^{1}H and ^{11}B nmr spectra were obtained using the Bu_4N^+ salt.

Anal. Calcd for $[Et_4N]_2B_{18}C_2H_{18}$: B, 39.12; C, 43.47; H, 11.77; N, 5.64; equiv wt 248.6. Found: B, 38.51; C, 42.85; H, 11.88; N, 6.28; equiv wt 256.

The ^{11}B nmr spectrum of the Bu_4N^+ salt in acetonitrile consisted of a singlet of area 1 at −44.5 ppm and two doublets of area 4 at +18.3 and +23.6 ppm, respectively. The carborane CH in the ^{1}H nmr spectrum was observed at τ 5.68.

$B_{18}C_2H_{10}Cl_8^{2-}$. $(Et_4N)_2B_{18}C_2H_{18}$ (200 mg, 0.4 mmol) was dissolved in 50 ml of aqueous acetonitrile and passed through an acid ion-exchange column. The eluent was neutralized with NaOH and evaporated to a volume of 75 ml. Chlorine was bubbled through the solution for 2 hr at room temperature. The solution was neutralized with NaOH and treated with excess Et_4NBr. The white solid was collected by filtration and recrystallized from aqueous acetone. The yield of $(Et_2N)_2B_{18}C_2H_{10}Cl_8$ was 250 mg (81%).

Anal. Calcd for $[Et_4N]_2B_{18}C_2H_{10}Cl_8$: B, 25.11; C, 27.90; H, 6.76; Cl, 36.60; N, 3.63; equiv wt 387.4. Found: B, 24.81; C, 27.87; H, 6.49; Cl, 36.71; N, 3.53; equiv wt 383.

The ^{11}B nmr spectrum consisted of a singlet of area 1 at −24.0 ppm, a singlet of area 4 at +5.7 ppm, and a doublet of area 4 at +9.4 ppm. The carborane CH was observed at τ 5.42.

$B_9CH_5Cl_5^-$. $(Et_4N)B_9CH_{10}$ (250 mg, 1 mmol) was converted to the Na^+ salt by passage through an acid ion-exchange column with aqueous acetonitrile and neutralization of the eluent with NaOH. The solution was evaporated to about 75 ml and treated as described above for the halogenation of $B_{18}C_2H_{18}^{2-}$. The yield of $(Et_4N)B_9CH_5Cl_5$ was 0.35 g (83%). The ^{11}B nmr exhibited a singlet of area 1 at −23.1 ppm, a singlet of area 4 at +7.3 ppm, and a doublet of area 4 at +12.6 ppm. The equivalent weight was found to be 423, which compares well with that calculated for the $(Et_4N)B_9CH_5Cl_5$ of 421.9.

$B_{10}CH_{12}NHCOCH_3^-$. In a typical experiment $CsB_{10}CH_{13}$ (2.49 g, 9.37 mmol) was exhaustively electrolyzed at +1.75 V *vs.* sce. Integration of the current indicated $n = 2.14$ equiv/mol. The electrolysis solution was added to 200 ml of H_2O containing excess Et_4NBr and neutralized with NaOH. The aqueous solution was extracted with two 100-ml portions of CH_2Cl_2. The CH_2Cl_2 solution was washed with three 100-ml portions of H_2O, dried with $MgSO_4$, and evaporated to dryness. The oily residue was dissolved in EtOH, filtered, and diluted with Et_2O. A white flocculent precipitate formed which was collected by filtration. The yield of $(Et_4N)B_{10}CH_{12}NHCOCH_3 \cdot H_2O$ was 2.8 g (88%).

Anal. Calcd for $[Et_4N]B_{10}CH_{12}NHCOCH_3 \cdot H_2O$: B, 31.93; C, 39.03; H, 11.31; N, 8.27; equiv wt 338.5. Found: B, 31.32; C, 38.48; H, 10.86; N, 7.41; equiv wt 347.

The infrared spectrum of $Et_4NB_{10}CH_{12}NHCOCH_3 \cdot H_2O$ included absorptions at 3500 (H_2O), 3250 (NH), 2550 (BH) and 1620 cm^{-1} (CO) which is consistent with the above formulation. The ^{11}B nmr exhibited a singlet at +3.0 ppm for the substituted boron and nine additional doublets, each of area 1, which is expected for an asymmetrically substituted open 11-particle polyhedral structure.

Registry No. $Cs(1\text{-}B_9CH_{10})$, 38192-38-0; $(Et_4N)_2B_{18}C_2H_{18}$, 38192-39-1; $(Bu_4N)_2B_{18}C_2H_{18}$, 38192-40-4; $(Et_4N)_2B_{18}C_2H_{10}Cl_8$, 38192-41-5; $(Et_4N)B_9CH_{10}$, 38192-43-7; $(Et_4N)B_9CH_5Cl_5$, 38192-42-6; $CsB_{10}CH_{13}$, 38192-44-8; $(Et_4N)B_{10}CH_{12}NHCOCH_3$, 37-239-397; $CsB_{11}CH_{12}$, 38192-46-0; $(Et_4N)B_{10}CH_{11}$, 38192-45-9.

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Unsymmetrically B-Substituted Borazines. Nuclear Magnetic Resonance Characterization

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The proton nmr spectra of ten B-substituted *N*-trimethylborazines were determined in noninteracting (CCl_4) and interacting (C_6H_6 or C_6D_6) solvents. The differences in the spectra are attributed to the association of anisotropic benzene molecules with molecular dipoles of the borazines. The spectra obtained on CCl_4 solution have been analyzed on the basis of characteristic group contributions to the chemical shift of the probe substituents. A discussion of the effect of substituents on the electronic environment of the borazine nucleus is presented.

Introduction

In the course of preparing a series of unsymmetrically B-substituted *N*-trimethylborazines for other purposes, we have also investigated the ^{1}H nmr spectra of these substances in an attempt to provide a simpler basis for their characterization and a method for identifying these substances in reaction mixtures.

Experimental Section

All spectra were recorded at ambient temperature on a Varian A-60 spectrometer at 60-MHz frequency. The chemical shifts are reported in cycles per second downfield from an internal standard of tetramethylsilane in benzene and in carbon tetrachloride as solvents. Preliminary studies showed that concentration-dependent chemical shifts of about 2 cps occurred at concentrations greater than 15%; consequently all subsequent spectra were recorded in the concentration range 8–5% and were comparable with those obtained at infinite dilution. Instrumental error was less than 1.0 cps over a 500-cps sweep and less than 0.5 cps over the range 0–250 cps on a 500-cps sweep. The chemical shifts (±0.2 cps) are average values obtained from several spectra recorded for each compound. All samples were pure borazines except 2,6-dimethyl-4-chloro-1,3,5-trimethylborazine which contained approximately 10% hexamethylborazine. Deuterated benzene (99.5%) was used as solvent for the phenyl derivatives and benzene was used for the other samples. An independent study indicated that a solvent isotope effect was not present in these systems, an observation that is in agreement with other observations.[1] The proton chemical shifts are given in Tables I–III.

The details of the preparation and purification of the unsymmetrically B-substituted borazines are described in a previous paper.[2]

Discussion

As a matter of convenience, the ^{1}H nmr spectra of the unsymmetrically B-substituted *N*-trimethylborazines are discussed with reference to the numbering system shown in I.

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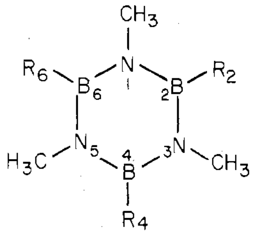
[1] P. Lazlos and D. H. Williams, *J. Amer. Chem. Soc.*, 88, 2799 (1966).

[2] L. A. Melcher, J. L. Adcock, and J. J. Lagowski, *Inorg. Chem.*, 11, 1247 (1972).

Table I. Chemical Shift (cps) by Compound

B-Substituents on 1,3,5-trimethylborazine (I)				Ring position			
R_2	R_4	R_6	Solvent	1	2 and 6	3 and 5	4
Me	Me	Me	CCl_4	172.0	27.0	172.0	27.0
			C_6H_6	167.5	29.2	167.5	29.2
			Δ	+4.5	−2.2	+4.5	−2.2
Cl	Cl	Cl	CCl_4	188.8		188.8	
			C_6H_6	173.0		173.0	
			Δ	+15.8		+15.8	
Ph	Ph	Ph	CCl_4	152.0	438.0	152.0	438.0
			C_6D_6	163.0	438.0	163.0	438.0
			Δ	−11.0	0.0	−11.0	0.0
Ph	Me	Ph	CCl_4	146.5	435.5	165.5	34.0
			C_6D_6	158.3	437.5	165.0	30.7
			Δ	−11.8	−2.0	+0.5	+3.3
Ph	Cl	Ph	CCl_4	149.5	437.5	171.8	
			C_6D_6	151.3	433.0	172.0	
			Δ	−2.8	+4.5	−0.2	
Cl	Me	Cl	CCl_4	186.5		181.5	34.5
			C_6H_6	181.5		165.2	13.7
			Δ	+5.0		+16.3	+20.8
Cl	Ph	Cl	CCl_4	191.7		168.5	437.5
			C_6D_6	185.6		163.2	432.2
			Δ	+6.1		+5.3	+4.3
Me	Ph	Me	CCl_4	177.0	30.0	159.5	434.0
			C_6D_6	169.5	29.0	161.0	437.0
			Δ	+7.5	+1.0	−1.5	−3.0
Me	Cl	Me	CCl_4	173.8	30.5	179.5	
			C_6H_6	160.5	21.5	173.5	
			Δ	+13.3	+9.0	+6.0	
Ph	Me	Cl	CCl_4	165.8	435.6	162.2, 184.5	33.5
			C_6D_6	169.7	434.2	154.9, 177.2	22.2
			Δ	−3.9	+1.4	+7.3, +7.3	+11.3
Me	C_6Me_5	Me	CCl_4	177.8	30.0	154.8	
			C_6H_6	171.3	31.8	164.5	
			Δ	+6.5	−1.8	−9.7	
Me	$B_3N_3Me_5$	Me	CCl_4	175.0	28.0	172.0	
			C_6H_6	171.0	31.5	177.0	
			Δ	+4.0	−3.5	−5.0	
Me	$OB_3N_3Me_5$	Me	CCl_4	163.5	26.0	172.0	
			C_6H_6	166.1	29.5	166.5	
			Δ	−2.6	−3.5	+5.5	



I

Solvent Effects. The proton nmr spectra of several borazines determined in several solvents with varying dielectric constants were virtually identical, the lone exceptions being the spectra determined in benzene solution. These results suggest that the differences in chemical shifts between saturated solvents and benzene arise from the anisotropy of benzene molecules. Similar solvent effects have been reported for other dipolar molecules.[3,4] This solvent effect has been attributed to the formation of transitory complexes in which hydrogen atoms on the dipolar solute molecules are found in different magnetic environments arising from the preferential association of the solvent molecules.[3] The solvent effect reported here does not appear to be related to the dielectric constant of the solvent.

Table II. Ortho Substituent Effects

B-Substituents			N_1-Methyl chemical shift, cps				
Para	Ortho		Benzene		Carbon tetrachloride		Net substituent change, CCl_4
R_4	R_2	R_6	δ	δ′	δ	δ′	
Me	Me	Me	167.5		172.0		
				+6.0		+7.5	−Me + Cl
Me	Me	Cl	173.5		179.5		
				+8.0		+7.0	−Me + Cl
Me	Cl	Cl	181.5		186.5		
Cl	Me	Me	160.5		173.8		
				+4.7		+7.7	−Me + Cl
Cl	Me	Cl	165.2		181.5		
				+7.8		+7.3	−Me + Cl
Cl	Cl	Cl	173.0		188.8		
Me	Me	Me	167.5		172.0		
				−6.5		−12.5	−Me + Ph
Me	Me	Ph	161.0		159.5		
				−2.7		−13.0	−Me + Ph
Me	Ph	Ph	158.3		146.5		
Ph	Me	Me	169.5		177.5		
				−4.0		−12.0	−Me + Ph
Ph	Me	Ph	165.5		165.5		
				−2.5		−13.5	−Me + Ph
Ph	Ph	Ph	163.0		152.0		
Cl	Cl	Cl	173.0		188.8		
				−9.8		−20.3	−Cl + Ph
Cl	Cl	Ph	163.2		168.5		
				−11.9		−19.0	−Cl + Ph
Cl	Ph	Ph	151.3		149.5		
Ph	Cl	Cl	185.6		191.7		
				−13.6		−19.9	−Cl + Ph
Ph	Cl	Ph	172.0		171.8		
				−9.0		−19.8	−Cl + Ph
Ph	Ph	Ph	163.0		152.0		

It has been demonstrated[3,5,6] that benzene molecules solvate a dipolar species in one of two ways. The face of the benzene molecule, which contains the π-electron density, is repelled by the negative end of the dipole but is attracted by the positive end of the dipole. The edge of the benzene molecule is attracted to the negative site. This preferred orientation of benzene molecules about a dipolar solute affects the magnetic environment of the protons on the solute molecules depending upon their orientation with respect to the anisotropic solvent molecule. Solute protons near the face of the benzene molecule should be more shielded by its π-electron density (*i.e.*, their resonance absorption will move upfield) than if they were not in that environment; conversely a solute proton near the edge of the benzene molecule should be deshielded. Because they are planar molecules, symmetrically B-substituted *N*-trimethylborazines (I) should not have a net molecular dipole moment even though the individual bond moments may be of considerable magnitude. Unsymmetrical borazines must exhibit a net molecular dipole moment. The relative displacements of the chemical shifts of the *N*-methyl protons in the B-substituted *N*-trimethylborazines are consistent with the existence of a molecular dipole moment in the substances.

The chemical shifts of 13 borazines as determined in CCl_4

(3) D. H. Williams, J. Ronayne, H. W. Moore, and H. R. Sheldon, *J. Org. Chem.*, 33, 998 (1968).

(4) R. Keat and R. A. Shaw, *J. Chem. Soc. A*, 703 (1968).

(5) J. Ronayne and D. H. Williams, *J. Chem. Soc. B*, 805 (1967).

(6) J. Ronayne and D. H. Williams, *J. Chem. Soc. B*, 540 (1967).

Table III. Para Substituent Effects

B-Substituents			N_1-Methyl chemical shift, cps				
Ortho		Para	Benzene		Carbon tetrachloride		Net substituent change, CCl_4
R_2	R_6	R_4	δ	δ'	δ	δ'	
Me	Me	Me	167.5	−7.0	172.0	+1.8	−Me + Cl
Me	Me	Cl	160.5		173.8		
Cl	Me	Me	173.5	−8.3	179.5	+2.0	−Me + Cl
Cl	Me	Cl	165.2		181.5		
Cl	Cl	Me	181.5	−8.5	186.5	+2.3	−Me + Cl
Cl	Cl	Cl	173.0		188.8		
Me	Me	Me	167.5	+2.0	172.0	+5.5	−Me + Ph
Me	Me	Ph	169.5		177.5		
Me	Ph	Me	161.0	+4.0	159.5	+6.0	−Me + Ph
Me	Ph	Ph	165.0		165.5		
Ph	Ph	Me	158.3	+4.7	146.5	+5.5	−Me + Ph
Ph	Ph	Ph	163.0		152.0		
Cl	Cl	Cl	173.0	+12.6	188.8	+2.9	−Cl + Ph
Cl	Cl	Ph	185.6		191.7		
Cl	Ph	Cl	163.2	+8.8	168.5	+3.3	−Cl + Ph
Cl	Ph	Ph	172.0		171.8		
Ph	Ph	Cl	151.3	+11.7	149.5	+2.5	−Cl + Ph
Ph	Ph	Ph	163.0		152.0		

and C_6H_6 (C_6D_6) solution are listed in Table I. The quantity Δ is defined as the difference between the chemical shift observed in CCl_4 and in C_6H_6, all expressed in cps relative to TMS. A positive value of Δ corresponds to an up-

$$\Delta = \delta_{CCl_4} - \delta_{C_6H_6} \tag{1}$$

field shift indicating that the hydrogen atoms at the positive end of the molecular dipole are nearest the face of the benzene molecule. Using these criteria 4-methyl-2,6-dichloro-, 4-methyl-2,6-diphenyl-, and 4-chloro-2,6-diphenyl-1,3,5-trimethylborazine and $[(CH_3)_3N_3B_3(CH_3)_2]_2O$ exhibit molecular dipoles which lie along the B_4–N_1 axis of the borazine nucleus (I), the boron site being positive with respect to the nitrogen site. On the other hand 4-phenyl-2,6-dimethyl-, 4-chloro-2,6-dimethyl-, 4-pentamethylphenyl-2,6-dimethyl-, and 4-(1,2,3,4,5-pentamethylborazinyl)-2,6-dimethyl-1,3,5-trimethylborazine possess a reverse orientation of the dipole moment along the same axis ($B_4 \rightarrow N_1$). The latter compound has no net dipole because of its symmetry. The methyl substituents in 4-phenyl-2,6-dichloro-1,3,5-trimethylborazine are shifted upfield by approximately the same amount which indicates that this substance has no or, at most, a small dipole moment. The dipole moment of 2-phenyl-4-methyl-6-chloro-1,3,5-trimethylborazine lies between the phenyl and chloro substituents in the 1,4 direction with the negative end at the 1-methyl group. Qualitatively, these data suggest that phenyl and chloro substituents withdraw electrons from the ring more than do methyl groups.

A solvent effect is also observed in the nmr spectra of the symmetrically substituted borazines. Since an internal standard of tetramethylsilane was used, the bulk susceptibility of the benzene is probably not the source of the shift.[7] A more likely cause of this effect is the higher probability of a solute molecule associating with the face of a benzene molecule rather than its edge, which could affect individual bond dipoles.

Additivity Effects. The *N*-methyl and *B*-methyl chemical shifts, as determined in CCl_4, are dependent upon the nature of the remaining boron substituents. The change in the electronic density at a given substituent ring site is a complex function of mesomeric and inductive effects, group magnetic anisotropies, localized van der Waals forces, and field effects of the introduced substituents.[8] Although a characteristic shift associated with a given B-substituent could be established, it was not possible to separate them into these components unambiguously.

Since benzene interacts strongly with these borazines and one of the substituents in some of the borazines investigated here is a phenyl group, it is not surprising that an additivity effect is not observed in benzene solutions. Tables II and III summarize the relationship found in carbon tetrachloride solutions between the chemical shift of *N*-methyl groups in borazines containing different boron substituents. The values obtained in benzene solutions reflect the complex nature of the solute–solvent interaction and are included for comparison.

The chemical shift (in cycles per second downfield from tetramethylsilane) for the *N*-methyl group in the 1 position (I) is given in Tables II and III; the difference between the chemical shifts of the 1-methyl groups for the various derivatives in the same solvent is designated δ'. The compounds are listed in groups of three which correspond to the successive replacement of the ortho boron substituents (R_2 and R_6 in I) by the same group. For example, in the triad of compounds listed, the second compound represents the replacement of an ortho methyl by an ortho chloro; the other ortho methyl group has been replaced in the third compound. In the third series of compounds, the data indicate that the replacement of an ortho methyl by a chloro group leads to a downfield shift of the 1-methyl resonance by 7.3 cps. Replacement of an ortho methyl by a phenyl group causes the 1-methyl resonance to shift upfield by 12.7 cps. If the substituent effects are additive, it might be expected that replacement of an ortho chloro by a phenyl group should lead to a shift of the 1-methyl resonance upfield by 20.0 cps. An average

Change in O-substituent	Numerical value
(−Me + Ph)	(−12.7 cps)
−(−Me + Cl)	−(+7.3 cps)
(−Cl + Ph)	(−20.0 cps)

upfield shift of 19.8 cps was observed experimentally for this substitution (Table II).

Similar results are obtained when para boron (R_4 in I) substituents are considered (Table III). The effect of substituting at the meta positions (R_2 and R_6 of I) to a methyl group at R_4 (Table IV) also yields similar results, but unfortunately the relative number of compounds available is smaller than in the other cases.

The addition of an ortho or para chloro or a para phenyl substituent leads to a downfield chemical shift of the 1-

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[7] F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy," Academic Press, New York, N. Y., 1969, pp 64–71.

[8] W. R. Smith and J. L. Roark, *J. Amer. Chem. Soc.*, **89**, 5018 (1967).

Table IV. Meta Substituent Effects

B-Substituents			B_4-Methyl chemical shifts, cps				Net substituent change, CCl_4
			Benzene		Carbon tetrachloride		
R_4	R_2	R_6	δ	δ'	δ	δ'	
Me	Me	Me	29.2		27.0		
				−7.7		+3.5	−Me + Cl
Me	Me	Cl	21.5		30.5		
				−7.8		+3.5	−Me + Cl
Me	Cl	Cl	13.7		34.0		
Me	Me	Me	29.2		27.0		
				−0.2		+3.0	−Me + Ph
Me	Me	Ph	29.0		30.0		
				+1.7		+4.0	−Me + Ph
Me	Ph	Ph	30.7		34.0		
Me	Cl	Cl	13.7		34.0		
				+8.5		−0.5	−Cl + Ph
Me	Cl	Ph	22.2		33.5		
				+8.5		+0.5	−Cl + Ph
Me	Ph	Ph	30.7		34.0		

methyl protons, suggesting an overall decrease in electron density at this position. An ortho phenyl group causes the resonance of the 1-methyl group to move upfield which corresponds to an increase in the electron density experienced by the methyl group. These relations are summarized in eq 2, where A is the number of ortho chloro

$$\delta_{N-Me}(\text{cps}) = 172.0 + 7.3A - 12.7B + 2.2C + 5.4D \qquad (2)$$

groups, B the number of ortho phenyl groups, C the number of para chloro groups, and D the number of para phenyl groups. A similar relationship (eq 3) is obtained for *B*-

$$\delta_{B-Me}(\text{cps}) = 27.0 + 3.5X + 3.5Y \qquad (3)$$

methyl chemical shifts; in this expression X represents the number of meta chloro groups and Y the number of meta phenyl groups. The values of the chemical shifts calculated from eq 2 and 3 agree with the observed values with an average error of 0.3 cps, which is of the order of the error involved in reading the chart paper.

Both meta chloro and phenyl groups (Table IV, eq 3) shift the resonance of the boron methyl group downfield by 3.5 cps suggesting that these substituents inductively withdraw electron density from the borazine ring to the same extent. The *N*-methyl group located between the probe *B*-methyl group and the other B-substituent blocks the latter's magnetic field effect.[9] These results suggest that chloro and phenyl groups exhibit the same inductive effect through the σ framework because the meta position in an aromatic system is not as influenced by resonance effects as are the ortho and para positions. The effect on the *N*-methyl group by a para substituent (Table III) also should be transmitted through the bonds and not related to the field of the substituent.[8,10] Qualitatively the difference in magnitude of the chemical shift implies that a para phenyl group withdraws electrons at least twice as well as a para chloro group. While this could imply that a phenyl group has a larger inductive effect than the chloro group, it is recognized that in planar boron compounds containing a *B*-Cl unit that the chloro group can denote electron density back to the boron atom through a π system. The interaction of a phenyl group with a borazine ring is geometrically unfavorable because the rings are perpendicular to each other; π conjugation between the phenyl and borazine rings is negligible.[11] The difference in magnitude in chemical shift between para chloro and para phenyl substituents can more likely be attributed to the larger resonance effect of the chloro substituent through the π framework. The presence of ortho phenyl substituents (Table II) causes the methyl protons to shift to higher field. There is no reason to suspect that the direction of the boron-phenyl bond moment has changed, *i.e.*, that the phenyl group is now releasing electron density into the borazine ring. A more reasonable explanation for this observation is that the plane of the phenyl ring is perpendicular to that of the borazine ring; in this configuration the ortho methyl group lies in the shielding portion of the aromatic magnetic cone.[12,13]

The previous argument concerning the relative electron-withdrawing ability of phenyl and chloro substituents perhaps should not be considered final because the observed differences in the chemical shift of the *B*-methyl group as the meta substituent changes and the *N*-methyl group as the para substituent changes may be related to a difference in the ability of boron and nitrogen atoms to accommodate electron density. N meta and B ortho and para substituent effects were not investigated because of the difficulty in preparing unsymmetrically N-substituted borazines.

Registry No. Hexamethylborazine, 877-07-6; 2,4,6-trichloro-1,3,5-trimethylborazine, 703-86-6; 2,4,6-triphenyl-1,3,5-trimethylborazine, 909-21-7; 4-methyl-2,6-diphenyl-1,3,5-trimethylborazine, 28075-19-6; 4-chloro-2,6-diphenyl-1,3,5-trimethylborazine, 36972-51-7; 4-methyl-2,6-dichloro-1,3,5-trimethylborazine, 7387-21-5; 4-phenyl-2,6-dichloro-1,3,5-trimethylborazine, 36972-50-6; 4-phenyl-2,6-dimethyl-1,3,5-trimethylborazine, 32386-02-0; 4-chloro-2,6-dimethyl-1,3,5-trimethylborazine, 13058-05-4; 2-phenyl-4-methyl-6-chloro-1,3,5-trimethylborazine, 36972-52-8; 4-(pentamethylphenyl)-2,6-dimethyl-1,3,5-trimethylborazine, 36972-54-0; 4-(1,2,3,4,5-pentamethylborazinyl)-2,6-dimethyl-1,3,5-trimethylborazine, 21305-33-9; 1,2,3,4,5-pentamethylborazinyl ether, 15270-88-9.

Acknowledgment. This work was supported by the National Science Foundation and the Robert A. Welch Foundation.

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[9] H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, 35, 731 (1961).

[10] F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy," Academic Press, New York, N. Y., 1969, p 80.

[11] H. J. Becher and S. Frick, *Z. Phys. Chem.* (*Frankfurt am Main*), 12, 241 (1957).

[12] I. M. Butcher, W. Gerrard, J. B. Leane, and E. F. Mooney, *J. Chem. Soc.*, 4528 (1964).

[13] H. K. Watanabe, K. Ito, and M. Kubo, *J. Amer. Chem. Soc.*, 82, 3294 (1960).