

Isomeric Borabicyclo[4.3.0]nonanes from Bis(9-borabicyclo[3.3.1]nonane) by Gas-Phase Pyrolysis¹⁾

Mohamed Yalpani*^a, Roland Boese^b, and Roland Köster^a

Max-Planck-Institut für Kohlenforschung^a,
Kaiser-Wilhelm-Platz 1, D-4330 Mülheim an der Ruhr

Institut für Anorganische Chemie der Universität Essen^b,
Universitätsstraße 5–7, D-4300 Essen 1

Received November 7, 1986

The gas-phase pyrolysis of bis(9-borabicyclo[3.3.1]nonane) (**1**)₂ has been studied in the range of 400–620°C. At 490°C approximately equal amounts of 1-borabicyclo[4.3.0]nonane (**2**) and 8-borabicyclo[4.3.0]nonane (**3**) are formed (yield >95%). Heating of **3** which presumably exists as the dimer (**3**)₂ with a 1,1:2,2-diborane(6) structure or as an oligomer with mixed 1,1:2,2- and 1,2:1,2-diborane(6) structure **4**, in the condensed phase to above 100°C results in the formation of the air and hydrolysis stable **5** with a 1,2:1,2-diborane(6) structure. The structure of **5** has been determined by X-ray analysis. The pyrolysis of 9-alkyl-9-borabicyclo[3.3.1]nonanes **6** [alkyl = ethyl (**6a**), 1,2-dimethylpropyl (**6b**), and isopinocampheyl (**6c**)] gives **2** and small amounts of (**1**)₂. The formation of **2** from (**1**)₂ as well as **2** and (**1**)₂ from **6** indicate that monomeric 9-borabicyclo[3.3.1]nonane **1** is an intermediate.

The chemistry of bis(9-borabicyclo[3.3.1]nonane) [(9-BBN)₂ (**1**)₂], which has been known since 1960²⁾ and been widely and extensively used as a facile reagent for various hydroboration³⁾ and borylating⁴⁾ reactions, has itself received very little attention. In particular the thermal chemistry of this molecule has been completely neglected probably due to an early report on its thermal stability⁵⁾. During an investigation on the reductive carbon monoxide oligomerization with (**1**)₂ we noticed that already at moderate temperatures (120–150°C) in a fast dehydro-hydroboration reaction the bicyclic ring is reversibly cleaved⁶⁾. At higher temperatures (≥170°C) irreversible intermolecular hydroboration of C–C single bonds of the C₈ ring of (**1**)₂ results in the formation of homologous 9-alkyl-9-BBN's⁷⁾. In these reactions some of the results obtained pointed to at least a partial persistence of the hydride bridged dimeric structure. It has further been observed that this dimeric structure continues to persist even in the gas phase as indicated by the mass spectrum of (**1**)₂, showing a molecular ion at *m/z* = 244 with 60% abundance⁸⁾.

In contrast to these findings, kinetic experiments on the hydroboration of alkenes^{9a)} or alkynes^{9b)} with (**1**)₂ have shown that the monomer **1** is in equilibrium with the dimer (**1**)₂¹⁰⁾ in polar or non-polar solvents.

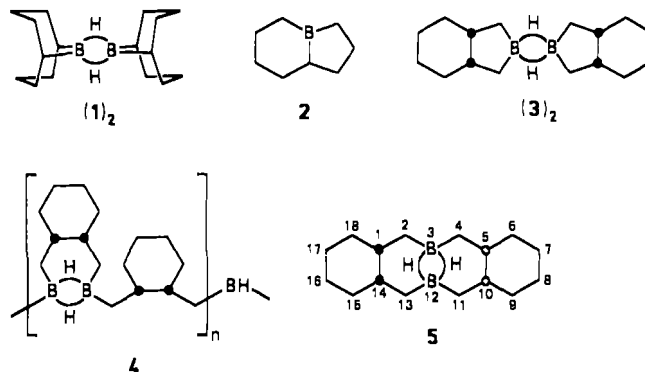
In this report we describe results on the high temperature gas-phase reactions of (**1**)₂ and of the three 9-alkyl-9-borabicyclo[3.3.1]nonanes **6a–c**. The products isolated suggest the intermediate formation of the monomer **1**.

Isomere Borabicyclo[4.3.0]nonane aus Bis(9-borabicyclo[3.3.1]nonan) bei der Gasphasen-Pyrolyse¹⁾

Die zwischen 400 und 620°C untersuchte Pyrolyse des gasförmigen Bis(9-borabicyclo[3.3.1]nonans) (**1**)₂ liefert bei ca. 490°C in hohen Ausbeuten (>95%) 1-Borabicyclo[4.3.0]nonan (**2**) und 8-Borabicyclo[4.3.0]nonan (**3**), das vermutlich als Dimer (**3**)₂ mit 1,1:2,2-Diboran(6)-Struktur bzw. als Oligomer **4** mit 1,1:2,2- sowie 1,2:1,2-Diboran-Struktur anfällt. (**3**)₂ und **4** isomerisieren in kondensiertem Zustand oberhalb ca. 100°C zu den Luft- und Hydrolyse-resistenten Verbindungen **5** mit ausschließlich 1,2:1,2-Diboran(6)-Struktur. Von **5** liegt eine Röntgenstrukturanalyse vor. Die Pyrolyse der 9-Alkyl-9-borabicyclo[3.3.1]nonane **6** [Alkyl = Ethyl (**6a**), 1,2-Dimethylpropyl (**6b**) und Isopinocampheyl (**6c**)] liefert **2** sowie kleinere Anteile an (**1**)₂. Sowohl die Bildung von **2** aus (**1**)₂ als auch von **2** und (**1**)₂ aus **6** weisen auf das Auftreten des monomeren 9-Borabicyclo[3.3.1]nonans **1** während der Pyrolyse hin.

Results and Discussion

Passing gaseous (**1**)₂ with a slow stream of argon gas through a heated quartz tube at temperatures higher than 350°C resulted in the formation of products which were collected on a cold finger at –178°C. Above 620°C only a complex mixture of olefinic hydrocarbons having elemental compositions of C₈H₁₂ (GC-MS) could be detected. At intermediate temperatures, e.g. 490°C, and low internal pressures (<0.01 mbar) the pyrolysate was a colourless and slightly viscous liquid. The infrared spectrum of the product showed an absorption band for ν_{BH₂B} at 1590 cm⁻¹ and the ¹¹B-NMR spectrum showed two signals at δ = 90.5 and 27 of nearly equal intensity [for (**1**)₂ ν_{BH₂B} = 1567 cm⁻¹¹¹⁾, and δ¹¹B = 28¹²⁾].



Fractional distillation gave a low boiling fraction (a) (b.p. $\approx 30^\circ\text{C}/10^{-4}$ mbar) which was an analytically pure colourless liquid ($\approx 50\%$ yield). It showed no >BH absorption band in its infrared spectrum. Elemental analysis and the molecular mass at $m/z = 122$ suggested a structure isomeric with **1**. From the ^{11}B - and ^{13}C -NMR spectra of this new compound as well as from the ^{11}B -, ^1H -, and ^{13}C -NMR spectra of its 1:1 addition complex with quinuclidine, the 1-borabicyclo[4.3.0]nonane structure (**2**) was deduced.

The second, higher boiling fraction (b) (b.p. $\approx 100^\circ\text{C}/10^{-4}$ mbar), a viscous and colourless liquid ($\approx 45\%$ yield) partially crystallized on cooling. On separation and recrystallization from boiling ethanol ($\approx 20\%$ yield) the resulting crystals (m.p. $121\text{--}122^\circ\text{C}$) showed an intense infrared absorption band for BH_2B at 1620 cm^{-1} . The mass spectrum with the molecular mass at $m/z = 244$ (no $M^+/2$), the elemental composition ($\text{C}_{16}\text{H}_{30}\text{B}_2$), and further analytical data (^{11}B and ^{13}C NMR) as well as its stability to air and protonic solvents suggested the structure **5** with a 1,2:1,2-bis(1,4-butanediyl)diborane(6) bridge which is isomeric with (**1**)₂.

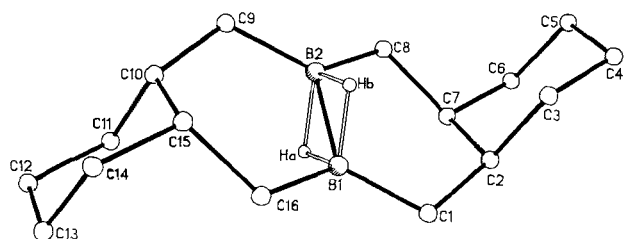


Figure 1. Perspective view of **5** showing the numbering scheme

Table 1. Bond lengths (Å) and angles ($^\circ$) for the borane bridge of **5**, (**1**)₂, 1,2:1,2-bis(biphenyl-2,2'-diyl)diborane(6) (BBDDDB), and diborane(6) (DB)

	5	(1) ₂	BBDDDB	DB
d_{BC}	1.576(2)	1.567(1)	1.569(3)	—
d_{BH}	1.230(13)	1.25(2)	1.25(2)	1.321(5)
d_{BB}	1.799(3)	1.818(3)	1.779(2)	1.770(5)
$\angle\text{CBC}$	128.0(9)	121.8(3)	131.4(3)	—
$\angle\text{BHB}$	91.9(9)	94.0(4)	90.5(2)	84.0(5)
$\angle\text{HBB}$	87.0(9)	86.0(2)	89.3(2)	96.0(5)

The above structural assignment of **5** was further confirmed by X-ray determination which is shown in Figure 1. The structure represents a 1,6-diboracyclodecane with two fused cyclohexane rings (linearly annelated in which the boron atoms are bridged by two hydrogen atoms. The central bonds around the borane bridge have, as shown in Table 1, similar bond lengths as reported for (**1**)₂¹³, for 1,2:1,2-bis(biphenyl-2,2'-diyl)diborane(6)¹³, and for diborane(6)¹⁴. The bond angles show small variations as required by the structure of the substituents on the boron atoms. The methylene carbon atoms C1, C8 and C9, C16 (cf. Figure 1), respectively, are *cis*-substituted to the peripheral cyclohexane rings. Fi-

nally, these cyclohexane rings are fused in an *anti* configuration to the central 1,6-diboracyclodecane ring.

The viscous filtrate (c) obtained after separation of crystalline **5** from the fraction (b) showed the same spectral characteristics (IR, MS, and ^{11}B NMR) as found for **5**. It consists, however, of a mixture of *cis/trans*-fused C_6 -ring isomers of **5**, based on the products of alkaline hydrogen peroxide oxidation, which gives a 7:1 mixture of *cis*- and *trans*-1,2-bis(hydroxymethyl)cyclohexanes.

The IR spectrum of the pyrolysate mixture before distillation, i.e. before heating, and also that of the residue after removal of the low boiling fraction (a) at 30°C , showed a strong BH_2B absorption band at 1590 cm^{-1} which on heating to above 100°C disappeared giving rise to a similarly strong band at 1620 cm^{-1} . The oxidation of this high boiling fraction, before and after heat treatment, with alkaline hydrogen peroxide, gave a 10:1 mixture of *cis*- and *trans*-1,2-bis(hydroxymethyl)cyclohexanes as the sole oxidation products. These results suggest the basic structure **3** which may be present in the product mixture before distillation as the dimer (**3**)₂ or the oligomer **4**.

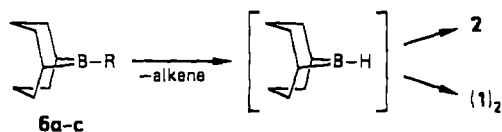
Therefore, **5** is not the primary gas-phase pyrolysis product rather it forms in the aggregate form of (**3**)₂ or **4** during the distillation. Such a rearrangement and substituent exchange on the boron atom has been previously reported¹⁵.

The formation of **2**, an isomer of **1**, in the gas-phase pyrolysis of (**1**)₂ suggests an at least partial dissociation of the borane bridge of (**1**)₂. This process could be enhanced by carrying out the pyrolysis (at 460°C) over activated surfaces such as granulated molecular sieves or glass wool. The product obtained in this way was mainly ($\approx 80\%$) **2**. It can be assumed that the interaction of the boron atoms of (**1**)₂ with the oxygen atoms on the surfaces used promote the dissociation into the monomer **1** which then rearranges to **2**.

Another evidence for a more than transitory existence of the monomer **1** under these conditions was obtained from the pyrolysis of the three 9-alkyl-9-BBN derivatives **6a–c**. At high temperatures dehydroboration results in the release of an alkene and the formation of **1** which isomerizes to **2**. The extent of the dehydroboration and therefore formation of **2** is not only dependent on the temperature but also on the structure of the 9-alkyl substituents. 9-Ethyl-9-BBN (**6a**) is only minimally dehydroborated at 500°C and only about 5% of **2** is formed. An increase of temperature leads, however, to complete dehydroboration and formation of C_8 olefins. With **6b** dehydroboration becomes detectable at 375°C ($\approx 2\%$) and the conversion to **2** is complete at about 500°C . Interestingly, at intermediate temperatures ($430\text{--}450^\circ\text{C}$) the initial dehydroboration product, the monomer **1**, is only partially rearranged to **2**. A significant amount of **1** survives the further thermal reaction and can be isolated ($\approx 10\%$) as the solid dimer (**1**)₂ from the cold finger on warming to room temperature.

In the case of **6c**, the dehydroboration to **1** and its subsequent dimerization is already observed during vacuum distillation of **6c** at 110°C and 10^{-4} mbar. The distillate consists of a mixture of α -pinene and crystalline (**1**)₂. Since solid formation could not be observed in any part of the

distillation head but in the cooled receiving flask, it can be assumed that monomer **1** once formed in the gas phase survives the passage through the relatively warm parts of the distillation apparatus and dimerization and crystallization first occurs in the cooled receiver.

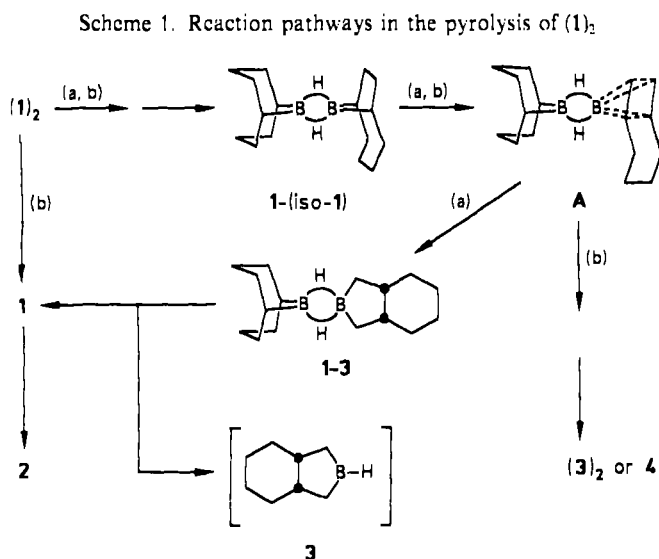


	R
a	C ₂ H ₅
b	$\begin{array}{c} \text{H}_3\text{C}-\text{CH}-\text{CH}- \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$
c	Isopinocampheyl

For the conversion of **1** to **2**, in analogy to other known thermal rearrangements of dialkylhydroboranes to trialkylboranes¹⁶, a four centered transition state, involving the migration of a methylene radical from C1 to the boron atom and of a hydrogen atom from boron to C1, can be assumed.

In the thermal transformation of (1)₂ to **3** the monomer **1** is not an intermediate, since in the pyrolysis products of derivatives of **6** or of (1)₂ over active surfaces compound **3** could not be found. Therefore for the formation of the latter two pathways both involving dimeric species can be formulated:

a) The reaction is initiated by a dehydro-hydroboration in one of the two rings of (1)₂ to form 9-borabicyclo[4.2.1]nonane bound to **1**, depicted in Scheme 1 as 1-(iso-1). Suprafacial migration of the boron atom as in A would lead to compound 1-3, in which a **3** moiety with a *cis* junction onto the cyclohexane ring is bridged to **1** with a BH₂B bond. At this stage the cleavage of the diborane bridge would release **3**, collected from the cold finger as the dimer (3)₂ (or



the oligomer **4**), and the monomer **1** which can undergo rearrangement to **2**.

b) The dimer (1)₂ dissociates in part to **1** followed by further rearrangement to **2**. Both of the bicyclic rings of the remaining undissociated (1)₂ undergo concurrently or consecutively a double isomerization to (iso-1)₂ followed by the series of reactions described under pathway (a) without dissociation of the borane bridge to form directly (3)₂.

The formation of approximately equal amounts (¹¹B NMR and isolation) of **2** and (3)₂ or **4**, respectively, in the pyrolysis at 490°C would tend to favour pathway (a). However, since the analysis of yields of **2** and **3** in the product mixture are complicated by the presence of unreacted (1)₂ at much lower and olefine formation at much higher temperatures, it is not possible to conclude that the 1:1 ratio, as required by pathway (a), holds at all temperatures.

Furthermore, it should be noted that the proposed suprafacial mode of migration of boron only rationalizes the formation of *cis*-fused **3**. For the approximately 10% of *trans*-fused **3** found a probably more complex transition must be invoked.

Experimental

Melting points: sealed capillary tubes, Büchi melting point apparatus, uncorrected. — Gas chromatograms: Siemens Sinchromat 1 instrument with a 20 m PS 240 capillary column, injection port at 150°C, oven at 40–300°C, programmed at 4°/min, helium as carrier gas. — Mass spectra: MAT CH 7A. — ¹¹B-NMR spectra: Varian XL 100. — ¹³C-NMR spectra: Bruker WM 300 spectrometer. — All operations were performed under argon. — The pyrolysis apparatus consisted of a quartz tube (50 cm long, 18 mm o.d.) fused to a Dewar vessel with a rotatable cold finger, a pyrolysis tube oven (20 cm length) and a preheating oven (20 cm length). The system was evacuated by means of a double stage rotary and an oil diffusion pump. A slow stream of argon through a capillary was passed over the substrate which also regulated the vacuum to about 10⁻³ mbar.

General Procedure for Gas-Phase Pyrolyses: The substrate (2–8 g) was volatilized from a porcelain boat in the preheating section of the quartz tube and passed through the pyrolysis section, and the pyrolysate was collected on the cold finger cooled to –196°C. On completion of the sublimation and warming of the cold finger to room temperature the pyrolysate dripped into a receiving flask immediately below the cold finger. In all cases the recovery was quantitative.

Pyrolysis of (1)₂, Isolation of 1-Borabicyclo[4.3.0]nonane (2): Via general procedure 8.0 g (21.3 mmol) of (1)₂ was sublimed (90–100°C/10⁻³ mbar) and pyrolysed at 490°C during 6 h. The pyrolysate was a colourless liquid [IR (film): 1590 cm⁻¹. — ¹¹B NMR (hexane): δ = 90.5 and 27.0 (≈ 1:1)]. Vacuum distillation at room temperature and 10⁻⁴ mbar gave **2** as a colourless liquid, fraction (a) (4.0 g, ≈ 50% yield). — ¹¹B NMR (hexane): δ = 90.5. — ¹³C NMR (CDCl₃): δ = 22.0 (br, t); 24.6 (br, t); 25.2 (t); 25.9 (t); 28.0 (t); 31.2 (t); 33.9 (t); 42.1 (br, d). — MS: *m/z* (%) = 122 (B⁺, M⁺, 40); 94 (100).

C₈H₁₅B (122.0) Calcd. C 78.75 H 12.39
Found C 78.83 H 12.08

Quinuclidine Adduct of 2: To 20 ml of an ether solution of 1.0 g (8.2 mmol) of **2** was added 1.0 g (9.0 mmol) of quinuclidine. After

stirring at room temperature for 30 min the solution was cooled to -78°C and the microcrystalline solid separated (1.8 g, 94%), m. p. $130-131^{\circ}\text{C}$. — ^1H NMR (CDCl_3 , 60 MHz): $\delta = 3.0$ (t, 6H); $0.2-2.0$ (m, 22 H). — ^{13}C NMR (CDCl_3): signals for quinuclidine moiety $\delta = 20.71$ (d); 24.92 (t); 47.36 (t); signals for **2** moiety $\delta = 24.67$ (t); 25.18 (t); 27.25 (t); 30.81 (t); 36.20 (t); signals for B—C carbons very broad. — MS: Decomposition to spectra for **2** and for quinuclidine.

$\text{C}_{15}\text{H}_{28}\text{BN}$ (233.2) Calcd. C 77.26 H 12.10 B 4.67
Found C 77.01 H 12.22 B 4.80

anti-3,12-Diboratricyclo[12.4.0.0^{5,10}]octadecane (5): The distillation residue from above [IR (film): 1590 cm^{-1} and ^{11}B NMR (hexane): $\delta = 27.0$, ^{13}C NMR (CDCl_3): $\delta = 23.14$ (t), 29.62 (t), 35.39 (d)] was further distilled at 100°C and 10^{-4} mbar to yield fraction (b). The colourless, initially liquid distillate (3.2 g, $\approx 40\%$) partially crystallized on standing. Separation from filtrate (c) and recrystallization from ethanol gave 1.6 g of **5** ($\approx 20\%$), m. p. $121-122^{\circ}\text{C}$. — IR (film): 1620 cm^{-1} . — ^1H NMR (CDCl_3 , 200 MHz): $\delta = 1.81$ (m, 4H); 1.59 (m, 4H); 1.34 (m, 12H); 1.00 (br, 2H); 0.79 (m, 8H). — ^{11}B NMR (hexane): $\delta = 27.0$. — ^{13}C NMR (CDCl_3): $\delta = 19.4$ (br, t); 23.88 (t); 31.38 (t); 36.95 (d). — MS: m/z (%) = 244 (B_2 , M⁺, 55); 230 (B₁, 30); 122 (44); 120 (100).

$\text{C}_{16}\text{H}_{30}\text{B}_2$ (244.0) Calcd. C 78.75 H 12.39
Found C 78.70 H 12.43

Filtrate (c): 1.6 g (20%) mixture of *cis* and *trans* isomers of **5**. — IR (film) = 1620 cm^{-1} . — ^{11}B NMR (hexane) $\delta = 27.0$. — MS: m/z (%) = 244 (B_2 , 35); 230 (B₁, 20); 122 (40); 120 (100).

Oxidation of Distillation Fraction (b): To 5 ml of a methanol solution of 0.5 g of distillation fraction (b) at 0°C was added dropwise a solution of 4 ml of 30% hydrogen peroxide in 5 ml of methanol. After stirring for 1 h at 0°C the mixture was refluxed for 3 h. The product obtained on ether extraction was acetylated with acetic anhydride/pyridine mixture and analyzed by GC-MS: Two peaks, both with a molecular mass at $m/z = 228$, identical to authentic *cis*- and *trans*-bis(acetoxymethyl)cyclohexane, ratio 10:1.

Oxidation of Filtrate (c): As above, gave a *cis-trans* ratio of 7:1.

X-ray Structure Determinations: Data collection and calculations were carried out on a Syntex R 3 four cycle diffractometer with a Nova 3:12 (Data General), Nicolet P 3 SHELXTL software¹⁷⁾. The structure solutions were carried out by direct method and hydrogen atoms were included as rigid groups. The isotropic temperature factors of the H atoms were taken as the 1.2 fold U_{eq} of the corresponding C atoms. Hydrogen atoms attached to boron were taken from difference Fourier syntheses and refined with unique temperature factor of 0.039 (3) \AA^{-2} . Compound **5**, $\text{C}_{16}\text{H}_{30}\text{B}_2$, monoclinic, $P 2_1/n$; $a = 5.409$ (1), $b = 11.525$ (3), $c = 24.278$ (5) \AA , $\beta = 90.44$ (2) $^{\circ}$, $V = 1513.4$ (6) \AA^3 , $D_x = 1.07\text{ g cm}^{-3}$, $\mu = 0.53\text{ cm}^{-1}$ [Mo- K_{α} , (graphite monochromator)], 2663 unique reflections of which 1857 were observed [$F_o \geq 3.5\sigma(F)$]. $R = 0.048$, $R_w = 0.047$ [$w^{-1} = \sigma^2(F) + 0.00024 \cdot F^2$], maximal residual electron density $0.18\text{ e}\text{\AA}^{-3}$. The atom coordinates for **5** are shown in Table 2¹⁸⁾.

Table 2. Atomic coordinates and isotropical temperature parameters ($\text{pm}^2 \cdot 10^{-1}$) for **5**

	x/a	y/b	z/c	U
C(1)	2486(3)	5763(1)	2128(1)	44(1)*
C(2)	2841(3)	6278(1)	1549(1)	41(1)*
C(3)	4963(3)	5719(1)	1234(1)	50(1)*
C(4)	5032(4)	6133(2)	636(1)	67(1)*
C(5)	5103(4)	7448(2)	596(1)	62(1)*
C(6)	3074(3)	8014(2)	931(1)	57(1)*
C(7)	3091(3)	7609(1)	1534(1)	44(1)*
C(8)	5345(3)	8102(1)	1849(1)	47(1)*
C(9)	7564(3)	8079(1)	2908(1)	45(1)*
C(10)	7165(3)	7579(1)	3490(1)	42(1)*
C(11)	5014(3)	8156(1)	3789(1)	49(1)*
C(12)	4904(4)	7763(2)	4388(1)	66(1)*
C(13)	4814(4)	6451(2)	4441(1)	67(1)*
C(14)	6863(4)	8102(1)	5868(2)	60(1)*
C(15)	6912(3)	6252(1)	3515(1)	44(1)*
C(16)	4685(3)	5747(1)	3189(1)	46(1)*
B(1)	4228(3)	6256(2)	2597(1)	40(1)*
B(2)	5818(3)	7585(2)	2440(1)	40(1)*
H(a)	3752(25)	7309(12)	2635(5)	39(3)
H(b)	6219(24)	6537(11)	2401(5)	39(3)

* Equivalent isotropic U calculated as $1/3$ of the U_{ij} tensor.

CAS Registry Numbers

(1): 21205-91-4 / 2: 5731-84-0 2-quinuclidine: 106904-69-2 / *cis*-**5**: 106880-59-5 / *trans*-**5**: 106972-41-2 / **6a**: 52102-17-7 / **6b**: 63942-78-9 / **6c**: 100347-98-6 / *cis*-bis(acetoxymethyl)cyclohexane: 98516-00-8 / *trans*-bis(acetoxymethyl)cyclohexane: 106880-60-8

¹¹⁾ Part 74 of the series *Boron Compounds*: For part 73 see R. Köster, K. Angermund, A. Sporzyński, J. Serwatowski, *Chem. Ber.* **119** (1986) 1931.

^{2a)} R. Köster, *Angew. Chem.* **72** (1960) 626. — ^{2b)} For a survey cf. R. Köster in *Methoden der Organischen Chemie* (Houben-Weyl-Müller), R. Köster, Ed., Vol. XIII/3a, p. 329f, Thieme, Stuttgart 1982.

^{3a)} H. C. Brown, C. F. Lane, *Heterocycles* **7** (1977) 453. — ^{3b)} For review cf. R. Köster in *Methoden der Organischen Chemie* (Houben-Weyl-Müller), R. Köster, Ed., Vol. XIII/3c, p. 620, Thieme, Stuttgart 1984.

⁴⁾ See ref. ^{2a)}, pp. 596, 574, and 553.

⁵⁾ E. F. Knights, H. C. Brown, *J. Am. Chem. Soc.* **90** (1968) 5280.

⁶⁾ R. Köster, M. Yalpani, *Angew. Chem.* **90** (1985) 600; *Angew. Chem. Int. Ed. Engl.* **24** (1985) 572.

⁷⁾ R. Köster, M. Yalpani, *J. Org. Chem.* **51** (1986) 3054.

⁸⁾ D. Henneberg, Max-Planck-Institut für Kohlenforschung, Mülheim an der Ruhr, unpublished results.

^{9a)} K. K. Wang, H. C. Brown, *J. Org. Chem.* **45** (1980) 5303. — ^{9b)} K. K. Wang, C. G. Scouten, H. C. Brown, *J. Am. Chem. Soc.* **104** (1982) 531.

¹⁰⁾ A mixture of equal amounts of (1)₂ ($\nu_{\text{B-H,B}}$: 1567 cm^{-1} ¹¹⁾) and (1D)₂ ($\nu_{\text{B-D,B}}$: 1149 cm^{-1} ¹⁹⁾) in THF at about 20°C rapidly reacts to give 1—1D; the infrared spectrum shows the $\nu_{\text{B-H,D,B}}$ absorption bands at 1640 and 1172 cm^{-1} ; M. Yalpani, Max-Planck-Institut für Kohlenforschung, Mülheim an der Ruhr, unpublished results; cf. also ref. ¹¹⁾.

¹¹⁾ See ref. ^{3b)}, p. 441.

¹²⁾ See ref. ^{3b)}, p. 446.

¹³⁾ See ref. ^{3b)}, p. 447.

¹⁴⁾ Gmelin, 8. Ed., Vol. 52/18, p. 72 (1978).

¹⁵⁾ See ref. ^{2b)}, p. 336.

¹⁶⁾ See ref. ^{2b)}, p. 27.

¹⁷⁾ G. M. Sheldrick, SHELXTL (1981). An integrated system for solving, refining, and displaying crystal structures from diffraction data, University of Göttingen.

¹⁸⁾ Further details and basis data concerning the X-ray analysis may be obtained from Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2 (W-Germany), by specifying registry number CSD 52247, the authors, and the reference to this publication.

¹⁹⁾ See ref. ^{2b)}, p. 339.

[289;86]