

from 2540 cm^{-1} for the terminal B-H stretching to 1870 cm^{-1} for the corresponding B-D stretching is in agreement with the predicted effect of the heavier isotope.¹ The similar shift, from 2470 cm^{-1} for dihexylborane to 1820 cm^{-1} for the corresponding deuterium derivative **2**, supports the assignment of these absorptions to the stretching frequencies for the monomeric species. The monomeric nature of dihexylborane was further established by ^{11}B nmr, which exhibits a doublet centered at 81.3 ppm ($J = 110\text{ Hz}$) downfield relative to $\text{BF}_3 \cdot \text{OEt}_2$.

That dihexylborane exists as an unassociated monomer rather than the THF complex was established by its synthesis in the absence of THF. The reaction of TME with preformed neat dihexyldiborane in the 30:1 molar ratio (TME:B = 16:1) produced slowly (24 hr) at 25° dihexylborane which exhibits the same ir features in the $2600\text{--}2400\text{-}$ and $1600\text{--}1500\text{-cm}^{-1}$ regions as the sample prepared in THF. The molecular weight of the product in TME, determined by osmometry, was 185, in excellent agreement with the theoretical value 182 for the monomer.

Existence in monomeric form appears to be a general phenomenon for dialkylboranes containing bulky alkyl groups. Thus, thexylmonoalkylboranes, derived from hydroboration of bulky olefins with thexylborane,¹² exhibit the ir band attributable to monomeric dialkylboranes at 2470 cm^{-1} in varying intensities. The ratio of intensities of the band at 2470 cm^{-1} to that in the $1600\text{--}1500\text{-cm}^{-1}$ region increases in the following order and seems to correlate with the steric requirements of olefins: isobutylene < cyclopentene < 2-butene < 1-methylcyclopentene < norbornene < 2-methyl-2-butene. These results strongly support the conclusion that the large steric requirements of the two alkyl groups are primarily responsible for the existence of such monomeric dialkylboranes. We are currently exploring the consequences of the monomeric nature of these dialkylboranes.

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Nonequivalent Tin Coupling to Anisochronous Protons

Sir:

We have been interested in the anisochronous behavior exhibited by chemically equivalent protons in

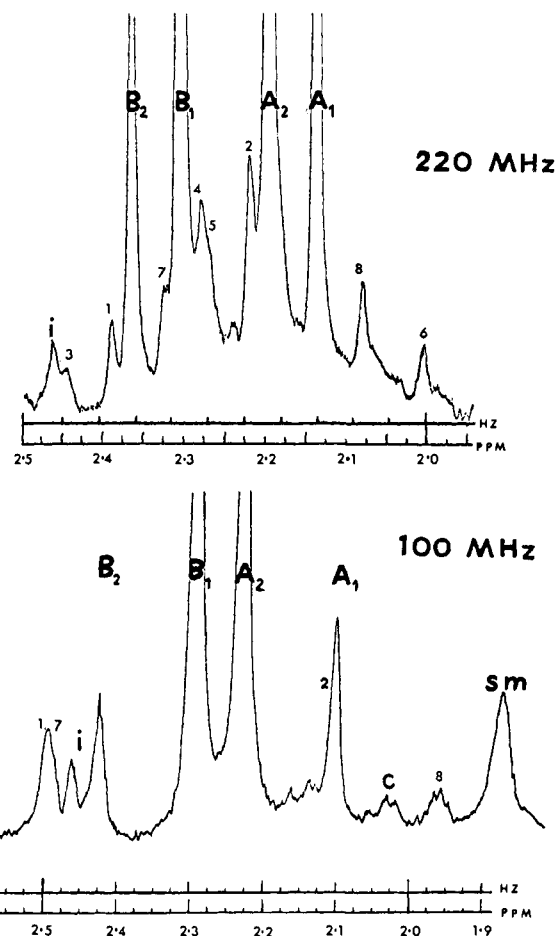


Figure 1. Neophyl methylene proton resonance spectra: sm = starting material, i = impurity, C = downfield ^{13}C satellite of *tert*-butyl protons.

dissymmetric environments. In many cases involving a chiral tin atom, the expected anisochronous behavior fails to occur.^{1,2} However, in certain of these cases we have observed a measurable asymmetry in the tin satellite spectrum of methylene groups bonded to the chiral tin atom. Thus, the upfield satellite component is somewhat broader than the downfield component. A close examination of the nmr spectrum of *tert*-butylphenylneophyltin(IV) iodide has shown that this asymmetry is due to nonequivalent geminal coupling between the tin atom and the anisochronous protons.

The compound was prepared by a method developed elsewhere.³ The analytically pure starting material, *tert*-butyldiphenylneophyltin(IV), was carefully cracked with iodine at 0° . The resulting solution in carbon tetrachloride was eluted through a short alumina column and concentrated by evaporation. Spectra were obtained on a Varian HA-100 using a TMS lock signal and reference, all shifts reported being downfield. The *tert*-butyl methyl peaks were found at 1.12 ppm with $J_{\text{Sn-H}}$ couplings of 87.0 (117) and 91.0 (119). Neophyl methyl groups appeared as a doublet, as in some other dissymmetric tin complexes,^{1,2} at 1.40 and 1.43 ppm with $J_{\text{Sn-H}}$ coupling approximately 3-4 Hz. All phenyl peaks were found in the usual region (7.0-7.3 ppm). Small amounts of impurity plus some

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Table I. Tin Satellite Pmr Spectra of Neophyl Methylene Groups

Line ^a	100-MHz spectra			220-MHz spectra				
	Calcd	Energy, ^b Hz	Obsd	Calcd rel intensity	Calcd	Energy, ^b Hz	Obsd	Calcd rel intensity
1	-23.0		-22.5	1.93	-29.3		-30.0	1.44
2	+14.8		14 to 15	1.46	+6.4		+6.5	1.29
3	-36.0		Not seen	0.07	-42.3		-43.0	0.51
4	+1.8		Obscured	0.54	-6.6		-7	0.71
5	-9.0		Not seen	0.07	-2.7		~ -4	0.51
6	+43.2		Obscured	0.54	+51.6		+53.0	0.71
7	-22.0		-22.5	1.93	-15.7		-16	1.49
8	+32.2		+31.0	1.46	+38.6		+38.0	1.29

^a Labeled according to ref 6. ^b Calculated using the following parameters (relative to $1/2(\nu_A + \nu_B)$): geminal proton-proton, $J_{AB} = -13.1$ Hz, $\Delta\nu_{AB} = 0.151$ ppm; geminal tin-proton, $J_{AX} = 55 \pm 1$ Hz, $J_{BX} = 35 \pm 1$ Hz.

starting material were present; the positions of these were checked at 60 and 220 MHz.⁴

The region of interest, that of the neophyl methylene protons, is shown in Figure 1 for both the 100- and 220-MHz scans. Peak positions are labeled A₁, A₂, B₁, and B₂ for the central AB quartet of the anisochronous methylene protons, for which the tin atom has zero spin. The satellite spectra due to the tin isotopes (117 and 119) of spin one-half are the AB parts of overlapping ABX spectra. To avoid confusion, the average position of the satellite spectra has been labeled, and these positions were used to calculate tin-proton coupling. The relationship between the tin (117 and 119) couplings is simply $J(117) = 0.956 J(119)$. We observe nonequivalent coupling between the tin and the methylene protons (J_{AX} and J_{BX}), with values of 55 and 35 ± 1 Hz, respectively. The ABX line positions have been labeled from 1 to 8 to correspond to the eight possible resonances in the AB part of an ABX spectrum. It is most important to remember that the tin-proton couplings cannot be obtained directly from the spectrum.⁵ Table I contains calculated and observed line positions. The numbering refers directly to the eigenfunctions and eigenvalues obtainable from the literature.⁶ Only the relative signs of J_{AX} and J_{BX} are obtainable from the spectra. All other signs must be inferred from other data. Geminal proton-proton couplings of saturated hydrocarbons are known to be negative, and geminal tin-proton couplings across a carbon atom are known to be positive in methyltin derivatives.⁷

Addition of small amounts of pyridine causes rapid isomerization of the enantiomers of the tin compound.^{1,2} The resulting trivial AA'X spectrum of the neophyl methylene protons yields only the average value of the two geminal tin-proton spin coupling parameters. This is found to be 46 ± 1 Hz which is in good agreement with the expected value from the uncollapsed spectrum.

The large difference in coupling between tin and two chemically equivalent but anisochronous protons poses several questions, not the least of which is the significance of such coupling constants when used to infer hybridization parameters of the tin atom. Clearly, two quite different hybridization parameters

can be obtained for one tin-carbon bond in this present example. Using the collapsed and averaged tin-proton coupling of the compound would yield yet a third. Obviously angle dependence of the coupling constant is important, and the probability of contributions other than Fermi contact cannot be ignored. Both of these factors are tacitly overlooked in correlations of $^2J_{Sn-H}$ and per cent s orbital character. A correlation between $^2J_{Sn-H}$ and J_{Sn-C} has previously indicated that one of them contains contributions other than the Fermi contact term. An extrapolated value of about $+25$ Hz for $^2J_{Sn-H}$ when J_{Sn-C} approaches zero suggests an order of magnitude for these contributions.⁷ It is significant that the difference between the tin-methylene proton couplings in our compound is of the same order.

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A Model for the Mechanism of Action of Coenzyme B₁₂ Dependent Enzymes. Evidence for $\sigma \rightleftharpoons \pi$ Rearrangements in Cobaloximes

Sir:

Most vitamin B₁₂ coenzyme dependent enzymes catalyze a net substrate rearrangement in which hydrogen migrates to an adjacent carbon atom, while an alkyl, acyl, or electronegative group (X) migrates in the opposite direction (**4** → **8**, Scheme I).¹⁻⁵ Numerous proposals have been made concerning the possible mode of migration of the X group,^{1-4,6-12}

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