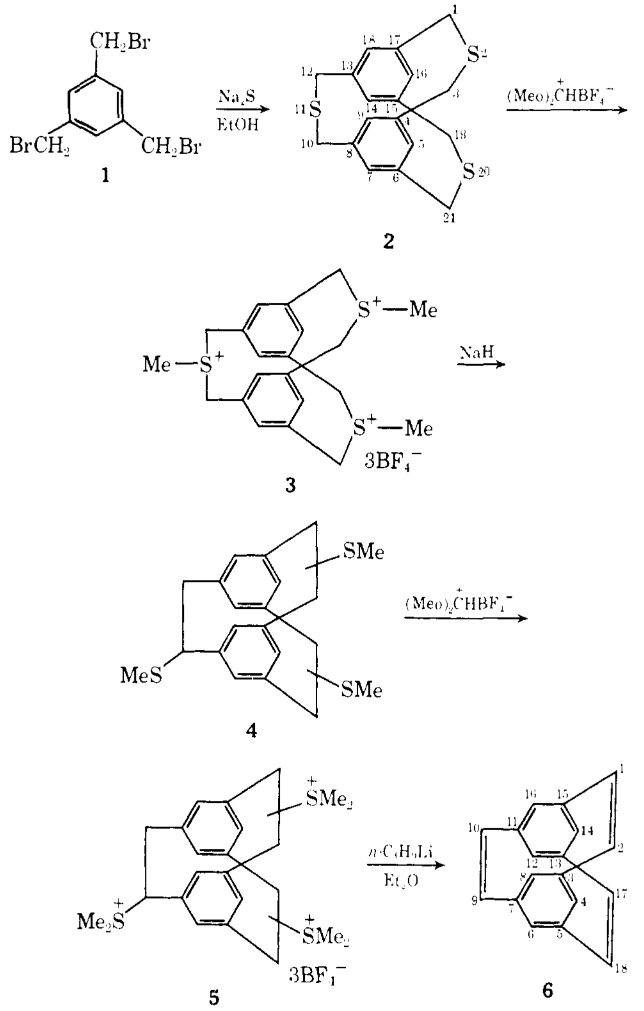
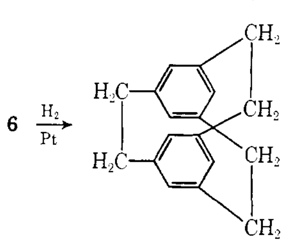
which the two benzene rings are held face to face in very close proximity by the three ethylene bridges, its nmr spectrum seemed at first glance to be singularly unexciting. However, since the assignment of which signal represented the vinyl protons and which represented the aromatic protons could not be made *a priori*, it seemed worthwhile to carry out a deuterium labeling experiment to settle this point.

Reduction of trimethyl 1,3,5-benzenetricarboxylate with lithium aluminum deuteride gave the corresponding deuterated 1,3,5-tris(hydroxymethyl)benzene. This, on treatment with phosphorus tribromide, gave 1,3,5-tris(bromomethyl)benzene, **1**, in which all of the benzylic hydrogens are replaced by deuterium. When the deuterated derivative of **1** was carried through the same reaction sequence as shown above, it gave a sample of **6** in which all of the vinyl hydrogens are replaced by deuterium. Examination of the nmr spectrum of this deuterated derivative of **6** showed a singlet at τ 3.76. Thus, it can be stated unambiguously that the aromatic protons of **6** appear at τ 3.76, whereas the vinyl protons appear as a singlet at τ 2.63. Actually, the upfield shift of the aromatic protons to τ 3.76 is not unexpected, since such upfield shifts of aromatic protons are a common consequence of bringing two benzene rings face to face in a *cis* relationship.[8-10] The more unusual observation is the downfield shift of the vinyl protons. Presumably, this is related to the unusual strain present in the rigid tris-bridged, *cis*-metacyclophane structure of **6**. In this regard the strain present in **6** should exceed that of [2.2]paracyclophane-1,9-diene, a molecule which previously had represented the outstanding example of severe ring-bridged strain.[11]



Since the aromatic protons of **6** probably are deshielded by the bridging vinyl groups, it was of interest to hydrogenate **6**. This occurred readily over a platinum catalyst to give **7** as white crystals, mp 204–206°. The nmr spectrum of **7** shows two singlets at τ 4.27, corresponding to the aromatic protons, and at 7.25, corresponding to the benzylic protons. To the extent that the upfield shift of aromatic protons is a measure of the proximity of two aromatic rings, the two aromatic rings of **7** (Ar-*H*, τ 4.27) are appreciably closer than in [2.2]paracyclophane (Ar-*H*, τ 3.63).[9]



7

In view of the extensive theoretical interest in the long wavelength (302 nm) band of [2.2]paracyclophane,[12-14] it should be noted that both **6** and **7** show a similar band but at even longer wavelength. Thus, the ultraviolet spectrum of **6** in hexane shows absorption maxima at 252 (ϵ 1960) and 325 nm (ϵ 90), while a solution of **7** in hexane has absorption maxima at 258 (ϵ 1340) and 312 nm (ϵ 14).

Further studies of the physical and chemical properties of **6** and **7** are under investigation.

Acknowledgment. We thank the National Science Foundation for their support of this investigation.

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Nuclear Magnetic Resonance Disclosure of the Anomalous Hydrogen in Pentaborane(11)

Sir:

The structure of pentaborane(11) has been generally settled, except for the nature of one particular hydrogen which is believed to be located somewhere in the vicinity of boron atoms 1, 2, and 5. The X-ray data[1] suggest

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(1) (a) L. R. Levine and W. N. Lipscomb, *J. Chem. Phys.*, **21**, 2087 (1953); **22**, 614 (1954); (b) E. B. Moore, Jr., R. E. Dickerson, and W. N. Lipscomb, *ibid.*, **27**, 209 (1957).

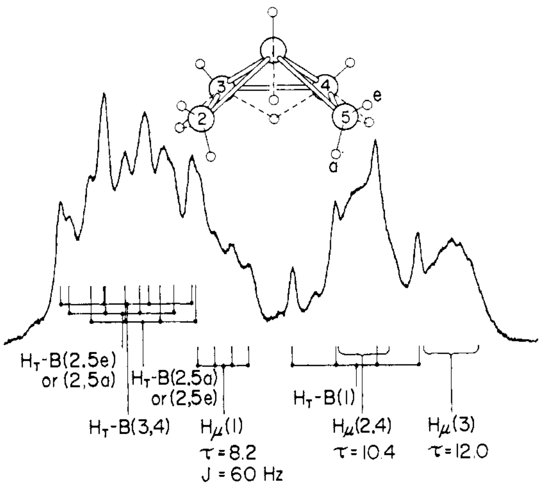

Figure 1. Proton nmr spectrum (220 MHz) and ball and stick model of B_5H_{11}.

that this hydrogen is bonded somewhat strongly to the apex boron atom and also bonded weakly, but perhaps equally, to boron atoms 2 and 5. The boron nmr data[2-4] suggest that the bonding of this hydrogen to any of the mentioned boron atoms is rather weak, for no direct coupling is observed. To add to this perplexity, no direct observation of this anomalous hydrogen in the proton nmr has heretofore been confirmed. This can be attributed to the labyrinth of overlapping resonances at the field strengths previously used, thus not allowing for a transpicuous assignment.[2-5]

From both the 220-MHz proton nmr spectrum (Figure 1) and decoupling experiments at 100 MHz we have been successful in locating the resonance of this anomalous proton. The quartet of resonances located at τ 8.2 can be collapsed by double-resonance experiments affecting the apex boron only. Preferential irradiation of the basal borons in triple-resonance studies sharpens the other assigned bridge resonances at τ 10.4 and 12.0.[6] From these observations and also from the coupling constant, $J_{\mathrm{H-B(1)}} = 60$ Hz, for the resonance at τ 8.2, the position for the anomalous hydrogen can be unambiguously assigned. The apparent stronger coupling of this hydrogen to the apex boron atom than to the basal boron atoms is consistent with the relative bond distances suggested by the X-ray studies.[1] The magnitude of the coupling constant is somewhat higher than is found for bridge hydrogens (usually *ca.* 30–40 Hz) in the boron hydrides and considerably smaller than that found for terminal hydrogens at apically situated borons (usually *ca.* 170–180 Hz). Following this comparison, the moot question of categorizing the nature of this anomalous hydrogen within the context of these previously known bonding types is left up to the catechism of the reader.

The chemical shift of the anomalous hydrogen is unusually low when compared to the other bridge hydrogens in pentaborane(11) or when compared to bridge hydrogens in other boron hydrides. It is also at significantly lower field than other apically bonded terminal hydrogens in other pyramidal boron hydrides.[7] Any simple explanation of this shift is subject to some degree of imputation; however, we would like to suggest that the low-field appearance of this resonance may indicate a higher amount of protonic character than in most bridge (or terminal apical) hydrogens. It is to be noted that in previous structures assigned to pentaborane(11) this hydrogen is depicted in a fashion so as to suggest a localization of two of the six electrons bonding the apex boron to the basal boron framework. By assigning a high measure of protonic character to this hydrogen, the partially relinquished pair of electrons may be better able to stabilize the framework through extensive delocalization analogous to that observed for related pyramidal systems.[8]

Acknowledgment. This work was supported, in part, by a grant from the Office of Naval Research. The HR-220 nmr instrument was available at California Institute of Technology through a grant by the National Science Foundation, No. GP-8540. The HA-100 nmr instrument at CSCLA was available through a grant by the National Science Foundation, No. GP-8347.

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(6) The details of the irradiation experiments will be published at a later date.

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The 220-MHz Proton Resonance Spectra of the Volatile Boron Hydrides

Sir:

We have recently obtained 220-MHz pmr spectra of B_4H_{10}, B_5H_9, B_5H_{11}, B_6H_{10}, B_6H_{12}, B_8H_{12}, B_8H_{18}, n-B_9H_{15}, i-$B_{10}H_{16}$, $^{10}B_4H_{10}$, $^{11}B_4H_{10}$, $^{11}B_5H_{11}$, and n-$B_9H_{10}D_5$. New features are resolved at this frequency which greatly enhance the value of pmr for structural studies in the boron hydride field. In contrast to spectra observed at lower fields, the 220-MHz spectra can, in favorable cases, resolve bridge regions into separated peaks corresponding to structurally nonequivalent bridging protons. For example, in Figure 1 the bridge region of $^{11}B_5H_{11}$ is resolved into two peaks of ratio 2:1. Assignment of the bridging protons is confirmed not only by the relative intensity of the peaks, but also by the appearance of fine structure on the peak at highest field, corresponding to splitting into a septet ($J = 36$ cps) of relative intensity 1:2:3:4:3:2:1 by the 3,4 boron atoms.[1] This ^{11}B–^{1}H–^{11}B bridge coupling is confirmed in the 70.58-MHz spectrum[2] (Figure 2) of $^{11}B_5H_{11}$, where a splitting of 36 cps is clearly observed on the doublet arising from the 3,4 boron atoms. Furthermore, the "unique terminal" proton is clearly visible,

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(1) All boron cage nomenclature and numbering orders are those set forth under the new rules which appeared in *Inorg. Chem.*, **7**, 1945 (1968).

(2) The ^{11}B spectra of the above compounds were obtained with an experimental 70.58-MHz probe built by Mr. A. O. Clouse of this laboratory.