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Preparation and Conformation of B-Triethynylborazine Derivatives

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B-Triethynylborazine derivatives were prepared and characterized. N.m.r. spectra and ultraviolet spectra showed that the phenyl group directly attached to the borazine ring inclines at a large angle depending on the size of *ortho* substituents and that insertion of a C≡C group between the two rings releases the steric hindrance to allow a coplanar structure. These borazines were submitted to a preliminary hydrolysis experiment to appraise the resonance effect on their stabilities.

Although the general synthesis of B-trisubstituted borazines by the Grignard reaction[1,2] has been known for a long time, reports of borazines with unsaturated aliphatic substituents have been confined to vinyl derivatives.[3] The only example involving ethynyl substituents is the B-triethynyl-N-triphenylborazine prepared by Seyferth and Yamazaki.[4] The present paper includes the preparation and the conformation determination of ethynylborazine derivatives.

The great majority of work on the hydrolytic stability of B–N bonds has dealt with stabilization by steric effects or inductive effects of substituents, but the resonance effect of a substituent must also be a significant factor influencing the hydrolytic stability. Of borazine derivatives, B- and N-triphenylborazine have so far been the most typical examples of resonance structures. Even in these molecules it does not seem reasonable to assume that the borazine ring would be in full conjugation with the phenyl ring in view of the fact that the two phenyl rings of biphenyl are twisted at 41.6° by steric hindrance in the gas phase.[5] The insertion of a C≡C group between the two rings would release the steric hindrance and allow an essentially planar conformation to the molecule. Thus, the ethynylborazines are expected to afford better choices to appraise the resonance effect in increasing the hydrolytic stability of the borazine ring.

From the purely preparative point of view, compounds containing the C≡C—B grouping should be valuable intermediates in the syntheses of new borazine derivatives, *e.g.*, *sym*-B-tris(*cis*-phenylvinyl)-N-triphenylborazine. A subsequent paper will describe the hydrogenation of these derivatives and the stereochemistry of the reaction products.

The preparative method used here is virtually identical with that described by Ryschkewitsch, *et al.*,[1] and by Haworth and Hohnstedt[2] and may be summarized as

$$\begin{tikzcd} & \mathrm{RNH_2\ (or\ NH_4Cl) + BCl_3} \arrow[r] & \mathrm{B_3Cl_3N_3R_3} \arrow[d] \\ \mathrm{R'C{\equiv}CH + C_2H_5MgBr} \arrow[r] & \mathrm{R'C{\equiv}CMgBr} \arrow[r] & \mathrm{B_3(C{\equiv}CR')_3N_3R_3} \end{tikzcd}$$

The derivatives thus obtained are listed in Table I, together with their yields, melting points, molecular weights, and analytical data.

The ethynylborazines were subjected to catalytic hydrogenation to identify the product with the corresponding alkyl derivatives prepared from alkyl Grignard reagents and B-trichloroborazines.[6] Further confirmation and more details on the molecular structures of these derivatives were obtained from their ultraviolet, infrared, and n.m.r. spectra.

Experimental

Materials.—B-Trichloroborazine, B-trichloro-N-triphenylborazine, and B-trichloro-N-trimethylborazine were prepared according to the directions of Brown and Laubengayer,[7] Jones and Kinney,[8] and Turner and Warne.[9]

Preparation of Ethynylborazines.—The procedure of preparation will be sufficiently illustrated by a brief description for one derivative, as it is simple and similar for all the compounds. In a typical experiment, 2.86 g. (0.028 mole) of phenylacetylene in 10 ml. of ethyl ether was added in small portions with stirring over a period of 20 min. to the Grignard reagent prepared in the usual manner from 0.75 g. of magnesium and 3.3 g. (0.03 mole) of ethyl bromide. The reaction mixture was then refluxed for 1.5 hr. until evolution of ethane ceased. After the mixture was cooled, 2.0 g. (0.0088 mole) of B-trichloro-N-trimethylborazine in benzene was added dropwise over 40 min., during which the color of the mixture changed from light brown to dark green. Then, the mixture was refluxed for 4 hr. and allowed to stand overnight at room temperature. Colorless needles, if deposited from the solution, were dissolved with benzene, and the solution was filtered through a sintered-glass funnel. The solvent was removed from the filtrate under reduced pressure and the residue was recrystallized from benzene–petroleum ether mixed solvent.

Catalytic Reduction.—In a typical experiment, a mixture of 1.0 g. of B-trisphenylethynyl-N-triphenylborazine and 0.1 g. of palladium black was subjected to hydrogenation at room temperature and atmospheric pressure. Removal of the catalyst and the solvent left colorless crystals which on recrystallization from ether–methanol gave 0.93 g. of needles. This was identical in infrared spectrum and in melting point (225–226°) with the substance prepared by the Grignard reaction[6] between B-trichloro-N-triphenylborazine and β-phenylethylmagnesium bromide.

Analytical.—The usual micro-Dumas method was used for the determination of nitrogen without any particular precautions, whereas carbon and hydrogen were determined by a modifica-

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[9] H. S. Turner and R. J. Warne, *Chem. Ind.* (London), 526 (1958).

TABLE I

ETHYNYLBORAZINES, $B_3R_3N_3R_3'$

Sub. on B R	Sub. on N R′	Yield, %	M.p., °C.	% C Calcd.	% C Found	% H Calcd.	% H Found	% N Calcd.	% N Found	Mol. wt. Calcd.	Mol. wt. Found
$C{\equiv}CC_6H_5$	H	64	139–140	75.67	75.84	4.77	5.04	11.03	10.50	381	377
$C{\equiv}CC_6H_5$	CH_3	81	217–218	76.66	76.89	5.73	5.94	9.94	10.13	424	419
$C{\equiv}CC_6H_5$	C_6H_5	83	240–242	82.80	83.28	4.97	5.26	6.90	6.76	609	598
$C{\equiv}CCH_3$	H	24	100–102	55.53	54.97	6.21	6.57	21.59	20.72	195	169
$C{\equiv}CCH_3$	CH_3	82	187–189	60.86	60.55	7.68	7.78	17.75	17.61	237	241
$C{\equiv}CCH_3$	C_6H_5	38	245–246	76.66	76.57	5.73	5.85	9.94	10.16	423	464
$CH{=}CHCH_3$	C_6H_5	79[a]	177–179	75.58	75.69	7.06	7.38	9.80	9.37		

[a] Yield for the reduction process.

TABLE II

INFRARED SPECTRA OF B-TRIETHYNYLBORAZINES, $B_3(C{\equiv}CR)_3N_3R_3'$

R R′ C_6H_5 H	R R′ C_6H_5 CH_3	R R′ C_6H_5 C_6H_5	R R′ CH_3 H	R R′ CH_3 CH_3	R R′ CH_3 C_6H_5	Assignment
3453 m			3438 m			NH stretch
3096 w	3104 w	3074 w			3065 w	Ring CH stretch
3036 w	3036 w	3036 w			3036 w	
	2954 w		2966 w	2932 w		CH₃ stretch
			2915 w	2905 w	2905 w	
	2854 w		2852 w	2850 w	2845 w	
2195 m	2189 m	2189 m	2208 s	2202 m	2195 m	C≡C stretch
1598 w	1599 w	1600 w			1598 w	Phenyl ring CC stretch
	1576 w	1577 w				
1495 s	1493 m	1494 m			1495 m	
				1462		CH_3 deform.
	1448 s		1445 s	1445 s	1453 w	
1472 vs		1397 vs	1483 vs	1411 vs	1390 vs	Borazine ring BN stretch
1464 vs	1408 vs	1382 vs	1472 vs	1406 vs	1383 vs	
1327 s			1323 s			NH in-plane bend
1069 m	1069 m	1069 m			1073 m	Phenyl ring CH in-plane bend
1026 w	1028 w	1027 w			1025 m	
756 m	757 m	758 m			765 m	Phenyl ring CH out-of-plane bend
739 s			741 m			NH out-of-plane
	713 w	720 w		715 w	723 w	Borazine ring in-plane and/or out-of-plane deform.
708 w	702 m	713 m	706 w	706 m	715 m	
		694 m			695 m	N—C_6H_5 ring
687 m	687 m	689 m				≡C—C_6H_5 ring

tion[10] of the usual microdetermination method which was improved to prevent the low carbon analyses observed for some borazine derivatives.[11]

Molecular Weight Determination.—The molecular weight was measured by the boiling point elevation in benzene with an ebulliometer from the Shibayama Kagaku Co., Ltd., Tokyo, for all the samples except B-trismethylethynylborazine (IV) and B-trismethylvinyl-N-triphenylborazine (VII), for which a Mechrolab Model 301A vapor pressure osmometer was employed.

Infrared Spectra.—Infrared spectra were recorded in carbon tetrachloride and carbon disulfide solution over the rock salt region on a DS-201B type spectrophotometer from Japan Spectroscopic Co., Ltd., Tokyo, Japan. Table II gives the frequencies in cm.$^{-1}$ of the major absorption peaks of the ethynylborazines in carbon disulfide solution except in the regions where the solvent showed its own absorptions.

N.m.r. Spectra.—The proton magnetic reonance spectra were recorded at room temperature with a Varian A-60 high resolution n.m.r. spectrometer operating at 60 Mc. In these experiments, 10% carbon tetrachloride solutions were used with tetramethylsilane as an internal reference. The integrator was also employed for comparison of the signal intensities to determine the relative number of protons in various groups. The signals were unequivocally assigned by comparison of the charts with each other. The results are summarized in Table III.

Ultraviolet Spectra.—The ultraviolet spectra were recorded in ethyl ether solution over the region 220 to 500 mμ, using a Hitachi Model EPS-2 recording spectrophotometer. The spectra of phenylethynylborazines are shown in Figure 1 together with that of N-triphenylborazine[12] for comparison.

TABLE III

N.M.R. SPECTRA OF B-TRIETHYNYLBORAZINES $B_3(C{\equiv}CR)_3N_3R_3'$

Compound	Chemical shift, τ R	Chemical shift, τ R′	Relative intensity R	Relative intensity R′
$B_3(C{\equiv}CC_6H_5)_3N_3H_3$	2.4–2.9	4.47	5 (5)	0.93 (1)
$B_3(C{\equiv}CC_6H_5)_3N_3(CH_3)_3$	2.4–2.9	6.62	5 (5)	3.2 (3)
$B_3(C{\equiv}CC_6H_5)_3N_3(C_6H_5)_3$	2.4–3.0		...	...
$B_3(C{\equiv}CCH_3)_3N_3H_3$	8.15	4.9 br	3 (3)	1 (1)
$B_3(C{\equiv}CCH_3)_3N_3(CH_3)_3$	8.00	6.84	1 (1)	1 (1)
$B_3(C{\equiv}CCH_3)_3N_3(C_6H_5)_3$	8.60	2.7–3.05	2.3 (3)	5 (5)

Discussion

The assignment of the ethynylborazine structure to the products rests on analytical data, molecular weight determination, and the conversion to the corresponding saturated borazines by catalytic reduction. The infrared spectra afford further support for the structure.

The two N-hydrogen borazines exclusively show a sharp band due to N–H stretching at 3453 and 3438 cm.$^{-1}$, respectively, and borazines containing methyl groups give rise to a group of CH_3 stretching bands (2845–2966 cm.$^{-1}$) in the normal range and CH_3 asym-

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

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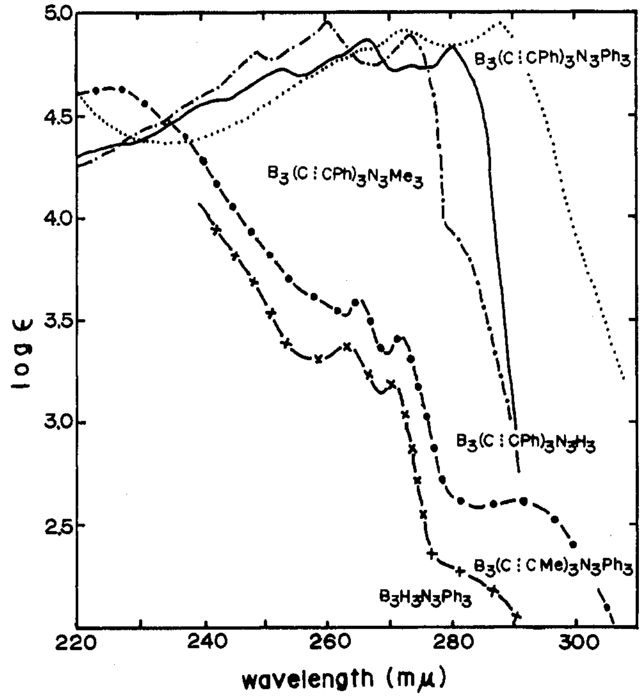
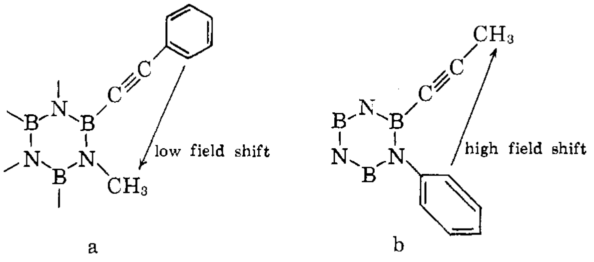


Figure 1.—The ultraviolet spectra of ethynylborazine derivatives.



a b

Figure 2.—Magnetic shielding effect of phenyl ring.

metric deformation bands at about 1450 cm.$^{-1}$. For N-triphenyl- and B-trisphenylethynylborazines, aromatic C–H stretching bands occur at 3036 and 3065–3104 cm.$^{-1}$, and ring C–C stretching bands are easily recognized at about 1600, 1577, and 1495 cm.$^{-1}$. A medium intensity band at about 2200 cm.$^{-1}$ for each compound is undoubtedly due to the $C\equiv C$ stretching vibration.

These compounds are too complex to permit unequivocal assignments of low-frequency bands to various modes of vibration, but extensive investigation of the infrared spectra of borazines[13] facilitates the assignments of the characteristic borazine-ring vibrations of the 1400 and 700 cm.$^{-1}$ regions. These bands have weaker satellite bands due to isotope shift. The remaining NH in-plane and out-of-plane bending bands were assigned by comparison with each other and with those reported.[13] Thus, the major bands of these compounds have been explained to support the expected structures.

Confirmatory evidence for the structure was obtained by a simple survey of the n.m.r. spectra. Each signal appeared at the position expected from the molecular structure with the appropriate intensity, and was unequivocally assigned as shown in Table III. Phenyl groups in each compound gave rise to complex signals spread over a range and no effort was made to analyze them. Closer examination of Table III provides evidence for the orientation of the phenyl rings attached to the ethynyl group and to the ring nitrogen. Ultraviolet[12] and n.m.r.[14,15] spectra suggest that the phenyl groups of N- and B-triphenylborazine are considerably inclined to the borazine ring plane and that the introduction of substituents onto the *ortho* positions of either ring results in a larger inclination angle owing to the increased steric hindrance. In contrast to the phenyl groups directly bonded to a borazine ring, the phenyl groups bonded through ethynyl groups would be free from the steric hindrance between the N-substituents and the phenyl groups to allow their coplanar structure.

The chemical shift data given in Table III can be adduced to support this expectation. The methyl signal of B-trisphenylethynyl-N-trimethylborazine appearing at τ 6.62 is located at a field lower by 0.22 p.p.m. than that of B-trismethylethynyl-N-trimethylborazine, τ 6.84. This difference can be explained as a consequence of the magnetic anisotropy associated with the phenyl groups coplanar with the borazine ring as illustrated in Figure 2a. A similar relation holds for the hydrogen atoms on the ring nitrogens of the pair B-trisphenylethynylborazine and B-trismethylethynylborazine, though the difference in τ value is somewhat larger. Contary to these low-field shifts, the substitution of phenyl groups for the methyl groups or hydrogen atoms attached to ring nitrogens causes the methylethynyl signal to shift in the opposite direction, as can be seen by comparing the τ value of 8.00 for B-trismethylethynyl-N-trimethylborazine or of 8.15 for B-trismethylethynylborazine with that of 8.60 for B-trismethylethynyl-N-triphenylborazine. This is consistent with the nonplanar structure as shown in Figure 2b.

The large conjugated system in B-trisphenylethynylborazines mentioned above should be reflected in the ultraviolet spectra. Platt, *et al.*,[16] investigated the ultraviolet absorptions of borazine and its methyl derivatives to conclude that the replacement of the N-hydrogen by a methyl group gives rise to a red shift of the absorption maximum at 1950 Å. as a consequence of increased aromatic character. In contrast, Becher, *et al.*,[12] described that a similar replacement

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[13] B. L. Crawford, Jr., and J. T. Edsall, *J. Chem. Phys.*, **7**, 223 (1939); W. C. Price, R. D. B. Fraser, T. S. Robinson, and H. C. Longuet-Higgins, *Discussions Faraday Soc.*, **9**, 131 (1950); R. A. Spurr and S. Change, *J. Chem. Phys.*, **19**, 518 (1951); H. J. Becher and S. Frick, *Z. anorg. allgem. Chem.*, **295**, 83 (1958); H. Watanabe, M. Narisada, T. Nakagawa, and M. Kubo, *Spectrochim. Acta*, **16**, 78 (1960); H. Watanabe, T. Totani, T. Nakagawa, and M. Kubo, *ibid.*, **16**, 1076 (1960); H. Watanabe, Y. Kuroda, and M. Kubo, *ibid.*, **17**, 454 (1961); W. Gerrard, H. R. Hudson, E. F. Mooney, I. M. Stripp, and H. A. Willis, *ibid.*, **18**, 149 (1962); W. Gerrard, E. F. Mooney, and H. A. Willis, *ibid.*, **18**, 155 (1962); I. M. Butcher, W. Gerrard, E. F. Mooney, R. A. Rothenbury, and H. A. Willis, *ibid.*, **18**, 1487 (1962); J. E. Burch, W. Gerrard, M. Goldstein, E. F. Mooney, D. E. Pratt, and H. A. Willis, *ibid.*, **19**, 889 (1963); D. W. Aubrey, M. F. Lappert, and H. Pyszora, *J. Chem. Soc.*, 1931 (1961).

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results in an opposing influence for the case of B- or N-triphenylborazine. The explanation for this blue shift was that replacement of methyl groups for hydrogens on the ring nitrogen or boron prevents the adjacent phenyl groups from achieving coplanarity to cause a blue shift of the π–π^* transition band which was red-shifted by the conjugation of the phenyl groups.

The insertion of ethynyl groups between the borazine and the phenyl rings of N-triphenylborazines can release the steric hindrance to allow coplanarity and displace the π–π^* band to longer wave lengths, as Figure 1 has already shown. This affords another support for the coplanar structure. It is worthwhile to note that the methyl substitution in B-trisphenylethynylborazine results in a blue shift of the π–π^* band at 290 mμ, contrary to what is predicted from the methyl substitution effect observed for borazine itself.[12] This shift cannot be ascribed to steric hindrance. A possible explanation for this may be offered by the hyperconjugation or inductive effect of the methyl substituents on the ring nitrogens. A simple Hückel MO calculation, using the parameters[17–19] listed in Table IV, shows that the transition responsible for the 290 mμ band is accompanied by a charge transfer from the phenylethynyl groups to the borazine ring. Then, it is likely that the introduction of methyl groups onto the ring nitrogen increases the electron density of the borazine ring and opposes the charge transfer from the phenylethynyl groups to the borazine ring.

Table IV
Parameters

Bond	Overlap integral	Resonance integral (β/β_{CC})
CC (benzene)	0.250	1
BN (borazine)	0.219	0.88
$\equiv$B—C$\equiv$	0.268	1.07
—C$\equiv$C—	0.335	1.34
$\equiv$C—C$\equiv$	0.231	0.92
Coulomb integral	$\alpha_B = \alpha - \beta_{CC}$	$\alpha_N = \alpha + 1.5\beta_{CC}$

The ultraviolet spectra of B-trismethylethynyl-N-triphenylborazine and N-triphenylborazine closely resemble each other and differ markedly from that of B-trisphenylethynyl-N-trimethylborazine. These spectra suggest that in the two N-triphenylborazines the phenyl groups are inclined toward the borazine ring to the same extent.

The triethynylborazines in ether solution were hydrolyzed on contact with water according to the overall equation

$$(NRBR')_3 + 9H_2O = 3NRH_2 + 3B(OH)_3 + 3HR'$$

where R = alkyl, phenyl, or H and R' = methylethynyl or phenylethynyl. In all cases examined, more than 80% of the reaction products were recovered. The progress of the reaction can be followed by measuring the changes in absorption coefficient in the range 270 to 290 mμ. The half-lives in the dioxane (80%)–water (20%) solution at 23° are 28 × 10^4 sec. for $B_3(C{\equiv}CCH_3)_3N_3(C_6H_5)_3$, 3.3 × 10^4 sec. for $B_3(C{\equiv}CC_6H_5)_3N_3(C_6H_5)_3$, 3.6 × 10^4 sec. for $B_3(C{\equiv}CC_6H_5)_3$-$N_3(CH_3)_3$, and 6.3 × 10^4 sec. for $B_3(C{\equiv}CC_6H_5)_3N_3H_3$. Comparison of these results with the half-lives of some borazines without ethynyl substituents[20] indicates that the resonance energies of ethynylborazines deter the hydrolysis to some extent but are not sufficient for thermodynamical stabilization. More extensive and strict hydrolysis experiments are now in progress.

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