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	$1\text{-}\overset{O}{\overset{\|}{\mathrm{C}}}\text{-}\overset{|}{\mathrm{N}}\text{-}$
Small	−3	1 N^3, 2 N^4	$2\text{-}\overset{O}{\overset{\|}{\mathrm{C}}}\text{-}\overset{|}{\mathrm{N}}\text{-}$
Larger	−10	2 N^4, $1\text{-}\overset{O}{\overset{\|}{\mathrm{C}}}\text{-}\overset{|}{\mathrm{N}}\text{-}$	$\mathrm{No}\text{-}\overset{O}{\overset{\|}{\mathrm{C}}}\text{-}\overset{|}{\mathrm{N}}\text{-}$
Largest	−16	2 N^4, $1\text{-}\overset{O}{\overset{\|}{\mathrm{C}}}\text{-}\overset{|}{\mathrm{N}}\text{-}$	$1\text{-}\overset{O}{\overset{\|}{\mathrm{C}}}\text{-}\overset{|}{\mathrm{N}}\text{-}$

[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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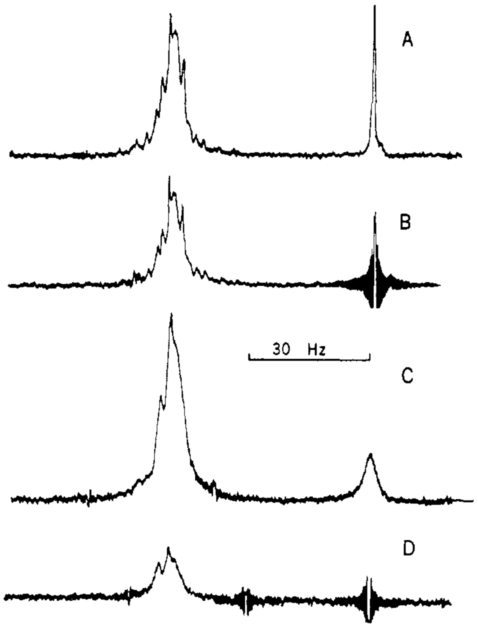

Figure 1. Nmr spectra of the CH_2CH_2OH group in 2-phenoxyethanol (0.53 *M*) and the OH group in *t*-butyl alcohol (0.53 *M*) dissolved in CS_2 at 25° and 60 MHz. The methyl protons in *t*-butyl alcohol were used as locking signal. The phenyl protons of 2-phenoxyethanol are not shown: (A) the spectrum in CS_2; (B) the spectrum in CS_2, with the OH proton in *t*-butyl alcohol irradiated; (C) the spectrum in CS_2 with 4.0×10^{-6} *M* trifluoroacetic acid; (D) same as C, with the OH proton in *t*-butyl alcohol irradiated.

Let us represent the ratio between the intensity of II after and before the irradiation of I by r.[8] If there is no proton exchange, the irradiation of I would not influence the intensity of II ($r = 100\%$). If the indirect spin saturation process is limited to the protons involved in chemical exchange, r would be at the smallest 80%. If there is a transference of demagnetization from the OH proton to the α-CH protons in II due to spin–spin interaction,[1] but the β-CH protons are not affected, r would be at the smallest 40%. However, if the transference of demagnetization can propagate along the chain, we expect that the β-CH protons could be partly or completely "spin saturated." Then r may be brought to a value smaller than 40% under suitable conditions.

For a solution of 0.53 *M* 2-phenoxyethanol and 0.53 *M* *t*-butyl alcohol in carbon disulfide, $r = 73 \pm 2\%$ (Figure 1A and B). For the same concentration of alcohols, r was reduced to $28 \pm 2\%$ when there was 4.0×10^{-6} *M* trifluoroacetic acid in the solvent (Figure 1C and D). This striking result shows that the indirect spin saturation in II is not limited to the OH and the α-CH protons; the demagnetization process is transferred at least partly to the β-CH protons. An intermolecular Overhauser effect is not likely to be operative in the saturation of the nmr signal, because the effect would be quite small in dilute solutions and would hardly increase much on adding a trace of acid. The transference of demagnetization in 2-phenoxyethanol must be caused by spin–spin couplings in the molecule.[1] Since the direct or long-range coupling between the OH and the β-CH protons in II is expected to be very small, the cause of this is likely due to the coupling between the two methylene groups. The mechanism of the indirect spin saturation process can then be described as the following. When I is irradiated at its resonance frequency, the proton exchange between I and the OH proton in II would destroy the magnetization of the latter. The completeness of this process is strongly dependent upon the rate of proton exchange. The coupling between the OH and the α-CH protons, and the coupling between the α-CH and the β-CH protons in II, would transfer the information along the chain. We call this "propagation of demagnetization." The necessary condition for this is the existence of strong coupling (*i.e.*, coupling constants comparable to the chemical shift) between neighboring magnetic nuclei in a compound. In order to clearly observe the phenomenon, however, it is required that one of the coupled nuclei be in chemical exchange at a suitable rate with a nucleus of the same kind at another site. Then, when the latter is irradiated at its resonance frequency, the indirect saturation of the former group can be observed. On the other hand, unambiguous results cannot be obtained if one of a group of closely spaced signals is directly irradiated.

It has been demonstrated that the effectiveness of the transference of demagnetization depends strongly upon the extent of the mixing of spin states.[1] The mechanism of the transference has its origin in the $J_{jk}\mathbf{I}_j \cdot \mathbf{I}_k$ term in the spin Hamiltonian.[9] Therefore, as the OH signal of II moved away from the methylene signals (either upfield by decreasing the concentration of the alcohols or downfield by increasing the concentration), the ratio between J_{BX} and δ_{BX} decreased and r took greater values. Because of the complexity of the present system, it is not possible to obtain a simple compact solution of the density matrix equations for the proton exchange process. A detailed analysis of a simpler system will be discussed elsewhere.[9]

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(8) In order to avoid the change in the intensity of the whole spectrum due to the application of a strong radiofrequency field, the irradiating field (H_2) was always on while taking the spectra. When the OH proton in *t*-butyl alcohol was irradiated, H_2 was set at its resonance frequency. When the irradiation was "off", H_2 was set at 180 Hz apart (upfield) from the previous frequency. The areas of the signals were obtained by electronic integration.

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