chloride, respectively, to yield polymers whose infrared spectra show a strong P–O–P absorption. The polymerization is described by the preceding equation where R = H or C_2H_5. Although the infrared spectra of the two polymers were very similar, the softening point of the III–VII polymer was 220–300°, while the softening point of the III–V polymer was only 100–120°. The polymer structures should be the same, but end-group analysis (terminal chloride) of the two materials indicates that the III–VII polymer has the higher molecular weight.

From this work, we have described a one-step synthesis of a difunctional phosphonitrilic tetramer which will react with several diols to form thermally stable low polymers. It has also been shown that small amounts of phloroglucinol, acting as a cross-linking agent, will raise the softening point of the resulting polymer approximately 200°, and that the cross-linked material may be molded conveniently. Hexaphenyldichlorophosphonitrilic tetramer will also copolymerize with the dialkoxy and dihydroxy derivatives.

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Reduction of B-Triethynylborazine Derivatives

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The catalytic hydrogenation of B-triethynylborazine derivatives was employed for the preparation of B-tris(*cis*-methyl vinyl)- and B-tris(*cis*-phenylvinyl)borazine derivatives which were not attainable by the usual Grignard reaction. The configurations and conformations at the vinyl groups were determined on the basis of the n.m.r., infrared, and ultraviolet spectra.

It was found[1] that a Grignard reagent prepared from *cis*- or *trans*-β-bromostyrene gives a mixture of *cis*- and *trans*-styryl compound by an appropriate subsequent reaction. This fact suggests difficulties in the preparation of pure B-tris-*cis*- and B-tris-*trans*-styrylborazines by the usual Grignard reaction. Furthermore, in a preliminary experiment, B-tris(phenylethynyl)-N-triphenylborazine was the main product of the reaction between B-trichloro-N-triphenylborazine and the Grignard reagent prepared from *cis*-β-bromostyrene in tetrahydrofuran. In a previous paper,[2] the preparation and properties of B-tris(phenylethynyl)borazine derivatives were described and a new route was suggested for the preparation of B-trivinylborazine derivatives by hydrogenating the B-triethynylborazines. The present work deals with the catalytic reduction of ethynyl groups on borazines and the conformation determination of B-trivinylborazines obtained therefrom.

An attempt to reduce B-tris(phenylethynyl)-N-triphenylborazine with sodium in liquid ammonia was unsuccessful due to the instability of the borazine ring. In contrast, B-tris(phenylethynyl)borazines and B-tris(alkylethynyl)borazines underwent the usual catalytic hydrogenation in tetrahydrofuran to give the corresponding vinyl derivatives. The compounds listed in Table I were prepared by the catalytic reduction of ethynylborazines except B-tris(*trans*-phenylvinyl)-N-triphenylborazine, which was prepared for comparison by the Grignard reaction between B-trichloro-N-triphenylborazine and *trans*-styrylmagnesium bromide. Here, the procedure of Yoshino and Manabe[1] was followed to retain *trans* configuration at the double bond of the styryl group in good yield. The product was referred to and shown to be different from that obtained by the catalytic reduction. For these reduction products, four different structures are conceivable with respect to the configuration and the relative orientation of the three vinyl groups, as illustrated in Figure 1, when three vinyl groups in the molecule are solely of *cis* or *trans* configuration and the rotation around the B—C= bond is restricted.

Various chemical and physicochemical data showed that the hydrogenation products are the monomeric B-trivinylborazine derivatives and the three vinyl groups on boron atoms are of *cis* configuration and of symmetric conformation. In contrast, the Grignard reaction product was proved to be the *trans* isomer in which the rotation around the B—C= bond would be sterically allowed. Both of the *cis* and *trans*

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(1) T. Yoshino and Y. Manabe, *J. Am. Chem. Soc.*, **85**, 2860 (1963).

(2) H. Watanabe, T. Totani, and T. Yoshizaki, *Inorg. Chem.*, **4**, 657 (1965).

TABLE I

VINYLBORAZINES, $N_3R'_3B_3(CH{=}CH \cdot R)_3$

Compound			Yield,	M.p., °C.	C, %		H, %		N, %		Mol. wt.	
No.	R'	R	%	[b.p. (mm.)]	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.
I	H	CH_3	60	[100 (1)]	...	...	...	...	...	...	208	201
II	H	C_6H_5	65	Oil	74.74	74.50	6.74	6.25	9.96	10.86	335	387
III	CH_3	CH_3	15	Oil	59.06	59.36	10.27	9.96	17.07	17.31	254	243
IV	CH_3	C_6H_5	37	72–74	75.60	75.59	7.29	7.05	9.39	9.80	383	429
V	C_6H_5	CH_3	81	177–179	75.80	75.59	7.46	7.05	10.23	9.80	470	429
VI	C_6H_5	C_6H_5 (*cis*)	5	172–173	82.25	82.00	6.42	5.90	7.07	6.83	623	615
VII	C_6H_5	C_6H_5 (*trans*)	10	292–293	82.32	82.00	6.06	5.90	6.50	6.83	619	615

TABLE II

PROTON CHEMICAL SHIFTS, RELATIVE INTENSITIES, AND SPIN COUPLING CONSTANTS OF B-TRIVINYLBORAZINE DERIVATIVES, $(R'NBCH{=}CHR)_3$

	Chemical shifts, τ				Relative intensities						J, c.p.s	
					R		R'		H(a)[b] + H(b)[b]			
No.[a]	R	R'	H(a)[b]	H(b)[b]	Found	Calcd.	Found	Calcd.	Found	Calcd.	J_{a-b}[b]	J_{b-c}[b]
I	8.145	5.12	4.465	3.80	1.5	1.5	0.4	0.5	1.0	1.0	14.0	6.6
II	2.39–2.80	4.73	2.85, 3.61		...	...	...	...	...	...	18.0	...
III	8.385	7.17	3.64–4.41		1.48	1.5	1.55	1.5	1.0	1.0	...	5.4
IV	2.75	7.28	3.05, 4.06		2.45	2.5	1.36	1.5	1.0	1.0	15.0	...
V	8.66	2.71–3.13	4.45–4.97		1.65	1.5	2.69	2.5	1.0	1.0	...	4.8
VI	2.66–3.58		3.78, 4.58		...	...	...	...	...	...	14.4	...
VII	2.69–3.33		4.15 (singlet)		...	...	...	...	...	...	...	...

[a] See Table I for identification of compounds. [b] B—CH(a)=CH(b)—R(c).

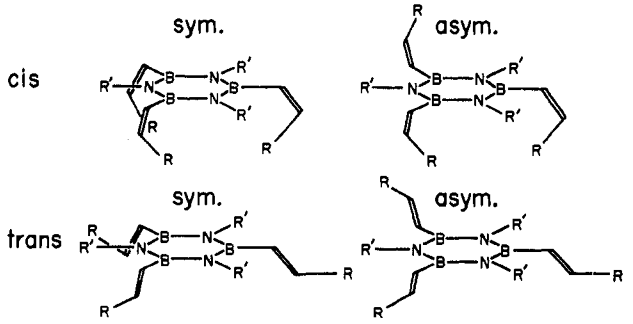

Figure 1.—Structures of B-trivinylborazine derivative.

isomers were subjected to further catalytic hydrogenation to give the same product, B-tris(phenylethyl)-N-triphenylborazine.

Experimental

Hydrogenation of B-Triethynylborazine Derivatives.—Hydrogenation was carried out essentially in a similar way for all the compounds. In a typical experiment, a mixture of 0.6 g. (0.00142 mole) of B-tris(methylethynyl)-N-triphenylborazine and 0.15 g. of Lindlar catalyst[3] was subjected to hydrogenation in tetrahydrofuran at room temperature and atmospheric pressure. Hydrogenation was monitored by infrared spectroscopy and stopped when the C≡C stretching band at 2195 cm.$^{-1}$ disappeared. Removal of the catalyst and the solvent left colorless crystals which, on recrystallization from ether–methanol mixed solvent, gave 0.49 g. (0.00115 mole) of B-tris(methylvinyl)-N-triphenylborazine.

Palladium black was used in place of Lindlar catalyst for B-tris(phenylethynyl)-N-triphenylborazine and B-tris(phenylethynyl)-N-trimethylborazine, and 5% palladium charcoal for B-tris(methylethynyl)-N-trimethylborazine.

Because B-tris(methylvinyl)-N-trimethylborazine failed to crystallize, another technique was employed for its purification. After the precipitate was filtered off from the reaction mixture, the solvent was distilled under reduced pressure and the residue was extracted with petroleum ether. The extract was washed with water and, after removal of the solvent, distilled to yield the oily product. This procedure was repeated until the n.m.r. spectrum showed the product to be pure by its simple chart.

Hydrogenation of B-Tris(phenylvinyl)-N-triphenylborazines.—Hydrogenations of the *cis* and *trans* isomers, VI and VII, were carried out in a manner similar to that described above. Both of the products were shown to be B-tris(β-phenylethyl)-N-triphenylborazine by comparing their n.m.r. and infrared spectra with those of an authentic sample prepared by Grignard reaction.[4] No depression in m.p. (225–226°) was observed in admixture of any pair of the three.

B-Tris(*trans*-phenylvinyl)-N-triphenylborazine.—A tetrahydrofuran solution of *trans*-styrylmagnesium bromide was prepared from 0.73 g. (0.03 g.-atom) of magnesium and 5.5 g. (0.03 mole) of *trans*-β-bromostyrene in a manner similar to that of Yoshino and Manabe[1] to retain the *trans* configuration. The Grignard reagent was added in small portions to 4.1 g. (0.01 mole) of B-trichloro-N-triphenylborazine in 20 ml. of tetrahydrofuran, and the reaction mixture was refluxed for 6 hr. After removal of the precipitate the solution was evaporated to dryness under reduced pressure, and the residue was recrystallized from methanol–ether mixed solvent to give 0.62 g. of colorless needles.

Analytical.—The usual micro-Dumas method was used for the determination of nitrogen without any particular precaution, whereas carbon and hydrogen were determined by a modification of the usual microdetermination method which was improved to prevent low carbon analyses[5] observed for some borazine derivatives.[6]

N.m.r. Spectra.—The proton magnetic resonance spectra were recorded at room temperature with a Varian A-60 high resolution n.m.r. spectrometer operating at 60 Mc. The results are summarized in Table II.

Ultraviolet Spectra.—The ultraviolet spectra were obtained over the region 220–320 mμ, using a Hitachi Model EPS-2 recording spectrophotometer. The typical spectra of these compounds in ethyl ether solution are shown in Figure 2, together with that of B-tris(phenylethynyl)-N-triphenylborazine for comparison.

Infrared Spectra.—Infrared spectra were taken in both carbon disulfide and carbon tetrachloride solution. Assignments of some of the absorption bands are indicated in Table III. The

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(3) H. Lindlar, *Helv. Chim. Acta*, **35**, 446 (1952).

(4) S. J. Groszos and S. F. Stafiej, *J. Am. Chem. Soc.*, **80**, 1357 (1958).

(5) W. Gerrard, H. R. Hudson, and E. F. Mooney, *J. Chem. Soc.*, 113 (1962).

(6) S. Mizukami and T. Ieki, *Microchem. J.*, **7**, 485 (1963).

Table III

Assignments of Infrared Absorption Bands of B-Trivinylborazine Derivatives

	Sample no.^{a}						
	I	II	III	IV	V	VI	VII
NH stretch	3438 m	3434 w					
C=C stretch	1629 s	1621 m	1626 m	1611 w	1632 w	1618 w	1616 s
C_6H_5					1598 w	1600 w	1597 w
		1579 w		1574 w		1577 m	1578 w
		1497 m		1495 m	1495 m	1496 m	1494 m
		1450 m		1455 m^b	1456 m	1457 w	1450 w
N—CH_3 asym.			1475 m	1470 m^b			
C—CH_3 asym.	1452 m^b		1446^c	1445 s	1447 m		
			1410 s	1411 s	1411 s	1416 s	
B—N stretch	1475 vs	1467 vs	1446 vs	1372 vs	1350 vs	1368 vs	1372 vs
C—CH_3 sym.	1393 m		1383 m		1376 s		
	1364 m	1350 m	1356 s				
			1285 w	1287 m			
N—CH_3 rock			1099 m	1097 s			
NH in-plane	1085 w	1087 w					
C_6H_5		1074 w		1073 w	1072 w	1072 w	1070 w
		1028 w		1028 w	1027 w	1027 w	1027 w
	1038 w		1037 w	1033 m	1037 w^b		
NH out-of-plane	983 w	985 m					
Vinyl C—H out-of-plane	815 w	854 m	800 w	763 m	743 w	776 w	991 m
C_6H_5		912 vw		908 vw		910 vw	895 vw
		842 vw		844 vw			843 vw
		835 vw		833 vw		830 vw	835 vw
B_3N_3 ring	765 s	754 s	716 m	756 m	753 m	755 m	756 s
BN, NH out-of-plane	721 m	708 s					
C_6H_5		692 m		698 s	700 m	700 m	699 s

^{a} See Table I for identification of compounds. ^{b} Shoulder. ^{c} Masked.

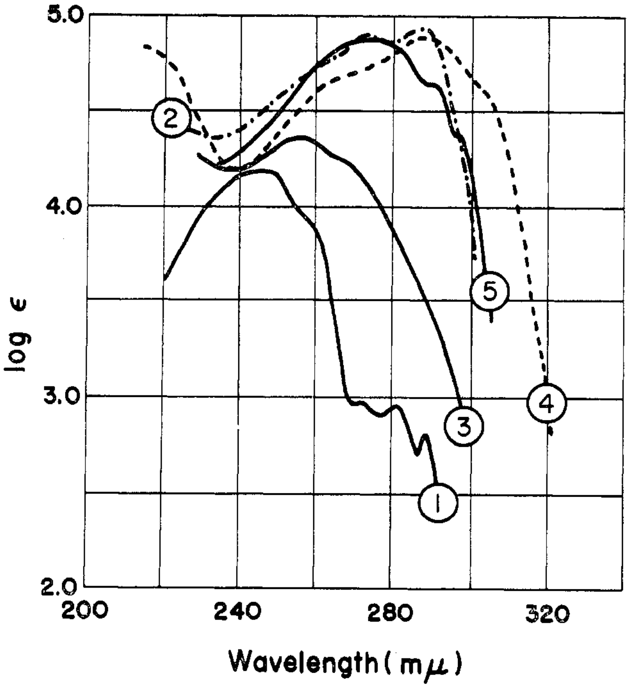

Figure 2.—Ultraviolet spectra of 1, styrene; 2, $B_3(C{\equiv}C{-}C_6H_5)_3N_3(C_6H_5)_3$; 3, B_3(*cis*-$CH{=}CH{-}C_6H_5)_3N_3(C_6H_5)_3$ (VI); 4, B_3(*trans*-$CH{=}CH{-}C_6H_5)_3N_3(C_6H_5)_3$ (VII); and 5, B_3(*cis*-$CH{=}CH{-}C_6H_5)_3N_3H_3$ (II).

wave numbers are of the solution in carbon disulfide except in regions where the solvent showed its own absorptions.

Discussion

A number of possible structures may be written for the hydrogenation products. Simple n.m.r. charts of the hydrogenation products, which will be referred to later, exclude the possibility that the three substituents of a molecule are a mixture of *cis* and *trans* configurations. Therefore, the four structures sketched in Figure 1 seem highly probable and will be given serious consideration.

It is well-known that catalytic hydrogenation of an acetylenic derivative results in *cis* addition of two hydrogen atoms to afford only a *cis*-olefinic derivative,[7] and the hydrogenation products in Table I are expected to be of *cis* configuration. Chemical support for the *cis* configurations is that the hydrogenation product of B-tris(phenylethynyl)-N-triphenylborazine is different in n.m.r. spectrum, in infrared spectrum, and in melting point from the *trans* isomer (VII) prepared by the Grignard reaction.

The ultraviolet spectra afford other support for the *cis* structure. B-Tris(*trans*-phenylvinyl)-N-triphenylborazine (VII) displays a π–π^* transition band at 288 mμ (log ε 4.9) similar to that of B-tris(phenylethynyl)-N-triphenylborazine which constitutes a large conjugated system.[2] In contrast, the *cis* isomer (VI) exhibits intense absorption at a shorter wave length, 255.5 mμ (log ε 4.36), the wave length being rather close to that of styrene (248 mμ, log ε 4.146). These correspondences suggest that in the *trans* isomer (VII) the three styryl groups conjugate and hence are nearly coplanar with the borazine ring, and that in the *cis* isomer (VI) they are not in conjugation with the borazine ring and skew at the =C—C(phenyl) or B—C= bonds. The spectrum of B-tris(phenylvinyl)-N-trimethylborazine (IV) agreed closely with that of VI to suggest a similar conformation at the styryl groups.

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[7] G. C. Bond and J. Sheridan, *Trans. Faraday Soc.*, **48**, 651, 658 (1952).

In this connection, the N-hydrogen borazines (I and II) can be expected to take more planar structures than the N-substituted B-trivinylborazines, because the van der Waals radius of hydrogen is smaller than that of the other substituents. This expectation is supported by the ultraviolet absorption curve of B-tris(*cis*-phenylvinyl)borazine, which has a strong resemblance to that of B-tris(phenylethynyl)-N-triphenylborazine.

Further evidence is obtained by comparing the infrared spectra of the two isomers of B-tris(phenylvinyl)-N-triphenylborazine. The band at 776 cm.$^{-1}$ of the hydrogenation product (VI) and that at 991 cm.$^{-1}$ of the Grignard reaction product (VII) can readily be assigned to the characteristic out-of-plane bending vibration of *cis* and *trans* olefinic CH groups. These assignments are made on the basis[8] that the *cis* olefinic CH bending appears near 690 cm.$^{-1}$ and the *trans* one at about 960 to 970 cm.$^{-1}$. In any of the infrared spectra of the other hydrogenation products, we did not find bands assignable to the *trans* olefinic out-of-plane bending. Thus, the partial hydrogenation onto the ethynyl groups of borazine derivatives results in the *cis* addition.

The n.m.r. data given in Table II can also be adduced effectively to determine the configurations and conformations of the vinyl groups. As for a –CH=CH– group, we expect signals to appear as a single quartet for the isomers having three substituents symmetrically. On the other hand, the isomers with unsymmetrically oriented substituents would afford two quartets with a relative intensity of 1:2. In a similar way, the N-methyl protons of unsymmetrical isomers may give rise to two peaks and those of symmetric ones to a single singlet. The observations of an N-methyl singlet and a single quartet of vinyl protons indicate symmetric conformations for all the compounds in Table I.

Here, it should be mentioned that examination of the molecular model shows that internal rotation around B—C= bonds of the *trans* vinyl isomer (VII) is almost free in the sense of steric hindrance and that one might be unable to distinguish the two *trans* isomers (conformers) in Figure 1, at room temperature. The internal rotation seems to be only slightly restricted in the molecules of N-hydrogen borazines (I and II) and may average out the magnetic environment of the vinyl protons to give a single quartet. Therefore, the symmetric structure cannot be concluded from the n.m.r. data alone for these three molecules.

It is worthwhile to note that the coupling constants between the two vinyl protons are larger than those observed in the usual *cis* olefinic compounds.[9]

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(8) R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," John Wiley and Sons, Inc., New York and London, 1963, p. 59.

(9) Reference 8, p. 87.

CONTRIBUTION FROM CHEMISTRY HALL,
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The Nuclear Magnetic Resonance Spectra of Some Boron Complexes

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Chemical shifts and coupling constants of a number of boron complexes are presented and discussed. Where available, shifts are compared with enthalpies of formation of the complexes. While B^{11} resonance proves to be a poor criterion of stability, groups on the boron or groups in the ligand give shifts that can be correlated with enthalpies where available, provided the variations in structure of the compounds compared are held within narrow limits.

Many authors make reference to chemical shifts or differences in chemical shifts as a criterion of relative stability of donor–acceptor complexes. This reasoning is based on the concept that chemical shift is a measure of electron density. While the concept is frequently challenged on the basis of both theoretical and empirical grounds, the reasons for this failure are not readily understood. Precise data on a series of closely related compounds could be of assistance in this respect. Moreover, it might be possible to establish a set of limits to the variations in the structure of a series of molecules, within which limits correlations between stability and chemical shift would be valid.

Since the beginning of this work, Coyle and Stone have reported observations similar to those presented here.[2] However, since many of the compounds considered are different, and there are some variations in the conclusions, it was decided to report the present data and include the boron resonances.

Experimental

The BF_3 and $B(CH_3)_3$ complexes were prepared by direct combination of the borane and ligand in a vacuum line. Triethylamine, trimethylamine, and ammonia from commercial

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(1) E. I. du Pont de Nemours and Co., Explosives Department, Experimental Station Laboratory, Wilmington, Del.

(2) T. D. Coyle and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 4138 (1961).