Structural studies of organoboron compounds LXII.[1] Synthesis and structure of various *N*-alkylated 1,3-dioxa-4-aza-2-boracyclohexanes

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The synthesis of a number of variously substituted *N*-alkyl 2-hydroxyaminoalkanols **3** and their reactions with phenylboronic acid are detailed. The crystalline products proved to be 1:2 condensates **4** in a few cases and 1:1 condensates **5** in all the other cases studied. Crystals of 2-mesityl-6,6-pentamethylene-1,3-dioxa-4-aza-2-boracyclohexane, **5*l***, are triclinic, a = 11.540(2), b = 10.402(3), c = 8.440(2) Å, α = 108.86(2)°, β = 97.62(2)°, γ = 89.36(2)°, Z = 2, space group $P\bar{1}$; and those of 4,4′-methylenebis(6,6-pentamethylene-2-phenyl-1,3-dioxa-4-aza-2-boracyclohexane) benzene solvate, **15a**·C_6H_6, are monoclinic, a = 22.690(1), b = 16.867(1), c = 8.4783(9) Å, β = 104.912(8)°, Z = 4, space group *C*2/*c*. The structures were solved by direct methods and refined by full-matrix least-squares procedures to R = 0.037 and 0.035 (R_w = 0.035 and 0.044) for 3190 and 2084 reflections with $I \geq 3\sigma(F^2)$. respectively.

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On décrit la synthèse d'un certain nombre de *N*-alkyl 2-hydroxyaminoalcanols substitués (**3**) ainsi que leurs réactions avec l'acide phénylboronique. Il s'avère que, dans quelques cas, les produits cristallins obtenus sont les produits de condensation 1 : 2 (**4**) alors que, dans tous les autres cas étudiés, ce sont les produits de condensation 1 : 1 (**5**). Les cristaux du 2-mésityl-6,6-pentaméthylène-1,3-dioxa-4-aza-2-boracyclohexane, **5*l***, sont tricliniques, groupe d'espace $P\bar{1}$, avec a = 11,540(2), b = 10,402(3), c = 8,440(2) Å, α = 108,86(2)°, β = 97,62(2)° et γ = 89,36(2)° et Z = 2; ceux du 4,4′-méthylènebis(6,6-pentaméthylène-2-phényl-1,3,-dioxa-4-aza-2-boracyclohexane) solvaté par le benzène, **15*a***·C_6H_6, sont monocliniques, groupes d'espace *C*2/*c*, avec a = 22,690(1), b = 16,867(1) et c = 8,4783(9) Å, β = 104,912(8)° et Z = 4. On a résolu les structures par des méthodes directes et on les a affinées par la méthode des moindres carrés jusqu'a des valeurs de R = 0,037 et 0,035 (R_w = 0,035 et 0,044) pour respectivement 3190 et 2084 reflexions avec $I \geq 3\sigma(F^2)$.

[Traduit par la rédaction]

Introduction

In a previous work (1) we described the synthesis of two *N*-alkylated 2-hydroxylaminoalkanols of type **3**, and the products of their reactions with phenylboronic acid. These products turned out to possess different molecular structures: in one case a bicyclic pyroboronate structure **4**, formed by the incorporation of two phenylboronic acid moieties and a transannular N→B coordinative bond, and in another a monocyclic phenylboronate structure **5** that exists in the solid state as a BONBON dimer of type **8**, in which two chair-form BONCCO rings are joined by a pair of N→B bonds. Both molecular structures, **4** and **8**, have been established by X-ray crystallographic analyses (1). The monomeric BONCCO boronate ring system of type **5** had already been obtained from certain hydroxamic acid derivatives **3** (R = acyl) (2) as well as from the use of the sterically hindered mesitylboronic acid in the condensation reaction with *N*-unsubstituted 2-hydroxyaminoalkanols **3** (R = H) (3). The semiplanar "sofa" conformation adopted by these BONCCO cycloboronates **5** is consistent with that reported for other diol-boronates (cf. refs. 2, 3). In order to produce additional examples of the six-membered BONCCO cycloboronate ring system we synthesized a number of variously substituted *N*-alkyl 2-hydroxyaminoalkanols **3**(*a–p*) by reduction of the nitrones **1** or **2** with KBH_4 or $LiAlH_4$, and reacted them with phenylboronic acid. The crystalline products proved to be 1:2 condensates in a few cases (**4*a–c***) and 1:1 condensates in all the other cases studied (**5*d–p***). The bicyclic structure of **4**, characterized in detail by an X-ray crystallographic study (1), is confirmed by the ^{11}B nmr spectra that display two signals of equal peak area: one near $\delta(Et_2OBF_3) \approx 29$ ppm indicative of a trivalent sp^2 boron, and another near 15 ppm, indicative of the presence of a tetracoordinated sp^3 boron in the compounds **4**.

The 1:1 reaction products give ^{1}H nmr spectra consistent with the different possible structures **5–9**. From the considerations and findings discussed in our previous work (1) it could be assumed that the constitution **5** and its dimeric form **8**, respectively, are the most probable ones. The ^{11}B nmr spectra of the examples **5*h,i,k,l,m***, and ***n*** show the expected signals for tricoordinated (sp^2) boron at $\delta(Et_2OBF_3)$ = 27.5, 27.3, 27.5, 28.3, 27.6 and 27.9 ppm, respectively, confirming the cycloboronate structure **5**, at least in solution. Dimeric associates of type **8** in the solid state, however, could not be ruled out. The infrared spectra (KBr pellets) corroborate the monomeric character of **5** in the solid state (with the exception of **5*d*** and **5*e***, see Experimental) because of the strong ν_{16} phenyl ring stretching vibrations at 1600 cm^{-1} which are normally found in the spectra of trigonal planar phenylboronates (ref. 1, and references therein). An X-ray crystallographic analysis of one of the 1:1 condensation products, **5*l***, has been performed in order to provide unambiguous proof of the cycloboronate structure **5** in the solid state.

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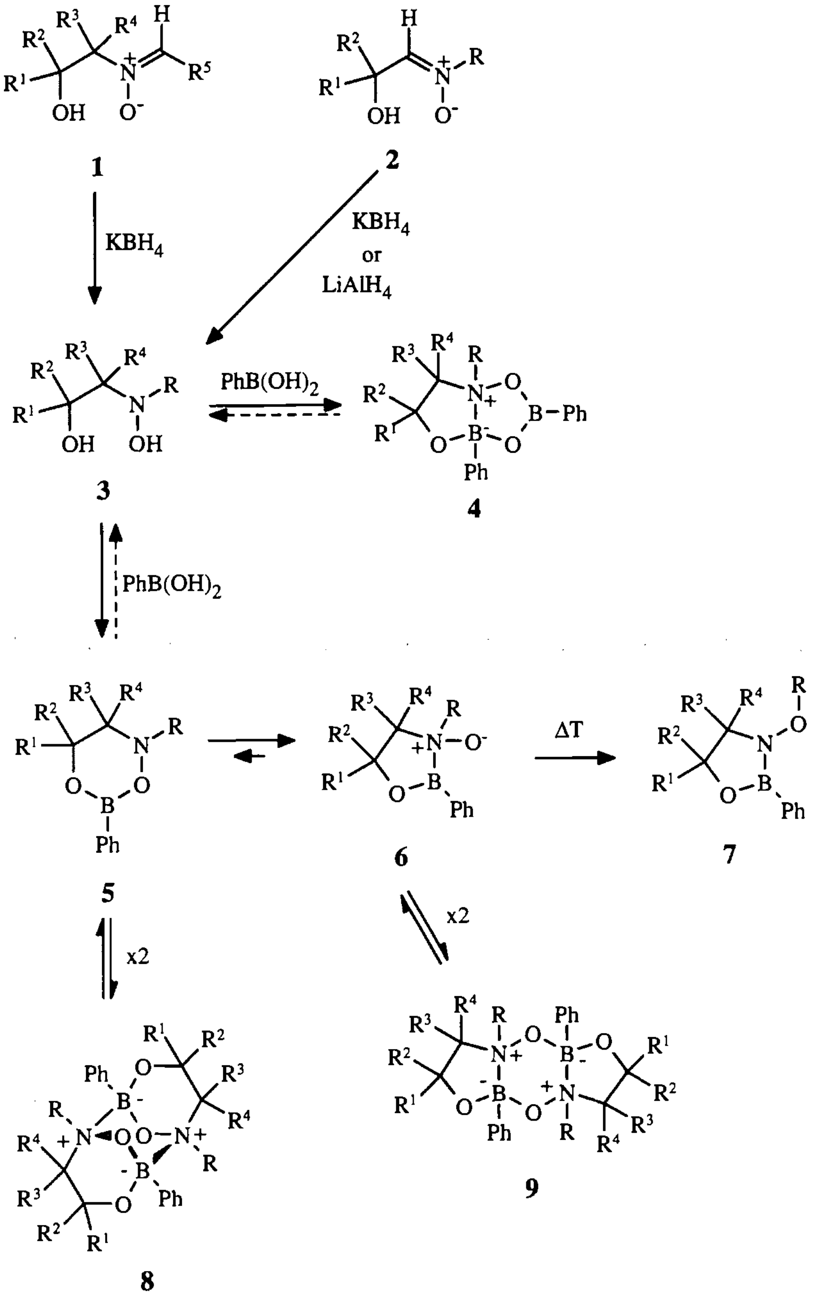
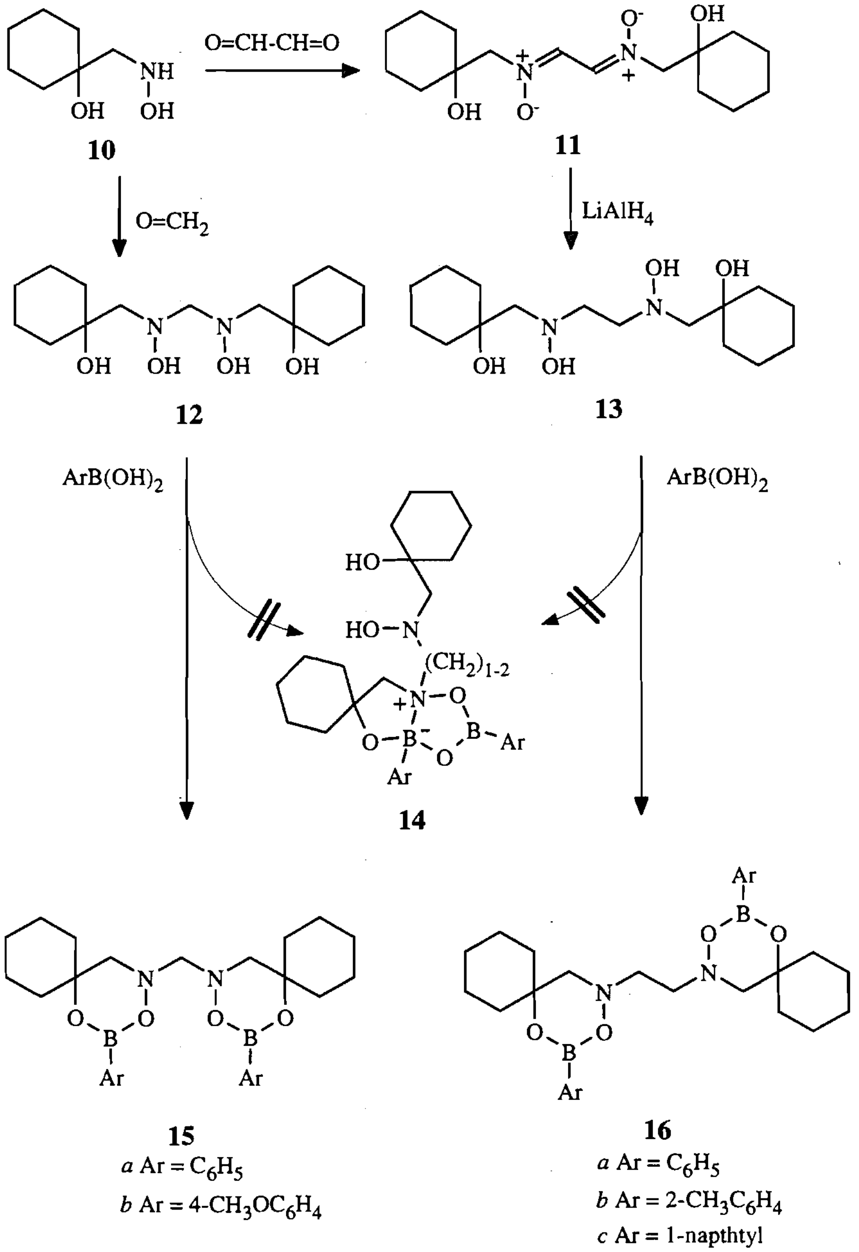
[1] Previous paper in this series; ref. 13.



3 and 4/5	R	R^1	R^2	R^3	R^4
a	C_6H_{11}	H	CH_3	H	H
b	$CH_2C_6H_5$	H	H	H	H
c	$CH_2C_6H_5$	H	H	H	CH_3
d	CH_3	H	H	H	H
e	CH_3	—$(CH_2)_5$—		H	H
f	C_2H_5	—$(CH_2)_5$—		H	H
g	C_6H_{11}	H	H	H	H
h	$CH_2C_6H_{11}$	—$(CH_2)_5$—		H	H
i	$CH_2C_6H_5$	H	H	CH_3	CH_3
j	$CH_2C_6H_5$	H	CH_3	CH_3	CH_3
k	$CH_2C_6H_5$	—$(CH_2)_5$—		H	H
l	$CH_2C_6H_4$-4-Cl	—$(CH_2)_5$—		H	H
m	$CH_2C_6H_4$-4-NO_2	H	H	CH_3	CH_3
n	$CH_2C_6H_4$-4-NO_2	—$(CH_2)_5$—		H	H
o	$CH_2C_6H_4$-4-$N(CH_3)_2$	—$(CH_2)_5$—		H	H
p	$CH(C_6H_5)_2$	H	CH_3	H	H



15
a Ar = C_6H_5
b Ar = 4-$CH_3OC_6H_4$

16
a Ar = C_6H_5
b Ar = 2-$CH_3C_6H_4$
c Ar = 1-napthtyl

A related structural problem arose from the reaction of arylboronic acids with compounds containing two *N*-alkylhydroxylaminoalkanol groups in a geminal or vicinal arrangement, namely the aminal **12** and the ethylenediamine derivative **13**. The aminal **12** could be prepared as a 2:1 condensation product of the hydroxylamine **10** and formaldehyde.[2] Compound **13** was synthesized by reduction of the glyoxal-bisnitrone **11** with $LiAlH_4$. Both of the tetrahydroxy compounds, **12** and **13**, gave bisarylboronates upon reaction with arylboronic acids. The elemental analyses as well as the infrared, ^{1}H nmr, and ^{11}B nmr spectra show that all of the four hydroxyl functions in each molecule are involved in the condensation reaction, so that a pyroboronate formation at only one of the "1,3-diol" groupings (**14**), as for type **4** compounds, can be excluded. Thus, structures **15** and **16** seemed very likely, although there are other possibilities of biscycloboronate condensation products as formulated in **17**–**20**. Further support for **15** and **16** comes from the strong ν_{16} phenyl ring stretching bands at 1600 cm^{-1} in the infrared spectra that are typical for non-tetracoordinated phenylboronates (like compound **5** (ref. 1, and references therein)). The EI mass spectra of **15** and **16**, however, give only very small molecular peaks (M^+). Both types of compound display a parent peak of a methyleniminium ion (Fig. 1), indicating an

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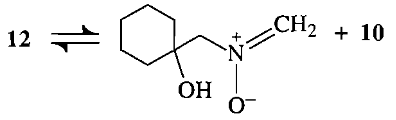
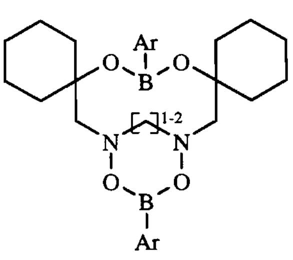
[2] As shown by ^{1}H nmr and mass spectrometry, the aminal **12** dissociates easily into a formaldehyde nitrone and the hydroxylamine **10**, in an elimination/addition equilibrium:



This kind of dissociation in solution or gaseous state has been reported for other *N*,*N*′-dihydroxyaminals (4).



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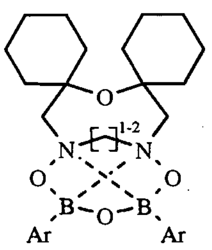

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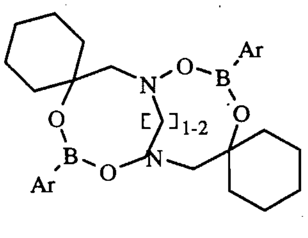

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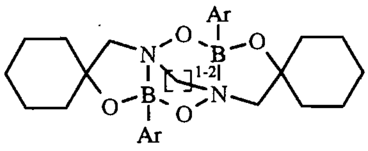

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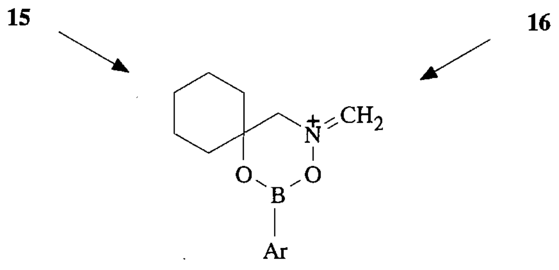

(100% relative abundance)

FIG. 1. Mass spectral fragmentation pattern of **15** and **16**.

easy dissociation of a C—N aminal bond in the case of **15**,[3] and of the C—C ethylene bond connecting the two BONCCO rings in **16**. To provide additional structural certainty, especially for the pyroboronate type **15** (with a relatively labile aminal function), an X-ray crystallographic analysis of **15***a*, which formed good crystals as a 1:1 benzene solvate, was carried out.

Experimental

N-*Benzylidene-3-hydroxy-2-methyl-2-butanamine* N-*oxide (1,*$R^1 = H$, $R^2 = R^3 = R^4 = CH_3$, $R^5 = C_6H_5$)

3-Hydroxyamino-3-methyl-2-butanol (5) (0.24 g, 2 mmol) and benzaldehyde (0.21 g, 2 mmol) are reacted as described previously (5). Yield: 0.34 g (82%) of colorless crystals. Mp 67°C (from benzene/petroleum ether), Infrared (KBr): 3220 (O—H), 1585 cm^{-1} (C=N). ^{1}H nmr (90 MHz, $CDCl_3$/TMS): δ (ppm) = 1.19 (d, *J* = 7 Hz, O—C—CH_3), 1.54 and 1.61 (s and s, $C(CH_3)_2$), 3.89 (q, *J* = 7 Hz, O—CH), 4.58 (s, broad, exchangeable, OH), 7.17–7.37 (m, 4 aromatic H and N=CH), 8.05–8.02 (m, 2 aromatic H). Anal. calcd. for $C_{12}H_{17}NO_2$: C 69.54, H 8.27, N 6.76; found: C 69.39, H 8.29, N 6.76.

N-*(2-Hydroxyethylidene)methanamine* N-*oxide (2*a, $R = CH_3$, $R^1 = R^2 = H$)

Glycolaldehyde (1.20 g, 20 mmol) and *N*-methylhydroxylamine hydrochloride (1.67 g, 20 mmol) are dissolved in 20 mL of ethanol (96%). A solution of K_2CO_3 (1.38 g, 10 mmol) in 5 mL of water is added under stirring. After 48 h the precipitated KCl is filtered off and the solvent removed in vacuo. The residue is taken up in 50 mL of absolute ethanol, and after filtration the ethanol is distilled off. The remaining oil is not purified further and is used in subsequent reactions as a crude product (see below). ^{1}H nmr (90 MHz, $CDCl_3$/TMS): δ (ppm) = 3.65 (s, NCH_3), 4.15 (s, broad, exchangeable, OH), 4.35 (d, *J* = 4 Hz, CH_2O), 6.92 (t, *J* = 4 Hz, N=CH).

N-*(2-Hydroxyethylidene)cyclohexanamine* N-*oxide (2*b, $R = C_6H_{11}$, $R^1 = R^2 = H$)

Glycolaldehyde (0.60 g, 10 mmol) and *N*-cyclohexylhydroxylamine (1.14 g, 10 mmol) are dissolved in 50 mL of absolute ethanol and refluxed for 1 h. After removal of solvent in vacuo, the oily residue is taken up in a small amount of ethanol and ether and stored 24 h at −18°C. Yield: 0.76 g (49%) colorless needles. Mp 127°C (from ethanol/ether). Infrared (KBr): 3280 (O—H), 1615 cm^{-1} (C=N). ^{1}H nmr (90 MHz, $CDCl_3$): δ (ppm) = 1.03–2.22 (m, $(CH_2)_5$), 3.44–3.84 (m, =N—CH), 4.39 (d, *J* = 4 Hz, O—CH_2), 4.89 (s, broad, exchangeable, OH), 6.98 (t, *J* = 4 Hz, N=CH). Anal. calcd. for $C_8H_{15}NO_2$: C 61.12, H 9.62, N 8.91; found: C 61.02, H 9.84, N 8.67.

N-*(2-Hydroxypropylidene)cyclohexanamine* N-*oxide (2*c, $R = C_6H_{11}$, $R^1 = H$, $R^2 = CH_3$)

2-Hydroxypropanal (6) (2.22 g, 30 mmol) and *N*-cyclohexylhydroxylamine (3.45 g, 30 mmol) are dissolved in 30 mL of absolute ethanol and stirred at room temperature for 48 h. The solvent is removed in vacuo, and the residue recrystallized from ethanol. Yield: 4.42 g (86%) of colorless needles. Mp 129°C (from absolute ethanol). Infrared (KBr): 3210 (O—H), 1605 cm^{-1} (C=N). ^{1}H nmr (90 MHz, $CDCl_3$/TMS): δ (ppm) = 1.04–2.02 (m, $(CH_2)_5$), 1.39 (d, *J* = 7 Hz, O—C—CH_3), 3.64 (m, =N—CH), 4.71 (m, O—CH), 5.61 (s, exchangeable,

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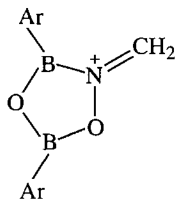
[3] The relatively high stability of the methyleniminium cation and the dissociation of the aminal **15** is reminiscent of the dissociation pattern of the corresponding *N,N'*-dihydroxyaminals **12** (see footnote 2) and also the mass spectral fragments of aminal-derived pyroboronates (4):



OH), 6.85 (d, $J = 5$ Hz, N═CH). Anal. calcd. for $C_9H_{17}NO_2$: C 63.13, H 10.01, N 8.18; found: C 63.09, H 10.15, N 7.97.

N-(2-Hydroxyethylidene)phenylmethanamine N-oxide (2d, R = $CH_2C_6H_5$, $R^1 = R^2 = H$)

Glycolaldehyde (1.20 g, 20 mmol) and *N*-benzylhydroxylamine hydrochloride (1.38 g, 10 mmol) are reacted as described for **2***a*, and the remaining residue is recrystallized from absolute ethanol and ether. Yield: 2.30 g (70%) of colorless platelets. Mp 82–84°C (from ethanol/ether). Infrared (KBr): 3300, 3170 (broad, O—H), 1610 cm^{-1} (C═N). ^1H nmr (90 MHz, $CDCl_3$/TMS): δ (ppm) = 4.15 (s, very broad, exchangeable, OH), 4.35 (d, $J = 5$ Hz, O—CH_2), 4.83 (s, N—CH_2), 6.88 (t, $J = 5$ Hz, N═CH), 7.37 (s, 5 aromatic H). Anal. calcd. for $C_9H_{11}NO_2$: C 65.44, H 6.71, N 8.48; found: C 65.41, H 6.71, N 8.57.

N-(2-Hydroxypropylidene)diphenylmethanamine N-oxide (2e, R = $CH(C_6H_5)_2$, $R^1 = H$, $R^2 = CH_3$)

2-Hydroxypropanal (1.48 g, 20 mmol) and *N*-benzhydrylhydroxylamine (7) (3.98 g, 20 mmol) are reacted as described for **2***c*. Yield: 4.21 g (82%) of colorless crystals. Mp 110–111°C (from ethanol/ether). Infrared (KBr): 3290 (O—H), 1590 cm^{-1} (C═N). ^1H nmr (90 MHz, $CDCl_3$/TMS): δ (ppm) = 1.34 (d, $J = 7$ Hz, CH_3), 4.71 (m, O—CH), 5.47 (s, broad, exchangeable, 2 OH), 6.15 (s, N—CH), 6.82 (d, $J = 5$ Hz, N═CH), 7.32 (s, 10 aromatic H). Anal. calcd. for $C_{16}H_{17}NO_2$: C 75.27, H 6.71, N 5.49; found: C 75.47, H 6.71, N 5.64.

1-(N-Cyclohexyl-N-hydroxyamino)-2-propanol (3a)

To a solution of **2***c* (1.71 g, 10 mmol) in 60 mL of methanol a solution of KBH_4 (1.08 g, 20 mmol) in 15 mL of water is added dropwise over a period of 30 min. After 24 h the excess KBH_4 is decomposed with tartaric acid, the methanol distilled off in vacuo, and the remaining aqueous solution brought to pH 9–10 using aqueous Na_2CO_3, solution. After extraction with 3 × 70 mL of dichloromethane, the collected dichloromethane solutions are dried with $MgSO_4$ and evaporated in vacuo. The residue is crystallized from benzene/petroleum ether. Yield: 1.56 g (90%). Mp 79°C. Infrared (KBr): 3250 cm^{-1} (O—H). ^1H nmr (90 MHz, $CDCl_3$/TMS): δ (ppm) = 1.03–2.17 (m, —$(CH_2)_5$—), 1.18 (d, $J = 7$ Hz, CH_3), 2.62 (m, N—CH_2C and N—CH(C,C)), 4.05 (m, O—CH), 5.28 (s, broad, exchangeable, OH). Anal. calcd. for $C_9H_{19}NO_2$: C 62.39, H 11.05, N 8.08; found: C 62.36, H 11.18, N 7.96.

2-(N-Benzyl-N-hydroxyamino)ethanol(3b)

2*d* (0.66 g, 4 mmol) and KBH_4 (0.54 g, 10 mmol) are reacted as described for **3***a* (see above). The oily residue is not purified further and is used as crude product in subsequent reactions. ^1H nmr (90 MHz, $CDCl_3$/TMS): δ (ppm) = 2.75 (t, $J = 5$ Hz, N—CH_2CO), 3.62 (t, $J = 5$ Hz, O—CH_2), 3.69 (s, N—CH_2(Ph)), 4.40 (s, very broad, exchangeable, 2 OH), 7.17 (s, 5 aromatic H).

2-(N-Benzyl-N-hydroxyamino)-1-propanol (3c)

N-Benzylidene-1-hydroxy-2-propanamine *N*-oxide (**1**, $R^1 = R^2 = R^3 = H$, $R^4 = CH_3$, $R^5 = C_6H_5$) (5) (2.15 g, 12 mmol) and KBH_4 (3.24 g, 60 mmol) are reacted as described for **3***a*. The oily residue is analytically pure. Yield: 2.05 g (94%) of a colorless oil. Infrared (film): 3100–3600 cm^{-1} (broad, O—H). ^1H nmr (90 MHz, $CDCl_3$/TMS): δ (ppm) = 1.05 (d, $J = 6$ Hz, CH_3), 2.91 (m, $J = 6$ Hz, O—CH), 3.49 (d, $J = 6$ Hz, CH_2CO), 3.65 and 3.96 (d and d, $J = 12$ Hz, N—CH_2 (Ph)), 4.53 (s, very broad, exchangeable, 2 OH), 7.30 (s, 5 aromatic H). Anal. calcd. for $C_{10}H_{15}NO_2$: C 66.27, H 8.34, N 7.73; found: C 66.34, H 8.19, N 7.43.

2-(N-Hydroxy-N-methylamino)ethanol (3d)

2*a* (crude product, 0.9 g, 10 mmol) and KBH_4) (1.08 g, 20 mmol) are reacted as described for **3***a*. The oily residue is not further purified and is used as crude product in subsequent reactions. ^1H nmr (90 MHz, $CDCl_3$/TMS): δ (ppm) = 2.4 (m_c, N—CH_3 and N—CH_2C), 3.5 (m_c, O—CH_2 and 2 OH).

1-(N-Hydroxy-N-methylaminomethyl)cyclohexanol (3e)

3-Hydroxy-5,5-pentamethylene-1,3-oxazolidine[4] (9) (1.57 g, 10 mmol) and KBH_4 (1.08 g, 20 mmol) are reacted as described for **3***a*. The oily residue is used as crude product in further reactions.

1-(N-Ethyl-N-hydroxyaminomethyl)cyclohexanol (3f)

N-Ethylidene-(1-hydroxycyclohexyl)methanamine *N*-oxide (**1**, $R^1 + R^2$ = —$(CH_2)_5$—, $R^3 = R^4 = H$, $R^5 = CH_3$) (8) (1.71 g, 10 mmol) and KBH_4 (1.08 g, 20 mmol) are reacted as described for **3***a*. The oily residue is used as crude product in further reactions.

2-(N-Cyclohexyl-N-hydroxyamino)ethanol (3g)

2*b* (3.14 g, 20 mmol) and $LiAlH_4$ (0.76, 20 mmol) are suspended in 150 mL of dry ether. After refluxing for 5 h, hydrolysis is carried out with water under cooling with ice, and subsequent acidification with 6N HCl. The mixture is neutralized with $NaHCO_3$, the ether layer separated, and the aqueous phase extracted with an additional 3 × 40 mL of ether. The combined ether solutions are dried over Na_2SO_4 and evaporated in vacuo. The reside is crystallized from benzene/petroleum ether. Yield: 2.04 g (65%) of colorless crystals. Mp 60–62°C. Infrared (KBr): 3500–2600 cm^{-1} (broad, O—H). ^1H nmr (90 MHz, $CDCl_3$/TMS): δ (ppm) = 0.71–2.17 (m, —$(CH_2)_5$—), 2.32–2.70 (m, N—CH(C,C)), 2.87 (t, $J = 5$ Hz, N—CH_2), 3.79 (t, $J = 5$ Hz, O—CH_2), 6.11 (s, exchangeable, 2 OH). Anal. calcd. for $C_8H_{17}NO_2$: C 60.35, H 10.76, N 8.80; found: C 60.52, H 11.17, N 8.60.

1-(N-Cyclohexylmethyl-N-hydroxyaminomethyl)cyclohexanol (3h)

N-Cyclohexylmethylene-(1-hydroxycyclohexyl)methanamine *N*-oxide (**1**, $R^1 + R^2$ = —$(CH_2)_5$—, $R^3 = R^4 = H$, $R^5 = C_6H_{11}$) (8) (1.20 g, 5 mmol) and KBH_4 (0.54 g, 10 mmol) are reacted as described for **3***a*. The residue is crystallized from absolute ethanol. Yield: 0.91 g (75%) of colorless crystals. Mp 74°C. Infrared (KBr): 3410, 3250 cm^{-1} (O—H). ^1H nmr (90 MHz, $CDCl_3$/TMS): δ (ppm) = 0.66–1.98 (m, —$(CH_2)_5$— and C_6H_{11}), 2.52 (d, $J = 6$ Hz, N—$CH_2C_6H_{11}$), 2.71 (s, N—CH_2CO), 3.31 and 5.70 (s and s, broad, exchangeable, 2 OH). Anal. calcd. for $C_{14}H_{27}NO_2$: C 69.67, H 11.28, N 5.80; found: C 69.67, H 11.35, N 5.71.

2-(N-Benzyl-N-hydroxyamino)-2-methylpropanol (3i)

N-Benzylidene-1-hydroxy-2-methyl-2-propanamine *N*-oxide (**1**, $R^1 = R^2 = H$, $R^3 = R^4 = CH_3$, $R^5 = C_6H_5$) (5) (0.97 g, 5 mmol) and KBH_4 (1.08 g, 20 mmol) are reacted as described for **3***a*. The residue is crystallized from benzene/petroleum ether. Yield: 0.90 g (92%) of colorless crystals. Mp 107°C. Infrared (KBr): 3460, 3360 cm^{-1} (O—H). ^1H nmr (90 MHz, $CDCl_3$/TMS): δ (ppm) = 1.12 (s, 2 CH_3), 3.12 (s, very broad, exchangeable, OH), 3.38 (s, OCH_2) 3.70 (s, NCH_2), 4.88 (s, very broad, exchangeable, OH), 7.26 (s, 5 aromatic H). Anal. calcd. for $C_{11}H_{17}NO_2$: C 67.66, H 8.78, N 7.17; found: C 67.72, H 8.82, N 6.97.

3-(N-Benzyl-N-hydroxyamino)-3-methyl-2-butanol (3j)

N-Benzylidene-3-hydroxy-2-methyl-2-butanamine *N*-oxide (**1**, $R^1 = H$, $R^2 = R^3 = R^4 = CH_3$, $R^5 = C_6H_5$) (this work, see above) (1.04 g, 5 mmol) and KBH_4 (1.08 g, 20 mmol) are reacted as described for **3***a*. The residue is crystallized from benzene/petroleum ether. Yield: 0.72 g (69%) of colorless crystals. Mp 86°C. Infrared (KBr): 3460, 3360 cm^{-1} (O—H). ^1H nmr (90 MHz, $CDCl_3$/TMS): δ (ppm) = 1.09 (s, 2 CH_3), 1.10 (d, $J = 6$ Hz, $OCCH_3$), 3.37 (s, very broad, exchangeable, OH), 3.78 (q, $J = 6$ Hz, OCH), 3.79 (s, NCH_2), 5.10 (s, very broad, exchangeable, OH) 7.30 (s, 5, aromatic H). Anal. calcd. for $C_{12}H_{19}NO_2$: C 68.87, H 9.15, N 6.69; found: C 68.90, H 9.17, N 6.55.

1-(N-Benzyl-N-hydroxyaminomethyl)cyclohexanol (3k)

N-Benzylidene-(1-hydroxycyclohexyl)methanamine *N*-oxide (**1**, $R^1 + R^2$ = —$(CH_2)_5$—, $R^3 = R^4 = H$, $R^5 = C_6H_5$) (5) (1.16 g, 5 mmol)

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[4] This is the ring tautomer of *N*-methylene-(1-hydroxycyclohexyl)-methanamine *N*-oxide (**1**, $R^1 + R^2$ = —$(CH_2)_5$—, $R^3 = R^4 = R^5 = H$). The ring/chain tautomerism of other aliphatic aldonitrones of this type has already been reported (8).

and $\mathrm{KBH_4}$ (0.54 g, 10 mmol) are reacted as described for **3**_a_. The residue is crystallized from benzene/petroleum ether. Yield: 0.76 g (66%) of colorless platelets. Mp 85–86°C. Infrared (KBr): 3470, 3210 cm^{-1} (O—H). ^{1}H nmr (90 MHz, $\mathrm{CDCl_3}$/TMS): δ (ppm) = 1.03–1.88 (m, —$\mathrm{(CH_2)_5}$—), 2.71 (s, $\mathrm{NCH_2CO}$), 3.40 (s, broad, exchangeable, OH), 3.82 (s, $\mathrm{NC}\mathit{H}_2\mathrm{C_6H_5}$), 6.02 (s, broad, exchangeable, OH), 7.11–7.40 (m, 5 aromatic H). Anal. calcd. for $\mathrm{C_{14}H_{21}NO_2}$: C 71.45, H 8.99, N 5.95; found: C 71.40, H 9.15, N 5.74.

*1-[*N*-(4-Chlorophenylmethyl)-*N*-hydroxyaminomethyl]cyclohexanol* (**3**l)

N - (4 - Chlorophenylmethylene) - (1 - hydroxycyclohexyl)methanamine *N*-oxide (**1**, $\mathrm{R^1 + R^2}$ = —$\mathrm{(CH_2)_5}$—, $\mathrm{R^3 = R^4 = H}$, $\mathrm{R^5}$ = 4-$\mathrm{ClC_6H_4}$) (5) (1.34 g, 5 mmol) and $\mathrm{KBH_4}$ (0.54 g, 10 mmol) are reacted as described for **3**_a_. The residue is crystallized from benzene. Yield: 1.00 g (74%) of colorless small needles. Mp 113°C. Infrared (KBr): 3390, 3180 cm^{-1} (O—H). ^{1}H nmr (90 MHz, $\mathrm{CDCl_3}$/TMS): δ (ppm) = 1.07–1.83 (m, —$\mathrm{(CH_2)_5}$—), 2.17 (s, $\mathrm{NCH_2CO}$), 3.04 (s, broad, exchangeable, OH), 3.78 (s, $\mathrm{C}\mathit{H}_2\mathrm{C_6H_4Cl}$), 5.64 (s, very broad, exchangeable, OH), 7.21 (s, 4 aromatic H). Anal. calcd. for $\mathrm{C_{14}H_{20}ClNO_2}$: C 62.33, H 7.47, N 5.19; found: C 62.17, H 7.49, N 5.00.

*2-[*N*-Hydroxy-*N*-(4-nitrophenylmethyl)amino]-2-methylpropanol* (**3**m)

1-Hydroxy-2-methyl-*N*-(4-nitrophenylmethylene)-2-propanamine *N*-oxide (**1**, $\mathrm{R^1 = R^2 = H, R^3 = R^4 = CH_3, R^5}$ = 4-$\mathrm{NO_2C_6H_4}$) (5) (2.38 g, 10 mmol) and $\mathrm{KBH_4}$ (1.08 g, 20 mmol) are reacted as described for **3**_a_. The residue is crystallized from benzene. Yield: 1.17 g (49%) of yellowish crystals. Mp 113–114°C. Infrared (KBr): 3600–3200 (broad, O—H), 1525 cm^{-1} ($\mathrm{NO_2}$). ^{1}H nmr (90 MHz, $\mathrm{CDCl_3}$/TMS): δ (ppm) = 1.12 (s, 2 $\mathrm{CH_3}$), 2.70 (s, broad, exchangeable, OH), 3.43 (s, $\mathrm{NCH_2}$), 3.83 (s, $\mathrm{OCH_2}$), 5.30 (s, broad, exchangeable, OH), 7.45 and 8.07 (d and d, *J* = 8 Hz, AA′BB′ system, 4 aromatic H). Anal. calcd. for $\mathrm{C_{11}H_{16}N_2O_4}$: C 54.99, H 6.71, N 11.66; found: C 55.58, H 6.87, N 11.36.

*1-[*N*-Hydroxy-*N*-(4-nitrophenylmethyl)aminomethyl]cyclohexanol* (**3**n)

(1-Hydroxycyclohexyl)-*N*-(4-nitrophenylmethylene)methanamine *N*-oxide (**1**, $\mathrm{R^1 + R^2}$ = —$\mathrm{(CH_2)_5}$—, $\mathrm{R^3 = R^4 = CH_3, R^5}$ = 4-$\mathrm{NO_2C_6H_4}$) (5) (1.39 g, 5 mmol) and $\mathrm{KBH_4}$ (1.08 g, 20 mmol) are reacted as described for **3**_a_. The residue is crystallized from benzene. Yield: 1.13 g (81%) of yellow needles. Mp 125–126°C. Infrared (KBr): 3380, 3140 (O—H), 1510 cm^{-1} ($\mathrm{NO_2}$). ^{1}H nmr (90 MHz, $\mathrm{CDCl_3}$/TMS): δ (ppm) = 1.08–1.86 (m, —$\mathrm{(CH_2)_5}$—), 2.81 (s, $\mathrm{NCH_2CO}$), 2.96 (s, broad, exchangeable, OH), 3.95 (s, $\mathrm{NC}\mathit{H}_2\mathrm{C_6H_4NO_2}$), 5.83 (s, broad, exchangeable, OH), 7.51 and 8.14 (d and d, *J* = 8 Hz, AA′BB′ system, 4 aromatic H). Anal. calcd. for $\mathrm{C_{14}H_{20}N_2O_4}$: C 59.99, H 7.19, N 9.99; found: C 60.01, H 7.29, N 9.87.

*1-[*N*-(4-Dimethylaminophenylmethyl)-*N*-hydroxyaminomethyl]cyclohexanol* (**3**o)

N-(4-Dimethylaminophenylmethylene)-(1-hydroxycyclohexyl)methanamine N-oxide (**1**, $\mathrm{R^1 + R^2}$ = —$\mathrm{(CH_2)_5}$—, $\mathrm{R^3 = R^4 = CH_3, R^5}$ = 4-$\mathrm{CH_3)_2NC_6H_4}$) (5) (1.38 g, 5 mmol) and $\mathrm{KBH_4}$ (1.62 g, 30 mmol) are reacted as described for **3**_a_. The residue is crystallized from benzene/petroleum ether. Yield: 0.75 g (54%) of colorless crystals. Mp 69–70°C. Infrared (KBr): 3370, 3250 cm^{-1} (O—H). ^{1}H nmr (90 MHz, $\mathrm{CDCl_3}$/TMS): δ (ppm) = 1.19–1.77 (m, —$\mathrm{(CH_2)_5}$—), 2.72 (s, $\mathrm{NCH_2CO}$), 2.94 (s, $\mathrm{N(CH_3)_2}$), 3.75 (s, $\mathrm{NC}\mathit{H}_2\mathrm{C_6H_4N(CH_3)_2}$), 6.67 and 7.17 (d and d, *J* = 9 Hz, AA′BB′ system, 4 aromatic H); OH signals not observed.

*1-(*N*-Benzhydryl-*N*-hydroxyamino)-2-propanol* (**3**p)

2_e_ (1.53 g, 6 mmol) and $\mathrm{KBH_4}$ (0.65 g, 12 mmol) are reacted as described for **3**_a_. The residue is crystallized from benzene. Yield: 1.35 g (87%) of colorless crystals. Mp 137–138°C. Infrared (KBr): 3430, 3300 cm^{-1} (O—H). ^{1}H nmr (90 MHz, $\mathrm{CDCl_3}$/TMS): δ (ppm) = 1.09 (d, *J* = 6 Hz, $\mathrm{CH_3}$), 2.62 (d, *J* = 5 Hz, $\mathrm{NCH_2}$), 3.14 (s, broad, exchangeable, OH), 4.07 (m, OCH), 4.37 (s, $\mathrm{NC}\mathit{H}\mathrm{Ph_2}$), 5.26 (s, broad, exchangeable, OH), 7.08–7.51 (m, 10 aromatic H). Anal. calcd. for $\mathrm{C_{16}H_{19}NO_2}$: C 74.68, H 7.44, N 5.44; found: C 74.70, H 7.44, N 5.45.

1-Cyclohexyl-7-methyl-3,5-diphenyl-2,4,6-trioxa-1-azonia-3-bora-5-boratabicyclo[3.3.0]octane (**4**a)

3_a_ (0.51 g, 3 mmol) and phenylboronic acid 0.73 g, 6 mmol) are dissolved in 20–30 mL of benzene and refluxed for 1 h with continuous removal of water using a Dean Stark trap. After evaporation in vacuo the residue is crystallized from benzene/petroleum ether. Yield: 0.85 g (78%) of colorless needles. Mp 130°C. Infrared (KBr): 1605 cm^{-1} (phenyl C═C). ^{1}H nmr (90 MHz, $\mathrm{CDCl_3}$/TMS): δ (ppm) = 0.74–2.10 (m, —$\mathrm{(CH_2)_5}$—), 1.42 (d, *J* = 6 Hz, $\mathrm{CH_3}$), 2.67 (m, NCH and 1 H of $\mathrm{NCH_2}$), 3.32 and 3.45 (d and d, 1 H of $\mathrm{NCH_2}$), 4.27 (m, OCH), 7.18–7.53 (m, 6 aromatic H), 7.57–7.77 (m, 2 aromatic H), 7.81–8.01 (m, 2 aromatic H). ^{11}B nmr (64.2 MHz, $\mathrm{CDCl_3/Et_2OBF_3}$): δ (ppm) = 29.2 ($w_{1/2}$ = 640 Hz) and 14.5 ($w_{1/2}$ = 300 Hz); ratio of peak areas: 1:1. Anal. calcd. for $\mathrm{C_{21}H_{27}B_2NO_3}$: C 69.47, H 7.50, B 5.96, N 3.86; found: C 69.36, H 7.50, B 6.19, N 4.01.

1-Benzyl-3,5-diphenyl-2,4,6-trioxa-1-azonia-3-bora-5-boratabicyclo[3.30]octane (**4**b)

3_b_ (crude product, 0.50 g, 3 mmol) and phenylboronic acid (0.73 g, 6 mmol) are reacted as described for **4**_a_. Yield: 0.91 g (85%) of colorless crystals. Mp 128–129°C (from benzene/petroleum ether). Infrared (KBr): 1600 cm^{-1} (phenyl C═C). ^{1}H nmr (90 MHz, $\mathrm{CDCl_3}$/TMS): δ (ppm) = 3.04 (m, $\mathrm{NCH_2CO}$), 3.44 and 3.94 (d and d, *J* = 15 Hz, AB system, $\mathrm{NC}\mathit{H}_2\mathrm{Ph}$), 4.07 (m, $\mathrm{OCH_2}$), 7.17–7.53 (m, 11 aromatic H), 7.61 – 7.78 (m, 2 aromatic H), 7.80–7.98 (m, 2 aromatic H). ^{11}B nmr (64.2 MHz, $\mathrm{CDCl_3/Et_2OBF_3}$): δ (ppm) = 29.2 ($w_{1/2}$ = 640 Hz) and 14.7 ($w_{1/2}$ = 340 Hz); ratio of peak areas: 1:1. Anal. calcd. for $\mathrm{C_{21}H_{21}B_2NO_3}$: C 70.65, H 5.93, N 3.92; found: C 70.64, H 5.94, N 3.94.

1-Benzyl-8-methyl-3,5-diphenyl-2,4,6-trioxa-1-azonia-3-bora-5-boratabicyclo[3.3.0] octane (**4**c)

3_c_ (0.72 g, 4 mmol) and phenylboronic acid (0.98 g, 8 mmol) are reacted as described for **4**_a_. Yield: 1.18 g (80%) of colorless crystals. Mp 126°C (from benzene/petroleum ether). Infrared (KBr): 1600 cm^{-1} (phenyl C═C). ^{1}H nmr (90 MHz), $\mathrm{CDCl_3}$/TMS): δ (ppm) = 0.68 (d, *J* = 6 Hz, $\mathrm{CH_3}$), 3.16–4.15 (m, $\mathrm{CH_2CHN}$), 3.54 and 3.88 (d and d, *J* = 14 Hz, AB system, $\mathrm{NC}\mathit{H}_2\mathrm{Ph}$), 7.11–7.50 (m, 11 aromatic H), 7.56–7.72 (m, 2 aromatic H), 7.81–8.00 (m, 2 aromatic H). ^{11}B nmr (64.2 MHz, $\mathrm{CDCl_3/Et_2OBF_3}$): δ (ppm) = 28.6 ($w_{1/2}$ = 640 Hz) and 15.1 ($w_{1/2}$ = 340 Hz); ratio of peak areas: 1:1. Anal. calcd. for $\mathrm{C_{22}H_{23}B_2NO_3}$: C 71.21, H 6.25, N 3.78; found: C 71.23, H 6.25, N 3.85.

4-Methyl-2-phenyl-1,3-dioxa-4-aza-2-boracyclohexane (**5**d)[5]

3_d_ (0.27 g, 3 mmol) and phenylboronic acid (0.37 g, 3 mmol) are reacted as described for **4**_a_. The residue was crystallized from absolute ethanol. Yield: 0.25 g (47%) of colorless thin needles. Mp 126°C. ^{1}H nmr (90 MHz, $\mathrm{CDCl_3}$/TMS): δ (ppm) = 2.87 (s, $\mathrm{CH_3}$), 3.00 (t, *J* = 4 Hz, $\mathrm{NCH_2C}$), 4.24 (t, *J* = 4 Hz, $\mathrm{OCH_2}$), 7.15–7.40 (m, 3 aromatic H), 7.57–7.77 (m, 2 aromatic H). Anal. calcd. for $\mathrm{C_9H_{12}BNO_2}$: C 61.07, H 6.83, N 7.91; found: C 61.06, H 6.93, N 7.80.

4-Methyl-6,6-pentamethylene-2-phenyl-1,3-dioxa-4-aza-2-boracyclohexane (**5**e)

3_e_ (0.48 g, 3 mmol) and phenylboronic acid (0.37 g, 3 mmol) are reacted as described for **4**_a_. Yield: 0.57 g (78%) of colorless oil, the crystallization of which could not be induced. Infrared (film): 1600

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[5] The solid state infrared spectrum (KBr pellet) of **5**_d_, which lacks the ν_{16} band, and the X-ray crystallographic analysis of a homologous compound that has a comparable infrared spectrum (1) suggest that **5**_d_ should also exist as a dimer of the type **8** in the crystalline state and should be named: *1,6-dimethyl-2,7-diphenyl-3,8,11,12-tetraoxa-1,6-diazonia-2,7-diboratatricyclo[5.3.1.1*^{2,6}*]dodecane.*

cm^{-1} (phenyl C═C). ^{1}H nmr (90 MHz, $CDCl_3$/TMS): δ (ppm) = 1.17–2.05 (m, —$(CH_2)_5$—), 2.74 (s, CH_3), 2.78 (s, NCH_2CO), 7.03–7.32 (m, 3 aromatic H), 7.50–7.73 (m, 2 aromatic H). Anal. calcd. for $C_{14}H_{20}BNO_2$: C 68.60, H 8.22, N 5.71; found: C 68.86, H 8.25, N 5.38.

4-Ethyl-6,6-pentamethylene-2-phenyl-1,3-dioxa-4-aza-2-boracyclohexane (5f)

3*f* (0.52 g, 3 mmol) and phenylboronic acid (0.37 g, 3 mmol) are reacted as described for **4***a*. The residue was crystallized from absolute ethanol. Yield: 0.49 g (63%) of colorless crystals. Mp 36°C. Infrared (KBr): 1600 cm^{-1} (phenyl C═C). ^{1}H nmr (90 MHz, $CDCl_3$/TMS): δ (ppm) = 1.10–2.02 (m, —$(CH_2)_5$—), 1.27 (t, J = 7 Hz, CH_3), 2.78 (s, NCH_2CO), 2.89 (q, J = Hz, NCH_2CH_3), 7.13–7.38 (m, 3 aromatic H), 7.63–7.81 (m, 2 aromatic H). Anal. calcd. for $C_{15}H_{22}BNO_2$: C 69.52, H 8.56, B 4.17, N 5.40; found: C 69.49, H 8.60, B 4.16, N 5.31.

4-Cyclohexyl-2-phenyl-1,3-dioxa-4-aza-2-boracyclohexane (5g)

3*g* (0.80 g, 5 mmol) and phenylboronic acid (0.61 g, 5 mmol) are reacted as described for **4***a*. The residue was crystallized from absolute ethanol. Yield: 0.82 g (67%) of colorless crystals. Mp 73°C. Infrared (KBr): 1605 cm^{-1} (phenyl C═C). ^{1}H nmr (90 MHz, $CDCl_3$/TMS): δ (ppm) = 0.92–2.32 (m, —$(CH_2)_5$—), 2.45–2.82 (m, NCH(C,C)), 3.02 (t, J = 4 Hz, NCH_2), 4.13 (t, J = 4 Hz, OCH_2), 7.10–7.38 (m, 3 aromatic H), 7.57–7.71 (m, 2 aromatic H). Anal. calcd. for $C_{14}H_{20}BNO_2$: C 68.60, H 8.22, N 5.71; found: C 68.63, H 8.37, N 5.78.

4-Cyclohexylmethyl-6,6-pentamethylene-2-phenyl-1,3-dioxa-4-aza-2-boracyclohexane (5h)

3*h* (0.72 g, 3 mmol) and phenylboronic acid (0.37 g, 3 mmol) are reacted as described for **4***a*. The residue was crystallized from absolute ethanol. Yield: 0.69 g (70%) of colorless crystals. Mp 81°C. Infrared (KBr): 1600 cm^{-1} (phenyl C═C). ^{1}H nmr (90 MHz, $CDCl_3$/TMS): δ (ppm) = 0.79–2.03 (m, C_6H_{11} and —$(CH_2)_5$—), 2.63 (d, J = 7 Hz, $NCH_2C_6H_{11}$), 2.75 (s, NCH_2CO), 7.17–7.37 (m, 3 aromatic H), 7.60–7.81 (m, 2 aromatic H). ^{11}B nmr (64.2 MHz, $CDCl_3$/Et_2OBF_3): δ (ppm) = 27.5 ($w_{1/2}$ = 420 Hz). Anal. calcd. for $C_{20}H_{30}BNO_2$: C 73.40, H 9.24, N 4.28; found: C 73.45, H 9.31, N 4.49.

4-Benzyl-5,5-dimethyl-2-phenyl-1,3-dioxa-4-aza-2-boracyclohexane (5i)

3*i* (0.20 g, 1 mmol) and phenylboronic acid (0.12 g, 1 mmol) are reacted as described for **4***a*. The residue was crystallized from absolute ethanol. Yield: 0.20 g (71%) of colorless platelets. Mp 86–87°C. Infrared (KBr): 1600 cm^{-1} (phenyl C═C). ^{1}H nmr (90 MHz, $CDCl_3$/TMS): δ (ppm) = 1.26 (s, 2 CH_3), 3.88 (s, NCH_2CH_2O), 7.19–7.45 (m, 8 aromatic H), 7.53–7.71 (m, 2 aromatic H). ^{11}B nmr (64.2 MHz, $CDCl_3$/Et_2OBF_3): δ (ppm) = 27.5 ($w_{1/2}$ = 360 Hz). Anal. calcd. for $C_{17}H_{20}BNO_2$: C 72.62, H 7.17, N 4.98; found: C 72.61, H 7.21, N 4.99.

4-Benzyl-5,5,6-trimethyl-2-phenyl-1,3-dioxa-4-aza-2-boracyclohexane (5j)

3*j* (0.21 g, 1 mmol) and phenylboronic acid (0.12 g, 1 mmol) are reacted as described for **4***a*. The residue was crystallized from absolute ethanol. Yield: 0.25 g (85%) of colorless crystals. Mp 97°C. Infrared (KBr): 1600 cm^{-1} (phenyl C═C). ^{1}H nmr (90 MHz, $CDCl_3$/TMS): δ (ppm) = 1.15 and 1.25 (s and s, $C(CH_3)_2$), 1.36 (d, J = 6 Hz, CH_3CO), 3.92 (s, NCH_2), 4.11 (q, J = 6 Hz, OCH), 7.13–7.46 (m, 8 aromatic H), 7.52–7.72 (m, 2 aromatic H). Anal. calcd. for $C_{18}H_{22}BNO_2$: C 73.24, H 7.51, N 4.75; found: C 73.30, H 7.51, N 4.80.

4-Benzyl-6,6-pentamethylene-2-phenyl-1,3-dioxa-4-aza-2-boracyclohexane (5k)

3*k* (0.54 g, 2 mmol) and phenylboronic acid (0.24 g, 2 mmol) are reacted as described for **4***a*. The residue was crystallized from benzene/petroleum ether. Yield: 0.59 g (92%) of colorless crystals. Mp 76–78°C. Infrared (KBr): 1600 cm^{-1} (phenyl C═C). ^{1}H nmr (90 MHz, $CDCl_3$/TMS): δ (ppm) = 1.01–2.04 (m, —$(CH_2)_5$—), 2.78 (s, NCH_2CO), 4.04 (s, NCH_2Ph), 7.12–7.47 (m, 8 aromatic H), 7.62–7.81 (m, 2 aromatic H). ^{11}B nmr (64.2 MHz, $CDCl_3$/Et_2OBF_3): δ (ppm) = 27.5 ($w_{1/2}$ = 380 Hz). Anal. calcd. for $C_{20}H_{24}BNO_2$: C 74.78, H 7.53, N 4.26; found: C 74.75, H 7.61, N 4.26.

4-(4-Chlorophenylmethyl)-6,6-pentamethylene-2-phenyl-1,3-dioxa-4-aza-2-boracyclohexane (5l)

3*l* (0.27 g, 1 mmol) and phenylboronic acid (0.12 g, 1 mmol) are reacted as described for **4***a*. The residue was crystallized from absolute ethanol/ether. Yield: 0.33 g (92%) of colorless crystals. Mp 86°C. Infrared (KBr): 1600 cm^{-1} (phenyl C═C). ^{1}H nmr (90 MHz, $CDCl_3$/TMS): δ (ppm) = 1.04–2.05 (m, —$(CH_2)_5$—), 2.76 (s, NCH_2CO), 4.00 (s, $CH_2C_6H_4Cl$), 7.11–7.38 (m, 7 aromatic H), 7.57–7.78 (m, 2 aromatic H). ^{11}B nmr (64.2 MHz, $CDCl_3$/Et_2OBF_3): δ (ppm) = 28.3 ($w_{1/2}$ = 430 Hz). Anal. calcd. for $C_{20}H_{23}BClNO_2$: C 67.54, H 6.52, B 3.04, Cl 9.97, N 3.94; found: C 67.37, H 6.63, B 3.18, Cl 9.88, N 3.82. Crystals suitable for X-ray analysis were obtained by slow recrystallization from ethanol (99.5%).

4-(4-Nitrophenylmethyl)-5,5-dimethyl-2-phenyl-1,3-dioxa-4-aza-2-boracyclohexane (5m)

3*m* (0.24 g, 1 mmol) and phenylboronic acid (0.12 g, 1 mmol) are reacted as described for **4***a*. The residue was crystallized from absolute ethanol. Yield: 0.26 g (79%) of yellowish crystals. Mp 94°C. Infrared (KBr): 1605, 1600 (aryl C═C), 1515 cm^{-1} (NO_2). ^{1}H nmr (400 MHz, $CDCl_3$/TMS): δ (ppm) = 1.22 (s, $C(CH_3)_2$), 3.90 (s, OCH_2), 4.01 (s, NCH_2), 7.18–7.40 (m, 3 aromatic H), 7.56–7.61 (m, 2 aromatic H), 7.64 and 8.25 (d, and d, J = 9 Hz, AA′BB′ system, $C_6H_4NO_2$). ^{11}B nmr (64.2 MHz, $CDCl_3$/Et_2OBF_3): δ (ppm) = 27.6 ($w_{1/2}$ = 380 Hz). EI mass spectrum (70 eV): m/z = 326 (58%, M^+), 311 (100%, $M^+ - CH_3$), 240 (5%), 191 (26%), 136 (62%, $CH_2C_6H_4NO_2$), 120 (64%), 106 (16%), 90 (14%), 78 (22%).

4-(4-Nitrophenylmethyl)-6,6-pentamethylene-2-phenyl-1,3-dioxa-4-aza-2-boracyclohexane (5n)

3*n* (0.56 g, 2 mmol) and phenylboronic acid (0.24 g, 2 mmol) are reacted as described for **4***a*. The residue was crystallized from absolute ethanol. Yield: 0.59 g (80%) of yellowish crystals. Mp 116°C. Infrared (KBr): 1605, 1600 (aryl C═C), 1515 cm^{-1} (NO_2). ^{1}H nmr (90 MHz, $CDCl_3$/TMS): δ (ppm) = 1.21–2.08 (m, —$(CH_2)_5$—), 2.87 (s, NCH_2CO), 4.09 (s, $NCH_2C_6H_4NO_2$), 7.11–7.35 (m, 3 aromatic H), 7.45–7.68 (m, 2 aromatic H), 7.56 and 8.16 (d and d, J = 9 Hz, AA′BB′ system, $C_6H_4NO_2$). ^{11}B nmr (64.2 MHz, $CDCl_3$/Et_2OBF_3): δ (ppm) = 27.9 ($w_{1/2}$ = 390 Hz). Anal. calcd. for $C_{20}H_{23}BN_2O_4$: C 65.59, H 6.33, B 2.95, N 7.65; found: C 65.61, H 6.43, B 3.06, N 7.61.

4-(4-Dimethylaminophenylmethyl)-6,6-pentamethylene-2-phenyl-1,3-dioxa-4-aza-2-boracyclohexane (5o)

3*o* (0.28 g, 1 mmol) and phenylboronic acid (0.12 g, 1 mmol) are reacted as described for **4***a*. The residue was crystallized from absolute ethanol. Yield: 0.30 g (82%) of colorless crystals. Mp 92°C. Infrared (KBr): 1610, 1600 cm^{-1} (aryl C═C). ^{1}H nmr (90 MHz, $CDCl_3$/TMS): δ (ppm) = 1.22–2.01 (m, —$(CH_2)_5$—), 2.75 (s, NCH_2CO), 2.95 (s, $N(CH_3)_2$), 4.01 (s, $NCH_2C_6H_4NMe_2$), 6.69 (d, J = 9 Hz, AA′BB′ system, 2 aromatic H), 7.17–7.42 (m, 5 aromatic H), 7.69–7.86 (m, 2 aromatic H). Anal. calcd. for $C_{22}H_{29}BN_2O_2$: C 72.53, H 8.02, N 7.69; found: C 72.53, H 8.09, N 7.69.

4-Benzhydryl-6-methyl-2-phenyl-1,3-dioxa-4-aza-2-boracyclohexane (5p)

3*p* (0.51 g, 2 mmol) and phenylboronic acid (0.24 g, 2 mmol) are reacted as described for **4***a*. The residue was crystallized from absolute benzene. Yield: 0.51 g (74%) of colorless crystals. Mp 185–186°C. Infrared (KBr): 1600, 1595 cm^{-1} (shoulder, aryl C═C). ^{1}H nmr (90 MHz, $CDCl_3$/TMS): δ (ppm) = 1.30 (d, J = 6 Hz, CH_3), 2.50/2.64 and 3.02/3.15 (d/d and d/d, J = 12/8 Hz, NCH_2), 4.44 (m, OCH), 4.80 (s, $NCHPh_2$), 7.09–7.54 (m, 15 aromatic H). Anal. calcd. for $C_{22}H_{22}BNO_2$: C 76.99, H 6.46, N 4.08; found: C 77.02, H 6.48, N 4.15.

N,N′-*Ethanediylidenebis[1-hydroxycyclohexyl)methylamine]* N,N′-*dioxide (11)*

1-(*N*-Hydroxyaminomethyl)cyclohexanol **10** (5) (1.45 g, 10 mmol) and glyoxal monohydrate (0.38 g, 5 mmol) are dissolved in 20 mL of ethanol. After 1 day at room temperature the solution is partially evaporated in vacuo and cooled down for crystallization which is complete after a few days. Yield: 1.56 g (100%) of colorless crystals. Mp 188–189°C. Infrared (KBr): 3370 (O—H), 1530 cm^{-1} (C—N). ^{1}H nmr (60 MHz, d_6-DMSO/TMS): δ (ppm) = 1.40 (m$_c$, 2 —(CH$_2$)$_5$—), 3.86 (s, 2 NCH$_2$), 4.70 (s, exchangeable, 2 OH), 7.80 (s, N=CH). EI mass spectrum (70 eV, 240°C): *m/z* = 312 (3%, M$^+$), 197 (38%), 156 (19%), 140 (16%), 99 (100% $C_6H_{11}O$), 95 (41%) 81 (63%). Anal. calcd. for $C_{16}H_{28}N_2O_4$: C 61.51, H 9.03, N 8.96; found: C 61.19, H 9.02, N 8.93.

N,N′-*Dihydroxy*-N,N′-*bis(1-hydroxycyclohexylmethyl)methanediamine (12)*

1-*N*-Hydroxyaminomethyl)cyclohexanol **10** (5) (0.28 g, 2 mmol) and formaldehyde (0.1 g 35% aqueous solution, 1 mmol) are dissolved in 20 mL ethanol and stored at room temperature for 1 day. After evaporation in vacuo the residue is crystallized from benzene. Yield: 0.28 g (93%) of colorless crystals. Mp 104–105C. ^{1}H nmr (100 MHz, CDCl$_3$/TMS)[6]: δ (ppm) = 1.2–2.9 (m, 2 —(CH$_2$)$_5$—), 2.75 (s, 44% of NCH$_2$CO of **12**), 2.94 (s, 56% of NCH$_2$ of **10**), 3.63 (s, 44% of NCH$_2$N of **12**), 3.76 (s, 56% of NCH$_2$CO of the formaldehyde nitrone of **10**; cf. footnote 2), 4.3–4.9 (m, broad, exchangeable, 4 OH), 6.41 (q, AB system, 56% of N=CH$_2$ of the formaldehyde nitrone of **10**). EI mass spectrum (70 eV, 120C): *m/z* = 157 (100%, $H_2C{=}N(O)CH_2C(OH)(CH_2)_5$=formaldehyde nitrone of **10**), 140 (41%), 139 (55%), 127 (67%), 114 (39%), 112 (49%), 99 (73%, $C_6H_{11}O$), 95 (82%), 81 (95%). Molecular mass (cryoscopic determination in CHCl$_3$): 157 (formaldehyde nitrone of **10**, see footnote 2). Anal. calcd. for $C_{15}H_{30}N_2O_4$: C 59.57, H 9.99, N 9.26; found: C 59.17, H 9.90, N 9.10. Determination of the formaldehyde content (gravimetrically with dimedone (10)), after hydrolysis: calcd. for **12**: 10%; found: 12%.

N,N′-*Dihydroxy*-N,N′-*bis(1-hydroxycyclohexylmethyl)-1,2-ethanediamine (13)*

11 (3.12 g, 10 mmol) and LiAlH$_4$ (0.76 g, 20 mmol) are suspended in 100 mL of dry ether and refluxed for 6 h. After 24 h stirring at room temperature the reaction mixture is hydrolyzed with water and ice-cooling, and subsequently mixed with 6N HCl until the Al(OH)$_3$ precipitate redissolves. The mixture is brought to pH 7–8 using NaHCO$_3$ and the solid product that forms in the layer between the two phases is separated. The ether phase is dried over Na$_2$SO$_4$ and evaporated in vacuo. The residue is combined with the previously separated product. Yield: 1.77 g (56%) of colorless crystals. Mp 153°C (from absolute ethanol). Infrared (KBr): 3460, 3160 cm^{-1} (O—H). ^{1}H nmr (90 MHz, d_6-DMSO/TMS): δ (ppm) = 1.50 (m, 2 —(CH$_2$)$_5$—), 2.60 (s, 2, NCH$_2$CO), 2.81 (s, NCH$_2$CH$_2$N), 3.89 (s, exchangeable, 2 OH), 7.77 (s, exchangeable, 2 OH). Anal. calcd. for $C_{16}H_{32}N_2O_4$: C 60.73, H 10.19, N 8.85; found: C 60.47, H 10.39, N 8.61.

4,4′-Methylenebis(6,6-pentamethylene-2-phenyl-1,3-dioxa-4-aza-2-boracyclohexane) (15a)

12 (0.60 g, 2 mmol) and phenylboronic acid (0.49 g, 4 mmol) are dissolved in 20 mL of benzene and refluxed for 1 h with continuous removal of water using a Dean-Stark trap. The solvent is partially (about 1/2 of the volume) distilled off, and after the addition of petroleum ether the solution is stored at −18°C. The crystallization (after a few days) yields 0.52 g (55%) of colorless crystals which are recrystallized from ethanol. Mp 78–81°C. Infrared (KBr): 1600 cm^{-1} (phenyl C=C). ^{1}H nmr (90 MHz, CDCl$_3$/TMS): δ (ppm) = 1.14–2.04 (m, 2 —(CH$_2$)$_5$—), 3.12 (s, 2 NCH$_2$CO), 4.17 (s, NCH$_2$N), 7.18–7.42 (m, 6 aromatic H), 7.62–7.81 (m, 4 aromatic H). ^{11}B nmr (64.2 MHz, CDCl$_3$/Et$_2$OBF$_3$): δ (ppm) = 27.5 ($w_{1/2}$ = 640 Hz). EI mass spectrum (70 eV, 150°C); *m/z* = 474 (0.7%, M$^+$), 244 (100%, M$^+$ − PhB[ONCH$_2$C(CH$_2$)$_5$O]) 140 (2%), 105 (3%, PhBOH), 95 (6%), 81 (3%). Anal. calcd. for $C_{27}H_{36}B_2N_2O_4$: C 68.39, H 7.65, N 5.91; found: C 68.50, H 7.74, N 6.04

Crystals suitable for X-ray analysis were obtained by recrystallization from benzene/petroleum ether, and contain 1 mol of benzene. Mp 55–56°C. The ^{1}H nmr spectrum of **15***a*·C$_6$H$_6$ in CDCl$_3$ (TMS) shows an additional signal: δ (ppm) = 7.31 (s, 6 aromatic H). Anal. calcd. for $C_{27}H_{36}B_2N_2O_4{+}C_6H_6$: C 71.76, H 7.67, B 3.91, N 5.07; found: C 71.47, H 7.78, B 3.83, N 4.99.

4,4′-Methylenebis[2-(4-methoxyphenyl)-6,6-pentamethylene-1,3-dioxa-4-aza-2-boracyclohexane] (15b)

12 (0.30 g, 1 mmol) and 4-methoxyphenylboronic acid (0.30 g, 2 mmol) are reacted as described for **15***a*. Yield: 0.45 g (84%) of colorless crystals. Mp 134–135°C (from benzene/petroleum ether). Infrared (KBr): 1600 cm^{-1} (slightly broadened, aryl C=C). ^{1}H nmr (90 MHz, CDCl$_3$/TMS): δ (ppm) = 1.15–2.03 (m, 2 —(CH$_2$)$_5$—), 3.10 (s, 2 NCH$_2$CO), 3.78 (s, 2 OCH$_3$), 4.15 (s, NCH$_2$N), 6.82 and 7.65 (d, and d, *J* = 8 Hz, AA′BB′ system, 8 aromatic H), EI mass spectrum (70 eV, 125°C): *m/z* = 534 (0.2%, M$^+$), 274 (100%, M$^+$ − 4-MeOC$_6$H$_4$-BOCH$_2$C(CH$_2$)$_5$O), 134 (8%, 4-MeOC$_6$H$_4$BO), 124 (6%), 95 (16%), 81 (4%). Anal. calcd. for $C_{29}H_{40}B_2N_2O_6$: C 65.20, H 7.55, N 5.24, found: C 65.25, H 7.67, N 5.30.

4,4′-Ethylenebis(6,6-pentamethylene-2-phenyl-1,3-dioxa-4-aza-2-boracyclohexane) (16a)

13 (0.32 g, 1 mmol) and phenylboronic acid (0.24 g, 2 mmol) are dissolved in 50 mL of benzene and refluxed for 10 min. Crystallization commences in the boiling solution and is complete after cooling down to room temperature. The precipitate is separated and recrystallized. Yield: 0.46 g (94%) of colorless crystals. Mp 169°C (from CHCl$_3$/petroleum ether). Infrared (KBr): 1600 cm^{-1} (phenyl C=C). ^{1}H nmr (90 MHz, CDCl$_3$/TMS): δ (ppm) = 1.14–2.11 (m, 2 —(CH$_2$)$_5$—), 2.92 (s, 2 NCH$_2$CO), 3.29 (s, NCH$_2$CH$_2$N), 7.13–7.41 (m, 6 aromatic H), 7.63–7.82 (m, 4 aromatic H). ^{11}B nmr (64.2 MHz, CDCl$_3$/Et$_2$OBF$_3$): δ (ppm) = 28.9 ($w_{1/2}$ = 640 Hz). EI mass spectrum (70 eV, 125°C): *m/z* = 488 (0.1%, M$^+$), 411 (14%, M$^+$ − C$_6$H$_5$), 393 (7%), 285 (4%), 258 (6%), 244 (100%, 1/2 M$^+$), 228 (4%), 168 (6%), 140 (8%), 105 (5%, PhBOH), 95 (18%) 81 (4%). Anal. calcd. for $C_{28}H_{38}B_2N_2O_4$: C 68.88, H 7.85, B 4.43, N 5.74; found: C 68.71, H 7.95, B 4.60, N 5.62.

4,4′-Ethylenebis[2-(2-methylphenyl)-6,6-pentamethylene-1,3-dioxa-4-aza-2-boracyclohexane] (16b)

13 (0.32 g, 1 mmol) and 2-methylphenylboronic acid (0.27 g, 2 mmol) are reacted as described for **16***a*. Yield: 0.47 g (86%) of colorless small needles. Mp 145–146°C (from CHCl$_3$/petroleum ether). Infrared (KBr): 1600 cm^{-1} (aryl C=C). ^{1}H nmr (90 MHz, CDCl$_3$/TMS): δ (ppm) = 1.07–2.08 (m, 2 —(CH$_2$)$_5$—), 2.53 (s, 2 CH$_3$), 2.92 (s, 2 NCH$_2$CO), 3.27 (s, NCH$_2$CH$_2$N), 6.89–7.32 (m, 6 aromatic H), 7.61–7.78 (m, 2 aromatic H). ^{11}B nmr (64.2 MHz, CDCl$_3$/Et$_2$OBF$_3$): δ (ppm) = 28.1 ($w_{1/2}$ = 640 Hz). Anal. calcd. for $C_{30}H_{42}B_2N_2O_4$: C 69.79, H 8.20, B 4.19, N 5.43; found: C 69.79, H 8.40, B 4.24, N 5.33.

4,4′-Ethylenebis[2-(1-naphthyl)-6,6-pentamethylene-1,3-dioxa-4-aza-2-boracyclohexane] (16c)

13 (0.32 g, 1 mmol) and 1-naphthylboronic acid (0.35 g, 2 mmol) are reacted as described for **16***a*. Yield: 0.58 g (91%) of colorless crystals. Mp 189–200°C (from CHCl$_3$/petroleum ether). Infrared (KBr): 1595, 1580 cm^{-1} (weak, strong, aryl C=C). ^{1}H nmr (90 MHz, CDCl$_3$/TMS): δ (ppm) = 1.01–2.12 (m, 2 —(CH$_2$)$_5$—), 3.02 (s, 2 NCH$_2$CO), 3.37 (s, NCH$_2$CH$_2$N), 7.22–7.52 (m, 6 aromatic H), 7.63–8.04 (m, 6 aromatic H), 8.56–8.80 (m, 2 aromatic H). ^{11}B nmr (64.2 MHz, CDCl$_3$/Et$_2$OBF$_3$): δ (ppm) = 27.7 ($w_{1/2}$ = 640 Hz). Anal. calcd. for $C_{36}H_{42}B_2N_2O_4$: C 73.49, H 4.76, B 3.67, N 4.76; found: C 73.56, H 7.49, B 3.65, N 4.84.

X-ray crystallographic analysis of 5l and 15a·C$_6$H$_6$

Crystallographic data appear in Table 1. The final unit-cell parameters were obtained by least-squares on the setting angles for 25 reflections with 2θ = 36.1–38.9° for **5***l* and 56.6–82.3° for **15***a*. The

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[6] In solution (CDCl$_3$) the aminal **12** dissociates into the hydroxylamine **10** and the formaldehyde nitrone of **10** (see footnote 2).

TABLE 1. Crystallographic data[a]

Compound	**5*l***	**15*a***·C_6H_6
Formula	$C_{20}H_{23}BClNO_2$	$C_{33}H_{42}B_2N_2O_4$
fw	355.67	552.33
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$
a, Å	11.540(2)	22.690(1)
b, Å	10.402(3)	16.867(1)
c, Å	8.440(2)	8.4783(9)
α, deg	108.86(2)	90
β, deg	97.62(2)	104.912(8)
γ, deg	89.36(2)	90
V, Å^3	949.8(4)	3135.6(4)
Z	2	4
ρ_{calc}, g/cm^3	1.244	1.170
F(000)	376	1184
Radiation	Mo-K_α	Cu-K_α
μ, cm^{-1}	2.13	5.59
Crystal size, mm	0.30 × 0.45 × 0.50	0.30 × 0.30 × 0.35
Transmission factors (relative)	0.89–1.00	0.95–1.00
Scan type	ω–2θ	ω–2θ
Scan range, deg in ω	1.30 + 0.35 tan θ	1.00 + 0.20 tan θ
Scan speed, deg/min	32	32
Data collected	$\pm h$, $+k$, $\pm l$,	$+h$, $+k$, $\pm l$
$2\theta_{max}$, deg	60	155
Crystal decay, %	2.6	2.8
Total reflections	5821	3536
Total unique reflections	5529	3450
R_{merge}	0.019	0.018
Reflections with $I \geq 3\sigma(I)$	3190	2084
No. of variables	318	215
R	0.037	0.035
R_w	0.035	0.044
gof	2.70	1.64
Maximum Δ/σ (final cycle)	0.0003	0.09
Residual density e/Å^3	−0.29 to 0.17	−0.10 to 0.17

[a] Temperature 294 K, Rigaku AFC6S diffractometer, Mo-K_α (λ = 0.71069 Å) or Cu-K_α (λ = 1.54178 Å) radiation, graphite monochromator, takeoff angle 6.0°, aperture 6.0 × 6.0 mm at a distance of 285 mm from the crystal, stationary background counts at each end of the scan (scan/background time ratio 2:1, up to 8 rescans), $\sigma^2(F^2) = [S^2(C + 4B)]/\mathrm{Lp}^2$ (S = scan rate, C = scan count, B = normalized background count), function minimized $\Sigma w(|F_o| - |F_c|)^2$ where $w = 4F_o^2/\sigma^2(F_o^2)$, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$, and gof $= [\Sigma w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$. Values given for R, R_w, and gof are based on those reflections with $I \geq 3\sigma(F^2)$.

intensities of three standard reflections, measured every 200 reflections throughout the data collections, decayed linearly by 2.6% and 2.8% for **5*l*** and **15*a***, respectively. The data were processed,[7] corrected for Lorentz and polarization effects, decay and absorption (empirical, based on azimuthal scans for three reflections).

The structures were solved by direct methods, the coordinates of the non-hydrogen atoms being determined from an E-map or from subsequent difference Fourier syntheses. The structure analysis of **15*a***·C_6H_6 was initiated in the centrosymmetric space group $C2/c$ on the basis of the E-statistics. This choice was confirmed by the subsequent successful solution and refinement of the structure. The **15*a*** molecule has exact C_2 symmetry. The benzene solvate molecule in **15*a***·C_6H_6 is twofold disordered about a crystallographic C_2 axis. A split-atom anisotropic model was employed, the site occupancy factors being adjusted as the refinement progressed to result in approximately equal thermal parameters for the two components of the disorder. Non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms of **5*l*** were refined with isotropic thermal parameters and those of **15*a***·C_6H_6 were fixed in idealized positions (C—H = 0.98 Å, $B_H = 1.2B_{\text{bonded atom}}$). A correction for secondary extinction was applied for **15*a***·C_6H_6, the final value of the extinction coefficient being 6.13(6) × 10^{-6}. Neutral atom scattering factors for all atoms (11*a*) and anomalous dispersion corrections for the non-hydrogen atoms (11*b*) were taken from the International tables for X-ray crystallography. Final atomic coordinates and equivalent isotropic thermal parameters, bond lengths, bond angles, and intra-annular torsion angles appear in Tables 2–5, respectively. Stereoviews of the **5*l*** and **15*a*** molecules are shown in Figs. 2 and 3, respectively. Hydrogen atom parameters, anisotropic thermal parameters, torsion angles, intermolecular contacts, and least-squares planes are included as supplementary material.[8] Measured and calculated structure factor amplitudes are available from the authors.

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[7] *teXsan*: Crystal structure analysis package. Molecular Structure Corp. The Woodlands, TX. 1985 & 1992.

[8] Supplementary material mentioned in the text may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2, Canada.

Tables of hydrogen atom coordinates and bond lengths and angles involving hydrogen atoms have also been deposited with the Cambridge Crystallographic Data Centre and can be obtained on request from The Director, Cambridge Crystallographic Data Centre, University Chemical Laboratory, 12 Union Road, Cambridge CB2 1EZ, UK.

TABLE 2. Final atomic coordinates (fractional) and B_{eq} (Å^2)^a

Atom	x	y	z	B_{eq}	Occupancy
		5*l*			
Cl(1)	−0.11091(5)	−0.36876(5)	0.19633(7)	5.91(2)	
O(1)	0.26241(10)	0.17706(10)	0.42123(13)	4.04(4)	
O(2)	0.32724(9)	0.41041(9)	0.55526(12)	3.47(4)	
N(1)	0.18641(11)	0.21676(12)	0.2932(2)	3.71(5)	
C(1)	0.2497(2)	0.3242(2)	0.2604(2)	3.88(6)	
C(2)	0.26699(13)	0.45020(14)	0.4165(2)	3.34(5)	
C(3)	0.15170(15)	0.5109(2)	0.4673(2)	4.15(6)	
C(4)	0.1687(2)	0.6412(2)	0.6176(3)	4.87(8)	
C(5)	0.2431(2)	0.7458(2)	0.5832(3)	5.07(8)	
C(6)	0.3605(2)	0.6880(2)	0.5366(3)	4.51(7)	
C(7)	0.3455(2)	0.5555(2)	0.3892(2)	4.00(7)	
C(8)	0.1740(2)	0.0932(2)	0.1461(2)	4.27(7)	
C(9)	0.10617(14)	−0.0201(2)	0.1701(2)	3.70(6)	
C(10)	0.0168(2)	0.0025(2)	0.2688(2)	4.21(6)	
C(11)	−0.0492(2)	−0.1028(2)	0.2800(2)	4.34(7)	
C(12)	−0.0262(2)	−0.2341(2)	0.1895(2)	4.03(6)	
C(13)	0.0625(2)	−0.2603(2)	0.0921(3)	5.43(8)	
C(14)	0.1283(2)	−0.1530(2)	0.0833(3)	5.12(8)	
C(15)	0.39793(13)	0.23310(15)	0.6895(2)	3.34(5)	
C(16)	0.4171(2)	0.0966(2)	0.6663(2)	4.54(7)	
C(17)	0.4861(2)	0.0554(2)	0.7862(3)	5.49(8)	
C(18)	0.5366(2)	0.1489(2)	0.9323(3)	5.15(8)	
C(19)	0.5176(2)	0.2840(2)	0.9613(3)	5.89(9)	
C(20)	0.4498(2)	0.3251(2)	0.8393(2)	5.08(8)	
B(1)	0.3246(2)	0.2787(2)	0.5492(2)	3.34(6)	
		15*a*·C_6H_6			
O(1)	0.06953(5)	0.15335(6)	0.50190(11)	4.56(4)	
O(2)	0.14930(4)	0.25083(6)	0.57213(11)	4.11(4)	
N(1)	0.04100(6)	0.20244(7)	0.36261(14)	4.18(5)	
C(1)	0	0.14930(13)	1/4	4.9(1)	0.50
C(2)	0.08913(7)	0.23397(9)	0.2963(2)	4.46(7)	
C(3)	0.12768(7)	0.29180(9)	0.4168(2)	3.91(6)	
C(4)	0.09083(7)	0.36352(9)	0.4441(2)	4.28(6)	
C(5)	0.12992(8)	0.42369(9)	0.5588(2)	4.83(7)	
C(6)	0.18379(8)	0.45017(10)	0.4962(2)	5.49(8)	
C(7)	0.22171(7)	0.37926(11)	0.4721(2)	5.32(8)	
C(8)	0.18344(7)	0.31746(10)	0.3617(2)	4.80(7)	
C(9)	0.14368(7)	0.14208(8)	0.7731(2)	3.87(6)	
C(10)	0.11015(8)	0.08161(9)	0.8196(2)	4.92(7)	
C(11)	0.12929(9)	0.04439(10)	0.9695(2)	5.92(9)	
C(12)	0.18281(10)	0.06747(11)	1.0765(2)	5.94(9)	
C(13)	0.21714(8)	0.12649(11)	1.0343(2)	5.69(8)	
C(14)	0.19775(7)	0.16351(10)	0.8837(2)	4.82(7)	
B(1)	0.12007(8)	0.18557(10)	0.6063(2)	3.85(7)	
C(15)	1/2	0.2360(13)	1.2500	7.0(5)	0.335
C(16)	0.4508(5)	0.2012(9)	1.1510(13)	6.5(3)	0.67
C(17)	0.4529(3)	0.1167(3)	1.1517(10)	7.5(5)	0.67
C(18)	1/2	0.0785(11)	1.2500	12(2)	0.335
C(15a)	0.4755(14)	0.216(2)	1.202(4)	16(3)	0.33
C(16a)	0.4483(8)	0.1534(7)	1.141(2)	7.6(8)	0.33
C(17a)	0.4808(10)	0.0778(13)	1.185(3)	6.3(7)	0.33

$^a B_{eq} = (8/3)\pi^2\Sigma\Sigma U_{ij}a_i{}^*a_j{}^*(\boldsymbol{a}_i\cdot\boldsymbol{a}_j)$.

Results and discussion

The X-ray analyses of **5*l*** and **15*a*** both confirm the presence of six-membered cycloboronate ring systems (Figs. 2 and 3). In each case a trigonal planar sp^2-hybridized boron atom forms part of the planar portion of the six-membered heterocycle that has a "sofa" (semiplanar) conformation, typical for this type of cyclic boronic ester. This 1,3-dioxa-4-aza-2-boracyclohexane ring type has so far only been found for *N*-*un*substituted derivatives having bulky enough (e.g. mesityl) *B*-aryl groups (3), or for *N*-acyl derivatives (2). Thus, **5*l*** and **15*a*** are the first examples of *N*-alkyl derivatives of this type of boron heterocycle to be characterized in the solid state by X-ray crystallography.

The other *N*-alkyl derivatives of the types **5**, **15**, and **16** can generally be assumed to possess similar cycloboronate moieties with trivalent sp^2 boron atoms. The *N*-methyl derivative **5*d***, however, appears to have a dimeric structure **8** with twofold

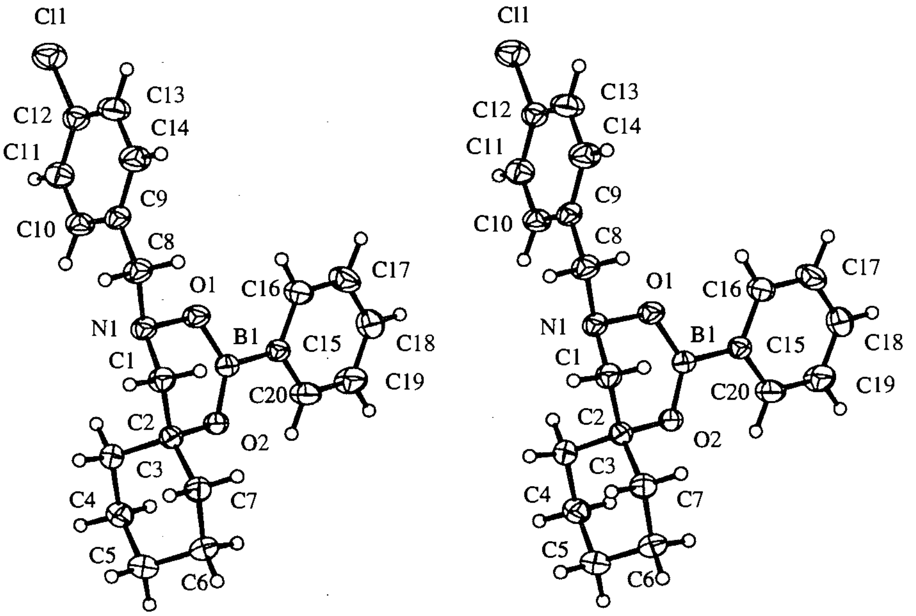

FIG. 2. Stereoview of 5*l*; 33% probability thermal ellipsoids are shown for the non-hydrogen atoms.

TABLE 3. Bond lengths (Å) with estimated standard deviations[a]

Atoms	Distance	Atoms	Distance
		5*l*	
Cl(1)—C(12)	1.738(2)	C(8)—C(9)	1.503(2)
O(1)—N(1)	1.462(2)	C(9)—C(10)	1.382(2)
O(1)—B(1)	1.369(2)	C(9)—C(14)	1.379(2)
O(2)—C(2)	1.456(2)	C(10)—C(11)	1.375(2)
O(2)—B(1)	1.354(2)	C(11)—C(12)	1.375(2)
N(1)—C(1)	1.460(2)	C(12)—C(13)	1.367(3)
N(1)—C(8)	1.463(2)	C(13)—C(14)	1.384(3)
C(1)—C(2)	1.521(2)	C(15)—C(16)	1.388(2)
C(2)—C(3)	1.520(2)	C(15)—C(20)	1.379(2)
C(2)—C(7)	1.521(2)	C(15)—B(1)	1.560(2)
C(3)—C(4)	1.521(3)	C(16)—C(17)	1.379(2)
C(4)—C(5)	1.516(3)	C(17)—C(18)	1.361(3)
C(5)—C(6)	1.524(3)	C(18)—C(19)	1.367(3)
C(6)—C(7)	1.522(2)	C(19)—C(20)	1.385(2)
		15*a*·C_6H_6	
O(1)—N(1)	1.451(1)	C(9)—C(14)	1.387(2)
O(1)—B(1)	1.368(2)	C(9)—B(1)	1.561(2)
O(2)—C(3)	1.456(2)	C(10)—C(11)	1.384(2)
O(2)—B(1)	1.354(2)	C(11)—C(12)	1.372(2)
N(1)—C(1)	1.457(2)	C(12)—C(13)	1.368(2)
N(1)—C(2)	1.452(2)	C(13)—C(14)	1.387(2)
C(2)—C(3)	1.517(2)	C(15)—C(16)	1.35(1)
C(3)—C(4)	1.522(2)	C(16)—C(17)	1.43(2)
C(3)—C(8)	1.520(2)	C(17)—C(18)	1.34(1)
C(4)—C(5)	1.523(2)	C(15a)—C(15a)″	1.20(6)
C(5)—C(6)	1.520(2)	C(15a)—C(16a)	1.27(4)
C(6)—C(7)	1.518(2)	C(16a)—C(17a)	1.47(3)
C(7)—C(8)	1.516(2)	C(17a)—C(17a)″	1.22(6)
C(9)—C(10)	1.389(2)		

[a] Primes and double primes refer (here and elsewhere) to symmetry operations: $-x$, $-y$, $1 - z$ and double primes: $1 - x$, $-y$, $2 - z$.

N→B coordination like that reported for the homologue **8** ($R = R^1 = CH_3$, $R^2 = R^3 = R^4 = H$) (1), at least for the solid state (cf. footnote 5). The other *N*-methyl compound, **5*e***, could not be obtained in crystalline form. Nevertheless, it seems that a small *N*-substituent, such as the methyl group in **5*d*** or in its previously reported homologue (1), and at least one ring C—H group (R^1 and/or R^2 = H) are necessary for the formation of the dimer **8**, stabilized by a pair of transannular C—H···O interactions in the solid state (1).

Some of the *N*-alkylhydroxylaminoalkanols **3** were observed to react preferentially with 2 mol of phenylboronic acid to give the bicyclic pyroboronates **4**, no matter what molar ratio of **3** and phenylboronic acid was applied (1). As already mentioned (1), it is not yet understood which competitive factors control of formation of the crystalline product, either **4** or **5**, out of the reaction equilibrium during the condensation of **3** and phenylboronic acid.

The six-membered BONCCO rings in **5*l*** and **15*a*** have slightly distorted "sofa" conformations (see Table 5) with C(1) and C(2) on the flaps, respectively. The five-atom BONCCO ring segments (excluding the carbon atoms on the flaps) are planar to within 0.071(2) Å for **5*l*** and 0.091(2) Å for **15*a***. Both compounds display a minor deviation from co-planarity of the *B*-phenyl ring and the planar O—B—O ring segment of the BONCCO heterocycle (the angles between normals to the boron coordination group and phenyl ring mean planes are 13.1° for **5*l*** and 7.7° for **15*a***). The B—C(phenyl) bond lengths of 1.560(2) Å for **5*l*** and 1.561(2) Å for **15*a*** are similar to those observed for other related phenylboronates. The boron coordination group is planar within experimental error in **15*a***, while that in **5*l*** shows a small (but statistically significant) deviation from planarity (maximum displacement 0.012(2) Å for B, χ^2 = 51.0 for CBO_2).

The N—O bonds in both compounds (**5*l***: 1.462(2) Å, **15*a***: 1.451(1) Å) are comparable to those in the *N*-unsubstituted mesitylboronate (3) (1.46(1) and 1.469(9) Å) that has a similar BONCCO ring system, but are considerably longer than those in the *N*-acyl derivatives (2) (1.402(3) and 1.401(1) Å). This difference between the N—O bond lengths is clearly a consequence of the *N*-alkyl substitution in contrast to the electron-withdrawing *N*-acyl substitution. The remaining geometric parameters of the BONCCO ring systems in **5*l*** and **15*a*** are in

TABLE 4. Bond angles (deg) with estimated standard deviations

Atoms	Angle	Atoms	Angle
		5*l*	
N(1)—O(1)—B(1)	117.1(1)	C(10)—C(9)—C(14)	117.6(2)
C(2)—O(2)—B(1)	120.4(1)	C(9)—C(10)—C(11)	121.8(2)
O(1)—N(1)—C(1)	106.7(1)	C(10)—C(11)—C(12)	119.1(2)
O(1)—N(1)—C(8)	103.5(1)	Cl(1)—C(12)—C(11)	120.2(1)
C(1)—N(1)—C(8)	110.9(1)	Cl(1)—C(12)—C(13)	119.2(1)
N(1)—C(1)—C(2)	110.6(1)	C(11)—C(12)—C(13)	120.6(2)
O(2)—C(2)—C(1)	107.8(1)	C(12)—C(13)—C(14)	119.4(2)
O(2)—C(2)—C(3)	108.1(1)	C(9)—C(14)—C(13)	121.4(2)
O(2)—C(2)—C(7)	107.2(1)	C(16)—C(15)—C(20)	116.8(2)
C(1)—C(2)—C(3)	112.4(1)	C(16)—C(15)—B(1)	121.0(1)
C(1)—C(2)—C(7)	110.5(1)	C(20)—C(15)—B(1)	122.2(1)
C(3)—C(2)—C(7)	110.8(1)	C(15)—C(16)—C(17)	121.5(2)
C(2)—C(3)—C(4)	112.5(1)	C(16)—C(17)—C(18)	120.3(2)
C(3)—C(4)—C(5)	111.2(2)	C(17)—C(18)—C(19)	119.9(2)
C(4)—C(5)—C(6)	110.6(2)	C(18)—C(19)—C(20)	119.7(2)
C(5)—C(6)—C(7)	111.8(2)	C(15)—C(20)—C(19)	121.9(2)
C(2)—C(7)—C(6)	113.2(1)	O(1)—B(1)—O(2)	123.8(1)
N(1)—C(8)—C(9)	113.4(1)	O(1)—B(1)—C(15)	115.4(1)
C(8)—C(9)—C(10)	122.9(1)	O(2)—B(1)—C(15)	120.7(1)
C(8)—C(9)—C(14)	119.4(2)		
		15*a*·C_6H_6	
N(1)—O(1)—B(1)	115.1(1)	C(10)—C(9)—C(14)	117.0(1)
C(3)—O(2)—B(1)	120.6(1)	C(10)—C(9)—B(1)	121.1(1)
O(1)—N(1)—C(1)	105.0(1)	C(14)—C(9)—B(1)	121.9(1)
O(1)—N(1)—C(2)	107.5(1)	C(9)—C(10)—C(11)	121.9(2)
C(1)—N(1)—C(2)	112.9(1)	C(10)—C(11)—C(12)	119.6(2)
N(1)—C(1)—N(1)′	104.1(2)	C(11)—C(12)—C(13)	120.0(2)
N(1)—C(2)—C(3)	109.6(1)	C(12)—C(13)—C(14)	120.1(2)
O(2)—C(3)—C(2)	107.8(1)	C(9)—C(14)—C(13)	121.4(2)
O(2)—C(3)—C(4)	108.1(1)	O(1)—B(1)—O(2)	124.0(1)
O(2)—C(3)—C(8)	107.4(1)	O(1)—B(1)—C(9)	115.8(1)
C(2)—C(3)—C(4)	111.7(1)	O(2)—B(1)—C(9)	120.2(1)
C(2)—C(3)—C(8)	111.0(1)	C(16)—C(15)—C(16)″	128(2)
C(4)—C(3)—C(8)	110.7(1)	C(15)—C(16)—C(17)	114(2)
C(3)—C(4)—C(5)	112.0(1)	C(16)—C(17)—C(18)	120(1)
C(4)—C(5)—C(6)	111.2(1)	C(17)—C(18)—C(17)″	122(1)
C(5)—C(6)—C(7)	110.5(1)	C(15a)″—C(15a)—C(16a)	123(1)
C(6)—C(7)—C(8)	111.7(1)	C(15a)—C(16a)—C(17a)	118(2)
C(3)—C(8)—C(7)	113.3(1)	C(16a)—C(17a)—C(17a)″	115(1)

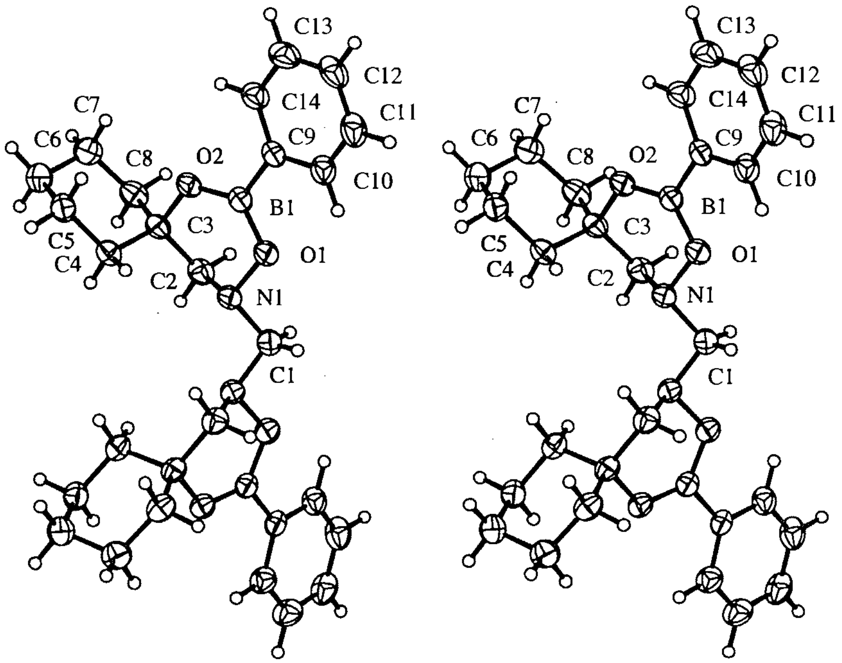

FIG. 3. Stereoview of **15***a* molecule; 33% probability thermal ellipsoids are shown for the non-hydrogen atoms.

TABLE 5. Intra-annular torsion angles (deg) with estimated standard deviations[a]

	Angle	
Atom	**5*l***	**15*a***
B(1)—O(1)—N(1)—C(a)	38.6(2)	44.9(2)
O(1)—N(1)—C(a)—C(b)	−65.4(2)	−67.6(1)
N(1)—C(a)—C(b)—O(2)	56.3(2)	55.0(1)
C(a)—C(b)—O(2)—B(1)	−21.1(2)	−21.1(2)
C(b)—O(2)—B(1)—O(1)	−3.5(2)	0.1(2)
O(2)—B(1)—O(1)—N(1)	−5.9(2)	−11.8(2)
C(g)—C(b)—C(c)—C(d)	−52.9(2)	−53.1(2)
C(b)—C(c)—C(d)—C(e)	56.2(2)	56.4(2)
C(c)—C(d)—C(e)—C(f)	−56.3(2)	−56.6(2)
C(d)—C(e)—C(f)—C(g)	54.7(2)	54.9(2)
C(e)—C(f)—C(g)—C(b)	−53.0(2)	−53.3(2)
C(f)—C(g)—C(b)—C(c)	51.3(2)	51.8(2)

[a] C(a–g) correspond, respectively, to C(1–7) for **5*l***, and to C(2–8) for **15*a***.

good agreement. In both compounds the oxygen substituent, O(2), is situated at an axial position of the spiro-connected cyclohexane ring. The cyclohexane rings in the two compounds have virtually identical, slightly distorted chair conformations (see Table 5).

The **15*a*** molecule has exact C_2 symmetry in the solid state, the twofold axis passing through the central aminal carbon atom C(1). The C—N bonds of the N—C—N (aminal) grouping in **15*a*** (1.457(2) Å) are not significantly different from those reported for the *N,N′*-dihydroxyaminal derived from *N*-methylhydroxylamine that has the same (C,O)N—C—N(C,O) moiety as **15*a*** (N—C = 1.452(3) Å) (12). The N—C—N angle in **15*a***, however, is somewhat compressed (to 104.1(2)°), presumably as a result of crystal packing effects.

The crystal structure of **5*l*** consists of discrete molecules separated by normal van der Waals distances, the shortest intermolecular distance between non-hydrogen atoms being Cl(1)···B(1)(−*x*, −*y*, 1 − *z*) = 3.409(2) Å. Compound **15*a*** crystallizes as a 1:1 benzene solvate with the benzene molecules disordered about a twofold axis (see Experimental). The packing in **15*a***·C_6H_6 is also dominated by van der Waals forces; the shortest distance between non-hydrogen atoms of the structural moieties involves a molecule of **15*a*** and a benzene molecule: B(1)···C(15a) (1/2 − *x*, 1/2 − *y*, 2 − *z*) = 3.45(3) Å.

Acknowledgements

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