0.62300 (10)	0.33186 (11)	0.62535 (5)	0.0155 (3)
H4A	0.638945	0.304962	0.657494	0.019*
H4B	0.684208	0.321657	0.606145	0.019*

C22	0.26936 (10)	0.69877 (14)	0.63369 (5)	0.0207 (3)
H22	0.218894	0.654525	0.649613	0.025*
C21	0.25508 (11)	0.82314 (14)	0.62480 (5)	0.0221 (3)
H21	0.195274	0.861639	0.634892	0.027*
C6	0.78352 (10)	0.52013 (13)	0.67616 (6)	0.0236 (3)
H6A	0.801667	0.434860	0.675946	0.035*
H6B	0.811589	0.558499	0.704089	0.035*
H6C	0.810525	0.559100	0.648130	0.035*
C8	0.47669 (12)	0.43301 (16)	0.72304 (6)	0.0311 (4)
H8A	0.440495	0.504437	0.712272	0.047*
H8B	0.446415	0.403817	0.752130	0.047*
H8C	0.472708	0.370187	0.699121	0.047*
B1	0.53820 (10)	0.50755 (13)	0.58960 (5)	0.0119 (3)
C9	0.64271 (14)	0.35359 (15)	0.74992 (6)	0.0345 (4)
H9A	0.635604	0.288080	0.727276	0.052*
H9B	0.614021	0.328939	0.779975	0.052*
H9C	0.713960	0.372554	0.754027	0.052*
C10	0.59141 (18)	0.55923 (17)	0.77124 (6)	0.0448 (5)
H10A	0.660967	0.585254	0.775764	0.067*
H10B	0.566082	0.523710	0.800285	0.067*
H10C	0.549936	0.628553	0.762762	0.067*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Si1	0.01541 (18)	0.01078 (17)	0.01295 (17)	-0.00045 (13)	-0.00323 (13)	-0.00092 (13)
N1	0.0150 (5)	0.0087 (5)	0.0127 (5)	0.0004 (4)	-0.0005 (4)	-0.0003 (4)
C11	0.0138 (6)	0.0115 (6)	0.0105 (6)	-0.0009 (5)	-0.0033 (4)	-0.0001 (5)
C19	0.0156 (6)	0.0136 (6)	0.0154 (6)	0.0021 (5)	-0.0050 (5)	-0.0010 (5)
C12	0.0149 (6)	0.0115 (6)	0.0114 (6)	-0.0008 (5)	-0.0037 (5)	0.0004 (5)
C24	0.0136 (6)	0.0130 (6)	0.0126 (6)	0.0001 (5)	-0.0036 (5)	-0.0005 (5)
C17	0.0173 (6)	0.0122 (6)	0.0144 (6)	-0.0028 (5)	-0.0054 (5)	0.0009 (5)
C18	0.0204 (7)	0.0112 (6)	0.0187 (7)	0.0011 (5)	-0.0055 (5)	0.0009 (5)
C13	0.0177 (6)	0.0132 (6)	0.0150 (6)	-0.0005 (5)	-0.0005 (5)	-0.0012 (5)
C16	0.0212 (7)	0.0133 (6)	0.0193 (7)	-0.0048 (5)	-0.0053 (5)	0.0046 (5)
C23	0.0177 (6)	0.0159 (6)	0.0162 (6)	-0.0014 (5)	-0.0013 (5)	0.0008 (5)
C14	0.0180 (6)	0.0195 (7)	0.0171 (6)	-0.0019 (5)	0.0020 (5)	-0.0027 (5)
C2	0.0200 (7)	0.0127 (6)	0.0224 (7)	-0.0042 (5)	-0.0023 (5)	-0.0027 (5)
C1	0.0204 (7)	0.0136 (6)	0.0152 (6)	-0.0005 (5)	-0.0034 (5)	0.0009 (5)
C3	0.0249 (7)	0.0088 (6)	0.0221 (7)	-0.0019 (5)	-0.0014 (5)	0.0007 (5)
C15	0.0210 (7)	0.0210 (7)	0.0164 (6)	-0.0092 (6)	0.0001 (5)	0.0030 (5)
C20	0.0209 (7)	0.0173 (7)	0.0219 (7)	0.0061 (5)	-0.0035 (5)	-0.0020 (5)
C7	0.0302 (8)	0.0196 (7)	0.0125 (6)	0.0011 (6)	0.0000 (5)	0.0005 (5)
C5	0.0262 (7)	0.0131 (6)	0.0190 (7)	-0.0001 (5)	-0.0063 (6)	-0.0036 (5)
C4	0.0204 (7)	0.0097 (6)	0.0164 (6)	0.0031 (5)	-0.0047 (5)	-0.0009 (5)
C22	0.0160 (7)	0.0259 (7)	0.0202 (7)	-0.0021 (6)	0.0014 (5)	-0.0003 (6)
C21	0.0168 (7)	0.0256 (7)	0.0238 (7)	0.0059 (6)	0.0002 (6)	-0.0042 (6)
C6	0.0174 (7)	0.0185 (7)	0.0349 (8)	-0.0013 (5)	-0.0076 (6)	0.0005 (6)



C8	0.0264 (8)	0.0412 (10)	0.0256 (8)	-0.0016 (7)	0.0092 (6)	0.0085 (7)
B1	0.0116 (6)	0.0116 (6)	0.0124 (6)	-0.0003 (5)	0.0016 (5)	0.0005 (5)
C9	0.0447 (10)	0.0350 (9)	0.0238 (8)	0.0081 (8)	0.0028 (7)	0.0144 (7)
C10	0.0817 (15)	0.0363 (10)	0.0165 (8)	-0.0084 (10)	0.0059 (9)	-0.0064 (7)

*Geometric parameters (Å, °)*

Si1—N1	1.7669 (11)	C1—H1B	0.9900
Si1—C7	1.9148 (14)	C1—B1	1.5863 (19)
Si1—C5	1.8606 (14)	C3—H3	0.9500
Si1—C6	1.8655 (15)	C3—C4	1.4988 (18)
N1—C4	1.4963 (16)	C15—H15	0.9500
N1—B1	1.4052 (17)	C20—H20	0.9500
C11—C12	1.4144 (17)	C20—C21	1.358 (2)
C11—C24	1.4108 (18)	C7—C8	1.535 (2)
C11—B1	1.5946 (18)	C7—C9	1.538 (2)
C19—C24	1.4370 (18)	C7—C10	1.539 (2)
C19—C18	1.3960 (19)	C5—H5A	0.9800
C19—C20	1.4304 (19)	C5—H5B	0.9800
C12—C17	1.4395 (18)	C5—H5C	0.9800
C12—C13	1.4300 (18)	C4—H4A	0.9900
C24—C23	1.4318 (18)	C4—H4B	0.9900
C17—C18	1.3940 (19)	C22—H22	0.9500
C17—C16	1.4286 (19)	C22—C21	1.421 (2)
C18—H18	0.9500	C21—H21	0.9500
C13—H13	0.9500	C6—H6A	0.9800
C13—C14	1.3646 (19)	C6—H6B	0.9800
C16—H16	0.9500	C6—H6C	0.9800
C16—C15	1.357 (2)	C8—H8A	0.9800
C23—H23	0.9500	C8—H8B	0.9800
C23—C22	1.3613 (19)	C8—H8C	0.9800
C14—H14	0.9500	C9—H9A	0.9800
C14—C15	1.422 (2)	C9—H9B	0.9800
C2—H2	0.9500	C9—H9C	0.9800
C2—C1	1.4947 (18)	C10—H10A	0.9800
C2—C3	1.3276 (19)	C10—H10B	0.9800
C1—H1A	0.9900	C10—H10C	0.9800
N1—Si1—C7	109.65 (6)	C19—C20—H20	119.5
N1—Si1—C5	112.07 (6)	C21—C20—C19	121.00 (13)
N1—Si1—C6	108.12 (6)	C21—C20—H20	119.5
C5—Si1—C7	108.35 (7)	C8—C7—Si1	109.95 (10)
C5—Si1—C6	107.16 (7)	C8—C7—C9	109.14 (13)
C6—Si1—C7	111.50 (7)	C8—C7—C10	108.36 (14)
C4—N1—Si1	112.36 (8)	C9—C7—Si1	114.47 (11)
B1—N1—Si1	130.21 (9)	C9—C7—C10	106.60 (14)
B1—N1—C4	117.43 (10)	C10—C7—Si1	108.10 (11)
C12—C11—B1	119.92 (11)	Si1—C5—H5A	109.5

C24—C11—C12	118.47 (11)	Si1—C5—H5B	109.5
C24—C11—B1	121.51 (11)	Si1—C5—H5C	109.5
C18—C19—C24	119.27 (12)	H5A—C5—H5B	109.5
C18—C19—C20	121.60 (12)	H5A—C5—H5C	109.5
C20—C19—C24	119.13 (12)	H5B—C5—H5C	109.5
C11—C12—C17	120.62 (12)	N1—C4—C3	113.90 (11)
C11—C12—C13	121.88 (11)	N1—C4—H4A	108.8
C13—C12—C17	117.49 (12)	N1—C4—H4B	108.8
C11—C24—C19	120.97 (12)	C3—C4—H4A	108.8
C11—C24—C23	121.44 (12)	C3—C4—H4B	108.8
C23—C24—C19	117.58 (12)	H4A—C4—H4B	107.7
C18—C17—C12	119.46 (12)	C23—C22—H22	119.8
C18—C17—C16	121.54 (12)	C23—C22—C21	120.48 (13)
C16—C17—C12	119.00 (12)	C21—C22—H22	119.8
C19—C18—H18	119.4	C20—C21—C22	120.28 (13)
C17—C18—C19	121.15 (12)	C20—C21—H21	119.9
C17—C18—H18	119.4	C22—C21—H21	119.9
C12—C13—H13	119.2	Si1—C6—H6A	109.5
C14—C13—C12	121.65 (12)	Si1—C6—H6B	109.5
C14—C13—H13	119.2	Si1—C6—H6C	109.5
C17—C16—H16	119.3	H6A—C6—H6B	109.5
C15—C16—C17	121.34 (12)	H6A—C6—H6C	109.5
C15—C16—H16	119.3	H6B—C6—H6C	109.5
C24—C23—H23	119.2	C7—C8—H8A	109.5
C22—C23—C24	121.53 (13)	C7—C8—H8B	109.5
C22—C23—H23	119.2	C7—C8—H8C	109.5
C13—C14—H14	119.8	H8A—C8—H8B	109.5
C13—C14—C15	120.36 (13)	H8A—C8—H8C	109.5
C15—C14—H14	119.8	H8B—C8—H8C	109.5
C1—C2—H2	119.7	N1—B1—C11	123.12 (11)
C3—C2—H2	119.7	N1—B1—C1	118.97 (11)
C3—C2—C1	120.60 (12)	C1—B1—C11	117.89 (11)
C2—C1—H1A	108.9	C7—C9—H9A	109.5
C2—C1—H1B	108.9	C7—C9—H9B	109.5
C2—C1—B1	113.30 (11)	C7—C9—H9C	109.5
H1A—C1—H1B	107.7	H9A—C9—H9B	109.5
B1—C1—H1A	108.9	H9A—C9—H9C	109.5
B1—C1—H1B	108.9	H9B—C9—H9C	109.5
C2—C3—H3	119.2	C7—C10—H10A	109.5
C2—C3—C4	121.63 (12)	C7—C10—H10B	109.5
C4—C3—H3	119.2	C7—C10—H10C	109.5
C16—C15—C14	120.11 (13)	H10A—C10—H10B	109.5
C16—C15—H15	119.9	H10A—C10—H10C	109.5
C14—C15—H15	119.9	H10B—C10—H10C	109.5
Si1—N1—C4—C3	143.11 (10)	C18—C17—C16—C15	-179.54 (13)
Si1—N1—B1—C11	12.58 (19)	C13—C12—C17—C18	-178.75 (12)
Si1—N1—B1—C1	-168.86 (9)	C13—C12—C17—C16	1.69 (18)

C11—C12—C17—C18	0.84 (18)	C13—C14—C15—C16	1.1 (2)
C11—C12—C17—C16	-178.72 (12)	C16—C17—C18—C19	177.47 (12)
C11—C12—C13—C14	178.38 (12)	C23—C22—C21—C20	0.2 (2)
C11—C24—C23—C22	179.33 (13)	C2—C1—B1—N1	20.11 (17)
C19—C24—C23—C22	0.77 (19)	C2—C1—B1—C11	-161.25 (12)
C19—C20—C21—C22	0.1 (2)	C2—C3—C4—N1	32.76 (19)
C12—C11—C24—C19	-2.54 (18)	C1—C2—C3—C4	-0.7 (2)
C12—C11—C24—C23	178.94 (12)	C3—C2—C1—B1	-25.46 (19)
C12—C11—B1—N1	83.53 (16)	C20—C19—C24—C11	-179.05 (12)
C12—C11—B1—C1	-95.05 (14)	C20—C19—C24—C23	-0.48 (18)
C12—C17—C18—C19	-2.07 (19)	C20—C19—C18—C17	-178.58 (13)
C12—C17—C16—C15	0.0 (2)	C7—Si1—N1—C4	-62.08 (10)
C12—C13—C14—C15	0.7 (2)	C7—Si1—N1—B1	117.35 (12)
C24—C11—C12—C17	1.44 (18)	C5—Si1—N1—C4	177.55 (9)
C24—C11—C12—C13	-178.99 (11)	C5—Si1—N1—B1	-3.01 (14)
C24—C11—B1—N1	-100.06 (15)	C4—N1—B1—C11	-168.01 (11)
C24—C11—B1—C1	81.36 (15)	C4—N1—B1—C1	10.55 (17)
C24—C19—C18—C17	0.99 (19)	C6—Si1—N1—C4	59.67 (10)
C24—C19—C20—C21	0.1 (2)	C6—Si1—N1—B1	-120.89 (12)
C24—C23—C22—C21	-0.6 (2)	B1—N1—C4—C3	-36.40 (16)
C17—C12—C13—C14	-2.04 (19)	B1—C11—C12—C17	177.96 (11)
C17—C16—C15—C14	-1.4 (2)	B1—C11—C12—C13	-2.47 (18)
C18—C19—C24—C11	1.37 (19)	B1—C11—C24—C19	-179.00 (11)
C18—C19—C24—C23	179.94 (12)	B1—C11—C24—C23	2.49 (18)
C18—C19—C20—C21	179.65 (13)		

### Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ )

*Cg*2, *Cg*5, *Cg*7 and *Cg*3 are the centroids of rings C11—C12/C17—C19/C24, C11—C18, C11—C24 and C12—C17, respectively.

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
C5—H5 <i>A</i> $\cdots$ <i>Cg</i> 2	0.98	2.86	3.4529 (15)	120
C5—H5 <i>A</i> $\cdots$ <i>Cg</i> 5	0.98	2.91	3.7305 (15)	142
C5—H5 <i>A</i> $\cdots$ <i>Cg</i> 7	0.98	2.88	3.4772 (15)	120
C2—H2 $\cdots$ <i>Cg</i> 3 <sup>i</sup>	0.95	2.92	3.6380 (15)	133
C4—H4 <i>B</i> $\cdots$ <i>Cg</i> 3 <sup>ii</sup>	0.99	2.97	3.9373 (15)	167

Symmetry codes: (i)  $-x+1, -y+1, -z+1$ ; (ii)  $-x+3/2, y-1/2, z$ .