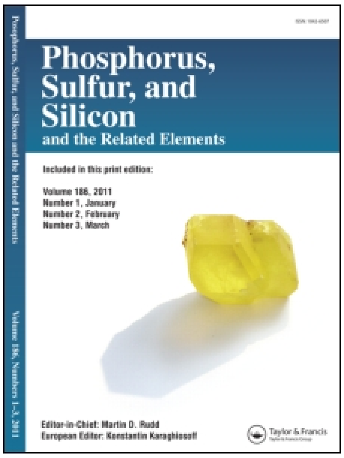

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HETEROCYCLES RELATED TO 2,4-DIBORA 1,3-DIAZAROBENZENE

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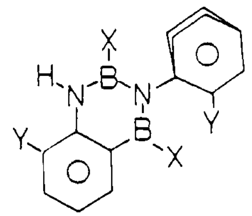
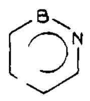
The reaction of ortho-substituted arylamines oY-$C_6H_4NH_2$ (Y = H, Cl, Br, Me) with BX_3, (X = F, Cl, Br, I) was investigated. By suitable choice of Y and X, this reaction may be directed to obtain, in a quantitative way, a new kind of heterocycle I instead of the expected trimeric species $(oYC_6H_4NBX)_3$. The formation of I was found to be related to the bulk of Y substituent and to the nature of X, increasing in the order $BCl_3 < BBr_3 < BI$, whereas BF_3 (X = F), with a tertiary amine added, always gives the corresponding borazines. Some derivatives of I were prepared (X = Me, Y = Br, Me) and characterized by NMR (^1H, ^{13}C and ^{11}B) and mass spectra.



In connection with this study, we were led to the question of atropisomerism in the N-triarylborazines $(oYC_6H_4NBX)_3$ when the starting arylamine bears an ortho substituent Y. As far as the compound Y = Me, X = Me is concerned, a sole isomer, the C_{3v} one, could be obtained instead of the two expected.

Previous lectures of Pf. Dr. W. Siebert and Pf. Dr. H. Binder gave new insights in two unexpected areas of boron chemistry. In a more classical way, the formal analogy between a boron-nitrogen bond with both atoms in the sp^2 state and a classical carbon—carbon double bond, despite its simplicity, still remains a quite useful pattern in aromatic chemistry. Thus, starting from a benzene molecule, one may obtain three kinds of heterocycles by replacing a carbon—carbon bond by the isoelectronic boron-nitrogen unit; let us add that we shall be interested only in those isomers where boron and nitrogen atoms are adjacent and alternate.



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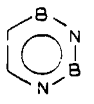

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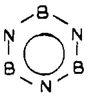

III

The symmetric compound III, or borazine, is well known and some derivatives of the latter are readily obtained, for instance, by reaction of amines with boron trichloride (tribromide):

$$RNH_2 + BX_3 \rightarrow 1/3(RNBX)_3 + 2HX \ (X = Cl, Br)$$

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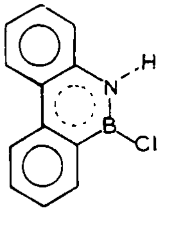
So far, heterocycle I has not yielded to isolation[1] but a great number of related compounds such as **1** could be obtained by Dewar and coworkers using a Friedel-Crafts reaction and a suitable aromatic amine with boron trichloride.[2] By comparison, quite a few derivatives of heterocycle II are described. The first example of "diboradiaza" heterocycle was reported by Köster and Iwasaki:[3] pyrolysis of a complex mixture gave rise to the B-ethyl derivative **2** with other isomeric material. In a quite different way, Turner and coworkers[4] found that addition of triethylamine to the adduct 2-methylaniline-boron trichloride gives the unexpected chloro derivative **3** together with the related chloroborazine $(o\text{-MeC}_6\text{H}_4\text{NBCl})_3$ but the separation of both compounds failed. If the same adduct was heated, borazine was the sole product obtained. In several previous papers,[5] we reported the reaction of 1-aminonaphthalene with boron trichloride (tribromide) that led to the isolation of the relevant heterocycle **4** with a quantitative yield. Quite noteworthy was the fact there was no formation of borazine under these conditions (refluxing in aromatic solvents). Unfortunately, the latter reaction appeared to be restricted to a few polycyclic primary amines such as 1-aminonaphthalene and 1-aminoanthracene.[6]



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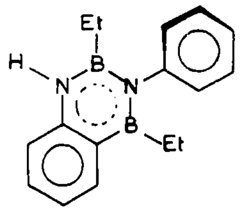

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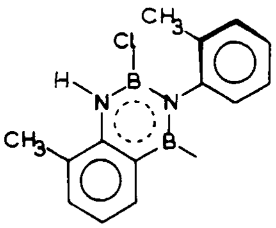

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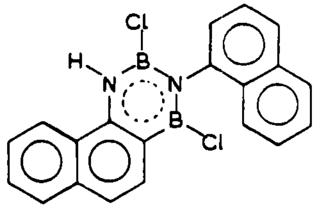

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Such limitations prompted us to investigate the haloboration reaction of substituted anilines. According to the literature, when an aniline is added to boron trichloride, for instance, a 1 : 1 complex is first obtained and the dehydrochlorination, either by heating or by an added tertiary base, occurs by a series of bimolecular reactions with the formation of linear intermediates, some of which have been isolated in special cases.[4] Thus, ring closure usually leads to borazine but the formation of diboradiaza heterocycle may be considered as a competitive process with 1-aminonaphthalene and, to a lesser extent with 2-methylaniline (Figure 1). On the following graph (Figure 2) are reported the values of π electronic density versus free valence index in the ortho position for various primary aromatic amines according to simple Hückel calculations. The figures obtained for 1-aminonaphthalene and 1-aminoanthracene are significantly different from those reported for

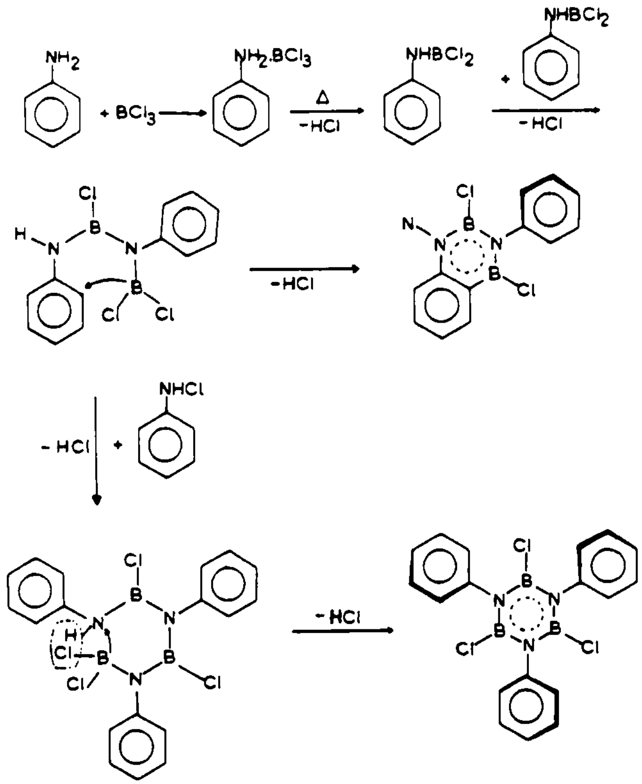

FIGURE 1

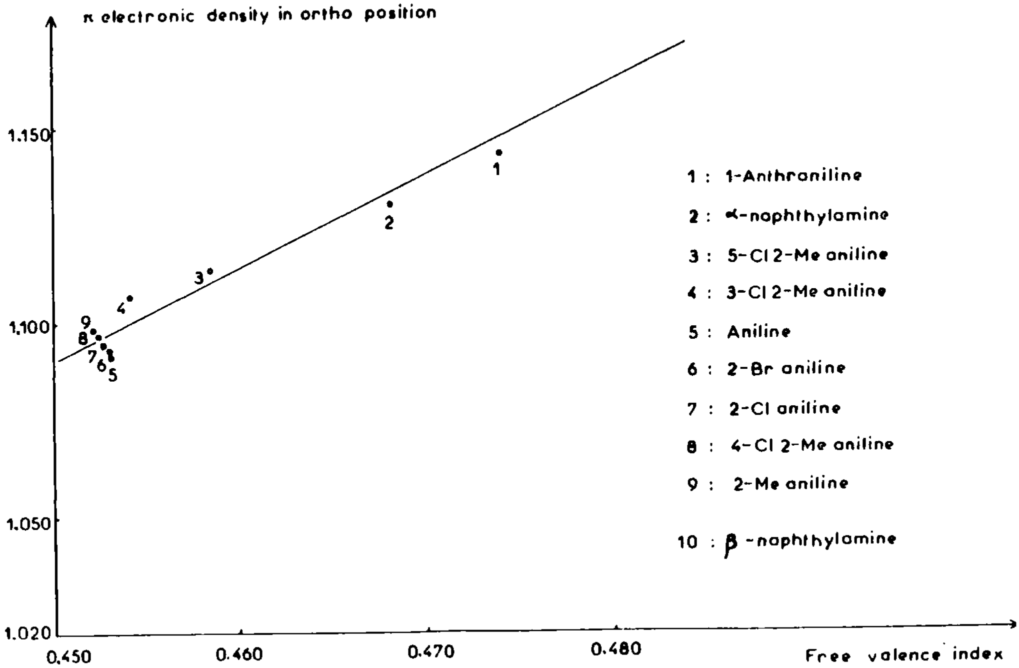

FIGURE 2

substituted anilines and may thus explain the unusual behavior of both amines towards boron trihalides but, of course, it is not possible to account for a difference in reactivity between aniline and 2-methylaniline, the values being quite similar. Hence, two other factors were retained:[7] first, the presence of a bulky substituent in the ortho position of the starting aniline strongly favors the formation of diazadibora heterocycle, probably by enhancing the stability of linear intermediates such as $H(o\text{-}YC_6H_4NBX)_2X$ ($X = Cl, Br$) for kinetic reasons. Secondly, the nature of boron trihalide used is also of prime importance; the formation of diboradiaza compound increasing in the order boron trichloride-boron triiodide, in agreement with the results of Blackborow and Lockhart[8] who identified, by means of mass spectrometry, the B iodo derivative **5** when aniline reacted with boron triiodide. By a somewhat more subtle reasoning, we may consider that the linear intermediates previously described $H(ArNBX)_nX$ ($X = Cl, Br, I$; $n = 2, 3$) behave as ambident nucleophiles. According to Pearson's HSAB terminology, nitrogen is the hard center and the ortho carbon the soft one. Hence, a hard acid like boron trichloride will react preferentially with the hard center that is to say with nitrogen, leading, after addition of another boron-nitrogen unit to the trimeric species whereas a soft acid like boron triiodide will rather react with the carbon atom in ortho position thus leading to the previous heterocycle. Of course, boron tribromide displays an intermediate behavior. These considerations are in good agreement with our experimental findings (Table I). With 1-aminonaphthalene, both the particular geometry of

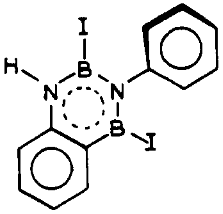

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TABLE I

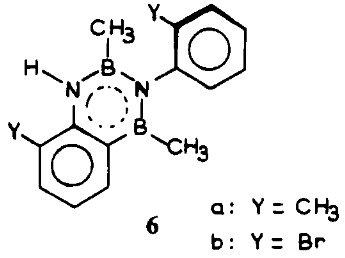
Formation of diboradiaza heterocycles (or borazines) by the reaction $ArNH_2 + BX_3$ ($X = Cl, Br$ or I)

$ArNH_2$	BCl_3	BBr_3	BI_3
1-naphthylamine	+	+	
1-anthraniline	+	+	
2-bromoaniline	–	+	
2-methylaniline	–	+[a]	
2-methyl-3-chloroaniline	–	+	
2-methyl-4-chloroaniline	–	+	
2-chloroaniline	–	–	
2-methyl-5-chloroaniline	–	–	
2-naphthylamine	–	–	
aniline	–	–	+[b]

Sign + is related to a quantitative yield of diboradiaza heterocycle, unless otherwise stated; sign – to a quantitative yield of borazine

[a] 98% of **6a** and 2% of trimer by VPC.

[b] 80% of **5** and 20% of trimer.



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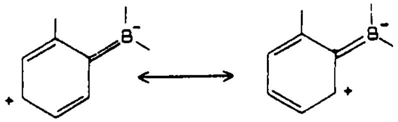
the amine and steric hindrance in ortho position are sufficient to give a quantitative yield of heterocycle II. With substituted anilines, the same reaction requires sufficient steric hindrance as is the case with Br and Me (but not with Cl) and the use of boron tribromide. Unfortunately, the data with boron triiodide are still limited but confirm earlier statements.

Having for the first time obtained in the pure state some derivatives of a new kind of heterocycle, we were led to study them thoroughly by means of NMR techniques. ^{13}C NMR enables ready identification of the seven primary carbons of the molecule **6a**, by comparison with the related borazine $(o\text{-}CH_3C_6H_4NBCH_3)_3$, by use of various decoupling methods and by using the fact that, in aromatic rings, $^2J_{CH} \ll {}^3J_{CH}$, that is to say the coupling constant between an aromatic carbon and the ortho hydrogen is usually much smaller than the coupling constant between the same carbon and the meta hydrogen.[9] Similar considerations apply for compound **6b**. Thus, in combination with high resolution proton NMR (360 MHz) and simulated spectra, was it possible to afford complete attribution for the chemical shifts of both derivatives **6a** and **6b**.[10] Interestingly, as far as the phenyl ring adjacent to the boron and nitrogen atoms is concerned, two atoms were deshielded and one shielded for **6a** and **6b**, which may be considered as a proof of the conjugation of boron with the adjacent aromatic ring as pictured by the two resonance patterns:



Such a hypothesis, indeed, is strongly supported by mass spectral data, the molecular peak being by far the most important for **6a** and **6b** whereas only a limited fragmentation is observed. We should also notice the importance of doubly charged ions. ^{11}B NMR, despite its lack of sensitivity, was a complementary tool, more especially as carbon bonded to boron could not be detected in ^{13}C NMR. It was possible, for the first time, to obtain two peaks of different width for the two boron atoms of the molecule of **6a** (or **6b**):[10] the broader one is the boron attached to the aromatic ring whereas the finer belongs to the boron atom between two nitrogen atoms, whose chemical shift is quite similar to the chemical shift of the related borazine. The reported values for those chemical shifts are also strongly dependant on the nature of the substituent on the boron atom.

During the course of this study, we were led to investigate the question of atropisomerism in *N*-triarylborazines. Indeed, according to the previously described

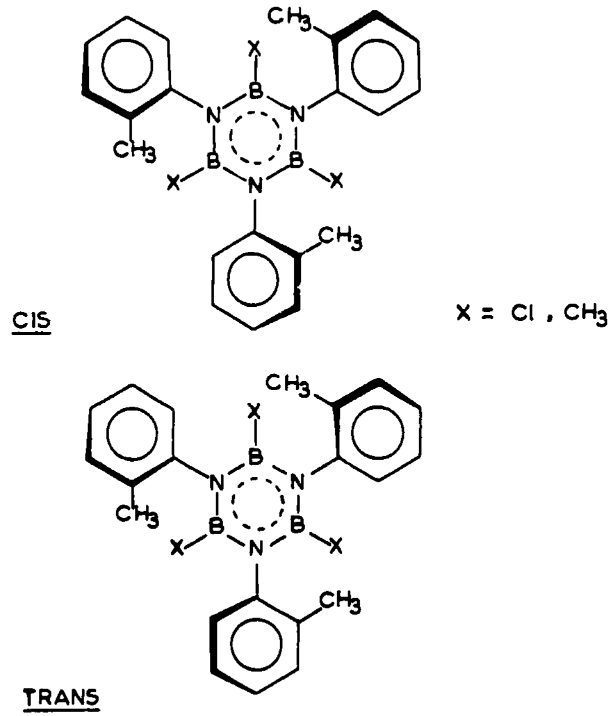
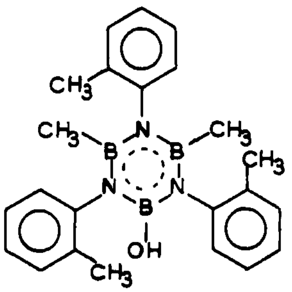


FIGURE 3

mechanism, when for instance, 2-methylaniline reacts with boron trichloride, two isomers are to be expected: one, the cis isomer with the three methyl groups above the plane of the borazine (C_{3v} symmetry) and the other, the trans isomer, with two methyl groups above the plane and one beneath (C_s symmetry) (Figure 3). However, when methylation of the chloroborazine was performed with the corresponding Grignard reagent, in diethyl ether, two main products were identified and separated by thin layer chromatography: the expected methyl derivative that corresponds to the cis isomer from its proton NMR spectrum consisting of two sharp peaks for the two different methyl groups; the other was a B-hydroxy by-product 7 whose formula



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was deduced from its proton NMR spectrum. ^{13}C NMR spectra of both compounds support these ideas: four peaks are obtained for the different primary carbons of the methyl derivative, as expected for a C_{3v} symmetry in the case of the cis isomer. Furthermore, the ^{13}C NMR spectrum of the hydroxy compound displays eleven peaks out of the twelve aromatic carbons required for a compound without a plane of symmetry.[11] Hence we may conclude that the trans isomer cannot be formed during the methylation reaction probably because of steric hindrance, thus leading to a hydroxy compound during the hydrolysis step.

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