melting points and other physical properties of the compounds would lead one to expect.

In conclusion, it appears that these trimers are both in the chair form with nearly coplanar arrangements of the valence bonds of the nitrogen atoms. The latter feature is not surprising, to judge from the dipole moments and other properties of aromatic amines which yield values of the nitrogen valency angle. The attachment of a phenyl group to nitrogen seems to widen the valency angle of that atom. Such attachment apparently causes a change in the nitrogen bonding orbitals from sp^3 to sp^2 hybridization, with the lone pair of nitrogen electrons now in symmetric p-orbitals at right angles to the plane of the bonding orbitals. In this situation, the contribution of the lone pair to the molecular moment diminishes and the calculations made above are the more valid.

Acknowledgments.—It is a great pleasure to acknowledge the friendly interest and advice given us by Drs. E. C. Wagner, E. R. Nixon, F. V. Brutcher and R. E. Hughes. For aid in the preliminary stages of the experimentation we are also indebted to Messrs. S. J. Rosoff and R. A. Brown.

PHILADELPHIA, PENNSYLVANIA

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA]

The Preparation of Di-*n*-butylboron Cyanide by the Interaction of Di-*n*-butylboron Chloride with Trimethylsilyl Cyanide[1]

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The interaction of $(n\text{-}C_4H_9)_2BCl$ with $(CH_3)_3SiCN$ results in the formation of the new polymeric compound $(n\text{-}C_4H_9)_2BCN$ which is a viscous liquid of high molecular weight. $(n\text{-}C_4H_9)_2BCN$ may also be prepared by the reaction of $(n\text{-}C_4H_9)_2BCl$ with AgCN. This substance when treated with sodium in liquid ammonia produces monomeric $(n\text{-}C_4H_9)_2BNH_2$, previously known only in a more highly polymerized form. $(CH_3)_3B$ and $(CH_3)_3SiCN$ react to produce a complex mixture of substances.

Introduction

In a preceding paper[2] it was shown that B_2H_6 reacts with trimethylsilyl cyanide to form an addition compound which, on heating, decomposes to form a polymeric substance, BH_2CN. Reaction proceeds according to the equation

$$(CH_3)_3SiCN\cdot BH_3 \longrightarrow (CH_3)_3SiH + BH_2CN \quad (1)$$

The present investigation was undertaken in an attempt to prepare less highly polymerized materials by replacing H with alkyl groups. For this purpose we have studied the reaction of trimethylsilyl cyanide with $(n\text{-}C_4H_9)_2BCl$ and $(CH_3)_3B$.

Results and Discussion

Di-*n*-butylboron chloride reacts rapidly and quantitatively with trimethylsilyl cyanide without the formation of any apparent addition compound under our experimental conditions. Reaction proceeds according to the equation

$$(n\text{-}C_4H_9)_2BCl + (CH_3)_3SiCN \longrightarrow (n\text{-}C_4H_9)_2BCN + (CH_3)_3SiCl \quad (2)$$

The new compound, $(n\text{-}C_4H_9)_2BCN$, may also be prepared conveniently by the metathetical reaction between di-*n*-butylboron chloride and silver cyanide. This method of preparation is similar to that used for the preparation of $B(OCN)_3$.[3]

Di-*n*-butylboron cyanide is a colorless, viscous liquid having a polymerization number of at least 20, judging by its cryoscopic behavior in benzene. The compound exhibits a well-defined $C\equiv N$ stretching frequency at 2280 cm.$^{-1}$, hence the cyanide group has not undergone any far reaching chemical transformation. Because of its polymeric nature it is not possible to designate the compound as either a normal or isocyanide since both the carbon and nitrogen atoms of each cyanide group are presumably attached to boron atoms.

Depolymerization of the di-*n*-butylboron cyanide may be effected by ammonia. A fairly mobile, non-volatile liquid of empirical composition $(n\text{-}C_4H_9)_2BCN\cdot NH_3$ is obtained on removing excess ammonia at room temperature.

It appears very likely that a reversible ammonolysis might take place in liquid ammonia, *viz.*

$$(n\text{-}C_4H_9)_2BCN\cdot NH_3 + NH_3 \rightleftarrows (n\text{-}C_4H_9)_2BNH_2 + NH_4CN \quad (3)$$

since treatment with sodium causes evolution of hydrogen and converts the cyanide to the corresponding monomeric amine, $(n\text{-}C_4H_9)_2BNH_2$, which previously has only been prepared in a more highly polymerized state.[4]

Just as NH_3 inhibits the polymerization of $(n\text{-}C_4H_9)_2BCN$ so also does $(CH_3)_3SiCN$ inhibit the polymerization of BH_2CN. When $(CH_3)_3SiCN\cdot BH_3$ is decomposed in the presence of $(CH_3)_3SiCN$, BH_2CN is not formed; instead there is produced $(CH_3)_3SiCN\cdot BH_2CN$, which is volatile at temperatures at which BH_2CN is completely involatile.[2] It therefore appears that the BH_2CN units, as formed, combine with $(CH_3)_3SiCN$ as indicated in equation 4 to form a monomeric material, instead of combining with themselves to form a polymer, *viz.*

$$(CH_3)_3SiCN + BH_2CN \longrightarrow (CH_3)_3SiCN\cdot BH_2CN \quad (4)$$

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(1) This research was supported by the Office of Naval Research, Contract No. Nonr-551(21). Reproduction in whole or in part is permitted for any purpose of the United States Government.

(2) E. Charles Evers, W. O. Freitag, W. A. Kriner, J. N. Keith, A. G. MacDiarmid and S. Sujishi, THIS JOURNAL, **81**, 4493 (1959).

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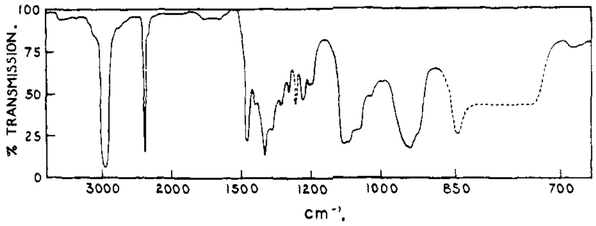

Fig. 1.—Infrared absorption spectrum of $(n\text{-}C_4H_9)_2BCN$. A Perkin–Elmer model 21 spectrophotometer with a sodium chloride prism was employed. A 20% solution in CCl_4 was used in a 0.114 cm. cell equipped with KBr windows. The frequencies observed were 2910 vs, C–H stretch; 2280 vs, C≡N stretch; 1462 vs, 1424 s, 1380 vs, 1350 s, 1310 s, 1225 s, 1205 s, all characteristic of $n\text{-}C_4H_9\text{-}B$ compounds; 934 vs; and impurities 1253 and 844 cm.$^{-1}$ probably due to $(CH_3)_3SiCl$ or $(CH_3)_3SiCN$ (dotted lines).

The highly polymeric nature of the cyanoborines BH_2CN[2] and $(n\text{-}C_4H_9)_2BCN$ is understandable since the linear nature of the B—C≡N → linkage does not permit small ring closures.

The compounds are also surprisingly stable thermally, in the sense that heating is apparently not effective in causing depolymerization to produce volatile fragments; instead, the cyanide group is reduced in the case of BH_2CN,[2] while the alkyl compound loses hydrocarbons.

In view of the reaction occurring between silyl cyanides and diborane as indicated by equation 1, it was expected that $(CH_3)_3SiCN$ and $(CH_3)_3B$ might react in an analogous manner to form $(CH_3)_4Si$ and $(CH_3)_2BCN$. Such, however, was not the case and reaction proceeded to give substances which could not be isolated in a sufficiently pure state for identification

Experimental

Apparatus and Materials.—When necessary, all studies were carried out in a Stock-type vacuum apparatus with rigid exclusion of air and moisture. Distillations at atmospheric pressure were carried out under dry nitrogen.

$(CH_3)_3SiCN$ was prepared as described previously.[2] The fraction distilling at atmospheric pressure in the range 116–118.8° was collected and refractionated in the vacuum system. $(n\text{-}C_4H_9)_2BCl$ (vapor pressure found, 7 mm., literature value,[5] 7 mm. at 47–48°) was prepared[5] by treating $(n\text{-}C_4H_9)_3B$[6] with BCl_3. The purity of the product was checked by hydrolyzing a sample in NaOH solution and then titrating with $AgNO_3$ solution. Found: Cl, 22.3. Calcd.: Cl, 22.1.

Preparation of $(n\text{-}C_4H_9)_2BCN$ from $(n\text{-}C_4H_9)_2BCl$ and $(CH_3)_3SiCN$.—$(n\text{-}C_4H_9)_2BCl$ (8.850 mmoles), $(CH_3)_3SiCN$ (55.50 mmoles) and pentane (3.569 g.) were combined at −196° and the temperature then was raised and held at −15° for one hour. The reaction vessel then contained only a clear homogeneous liquid phase. After three hours at room temperature and 18 hours at −78° the volatiles were completely removed at room temperature by continuous pumping during a period of three days. Fractionation of the volatile material yielded pentane (3.570 g.), $(CH_3)_3SiCN$ (46.64 mmoles; mol. wt. found, 99.0, calcd., 99.2), $(CH_3)_3SiCl$ (8.848 mmoles; mol. wt. found, 109, calcd., 109; confirmed by infrared spectrum[7]) and a few drops of an unidentified liquid. The non-volatile residue (8.695 mmoles) was a very pale yellow viscous liquid of composition corresponding to $(n\text{-}C_4H_9)_2BCN$ (Calcd.: C, 71.50; H, 12.00; N, 9.26; B, 7.18. Found: C, 69.21, 69.45; H, 12.37, 12.04; N, 10.48, 10.58; B, 7.86, 7.89).[8]

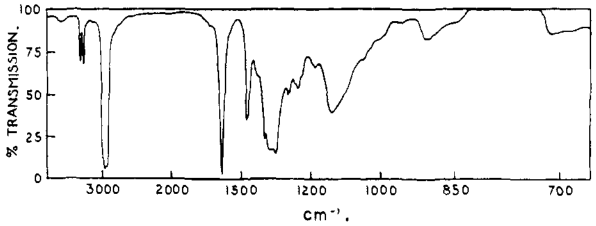

Fig. 2.—Infrared absorption spectrum of $(n\text{-}C_4H_9)_2BNH_2$. A Perkin–Elmer model 21 spectrophotometer with a sodium chloride prism was employed. A 20% solution in CCl_4 was used in a 0.114 cm. cell equipped with KBr windows. The frequencies observed were 3540, 3460 m, NH_2 stretch; 2940 vs, C–H stretch; 1608 vs, N–H bend; 1466 s, 1380 s, 1330 s, 1282 m, 1245 m, 1183 m, 1130 s, all characteristic of $n\text{-}C_4H_9\text{-}B$ compounds; 898 w.

Reaction therefore appears to occur under the above conditions according to equation 2 giving a 98.2% yield of di-*n*-butylboron cyanide based on the quantity of $(n\text{-}C_4H_9)_2BCl$ consumed.

In a second experiment, $(n\text{-}C_4H_9)_2BCl$ (71.0 mmoles) and $(CH_3)_3SiCN$ (90.5 mmoles) were combined at −196° and then brought rapidly to −10°, where a vigorous exothermic reaction occurred. After one hour the temperature was raised to 20° and all volatiles were removed. Fractionation yielded: $(CH_3)_3SiCN$ (21.9 mmoles; mol. wt. found, 103, calcd., 99.2; confirmed by infrared spectrum[9]), $(CH_3)_3SiCl$ (66.7 mmoles; mol. wt. found, 109, calcd., 109; confirmed by infrared spectrum[7]) and a trace of $(n\text{-}C_4H_9)_2BCl$, (approx. 0.1 mmole). The residue in the reaction vessel was similar in appearance to the product prepared in the first experiment. From the quantities of reactants and products involved it had a composition corresponding to $(n\text{-}C_4H_9)_2BCN$. The quantity of $(CH_3)_3SiCl$ measured corresponded to a yield of 97.1% based on the amount of $(CH_3)_3SiCN$ consumed according to equation 2.

The $(n\text{-}C_4H_9)_2BCN$ was soluble in common organic solvents and was hydrolyzed only slowly by a 10% NaOH solution at room temperature giving, after 20 hours, a clear solution containing a dispersion of oily droplets. Only 55% of the theoretical amount of free cyanide was detected in the hydrolysate by titration with $AgNO_3$.

In a third experiment $(n\text{-}C_4H_9)_2BCl$ (14.7 mmoles) and $(CH_3)_3SiCN$ (46 mmoles) were combined at −196°. On raising the temperature to 0° a vigorous reaction occurred. Reaction appeared complete after one hour at 0°. Volatiles were removed by pumping, first at room temperature and then at 80° for approximately 4 hours. Fractionation yielded $(CH_3)_3SiCN$ (approx. 31 mmoles), $(CH_3)_3SiCl$, (approx. 13 mmoles) and a small quantity of HCN (1.5 mmoles), all identified by their infrared spectra.[7,9,10]

The residue in the reaction vessel had the same appearance as the product prepared in the previous experiments. The yellow color was removed when a portion of the liquid was dissolved in benzene and passed through an alumina chromatographic column. Evaporation of the benzene yielded a completely colorless, viscous liquid. Infrared spectra of solutions of the colored and colorless liquids in CCl_4 were identical to the spectrum of the $(n\text{-}C_4H_9)_2BCN$ prepared in the previous experiment. A molecular weight of 3300 was obtained by a cryoscopic measurement in benzene solution.

Preparation of $(n\text{-}C_4H_9)_2BCN$ from $(n\text{-}C_4H_9)_2BCl$ and AgCN.—$(n\text{-}C_4H_9)_2BCl$ (26.5 g.) was treated in ether solution with an excess of AgCN in suspension. The reaction was allowed to proceed under ether reflux for several hours. Excess AgCN was removed by centrifugation and decantation, with minimum exposure to air. Removal of the solvent in

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[6] Rocky Mountain Research Corp., Denver, Colorado.

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[8] All analyses performed by Galbraith Micro-analytical Laboratories, Knoxville, Tennessee.

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vacuum left a yellow, sticky, viscous material. The infrared spectrum of this product in CCl_4 was identical to that obtained with the $(n\text{-}C_4H_9)_2BCN$ described above.

Reaction of $(n\text{-}C_4H_9)_2BCN$ with NH_3.—A sample of $(n\text{-}C_4H_9)_2BCN$ (2.34 mmoles) was treated with NH_3 (5.06 mmoles) at −35° for three hours. Excess NH_3 (2.89 mmoles; mol. wt. found, 17.6, calcd., 17.0) was removed. From the quantities of reactants involved, the clear, colorless, liquid residue had the composition $(n\text{-}C_4H_9)_2BCN \cdot 0.93NH_3$. It appeared to be less viscous than the starting material. An infrared spectrum of the product in CCl_4 solution showed the presence of $-NH_2$ frequencies and a shift of the $C{\equiv}N$ absorption to a lower frequency.

Reaction of $(n\text{-}C_4H_9)_2BCN$ with Na in liquid NH_3.—When Na was added to a solution of $(n\text{-}C_4H_9)_2BCN$ (approx. 14 mmoles) in liquid NH_3, H_2 (6.20 mmoles) was liberated. Fractionation of the volatiles yielded excess NH_3 and a slightly volatile oil which was identified as $(n\text{-}C_4H_9)_2BNH_2$ (approx. 3.2 mmoles; mol. wt. in benzene found 142, calcd., 141). Its composition was confirmed by estimating the NH_2 content by measuring the quantity of HCl gas consumed according to the equation

$$(n\text{-}C_4H_9)_2BNH_2 + HCl \longrightarrow (n\text{-}C_4H_9)_2BNH_2 \cdot HCl \quad (5)$$

The hydrochloride was then hydrolyzed and the boron content determined by titration with base in the presence of mannitol. The boron–nitrogen ratio in the amine was found to be 1.01.

The compound $(n\text{-}C_4H_9)_2BNH_2$ melted at −78°. On standing *in vacuo* for several hours at room temperature a portion of the $(n\text{-}C_4H_9)_2BNH_2$ changed to a more viscous non-volatile liquid. No new volatile material was liberated. It appears that some of the material may have polymerized. It is interesting to find that $(n\text{-}C_4H_9)_2BNH_2$ prepared from $(n\text{-}C_4H_9)_2BCl$ and Na in liquid NH_3[4] gave a material having a higher melting point and lower volatility than that described in the present paper. It therefore appears that $(n\text{-}C_4H_9)_2BNH_2$ can polymerize in a similar fashion to $(CH_3)_2BNH_2$ which is known both as a monomer and dimer.[11]

Reaction of $(n\text{-}C_4H_9)_2BCN$ with B_2H_6.—$(n\text{-}C_4H_9)_2BCN$ (2.94 mmoles) was treated with B_2H_6 (1.56 mmoles) at room temperature for 46 hours. Fractionation of the volatiles yielded only B_2H_6 (1.06 mmoles; mol. wt. found, 28.0, calcd., 27.7). This was returned to the vessel, together with 5 ml. of benzene, and the reaction was allowed to proceed for an additional 24 hours. Removal of the benzene and B_2H_6 (0.883 mmole; mol. wt. found 28.0, calcd., 27.7) left a clear viscous residue. The residue was heated at 100° for 8 hours. No apparent change occurred.

Thermal Decomposition of $(n\text{-}C_4H_9)_2BCN$.—$(n\text{-}C_4H_9)_2BCN$ (4.59 mmoles) was heated *in vacuo* in a vessel of approx. 50-ml. capacity fitted with a mercury manometer. After three hours at 100° a pressure of 3 mm. was recorded and the material had become dark orange in color. Heating for 14.5 hours at 170 to 240° produced approximately 0.5 mmole of a hydrocarbon gas of molecular weight 42.9. The residue had changed to a deep orange, clear, resinous solid. When the temperature was raised to 300–330° decomposition was at first rapid and then became slower over a period of three hours. Butane (1.54 mmoles; mol. wt. found, 53.5, calcd., 58.1; vapor pressure at −78°, found, 10 mm., literature value,[12] 10 mm.) was found. The residue was a dark brownish-black solid which was partly soluble in CCl_4.

Reaction of $(CH_3)_3SiCN$ with $(CH_3)_3B$.—$(CH_3)_3SiCN$ (3.725 mmoles) and $(CH_3)_3B$[6] (3.272 mmoles) were combined at −196° and warmed slowly to room temperature. A clear crystalline product, presumably an addition compound, was observed, together with a liquid. The above process was repeated until almost all the liquid had disappeared.

On distillation, $(CH_3)_3B$ (0.683 mmole; mol. wt. found, 52.4, calcd., 55.9; confirmed by infrared spectrum[13]) and $(CH_3)_3SiCN$ (1.48 mmoles; mol. wt. found, 95.1, calcd., 99.2) were recovered. The latter substance was contaminated with a small quantity of the addition compound from which it could not be separated even after repeated distillations.

The addition compound and the excess $(CH_3)_3SiCN$ were recombined and heated at 100° for four hours. A yellow brown liquid was formed. On distillation, $(CH_3)_3B$ (0.119 mmoles; mol. wt., found 56.5, calcd. 55.9, confirmed by infrared spectrum[13]) was found, together with a volatile oil and a non-volatile yellow brown liquid.

The volatile oil slowly and continuously liberated $(CH_3)_3B$ and formed a non-volatile oil either while standing at room temperature *in vacuo* or on distillation in the vacuum system. No consistent analysis of the volatile oil could therefore be obtained. Infrared spectra of samples of the volatile oil showed the presence of $(CH_3)_3Si$ and $B(CH_3)$ groupings. Cyanide stretching frequencies were absent. A 0.1086 g. sample of the oil (mol. wt. in benzene, 150) was treated with Cl_2 (1.25 mmoles) and the resulting mixture, consisting of a white solid and a liquid, was heated to 80°. Fractionation of the volatiles yielded $(CH_3)_3SiCl$ (0.681 mmoles; mol. wt. found, 108, calcd., 109; confirmed by infrared spectrum[7]). The yield of $(CH_3)_3SiCl$ agrees well with that expected (0.700 mmole) if the material has the structure $(CH_3)_3SiC(CH_3){=}NB(CH_3)_2$. The calculated molecular weight (155) is close to the experimental values (144–150) obtained cryoscopically for a number of samples in benzene.

The formation of this material, which undergoes slow continuous condensation with the elimination of $(CH_3)_3B$, could be caused by a rearrangement reaction such as that indicated below.

$$(CH_3)_3SiCN + (CH_3)_3B \longrightarrow \text{adduct} \longrightarrow (CH_3)_3SiC(CH_3){=}NB(CH_3)_2 \quad (6)$$

Acknowledgment.—The authors are indebted to Mr. Sheldon H. Isaac for preparation of the $(n\text{-}C_4H_9)_2BCl$ used in the present study and for the experiment on the interaction of $(n\text{-}C_4H_9)_2BCl$ with AgCN.

PHILADELPHIA, PA.

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