Syntheses and Identifications of the Ortho and Para Isomers of Some Unsymmetrically Substituted Borazines

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Abstract: The new borazine derivatives, $H_2ClB_3N_3H_2CH_3$, $HCl_2B_3N_3H_2CH_3$, $H_2[(CH_3)_2N]B_3N_3H_2CH_3$, and $H[(CH_3)_2N]_2B_3N_3H_2CH_3$, have been synthesized and fully characterized. The ortho and para isomers of $H_2ClB_3N_3H_2CH_3$ have been identified by their physical properties whereas the isomers of $H_2[(CH_3)_2N]B_3N_3H_2CH_3$ have been identified according to their ^1H nmr spectra as well as their physical properties. The para isomers of these two derivatives have been isolated in pure form, but samples containing the ortho isomer have always contained significant quantities of the corresponding para isomer. The isomers of $H[(CH_3)_2N]_2B_3N_3H_2CH_3$ have also been identified according to their ^1H nmr spectra. The relative amounts of the ortho and para isomers of $H_2ClB_3N_3H_2CH_3$ (70% para and 30% ortho) suggest that there is some type of directive influence operative during the course of the preparative reaction between $H_3B_3N_3H_2CH_3$ and $HgCl_2$.

Recent nuclear magnetic resonance studies[1,2] have suggested that the π electrons of borazine are delocalized, at least partially. Chemical evidence, such as a directive effect of a substituent on the course of a substitution reaction, could support this hypothesis of π electron delocalization. However, studies of this type require the syntheses and characterizations of the ortho and para isomers of *B*-monosubstituted-*N*-monosubstituted borazine derivatives, a difficult problem. There has been only one published report[3] of an attempted synthesis of a compound of this type, $H_2CH_3B_3N_3H_2CH_3$, but the material gave no indication of being a mixture of isomers.[3] This work has been repeated.[4] Isomeric compounds were not observed according to a gas chromatographic analysis.[4]

The variety of synthetic reactions and the unique spectral properties of some unsymmetrically substituted borazine derivatives suggest many avenues of approach for the preparation and identification of the ortho and para isomers of *B*,*N*-disubstituted borazines. In this paper we report the syntheses and identifications of the ortho and para isomers of $H_2ClB_3N_3H_2CH_3$ and $H_2[(CH_3)_2N]B_3N_3H_2CH_3$. For these syntheses, $H_3B_3N_3H_2CH_3$ was chosen as the starting material because it can be prepared in large quantities and is thermally stable.[5] On the basis of previous nmr data,[1] the derivative, $H_2[(CH_3)_2N]B_3N_3H_2CH_3$, was considered to be especially important for the identification of ortho and para isomers. The ortho and para NH ring protons of $H_2[(CH_3)_2N]B_3N_3H_3$ are clearly distinguished by ^1H nmr.[1] In the case of the isomers of $H_2[(CH_3)_2N]B_3N_3H_2CH_3$, the para isomer has NH ring protons which are only ortho to the dimethylamino group, whereas the ortho isomer has NH ring protons which are both ortho and para to the dimethylamino group.

Experimental Section

All compounds described in this investigation were manipulated in a vacuum system or a purified nitrogen atmosphere. The solvents and reagents were purified by conventional means.

Preparation of $H_3B_3N_3H_2CH_3$. The synthesis[5] of $H_3B_3N_3H_2CH_3$ from $NaBH_4$, NH_4Cl, and CH_3NH_3Cl in diglyme is similar to that previously reported, but the procedure[5] has been modified to handle larger quantities. In a typical preparation, 26.6 g (0.70 mol) of $NaBH_4$ was mixed with 100 ml of dry diglyme. Then, an intimate mixture of 18.7 g (0.35 mol) of NH_4Cl and 23.6 g (0.35 mol) of CH_3NH_3Cl was added to the stirred $NaBH_4$-diglyme mixture by means of a side arm dumper over a period of 40 min. After the amine hydrochloride addition was complete, the mixture was stirred for 1 hr at room temperature, then 2 hr at 55–60° and then slowly heated to reflux. The mixture was maintained at the reflux temperature for about 3 hr. The product, the mixture of the four possible borazines, was removed from the reaction flask by distillation using a 12-in. fractionating column packed with glass helices. This mixture of borazines was separated using an 18-in. spinning band distillation column. The isolated borazine, $H_3B_3N_3H_3$ (0.63 g), had a boiling point of 53–53.5°, whereas $H_3B_3N_3H_2CH_3$ (5.43 g) had a boiling point of 77–78°. The compounds, $H_3B_3N_3H(CH_3)_2$ and $H_3B_3N_3(CH_3)_3$, were not separated and purified because they were not needed for this investigation. The mass spectrum[5] and vapor pressure[5] of the $H_3B_3N_3H_2CH_3$ demonstrated the material to be pure.

Preparation and Separation of the Isomers of $H_2ClB_3N_3H_2CH_3$. The compound, $H_2ClB_3N_3H_2CH_3$, was prepared from $H_3B_3N_3H_2CH_3$ and $HgCl_2$. The reagent,[6] $HgCl_2$, has been used previously to convert $H_3B_3N_3H_3$ to $H_2ClB_3N_3H_3$. In a typical reaction, 3.302 g (31.9 mmol) of $H_3B_3N_3H_2CH_3$ was combined with 7.243 g (26.5 mmol) of $HgCl_2$ in 12 ml of *n*-pentane. After stirring the reaction mixture for 3 hr at room temperature the mixture was fractionated using −23, −46, −63, −78, and −196° traps. The −23 and −46° traps contained $HCl_2B_3N_3H_2CH_3$ (0.357 g) and the −63 and −78° traps contained $H_2ClB_3N_3H_2CH_3$ (0.367 g). The majority of the $H_2ClB_3N_3H_2CH_3$ was in the −63° trap. The −196° trap contained the solvent and unreacted $H_3B_3N_3H_2CH_3$.

Anal. Calcd for $H_2ClB_3N_3H_2CH_3$: N, 32.4; hydrolyzable H, 1.54. Found: N, 32.2; hydrolyzable H, 1.48. Calcd for $HCl_2B_3N_3H_2CH_3$: N, 25.6; hydrolyzable H, 0.610. Found: N, 25.2; hydrolyzable H, 0.610.

The $H_2ClB_3N_3H_2CH_3$ from the −63 and −78° traps was refractionated using traps of −23, −46, −63, −78, and −196° in an attempt to separate the ortho and para isomers. With the system under high vacuum and with no pumping the $H_2ClB_3N_3H_2CH_3$ transferred out of the −23° trap. During the early stages of distillation, the material in the −46° trap was a liquid. However, as the fractionation proceeded, the material in the −46° trap became a crystalline solid. When the entire contents of the −46° trap was crystalline, the distillation was stopped and the material in each of the −46, −63, and −78° traps was refractionated. Significant amounts of material were isolated in the −46 and −63° traps, but there was only a very small amount of material in the −78° trap. It must be emphasized that the material in the −46° trap is not stopped by the −46° trap, but was separated when the

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(1) O. T. Beachley, Jr., *J. Amer. Chem. Soc.*, **92**, 5372 (1970).

(2) O. T. Beachley, Jr., *ibid.*, **93**, 5066 (1971).

(3) H. I. Schlesinger, D. M. Ritter, and A. B. Burg, *ibid.*, **60**, 1296 (1938).

(4) A. D. Norman, Thesis, Indiana University, 1963.

(5) O. T. Beachley, Jr., *Inorg. Chem.*, **8**, 981 (1969).

(6) R. Maruca, O. T. Beachley, Jr., and A. W. Laubengayer, *ibid.*, **6**, 575 (1967).

Table I. Nuclear Magnetic Resonance Data

	$H_2[(CH_3)_2N]$-$B_3N_3H_2CH_3$ −46° fraction isomer	$H_2[(CH_3)_2N]B_3N_3H_2CH_3$ −63° fraction[7] isomer		$H_2[(CH_3)_2N]B_3N_3H_2CH_3$ −78° fraction[7] isomer		$H[(CH_3)_2N]_2B_3N_3H_2CH_3$ isomers	
	para	Para	Ortho	Para	Ortho	Ortho,ortho	Ortho,para
			Proton Data				
δ NH, ppm	−4.16	−4.18	−4.78	−4.18	−4.78	−3.92 (c)	
J, Hz	46	46	*b*	47	*b*	*d*	
δ BH, ppm	*a*	*a*	*a*	*a*	*a*	*a*	
J, Hz							
δ CH (ring CH_3)	−2.93	−2.93	−3.00	−2.93	−3.00	−2.78	−2.90
δ CH($N(CH_3)_2$)	−2.51	−2.51	−2.65	−2.51	−2.65	−2.56	−2.62, −2.48
Ratio of isomers in sample according to line intensities	1.00	0.66	0.34	0.62	0.38	0.45	0.55
			Boron-11 Data				
δ more intense line, ppm	−27.8[c,g]					−28.7[g]	
δ less intense line, ppm	−38.6[c,g]					*b*	

	$H_2ClB_3N_3H_2CH_3$ pure para isomer	$H_2ClB_3N_3H_2CH_3$ mixture of isomers	$HCl_2B_3N_3H_2CH_3$ mixture of isomers
		Proton Data	
δ NH, ppm	−5.17	−5.18	−5.20
J, Hz	55[e]	55[e]	54[e]
δ BH, ppm	−4.47	−4.41	*a*
J, Hz	138[f]	138[f]	
δ CH (ring CH_3)	−3.00	−3.00	−2.99
		Boron-11 Data	
δ more intense line, ppm	−30.3[g]	−30.5[g]	−31.9[g]
δ less intense line, ppm	−38.1[g]	−38.2[g]	*b*

[a] Not observable. [b] Poorly resolved. [c] Isomers not distinguished. [d] Singlet. [e] Triplet. [f] Quartet. [g] See ref 1 for interpretation.

contents were crystalline. All three fractions were shown to have the same parent molecular mass by their mass spectra. There was no evidence for any impurity of $HCl_2B_3N_3H_2CH_3$, $H_2ClB_3N_3H_3$, or $H_3B_3N_3H_2CH_3$. The physical properties of the −46, −63, and −78° fractions are given in a following section. The −46° fraction has been identified as the pure para isomer whereas the −63 and −78° fractions contain both the ortho and para isomers (see Results and Discussion).

The isomers of $HCl_2B_3N_3H_2CH_3$ could not be separated by vacuum distillation. The mixture of isomers, a liquid at room temperature, had a vapor pressure of 1.4 mm at 20°. The mass spectrum of the material showed it to be pure. It should be noted that it is difficult to remove all of the para isomer of $H_2ClB_3N_3H_2CH_3$ from $HCl_2B_3N_3H_2CH_3$.

Physical Properties of Fractions of $H_2ClB_3N_3H_2CH_3$. The −46° fraction (pure para isomer) has a melting point of 0–1° and a vapor pressure of 2.2 mm at 0° and 10.0 mm at 25°. The −63 and −78° fractions contained both the ortho and para isomers. Qualitative observations of these fractions indicated the presence of two components of different melting points. Furthermore, the vapor pressures of these fractions were not reproducible but depended on the length of time of factionation. For a given fractionation the −63 and −78° fractions had vapor pressures of 2.5 and 2.6 mm at 0°, respectively.

Preparation of $H_2[(CH_3)_2N]B_3N_3H_2CH_3$ and $H[(CH_3)_2N]_2B_3N_3H_2CH_3$. The dimethylamino derivatives of 1-methylborazine are readily prepared from the corresponding chloro derivatives by reaction with $N(CH_3)_2H$ in *n*-pentane at −78° according to a previously published procedure.[6] Each of the three fractions of $H_2ClB_3N_3H_2CH_3$, −46, −63, and −78°, was converted to $H_2[(CH_3)_2N]B_3N_3H_2CH_3$.[7] The physical properties of the various samples of $H_2(CH_3)_2NB_3N_3H_2CH_3$ are given in a following section.

Anal. Calcd for $H_2[(CH_3)_2N]B_3N_3H_2CH_3$: N, 40.6; hydrolyzable H, 1.45. Found: (−46° fraction)[7] N, 40.0; hydrolyzable H, 1.44; (−63° fraction)[7] N, 40.6; hydrolyzable H, 1.45. Calcd for $H[(CH_3)_2N]_2B_3N_3H_2CH_3$: N, 38.7; hydrolyzable H, 0.552. Found: N, 38.6; hydrolyzable H, 0.550.

Physical Properties of Fractions of $H_2[(CH_3)_2N]B_3N_3H_2CH_3$. The −46° fraction[7] (pure para isomer) had a melting point of 2–4° and a vapor pressure of 1.0 mm at 25°. The −63 and −78° fractions (mixtures of the ortho and para isomers) formed glasses at −46° as opposed to crystalline solids and had representative vapor pressures of about 1.4–1.5 mm at 25° depending upon the sample of $H_2ClB_3N_3H_2CH_3$ used for the preparation of $H_2[(CH_3)_2N]B_3N_3H_2CH_3$.

Mass Spectra. The mass spectra of the various fractions of $H_2ClB_3N_3H_2CH_3$, $H_2[(CH_3)_2N]B_3N_3H_2CH_3$, and $HCl_2B_3N_3H_2CH_3$ were recorded by using a Perkin-Elmer Hitachi Model RMU 6-E mass spectrometer. All spectra had the correct *m/e* cut-off values expected for the parent which confirmed the molecular mass and purity of the samples. Different samples of $H_2ClB_3N_3H_2CH_3$ had essentially identical spectra.

Infrared Spectra. The infrared spectra were recorded in the range 4000–630 cm^{-1} by means of a Beckman IR-5A spectrometer. The spectra of all compounds except $H[(CH_3)_2N]_2B_3N_3H_2CH_3$ were taken on samples in the gas phase in a 10-cm cell. The spectrum of $H[(CH_3)_2N]_2B_3N_3H_2CH_3$ was taken as a liquid film.

The spectra are given as follows [frequency, cm^{-1} (intensity, s = strong, m = medium, w = weak, sh = shoulder)].

$H_2ClB_3N_3H_2CH_3$ (−46° fraction): 3475 (m), 3010 (sh), 2975 (w), 2600 (sh), 2535 (sh), 2520 (m), 1496 (sh), 1460 (vs), 1440 (sh), 1420 (sh), 1385 (m), 1345 (w), 1340 (w), 1083 (sh), 1072 (m), 1062 (sh), 1038 (m), 935 (w), 908 (sh), 895 (m), 887 (sh), 738 (w), 730 (w), 715 (sh), 708 (m), 698 (sh).

$H_2ClB_3N_3H_2CH_3$ (−63° fraction): 3480 (m), 3025 (sh), 2960 (w), 2550 (m), 2525 (sh), 1485 (sh), 1470 (vs), 1460 (sh), 1440 (vs), 1408 (m), 1380 (m), 1370 (sh), 1078 (sh), 1070 (m), 1065 (sh), 1048 (m),

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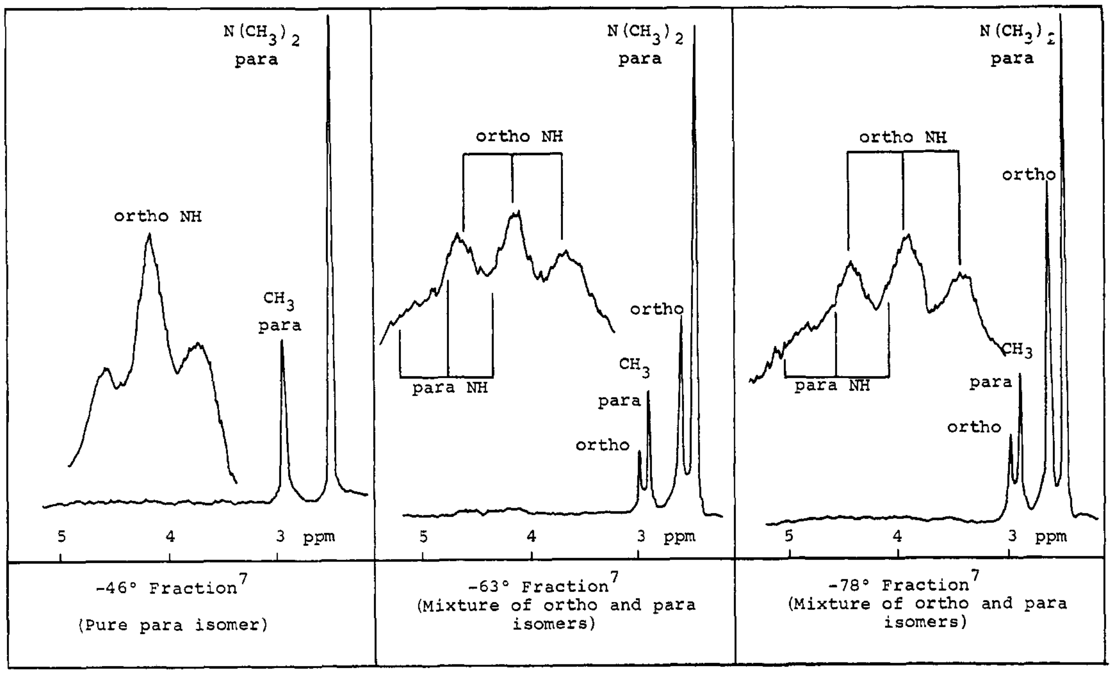
(7) Samples of $H_2[(CH_3)_2N]B_3N_3H_2CH_3$ are always designated according to the fraction of $H_2ClB_3N_3H_2CH_3$ used for their preparation, *i.e.*, −46, −63, and −78°.



-46° Fraction[7] (Pure para isomer)

-63° Fraction[7] (Mixture of ortho and para isomers)

-78° Fraction[7] (Mixture of ortho and para isomers)

Figure 1. 100-MHz nmr spectra of samples of $H_2(CH_3)_2NB_3N_3H_2CH_3$.

1038 (sh), 922 (sh), 910 (m), 900 (m), 890 (sh), 740 (w), 718 (sh), 708 (m), 692 (m), 680 (sh).

$H_2ClB_3N_3H_2CH_3$ (−78° fraction): 3480 (m), 3025 (sh), 3000 (w), 2550 (m), 2525 (sh), 1480 (vs), 1465 (vs), 1440 (vs), 1407 (m), 1380 (m), 1370 (sh), 1345 (sh), 1078 (m), 1075 (sh), 1068 (sh), 1047 (m), 922 (sh), 911 (m), 900 (m), 890 (sh), 726 (sh), 708 (sh), 703 (m), 692 (m), 682 (sh).

$HCl_2B_3N_3H_2CH_3$: 3480 (m), 2985 (w), 2560 (m), 1485 (sh), 1465 (vs), 1440 (vs), 1380 (m), 1350 (m), 1140 (w), 1087 (sh), 1063 (m), 1008 (m), 978 (m), 911 (sh), 908 (m), 899 (sh), 765 (m), 708 (sh), 700 (m), 690 (sh), 660 (w), 648 (w).

$H_2[(CH_3)_2N]B_3N_3H_2N]_2CH_3$ (−46° fraction[7]): 3480 (m), 3000 (w), 2915 (w), 2830 (w), 2510 (m), 1550 (sh), 1537 (s), 1480 (m), 1442 (s), 1425 (sh), 1360 (w), 1138 (m), 1132 (sh), 908 (sh), 898 (m), 888 (sh), 670 (m), 660 (sh).

$H_2[(CH_3)_2N]B_3N_3H_2CH_3$ (−63° fraction[7]): 3480 (m), 3000 (sh), 2960 (sh), 2910 (m), 2820 (sh), 2520 (m), 1532 (sh), 1512 (s), 1470 (sh), 1460 (s), 1440 (sh), 1345 (m), 1132 (m), 1072 (m), 1063 (m), 918 (sh), 908 (m), 898 (m), 888 (sh), 688 (sh), 670 (m), 665 (sh).

$H[(CH_3)_2N]_2B_3N_3H_2CH_3$: 3480 (m), 2980 (sh), 2885 (m), 2800 (m), 2500 (m), 1545 (sh), 1525 (vs), 1510 (sh), 1460 (s), 1456 (sh), 1430 (vs), 1405 (vs), 1390 (sh), 1320 (m), 1260 (m), 1210 (w), 1190 (m), 1150 (m), 1135 (sh), 1102 (m), 892 (m), 800 (m), 710 (sh), 693 (m), 680 (m), 645 (m).

Nuclear Magnetic Resonance Spectra. The ^1H nmr spectra were recorded at 100 MHz by means of a Varian Model HA-100 spectrometer. The ^{11}B nmr spectra were recorded at 15.871 MHz with a Varian Model HR-60 spectrometer. The reference compounds were tetramethylsilane and boron trifluoride diethyl etherate. The chemical shifts of the ^{11}B spectra were determined using the sideband technique. The nmr data are tabulated in Table I. Representative spectra of the fractions[7] of $H_2[(CH_3)_2N]B_3N_3H_2CH_3$ and $H[(CH_3)_2N]_2B_3N_3H_2CH_3$ are shown in Figures 1 and 2. All spectra were recorded as solutions in tetramethylsilane.

Results and Discussion

The unsymmetrically substituted borazines, $H_2ClB_3N_3H_2CH_3$ and $H_2[(CH_3)_2N]B_3N_3H_2CH_3$, exist as ortho and para isomers. The isomers have been identified on the basis of their physical and spectral properties. The para isomers of these two derivatives have been isolated but samples containing the ortho isomer have always been contaminated with a significant quantity of the corresponding para isomer. The pure para isomer has a sharp melting point, which is qualitatively higher than the melting point of the ortho isomer. Similarly, the vapor pressure of the para isomer is lower than the vapor pressures of samples of mixtures of the ortho and para isomers. The vapor pressure of the para isomer (the −46° fraction[7]) is reproducible from sample to sample, whereas the vapor pressures of the other fractions[7] (−63 and −78°) are not, indicating these fractions to be mixtures of the two isomers. It is well known that the para isomers of

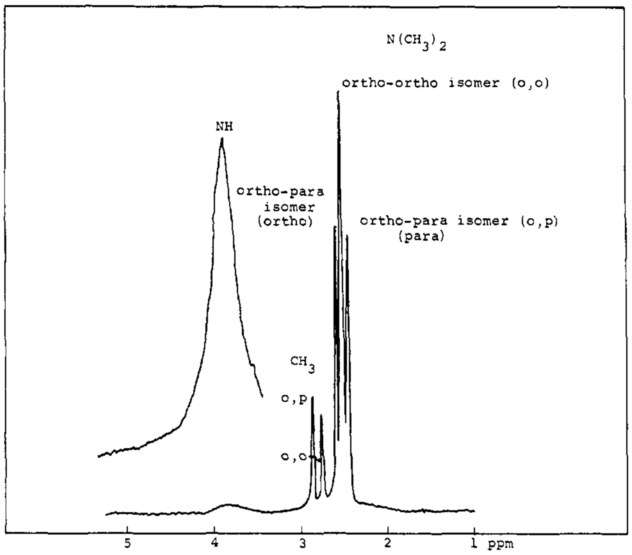
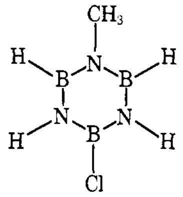
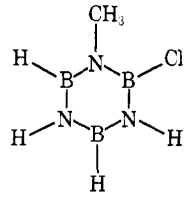


Figure 2. 100-MHz spectrum of $H[CH_3)_2N]_2B_3N_3H_2CH_3$.



para isomer

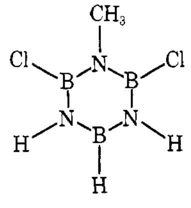


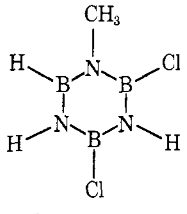
ortho isomer

benzene compounds have higher melting points and lower vapor pressures at a given temperature than the corresponding ortho isomers.

The ^1H nmr spectra of samples of $H_2[(CH_3)_2N]B_3N_3H_2CH_3$, prepared from the fractions[7] of $H_2ClB_3N_3H_2CH_3$, confirm the identification of the isomers based on their physical properties. The ^1H nmr spectra of the isomers of $H_2[(CH_3)_2N]B_3N_3H_2CH_3$ were different whereas the spectra of the isomers of $H_2ClB_3N_3H_2CH_3$ were identical (Table I). The spectrum of the para isomer of $H_2[(CH_3)_2N]B_3N_3H_2CH_3$ (Figure 1), prepared from the $-46°$ fraction of $H_2ClB_3N_3H_2CH_3$, had one line due to the ring methyl group (-2.93 ppm), one line due to the dimethylamino group (-2.51 ppm), and a well-resolved triplet for the ortho NH protons of the ring (-4.16 ppm). These assignments are consistent with the spectrum of $H_2[(CH_3)_2N]B_3N_3H_3$, which had a line for the $N(CH_3)_2$ group at -2.52 ppm, a line for the ortho NH protons at -4.28 ppm, and a line for the para NH proton at -4.80 ppm. The spectra of samples of $H_2[(CH_3)_2N]B_3N_3H_2CH_3$ containing both the para and ortho isomers (-63 and $-78°$ fractions[7]) had two lines, one for each isomer, for the ring methyl group (-2.93 (para) and -3.00 ppm (ortho)); two lines, one for each isomer, due to the dimethylamino group (-2.51 (para) and -2.65 ppm (ortho)); and a more complex set of lines for the NH protons on the ring. The spectrum of NH ring protons consisted of a well-resolved triplet at -4.18 ppm (ortho protons) and a poorly resolved triplet at -4.78 ppm (para proton). The similarity between the chemical shifts of the lines for the sample containing only the para isomer and the lines for the sample containing both isomers confirms the existence of isomers and their identification. It should be noted that the ^{11}B nmr spectrum and ^1H nmr spectrum of $H_2ClB_3N_3H_2CH_3$ could not distinguish the isomers. The ortho and para positions are not distinguished by the ^{11}B nmr spectra of monosubstituted borazines[5] nor by the ^1H nmr spectrum of $H_2ClB_3N_3H_3$. The infrared spectra do not help to identify the isomers either but one can certainly see differences between the spectrum of the para isomer and the mixture of ortho and para isomers especially in the bending frequency region, 950–650 cm^{-1}.

The derivatives, $HCl_2B_3N_3H_2CH_3$ and $H[(CH_3)_2N]_2B_3N_3H_2CH_3$, also exist as isomers, an ortho, ortho isomer and an ortho, para isomer. It has not been possible to separate these isomers but the ^1H nmr spectrum of a sample of $H[(CH_3)_2N]_2B_3N_3H_2CH_3$ is consistent with their presence (Figure 2). The lines at -2.78 (ring CH_3) and -2.56 ppm ($N(CH_3)_2$) are due to the ortho,ortho isomer. The areas of these lines are in the expected ratio of 1 to 4. The remaining lines at -2.90 (ring CH_3) and -2.62 and -2.48 ppm ($N(CH_3)_2$) are due to the ortho,para isomer. The areas of the lines at -2.90 and -2.62 or -2.48 ppm are in the expected ratio of 1 to 2, whereas the lines at -2.62 and -2.48 ppm are of equal intensity. The comparison of the chemical shifts of the lines due to the $N(CH_3)_2$ groups of the ortho,para isomer with those of the ortho and para isomers of $H_2[(CH_3)_2N]B_3N_3H_2CH_3$ suggest that the line at -2.62 ppm is due to the ortho $N(CH_3)_2$ group and the one at -2.48 ppm is due to the para $N(CH_3)_2$ group of $H[(CH_3)_2N]_2B_3N_3H_2CH_3$.


ortho, ortho isomer


ortho, para isomer

The dimethylamino group which is ortho to the ring methyl group might be expected to be differentiated from the para dimethylamino group by low temperature ^1H nmr spectra. If the rotation of the dimethylamino group is sufficiently slow, the ring CH_3 group will distinguish the two methyl groups of the dimethylamino group. However, if rotation is sufficiently fast, the line due to the ortho $N(CH_3)_2$ group will not be split into two components. No splitting of the lines due to the ortho dimethylamino groups in either $H_2[(CH_3)_2N]B_3N_3H_2CH_3$ or $H[(CH_3)_2N]_2B_3N_3H_2CH_3$ has been observed at temperatures as low as $-70°$, the lowest temperature we could attain. This observation would suggest that the extent of double bonding between the dimethylamino group and a boron of a borazine ring and an aminoborane are different. The methyl groups[8] of $(CH_3)_2NB(CHCH_2)Br$ are differentiated at 25°. This observation has been used to suggest that the boron–nitrogen bond in this aminoborane is essentially a double bond with restricted rotation.

The relative amounts of the ortho and para isomers in a given sample of the unsymmetrically substituted borazine, $H_2[(CH_3)_2N]B_3N_3H_2CH_3$, can be estimated from the relative intensities of the lines due to the various isomers, even though the two isomers could not be quantitatively separated. Furthermore, the relative amounts of the different isomers of the chloro derivatives are probably similar to the relative amounts of the isomers of the dimethylamino derivatives. The reaction for the preparation of the dimethylamino derivative uses extremely mild conditions and there is no evidence for any isomerization during the reaction. The sample of $H_2ClB_3N_3H_2CH_3$ assumed to be the pure para isomer according to its physical properties was still the pure para isomer after it was converted to $H_2[(CH_3)_2N]B_3N_3H_2CH_3$ on the basis of its ^1H nmr spectrum. Therefore, the ^1H nmr data for $H_2[(CH_3)_2N]B_3N_3H_2CH_3$ suggests that the reaction of $H_3B_3N_3H_2CH_3$ with $HgCl_2$ yields a total of 70% of the para isomer of $H_2ClB_3N_3H_2CH_3$ and only 30% of the ortho isomer. The relative amounts of the different isomers (70% para and 30% ortho) are based on the ^1H nmr data from batch lots of $H_2[(CH_3)_2N]B_3N_3H_2CH_3$ as well as the compilation of data from the various fractions from different preparative reactions. Thus, there must be some type of directive influence operative during the course of this reaction. If the reaction had been completely random, there should have been a 67% yield of the ortho isomer and a 33% yield of the para isomer due to the relative numbers of the different positions available for reaction. It is interesting to note that the chlorination of toluene[9] using iron(III) chloride leads to the formation of 87% *p*-chlorotoluene and 13% *o*-chlorotoluene. The directive influences in this reaction are based on a consideration of electronic and

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[8] K. Niedenzu, J. W. Dawson, G. A. Neice, W. Sawodny, D. R. Squire, and W. Weber, *Inorg. Chem.*, **5**, 2161 (1966).

[9] P. Kovacic and N. O. Brace, *J. Amer. Chem. Soc.*, **76**, 5491 (1954).

steric effects involving *all* reactants. The ^1H nmr spectrum of $H[(CH_3)_2N]_2B_3N_3H_2CH_3$ indicates the product to be 55% of the ortho,para isomer and 45% of the ortho,ortho isomer. These data might indicate that the dichloro derivative can be formed by more than one reaction path.

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Charge-Transfer Transitions in Para-Substituted Tribenzylboranes

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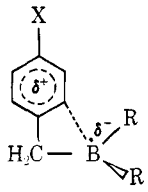
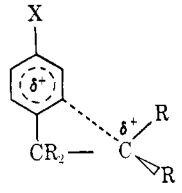
Abstract: The ultraviolet spectra of XC_6H_5-substituted tribenzylboranes (X is *p*-H, -F, and $-CH_3$, and CH_3O and 2,4,6-Me_3) in addition to the benzenoid ^1L_b transition maxima exhibit a medium intensity absorption maximum in the region 240–285 nm which is assigned to intramolecular charge transfer from aryl group to the boron vacant 2p orbital. This assignment is supported by a linear correlation of transition energy with XC_6H_5 ionization potential and by semiempirical molecular orbital calculations. A similar absorption maxima in the spectra of tribenzylamine and tribenzylphosphine may also be assigned to intramolecular charge transfer, from N or P lone-pair to antibonding vacant benzene π^* orbitals. A large red shift of the benzene ^1L_a transition of $(C_6H_5CH_2)_3B:NH_3$ is attributed to boron–carbon hyperconjugation.

Intramolecular charge transfer (CT) transition energies are well approximated by eq 1 in which I_p is the donor ionization potential, E_a is the acceptor electron affinity, and r is the distance between positive and negative charge. A linear dependence of electronic transition energy on donor group ionization potential is a generally accepted[2] criterion for assignment of an observed transition in a series of similar molecules to a charge-transfer transition. In a preliminary communication[3] we pointed out that the difference in r between triphenylboron and tribenzylboron, if applied in eq 1 to the observed CT transitions of triarylboranes near 300 nm, predicted a similar but less intense CT transition below 200 nm in tribenzylboranes. Indeed, tribenzylamine[4] and tribenzylphosphine[5] spectra have transitions near 247 and 248 nm which we have assigned[3] to charge-transfer transitions from nitrogen or phosphorus to the vacant π^* orbitals of benzene, *i.e.*, the reverse of the transition in tribenzylborane. The close analogy between the valence bond description of the CT excited state of a benzylborane **1** and the π complex intermediate or transition states such as **2** which have been suggested[6] in the solvolysis of some β-arylalkyl tosylates, etc., is readily apparent and provided a further cause for the study of these transitions. The success of this analogy is explored in a companion paper.



1



2

$$E_{CT} = I_p - E_a - e^2/r \qquad (1)$$

Results and Discussion

Because the two highest π orbitals of a para-disubstituted benzene are relatively close in energy there should in fact be two low-energy charge-transfer transitions in a monobenzylborane (six in the case of tribenzylborane). These orbitals are identified below as A′ or A′′, which are their symmetry representations under the C_s point group. This point group has as a single symmetry element a plane perpendicular through the substituted ring carbons, the CH_2, and the boron. By virtue of charge distribution[7] in the excited state, the lowest energy CT transition, CT_1, is from π orbital a′ to the boron vacant 2p orbital which is also a′; that is, A′ → A′. The second charge-transfer transition, CT_2, (orbitals a′′ → a′), should be slightly higher in energy and has the state notation A′ → A′′. Both a point-charge approximation from (e^2/r), eq 1, and semiempirical molecular orbital calculations discussed later, however, predict that the difference between the CT_1 and CT_2 transition energies will be only a few tenths (~0.3) electron volt and therefore smaller than the differences, 0.6–0.9 eV, calculated for the analogous transitions in arylboranes, -amines, or -arsenes.[7]

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