i.e., *cis*-2-butene leads to *trans*-2-azido-2-butene and *trans*-2-butene leads to *cis*-2-azido-2-butene. The vinyl azides were identified by spectral comparison with authentic materials.[3]

The ionic addition of BrN_3 to cyclohexene gives one adduct by vpc which is presumed to be *trans* on the basis of the results with the butenes and 2-cholestene. Bromine azide adds very slowly to chalcone under the ionic conditions; however acid catalysis allows the reaction to proceed at a useful rate. Further work on these and other systems are currently in progress.

(10) NASA Predoctoral Fellow, 1965–1967.

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Boron–Nitrogen Cage Structures. 1,2,4,5-Tetraaza-3,6-diborine Dimers

Sir:

Considerable interest in polyhedral boron hydrides and carboranes[1] has been evident in recent years. Boron–nitrogen compounds have also received much attention.[2] Although there are reports of bicyclic[3] and tricyclic[4] compounds containing boron and nitrogen, no polyhedral cage structures have been described. We wish now to present evidence for such structures.

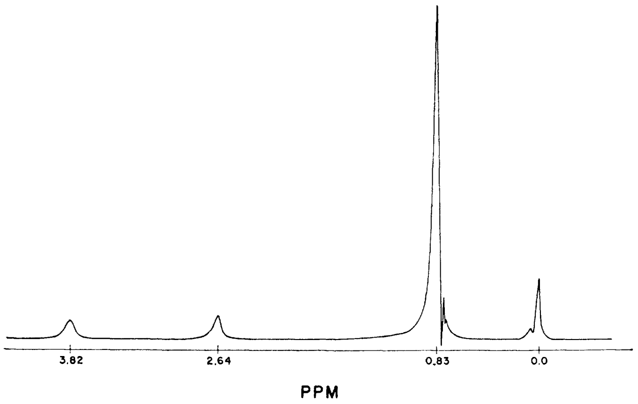
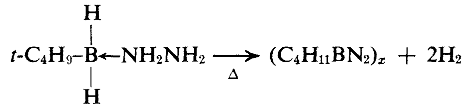


Figure 1.

Thermal decomposition of hydrazine *t*-butylborane at 140° causes evolution of hydrogen in amounts consistent with the following reaction and provides a white solid product, **1**, mp 161–163°. Elemental analysis of **1** is



$$t\text{-}C_4H_9\text{-}\underset{\text{H}}{\overset{\text{H}}{\text{B}}}\leftarrow NH_2NH_2 \xrightarrow[\Delta]{} (C_4H_{11}BN_2)_x + 2H_2$$

compatible with the empirical formula depicted, and infrared shows the presence of N–H bonds and the absence of B–H. Thermal tensimetry and mass spectral data indicate that the material is tetrameric. The proton nuclear magnetic resonance spectrum (Figure 1) shows that there are equal numbers of two types of hydrogen on nitrogen, and that all of the *t*-butyl groups are equivalent. All borons are also equivalent according to the B^{11} spectrum. Hydrolysis of **1** with aqueous acid gives *t*-butylboronic acid and hydrazine, thus demonstrating that no rearrangements occur.

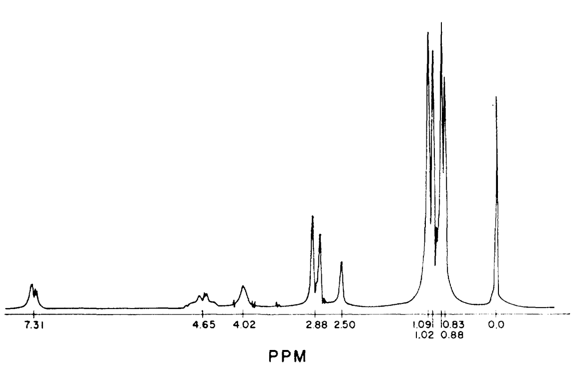
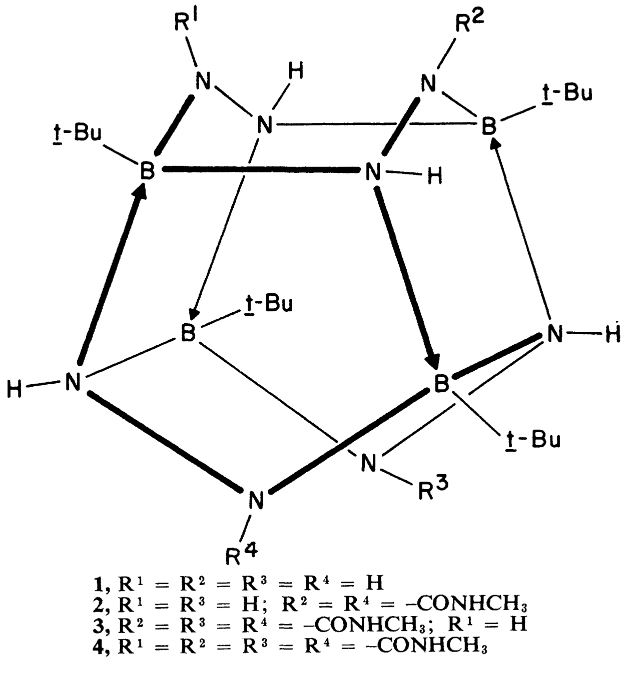


Figure 2.

Treatment of **1** with excess methyl isocyanate under mild conditions provides a new compound, **2**, mp 184–185°, which is composed of 2 equiv of the isocyanate and 1 equiv of compound **1**. The proton nmr spectrum of compound **2** (Figure 2) shows four separate peaks for the *t*-butyl groups and four types of hydrogen on nitrogen. There are at least seven separate H^1 shifts under suitable conditions. Spectra at 40 and 60 Mc demonstrate that the "splitting" of *t*-butyl resonances is the result of differences in chemical shift and not coupling. The structures shown below are proposed; these may be described as two six-membered rings in the boat form bonded to each other through four coordinate covalent nitrogen–boron bonds thus forming four five-membered rings. Only conventional kinds of bonds and bond angles are required in these structures and maximum coordination of boron and nitrogen is achieved. Dreiding models which approximate the



1, $R^1 = R^2 = R^3 = R^4 = H$
2, $R^1 = R^3 = H$; $R^2 = R^4 = \text{-CONHCH}_3$
3, $R^2 = R^3 = R^4 = \text{-CONHCH}_3$; $R^1 = H$
4, $R^1 = R^2 = R^3 = R^4 = \text{-CONHCH}_3$

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(1) Leading references to the chemistry of these systems can be found in M. F. Hawthorne, "The Chemistry of Boron and Its Compounds," E. L. Muetterties, Ed., John Wiley and Sons, Inc., New York, N. Y., 1967, Chapter 5.

(2) A recent survey of boron–nitrogen chemistry is available: H. Steinberg and R. J. Brotherton, "Organoboron Chemistry," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1966.

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angles and distances can be constructed with little difficulty. These structures are dimers of six-membered 1,2,4,5-tetraaza-3,6-diborine rings which are known products of the hydrazinolysis of some alkyl- and aryldiaminoboranes.[5,6]

Nucleophilic reactions of **1** should occur at the more basic and less hindered trigonal nitrogens. Compound **2** is the product of reaction of **1** with 2 equiv of isocyanate; reaction occurs at one trigonal nitrogen in each six-membered ring. All of the *t*-butyl groups of compound **2** should be different; two *t*-butyls are on borons bonded to nitrogens which now carry carbonyl groups, while the other two *t*-butyls are on borons bonded to hydrogen-carrying nitrogens. Only one member of each pair of *t*-butyls on boron has a carbonyl as next-nearest neighbor. Thus, there should be four separate *t*-butyl peaks which we have assigned as shown in Table I.

Table I. Shift from **1** in Cycles per Second

Expected	Obsd	Nearest neighbors[a]	Next-nearest neighbors
Unchanged	0	1 N^3, 2 N^4	$1\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{\vert}{N}\text{-}$
Small	−3	1 N^3, 2 N^4	$2\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{\vert}{N}\text{-}$
Larger	−10	2 N^4, $1\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{\vert}{N}\text{-}$	$\text{No}\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{\vert}{N}\text{-}$
Largest	−16	2 N^4, $1\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{\vert}{N}\text{-}$	$1\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{\vert}{N}\text{-}$

[a] N^3 is three-bonded nitrogen; N^4 four-bonded.

The nitrogen atoms which have attacked isocyanate will be partially double bonded to carbon; this will help shift the proton bonded to neighboring nitrogen (an N^4—already one of the downfield protons in **1**) further downfield. The peaks at 7.31 ppm are assigned to these, and again two peaks are observed because the protons are not identical on a next-nearest neighbor basis. The 2.88-ppm doublet and 4.65-ppm quartet are assigned to the CH_3NHCO– system based on spin–spin decoupling experiments. The spectrum of compound **2** shows two types of N–H (two protons each) which are not greatly changed from **1**. Exchange data on both compounds, as well as the spectra of compounds **3** and **4**, demonstrate that the 2.50-ppm peak is due to hydrogens on trigonal nitrogen and the 4.02-ppm peak to those on tetrahedral nitrogens.

Support for the above interpretation was obtained by the formation of compounds **3** and **4** from prolonged reactions of either **1** or **2** with methyl isocyanate. Compound **3**, mp 232° dec, is substituted at three trigonal nitrogens and compound **4**, mp 302° dec, at all four trigonal positions. The proton spectrum of **3** has three absorptions for *t*-butyl groups in a 1:2:1 ratio as expected from an examination of the structure; only one *t*-butyl absorption is present in the spectrum of compound **4**.

The existence of symmetry in compounds **1** and **4** is revealed by the single *t*-butyl absorption in each case. The presence of at least seven kinds of NH and four kinds of *t*-butyl groups (Figure 2) in the disubstituted compound, **2**, limits the symmetry of **1** to a single axis or plane. The indicated structure of S_4 symmetry is unique in fulfilling these requirements.

The synthesis, chemistry, and X-ray analysis of these new cage compounds are under investigation.

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Indirect Spin Saturation.[1] II. Propagation of Demagnetization

Sir:

The saturation of an nmr absorption, sometimes called "spin saturation" for simplicity, is essentially a process of equalizing the population of different nuclear spin states. It can be achieved by several methods. The most direct way is to apply a strong radiofrequency irradiation at the resonance frequency of the nucleus concerned. The irradiation may sometimes induce other transitions which are related to the one being directly irradiated ("negative" nuclear Overhauser effect).[2] When two kinds of nuclei undergo chemical exchange, the irradiation of one may cause the indirect saturation of the other.[1,3-6] If a third set of nuclei is strongly coupled to the second, their absorption could also be partly or completely saturated.[1,5] We now report that this kind of process, namely indirect spin saturation *via* spin–spin interaction, can "propagate" along an aliphatic chain.

The nonaromatic protons in 2-phenoxyethanol, $C_6H_5OCH_2CH_2OH$, form an AA′BB′X spin system. If *t*-butyl alcohol and 2-phenoxyethanol are dissolved in carbon disulfide, their hydroxyl protons undergo slow chemical exchange. The concentration of the alcohols can be adjusted to bring the signal of the hydroxyl proton of 2-phenoxyethanol arbitrarily close to the signal of the methylene groups (Figure 1A). The rate of proton exchange can be increased by adding a trace of acid (Figure 1C). When the OH group (I) in *t*-butyl alcohol was irradiated, the intensity of the CH_2CH_2OH group (II) in 2-phenoxyethanol decreased (Figure 1B and D).[7]

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