primarily on the difference in scattering power of atoms in 0, 0, 0 and $^2/_3$, $^1/_2$, $^1/_2$. If the Nd^{3+} and Na^+ ions in these sites are randomly intermixed, their contributions become zero and only those Na^+ ions in $\pm 0, 0, z$ contribute; these may be barely detectable as described above. Thus it is probable that the $NaMF_4$ crystals showing $P6_3/m$ symmetry (and also gagarinite) have very nearly, if not precisely, the $NaNdF_4$ structure, but with random mixing of the M^{3+} and Na^+ ions in 0, 0, 0 and $^2/_3$, $^1/_3$, $^1/_2$. The fact that their high-temperature forms have complete mixing of cations in the fluorite structure adds credence to this view. Some of the crystals were obtained from slowly cooled melts, while others were made by quenching, and indeed it may be possible to prepare all of these compounds in both forms; *i.e.*, the degree of randomness may be determined by the cooling rate.

Diffuse X-Ray Reflections.—The diffuse streaks observed in X-ray photographs of $NaNdF_4$ are of the type reported for the mineral wollastonite, $CaSiO_3$. A discussion of the origin of this phenomenon is given by Wooster.[21] An analogous explanation for $NaNdF_4$ is as follows. Consider the site at $^2/_3$, $^1/_3$, $^1/_2$, which is occupied by both Na^+ and Nd^{3+} ions. It is 3.71 Å. from the equivalent site in the next unit cell along **c**, but is 6.10 Å. from equivalent sites in the (001) plane. Thus, for example, when an Na^+ ion occupies the site, it is highly probable that Nd^{3+} ions will be at $\pm$**c**, but at adjacent sites in the (001) plane either kind of ion may be found with equal probability. This results in an ordered string of cations along **c** but permits parallel strings to be shift in the **c** direction by 3.71 Å. Willis[22] has studied the diffraction patterns obtained from this kind of disorder as a function of the probability that a shift occurs in going from one string to the next. By comparison with his examples the $NaNdF_4$ photographs indicate that this probability is about 0.5; *i.e.*, the shifts are completely random.

Acknowledgments.—The author wishes to thank R. E. Thoma for advice and encouragement in carrying out this study and G. M. Hebert for preparing the crystals. Computer programs were supplied by C. K. Johnson and R. D. Ellison.

---

[21] W. A. Wooster, "Diffuse X-Ray Reflections from Crystals," Clarendon Press, Oxford, 1962, pp. 118–121.

[22] B. T. M. Willis, *Proc. Roy. Soc.* (London), **A248**, 183 (1958).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
DUKE UNIVERSITY, DURHAM, NORTH CAROLINA

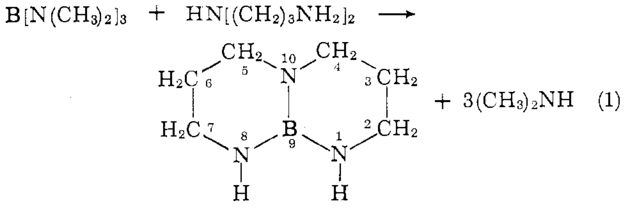
Boron–Nitrogen Compounds. XVII.[1,2] Reactions of 1,8,10,9-Triazaboradecalin

BY PETER FRITZ, KURT NIEDENZU, AND JOHN W. DAWSON

Received February 15, 1965

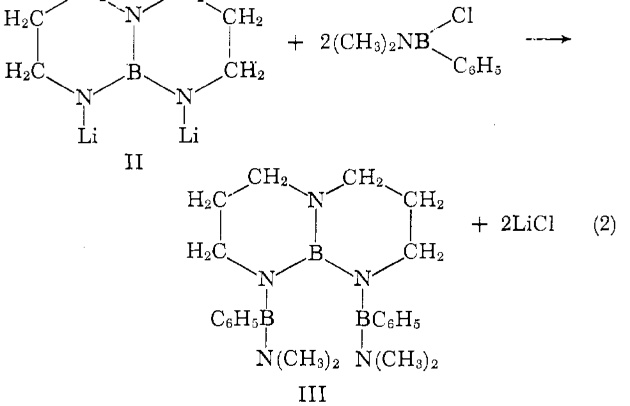
Several reactions of 1,8,10,9-triazaboradecalin which indicate a new route to the synthesis of unsymmetrically substituted borazines as well as for several new boron–nitrogen–carbon heterocycles have been studied. This research has also led to the discovery of a novel type of boron–nitrogen heterocycle, containing four nitrogen and three boron atoms as annular members, *i.e.*, the 1,3,5,6-tetraaza-2,4,7-triborine system.

Recently, the preparation of 1,8,10,9-triazaboradecalin (I) by a very simple method as illustrated in eq. 1 was reported.[1] We now wish to present a more detailed study of the chemical reactions of I.



I

The NH groups in I can be metallated by allowing that compound to react with lithium alkyl; the resultant dilithium salt, II, is extremely sensitive toward moisture. It, in turn, was allowed to react *in situ* with dimethylaminophenylchloroborane, to provide compound III, 1,8-bis(dimethylaminophenylboryl)-1,8,10,9-triazaboradecalin as shown in eq. 2. III, in like manner, reacts with aniline to yield the unsymmetrically substituted borazine, IV, hexahydro-1,2,3-



II

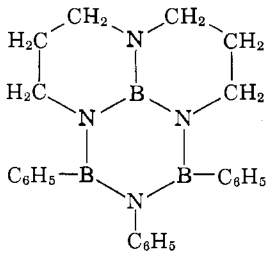
III

---

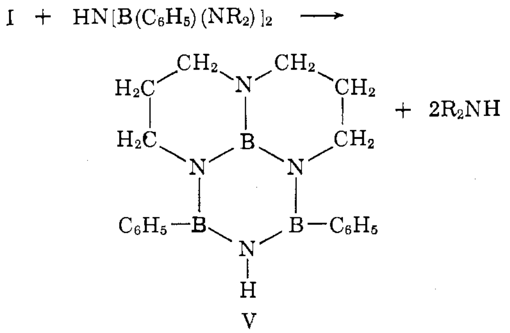
[1] Part XVI: K. Niedenzu, P. Fritz, and J. W. Dawson, *Inorg. Chem.*, **3**, 1077 (1964).

[2] Supported by the U. S. Army Research Office—Durham.

triphenyl-4H,7H-2,3a,6a,9a-tetraaza-1,3,9b-triboraphenalene,[3] by a transamination reaction.

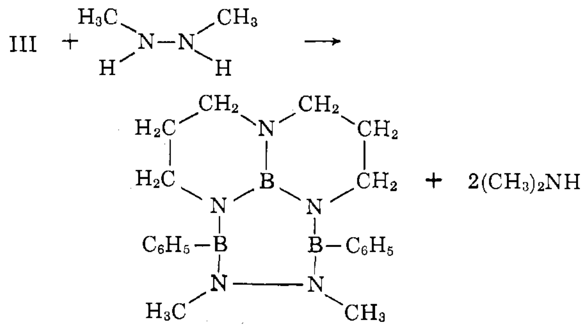

IV

The structure of IV has been confirmed by quantitative analysis and determination of its molecular weight. Additional evidence of structure is furnished by the infrared spectrum of the material. No NH vibration can be observed and a very strong band at 1408 cm.$^{-1}$ with a shoulder on the high-frequency side suggests the presence of a borazine ring vibration. This assignment finds support in the observation of a BN out-of-plane vibration in the 710 cm.$^{-1}$ region.[4] The validity of the latter assignment can be substantiated since (a) III does not exhibit this vibration and (b) this latter frequency is also observed in the borazine derivative V and hence cannot be due to a CH vibration of the phenyl ring attached to the nitrogen. Consequently, it seems reasonably certain that the product IV contains the fundamental borazine structure. Therefore, this method of preparation of IV constitutes a new procedure for the synthesis of unsymmetrical substituted borazines.


(3)

V

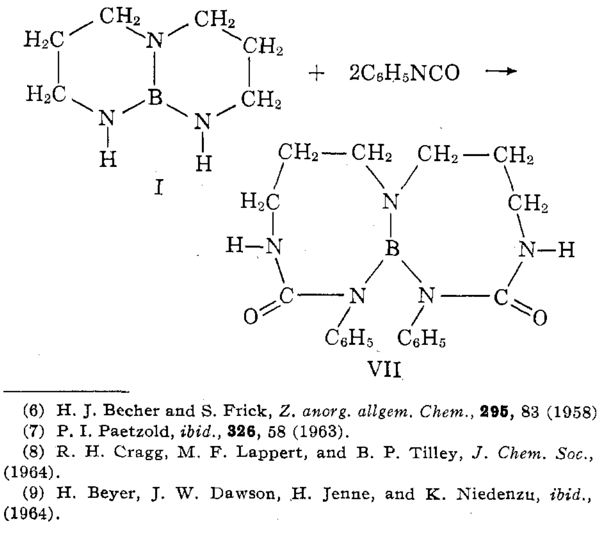
A similar borazine derivative, V (cited above), the hexahydro-1,3-diphenyl-4H,7H,2,3a,6a,9a-tetraaza-1,3,9b-triboraphenalene, has been obtained from the transamination of 1,8,10,9-triazaboradecalin (I) with bis(dimethylaminophenylboryl)amine[5] as illustrated in eq. 3. The infrared spectrum of V exhibits an NH vibration at 3480 cm.$^{-1}$. The strongest band of the spectrum, recorded at 1451 cm.$^{-1}$, was tentatively assigned to the borazine BN ring vibration. This shift of $\nu_{\text{BN ring}}$ to higher frequency appears remarkable when compared to the same vibration in IV. This shift seems to indicate an extensive weakening of the BN ring vibration on substituting the hydrogen of the 2-nitrogen atom in V by a phenyl group (IV). However, this observation is in agreement with a similar effect exhibited by B-triphenylborazine[6] (ν_{BN} = 1472 cm.$^{-1}$) on the one hand and B-triphenyl-N-triphenylborazine[7] (ν_{BN} = 1369 cm.$^{-1}$) on the other.


(4)

VI

1,8-Bis(dimethylaminophenylboryl)-1,8,10,9-triazaboradecalin (III) also was allowed to react with symmetrical dimethylhydrazine as shown in eq. 4. This transamination reaction yielded a novel boron–nitrogen heterocycle, VI, which is a derivative of the 1,3,5,6-tetraaza-2,4,7-triborine, containing three boron and four nitrogen atoms as annular members. The infrared spectrum of VI has been recorded. The general pattern of the spectrum is very similar to that of III. Due to the complexity of the spectrum and the lack of any comparative material, no attempt has been made to assign any characteristic frequency.

Unusual bicyclic boron–nitrogen–carbon heterocycles were obtained by allowing 1,8,10,9-triazaboradecalin (I) to react with isocyanates and isothiocyanates. This reaction appears to follow the course previously established for the reaction of isocyanates with simple acyclic aminoborane systems,[8,9] *i.e.*, the addition of a boron–nitrogen linkage across a carbon–nitrogen double bond. In principle, there are three boron–nitrogen bonds available in I for a reaction of this kind. With phenyl isocyanate, interaction of I occurs in a 2:1 molar ratio. This suggests the reaction of the 1,9 and 8,9 bonds of I as illustrated in eq. 5, leading to the formation of the bicyclic derivative VII.


(5)

VII

---

[3] The authors are grateful for the assistance rendered by Dr. K. L. Loening of *Chemical Abstracts* in naming the new compounds reported herein.

[4] H. Beyer, J. B. Hynes, H. Jenne, and K. Niedenzu, Advances in Chemistry Series, No. 42, American Chemical Society, Washington, D. C., 1964, p. 266.

[5] H. Jenne and K. Niedenzu, *Inorg. Chem.*, **3**, 68 (1964).

[6] H. J. Becher and S. Frick, *Z. anorg. allgem. Chem.*, **295**, 83 (1958).

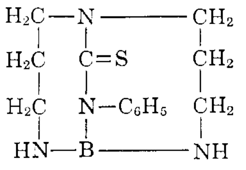
[7] P. I. Paetzold, *ibid.*, **326**, 58 (1963).

[8] R. H. Cragg, M. F. Lappert, and B. P. Tilley, *J. Chem. Soc.*, 2109 (1964).

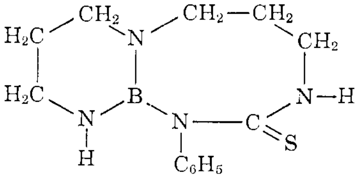
[9] H. Beyer, J. W. Dawson, H. Jenne, and K. Niedenzu, *ibid.*, 2115 (1964).

The structure of VII seems to be substantiated by infrared spectral data, since the product exhibits only one NH stretching vibration recorded near 3275 cm.$^{-1}$. Had one isocyanate molecule been added across the 9,10 linkage of I, one should expect two distinct NH stretching vibrations since the NH groups of the postulated product would not be expected to be equal. VII illustrates a new type of boron–nitrogen–carbon bicyclic system in which each ring contains eight annular atoms.

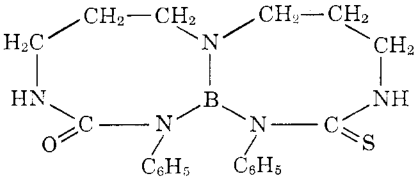
Strangely enough, however, I reacts only in a 1:1 molar ratio with phenyl isothiocyanate. The resultant product of that reaction can be formulated in two ways (VIII, IX). Since the infrared spectrum of the material exhibits two distinct NH vibrations at 3380 and 3270 cm.$^{-1}$, respectively, structure IX appears to be more reasonable. This conclusion is reinforced by the fact that the compound reacts with one mole of phenyl isocyanate. As illustrated by eq. 5 the formation of eight-membered cyclic systems seems to be preferred. Such a structure, X, will result from the reaction of phenyl isocyanate with IX but not with VIII. In addition, the product X exhibits only one NH stretching vibration near 3300 cm.$^{-1}$.



VIII



IX



X

Finally, 1,8,10,9-triazaboradecalin (I), on treatment with trinitrobenzene, gives a 1:1 molar addition complex. This dark brown to red material exhibits an e.s.r. signal at approximately 3400 gauss, suggesting the presence of unpaired electrons. It seems worth mentioning that the *g* value has the same order of magnitude as for organic free radicals. The infrared spectrum of the adduct is rather complex and no further elaboration can be made at this time. However, an examination of molecular models clearly reveals that the two fundamental parts of the adduct can be closely packed on top of each other.

Experimental[10]

1,8-Bis(dimethylaminophenylboryl)-1,8,10,9-triazaboradecalin (III).—A quantity (36.2 g., 0.26 mole) of 1,8,10,9-triazaboradecalin (I) was dissolved in 200 ml. of dry, thiophene-free benzene in an atmosphere of argon; 236.5 ml. of a 2.2 *M* solution of butyllithium in hexane was added with vigorous stirring. The reaction mixture was refluxed for 8 hr. A solution of 87 g. (0.52 mole) of dimethylaminophenylchloroborane in 100 ml. of dry benzene was added and refluxing was continued for an additional hour. The mixture was allowed to stand overnight and then filtered, and the solvents were stripped off. Rectification of the residue under vacuum yielded 27.8 g. (26.7%) of the desired product, III, b.p. 205–208° (1 mm.); m.p. 100–102° (softening starts at about 95°). *Anal.* Calcd. for $B_3N_5C_{22}H_{34}$: C, 65.9; H, 8.55; B, 8.1; N, 17.5; mol. wt., 401.0. Found: C, 65.8; H, 8.5; B, 8.1; N, 17.4; mol. wt., 406.

Hexahydro-1,2,3-triphenyl-4H,7H-2,3a,6a,9a-tetraaza-1,3,9b-triboraphenalene (IV).— A solution of 27.8 g. (69.3 mmoles) of III and 6.45 g. (69.3 mmoles) of aniline in 200 ml. of dry ether and 100 ml. of dry benzene was refluxed in an inert atmosphere for 10 hr. The solvents were stripped off and the residue was heated under vacuum at a temperature of about 200° for 15 min. The solid residue was then purified by repeated sublimation, yielding 8.4 g. (30%) of the desired compound, IV, m.p. 259–260°. *Anal.* Calcd. for $B_3N_4C_{24}H_{27}$: C, 71.35; H, 6.7; B, 8.0; N, 13.9; mol. wt.: 404.0. Found: C, 71.2; H, 6.9; B, 8.4; N, 13.9; mol. wt., 394.

Hexahydro-1,3-diphenyl-4H,7H-2,3a,6a,9a-tetraaza-1,3,9b-triboraphenalene (V).—A solution of 15.8 g. (56.75 mmoles) of bis(dimethylaminophenylboryl)amine and 7.81 g. (56.75 mmoles) of 1,8,10,9-triazaboradecalin (I) in 1000 ml. of dry benzene was refluxed for 3 hr. The benzene was stripped off and the residue was heated to 250°. Substantial quantities of dimethylamine were evolved and heating was continued until the material began to decompose as evidenced by the appearance of fumes. Subsequent distillation of the reaction product under vacuum afforded a fraction, boiling from 200 to 230° (3 mm.), which was rectified to yield 7.1 g. (38%) of V, b.p. 228–230° (3 mm.); m.p. 93–96°. *Anal.* Calcd. for $B_3N_4C_{18}H_{23}$: C, 65.9; H, 7.1; B, 9.9; N, 17.1; mol. wt., 327.9. Found: C, 65.9; H, 7.1; B, 9.8; N, 17.0; mol. wt., 328.

Octahydro-8,9-dimethyl-7,10-diphenyl-1H,4H-3a,6a,8,9,10a-pentaaza-7,10,10b-triboracyclohepta[*de*]naphthalene (VI).—A solution of 37.5 g. (93.5 mmoles) of III and 5.61 g. (93.5 mmoles) of anhydrous symmetrical dimethylhydrazine in 1000 ml. of anhydrous ether was refluxed in an argon atmosphere for 8 hr. On concentrating the solution a white crystalline material precipitated and was separated. Further concentration of the mother liquor yielded a second fraction of crystals. The combined precipitates where washed with several small portions of ether, yielding 24.3 g. (70%) of VI, m.p. 106–108°. *Anal.* Calcd. for $B_3N_5C_{20}H_{28}$: C, 64.8; H, 7.6; B, 8.75; N, 18.9; mol. wt., 370.9. Found: C, 64.8; H, 7.8; B, 8.4; N, 16.5; mol. wt., 369.

Octahydro-1,13-diphenyl[1,3,5,2]triazaborocino[1,2-*a*]1,3,5,2-triazaborocine-2,12(1H,13H)-dione (VII).—A solution of 6.9 g. (57.9 mmoles) of phenyl isocyanate in 10 ml. of benzene was added dropwise with stirring to a solution of 5.1 g. (36.7 mmoles) of 1,8,10,9-triazaboradecalin in 40 ml. of benzene. A white solid precipitated from the exothermic reaction. It was filtered off, washed with pentane, and dried under vacuum; yield, 92% of VII, m.p. 175° (softening begins at about 165°). *Anal.* Calcd. for $BN_5O_2C_{20}H_{24}$: C, 63.7; H, 6.4; B, 2.9; N, 18.6. Found: C, 63.9; H, 6.8; B, 3.0; N, 18.2.

Octahydro-1-phenyl[1,3,2]diazaborino[1,2-*a*]triazaborocine-2(1H)-thione (IX).—A solution of 7.85 g. (57.9 mmoles) of phenyl isothiocyanate in 50 ml. of benzene was added to a solution of 10.2 g. (57.9 mmoles) of 1,8,10,9-triazaboradecalin in 50 ml. of benzene. Upon adding pentane to the reaction mixture, a white precipitate was obtained which was filtered off, washed with

---

(10) Analysis were furnished by the Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y. Melting points were taken on a Mel-Temp block and are uncorrected; molecular weights were obtained by the cryoscopic method in benzene. Infrared spectra were recorded on a Perkin-Elmer Model 21 double-beam spectrophotometer using sodium chloride optics.

pentane, and dried under vacuum to yield 17 g. of material (IX), m.p. 110–112°. *Anal.* Calcd. for $BN_4SC_{13}H_{19}$: C, 56.9; H, 7.0; B, 3.95; N, 20.4; S, 11.7. Found: C, 57.2; H, 6.9; B, 4.0; N, 20.3; S, 11.7.

Octahydro-1,13-diphenyl-2-thio[1,3,5,2]triazaborocino[1,2-*a*]-[1,3,5,2]triazaborocine-2,12(1H,13H)-dione (X).—A solution of 5 ml. of phenyl isothiocyanate in 10 ml. of benzene was added to a solution of 5.12 g. (36.85 mmoles) of 1,8,10,9-triazaboradecalin in 30 ml. of benzene. The mixture was stirred and 3 ml. of phenyl isocyanate was added dropwise. Upon adding 75 ml. of pentane to the reaction mixture a white precipitate was obtained; it was filtered off and washed with pentane. After the material was dried under vacuum, it had a melting point of 115° with decomposition. *Anal.* Calcd. for $BN_5OSC_{20}H_{24}$: C, 61.1; H, 6.15; B, 2.75; N, 17.8; S, 8.15. Found: C, 61.2; H, 6.3; B, 2.6; N, 16.6; S, 8.1.

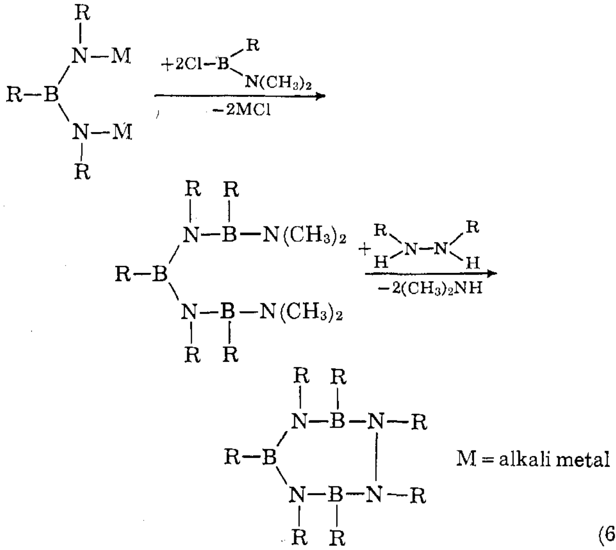
Adduct of 1,8,10,9-Triazaboradecalin with Trinitrobenzene.—A solution of 3.3 g. (14.4 mmoles) of trinitrobenzene in 50 ml. of benzene was added to a solution of 2 g. (14.4 mmoles) of 1,8,-10,9-triazaboradecalin in 100 ml. of benzene. A dark red color appeared. The benzene was stripped off under vacuum at room temperature and about 5 g. of red-brown crystals was obtained, m.p. 115–117° dec. On attempting to sublime the material, it exploded; the compound was analyzed without further purification. *Anal.* Calcd. for $BN_6O_6C_{12}H_{17}$: C, 40.9; H, 4.9; B, 3.1; N, 23.9. Found: C, 40.9; H, 4.8; B, 3.0; N, 23.7. The e.s.r. spectra of the addition compound were obtained from freshly prepared samples which were not actually isolated from the solution.

Discussion

On the basis of an examination of molecular models and spectroscopic data (to be published elsewhere), it is apparent that the BN_3 grouping in 1,8,10,9-triazaboradecalin (I) is planar or nearly planar, although the corresponding methylene groups of the two rings are not necessarily identical. On transition from I to III, molecular models reveal that the two terminal boron–nitrogen bonds in III are almost perpendicular to the B_2N_5 plane with the two phenyl rings favorably in the *trans* position, which permits the greatest free rotation of substituents. However, the *cis* position of the phenyl rings can readily be achieved. These two molecular arrangements could possess a slight difference in internal energy and this feature may explain the small discrepancies in line intensities of the infrared spectra of various samples of III.

The planarity of a borazine ring has been well established.[11] Hence, the presumed existence of a planar B–N–B–N–B arrangement in III would appear to favor the formation of a borazine ring, IV, in the described reaction. Virtually free rotation of the molecular parts exists in bis(dimethylaminophenylboryl)-amine, and it is reasonable to expect the combination of I and the diborylamine to yield the borazine derivative V in a transamination reaction. It is noteworthy, however, that the reaction illustrated in eq. 3 represents the first example of a transamination between a diborylamine and an aminoborane with the elimination of amine. This reaction might be considered as the first evidence to suggest that the formation of borazines occurs through preformed N–B–N systems rather than the condensation sequence as postulated by Wiberg.[12] This possibility has been noted briefly by Mikhailov[13] in a study of the reaction of isoamyldichloroborane with amines.

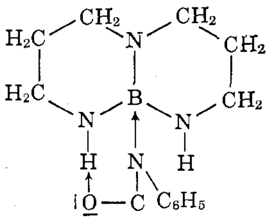
In VI, the boron and nitrogen atoms of the tetraazatriborine ring are not all planar. It seems reasonable to expect the synthesis of additional representatives of this system by the reaction scheme shown in eq. 6.



(6)

The bicyclic ureido derivatives VII, IX, and X represent novel boron–nitrogen–carbon heterocycles. It is noteworthy that the 9,10 linkage of I and the subsequent products is not attacked by additional isocyanate. This circumstance might be interpreted in terms of a greater inner stability of the eight-membered ring system as compared to a hypothetical ten-membered B–N–C cycle. This conclusion is not unreasonable since α,ω-diamines react with bisaminoboranes to yield heterocyclic derivatives in a smooth reaction[1] only if the resultant ring does not contain more than eight annular atoms. Otherwise, there seems to be a distinct preference for the formation of linear polymers.

The preferred addition of the 1,9 and 8,9 boron–nitrogen bonds of I (as opposed to the 9,10 bond) across the carbon–nitrogen double bond of isocyanates may be explained by the initial formation of a six-membered ring through hydrogen bonding, illustrated in XI, followed by rearrangement. The absence of a



XI

labile hydrogen on the 10-nitrogen prevents the operation of this mechanism and this suggests the inability of the 9,10 linkage in I to react with isocyanate.

---

[11] S. H. Bauer, *J. Am. Chem. Soc.*, **60**, 524 (1938).

[12] E. Wiberg, *Naturwissenschaften*, **35**, 182, 212 (1948).

[13] B. M. Mikhailov and T. K. Kozminskaia, *Dokl. Akad. Nauk SSSR* **121**, 656 (1958); *Chem. Abstr.*, **53**, 1209 (1959).