Journal of Organometallic Chemistry, 348 (1988) 149–156
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Syntheses and structures of two new dibenzobicyclic phenylboronates

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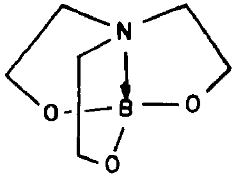
(Received August 12th, 1987; in revised form November 9th, 1987)

Abstract

The preparation, spectroscopic data and structure determination of (*N–B*)-phenyl[amino-2,2′-diphenolate-*O,O′,N*]borane (**3**) and of (*N–B*)-phenyl[*N*-methyl-amino-2,2′-diphenolate-*O,O′,N*]borane (**4**) derived from 2,2′-diphenolamine (**5**) and from *N*-methyl-2,2′-diphenolamine (**6**), respectively, are described. The structure of **3** was further demonstrated by X-ray diffraction studies.

In recent years we have been interested in the syntheses of bicyclic boron compounds derived from diethanolamines [1], phenolamines [2], iminodiacetic [3] and *N*-alkyl-*N*-(ethyl-2-hydroxy)-aminoacetic acids [4], as well as in studying intramolecular N→B coordination. In a continuation of these studies we describe in this paper the preparation and spectroscopic characterization of the 2,2′-diphenolamine and *N*-methyl-2,2′-diphenolamine esters derived from phenylboronic acid.

In contrast to triptychboroxazolidine (**1**) [5], the boric ester of 2,2′,2″-triphenolamine (**2**) [6] has been found not to have a N→B bond. The absence of coordination has been attributed to angular restrictions as well as to low nitrogen basicity. Therefore the 2,2′-diphenolamine (**5**) ligand in boron heterocycles is of interest in order to test whether N→B coordination is possible when a diaromatic amine is used as the ligand.



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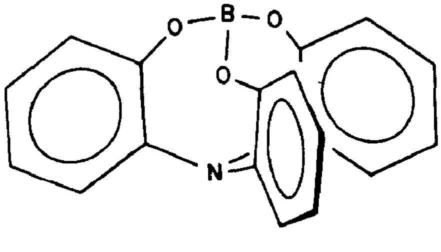

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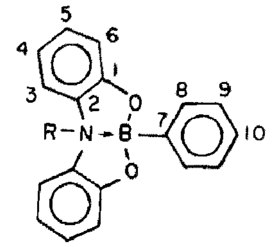
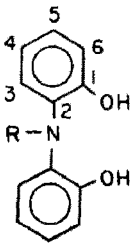
Table 1

^{13}C and ^{11}B NMR chemical shifts (ppm)

3 R=H

4 R=CH_3





5 R=H

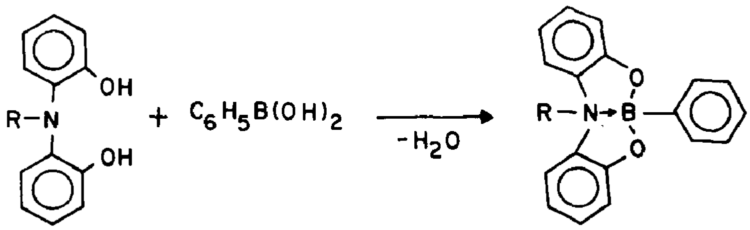
6 R=CH_3

^{13}C												^{11}B [a]
Compound	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)	R	
3 [c]	157.6	131.2	118.9 [d]	127.4	121.9 [d]	113.0	139.0	131.8	129.8	127.9	–	+13.7
4 [c]	157.2	136.2	119.2 [d]	127.7	119.4 [d]	114.8	143.0	133.1	130.1	128.8	47.5	+17.4
5 [b]	146.3	131.4	114.9 [d]	119.8 [e]	119.4 [e]	114.8 [d]	–	–	–	–	–	
6 [c]	150.1	137.2	121.0 [d]	125.9	122.6 [d]	116.1	–	–	–	–	41.9	

[a] In THF. [b] In DMSO-d_6. [c] In $CDCl_3$. [d,e] Assignments may be interchanged.

The new compounds described herein are (N–B)-phenyl[amino-2,2′-diphenolate-*O*,*O*′,*N*]borane (**3**) and (*N*–*B*)-phenyl[*N*-methylamino-2,2′-diphenolate-*O*,*O*′,*N*] borane (**4**). The structure of the former was also determined by a single crystal X-ray study. This structure provided information on the length of the N→B bond, thereby giving insight into problems encountered in the synthesis of stable boron chelates.

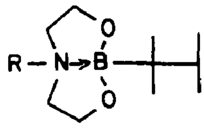
Compounds **3** and **4** were prepared from diphenolamines **5** and **6**, respectively, and phenylboronic acid:



5 R=H
6 R=CH_3

3 R=H
4 R=CH_3

In contrast to boronic esters derived from ethanolamines [1], such as **7**, which decompose readily in air at room temperature, **3** and **4** can be handled under the same conditions without decomposition.



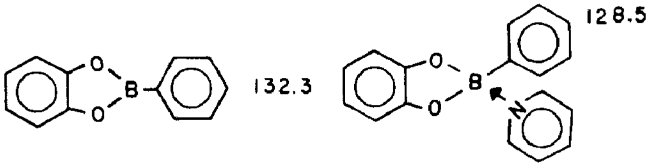
7 R=H,CH_3

These stable dibenzobicyclic boranes have a strong N→B intramolecular coordination between a dianilinic weak base and a phenylboronic weak acid. An explanation for this unusual behavior is that the rigid polycyclic structure brings the nitrogen and boron close together in space, thus constraining the coordination. This type of bonding was not observed in compound **2**, which does not form a N→B bond, in spite of the fact that both compounds share a common ligand.

NMR results

Evidence for intramolecular N→B coordination is based on the characteristic ^{11}B NMR data [7] (Table 1). Thus, the ^{11}B resonances for compounds **3** and **4** (δ +13.7 and +17.4 ppm, respectively) are shifted to higher fields with respect to phenylboronic acid (δ +28.4 ppm) [7], and therefore correspond to a four coordinated boron atom. These data are in agreement with other N→B bicyclic derivatives [1].

The ^{13}C NMR chemical shifts (Table 1) show a strong magnetic deshielding effect of the C(1) signal owing to the formation of a boron–oxygen bond that weakens the mesomeric donor ability of oxygen towards the phenyl ring [8]. On the other hand, C(2), shows a very small shielding effect owing to the nitrogen boron coordination ($\Delta\delta$ 0.2 for **3**, 1.0 ppm for **4**), when compared to the *N*-methylaniline borane (δ 148.3 ppm), which is shifted 1.9 ppm to high field referred to the free *N*-methylaniline (δ 150.2 ppm) [9]. Moreover, C(10) in **3** and **4** (127.9 and 128.8 ppm, respectively), which are *para* to the boron-phenyl group, also show the nitrogen-boron coordination, giving shifts of 4 to 5 ppm to higher fields, when compared with the same atom of the free phenylboronic acid (δ 132.7 ppm in $CDCl_3$) [10]. This shift can be attributed to an increase in electron density of the boron-phenyl group. A similar effect is observed for the phenylboronic ester of catechol (**8**), whose pyridine complex (**9**) is shielded by 3.8 ppm [10] (C *para* in phenylboron δ 132.3 ppm; pyridine complex δ 128.5 ppm).



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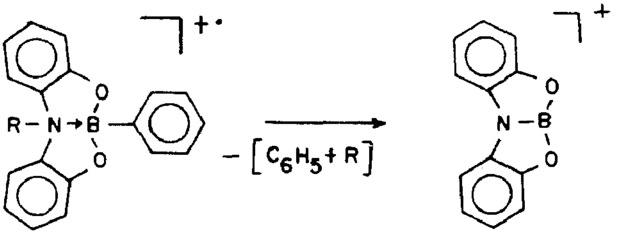
Mass spectra

Mass spectral fragmentation of **3** and **4** are similar, showing the initial loss of the phenyl and R groups to give the base peak **10** ($m/z = 209$) which is easily recognized as an ion containing a single boron atom ($^{10}B/^{11}B = 1/4$).



3 R=H

4 R=CH_3

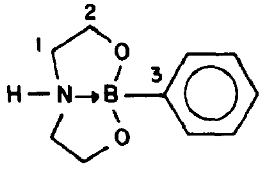
10

Infrared

Further evidence for the N→B coordination is obtained from IR data, since compounds **3** and **4** show the characteristic bands at 999 and 1019 cm^{-1}, respectively, attributed to the N→B bond [11].

X-Ray diffraction study

The structure determination of **3** by X-ray diffraction (Tables 2–4, Fig. 1) establishes the central bicyclic structure showing a N–B bond length of 1.699 Å. The value is comparable to the N→B bond length in its aliphatic analogue (**11**) (1.666 Å) [12].



11

The boron-phenyl and the NH groups in **3** are bent further away, as indicated by the bond angle values (H–N–B of 117.7° and N–B–C(7) of 114.1°), than in **11**

Table 2

Crystal data, collection and refinement parameters for (*N*–B)-phenyl(amino-2,2′-diphenolate-*O*,*O*′,*N*)borane

A. Crystal parameters	
chemical formula	$C_{18}H_{14}O_2NB$
molecular weight	286.13
crystal system	orthorhombic
space group	$Ccm2_1$
crystal size, mm	0.6×0.18×0.14
crystal color	pale brown
cell constants	
a, Å	9.6639(33)
b, Å	16.2866(57)
c, Å	9.1330(22)
α, deg	90.000 (00)
β, deg	90.000 (00)
γ, deg	90.000 (00)
cell volume, Å^3	1437.47
ρ(calc), g/cm^3	1.32
Z	4
F(000), e$^-$	596
B. Data collection parameters	
μ, cm^{-1}	6.9
scan width, below K_{α_1}, above K_{α_2}, deg	1.0, 1.2
2θ limits, deg	3°–110°
scan speed (variable), deg min^{-1}	(4.0, 29.3)
exposure time, h	22.87
total no. reflections collected	1090
no. unique reflections	498
C. Structure refinement	
reflections for final refinement	491
parameters refined	117
R(F), %	2.72
R_w(F), %	3.29
goodness of fit for the last cycle	1.215

Table 3

Atom coordinates ($\times 10^4$) and temperature factors ($Å^2 \times 10^3$) for ($N-B$)-phenyl(amino-2,2′-diphenolate-O,O',N – borane (**3**)

Atom	x	y	z	U_{eq}
C(1)	9780(2)	6145(1)	5268(3)	54(1) [a]
O	10970(1)	5741(1)	4957(3)	73(1) [a]
C(2)	8932(2)	5769(1)	6280(4)	48(1) [a]
N	9576(3)	5000	6769(4)	45(1) [a]
C(3)	7705(3)	6116(2)	6744(4)	61(1) [a]
C(4)	7336(3)	6865(2)	6144(4)	77(1) [a]
C(5)	8180(3)	7250(2)	5122(4)	74(1) [a]
C(6)	9410(3)	6898(2)	4656(4)	68(1) [a]
B	11112(4)	5000	5865(5)	53(1) [a]
C(7)	12428(3)	5000	6907(4)	48(1) [a]
C(8)	13021(2)	4277(2)	7406(4)	62(1) [a]
C(9)	14154(3)	4274(2)	8347(4)	81(1) [a]
C(10)	14696(3)	5000	8825(6)	85(2) [a]
H	9595(45)	5000	7636(74)	86(16)
H(3)	7052	5813	7553	99(11)
H(4)	6370	7156	6476	113(11)
H(5)	7868	7843	4677	90(9)
H(6)	10063	7199	3844	87(8)
H(8)	12588	3693	7048	65(7)
H(9)	14606	3694	8703	115(10)
H(10)	15563	5000	9588	221(30)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor

Table 4

Bond lengths (Å) and angles (deg.) for ($N-B$)-phenyl(amino-2,2′-diphenolate-O,O',N)borane (**3**)

C(1)–O	1.355(3)	C(1)–C(2)	1.380(4)
C(1)–C(6)	1.394(3)	O–B	1.471(3)
C(2)–N	1.468(3)	C(2)–C(3)	1.380(3)
N–B	1.699(5)	N–C(2+)	1.468(3)
C(3)–C(4)	1.383(4)	C(4)–C(5)	1.389(4)
C(5)–C(6)	1.387(4)	B–C(7)	1.588(5)
B–O+	1.471(3)	C(7)–C(8)	1.386(3)
C(7)–C(8+)	1.386(3)	C(8)–C(9)	1.392(4)
C(9)–C(10)	1.365(4)	C(10)–C(9+)	1.365(4)
N–H	0.792(67)		
O–C(1)–C(2)	115.4(2)	O–C(1)–C(6)	124.1(2)
C(2)–C(1)–C(6)	120.5(2)	C(1)–O–B	111.1(2)
C(1)–C(2)–N	109.3(2)	C(1)–C(2)–C(3)	122.3(2)
N–C(2)–C(3)	128.4(3)	C(2)–N–B	102.9(2)
C(2)–N–C(2+)	117.1(3)	B–N–C(2+)	102.9(2)
C(20–C(3)–C(4)	117.5(3)	C(3)–C(4)–C(5)	120.9(3)
C(4)–C(5)–C(6)	121.5(2)	C(1)–C(6)–C(5)	117.4(3)
O–B–N	101.1(2)	O–B–C(7)	114.4(2)
N–B–C(7)	114.1(3)	O–B–O+	110.3(3)
N–B–O+	101.1(2)	C(7)–B–O+	114.4(2)
B–C(7)–C(8)	121.9(2)	B–C(7)–C(8+)	121.9(2)
C(8)–C(7)–C(8+)	116.2(3)	C(7)–C(8)–C(9)	122.1(3)
C(8)–C(9)–C(10)	119.7(3)	C(9)–C(10)–C(9+)	120.1(4)
B–N–H	117.7(32)	C(20–N–H	108.3(14)

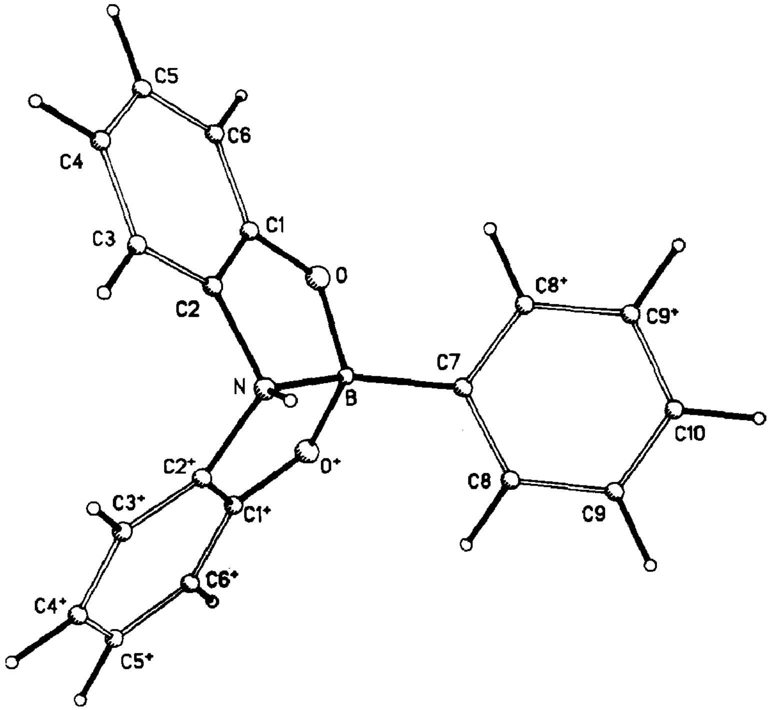


Fig. 1. Molecular structure of **3**.

(H–N–B of 111.0° and N–B–C(3) of 113.2°). The C–N–C angle is larger in **3** (C–N–C 117.1°) and the O–B–O angle is smaller (112.9°), when compared with those of **11** [12]. All the other structural features are in reasonable agreement with those of *o*-aminophenol hydrochloride [13].

Conclusion

Comparison of compound **3** with its aliphatic analogue **11** allows to conclude that basicity is not a decisive factor for the formation of stable N → B bonds. This in turn suggests that the main factor which precludes formation of a coordinate bond in **2** is angular restriction.

Experimental

NMR spectra were recorded with JEOL FX90Q (^{11}B, ^{13}C NMR) and Varian Associates EM-390 (^{1}H NMR) spectrometers. Chemical shifts are relative to $BF_3 \cdot Et_2O$ and TMS. Mass spectra were obtained with a Hewlett-Packard 5985-A spectrometer and infrared spectra were determined on a Nicolet MX-1 FT spectrophotometer in KBr pellets. The X-ray study was performed on a Nicolet R3m four-circle diffractometer using monochromated Cu-K_α radiation.

(N–B)-Phenyl[amino-2,2′-diphenolate-O,O′,N]borane (3)

A solution of 2,2′-diphenolamine (0.34 g, 1.7 m*M*) in 150 ml of dry benzene was placed into a 250 ml flask equipped with a stirrer and a Dean–Stark trap.

Phenylboronic acid (0.20 g, 1.7 m*M*) was added and the mixture was kept under reflux for 4 h. After removal of the solvents in vacuo, the product was recrystallized from benzene/acetone to give 0.42 g of the compound **3**, m.p. 190–192 °C. IR: ν(N→B) 999 cm^{-1}. ^1H NMR (in $CDCl_3$): 8.2–8.4 (m, 2H); 7.4–7.7 (m, 11H). MS: $m/z = 287$ $(M)^+$, 39%; 288 $(M+1)^+$, 7%; 286, 8%; 210, 18%; 209, 100%; 208, 15%.

*(N–B)Phenyl[N-methylamino-2,2′-diphenolate-O,O′,N]borane (**4**)*

In the procedure used for **2**, *N*-methyl-2,2′-diphenolamine (0.29 g, 1.3 m*M*) and phenylboronic acid (0.16 g, 1.3 m*M*) gave 0.22 g of compound **4**, m.p. 217–219 °C. IR: ν(N→B) 1019; ^1H NMR (in $CDCl_3$): 8.6–8.8 (m, 2H); 6.9–7.4 (m, 11H); 2.8 (s, 3H, N–CH_3). MS: $m/z = 301$ $(M)^+$, 64%; 302 $(M+1)^+$, 17%; 300, 18%, 224, 50%; 210, 17%; 209, 100%; 208, 28%.

Acknowledgements

We are grateful to Conacyt, to Proyectos Estratégicos-SEP and to COSNET-SEP (México), for financial support and to Ing. L. Velasco (UNAM) for mass spectra.

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