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1,3-DIAZA-2,4-DIBORETIDINES[1]. ISOCYANIDE - BORANE ADDUCTS. II[2].

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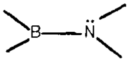
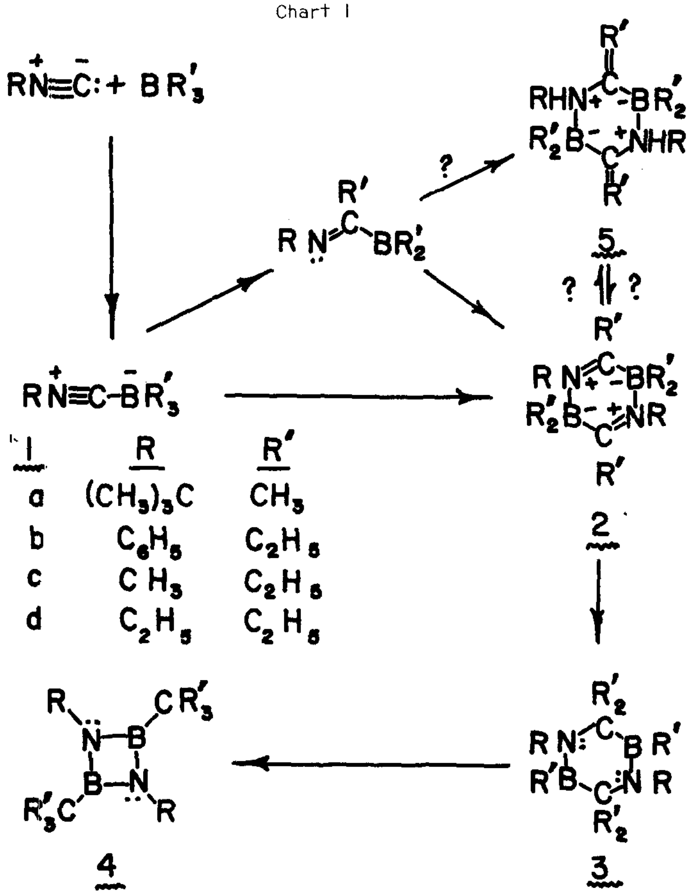
Heterocyclic compounds that formally satisfy the Hückel (4n+2) Rule, but in which the degree of aromaticity depends upon delocalization of  bonds into an extended π-system, have constituted an area of keen theoretical interest for many years[3,4]. Such systems containing the same number of boron and nitrogen atoms in an even number ring size are isoconjugate with corresponding carbocyclic aromatics. Depending upon the structure of the remainder of the ring, compounds have been reported as ranging from stable, with "marked similarity to the related 'normal' aromatic" in their physical properties (i.e., derivatives of 4,3-borazaroisoquinolines)[5] to unstable, with little similarity to the related aromatic (i.e., borazine)[6]. Prompted by the ease of entry into an N-B-C heterocyclic system via adducts of isocyanides and organoboranes[2,7], and encouraged by recent extended molecular orbital calculations on these compounds[3b,4b], we have directed efforts toward the preparation of derivatives of 1,4-diaza-2,5-diborine from the ring system 3,6-dihydro-1, -diaza-2-5 diborine **3**, shown on Chart I, in order to educe the degree of aromaticity in the former compounds. Ancillary to this objective, we have encountered a remarkable compound which we are compelled to formulate as 1,4-diphenyl-2,4-bis(triethylcarbinyl)-1,3-diaza-2,4-diboretidine **4**, a compound which is isoelectronic with the similarity substituted cyclobutadiene system. This ring system has been only recently discovered[8], and virtually none of its chemistry has been studied. The object of this report is to present evidence for the structure of **4**, and to record some observations of its surprising chemical stability.

Isocyanides behave as Lewis bases toward diborane and organoboranes, forming crystalline adducts 1 at low temperature[2]. These adducts undergo a series of isomerizations at successively increasing temperatures to produce compounds 2, 3 and 4, as illustrated in Chart I. The ease with which these successive isomerizations occur appears to be markedly dependent upon the nature of R and R'.

Chart I



1	R	R'
a	$(CH_3)_3C$	CH_3
b	C_6H_5	C_2H_5
c	CH_3	C_2H_5
d	C_2H_5	C_2H_5

Although adduct **1a** is converted to **2a**[9] slowly at room temperature, **1b** can be identified only fleetingly by its low temperature proton resonance spectrum. This rate difference may be related to a steric effect.

Compound **2a** decomposed rapidly at 100-150°, giving at least 6 different products (by thin-layer chromatography), however, compound **2b** was converted quantitatively to **3b** by a brief heating at 180°, mp. 203-204°, after crystallization from acetonitrile, as described by Hesse and Witte[7]. Compound **3b** was homogeneous by thin layer chromatography (TLC). When **3b**, in an evacuated sealed tube, was placed in an oven at 300° for 5 minutes, a new compound was formed in 96% yield, mp. 141-42° after crystallization from methanol. It was homogeneous by TLC, and much less polar than **3b**, and was soluble in chloroform, ether, acetone, benzene, and pyridine, but insoluble in water, hydrochloric acid, and sodium hydroxide. This compound is formulated as 1,3-diphenyl-2,4-bis(triethylcarbinyl)-1,3-diaza-2,4-diboretidine, **4b**, on the basis of the evidence below. The elemental analysis supported an empirical formula $C_{26}H_{40}N_2B_2$: Calc'd.: C, 77.63; H, 10.02; N, 6.96: Found, C, 77.48; H, 10.04; N, 6.82. Molecular weight (isopiestic)[10], in benzene: Found; 395: Molecular weight (Mecrolab Vapor Pressure Osmometer, Type 301A), in benzene: Found; 390. Calc'd. for $C_{26}H_{40}N_2B_2$; 402.26. A sample recovered from the isopiestic molecular weight measurement after three weeks was unchanged in melting point. The infrared spectrum of **4b** (CCl_4 solution) showed no N-H or O-H stretch and no -C≡N, -N≡C or -C=N- stretch, but absorption at 2920(C-H), 1575, 1475, 1380, and 700 cm.$^{-1}$. The ultraviolet absorption spectrum (see Chart II) falls in intensity and wavelength maximum close to anilinium ion[11], suggesting little extention of the aromatic system into the adjacent nitrogen atom.

Chart II

Ultraviolet Spectra of N-B-C Heterocycles

Compound	Absorption Maxima (mμ) (log ε)	Solvent
2b	230(4.23)	95% ethanol
3b	225(3.76)	95% ethanol
4b	253(2.29); 259(2.27);265(2.14)	95% ethanol

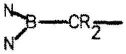
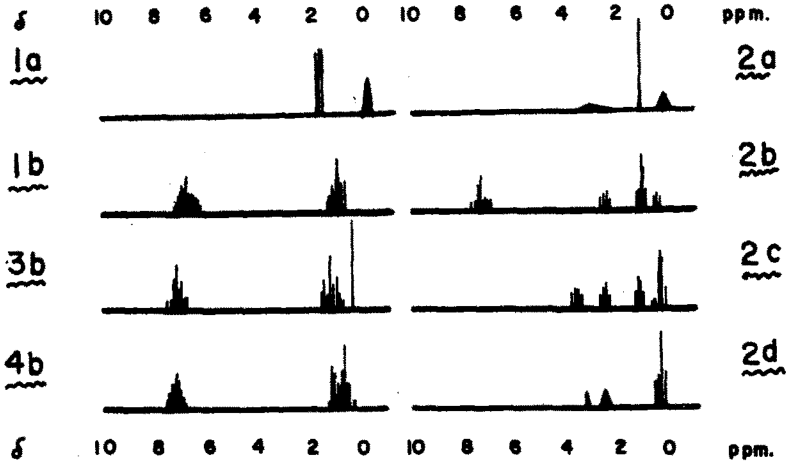
The proton resonance spectrum consisted of two broad complex regions of absorption centered at δ ≐ 7.10 ppm. and 1.0 ppm. (relative to tetramethylsilane), and in the ratio of 1:3 (see Chart III). These areas are attributed to aromatic and aliphatic proton resonances, respectively. The near coincidence of methyl and methylene proton chemical shifts is easily understood when one considers the low electronegativity of the  $(N)_2B{-}CR_2{-}$ group which is attached to the methylene carbon atom.

Chart III

Schematic Proton Resonance Spectra of N-B-C Heterocycles

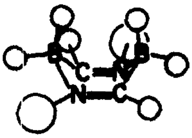


An atom or group of this nature raises the chemical shift of $-CH_2-$ into the $-CH_3$ region[12]. The B^{11} resonance spectrum ($\delta = -36 \pm 5$ ppm., relative $BF_3.O(C_2H_5)_2$ at $\delta = 0$) was a very broad single line, and suggests the presence of a boron atom attached to one carbon atom and two nitrogen atoms[13]. The high resolution mass spectrum of **4b** was very complex. No parent peak was observed, but prominent peaks at M-33±4 (loss of $-C_2H_5$), M-99 (loss of $-C(C_2H_5)_3$), M-123 (loss of $-C(C_2H_5)_3$ and $2C_2H_5$), M-153 ($N_2B_2H(C_6H_5)_2$, M-198 ($N_2B_2C_2(C_2H_5)_2C_6H_5$), M-235 ($N_2B_2CC_2H_5C_6H_5$), M-263 ($N_2B_2CC_6H_5$), and M-309 ($H_2NC_6H_5$) were in accord with the proposed structure. Fragments containing two boron atoms were further identified by the intensity of the P-1 and P-2 peaks. On the weight of this evidence we can write only structure **4b** for this compound. The isomerization of **3**$\rightarrow$**4** can be viewed as analogous to the Favorski Rearrangement.

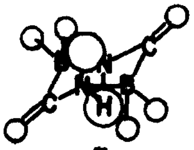
Compound **4** is virtually refractory to chemical change when treated with a wide variety of common reagents. It failed to form a salt with dry hydrogen chloride in ether solution. It was recovered unchanged (84%) after 3 hours of refluxing with 37% hydrochloric acid. It was recovered unchanged (92%) after 3 hours of refluxing with 50% methanolic potassium hydroxide. It failed to decolorize bromine in carbon tetrachloride. When 40 mg. of **4b** was allowed to stand overnight with 200 mg. of CrO_3 in 2.0 ml. of pyridine, a small amount of an oil was obtained from the neutral ether workup, identified as 3-pentanone as the 2,4-dinitrophenylhydrazone by melting point, mixed melting point, and TLC comparison with an authentic sample. When 40 mg. of **4b** in 15 ml. of ether and 0.5 ml. of chromic acid was stirred overnight, according to Brown's procedure[14] for the oxidation of alkylboranes, only unchanged **4b** was recovered in the ether phase. We can extend no rational for this unexpected chemical inertness.

While the lack of reactivity of compound 4b is unpredicted, a pattern of behavior for the isomerization sequence $1 \rightarrow 2 \rightarrow 3 \rightarrow 4$ emerges from examination of scale molecular models and considerations of the bond energy changes in the sequence. We have assumed that the bond lengths and angles of tetravalent C°, $B^{\ominus}$ and $N^{\oplus}$ are nearly identical in the following discussion. Chart IV illustrates the possible stereochemistry in these compounds. Compound 2 must exist in a boat or twist-boat conformation due to the C=N double bond.

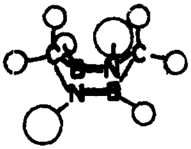
Chart IV



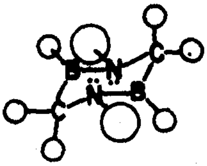
2



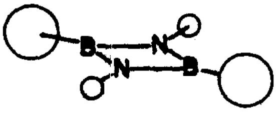
5



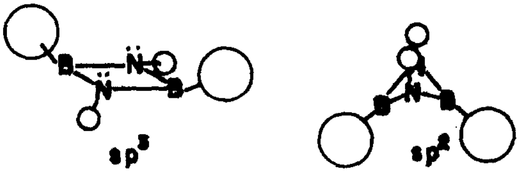
3-DELOCALIZED



3-LOCALIZED



4-DELOCALIZED



4-LOCALIZED

Since both alkyl groups on each boron atom are identical, considerable diaxial non-bonded interaction will be expected from either conformer. In addition, very bulky groups on nitrogen (such as the t-butyl group in 2a) will cause severe crowding and should result in substantial weakening of the B-N and/or B-C bond over that expected for an unsubstituted ring. This weakened bonding is reflected in the thermal instability[9] and complex fragmentation of 2a (*vide infra*). If the substituents on nitrogen are less bulky, but still aliphatic, another interesting reaction appears to occur. Bresadola and his collaborators recently reported[15] evidence to support structure 5d for a compound melting at 95-97° which they obtained in addition to the expected product, 2d, m.p. > 200°. Although these authors did not suggest it, compounds 2d and 5d are, in principle, related to each other as tautomers, a relation which may be illustrated by a partial structure as:

A rationale for this behavior is afforded by examination of structure 5 in Chart IV. Tautomerization can convert the boat conformer, 2, to into a chair conformer, 5, in which a considerable decrease of non-bonded interaction is anticipated. We have prepared Bresadola's compounds, and observed somewhat higher melting points than those reported. In our hands, compound 5d melted at 101-103° (recrystallized from benzene - ether), and compound 2d melted at 231-232° (recrystallized from benzene - methanol). Both materials were homogeneous by TLC, and gave the proton resonance spectra previously described[15].

However, the suspected equilibrium (2d $\rightleftharpoons$ 5d) could not be established from either pure 2d or pure 5d by thermal or catalytic means. Compound 2d, in ether solution at room temperature, was unaffected either by catalytic amounts of $BF_3.O(C_2H_5)_2$ or triethylamine, even after long standing. Compound 5d gave at least five different compounds in the presence of $BF_3.O(C_2H_5)_2$ but was unaffected by triethylamine. Compound 5d rapidly decolorized bromine in carbon tetrachloride. A similar behavior for compound 1c during its conversion to subsequent products (2c → 5c) has been observed in our laboratories, but this series has not been fully investigated. Stability of compound 2b (R = phenyl) relative to its tautomer, 5b can be accomodated by the fact that tautomerization in this case would require that the N═C double bond shift out of conjugation with the aromatic ring. Evidence for substantial conjugative overlap in 2b is seen from its ultraviolet absorption spectrum (Chart II). Our inability to interconvert compounds 2 and 5 suggests that 1 is first converted to a common intermediate, perhaps of the $RN{=}CR'BR_2'$ structure, which can either dimerized to 2, or tautomerize and dimerize to 5.

The conversion 2 → 3 provides an unusual case of a chemical reaction in which the reactant and product are homomorphic, if it is assumed that a substantial amount of back-bonding of electrons from nitrogen to boron is occurring. This situation is illustrated as structure 3-delocalized in Chart IV. In such a case, ΔS° would be near zero, and a substantial negative ΔH° should be involved. Unfortunately, the bond strengths of tri- and tetra-coordinated B-N bonds is so imperfectly known as to render highly questionable any estimate for ΔH° in this reaction[16]. Present evidence[4b,17] suggests that such extensive delocalization is not the encountered in similar compounds. Structure 3-localized in Chart IV depicts a shallow chair conformation for compound 3 in the case that both nitrogen and boron are hybridized intermediate between sp^2 and sp^3 to give pyramidal boron and nitrogen atoms. An interesting alternative formulation, not depicted in Chart IV, would permit a planar arrangement of atoms around each boron and nitrogen atom, but localization of electrons in the nitrogen p-orbital. Both formulations would effect a marked decreasenof eclipse interaction of substituents. The B^{11} resonance spectrum of 3b is a single line (δ = -41 ± 3 ppm., relative to $BF_3.O(C_2H_5)_2$ at δ = 0) and supports a structure with tricoordinate boron atom attached to two carbon atoms and one nitrogen atom, but neither confirms nor rejects significant back-bonding between nitrogen and boron[13]. The ultraviolet spectrum of 3b (Chart II), while suggesting little interaction between the aromatic ring and the adjacent nitrogen atom, may only reflect non-colinearity of the appropriate π-orbitals due to geometrical constraints imposed by the heteroring. Of the localized and delocalized structures for compound 3, molecular overcrowding is greatly diminished in 3-localized.

Considering the sensitivity of the isomeric transformations in this series to geometrical and bond energy changes, it is not surprising that upon strong heating 3b is converted to 4b. Examination of molecular models suggests substantially less crowding in this isomer. A large negative ΔH° would be anticipated in this transformation as well. Structures may be drawn for 4 which are analogous to the localized and delocalized structures drawn for 3. Although structure 4-delocalized requires that the groups attached to nitrogen and boron lie in the ring plane, structure 4-localized does not require that these groups be out of that plane. Steric considerations favor the out of plane arrangement, especially if the ring is itself planar. While preliminary evidence from the B^{11} resonance spectrum and ultraviolet spectrum of 4b does not suggest that back-bonding of nitrogen electrons to boron occurs to a large extent, the stereochemical constraints imposed on attainment of planarity of the three rings by severe overcrowding could decisively affect this conclusion. Hoffmann has suggested[18], from extended molecular orbital calculations, that the cyclic $(BHNH)_2$ molecular is a square plane. Kaufman[19a] and Niedenzu[19b], from theoretically and experimentally based calculations, respectively, have concluded that the introduction of an N-phenyl group brings about a considerable lowering of B-N bond order in phenyl-N-B compounds due to "resonance interaction of the unshared electron pair of the nitrogen atom with the adjacent phenyl group." On the other hand, appreciable experimental evidence exists from bond energy data[16a], bond length measurement[20], infrared analysis[21], and proton resonance spectroscopy[22] to indicate a considerable amount of π-bonding in the tricoordinate B-N bond. Studies to determine the effect of sterochemistry on the nature of the isomerization reactions and on ring geometry are in progress.

References

(1) We have adopted the nomenclature recommended by the IUPAC 1957 Rules (Section B-1) rather than the replacement name "azaboracyclobutane." Inconsistencies which arise from the use of replacement names in boron heterocycles have been adequately discussed (consult M. J. S. Dewar, reference 3b, p. 228).

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(b) M. J. S. Dewar and W. H. Poesche, *J. Org. Chem.*, **24**, 1757 (1964).

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(b) See also reference 3b, Chapter 24.

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(9) In reference 2, the compound here described as **2a** was tentitively identified as a monomer by its mass spectrum. Subsequent isopiestic molecular weight measurement and B^{11} - resonance spectrum identify it as the dimer. It is probably that under the conditions of high vacuum and heated inlet in the mass spectrometer **2a** was converted to the monomer before being ionized. Examination of scale molecular models suggest very severe molecular overcrowding in **2a** and renders unlikely the possibility that B-N bonding here is especially strong.

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(18) R. Hoffman, reference 3b, p. 83.

(19) (a) J. J. Kaufman and J. R. Hamann, reference 3b, p. 97;
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