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Photochemical Study of the *N*-Methylborazines

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Photolysis of *N*-methylborazine with 1849-Å radiation yields H_2, CH_4, borazanaphthalene, *N*-methylborazanaphthalene, and *N*-dimethylborazanaphthalene. Photolysis of *N*-methylborazine in the presence of ammonia, methanol, or dimethylamine yields predominantly a B-monosubstituted derivative. The relative quantities of ortho to para isomers in the products were determined by NMR. The photochemical reactions of *N*-dimethylborazine and *N*-trimethylborazine with ammonia were also investigated. Suggested mechanisms for these reactions are discussed.

Introduction

In 1967 Lee and Porter reported the synthesis of *B*-aminoborazine in a gas-phase photochemical reaction of borazine with ammonia using 1849-Å radiation.[1] Other B-monosubstituted borazines, including *B*-methoxyborazine[2] and *B*-dimethylaminoborazine,[3] have also been prepared photochemically. In 1972, Neiss and Porter presented a quantitative analysis of the effect of 1849-Å radiation on borazine in the absence of a second reagent[4] and also reported on a quantum yield study of the borazine–ammonia reaction.[5] The early 1970's showed an upsurge of interest in the characterization of *N*-methylborazine derivatives,[6-10] due in part to the development of a facile large-scale synthesis and purification procedure for the *N*-methylborazines by Beachley.[11] The uv absorption spectrum of *N*-trimethylborazine has been published[12] and is similar to that of borazine, except that its maximum is red shifted (ϵ_{max} 1650 Å for borazine, 1860 Å for *N*-trimethylborazine). A number of theoretical studies have been reported on this compound[8,12-17] and on *N*-methylborazine and *N*-dimethylborazine.[18] These studies predict an increase in electron density on the boron atoms adjacent to the *N*-methyl group, relative to the parent borazine molecule. The present paper attempts to probe the effect of this methyl substitution on the photochemical reaction mechanism of the *N*-methylborazines.

Experimental Procedures

The *N*-methylborazines were prepared from $NaBH_4$ (Alpha Chemical Co.) and CH_3NH_3Cl and NH_4Cl (Fisher Scientific) under a helium atmosphere using $NaBH_4$-dried dimethoxyethane (Eastman Chemicals) as solvent, according to the method of Beachley.[11] The mixture of borazine and all the possible *N*-methylborazines was purified by gas chromatography (acid-washed firebrick with 15% Apiezon). *N*-Trimethylborazine, prepared separately by similar reaction of CH_3NH_3Cl and $NaBH_4$, was purified by vacuum distillation through traps maintained at −23, −80, and −196°. The −23° trap contained pure *N*-trimethylborazine while the −80° trap contained some of this compound and the dimethoxyethane solvent. *B*-Trideuterio-*N*-trimethylborazine was prepared by the photolysis of D_2 (Matheson, reagent grade) with *N*-trimethylborazine.[19] Methyl alcohol (Mallinckrodt) and ammonia and dimethylamine (Matheson) were distilled prior to use and were analyzed for purity by ir and mass spectra.

The photolysis cell for study of *N*-methylborazine was a 500-ml vessel (Figure 1) equipped with a quartz immersion well which transmitted light down to 1800 Å. The photolysis chamber was separated by a stopcock from a 100-ml bulb used to collect noncondensable product gases. Reactions were run for 1 hr with *N*-methylborazine pressures ranging from 2 to 5 mm, using a Hanovia medium-pressure mercury lamp purged with dry N_2. The photolysis vessel was cooled to liquid nitrogen temperatures after the photolysis and the noncondensable products expanded into the 100-ml bulb. Mass spectra were taken of the noncondensable products. The material remaining in the photolysis vessel was pumped through traps maintained at −45, −80, and −196°. The contents of these traps were analyzed mass spectrometrically.

Mixtures of *N*-methylborazine and a second reagent (NH_3, CH_3OH, or $NH(CH_3)_2$) were photolyzed for about 1 hr in a 2-l. vessel. Typical reactant pressures were in the range 2–3 mm *N*-methylborazine and 2–10 mm reagent, with total pressures ranging from 4 to 12 mm. *N*-Dimethylborazine–ammonia mixtures (ratio 1:5, total pressure 12 mm) were also photolyzed. The photolysis products were pumped through traps maintained at −45, −80, and −196°. The contents of the −45° trap were analyzed by ir, mass, and proton NMR spectra.

N-Trimethylborazine–ammonia mixtures were photolyzed for 30 min and volatile products collected in a −23° trap. Nonvolatile crystalline products found on the walls of the photolysis vessel were soluble in $CDCl_3$. In one experiment ND_3 was photolyzed with *B*-trideuterio-*N*-trimethylborazine. For this reaction the vacuum-line manifold was preconditioned with ND_3 before the measured reagents were added. *B*-Amino-*N*-trimethylborazine, a product from the reaction of ammonia with *N*-trimethylborazine, was photolyzed for 30 min in a photolysis vessel saturated with mercury vapor. Crystalline products deposited on the walls of the reaction vessel and the contents of the traps from all of these reactions were analyzed by mass, infrared, and proton NMR spectra.

Infrared spectra were taken on a Perkin-Elmer 521 Grating spectrophotometer with gas samples in a 10-cm cell or with mulls between two NaCl plates. Mass spectra of gas samples were obtained using a CEC 21-103A mass spectrometer, while those of solid samples

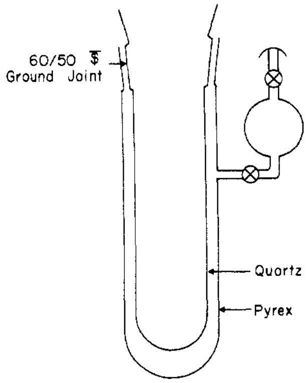


Figure 1. Photolysis vessel.

were obtained on an AEI-MS902/CIS-2 mass spectrometer with probe temperature at 50°. NMR samples were made up of 1–5% solutions in $CDCl_3$ and sealed in 5-mm tubes. The 0.2% impurity of $CHCl_3$ and $CDCl_3$ was used as a reference peak. Proton spectra with peak integrations were obtained on a Varian A-60A NMR spectrometer. All proton chemical shifts reported here have been converted to δ_{TMS} values by the formula, $\delta_{TMS} = 7.28 + \delta_{CHCl_3}$. In all cases the downfield shifts are taken as positive. Uncertainties quoted in chemical shifts reflect only the precision of measurements in $CDCl_3$ solvent.

The extinction coefficients of *N*-methylborazine, *N*-dimethylborazine, and *N*-trimethylborazine at 1849 Å were determined using the quantum yield apparatus designed by Neiss.[4] Absorption measurements (I_0/I) were taken for samples in the pressure range 0.01–1.00 mm. Sample pressures were determined from a calibrated manifold:cell volume ratio. A buildup of polymer on the cell windows was observed even during the short times required for measurements.

Results

The photolysis of *N*-methylborazine in the absence of a second reagent produced two noncondensable gases, H_2 and CH_4, identified by mass spectra. Mass spectra of the products in the −45° trap showed three different peak envelopes. Considering the natural isotopic abundance of boron (80% ^{11}B, 20% ^{10}B), the peak envelopes are interpreted as characteristic of a five-boron pattern, with the $^{11}B_5$ parent peaks at *m/e* 133, 147, and 161. We interpret these spectra as parent molecular ions of borazanaphthalene, *N*-methylborazanaphthalene, and *N*-dimethylborazanaphthalene subsequently referred to as I, II, and III, respectively. The mass spectrum of I has been reported.[20] By analogy to the photochemical reaction of borazine which produces I,[4] II and III are probable reaction products. Mass spectral analyses of the contents of the −80 and 196° traps showed the presence of unreacted *N*-methylborazine and the photochemical products borazine, *N*-dimethylborazine, and *N*-trimethylborazine. The ratio of H_2:CH_4 and the ratio of compounds I:II:III produced in a given photolysis were found to be dependent upon the pressure of *N*-methylborazine used (see Table I). In separate photolysis experiments where the *N*-methylborazine pressure was changed from 2 to 5 mm, the H_2:CH_4 ratio changed from 4:1 to 8.5:1, while the ratio I:II:III varied from 4:4:1 to <0.1:4:1. It can be noted from these data that the amount of H_2 relative to CH_4 increased as the pressure was increased, while the amount of I decreased. In all cases studied, III appeared as approximately 25% of II.

Analysis of the contents of −45° trap from the photolysis of *N*-methylborazine with ammonia reveals two isomers of a new compound identified as *B*-amino-*N*-methylborazine. The mass spectrum of this compound shows an $^{11}B_3$ parent peak at *m/e* 110 and a base peak at *m/e* 109 for the $^{11}B_3$ (parent − H)$^+$ molecular ion. This derivative exhibits rapid hydrolysis by water adsorbed on the glass surface of the mass spectrometer inlet system. The proton NMR spectrum of the product contains two peaks whose ratios vary according to the amount of NH_3 and *N*-methylborazine used in the photolysis. These peaks have been assigned to the methyl group ortho (δ 2.84 ± 0.01 ppm) and para (δ 2.98 ± 0.01 ppm) to the substituted boron. These assignments were verified using ^{15}N-labeled *N*-methylborazine in the photolysis with ammonia, as described elsewhere.[21] The infrared spectrum of *B*-amino-*N*-methylborazine is shown in Figure 2.

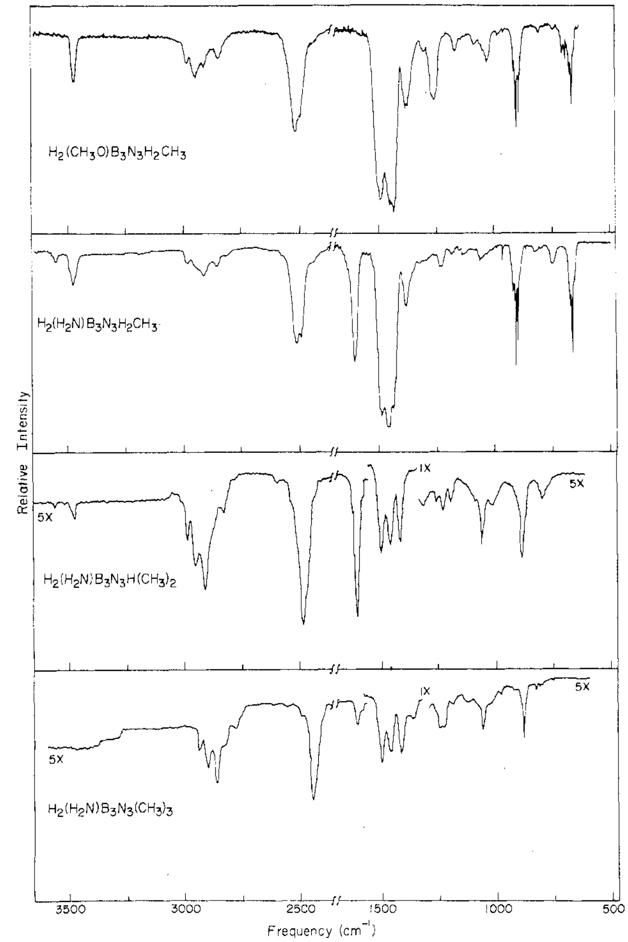


Figure 2. Infrared spectra of *N*-methyl-*B*-methoxyborazine, *N*-methyl-*B*-aminoborazine, *N*-dimethyl-*B*-aminoborazine, and *N*-trimethyl-*B*-aminoborazine.

N-Methylborazine photolyzed with CH_3OH and with $NH(CH_3)_2$ produced *B*-methoxy-*N*-methylborazine and *B*-dimethylamino-*N*-methylborazine, respectively. The mass spectrum of the methoxy derivative shows a parent grouping beginning at *m/e* 125, while the dimethylamino derivative has a parent grouping beginning at *m/e* 138, as expected. The proton NMR spectrum of the methoxy derivative reveals the presence of two isomers, with resonances assigned as follows: CH_3, δ_{ortho} 2.91 ± 0.01 ppm, δ_{para} 3.08 ± 0.01 ppm; OCH_3, δ_{ortho} 3.61 ± 0.01 ppm, δ_{para} 3.55 ± 0.01 ppm. The ratio of the peak areas of the ortho and para CH_3 resonances to each other (2:1) was the same as that of the two OCH_3 resonances (2:1). The assignment of the chemical shifts of the para isomer is based on the near coincidence of these shifts with those of the monosubstituted borazines *N*-methylborazine (δ_{CH_3} 3.01 ± 0.01 ppm) and *B*-methoxyborazine (δ_{OCH_3} 3.53 ± 0.01 ppm). An attempt was made to produce *B*-methoxy-*N*-trimethylborazine photochemically to check the chemical shift of the methyl protons ortho and para to the substituted boron, but the photolysis did not lead to the desired product. A study of the proton NMR spectrum of the photochemically produced *B*-dimethylamino-*N*-methylborazine shows it to be >90% para isomer. Identification of this compound is based on a comparison of the chemical shifts of the ring CH_3 (δ 3.05 ± 0.01 ppm) with that in *N*-methylborazine (δ 3.01 ± 0.01 ppm) and

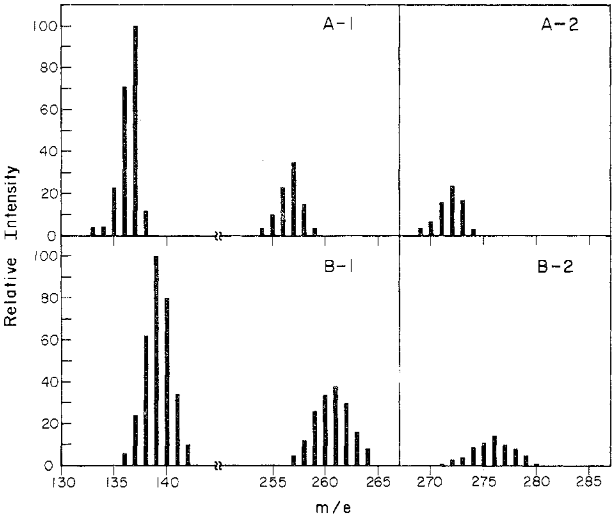
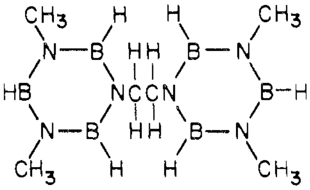
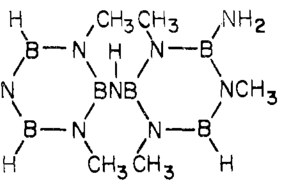


Figure 3. Portion of the mass spectra of (A-1) $[(CH_3)_3N_3B_3H_2]_2NH$, (A-2) $[(CH_3)_3N_3B_3H_2]NH[H(NH_2)B_3N_3(CH_3)_3]$, (B-1) $[(CH_3)_3N_3B_3D_2]_2ND$, and (B-2) $[(CH_3)_3N_3B_3D_2]ND[D(ND_2)B_3N_3(CH_3)_3]$.

the $N(CH_3)_2$ (δ 2.65 ± 0.01 ppm) with that in *B*-dimethylaminoborazine (δ 2.66 ± 0.01 ppm). A small amount of ortho isomer (δ_{CH_3} 2.86 ± 0.02 ppm, $\delta_{N(CH_3)_2}$ 2.44 ± 0.01 ppm) was noted. The infrared spectrum of *B*-methoxy-*N*-methylborazine is shown in Figure 2.

Mass spectra of the products of the ammonia–*N*-dimethylborazine and ammonia–*N*-trimethylborazine reactions collected in the −45° trap show the expected parent groupings beginning at *m/e* 125 and 138 for *B*-amino-*N*-dimethylborazine and *B*-amino-*N*-trimethylborazine, respectively. These derivatives were less sensitive to hydrolysis in the mass spectrometer than *B*-amino-*N*-methylborazine. The photochemically produced dimethyl derivative is shown by proton NMR to consist of two isomers, 1,3-dimethyl-2-aminoborazine (δ_{CH_3} 2.88 ± 0.01 ppm) and 1,3-dimethyl-4-aminoborazine (δ_{CH_3} 2.88 ± 0.01 ppm (ortho) and 2.98 ± 0.01 ppm (para)). The proton NMR spectrum of *B*-amino-*N*-trimethylborazine shows two peaks, δ_{CH_3} 2.85 ± 0.01 ppm (ortho) and 2.95 ± 0.01 ppm (para), in a 2:1 ratio. Figure 2 shows the infrared spectra of *B*-amino-*N*-dimethylborazine and *B*-amino-*N*-trimethylborazine. The crystalline products formed in the photolysis of *N*-trimethylborazine and ammonia were analyzed by mass, infrared, and NMR spectra and shown to be a mixture of 1,3-bis(3',5'-dimethylborazinyl)ethane(IV), also referred to as DMBE, bis(*N*-trimethylborazinyl)amine (V), and a small amount of a third compound (VI) believed to be an amino derivative of V. Compound IV has previously been characterized.[19] Figure 3 shows the major peaks in the mass spectrum assigned to compound V (A-1 and B-1) and the peaks assigned as the parent envelope of compound VI (A-2 and B-2). The top spectrum (A) was obtained from the products formed when *N*-trimethylborazine reacted with NH_3 and the bottom spectrum (B) when *B*-trideuterio-*N*-trimethylborazine reacted with ND_3. Analysis of these spectra verifies the structural assignments. Compound V exhibits in $^{11}B_6$ parent mass at *m/e* 259 with the highest peak in the grouping at *m/e* 257, as is expected for a six-boron structure which preferentially forms a (parent − H)$^+$ molecular ion. The mass spectrum of the product obtained with isotopically labeled $D_3B_3N_3(CH_3)_3$ and ND_3 as reagents shows the parent envelope for compound V (Figure 3, B-1) beginning 5 mass units higher due to the four deuterium labels on the boron atoms and one deuterium label on the nitrogen which links the two rings. A peak envelope due to the loss of $B_3N_3C_3H_{10}$ is observed for compound V at *m/e* 138. A similar fragment has been observed in the mass spectrum of unsubstituted diborazinylamine at *m/e* 96 indicating the loss of $B_3N_3H_4$.[22] The product of $^{11}B_6$ parent mass *m/e* 274 (Figure 3, A-2) is identified as *N*-trimethylborazinyl-*N*-trimethyl-*B*-aminoborazinylamine, VI. The mass spectrum of the sample labeled with deuterium (Figure 3, B-2) shows an increase of 6 units for the parent mass. This increase can be ascribed to deuterium atoms on the three unsubstituted borons, an exocyclic ND_2 and an ND group joining the two rings. The NMR spectrum of the crystalline mixture shows four peaks: one pair at δ 2.88 ± 0.01 and 2.98 ± 0.01 ppm in a ratio of 2:1 which are quite similar to the chemical shifts of *B*-amino-*N*-trimethylborazine, δ 2.85 ± 0.01 (ortho) and 2.95 ± 0.01 ppm (para), and another pair at δ 3.10 ± 0.01 and 3.36 ± 0.01 ppm in a ratio of 3:1. This latter compound is identified as DMBE (IV) by chemical shift and peak ratios. In the infrared spectrum of the crystals, a band at 1600 cm^{-1} is characteristic of an N–H bending vibration of an exocyclic amine.[23] Furthermore, bands at 3535 and 3455 cm^{-1} suggest that one component of the crystalline material has an exocyclic NH_2 group.[23] The remaining peaks in the infrared spectrum are identical with those for DMBE.


IV


V

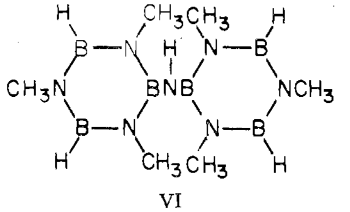

VI

Table I. Photochemical Products from the Reaction of the *N*-Methylborazines in the Absence or Presence of a Second Reagent

Reactants pressure ratios	Product
N-Methylborazine	
2 mm	H_2:CH_4 (4:1), I:II:III (4:4:1)
5 mm	H_2:CH_4 (8.5:1), I:II:III (^{a}:4:1)
N-Methylborazine:NH_3	
2:2	*N*-Methyl-*B*-aminoborazine (>90% ortho)
2:5	*N*-Methyl-*B*-aminoborazine (85% ortho)
N-Methylborazine:CH_3OH	
2:1	*N*-Methyl-*B*-methoxyborazine (67% ortho)
N-Methylborazine:$NH(CH_3)_2$	
3:3	*N*-Methyl-*B*-dimethylaminoborazine (>90% para)
N-Dimethylborazine:NH_3	
2:12	*N*-Dimethyl-*B*-aminoborazine (60% ortho–ortho)
N-Trimethylborazine:NH_3	
2:10	*N*-Trimethyl-*B*-aminoborazine Bis(*N*-trimethylborazinyl)amine 1,2-Bis(3',5'-dimethylborazinyl)ethane (DMBE) *N*-Trimethylborazinyl-*N*-trimethyl-*B*-aminoborazinylamine

^{a} Amount too small to determine.

A summary of the photochemical reactions presented in this study is given in Table I. Table II lists chemical shift data for the compounds reported here, along with that for related compounds used for comparison purposes.

Table II. Chemical Shifts of Methyl Protons in a Series of *N*-Methylborazine Derivatives (ppm from TMS)

Compd	Chem shift, ppm
N-Methylborazine	3.01 ± 0.01
N-Dimethylborazine	3.11 ± 0.01
N-Trimethylborazine	3.08 ± 0.01
1-Methyl-2-aminoborazine	2.84 ± 0.01
1-Methyl-4-aminoborazine	2.98 ± 0.01
1,3-Dimethyl-2-aminoborazine	2.88 ± 0.01
1,3-Dimethyl-4-aminoborazine	2.88 ± 0.01, 2.98 ± 0.01
1,3,5-Trimethyl-2-aminoborazine	2.85 ± 0.01, 2.95 ± 0.01
1-Methyl-2-methoxyborazine	
(CH_3)	2.91 ± 0.01
(OCH_3)	3.63 ± 0.01
1-Methyl-4-methoxyborazine	
(CH_3)	3.08 ± 0.01
(OCH_3)	3.61 ± 0.01
2-Methoxyborazine (OCH_3)	3.55 ± 0.01
1-Methyl-2-dimethylaminoborazine	
(CH_3)	2.86 ± 0.02
($N(CH_3)_2$)	2.45 ± 0.02
1-Methyl-4-dimethylaminoborazine	
(CH_3)	3.05 ± 0.01
($N(CH_3)_2$)	2.65 ± 0.01
1,3,5-Trimethyl-2-dimethylaminoborazine	
(CH_3)	2.87 ± 0.01, 3.08 ± 0.01
($N(CH_3)_2$)	2.44 ± 0.01
2-Dimethylaminoborazine ($N(CH_3)_2$	2.66 ± 0.01
1,2-Bis(3′,5′-dimethylborazinyl)ethane	
(CH_3)	3.10 ± 0.01
(CH_2)	3.36 ± 0.01
Bis(1,3,5-trimethylborazinyl)amine	2.88 ± 0.01, 2.98 ± 0.01

Extinction Coefficients

The extinction coefficients at 1849 Å of the *N*-methylborazines calculated from a Beer's law plot of the variation of log (I_0/I) with concentration are as follows: *N*-methylborazine, 4100 l. mol^{-1} cm^{-1}; *N*-dimethylborazine, 8400 l. mol^{-1} cm^{-1}; *N*-trimethylborazine, 36,000 l. mol^{-1} cm^{-1}. The values reported here are only accurate to about 15% due to experimental difficulties arising from loss of small quantities of *N*-methylborazines by adsorption on the cell walls and by photolysis which occurred during the measurements. These extinction coefficients and that reported for ammonia by Neiss[4] (ϵ 1210 l. mol^{-1} cm^{-1}) were used to determine the percent of the total 1849-Å radiation absorbed by each reagent in a given photolysis. Table III lists sets of experimental conditions for the photochemical reaction of *N*-methylborazine or *N*-dimethylborazine with NH_3 and the calculated, experimental, and statistical percent of ortho isomer in the product. Using the relationship

$$\text{fraction of light absorbed by A} = \frac{P_A\epsilon_A}{P_A\epsilon_A + P_B\epsilon_B + \ldots}$$

the percentage of light absorbed by each reagent was calculated. The calculated percent ortho isomer in the product was based on the following considerations: (1) the light absorbed by the *N*-methylborazine was assumed to produce 100% ortho isomer (this was determined experimentally); (2) light absorbed by ammonia was assumed to produce a statistical distribution of products. The experimental percent ortho isomer was determined from integrated peak intensities in the proton NMR spectra of these derivatives.

Discussion

In 1972, Neiss and Porter[4] published a study of the photolysis of borazine with 1849-Å radiation. They gave evidence for the production of H_2, borazanaphthalene, diborazinyl, and a polymer. They explained their results in terms of the unimolecular decomposition of excited borazine into H_2 and a borazyne intermediate, $B_3N_3H_4$. This intermediate could react rapidly with another borazine molecule either by a Diels–Alder type mechanism to form borazanaphthalene ($B_5N_5H_8$) and a polymer (produced from the remaining HBNH units) or by a proton-transfer mechanism to form diborazinyl. By analogy with the borazine photochemistry, *N*-methylborazine can be expected to produce H_2 + borazyne and CH_4 + *N*-methylborazyne in a unimolecular decomposition of the excited molecule ($H_3B_3N_3H_2CH_3'$). The fact that the H_2:CH_4 ratio is larger than one would predict on a statistical basis suggests a greater stability of *N*-methylborazyne over borazyne. The borazyne or *N*-methylborazyne can then react by collision with an *N*-methylborazine molecule, eliminating HBNH or $HBNCH_3$ to form polymer. In this manner, a borazyne intermediate would produce borazanaphthalene + $HBNCH_3$ or *N*-methylborazanaphthalene + HBNH, while an *N*-methylborazyne would produce *N*-methylborazanaphthalene + $HBNCH_3$ or *N*-dimethylborazanaphthalene + HBNH. All of these borazanaphthalenes were observed in the −45° trap after photolysis. The relative increase of H_2 and *N*-methylborazanaphthalene production with increasing pressure, and the simultaneous decrease of CH_4 and borazanaphthalene can be explained in terms of the higher concentration of *N*-methylborazyne intermediate present. It does not seem that the data are sufficiently quantitative to determine whether the loss of HBNH or of $HBNCH_3$ to form polymer is more highly favored. Analogy with the mass spectral fragmentation pattern of *N*-methylborazine and *N*-dimethylborazine[11] suggests that the loss of $HBNCH_3$ would be favored.

Analysis of the contents of −80 and −196° traps from the photolysis of *N*-methylborazine revealed the products of a disproportionation reaction. Borazine was found in the −196° trap along with unreacted *N*-methylborazine. *N*-Dimethylborazine and *N*-trimethylborazine were found in the −80° trap. The absence of these products when pure *N*-methylborazine gas samples were analyzed after remaining several days at room temperature indicates they are photochemical not thermal products. The products were also absent when pure *N*-methylborazine was condensed at liquid nitrogen temperatures and then rewarmed to room temperature, proving that disproportionation does not occur in the condensed phase within the time period of the experiment. In this connection, Wagner and Bradford[24] have reported a thermal disproportionation of the nitrogen substituents after the pyrolysis of 1,2,3,4,6-pentamethylborazine at 400° for 16 hr. The photochemical disproportionation reaction of *N*-methylborazine is very efficient (~10% conversion in 1 hr of photolysis). It may occur during collisional exchange of an electronically or highly vibrationally excited *N*-methylborazine molecule with a ground-state molecule. Previous photochemistry with borazine

Table III

	Methylborazine		NH_3		Percent ortho isomer		
	Pressure, mm	Percent light absd	Pressure, mm	Percent light absd	Calcd	Exptl	Statistical
N-Methylborazine	2	57	5	43	85	~85	66.7
N-Methylborazine	2	77	2	23	92	>90	66.7
N-Dimethylborazine	2	54	12	46	70	~60	33.3 (ortho–ortho)

has always involved reaction at the boron site. The disproportionation reaction observed for *N*-methylborazine is the first evidence for a photochemical exchange occurring at the nitrogen site.

Photolysis of *N*-methylborazine with ammonia yields the ortho isomer of *B*-amino-*N*-methylborazine predominantly. Under conditions where *N*-methylborazine absorbs all the light, the ortho isomer is the only product. Mechanism I is proposed

Mechanism I

$$H_3B_3N_3H_2CH_3 \xrightarrow{h\nu} H_3B_3N_3H_2CH_3{}^* \qquad (1)$$

$$H_3B_3N_3H_2CH_3{}^* \rightarrow H_3B_3N_3H_2CH_3{}' \qquad (2)$$

$$NH_3 + H_3B_3N_3H_2CH_3{}' \rightarrow \underset{\text{ortho isomer}}{H_2NH_2B_3N_3H_2CH_3} + H_2 \qquad (3)$$

to explain this result. The absorption of light by *N*-methylborazine produces an electronically excited species ($H_3B_3N_3H_2CH_3$) which may convert to a longer lived state ($H_3B_3N_3H_2CH_3'$), which in turn may undergo reaction by collision with ammonia. Competing with this process are the free-radical reactions 4–8 proposed in Mechanism II. Absorption of 1849-Å radiation by ammonia is known to produce NH_2 and H radicals[25] which can initiate the chain. A statistical distribution of ortho and para isomers of the radical $\cdot H_2B_3N_3H_2CH_3$ and of the product $H_2NH_2B_3N_3H_2CH_3$ is postulated on the basis of the lower specificity observed in free-radical reactions. The prediction agrees well with experimental data, as previously shown in Table III.

Mechanism II

$$NH_3 \xrightarrow{h\nu} NH_2 + H \qquad (4)$$

$$NH_2 + H_3B_3N_3H_2CH_3 \rightarrow \cdot H_2B_3N_3H_2CH_3 + NH_3 \qquad (5)$$

$$H + H_3B_3N_3H_2CH_3 \rightarrow \cdot H_2B_3N_3H_2CH_3 + H_2 \qquad (6)$$

$$NH_3 + \cdot H_2B_3N_3H_2CH_3 \rightarrow H_2NH_2B_3N_3H_2CH_3 + H \qquad (7)$$

$$NH_2 + \cdot H_2B_3N_3H_2CH_3 \rightarrow H_2NH_2B_3N_3H_2CH_3 \qquad (8)$$

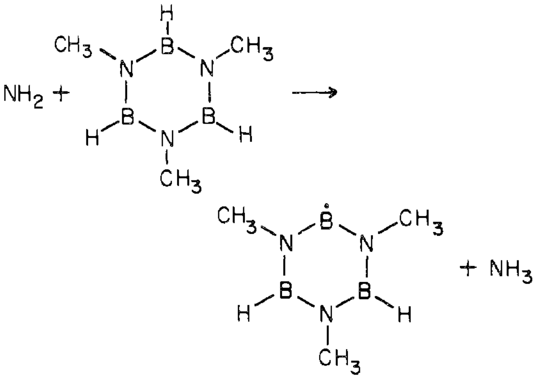
The trend of ortho substitution is also observed when *N*-dimethylborazine–ammonia mixtures are photolyzed to yield *B*-amino-*N*-dimethylborazine. The major isomer produced in this case is the one in which the amino group is between the two *N*-methyl groups (ortho–ortho isomer). Statistically, one would have expected 33% ortho–ortho substitution. Under one set of experimental conditions 60% ortho–ortho isomer was obtained (Table III).

Preferred substitution at the site ortho to the methyl group (Mechanism I) is unexpected initially. Beachley had observed 70% para *B*-chloro-*N*-methylborazine in the substitution reaction of $HgCl_2$ with *N*-methylborazine in *n*-pentane solution.[7] In addition, one expects the lone pair of the ammonia molecule to attack preferentially that boron atom of $H_3B_3N_3H_2CH_3'$ which has the lowest electron density. Theoretical calculations on *N*-methylborazines suggest a higher electron density on the ortho boron than on the para boron.[13,18] There is, however, some experimental evidence based on NMR data, regarding ^{11}B chemical shifts and ^1H–^{15}N coupling constants, discussed elsewhere[21] which appears contrary to the theoretical predictions. The photochemical data presented here also indicate that the boron atoms adjacent to the methyl group have the lowest electron density. The discrepancy between Beachley's results and the gas-phase photochemistry can be due to two factors: (1) solvent–borazine interactions and (2) sterically hindered attack of $HgCl_2$ at the ortho site. Anderson and Lagowski[26] have shown that the reaction of *N*-trimethylborazine with heavy metal halides such as $HgCl_2$ goes through a concerted bimolecular exchange mechanism. This would make ortho substitution for *N*-methylborazine sterically hindered and, therefore, less favored than para attack.

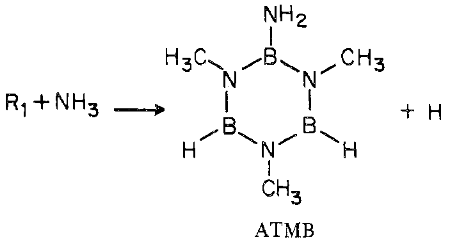
The photolysis of CH_3OH with *N*-methylborazine produces a statistical distribution of products (67% ortho, 33% para). Since *N*-methylborazine absorbs essentially all the light,[27] a lower energy barrier for the CH_3OH reaction relative to the NH_3 reaction may account for the para isomer observed. There may also be some steric factor in the CH_3OH + *N*-methylborazine reaction.

Although the photochemical reactions of NH_3 and of CH_3OH with *N*-methylborazine involve predominantly ortho substitution, the reaction product of *N*-methylborazine–dimethylamine photolysis is greater than 90% para isomer. This is explained by the sterically hindered approach of the dimethylamine to the boron ortho to the substituted nitrogen, thus making para attack preferred. This parallels the steric effect in Beachley's reaction.[6] In this connection, it is interesting to note that toluene shows a preference for meta or para substitution when allowed to react with $HN(CH_3)_2$ in solution.[28]

A radical mechanism provides the best explanation for the crystalline material produced in the photolysis of *N*-trimethylborazine with ammonia. We have previously reported[19] on the free-radical mechanism involved in the Hg-sensitized photochemical reaction of H_2 with *N*-trimethylborazine to form DMBE. Hydrogen atoms, produced by mercury sensitization,[29] initiate the chain. The present reaction is shown to be mercury sensitized by the use of a Vycor filter which eliminates radiation below 2200 Å, essentially eliminating light absorption by *N*-trimethylborazine. The decomposition of NH_3 by 1849-Å radiation[25] or by mercury sensitization[30] produces NH_2 and H radicals. The amino radical could initiate steps 9 and 10 which suggest one pathway for the formation of *B*-amino-*N*-trimethylborazine (ATMB). It cannot be determined from the present data whether this is a one- or two-step process. Another possible pathway for the formation of ATMB is shown in step 11. Some of this derivative is also expected to be formed by the reaction of NH_3 with *N*-trimethylborazine excited by 1849-Å radiation. The mercury-sensitized photolysis of *B*-amino-*N*-trimethylborazine in the absence of H_2 or NH_3 failed to produce any crystalline products. This implies that a radial such as R_1 produced in (9) is responsible for the formation of the diborazinylamine V by a reaction such as (12). The strength of the B–N bond formed in this step would be more than enough to compensate energetically for the N–H bond broken. The mechanism of formation of the amino-



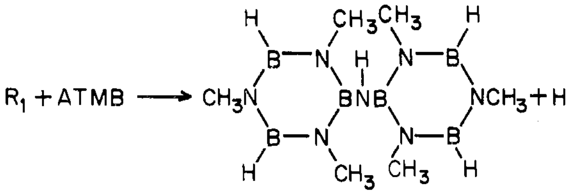
(9)



(10)

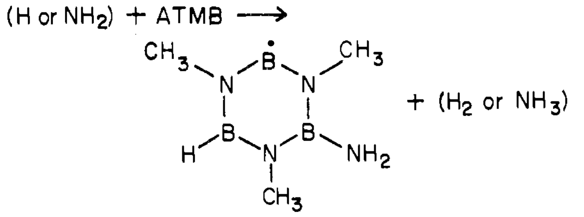
ATMB

$$R_1 + NH_2 \rightarrow ATMB \qquad (11)$$


(12)

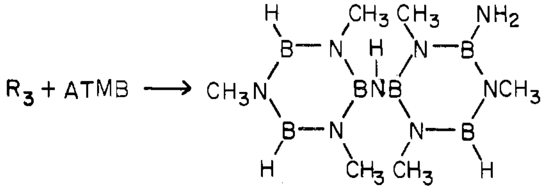
V

substituted diborazinyl amine VI is not clear. Reactions 13


(13)

R_3

and 14 represent one possible pathway.


(14)

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Registry No. *N*-Methylborazine, 21127-94-6; *N*-dimethylborazine, 23208-28-8; *N*-trimethylborazine, 1004-35-9; 1-methyl-2-aminoborazine, 54517-68-9; 1-methyl-4-aminoborazine, 54517-69-0; 1,3-dimethyl-2-aminoborazine, 54517-70-3; 1,3-dimethyl-4-aminoborazine, 54517-71-4; 1,3,5-trimethyl-2-aminoborazine, 54517-72-5; 1-methyl-2-methoxyborazine, 54517-73-6; 1-methyl-4-methoxyborazine, 54517-74-7; 2-methoxyborazine, 18277-68-4; 1-methyl-2-dimethylaminoborazine, 37013-94-8; 1-methyl-4-dimethylaminoborazine, 37133-10-1; 1,3,5-trimethyl-2-dimethylaminoborazine, 54517-75-8; 2-dimethylaminoborazine, 15127-53-4; 1,2-bis(3',5'-dimethylborazinyl)ethane, 54517-76-9; bis(1,3,5-trimethylborazinyl)amine, 54517-77-0; I, 253-18-9; II, 54517-22-5; III, 54517-23-6; VI, 54517-78-1; borazine, 6569-51-3; NH_3, 7664-41-7; CH_3OH, 67-56-1; $NH(CH_3)_2$, 124-40-3.

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Polarized Infrared and Raman Studies of Some Tri-μ-chloro-bis(trichlorochromate(III)) Single Crystals and Normal-Coordinate Analysis of the $Cr_2Cl_9{}^{3-}$ Ion

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The polarized infrared reflectance and Raman spectra of single crystals having the general formula $A_3Cr_2Cl_9$ (A = K, Rb, Cs) have been recorded at 300 and 77°K. Nearly all of the 30 fundamental modes of vibration, predicted by factor group analysis, are observed for each complex and unambiguously assigned to their respective symmetry species. A normal-coordinate analysis of the $Cr_2Cl_9{}^{3-}$ anion using a Urey–Bradley potential function produced calculated frequencies and symmetry species which gave good agreement with the vibrational data observed for the cesium complex.

Introduction

Although the vibrational spectra of dimetalate complexes having the general formula $A_3M_2X_9$ (A = alkali metal or tetraalkylammonium ion; M = Ti, Cr, Mo, W, Rh, Tl; X = Cl, Br) have been previously recorded,[2–8] the majority of this work has been concerned only with the infrared region down to 150 cm^{-1}. Recently more detailed studies of the infrared and Raman spectra of complexes containing $Cr_2Cl_9{}^{3-}$, $W_2Cl_9{}^{3-}$, and $Tl_2Cl_9{}^{3-}$ ions have been reported.[3,8] However, with the exception of a single-crystal Raman study on $Cs_3Tl_2Cl_9$[3] previous symmetry assignments have been based on spectral data obtained from powdered solids. This has led to the observation of far fewer bands than theoretically predicted and, in some cases, erroneous assignments.

There have been two previous reports of normal-coordinate analysis of complexes containing $M_2Cl_9{}^{3-}$ ions. Beattie et al.[3]