SYNTHESIS AND CHARACTERIZATION OF 2,4,6-TRIS{[BIS(ISOPROPYLAMINO)BORYL](ISOPROPYL)AMINO}BORAZINE

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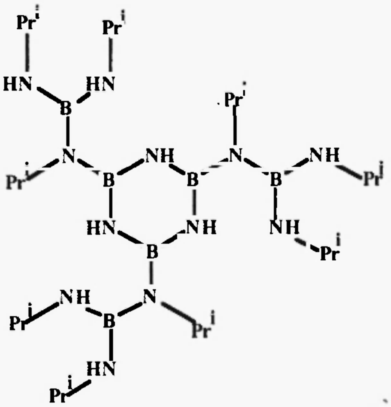
Abstract. The B–substituted borazine 2,4,6-$[(NHPr^i)_2$-B-$(NPr^i)]_3$-$B_3N_3H_3$ (**1**) was prepared by the reaction of 2,4,6-trichloroborazine with tris(isopropylamino) borane in a 1:3 molar ratio. Compound **1** was characterized by elemental analysis, mass spectroscopy, F.T.I.R. and multinuclear N.M.R. spectroscopy. This borazine consists of a B_3N_3 ring linked by amino bridges to three $B(NHPr^i)_2$ groups. These aminoboryl groups and the borazine ring are presumably strongly twisted or oriented orthogonally as shown by ^{11}B and ^1H N.M.R. spectra.

The borazinic polymer route was shown suitable for obtaining specific boron nitride morphologies, e.g. coatings, foams, matrices and fibers. The polyborazines display various structures, the connection between borazine rings depending upon the reactive groups bound to the B_3N_3 ring and the reaction conditions [1]. The requirement of high quality BN final material has prompted us to research new borazine-based monomers. We have focused our attention on the preparation of a B-substituted borazine with three diaminoboryl ligands. There is little data for this kind of derivatives; in 1978, Nöth and Wrackmeyer [2] have reported the existence of a B-substituted mono(aminoboryl)borazine $[CH_3]_2$ $[(CH_3)_2BN(CH_3)]$ $B_3N_3[CH_3]_3$ and most recently Nöth and coworkers [3] have prepared some N,N',N"–borylated borazines, $R_3B_3N_3(BR_2)_3$, from aminoboranes or diborylamines. These borazines display interesting structural properties with boryl group planes oriented orthogonally to or strongly twisted with respect to the borazine ring plane. We report here the synthesis and the characterization of 2,4,6-tris{[bis(isopropylamino)boryl](isopropyl) amino}borazine (1).

The behaviour of related compounds indicates that the reaction of aminoborane with halogenated boron derivatives, particularly 2,4,6-trichloroborazine (TCB), could proceed in different ways. Bis(amino)halogenoboranes, $XB(NR_2)_2$, were obtained by mixing tris(amino)boranes, $B(NR_2)_3$, with boron trihalides, BX_3 [4], and several exchange reactions of substituted borazines with other substituted borazines or boron trihalides have also been reported [5]. Such exchange reactions could be expected between TCB and tris(isopropyl-amino)-borane but no trace of B-(alkylamino)borazine and bis(alkylamino)chloroborane was detected. Assuming $B(NHPr^i)_3$ acts as a particular amine, the other potential reaction pathway is similar to the well known exchange reaction of chlorine atoms of TCB for alkylamino groups readily giving the corresponding B-(alkylamino)borazine. We have found that this reaction could be extended to the amino group of $B(NHPr^i)_3$.

Thus, (1) was obtained by reacting 2,4,6-trichloroborazine and tris(isopropylamino)borane in dry toluene in a 1:3 molar ratio, in the presence of triethylamine, in order to remove hydrogen chloride formed. The amount of triethylamine hydrochloride collected was exactly that expected for a 100% recovery. No chloride was detected in (1).



Schematic representation of 2,4,6-$[(NHPr^i)_2$-B-$(NPr^i)]_3$-$B_3N_3H_3$ (1)

The infrared spectrum exhibits absorptions typical of a borazine ring [6] and of B-N bonds of tris-(isopropylamino)borane[7]. The ν(B-Cl) band, at 743 cm^{-1} for TCB [8] was replaced by a band at 805 cm^{-1}. Therefore, this new absorption, absent in both the spectra of TCB and $B(NHPr^i)_3$, was tentatively assigned to a B*(borazine)*-N extracyclic vibration of (1). The nature of (1) was unambiguously confirmed by mass spectrometry (EI). The mass spectrum displays the parent molecular ion at *m/z* = 630 without any ion of higher molecular mass ; the major fragment ion at *m/z* = 615 results from the loss of a single CH_3 group from the parent molecular ion. The ^{11}B NMR spectrum of (1) exhibits two peaks in a relative 1:1 intensity consistently with the presence of two types of boron atoms in an equivalent ratio. The position of the signal of the boron atoms of the borazine ring is in good agreement with previously reported values for tris(isopropylamino)-borazine [7]. There is only a little shift (0.3 ppm) to low field of the signal of the boron atoms of the boryl substituents compared with pure tris(isopropyl-amino)borane [7, 9]. That indicates only a weak perturbation of the partial π-system of aminoboryl groups compared to tris-(isopropyl-amino)borane. This observation can be paralleled with the results reported by Nöth and coworkers for the other borylated borazines: (a) there is only little (if any) interaction between the two BN π-systems. (b) the free electron pair of the sp^2 nitrogen bridging atom should not interact with the B_3N_3 system provided that the 2 planes are orthogonals [2]. These conclusions are in accordance with our ^{11}B NMR results suggesting that the two BN π-systems are too sterically encumbered to allow a coplanar arrangement even if the orthogonality of the borazine ring and the aminoboryl group planes could not be shown. The ^{13}C spectrum at room temperature shows a singlet for the CH of bridging groups whereas two close resonances appear for each other carbon atoms ($\underline{C}H$ amino, $\underline{C}H_3$ amino and $\underline{C}H_3$ bridge). The splitting observed indicates that the magnetic environments of the involved atoms are not equivalent. The configurational and conformational situation of (**1**) in solution is probably responsible of these patterns by taking into account the twist of the aminoboryl planes to the borazine ring according to the ^1H NMR spectrum. The latter displays complex signals for the methyls of both bridging and terminal groups instead of the only two expected doublets and the methynic protons area shows two broad poorly resolved multiplets. Variable-temperature ^1H NMR has been performed at temperatures from 243 K to 323 K and has revealed significant changes only in the methylic region. Within this range, we have noticed a progressive splitting of each complex signal into a pair of doublets whereas each of them sharpens as the temperature increases with no change in the overall integration ratio. The chemical shift differences between the two doublets of each type were too small to permit integration. The sharpening of the resonances reveals that some hindered rotations are temperature dependant whilst their persistent splitting is consistent with the existence of steady conformations. Related examples of atropisomerism have been reported in the literature for N-aryl substituted borazines [10] and B-aryl substituted borazines [11] which have sufficient steric hindrance to prevent rotation about the B-C bonds. Taking account of the ^{11}B NMR results, we concluded that the aminoboryl substituents are bulky enough to preclude rotation about the B*(borazine)*-N bonds. Consequently, stereoisomerism may be expected and (**1**) should exist as a pair of atropisomers. The cis isomer would display all of the $B(NHPr^i)_2$ on the same side of a plane defined by the $(BN)_3$ cycle, and the trans isomer would have two $B(NHPr^i)_2$ groups on the same side of the borazine ring and one on the opposite side. Although the geometric features of (**1**) are undoubtedly responsible of the splitting of some resonances, further investigations with other tris(alkylamino)boranes and modelisation studies are required to confirm this hypothesis.

Materials and methods

All experiments were performed under atmosphere of pure argon and anhydrous conditions using standard vacuum-line and Schlenk techniques. The ^{11}B N.M.R. spectra were recorded on a Brüker AM300 spectrometer at 96.28 MHz with $Et_2O.BF_3$ as an external reference (positive values downfield) in toluene and/or C_6D_6 solutions. The ^1H and ^{13}C spectra were obtained at 300 MHz and 75 MHz respectively in $CDCl_3$. The infrared spectra were obtained on an IR-FT Nicolet Magna 550 spectrometer as nujol mulls. Mass spectra were recorded on a Varian Mat 311 spectrometer by electronic impact (70 eV) at the C.R.M.P.O. (Rennes, France). Analytical data were obtained from the S.C.A. du C.N.R.S.

Synthesis and spectroscopic data of (1)

Triethylamine (1.80 g, 17.82 mmol) was added to a solution of 2,4,6-trichloroborazine (TCB) (0.98 g, 5.33 mmol) in toluene (50 ml), then a solution of tris(isopropylamino)borane (2.97 g, 16.07 mmol) in toluene (30 ml) was dripped into the TCB solution previously cooled at –20 °C. The mixture was stirred for 2 h at –20°C and allowed to warm to 25 °C ; the total reaction time was 24 h. The resulting mixture was filtered under argon. The residue was washed with toluene (50 ml). The combined filtrate and extract solutions were evaporated yielding a viscous liquid, 2,4,6-$[(NHPr^i)_2$-B-$(NPr^i)]_3$-$B_3N_3H_3$ (**1**). Yield 3.12 g, 93 %. *Anal*. Found: C, 51.8; H, 11.9; B, 10.1; N, 26.7. Calc. For $C_{27}H_{72}B_6N_{12}$: C, 51.5; H, 11.4; B, 10.3; N, 26.7. NMR data (δ, ppm): ^{11}B (C_6D_6): 26.3 (borazine core, 1B); 22.6 (aminoboryl groups, 1B). ^1H ($CDCl_3$) 293 K: 3.36 (m, C*H* bridge, *J*HCCH = 6.55 Hz, bs, C*H* amino and N*H* borazine, 10H); 3.06 (m, C*H* amino, 2H); 2.09 (d, N*H* amino, *J*HNCH = 10.25 Hz, 6H); 1.14 (m, CH_3 bridge, 18H); 1.05 (m, CH_3 amino, 36H). IR (cm^{-1}): 3443 (vNH); 2961, 2930, 2869 (vCH); 1493 (vBN amino); 1462 (vBN ring); 805, 822 shoulder (vB*(borazine)*-N extracyclic). HRMS (*m/z*, EI): $[\mathbf{1}]^+$(21%), $[\mathbf{1}\text{-}CH_3]^+$(100%), $[\mathbf{1}\text{-}Pr^i]^+$(9%), $[\mathbf{1}\text{-}B(NHPr^i)_2\text{-}CH_3]^+$(18%).

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