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THERMAL OLIGOMERIZATION OF UNSYMMETRICALLY B-TRISUBSTITUTED BORAZINES

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Abstract. The B-alkylaminosubstituted borazines $(\text{NEt}_2)_3\text{B}_3\text{N}_3\text{H}_3$ (**1**), $(\text{NEt}_2)_2(\text{NHPr}^i)\text{B}_3\text{N}_3\text{H}_3$ (**2**), $(\text{NEt}_2)(\text{NHPr}^i)_2\text{B}_3\text{N}_3\text{H}_3$ (**3**) and $(\text{NMe}_2)(\text{NHMe})_2\text{B}_3\text{N}_3\text{H}_3$ (**4**) have been prepared and characterized by spectroscopic techniques. Their thermolyses at moderate temperature have been investigated in order to elucidate the effects of the nature of the B-alkylamino substituents on the resulting polyborazines backbone. Early stages of the degradations were accompanied by the elimination of primary and secondary amines for (**2**), (**3**) and (**4**). On the basis of ^{13}C NMR data, oligomerizations have been shown to occur mainly *via* the formation of direct inter-ring B-N bonds rather than classical deamination with formation of -N(R)- bridges between borazine rings. This phenomenon should be related to the presence of dialkylamino substituents on the boron atoms.

Boron- and nitrogen-containing polymers are of well-known interest for the preparation of boron nitride complex forms [1]. For example, BN matrices, coatings, fibres and composites were prepared by the polycondensation of borazinic molecular precursors subsequently followed by an appropriate thermal treatment [2]. The intermediate polyborazinic polymers display several structures including amino-bridged rings [3], linked-rings and fused rings [4] frameworks. The condensation reactions can be promoted by either the action of a reagent such as silazane [5] or ammonia [6] or by thermolysis of the monomers. Bulk thermal polymerization studies of B-tri(alkylamino)borazines $[(\text{RHN})\text{BN}(\text{H})]_3$ are relatively rare and lead to different conclusions. Kimura *et al.* reported that the thermal condensation of B-tri(methylamino)borazine yields a polymer in which borazine rings are linked through -NMe- bridges [7]. By contrast, Paciorek *et al.* found that direct B-N bonding between the rings is the predominant path in the early stages of the thermolysis of B-tri(anilino)borazine although some amino bridges were also formed [8]. As discussed by Paine and Sneddon [1], varying the nature of the substituent groups of the borazine can modify the structure of the polyborazines. However, the synthesis and characterization of unsymmetrically B-trisubstituted alkylaminoborazines have not been reported. One of the aims of our work was the determination of the dependence of the structure of the derived oligomers on B-mono- or di-alkylamino substitution of the borazine. Thus, we have explored bulk polycondensation reactions at moderate temperature of unsymmetrically B-trisubstituted alkylaminoborazines. Herein, we report preliminary results of the oligomerization of $(\text{NEt}_2)_3\text{B}_3\text{N}_3\text{H}_3$ (**1**), $(\text{NEt}_2)_2(\text{NHPr}^i)\text{B}_3\text{N}_3\text{H}_3$ (**2**), $(\text{NEt}_2)(\text{NHPr}^i)_2\text{B}_3\text{N}_3\text{H}_3$ (**3**) and $(\text{NMe}_2)(\text{NHMe})_2\text{B}_3\text{N}_3\text{H}_3$ (**4**). These compounds were heated under vacuum for 20 h at 140-145 °C whereas the evolved gas were continuously trapped at low temperature. In these cases, no NH_3 liberation has been observed during thermolysis that excludes any ring opening mechanism described by Paciorek *et al.* [8] and Toeniskoetter and Hall [9]. Spectroscopic data are consistent with the presence of borazine rings in the oligomers. Their FTIR spectra display B-N ring vibrations near 1500 and 700 cm^{-1} showing that the borazine rings remain unaffected during the thermolysis [10]. Because ^{11}B chemical shifts are slightly dependent of the type of alkylamino substitution, the inequivalent boron environments in the monomers are not resolved and give one resonance around 25 ppm, consistently with data reported for B-tri(alkylamino)borazines [11,12]. For the same reason, ^{11}B NMR spectra of the four oligomers exhibit only one resonance around 25 ppm, the broadening of which can be related to the oligomeric nature of these species. This pattern is also observed on ^1H NMR spectra and the resulting overlapping of the signals limits integration ratio determination. On the other hand, ^{13}C NMR appeared as a more reliable spectroscopic technique for the understanding of the path leading to the oligomers.

The thermal reactivity of $(\text{NEt}_2)_3\text{B}_3\text{N}_3\text{H}_3$ (**1**) has been previously described by Gerrard *et al.* [13]. In accordance with their findings, diethylamine was evolved and characterized by its

FTIR and ^1H NMR spectra showing that (1) oligomerizes via the formation of direct B-N bonds between two borazine rings (Fig. 1).

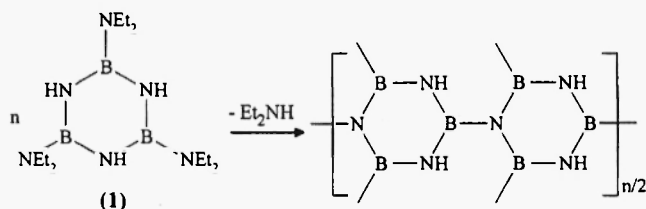


Fig. 1: Mechanism for thermal oligomerization of borazine (1)

As expected and considering the reactivity of borazine N-H hydrogen atoms demonstrated above, thermal polycondensation of compounds (2), (3) and (4) may proceed according to the two mechanisms depicted on Figure 2, previously proposed by Paciorek *et al.* for B-tri(anilino)borazine [8]: (a) formation of -N(R)- bridges; (b) formation of direct B-N bonds between two rings.

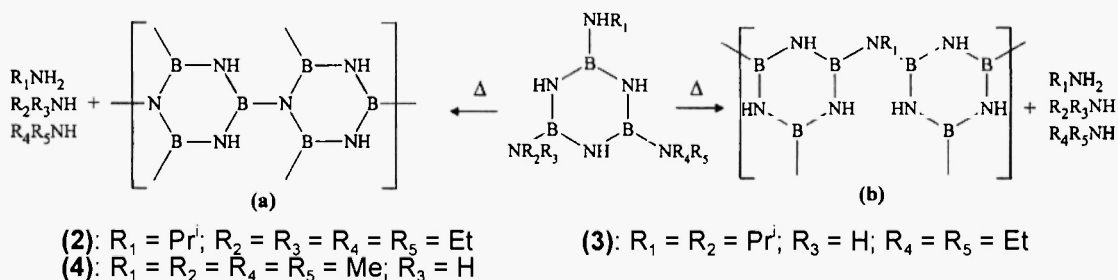


Fig. 2: Possible mechanisms for thermal oligomerization of borazines (2), (3) and (4).

Concerning the thermolysis of $(\text{NEt}_2)_2(\text{NHPr}^i)\text{B}_3\text{N}_3\text{H}_3$ (2) and $(\text{NEt}_2)(\text{NHPr}^i)_2\text{B}_3\text{N}_3\text{H}_3$ (3), the species evolved were identified as Pr^iNH_2 and Et_2NH , the latter being by far the major amine eliminated despite the 1:2 or 2:1 ratio in the monomer. This phenomenon can be related to the ease of displacement of secondary amine compared to primary amine [15] but can be produced by either the two possible mechanisms (Fig. 2). ^1H NMR spectrum of the oligomer obtained from (2) is complex and displays overlapping resonances but shows as expected a major doublet for the CH_3 of NPr^i groups and a small triplet for the CH_3 of NEt_2 groups. The ^{13}C NMR spectrum displays a single set of $-\text{NEt}_2$ and $-\text{NPr}^i$ resonances. The presence of one type of $-\text{NEt}_2$ groups, always in terminal position, was expected whatever the mechanism (a) or (b). The isopropyl CH and CH_3 , respectively at 42.2 and 26.8 ppm are characteristic of amino $-\text{NHPr}^i$ groups according to data reported for B-tri(isopropylamino)borazine [12] whereas other resonances which might be ascribed to $-\text{NPr}^i$ - bridges, namely around 46 ppm for CH and 25 ppm for CH_3 , are absent. For these assignments, we used results of a current parallel study involving the formation of $-\text{N(R)}$ - bridges between borazine rings [14]. Therefore, it appears that the oligomerization of $(\text{NEt}_2)_2(\text{NHPr}^i)\text{B}_3\text{N}_3\text{H}_3$ (2) proceeds mainly via the formation of B-N linked borazine rings (mechanism a). Concerning the oligomer derived from $(\text{NEt}_2)(\text{NHPr}^i)_2\text{B}_3\text{N}_3\text{H}_3$ (3), both ^1H and ^{13}C spectra are nearly the same as those of the oligomer derived from (2). The only noticeable difference in the case of (3) is that the signals characteristic of $-\text{NEt}_2$ groups are negligible showing that almost complete substitution of diethylamino groups took place during oligomerization. This observation is consistent with the amount of amines collected and with the lower ratio of $-\text{NEt}_2$ groups in (3) compared to (2). Thus we concluded that the thermolysis of (3) follows the same path as for (2), giving a polyborazine containing direct B-N bonds between the rings.

Likewise, the oligomerization of $(\text{NMe}_2)(\text{NHMe})_2\text{B}_3\text{N}_3\text{H}_3$ (4) yielded the expected mixture MeNH_2 - Me_2NH (major product). The ^1H NMR spectrum of the oligomer is complex but showed resonances characteristic of borazine rings, amino groups and different methylic hydrogen atoms. The ^{13}C spectrum is consistent with the results deduced from borazines (2) and (3) thermolysis. It displays two resonances at 27.58 and 37.01 ppm respectively assigned

to methyl carbon atoms of -NHMe and -NMe₂ groups in accordance with the shifts observed for the monomer (**4**) whereas the resonance of -NMe- bridge should appear at 31 ppm [14]. Consequently, no signals could be attributed to bridging -NMe- groups showing that borazine rings are bonded through direct B-N links (mechanism **a**). As otherwise stated, Kimura *et al.* [7] reported that thermolysis of tri(methylamino)borazine (MAB) at a similar temperature leads to a polyborazine in which the rings are bonded through -NMe- bridges. Thus, it appears that the substitution of one -NHMe for one -NMe₂ group on MAB results in direct B-N link establishment.

Thermal oligomerization of the four borazines was associated with primary and secondary amine liberation, the latter being always the major species evolved. Although the structures of the ultimate polymers are probably complex and cross-linked, the process of direct B-N link establishment occurs when the borazine boron atoms bear mono- and dialkylamino groups. These conclusions, consistently with those of Paciorek *et al.* stated above [8], are a crucial point for the choice of the polymerization process and for the identification of the most suitable borazines for preceramic polymer elaboration. In this undertaking, further works are in progress to determine the molecular weights of the oligomers and the influence of others thermolysis conditions on the structure of the obtained polyborazines.

Materials and methods

All experiments were performed under atmosphere of pure argon and anhydrous conditions using standard vacuum-line and Schlenk techniques with solvents purified by standard methods. ¹¹B, ¹H, ¹³C NMR spectra were recorded on a Bruker AM300 spectrometer at 96.28 MHz with Et₂O.BF₃ as an external reference (positive values downfield), at 300 MHz and 75 MHz, respectively. The infrared spectra were obtained on an FTIR Nicolet Magna 550 spectrometer as KBr pellets. Analytical data and Mass Spectra (E.I.) were obtained from the S.C.A. of the C.N.R.S.

Synthesis and characterisations of borazines

The B-trisubstituted borazines [(NR₂BNH)₃ and [(NRH)_x(NR'₂)_{3-x}B₃N₃H₃] were synthesised following procedures similar to those previously described in the literature for B-tri(alkylamino)borazines [13]. In a typical experiment, triethylamine (120 mmol) was added to a solution of 2,4,6-trichloroborazine (TCB) (38 mmol) in toluene (130 ml). A solution of the required stoichiometric amount of diethylamine or dimethylamine in toluene (10 ml) was dropped into the TCB solution. The mixture was stirred for 24 h at 25°C. Then, for the syntheses of (**2**), (**3**) and (**4**), a solution of the required stoichiometric amount of isopropylamine or methylamine in toluene (10 ml) was added to the mixture. After 24 h, the residue was filtered off and vacuum dried. The filtrate was evaporated yielding a waxy white solid or a white powder characterized as mainly the expected borazine. Attempted sublimation or recrystallisation of the borazines was unsuccessful. As isolated from the reactions, the compounds gave analyses corresponding closely to the calculated compositions and according to their NMR and mass spectra, the four compounds recovered were identified as the expected borazines containing traces of symmetrically trisubstituted borazines and solvent. Hence, the compounds appeared to be in a satisfactory state of purity to be used in the subsequent pyrolyses without further purification. Yields are calculated on the weights of triethylamine hydrochloride.

(NEt₂)₃B₃N₃H₃ (**1**). Yield 7.88g, 95%. *Anal.* Found: C, 48.2; H, 11.1; B, 10.9; N, 29.8. *Calc.* For C₁₂H₃₃B₃N₆: C, 49.1; H, 11.3; B, 11.0; N, 28.6. NMR (δ, ppm): ¹¹B (C₆D₆): 25.4. ¹H (CDCl₃): 1.05 (t, CH₃, 18H); 2.91 (q, CH₂, 12H); 3.22 (s, NH, 3H). ¹³C (CDCl₃): 16.1 (CH₃); 41.5 (CH₂). IR (cm⁻¹): 3455 (ν_{NH}); 2964, 2925, 2869 (ν_{CH}); 1498 (ν_{BN} + δ_{CH}); 700-685 (BN ring def.). MS (*m/z*, EI): 294 [1]⁺ (30%); 279 [1-CH₃]⁺ (100%).

(NEt₂)₂(NHPr)₁B₃N₃H₃ (**2**). Yield 10.56g, 98%. *Anal.* Found: C, 48.5; H, 12.1; B, 10.3; N, 29.1. *Calc.* For C₁₁H₃₁B₃N₆: C, 47.2; H, 11.1; B, 11.6; N, 30.1. NMR (δ, ppm): ¹¹B (C₆D₆): 25.4. ¹H (CDCl₃): 1.07 (m, CH₃ (Et + Pr), 18H); 1.82 (m, NH amino, 1H); 2.78 (m, NH boraz., 3H); 2.92 (q, CH₂, 8H); 3.23 (m, CH, 1H). ¹³C (CDCl₃): 16.5 (CH₃ (Et)); 27.0 (CH₃ (Pr)); 41.8 (CH₂); 43.0 (CH). IR (cm⁻¹): 3420 (ν_{NH}); 2965, 2926, 2869 (ν_{CH}); 1511 (ν_{BN} + δ_{CH}); 698-684 (BN ring def.). MS (*m/z*, EI): 279 [2]⁺ (15%); 236 [2-Pr]⁺ (100%).

(NEt₂)₁(NHPr)₂B₃N₃H₃ (**3**). Yield 10.15g, 95%. *Anal.* Found: C, 45.4; H, 9.7; B, 13.2; N, 31.7. *Calc.* For C₁₀H₂₉B₃N₆: C, 45.2; H, 10.9; B, 12.2; N, 31.7. NMR (δ, ppm): ¹¹B (C₆D₆): 25.5. ¹H (CDCl₃): 1.06 (m, CH₃ (Et + Pr), 18H); 1.79 (d, NH amino, 2H); 2.70 (m, NH boraz., 3H); 2.89 (q, CH₂, 4H); 3.18 (m, CH, 2H). ¹³C (CDCl₃): 16.4 (CH₃ (Et)); 26.9 (CH₃ (Pr)); 41.7 (CH₂); 42.3 (CH). IR (cm⁻¹): 3413 (ν_{NH}); 2961, 2925, 2867 (ν_{CH}); 1510 (ν_{BN} + δ_{CH}); 697-686 (BN ring def.). MS (*m/z*, EI): 265 [3]⁺ (20%); 236 [3-C₂H₅]⁺ (100%).

(NMe₂)(NMeH)₂B₃N₃H₃ (**4**). Yield 12.11g, 96%. *Anal.* Found: C, 27.6; H, 9.3; B, 16.9; N, 46.2. *Calc.* For C₄H₁₇B₃N₆: C, 26.4; H, 9.4; B, 17.9; N, 46.3. NMR (δ , ppm): ¹¹B (C₆D₆): 25.6. ¹H (CD₂Cl₂): 1.87 (s, NH amino, 2H); 2.57 (d, NHCH₃, 6H); 2.61 (s, N(CH₃)₂, 6H); 2.86 (m, NH boraz., 3H). ¹³C (CD₂Cl₂): 27.6 (NHCH₃); 37.1 (N(CH₃)₂). IR (cm⁻¹): 3446 (ν_{NH}); 2934, 2887, 2815 (ν_{CH}); 1510 ($\nu_{\text{BN}} + \delta_{\text{CH}}$); 708 (BN ring def.). MS (*m/z*, EI): 181 [4]⁺ (30%); 166 [4-CH₃]⁺ (100%).

Synthesis and characterisations of polyborazines

The borazines were heated under vacuum at 140°C with a mechanical stirring. The volatiles were trapped in liquid nitrogen. Then, the amine ratios were analysed either directly or after transformation into their hydrochloride salts. At least, all the oligomers were solid compounds at room temperature and soluble in CH₂Cl₂.

Oligomer obtained from (NEt₂)₃B₃N₃H₃ (**1**). NMR (δ , ppm): ¹¹B (C₆D₆): 25.3. ¹H (CD₂Cl₂): 1.06 (m, CH₃); 2.61 (m, CH₂); 2.89 (s, NH). IR (cm⁻¹): 3452 (ν_{NH}); 2966, 2927, 2870 (ν_{CH}); 1506 ($\nu_{\text{BN}} + \delta_{\text{CH}}$); 701 (BN ring def.). The volatile obtained during oligomerization was characterized as Et₂NH.

Oligomer obtained from (NEt₂)₂(NHPr')B₃N₃H₃ (**2**). NMR (δ , ppm): ¹¹B (C₆D₆): 25.3. ¹H (CD₂Cl₂): 1.05 (m, CH₃ (Et + Pr')); 1.85 (s, NH amino); 2.81 (m, NH boraz.); 2.91 (m, CH₂); 3.22 (m, CH). ¹³C (CD₂Cl₂): 16.2 (CH₃ (Et)); 26.7 (CH₃ (Pr')); 41.6 (CH₂); 42.3 (CH). IR (cm⁻¹): 3440 (ν_{NH}); 2964, 2924, 2868 (ν_{CH}); 1490 ($\nu_{\text{BN}} + \delta_{\text{CH}}$); 695-685 (BN ring def.). The volatiles obtained during oligomerization were characterized as Et₂NH (95% molar) and NH₂Pr' (5% molar).

Oligomer obtained from (NEt₂)(NHPr')₂B₃N₃H₃ (**3**). NMR (δ , ppm): ¹¹B (C₆D₆): 24.9. ¹H (CD₂Cl₂): 1.07 (d, CH₃ (Pr')); 1.80 (s, NH amino); 2.71 (m, NH boraz.); 3.17 (m, CH). ¹³C (CD₂Cl₂): 26.8 (CH₃ (Pr')); 42.2 (CH). IR (cm⁻¹): 3420 (ν_{NH}); 2970, 2924, 2867 (ν_{CH}); 1506 ($\nu_{\text{BN}} + \delta_{\text{CH}}$); 705 (BN ring def.). The volatiles obtained during oligomerization were characterized as Et₂NH (80% molar) and NH₂Pr' (20% molar).

Oligomer obtained from (NMe₂)(NMeH)₂B₃N₃H₃ (**4**). NMR (δ , ppm): ¹¹B (C₆D₆): 25.8. ¹H (CD₂Cl₂): 1.79 (s, NH amino); 2.57 (m, NHCH₃); 2.60 (m, N(CH₃)₂); 2.95 (m, NH boraz.). ¹³C (CD₂Cl₂): 27.6 (NHCH₃); 37.0 (N(CH₃)₂). IR (cm⁻¹): 3460 (ν_{NH}); 2976, 2896, 2840 (ν_{CH}); 1505 ($\nu_{\text{BN}} + \delta_{\text{CH}}$); 729-716 (BN ring def.). The volatiles obtained during oligomerization were characterized as Me₂NH (80%) and MeNH₂ (20%).

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- [14] Reaction of (NEt₂)(NHPr')₂B₃N₃H₃ (**3**) or (NMe₂)(NMeH)₂B₃N₃H₃ (**4**) with TCB yielded polyborazines containing -N(R)- bridges. ¹³C NMR data in CD₂Cl₂ (δ , ppm): -NPr'-bridges: 45.7 (CH), 24.9 (CH₃); -NCH₃- bridges: 31. *Unpublished results.*
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