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Synthesis and molecular structure of 2,4,6-tri[bis(diisopropylamino)boryl(methylamino)]borazine, $[(N^iPr_2)_2B(Me)N]_3B_3N_3H_3$

Bérangère Toury[1], David Cornu[1], Sylvain Lecocq[2] and Philippe Miele[1]*

[1]Laboratoire des Multimatériaux et Interfaces, UMR CNRS 5615, Université Claude Bernard–Lyon 1, 43 bd du 11 novembre 1918, 69622 Villeurbanne Cedex, France
[2]Laboratoire de Cristallographie, UMR CNRS 5078, Université Claude Bernard–Lyon 1, 43 bd du 11 novembre 1918, 69622 Villeurbanne Cedex, France

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Reaction of bis(diisopropylamino)(methylamino)borane, $(NH^iPr)_2B(NHMe)$, with 2,4,6-trichloroborazine $(ClBNH)_3$ affords 2,4,6-tri[bis(diisopropylamino)boryl(methylamino)]borazine, 2,4,6-$[(N^iPr_2)_2B(Me)N]_3B_3N_3H_3$, which is the first boryl-borazine structurally characterized. According to the X-ray single crystal structure and the chemical shifts of ^{11}B NMR resonances of boron atoms, compared with the aminoborane and borazine analogs, the borazine and boryl π-systems are not coplanar either in the solid state or in organic solution. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: borazine; boryl; X-ray structure; boron nitride; precursor

INTRODUCTION

Borazine ($H_3B_3N_3H_3$) and its derivatives are attractive molecular precursors to hexagonal boron nitride (*h*-BN) materials. These compounds offer advantages over other boron-containing monomers because they have been shown to lead to processable polymers that can be regarded as an assembly of B_3N_3 hexagons, the basic patterns of *h*-BN.[1] Therefore, borazine-based monomers and polymers derived therefrom are deemed to be the best precursors to *h*-BN processed forms such as coatings,[2,3] matrices,[4] and fibres.[5–8] The production of the latter remains the most difficult application, but this can be achieved through the use of melt-spinnable polyborazines.[9] From these studies, it emerges in addition that the required improvements in polymer processability are determined by the control of the nature of polyborazine backbone, including the kind of reactive groups linked to the rings and the way the rings are connected.[9,10] In order to achieve these goals, several routes have been envisaged, which can be summed up as being functionalization of either a polyborazine or a borazine.[9–11] Although both approaches are promising, we have focused our studies toward tailored borazinic derivatives that can give rise to novel preceramic polymers having enhanced processing properties. For example, we recently reported on the synthesis of 2,4,6-$[(NH^iPr)_2B(^iPr)N]_3B_3N_3H_3$, constituted of a B_3N_3 core surrounded by three aminoboryl groups,[12] as well as on its thermal polycondensation.[13] The resulting oligomer has been proven to be an interesting precursor of BN matrices and oxidation protective coatings,[13] while the presence of 'N—B—N' three-atom bridges between the rings could afford a promising outlook for the melt-spinning of polyborazine fibres. Along the same line as the investigation of the potential of these kinds of precursor for the preparation of BN fibres, our objective is thus to synthesize model molecules with the aim of understanding the polycondensation mechanisms better, particularly by means of high-resolution ^{11}B NMR analysis and single crystal X-ray diffraction. In this report, we describe the synthesis and complete characterization of the new boryl-borazine model molecule 2,4,6-$[(N^iPr_2)_2B(Me)N]_3B_3N_3H_3$ (**1**).

EXPERIMENTAL

Synthesis of 1

All experiments were carried out under anhydrous conditions using vacuum-line and Schlenk techniques. In a typical experiment, $Cl_3B_3N_3H_3$ (0.92 g, 5.0 mmol) and Et_3N (5 g, 49.5 mmol) in toluene (100 ml) were slowly added at −20 °C

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*Correspondence to: P. Miele, Laboratoire des Multimatériaux et Interfaces, UMR CNRS 5615, Université Claude Bernard–Lyon 1, 43 bd du 11 novembre 1918, 69622 Villeurbanne Cedex, France.
E-mail: miele@univ-lyon1.fr

to a solution of $(MeHN)B(N^{i}Pr_2)_2$ (3.62 g, 15.0 mmol) in toluene (50 ml). The mixture was stirred for 2 h at room temperature. The residue was filtered off and the filtrate was evaporated, yielding a white powder. By recrystallization in hexane, the product yields crystals of $[2,4,6\text{-}[(N^{i}Pr_2)_2B(Me)N]_3B_3N_3H_3]$ (**1**; 3.45 g, 86%/trichloroborazine).

Characterization of 1

Anal. Found: C, 58.9; H, 12.5; B, 7.2; N, 21.4. $C_{39}H_{96}B_6N_{12}$ requires C, 58.7; H, 12.1; B, 8.0; N, 21.2%. NMR: δ_B (96.28 MHz; solvent C_6D_6; standard $Et_2O{\cdot}BF_3$) 27.0 [1B, $[(^{i}Pr_2N)\mathit{B}(Me)N]_3B_3N_3H_3$], 31.7 [1B, $[(^{i}Pr_2N)B(Me)N]_3\mathit{B}_3N_3H_3$] (referenced to $Et_2O{\cdot}BF_3$); δ_H (300 MHz; solvent $CDCl_3$; standard $SiMe_4$) 1,15 [d, 24H, $C\mathit{H}_3$ isopropyl], 2.53 [s, 3H, $C\mathit{H}_3$ methyl], 3.28 [s, 1H, N*H* borazine], 3.49 [h, 4H, C*H*]; δ_C (75 MHz; solvent $CDCl_3$; standard $SiMe_4$), 25.1 [CH_3 isopropyl], 34.7 [CH_3 methyl], 47.2 [CH]. Mass spectrometry (EI), *m/z* 798 (M^+, 31%), 755 ($M-{}^{i}Pr$, 62).

Crystal structure determination of complex 1

A suitable crystal of **1** was covered with paratone oil in order to conduct X-ray experiments in an ambient atmosphere over some hours. Diffraction data were collected on a Nonius Kappa CCD diffractometer. All calculations were performed with DENZO,[14] SHELXS[15] and PLUTON.[16] Non-H atoms were refined anisotropically. H atoms were included at calculated positions and refined riding on C. The carbon C313 has a large B factor and, at the same time, the bond length C(311)–C(313) is shorter than usual, 1.400 Å. This can be due to a disorder between C(313) and H(313). The large value of R is due to the bad quality of the crystals and their rapid evolution during the data collection.

RESULTS AND DISCUSSION

As previously reported, the exchange reaction of chlorine atoms of trichloroborazine for borylamino groups yields the corresponding boryl-borazine.[12] Thus, compound **1** was prepared by reaction of one equivalent of 2,4,6-trichloroborazine with three equivalents of bis(diisopropylamino)-(methylamino)borane in dry toluene. The reaction is performed in the presence of an excess of triethylamine in order to precipitate the corresponding amine hydrochloride. This residue was filtered off and the filtrate evaporated to yield a white powder. This was recrystallized in hexane, yielding colourless crystals of **1**. Its nature was suggested by

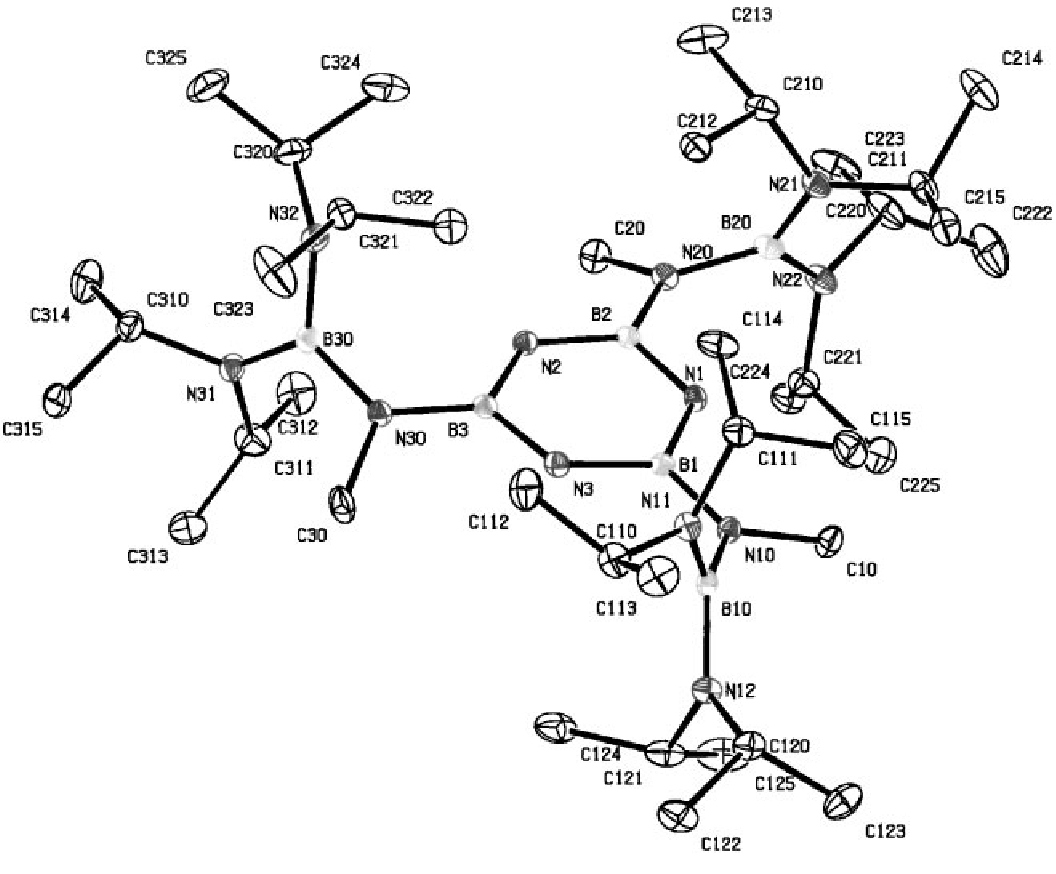

Figure 1. ORTEP drawing of the molecular structure of $[(^{i}Pr_2N)B(Me)N]_3B_3N_3H_3$.

Table 1. Crystallographic data and structure refinement for **1** (CCDC number 179760)

Formula	$C_{39}H_{96}B_6N_{12}$
Formula weight	798.14
Temperature (K)	123
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	13.592(3)
b (Å)	16.616(3)
c (Å)	26.752(5)
β (deg)	119.18(3)
Volume (Å^3)	5274.8(2)
Z	4
Density (calc.) (g cm^{-3})	1.005
Absorption coefficient (mm^{-1})	0.059
F(000)	1776
Crystal size (mm^3)	$0.24 \times 0.18 \times 0.17$
θ range for data collection (deg)	0.998 to 27.485
Index ranges	$0 \le h \le 17, -21 \le k \le 0, -34 \le l \le 29$
Reflections collected	12 056
Independent reflections	11 658
Goodness-of-fit on F^2	1.134
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0792$, $wR(F^2) = 0.1938$
R indices (all data)	$R_1 = 0.1304$, $wR(F^2) = 0.2125$

the mass spectrum, which displays the parent molecular ion at *m/z* 798 and a peak at *m/z* 755 resulting from the loss of a single $CH(CH_3)_2$ group from **1**. The high-resolution ^{11}B NMR spectrum obtained at 293 K shows a broad resonance centred at δ 26.8 with a shoulder at around δ 31. At 343 K, the resolution of the spectrum is significantly improved, since the signal splits into two peaks at δ 27.0 and δ 31.7 in a relative 1:1 intensity in accordance with the presence of two types of boron atom. Within this temperature range, the signals sharpen whilst the chemical shifts remain practically the same, which suggests that the magnetic environment of the boron atoms is nearly unchanged. A rapid examination of these data might lead to the erroneous attribution of the high-field signal (δ 27.0) to boron atoms pertaining to boryl groups, this chemical shift being equivalent to the value found for (MeHN)B(N^iPr_2)$_2$ (δ 27.2; Laboratoire des Multi-matériaux et Interfaces, Université Claude Bernard–Lyon 1, unpublished results), whereas the signal at δ 31.7 would then correspond to borazine boron atoms. However, this value is rather unusual for alkylaminoborazines [where boron atoms are more shielded than in borazine $H_3B_3N_3H_3$ (δ 29),[17] which have chemical shifts around δ 24–26.[17,18] These data may also be compared with ^{11}B NMR data for the similar boryl-borazine $[(^iPrHN)_2B(^iPr)N]_3B_3N_3H_3$ (*B*-boryl δ 22.6, *B*-borazine δ 26.3).[11] Thus, the ^{11}B NMR data for **1** were reinvestigated by considering that the coarse preliminary attributions of the two signals should be inverted. On this assumption, the high-field peak δ 27.0 would appear at a chemical shift more consistent with previously reported data for boron atoms of trialkylaminoborazines, whereas the signal at δ 31.7 would be assigned to deshielded boryl boron atoms. This value falls in the range of those reported for bis(amino)boranes and (halogeno)bis(amino)boranes.[17] This low-field shift, compared with the parent aminoborane $(N^iPr_2)_2B(NHMe)$ (δ 27.2), is presumably the consequence of an absence of π-interaction between the boryl boron atoms and bridging nitrogen atoms —N(Me)—, which should result in the loss of alignment of boron- and nitrogen-related *p*-orbitals. One may assume that sufficient overlap exists between lone pairs of electrons on bridging nitrogen atoms and the vacant *p*-orbital on connected borazine boron atoms to effect delocalization and consequent π-bonding. Thus, bridging nitrogen atoms adopt a trigonal planar geometry and the resulting planes are probably almost coplanar with the borazine ring plane.

The stable conformation adopted in organic solution for **1** has been confirmed by X-ray crystal structural analysis. The molecular structure, with the atomic numbering scheme, is shown in Fig. 1. The crystallographic data are summarized in Table 1, and selected bond lengths and angles are given in Table 2.

The borazine ring is planar and all $B_{borazine}$—N endo- and exo-ring bond lengths, respectively averaged to 1.434(3) Å and 1.437(3) Å, are consistent with bond orders greater than unity. These distances are identical within experimental error and are comparable to those found in $(HBNH)_3$,[19] $[ClBNH]_3$,[20] $(Me_2NBNH)_3$,[21] $(^iPr_2\ NBNH)_3$,[22] $[(H_2N)BN(Me)]_3$.[23] On the other hand, N—B—N endocyclic angles are more acute [av. 115.9(2)°] and B—N—B angles are more open [av. 124.1(2)°] in **1** than in the aforementioned species. Further, it is interesting to examine these angles by comparison with those reported for borazines in which boron atoms bear π-donor amino groups, namely $(Me_2NBNH)_3$[21] and $(^iPr\ NBNH)_3$.[22] In this series of compounds, we have noticed that N—B—N angles are more open and B—N—B angles are more compressed when the donating effect of the amino substituents increases, following the order $(N^iPr_2)_2B($-MeN)— <Me_2N— <$^iPr_2N$—. [The average values of N—B—N and B—N—B angles are respectively 115.9(2)° and 124.1(2)° for the $(N^iPr_2)_2B(Me)N$— substituent, 116.9(5)° and 123.4(5)° for the Me_2N— substituent, and 118.7(2) and 121.2(2)° for the $^iPr_2N$— substituent.] This phenomenon is presumably related partly to the resulting increase of the electron density around the accepting boron atoms; the steric bulk of the substituents is also probably involved in this phenomenon. Likewise, the distances found for the exo-ring B—N bonds in **1** are the longest and characterize the lowest degree of electrons delocalization along these bonds among

Table 2. Selected bond lengths and angles for **1**

Bond lengths	(Å)	Bond angles	(deg)
$N_{endo-ring}-B_{endo-ring}$	1.434(3) av.	B(2)−N(1)−B(1)	123.9(2)
N(10)−B(1)	1.434(3)	B(2)−N(2)−B(3)	123.8(2)
N(20)−B(2)	1.441(3)	B(3)−N(3)−B(1)	124.6(2)
N(30)−B(3)	1.435(3)	N(3)−B(1)−N(1)	115.6(2)
N(10)−B(10)	1.474(3)	N(2)−B(2)−N(1)	116.3(2)
N(20)−B(20)	1,470(3)	N(3)−B(3)−N(2)	115.7(2)
N(30)−B(30)	1.466(3)	N(10)−B(1)−N(3)	122.0(2)
N(11)−B(10)	1.435(3)	N(10)−B(1)−N(1)	122.3(2)
N(12)−B(10)	1.437(3)	N(2)−B(2)−N(20)	122.1(2)
N(21)−B(20)	1.433(3)	N(1)−B(2)−N(20)	121.6(2)
N(22)−B(20)	1.444(3)	N(3)−B(3)−N(30)	123.3(2)
N(31)−B(30)	1.438(3)	N(30)−B(3)−N(2)	121.1(2)
N(32)−B(30)	1.439(3)	N(10)−B(10)−N(11)	119.0(2)
		N(10)−B(10)−N(12)	120.0(2)
		N(11)−B(10)−N(12)	121.0(2)
		N(20)−B(20)−N(21)	119.5(2)
		N(20)−B(20)−N(22)	118.5(2)
		N(21)−B(20)−N(22)	122.0(2)
		N(30)−B(30)−N(31)	119.7(2)
		N(30)−B(30)−N(32)	118.9(2)
		N(31)−B(30)−N(32)	121.4(2)

the three derivatives. However, the exo-nitrogen atoms in **1** have a trigonal planar geometry,† as in $(Me_2NBNH)_3$[21] and $(^iPr_2\ NBNH)_3$,[22] but the main difference is that the related planes in **1** are slightly twisted with respect to the borazine ring plane. The dihedral angles, 14.14(1)°, 23.80(1)°, and 20.97(1)° for planes arising from N(10), N(20), and N(30) respectively, are sufficiently weak to allow electrons partial delocalization between the borazine boron atoms and bridging nitrogen atoms, and consequently π bonding.

In this molecular structure, one can also remark on the presence of other trigonal planes built from N(*X*0), B(*X*0), N(*X*1), and N(*X*2) atoms. [The maximum deviation of the position of the atoms B(*X*0), N(*X*0), N(*X*1) and N(*X*2) from the mean least-squares plane calculated from them is 0.0065(5) Å.] In each of these moieties, terminal B(*X*0)−NR_2 distances [av. 1.438(3) Å] are consistent with the presence of some degree of π-interaction, falling in the range found for aminoboranes.[17,24] As expected, B(*X*0)−N(*X*0) distances are significantly longer [av. 1.470(3) Å], indicating a weak double bond character and, consequently, that both *p*-orbitals of bridging nitrogen atoms and boryl boron atoms are out of alignment. The dihedral angles of the boryl planes with respect to the adjacent bridging nitrogen planes [64.27(1)°, 57.58(1)°, and 58.57(1)° respectively for B(10)-, B(20)- and B(30)-containing planes] confirm this hypothesis, in accordance with the assumptions based on the ^{11}B NMR results quoted above.

In conclusion, the data obtained for $[(N^iPr_2)_2B(Me)N]_3B_3N_3H_3$ (**1**) are consistent with the structural assumptions proposed for $[(^iPr\ HN)_2B(^iPr)N]_3B_3N_3H_3$,[12] namely that the whole of the aminoboryl groups, including the ^{i}Pr N− bridging groups, are greatly twisted with respect to the borazine ring plane, which precludes any interaction between the two BN π-systems and is in agreement with the findings by Nöth and Wrackmeyer.[17] Moreover, for **1**, the less bulky Me substituents on nitrogen bridging atoms allow an almost coplanar arrangement of the nitrogen bridging plane and the borazine ring, whereas the bulkiness of the ^{i}Pr N groups forces the boryl moieties to deviate greatly from the ring plane.

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† The maximum deviation of the position of the atoms B(*X*), N(*X*0), C(*X*0), and B(*X*0) from the mean least-squares plane calculated from them is 0.0484(2) Å.

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