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Aminoborane Polymers as Precursors of C-N-B Ceramic Materials

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Aminoborane polymers were prepared via condensation reactions between polyfunctional amines and either triethylborane or tris(dimethylamino)borane. The products were characterized by chemical and spectroscopic analyses. The thermal degradation of these materials was studied to establish pyrolytic pathways and to evaluate their potential as precursors to C-N-B ceramic materials. The borane condensation products with 4,4′-methylenedipyrazole, *o*-phenylenediamine, and 3,3′-diaminobenzidine produced relatively high ceramic yields at 800°C, whereas that with diethylenetriamine decomposed into partially volatile oligomers.

I. Introduction

The conversion of polymeric precursors into ceramic materials via thermal treatment is a synthetic approach pioneered during the early 1960s. A historical perspective of that period and a description of polymeric precursor research opportunities are given in Ref. 1. Research in this subject was greatly stimulated by the work of Yajima,[2] who demonstrated the formation of SiC fibers by the heat treatment of organosilicon polymers. At the present time, the convergence of organic and inorganic chemistry, polymer science, and materials science into a potentially rewarding area of research is evident, namely, the preparation of polymers as precursors of ceramic materials. It is within this framework that the present study was undertaken; its goal was the preparation of coatings or fibers of boron nitride or C-B-N materials from aminoborane polymers. It was also of interest to learn about pyrolytic pathways so that it will be possible to accumulate an empirical database for the design of appropriate precursors.

Earlier attempts to prepare polymers containing B-N moieties, not necessarily for conversion to ceramic materials, include the work of Mulvaney *et al.*[3] and the work described in Ref. 4. More recently, borazine-based polymers have been prepared and evaluated as sources of boron nitride.[5,6]

II. Experimental Procedure

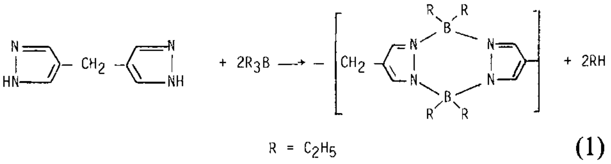
Polymeric materials containing B-N moieties were prepared by condensation reactions of a borane, either triethylborane or tris(dimethylamino)borane, and a bifunctional (or higher functionality) amine. The compound 4,4′-methylenedipyrazole was prepared by a modification of Trofimenko's procedure,[7] as described below. All other reagents were commercial products[*] and were used without further purification. The condensation reactions were conducted under reflux in toluene or xylene for 18 h using an argon stream to exclude moisture. The resulting polymeric materials were characterized by chemical analysis, infrared (IR) spectroscopy[†] (KBr pellets), and differential thermal analysis–thermogravimetric analysis (DTA–TGA). The products were subjected to pyrolysis in a quartz tube up to 800°C under a dynamic vacuum, heating in 100°C steps, and holding at temperature until the volatile evolution subsided. Condensable volatile decomposition products were collected in a U trap cooled to −196°C for subsequent separation and examination by IR. In one instance a pyrolysis experiment was conducted while passing a stream of helium and analyzing the volatiles by mass spectrometry (MS). Solid residues of the pyrolyses were subjected to chemical analysis and examined by powder X-ray diffraction (XRD). Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. In most cases the analyses accounted for ≥95 wt% of the material.

The preparation of 4,4′-methylenedipyrazole was performed by heating equimolar mixtures of CH_2Br_2 and pyrazole at 200°C in 2.54-cm-outside-diameter heavy-walled glass ampules of 40-mL capacity loaded with 20 g of the mixture. This differs from the method employed by Trofimenko,[7] who used an autoclave. (**Caution:** Steel pipes should be used to contain the ampules while heating.) The dipyrazole was recrystallized from hot water and sublimed under vacuum at 180°C: mp 199°C [reported[7] 194° to 196°C]; ^1H NMR (DMSO) δ 11.34 (NH), 3.59 (CH_2), 6.95 (ring protons), downfield from TMS, in a 1:1:2 relation. These compare with δ 11.8, 3.57, and 7.38, respectively, reported by Trofimenko.[7]

III. Results and Discussion

(1) *Pyrazabole Polymers*

Trofimenko,[7] in a study of the chemistry of pyrazolyl alkanes, described the preparation of pyrazabole polymers by the reaction of 4,4′-methylenedipyrazole and triethylborane (Et_3B) according to Eq. (1).



(1)

The product was described as being soluble in toluene, but it was not fully characterized other than by chemical analysis and thermal treatment under mild conditions. This material seemed attractive as a potential source of a ceramic material that could be obtained as a coating or as fibers. The preparation of the polymer was performed by mixing 25 mmol of dipyrazole and 50 mmol of Et_3B in 150 mL of toluene and heating under reflux for 18 h. Cooling the reaction mixture to room temperature separated 3.65 g of an initial solid fraction (polymer A); evaporation of the filtrate to half of its initial volume produced 2.5 g of a second fraction (polymer B). Polymer A proved to be, on the basis of chemical analyses and molecular weight determination, an oligomer containing an average of nine repeat units terminated at both ends with pyrazole units, whereas polymer B, also containing an average of nine units, had one pyrazole end capped by a >B–Et unit.

Polymer A, Anal. Calcd for $C_{142}H_{242}N_{40}B_{18}$ (wt%): C, 63.1; H, 8.96; N, 20.74; B, 7.20; MW 2704.3; N/B atomic ratio 2.22; C/B 7.89. Found: C, 62.99; H, 8.60; N, 20.84; B, 7.35; MW (osmometry in toluene) 2662; N/B 2.19; C/B 7.71. Polymer B, Anal. Calcd for $C_{144}H_{246}N_{40}B_{19}$ (wt%): C, 63.08; H, 8.98; N, 20.45; B, 7.49; MW 2739; N/B 2.106; C/B 7.58. Found: C, 62.86; H, 9.15; N, 20.19; B, 7.45; MW 2780; N/B 2.091; C/B 7.59. Alternatively, a $>BEt_2$ cap for polymer B is not significantly different.

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[*] Aldrich Chemical Co., Milwaukee, WI.

[†] Model 60 Digilab, BIORAD, Cambridge, MA.

The IR spectra of polymers A and B are very similar; bands were observed (cm^{-1}) at 3469 (NH), 3134 (C–H aromatic), 2945, 2906, 2870, 2827, 2721 (C–H aliphatic), 1674, 1576, 1458, 1425, 1360, 1276, 1126, 1057, 1024, 910, 852, 750, and 628. The aliphatic C–H stretching bands were more intense in polymer B, apparently on account of the additional >B-Et or $>BEt_2$ cap, whereas polymer A showed a stronger N–H stretching band.

Pyrolyses of polymer A were conducted in separate experiments under the following conditions: under dynamic vacuum up to 800°C, in a TGA-DTA apparatus under a stream of argon up to 1200°C, and in a system connected to a mass analyzer under a stream of helium up to 800°C with a constant 10°C/min ramp.

The residue from the dynamic vacuum pyrolysis to 800°C was 51.5% of the initial weight, amorphous by XRD, and consisted of friable, shiny black particles, a few millimeters in diameter, similar in appearance to vitreous carbon. Volatile condensable products from the pyrolysis collected at −196°C and later separated by fractional condensation at −63°, −130°, and −196°C gave, respectively, Et_3B and NH_3, HCN, and C_2H_4. Ammonia, which should not have condensed in the −63°C trap, apparently either was retained by Et_3B as an adduct or reacted later. Chemical analysis of this fraction showed nearly equimolar amounts of ammonia and boron.

A material balance showed that the condensable volatiles accounted for 83% of the weight loss; the balance apparently evolved as noncondensable species, such as hydrogen or methane. It is significant that the Et_3B that evolved was a relatively small fraction, about 10%, of the initial boron present, most of which is retained in the residue. Thus, it appears that no readily favorable mechanism is available for the evolution of volatile species containing boron. The main volatile components were C_2H_4 and HCN, produced to the extent of about 3 mol and 1 mol, respectively, per mole of repeat unit in the polymer.

The TGA-DTA experiment showed a very sharp and pronounced exothermic event at 432°C. This coincided with a sharp (TGA) weight loss. Cumulative weight losses amounted to 53% at 700°C and 76.7% at 1200°C (see Fig. 1). No additional weight loss was observed after holding at 1200°C for 30 min. The residue had an appearance similar to that of the vacuum pyrolysis. In this case a faint XRD pattern could be detected corresponding to graphite; however, additional faint lines with *d* values of 0.36, 0.56, and 0.61 nm (3.6, 5.6, and 6.1 Å) were also present. These lines could be due to a BN crystalline modification.[8]

Volatile evolution as a function of time and temperature monitored by MS showed the onset of decomposition at 330°C, reaching a maximum at 370°C, with a secondary maximum at 453°C. Evolution of volatiles subsided at 610°C. MS analyses of the species evolved showed HCN and C_2H_4 at both maxima, whereas Et_3B (parent peak at 98 with strong peaks at 69, 54, and 41) evolved only with the initial current maximum.

A sample of vacuum pyrolysis residue hot-pressed at 1400°C and 44 MPa under vacuum gave a friable pellet. Repressing at 1600°C and 44 MPa produced a nonfriable compact with a density of 1.41 g/cm^3, similar to amorphous carbon, but considerably lower than the 2.26 g/cm^3 value of graphite. The overall yield of the 1600°C compact from the polymer was 25%. The chemical analysis of the 1600°C residue showed the following (wt%): C, 51.85; H, 0.16; N, 21.59; B, 20.51; O, 1.73. The electrical conductivity of the compact was 1.1 S/cm, which is within the conductivity range of a number of pyrolyzed organic polymers.[9]

A translucent film, about 30 μm in thickness, formed by evaporation of a toluene solution of the polymer in a 70 by 25 mm quartz tray, was vacuum pyrolyzed at 800°C. This treatment produced isolated islands instead of a coherent coating because of shrinkage. Attempts to produce fibers by forcing a toluene solution of the polymer through a thin needle into a column containing chilled methanol failed. It seems that the failure to produce coatings might be due to the fact that the polymer does not melt. On the other hand, the competing combination of viscosity and surface tension in the polymer solution prevents formation of fibers.

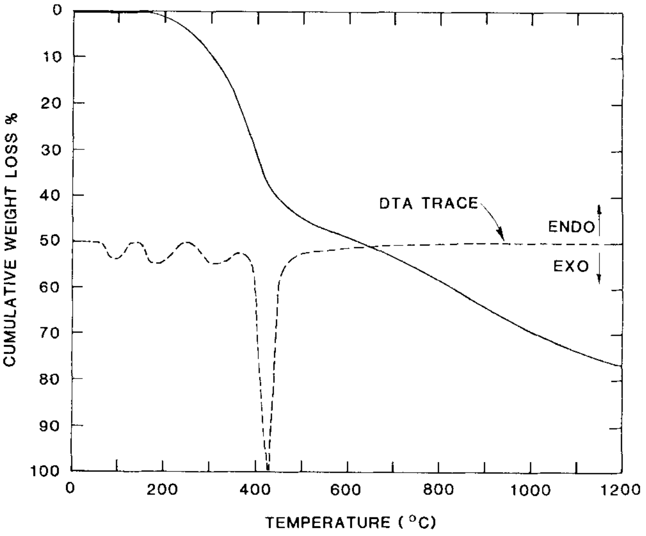
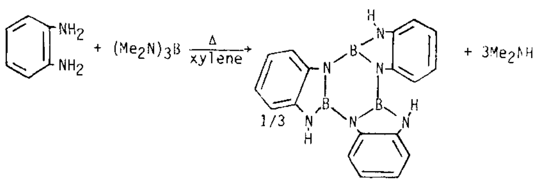


Fig. 1. TGA–DTA analysis of pyrazabole polymer.

(2) *Hydrobenzoboradiazole Polymers*

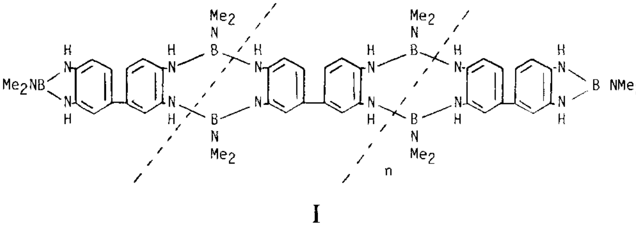
Condensation reactions of tris(dimethylamino)borane (TDMAB) with either *o*-phenylenediamine or 3,3′-diaminobenzidine were performed in the course of this study. These reactions are similar to those conducted by Mulvaney *et al.*,[3] who used tetra-*n*-butylbenzene-1,4-diboronate as the source of the boron. The reaction between TDMAB and *o*-phenylenediamine has been previously studied by Beyer *et al.*[10] The reaction produces, in high yield, an interesting fused ring system according to Eq. (2).



(2)

The pyrolysis of this borazine derivative produced a residue with an 85% yield in the form of adherent coatings on a variety of substrates such as quartz, silicon, titanium, and steel. As reported elsewhere,[11] the coatings were amorphous semiconductors containing carbon, nitrogen, and boron.

The reaction of 77 mmol of TDMAB and 39 mmol of 3,3′-diaminobenzidine produced, after 24-h reflux in toluene and room-temperature filtration, a condensation product whose idealized form is shown in structure I. (A more random linking of the repeat unit is likely.)



I

Anal. Calcd for $(C_{16}H_{22}N_6B_2)_n$ (wt%): C, 60.07; H, 6.88; N, 26.28; B, 6.76. Found: C, 58.75; H, 6.84; N, 25.78; B, 6.51 (Σ 97.38). The analysis indicates one terminal dimethylamino group per boron. This fact precludes the formation of the corresponding fused-ring borazine system as observed in the case of *o*-phenylenediamine. Steric effects and the presence of two reaction sites in the benzidine apparently favor polymerization instead of ring closure.

Thermal degradation of this material produced, at 265°C, a sublimate and Me_2NH equivalent to 1 mol per repeat unit of polymer, and a weight loss of 25.6%. Analysis of the residue showed the following (wt%): C, 59.48; H, 4.90; N, 22.97;

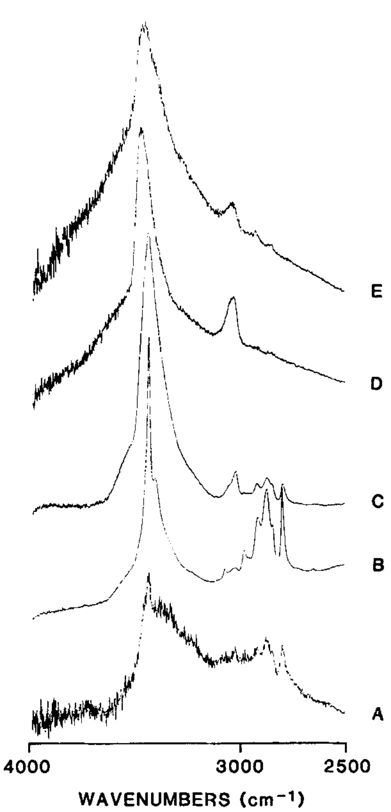
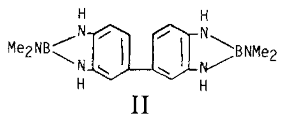


Fig. 2. IR spectra: (A) condensation product 3,3′-diaminobenzidine–TDMAB, (B) coupled benzodiazaborolene, (C) polymer A heated to 265°C, (D) polymer A heated to 800°C for 1 h, and (E) polymer A heated to 800°C for 4 h.

B, 7.97 (Σ 95.32). The sublimate analysis showed the following (wt%): C, 59.6; H, 6.84; N, 25.67; B, 6.50 (Σ 98.61). The sublimate is the coupled dimethylamino-1,3,2-benzodiazaboroline (structure II).



II

Anal. Calcd (wt%): C, 60.07; H, 6.88; N, 26.28; B, 6.76. MS supports the assignment showing the parent ion cluster caused by the boron isotopes with the highest peak at mass 320. The diazaboroline actually corresponds to a repeat unit of the initial polymer. The liberation of Me$_2$NH and the sublimate evidently leads to a cross-linked system. The initial polymer was soluble in dimethylformamide (DMF), but the residue of the thermal treatment could not be dissolved.

The release of 1 equiv of Me$_2$NH in the thermal treatment of the initial polymer suggests that the release of sublimate might also hold a similar relation; thus a calculation that incorporates a material balance shows that the molecular weight of the initial polymer would be about 2600, or 8 units, if the polymer produces 1 mol of sublimate or a molecular weight of about 5200 if it produces 2 mol of sublimate. An alternative explanation as to the origin of the sublimate is that it could be a byproduct of the initial reaction and not a fragment produced by the thermal treatment.

The IR of the sublimate is very similar to that of the initial polymer, but with better resolved bands (see Fig. 2). An attempt to obtain a ^{1}H NMR spectrum of the sublimate in deuterated dimethyl sulfoxide (DMSO) failed to produce additional structural evidence because the material reacted with the solvent. An attempt to determine the melting point of the sublimate in a sealed tube showed decomposition, without melting, up to 800°C.

Pyrolysis under dynamic vacuum of the initial polymer to 800°C produced sublimate, identical with the material obtained at 265°C and 2 equiv of Me$_2$NH per repeat unit of polymer, corresponding to a 41% weight loss. Analysis of the residue showed the following (wt%): C, 61.75; H, 3.29; N, 22.24; B, 8.84 (Σ 96.12). The material retained a considerable amount of hydrogen. The residue was a light tan powder. Evidence of carbonization was observed in parallel experiments only after holding for a few hours at 800°C. The IR of the 265° and 800°C residues showed changes consistent with the evolution of Me$_2$NH, that is, gradual disappearance of aliphatic C–H stretches, whereas N–H and aromatic C–H stretches were clearly evident, even in the product held for a few hours at 800°C (Fig. 2).

The TGA–DTA of the initial polymer conducted under argon up to 1200°C showed an endothermic event at 180°C with weight loss of about 15% of the initial weight and an exothermic event at 460°C with weight loss of 12%. There was no weight loss beyond 900°C. At that point, the cumulative weight loss amounted to 41%.

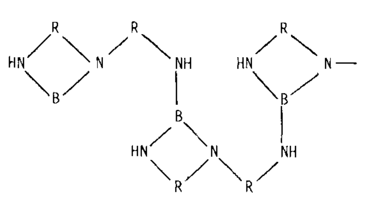
Attempts were made to cast a film of the polymer for subsequent pyrolysis. A reddish film produced by dissolution of the initial polymer in DMF and vacuum solvent evaporation at 115°C produced fluffy blisters with a ceramic yield of 68% upon pyrolysis at 800°C.

Transformation of the initial benzidine polymer by cleavage of dimethylamine at one or both ends of the chain produces a cross-linked material with very high thermal stability.

(3) Diethylenetriamine–TDMAB Condensation

The condensation of TDMAB and diethylenetriamine was studied in an attempt to produce a polymeric material with a higher B and N content than the previously discussed materials. One system with an even higher potential for producing a material with a relatively high B-N content would be the condensation product of melamine and TDMAB or triethylborane; however, these materials failed to react.

TDMAB reacted, in refluxing toluene, with diethylenetriamine using a 5:3 mole ratio of TDMAB to amine; this was designed to displace all the protons in the amine in order to produce a closed polymeric network. An idealized composition derived from the analysis showed the following. Anal. Calcd for $(C_{20}H_{47}N_{15}B_6)_n$ (wt%): C, 42.7; H, 8.36; N, 37.36; B, 11.53. Found: C, 42.4; H, 7.39; N, 36.34; B, 11.74 (Σ 97.87). This would imply that the actual reaction stoichiometry corresponded to a 6:5 mole ratio of TDMAB to amine. The analysis indicates that all the dimethylamino groups were displaced. A hypothetical portion of the network in this material is represented by structure III.



III

R = -CH$_2$-CH$_2$-.

The initial polymeric material was isolated by evaporating the toluene under vacuum, at room temperature, from the clear reaction mixture. That process left initially a thick liquid which eventually filled the flask with foamy blisters as additional solvent evaporated. A sample of the material was removed for IR and NMR analyses, and the balance was further dried under vacuum at 110°C. (The analysis given above corresponds to the dried material). The drying process evolved 8% residual toluene but no other volatile components. The dried material showed an IR different from the initial polymer, suggestive of internal rearrangement. The N–H stretching bands in the initial material at 3435, 3344, and 3269 cm^{-1} coalesced into a single, stronger band at 3441 cm^{-1} in the dried material. On the other hand, the dried material showed a significant enhancement of the bands at 1512, 1471, and 1428 cm^{-1}, indicative of an increased bond order of the B–N functionality present in the polymer.[12] It is possible that the drying caused additional bond formation through a conversion of the coordination environment around boron from trigonal to tetrahedral. The drying process also caused loss of solubility of the material in toluene.

The ^{1}H NMR and ^{13}C NMR spectra of the initial polymer did not show well-resolved peaks. The proton on nitrogen was not observed as is common with many amines. Attempts to determine the molecular weight of the initial polymer by vapor pressure osmometry failed, apparently because of hydrolytic decomposition of the material.

Pyrolysis of the dried polymer up to 800°C under dynamic vacuum led to the evolution of light volatiles, approximately 3% by weight, containing NH_3, C_2H_2, C_2H_4, and HCN. Also produced were heavy volatiles, in the form of droplets that did not leave the heating zone and a carbonaceous residue corresponding to 12% of the initial weight.

It is evident from the residue yield that the thermal stability of this aliphatic aminoborane polymer is lower than that of the aromatic materials examined.

IV. Conclusions

Aminoborane polymers, particularly those with a high aromatic hydrocarbon content, can be used as precursors of C-N-B ceramic materials which might be of interest because of their thermal or electronic characteristics. Their use as binders during sintering of boron nitride or silicon carbide powders might be of interest. The presence of a thermally robust organic backbone leads to a relatively high carbon content in the pyrolyzed product. Very little or no boron is evolved from the pyrolysis of aminoborane polymers, thus the boron concentration in the precursor polymer will be preserved or slightly increased in the pyrolyzed residue. Ceramic materials with relatively high B-N content might be better prepared from polymers containing borazine as the main structural feature.

Condensation reactions to produce aminoborane polymers examined in this study resulted in relatively low-molecular-weight products which prevented processing of these materials into coatings or fibers with the exception of the benzodiazaboroloborazine which produced coherent C-N-B coatings upon pyrolysis.

Pyrolytic pathways, apparently thermodynamically driven, favor loss of pendant groups that can form "good" leaving groups, such as ethane or triethylborane from the pyrazabole polymer and dimethylamine from the benzidine–TDMAB condensation product. Additional small molecules, such as NH_3, HCN, and $HC\equiv CH$, are likely products at higher temperatures.

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References

[1] R. W. Rice, "Ceramics from Polymer Pyrolysis, Opportunities and Needs—A Materials Perspective," *Am. Ceram. Soc. Bull.*, **62** [8] 889–92 (1983).

[2] S. Yajima, "Development of Ceramics, Especially Silicon Carbide Fibers, from Organosilicon Polymers by Heat Treatment," *Philos. Trans. R. Soc. London, A*, **294**, 419–26 (1980).

[3] J. E. Mulvaney, J. J. Bloomfield, and C. S. Marvel, "Polybenzborimidazolines," *J. Polym. Sci.*, **62**, 59–72 (1962).

[4] I. B. Atkinson and B. R. Currell, "Boron-Nitrogen Polymers," *Inorg. Macromol. Rev.*, **1**, 203–33 (1971).

[5] C. K. Narula, R. T. Paine, and R. Schaeffer, "Precursors to Boron-Nitrogen Macromolecules and Ceramics," *Mater. Res. Soc. Symp. Proc.*, **73**, 383–88 (1986).

[6] B. A. Bender, R. W. Rice, and J. R. Spann, "Evaluation of Potential BN Polymer Precursors," *Ceram. Eng. Sci. Proc.*, **6** [7–8] 1171–83 (1985).

[7] S. Trofimenko, "Geminal Poly(1-pyrazolyl)alkanes and Their Coordination Chemistry," *J. Am. Chem. Soc.*, **92** [17] 5118–26 (1970).

[8] S. S. Batsanov, G. E. Blokhina, and A. A. Deribas, "The Effects of Explosions on Materials—Structural Changes in Boron Nitride," *J. Struct. Chem. (Engl. Transl.)*, **6**, 209–13 (1965).

[9] C. B. Duke and H. W. Gibson, "Conductive Polymers"; pp. 769–93 in Kirk–Othmer Encyclopedia of Chemical Technology, 3d ed., Vol. 18. Wiley, New York, 1981.

[10] H. Beyer, K. Niedenzu, and J. W. Dawson, "Boron–Nitrogen Compounds, VIII. 2-Dimethylamino-1,3,2-benzodiazaboroline," *J. Org. Chem.*, **27**, 4701–702 (1962).

[11] L. Maya, "Semiconducting Amorphous Film Containing Carbon, Nitrogen, and Boron," *J. Electrochem. Soc.*, **135**, 1278 (1988).

[12] K. Niedenzu and J. W. Dawson, "The Chemistry of Boron–Nitrogen Compounds"; p. 393 in The Chemistry of Boron and Its Compounds. Edited by E. L. Muetterties. Wiley, New York, 1967. □