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THE N–B COORDINATION IN HINDERED CYCLIC THEXYLBORONIC ESTERS DERIVED FROM DIETHANOLAMINES

ROSALINDA CONTRERAS *, CIRILO GARCÍA, TERESA MANCILLA,

Centro de Investigación y de Estudios Avanzados del I.P.N., Apartado Postal 14-740, 07000-México, D.F. (México)

and BERND WRACKMEYER

Institut für Anorganische Chemie der Universität München, Meiserstr. 1, D-8000 München 2 (Germany)

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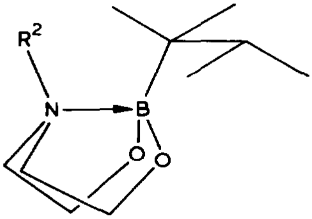
Summary

The reaction between thexylborane and diethanolamines in THF leads to cyclic thexylboronic esters. The intramolecular N–B coordination was demonstrated by dynamic ^{1}H and ^{11}B NMR spectroscopy.

The existence of steric interactions between the N-substituents and the *B*-thexyl group was indicated by the ^{1}H and ^{11}B NMR data.

Cyclic boronic esters derived from diethanolamines and monoalkylboron compounds are stabilized by nitrogen-boron coordination [1]. The N–B bond strength depends strongly on steric effects; bulky substituents at boron or nitrogen tend to weaken the N–B bond [2]. In this context the diethanolamine derivatives of thexylborane are of interest.

In the following, we report the synthesis and the characterization by NMR of the bicyclic structures of thexylboronic esters Ia and Ib.



(Ia, R^2 = H;
Ib, R^2 = CH_3)

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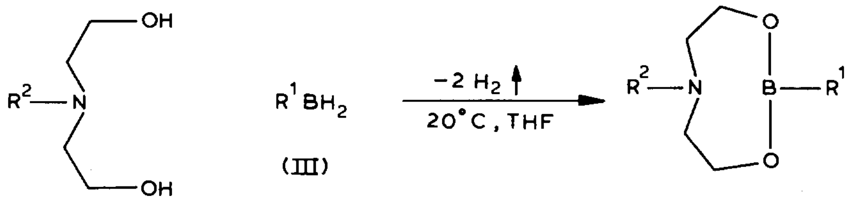
The reaction of diethanolamines (II) with thexylborane in tetrahydrofuran (THF) (III) leads to the heterocycles Ia, Ib, Ic (Scheme 1) from which compounds Ia, Ib, are isolated in the pure state. The NMR data (vide infra) point to intramolecular N–B coordination in Ia, Ib. This interaction appears to be absent in Ic and the difficulty in obtaining this compound in the pure state is reminiscent of the behaviour of other eight-membered cyclic organylboronic esters [3]. Compound Ia can be handled in air at room temperature while Ib and Ic are readily decomposed under the same conditions.

SCHEME 1



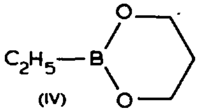
(IIa, R^2 = H;
IIb, R^2 = CH_3;
IIc, R^2 = C_6H_5)

(Ia, R^2 = H;
Ib, R^2 = CH_3;
Ic, R^2 = C_6H_5)

$R^1 = (CH_3)_2CCH(CH_3)_2$

NMR results

The evidence for N–B coordination as shown in Ia, Ib is mainly based on ^1H and ^{11}B NMR data. The ^{11}B chemical shifts are sensitive to the coordination number of the boron atom [4]. The ^{11}B resonances for compounds Ia, Ib are shifted to higher field with respect to Ic and also with respect to 2-ethyl-1,3,2-dioxaborinane (IV), for comparison:

Compound	Ia	Ib	Ic	IV	
$\delta(^{11}B)$ (25°C)	14.0	23.0	30.0	30.5	ppm
Solvent	THF	THF	THF	CH_3CN	

Furthermore, the nuclear shielding of the boron atom in compound Ib (in toluene) increases (from $\delta(^{11}B)$ 23.9 to 17.3 ppm) by lowering the temperature from +40 to −40°C. This demonstrates the existence of an equilibrium between species containing a trigonal and a tetracoordinate boron atom. There is no further increase in the shielding of the boron atoms in Ia, Ib below 22°C and −37°C, respectively. However, the precision of the $\delta(^{11}B)$ values is insufficient to calculate reliable data for the enthalpy of activation ($\Delta H^{\#}$) or the entropy of activation ($\Delta S^{\#}$). A negative sign of $\Delta S^{\#}$ is typical of adduct formation.

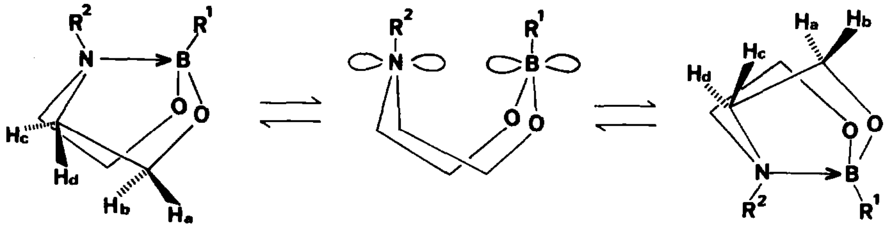


Fig. 1. Inversion of the bicyclic structure I.

A more precise picture emerges from variable temperature ^1H NMR studies of compounds Ia, Ib. At room temperature and above the pattern of the ^1H resonances for the OCH_2 and NCH_2 protons is simple. There is a triplet (OCH_2; $^3J(HCCH)$ and a quartet (NCH_2; $^3J(HCCH) \approx {}^3J(HNCH)$ in Ia, and there are two triplets in Ib. This can be explained in terms of a rapid (on the NMR time scale) dissociation of the N–B bond, followed by inversion and association as shown in Fig. 1. On lowering the temperature the ^1H resonances (OCH_2, NCH_2) broaden, coalescence is observed at 22 ± 2°C (Ia) and −37 ± 2°C (Ib), and a fairly complex multiplet structure is observed below the coalescence temperature. This is shown in Fig. 2 for the ^1H resonances of the OCH_2, NCH_2 and NH protons in compound Ia.

Homonuclear decoupling experiments $^1H\{^1H\}$ reduce the complex ^1H NMR

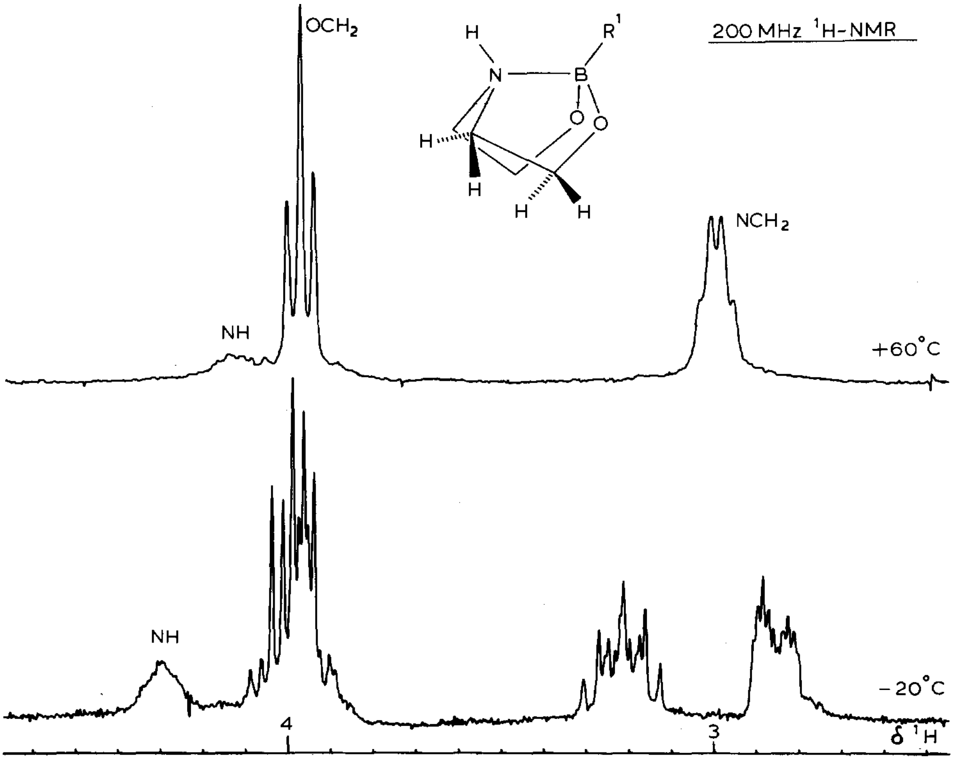
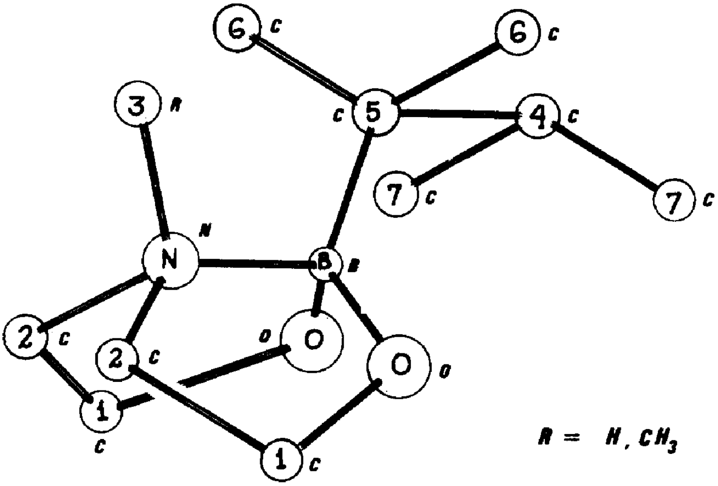


Fig. 2. 200 MHz ^1H-NMR spectra of Ia at +60°C and −20°C.

TABLE 1

^{1}H AND ^{13}C NMR PARAMETERS [a] FOR COMPOUNDS Ia, Ib



		(1)	(2)	(3)	(4)	(5)	(6)	(7)
Ia	$\delta(^{1}H)$	3.95 [b]	2.97 [c]	4.12 [d]	1.58	–	0.70	0.82
	$\delta(^{13}C)$	63.6	51.8	–	34.1	25.0	18.6	22.5
Ib	$\delta(^{1}H)$	3.84 [e]	2.82 [f]	2.74	1.51	–	0.67	0.74
	$\delta(^{13}C)$	63.0	59.7	47.4	36.1	27.1 [g]	19.2	22.7

[a] 30°C in $CDCl_3$, ca. 10% by weight, ^{1}H and ^{13}C in ppm relative to internal $(CH_3)_4Si$. [b] At −20°C: ^{1}H 4.03, 3.97; $^{2}J(HH)$ 10.5 Hz. [c] At −20°C: ^{1}H 3.23, 2.87; $^{2}J(HH)$ 11.5 Hz. [d] At −20°C: ^{2}H 4.33. [e] At −55°C; ^{1}H 3.88, 3.80; $^{2}J(HH)$ 10.5 Hz. [f] At −55°C: ^{1}H 2.88, 2.76; $^{2}J(HH)$ 11.3 Hz. [g] At −40°C: $^{13}C(5)$ 25.0.

spectra in the OCH_2 and NCH_2 region to simple AB-spin systems. Assuming that the peak separation $\Delta\nu$ and the rate constant k are larger than the band width (in the absence of exchange) the free energy of the activated complex $\Delta G^{\#}$ at coalescence can be calculated [5] as 59.6 ± 1 kJ/mole (Ia) and 49.2 ± 1 kJ/mole (Ib), respectively. These values reflect the steric interaction between the bulky thexyl group and the substituents at nitrogen. The $\Delta G^{\#}$ values of the *B*-phenyl derivatives corresponding to Ia, Ib are 80.6 and 73.1 kJ/mole, respectively [2c].

There is no appreciable change in the ^{13}C resonances for Ia, Ib with temperature. The assignment as given in Table 1 is based on the ^{1}H-coupled ^{13}C NMR spectra. The ^{13}C resonance of the quaternary carbon atom linked to boron is severely broadened by scalar relaxation of the second kind owing to the efficient quadrupole induced relaxation of the ^{10}B,^{11}B isotopes [6]. Reliable assignment was achieved by $^{13}C\{^{1}H,^{11}B\}$ heteronuclear triple resonance experiments.

Experimental

The NMR parameters (^{1}H, ^{11}B, ^{13}C) were obtained with a Bruker-WP 200 instrument operating in the PFT mode. Mass spectra were recorded at 20 eV with a

Hitachi–Perkin–Elmer RMU-7H spectrometer. The starting materials were commercial products (Ia, Ib, Ic) which were freshly distilled prior to use or have been prepared (III) via hydroboration of 2,3-dimethylbut-2-ene with BH_3 in THF [7].

(N–B)-Perhydro-2-thexyl-1,3-dioxa-6-aza-2-boracine (Ia)

Diethanolamine (2.0 ml, 20.8 mmol) in 40 ml of dry benzene is placed in a 50 ml flask equipped with a stirrer, a nitrogen inlet, and a connection to a gasimeter. Thexylborane in THF (20 ml, 23 mmol) is added dropwise at room temperature within 20 min. The exothermic reaction is finished in 20 min when two equivalents of H_2 are evolved. When the solvent and other volatile material have been removed in vacuo a colourless crystalline compound is left which gives upon recrystallization from dry benzene 3.37 g (81%) of compound Ia, m.p. 142°C. Found: C, 60.28; H, 11.08; N, 7.12. $C_{10}H_{22}BNO_2$ calcd.: C, 60.33; H, 11.14; N, 7.04%. MS: *m/e* 114 ($M^+ - 85$ (thexyl) 100%).

(N–B)-Perhydro-2-thexyl-6-methyl-1,3-dioxa-6-aza-2-boracine (Ib)

Following the same procedure as for Ia *N*-methyldiethanolamine (2.7 ml, 23.5 mmol) in 15 ml of dry benzene is allowed to react with thexylborane in THF (22.5 ml, 26 mmole) to give in quantitative yield the colourless crystalline compound Ib, m.p. 38°C Found: C, 61.64; H, 11.23; N, 6.65%. $C_{11}H_{24}BNO_2$ calcd.: C, 61.99; H, 11.35; N, 6.57%. MS: *m/e* 128 ($M^+ - 85$ (thexyl) 100%.)

(N–B)-Perhydro-2-thexyl-6-phenyl-1,3-dioxa-6-aza-2-boracine (Ic)

Following the same procedure as for Ia *N*-phenyldiethanolamine (5.0 g, 27.6 mmol) in 40 ml of dry benzene reacts with thexylborane in THF (26 ml, 30 mmol) to give a semisolid compound wich decomposes on standing $\delta(^{11}B)$ +30 ppm.

Acknowledgement

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