for H_3PBH_3 is significantly larger than the 1.67 kcal/mol value for CH_3SiH_3 although the P–B bond distance is 1.937 Å compared to the 1.863 Å distance found for the C–Si bond for these isoelectronic molecules. However, this increase of 0.8 kcal/molc an be rationalized by an examination of the nonbonded distances between the boron and phosphorus hydrogens. Because of the significant differences in the ∠HBP and ∠HCSi angles, the H···H distances of closest approach decrease by 0.5 Å for the phosphine-borane. Thus a significant increase in the contribution from the "hydrogen repulsive potential"[28] can be attributed to the shorter H···H distance which results in the marked increase in barrier height. Further *ab initio* calculations with better structural parameters should be carried out in order to provide better insight into the origin of barriers for single bonds.

Acknowledgment. The authors gratefully acknowledge the financial support of this work by the National Science Foundation by Grant GP-33780.

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Application of Line Narrowing to ^{11}B Nuclear Magnetic Resonance Spectra

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Abstract: The exponential line-narrowing technique is applied to ^{11}B nmr spectra, and previously unobservable splittings are resolved under the normally broad resonances. The line-narrowed 70.6-MHz ^{11}B nmr spectra of B_4H_{10}, B_5H_9, B_5D_9, B_5H_{11}, B_6H_{12}, $B_{10}H_{14}$, and n-B_9H_{15} are discussed in relation to their structures as liquids or in solution.

Recently the partially relaxed Fourier transform (PRFT) technique has been applied to ^{11}B nmr, and structural data not normally available have been obtained.[1] The technique reveals the previously unobservable ^{11}B 1:2:1 triplet, hidden by accidental overlap of other resonances, due to the $-BH_2$ group of n-B_9H_{15}. Certain problems are not resolved by this technique, however. For example, line widths of 60–100 Hz are common, and, as a result, one usually observes only splitting by the directly bonded terminal hydrogens.[2] Measurement of ^{11}B and ^{10}B relaxation times in B_5H_9 have shown that this broadening is probably caused by unresolved fine structure and not by quadrupolar relaxation.[3] Recently the ^{11}B(apex)–^{11}B(base) coupling constant in B_5H_9 was reported for the first time and found to be 19.4 Hz.[4] Splittings of this magnitude could easily overlap with envelopes of bridge hydrogen–boron couplings ($J_{^{11}B-^{1}H_{bridge}}$) to give line widths of 60–100 Hz. The research described here applies a new Fourier transform (FT) nmr technique which is especially applicable to the unresolved fine structure causing the broad lines in ^{11}B nmr spectra.

It has been known for some time that the free induction decay signal following a 90° pulse can be multiplied by an exponential function prior to the transform to increase the ratio of signal to noise at the expense of an artifically broadened line. Similarly, if the decay is retarded by multiplication of the raw signal by a function exponential in time, narrower lines are produced in the transform. This enhanced resolution is accompanied by a substantial reduction in signal/noise,[5] which is probably the reason why the technique has not been seriously applied before now. An example of the data manipulation is shown in Figure 1 for B_5H_9. The apodization function shown in the figure has been discussed elsewhere[6] and needs no further explanation. It should be noted that the data are collected in the usual manner, and the exponential multiplication is a mathematical operation performed by the computer on raw data.

We have applied this technique to a number of boron hydrides and have resolved ^{11}B–^{11}B couplings and ^{11}B–$^{1}H_{bridge}$ couplings under the broad ^{11}B resonances. The line-narrowed 70.6-MHz ^{11}B nmr spectra of B_4H_{10}, B_5H_9, B_5D_9, B_5H_{11}, B_6H_{12}, $B_{10}H_{14}$, and n-B_9H_{15} are discussed.

Experimental Section

The compounds studied in this experiment were readily available from laboratory samples. The spectra were obtained at 16° on a Varian Associates HR-220 spectrometer operating at 51.7 kG and using a "home-built" pulse apparatus operating at 70.6 MHz. A Nicolet 1080 computer was used to process the data, using Nicolet supplied software.

Results and Discussion

B_5H_9, Pentaborane(9). The normal 70.6-MHz ^{11}B nmr spectrum of B_5H_9 is shown in Figure 2. The

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(1) A. Allerhand, A. O. Clouse, R. R. Rietz, T. Roseberry, and R. Schaeffer, *J. Amer. Chem. Soc.*, **94**, 2445 (1972).

(2) R. Schaeffer, "Progress in Boron Chemistry," Vol. 1, H. Steinberg and A. L. McCloskey, Ed., Macmillan, New York, N. Y., 1964, p 422; (b) G. R. Eaton and W. N. Lipscomb, "NMR Studies of Boron Hydrides and Related Compounds," W. A. Benjamin, New York, N. Y., 1969.

(3) A. Allerhand, J. D. Odom, and R. E. Moll, *J. Chem. Phys.*, **50**, 5037 (1969).

(4) J. D. Odom, P. D. Ellis, and H. C. Walsh, *J. Amer. Chem. Soc.*, **93**, 3529 (1971).

(5) (a) R. R. Ernst, *Advan. Magn. Resonance*, **2**, 1 (1966); (b) T. C. Farrar and E. D. Becker, "Pulse and Fourier Transform NMR," Academic Press, New York, N. Y., 1971, p 75.

(6) Reference 5b, p 76.

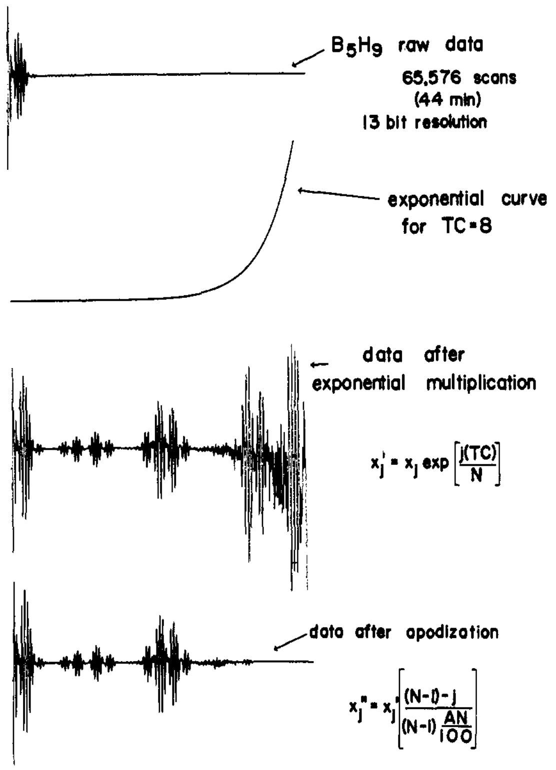

Figure 1. B_5H_9 data manipulation.

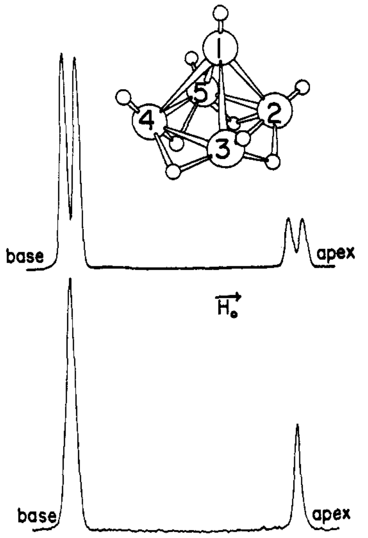

Figure 2. Structure and 70.6-MHz ^{11}B nmr spectra of B_5H_9 (top) and B_5D_9 (bottom).

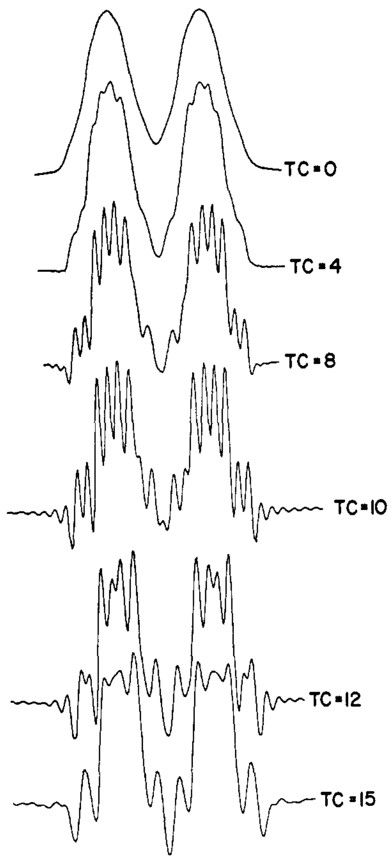

Figure 3. B_5H_9 base blowups, with apodization percentages varying from AN = 30 for TC = 4 to AN = 60 for TC = 15.

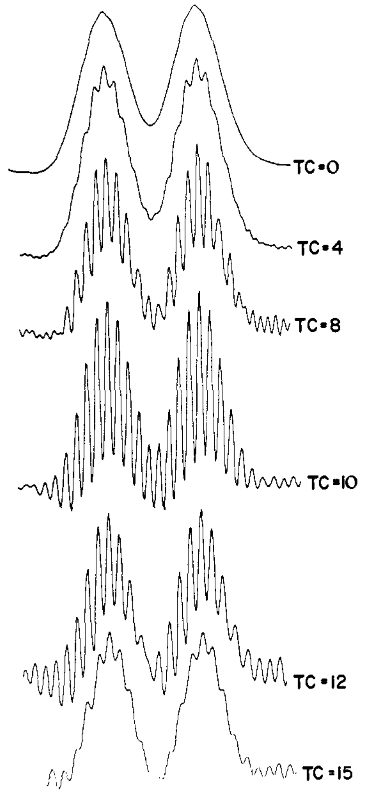

Figure 4. B_5H_9 apex blowups, with apodization percentages varying from AN = 30 for TC = 4 to AN = 60 for TC = 15.

only information obtained is that there are two distinct boron environments with relative intensities 4:1, each coupled to one terminal proton. There is no noticeable coupling between the different borons, nor is there any resolved coupling from the bridge protons. There is, however, a large degree of breadth of the resonances from these unresolved splittings. Figures 3 and 4 show the resolution of this fine structure as the exponential function is employed. As the exponent (TC) of the function increases, the fine structure develops, but the signal to noise ratio decreases drastically as the noise is multiplied along with the real signal. In this case when the time constant (TC) is ten, maximum resolution is obtained, but the signal to noise ratio is reduced from 1000/1 to 50/1. As

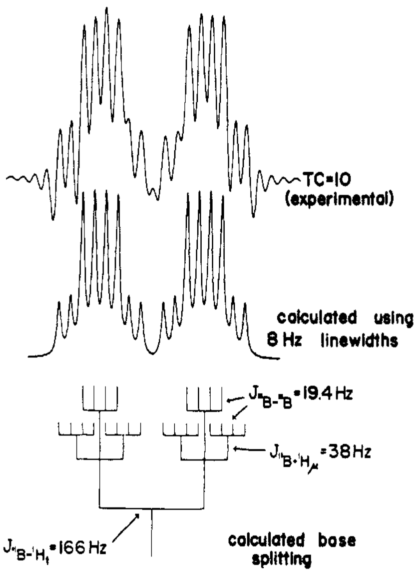

Figure 5. B_5H_9 base blowup.

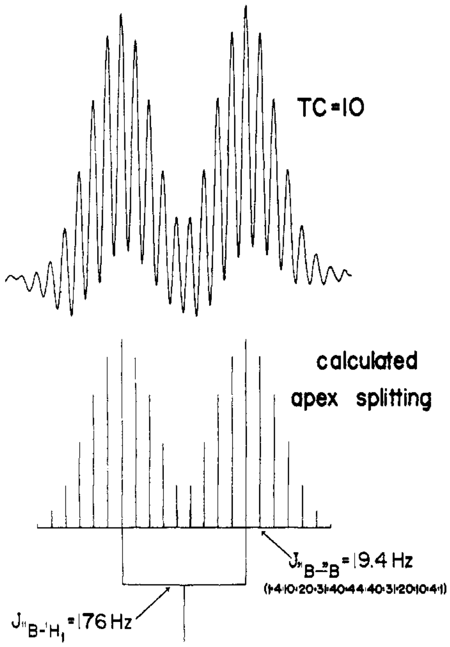

Figure 6. B_5H_9 apex blowup.

the exponent is made larger, the apodization (see Figure 1) must encompass a greater percentage of the data, and the part of the free induction decay which corresponds to the fine structure observed also becomes apodized; resolution again decreases. Thus two major factors must be considered: (1) the amount of signal to noise that one is willing or able to sacrifice and (2) the degree of apodization necessary to restore the overall exponential form of the free induction decay. The first of these is partially overcome since ^{11}B nuclei have very short relaxation times. Thus pulse repetition rates of 0.1 sec can very often be used and a large number of scans can be obtained in a relatively short period of time. The second factor varies for different exponents in the multiplication function and must be minimized separately for each multiplication operation with a new exponent.

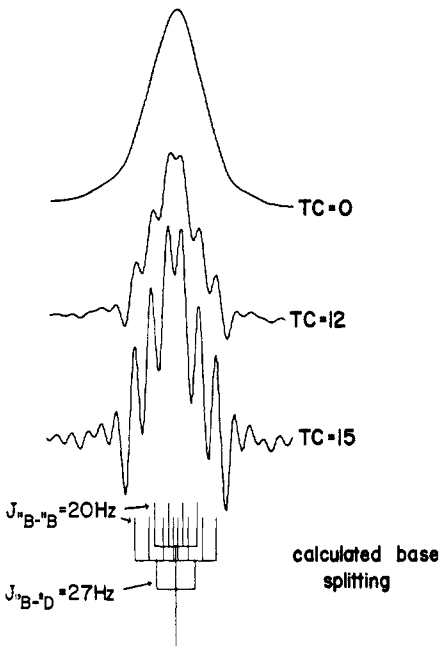

Figure 7. B_5D_9 base blowups, with apodization percentage AN = 55 for both TC = 12 and TC = 15.

The fine structure on the base resonance of B_5H_9 can be explained as a doublet of triplets of quartets (Figure 5). The large doublet is caused by coupling to a terminal hydrogen with a coupling constant of 166 Hz. The $^{11}B-H_{\mu}$(bridge) coupling of 39 Hz is responsible for the triplet fine structure, while the ^{11}B(base)–^{11}B(apex) coupling constant of 20 Hz furnishes the quartet structure. The calculated spectrum shown in Figure 5 was reconstructed using the previously reported ^{11}B(base)–^{11}B(apex) coupling constant of 19.4 Hz,[4] the ^{11}B(base)–H_t value of 166 Hz, and the estimated ^{11}B(base)–$^{1}H_{\mu}$ value of 38 Hz obtained from the bridge region of the 220-MHz ^1H nmr spectrum of pentaborane(9). This calculated spectrum shows a remarkable resemblance to the observed line-narrowed spectrum. The calculated apex pattern in Figure 6 also shows very good agreement with the observed spectrum. The apex boron is first coupled to the terminal proton with a coupling constant of 176 Hz and yields a doublet. Coupling with four equivalent basal borons (^{11}B = $^3/_2$ in 80% abundance) yields a 13 line pattern with relative intensities 1:4:10:20:31:40:44:40:31:20:10:4:1 and a coupling constant of 20 Hz. No noticeable contribution from $^{11}B-^{10}B$ coupling was encountered in either the base or the apex regions, but with the resolution of about 10 Hz which we obtained, there could be smaller couplings hidden (calcd $J_{^{11}B-^{10}B} \approx 6.5$ Hz).

B_5D_9, Pentaborane(9)-d_9. Theoretically the $^{11}B-^{1}H$ coupling is 6.514 times as large as the $^{11}B-^{2}D$ coupling;[7] thus the normal 70.6-MHz ^{11}B nmr spectrum of B_5D_9 (Figure 2) contains two broad singlets of relative intensity 4:1. Application of the line-narrowing technique reveals fine structure on the base resonance (Figure 7). The resolvable fine structure can be explained as resulting from splitting into a triplet of quartets. The $^{11}B-^{2}D_{\mu}$ coupling is now too small to be resolved and contributes to line broadening only.

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(7) F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy," Academic Press, New York, N. Y., 1969, p 90.

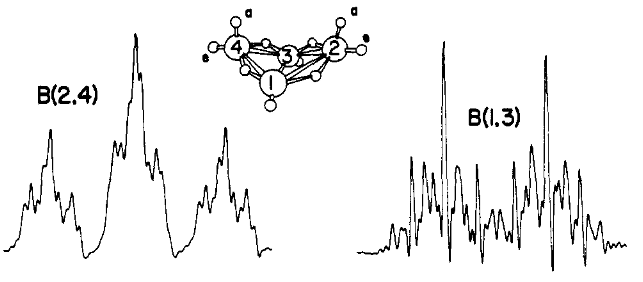

Figure 8. Blowup of line-narrowed FT ^{11}B nmr spectrum of $^{11}B_4H_{10}$.

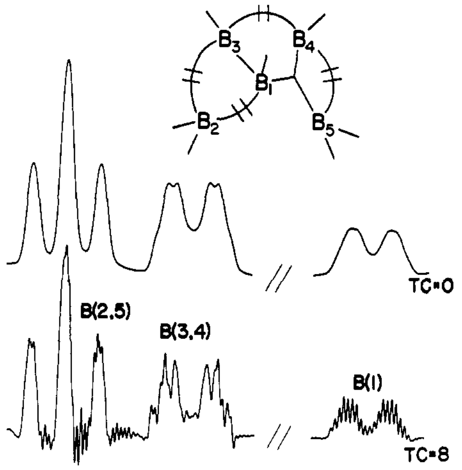

Figure 9. Normal and line-narrowed FT ^{11}B nmr spectra of $^{11}B_5H_{11}$.

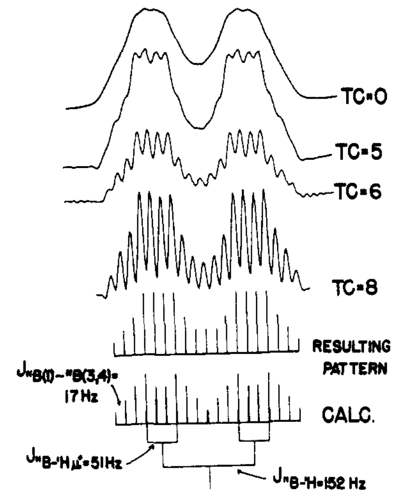

Figure 10. Blowup of the B(1) resonance of line-narrowed $^{11}B_5H_{11}$ spectra, with apodization percentage AN = 30 for TC = 8.

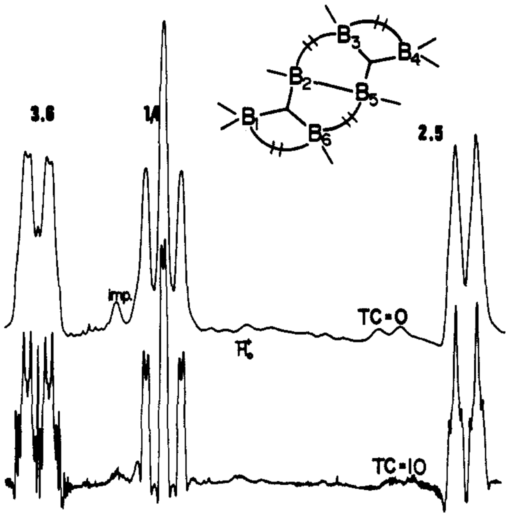

Figure 11. Normal and line-narrowed 70.6-MHz ^{11}B nmr spectra of B_6H_{12}.

The triplet results from terminal deuterium (I = 1) coupling to each basal boron, and the $^{11}B-^{11}B$ coupling constant remains approximately 20 Hz and is responsible for the quartet structure. The $^{11}B-^2D$ coupling constant observed is 27 Hz, which is in good agreement with a calculated ($J_{^{11}B-^2D} = J_{^{11}B-^1H}/6.514$) value of 25 Hz.

B_4H_{10}, Tetraborane(10). Analysis of the ^{11}B nmr of tetraborane(10) has proved to be a formidable problem.[8] The low-field resonance has been explained as a triplet of triplets, arising from the $-BH_2$ group coupled to the two bridge protons bonded to it. The upfield doublet exhibits fine structure which cannot be explained on a first-order basis. From the line-narrowed spectrum of 98% ^{11}B-enriched $^{11}B_4H_{10}$ shown in Figure 8, the complexity of this system is readily apparent, and even the low-field triplet exhibits fine structure which is uninterpretable at this time. It is felt that future studies of the $^{11}B_4H_{10}$ system with the line-narrowing technique will prove rewarding, but the problem is by no means trivial and will require an extensive study.

B_5H_{11}, Pentaborane(11). The 220-MHz pmr spectrum of $^{11}B_5H_{11}$ was recently reported and the "unique terminal" proton on the 1 position observed.[9,10] The normal ^{11}B nmr at 70.6 MHz shows only a doublet for the 1 boron, however (Figure 9). The 2,5 boron resonance indeed shows triplet structure for these $-BH_2$ groups, and the 3,4 resonance reveals some fine structure. The line-narrowed spectrum, also shown in Figure 9, contains much more information. The 3,4 resonance is now a very complex pattern and an exact interpretation of this pattern cannot be made at this time. However, a doublet of triplets of quartets can yield a pattern similar to that of the 3,4 resonance. The 1 boron also shows much more fine structure in the line-narrowed spectrum (Figure 10), and the coupling of the "unique terminal" hydrogen (μ^*) can now be observed. The overall pattern and intensities of the 1 resonance can be justified by a doublet ($J_{^{11}B-^1H_t}$ = 152 Hz) of doublets ($J_{^{11}B-H_{\mu^*}}$ = 51 Hz) of septets ($J_{^{11}B(1)-^{11}B(3,4)}$ = 17 Hz). There is probably some $^{11}B-^{11}B$ coupling between the 1 boron and the 2,5 borons, but it must be less than our resolution limit of approximately 10 Hz.

B_6H_{12}, Hexaborane(12). For most of the boron hydrides, the final structural confirmations have come from X-ray crystallographic studies. However, attempts to crystallize hexaborane(12) have proved unsuccessful.[10] Also an electron diffraction study on

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(8) R. C. Hopkins, J. D. Baldeschwieler, R. Schaeffer, F. N. Tebbe, and A. Norman, *J. Chem. Phys.*, 43, 975 (1965).

(9) R. R. Rietz, R. Schaeffer, and L. G. Sneddon, *J. Amer. Chem. Soc.*, 92, 3514 (1970); T. Onak and J. B. Leach, *ibid.*, 92, 3513 (1970).

(10) J. B. Leach, T. Onak, J. Spielman, R. R. Rietz, R. Schaeffer, and L. G. Sneddon, *Inorg. Chem.*, 9, 2170 (1970).

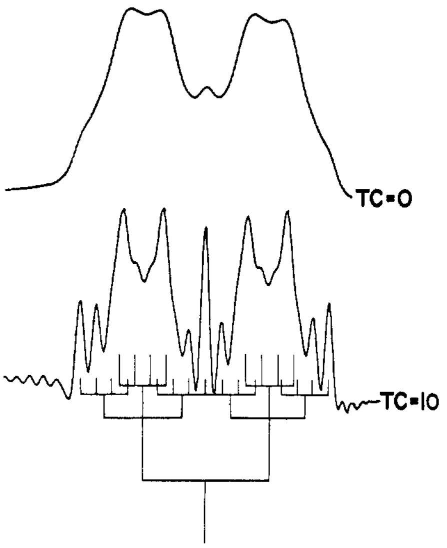

Figure 12. Blowup of B(3,6) resonance of line-narrowed B_6H_{12} spectra, with apodization percentage AN = 35 when TC = 10.

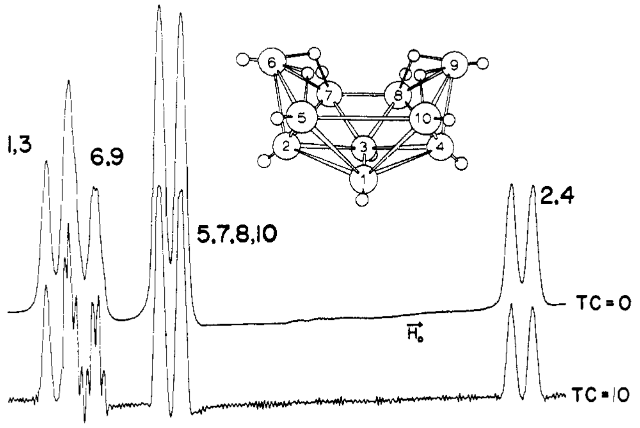

Figure 13. Normal and line-narrowed FT ^{11}B nmr spectra of $^{11}B_{10}H_{14}$.

gaseous B_6H_{12} failed to distinguish between the two 4212 formulations.[11] The ^{11}B and ^1H nmr studies[10,12] support the 4212 formulation shown in Figure 11. Also shown in Figure 11 are the normal and line-narrowed ^{11}B nmr spectra of B_6H_{12}. The normal spectrum shows a doublet, triplet, and another doublet at higher field, of relative intensities 2:2:2. Although this spectrum yields considerable structural information, the line-narrowed spectrum confirms the proposed structure with greater reliability than previously obtainable. The 1,4 resonance reveals no resolvable ^{11}B–^{11}B coupling but does exhibit doublet fine structures due to ^{11}B–$^1H_\mu$ coupling of 28 Hz. The 3,6 resonance in the line-narrowed spectrum shows a complex pattern which fits exactly with that of a doublet of triplets of quartets (Figure 12). The doublet undoubtedly evolves from ^{11}B–^1H_t coupling of 160 Hz. Although the two bridge protons bonded to the 3(6) position are not equivalent, they appear to couple to the 3(6) boron with very similar coupling constants. Thus with our resolution, we observe the triplet fine structure with spacings of approximately

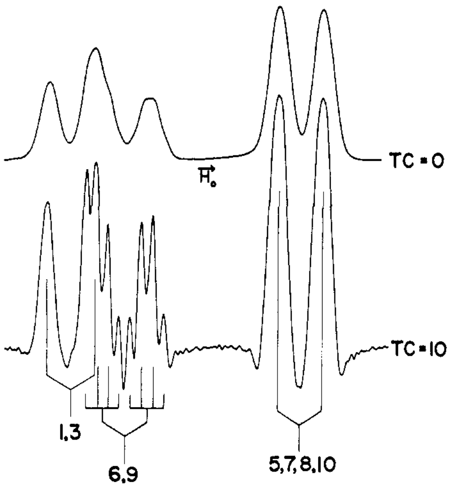

Figure 14. $^{11}B_{10}H_{14}$ fine structure gained through exponential filtering.

48 Hz. This value could be an average of the two slightly different coupling constants. The quartet fine structure on the 3,6 resonance probably involves ^{11}B–^{11}B coupling of 20 Hz. The B(5) could couple to the B(3), while B(2) couples to B(6). The overall effect of this coupling would be quartet fine structure (each resonance coupled to one ^{11}B (I = $^3/_2$)) on the 3,6 and 2,5 resonances. The 2,5 resonance exhibits fine structure which is basically consistent with a doublet ($J_{^{11}B-^1H_t}$) of doublets ($J_{^{11}B-^1H_\mu}$) of quartets ($J_{^{11}B-^{11}B}$); however, unresolved coupling (possibly to the 1(4) boron) limits the accuracy of the interpretation of the fine structure on this resonance.

A PRFT ^{11}B nmr study shows a first-order dependence of the amplitude of each of the three resonances on τ. The T_1 values obtained are $T_1(3,6)$ = 33.4 ± 2.0, $T_1(1,4)$ = 18.2 ± 0.6, and $T_1(2,5)$ = 50.0 ± 2.0 msec. This linear dependence diminishes the possibility of the other 4212 formulation being the correct structure since it requires accidental coincidence of both chemical shifts and T_1 values of two borons in significantly different environments.[12]

$B_{10}H_{14}$, Decaborane(14). The structure of decaborane(14) and the ^{11}B nmr of the 98% ^{11}B-enriched compound are shown in Figure 13. The normal ^{11}B nmr consists of two overlapping doublets (1,3 and 6,9), a larger doublet slightly upfield (5,7,8,10), and another doublet (2,4) at much higher field. The relative intensities of these doublets are 2:2:4:2, which are consistent with the structural assignments. The line-narrowed spectrum yields resolvable fine structure only for the 6,9 resonance. A blowup of this region of the spectrum can be seen in Figure 14. The quartet-like fine structure observed on the 6,9 resonance is undoubtedly a combination of complex coupling patterns involving many nuclei.[13] The interpretation of which nuclei are involved is not possible with any degree of accuracy since nothing is known about the magnitudes of the ^{11}B–$^1H_\mu$ couplings or

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(11) R. Foster, unpublished results.

(12) D. F. Gaines and R. Schaeffer, *Inorg. Chem.*, 3, 438 (1964).

(13) We have also noted this quartet-like pattern in *n*-B_9H_{15} and *nido*-5,6-$B_8C_2H_{12}$, but have been unable to ascertain the coupling involved. We do note that the nuclei involved, *i.e.*, the 6,9 positions in $B_{10}H_{14}$, the 9 position in *nido*-5,6-$B_8C_2H_{12}$, and the 5,8 (6,7) positions in *n*-B_9H_{15}, all contain nearly the same spacial arrangement of atoms, *i.e.*, an edge boron above an apex boron and between two bridge hydrogens.

the ^{11}B–^{11}B couplings in this molecule. Interpretation of this pattern would best be reserved until more of the parameters can be established. It is possible that a combination study involving proton decoupling and line narrowing could at least furnish information concerning the ^{11}B–^{11}B coupling constants. It is hoped that such a study can be undertaken in the near future.

n-B$_9$H$_{15}$, n-Nonaborane(15). The structure and ^{11}B nmr of n-B$_9$H$_{15}$ are shown in Figure 15. The complexity of the spectrum can be attributed to accidental overlap of B(5,6,7,8) and B(3) resonances. The line-narrowed spectrum of this region yields little interpretable data due to its complexity. The PRFT method[1] does, however, separate the B(3) triplet resonance from the rest of the overlapped resonances and, in this case, seems superior to the line-narrowing technique. But the B(4,9) resonance, which does not overlap with other resonances, does show a doublet fine structure ($J_{^{11}B-^{1}H_{\mu}}$) in the line-narrowed spectrum. Thus even in the large cage molecules like n-B$_9$H$_{15}$, there is still information to be gained through the use of this new technique.

The line-narrowing technique has been presented here for ^{11}B nmr only; however, the technique is not restricted to this one nucleus. It is thus felt that research in many other areas can benefit from the use of this line-narrowing technique, and it is hoped that there will be more applications in the near future.

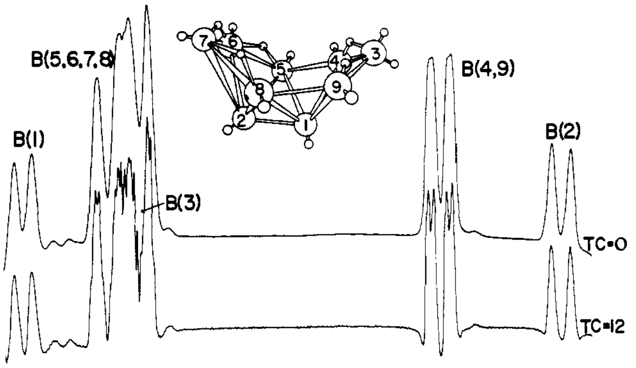

Figure 15. Normal and line-narrowed FT ^{11}B nmr spectra of n-B$_9$H$_{15}$.

Acknowledgments. This research was supported by Grant GP-24266X from the National Science Foundation. We thank Professor Adam Allerhand for his suggestion of this approach and for supplying the initial instrumentation used for line narrowing, supported by Grants GP-7922 and GP-17966 from the National Science Foundation.

Stabilization of 1,3-Dipoles by π-Complex Formation. Iron Carbonyl Derivatives of Thio- and Selenoketocarbenes

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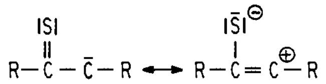
Received November 1, 1972

Abstract: *Trihapto*-1,2-diphenylthioketocarbenehexacarbonyldiiron, the first transition metal derivative of a 1,3-dipolar species, was obtained by the reaction of 1,4-dimethylnickel(II) bis(*cis*-stilbenedithiolate) or of diphenyl-1,2,3-thiadiazole with iron carbonyls on heating and light irradiation. The corresponding selenoketocarbene complex was prepared analogously from diphenyl-1,2,3-selenodiazole. The same method was used to synthesize the hexacarbonyldiiron complex of unsubstituted thioketocarbene. The complexed 1,3-dipoles form σ and π bonds with the iron carbonyl moieties and exhibit low residual reactivity, undergoing cycloaddition reactions with alkynes only on thermolysis. Ketocarbenes could not be stabilized analogously.

Although a large body of information on the reactivity and selectivity of "1,3-dipoles" is available,[2] the evidence for their existence is frequently indirect. Recently[3] we have reported on the synthesis and structure of *trihapto*-1,2-diphenylthioketocarbenehexacarbonyldiiron, the first transition metal complex of a thioketocarbene. Thioketocarbenes, whose ground state is described by the limiting valence-bond structures **1** and **2**, were first shown to be intermediates in the decomposition of 1,2,3-thiadiazoles[4] and have also been postulated to occur in certain reactions of chelates of 1,2-*cis*-ethylenedithiolates.[3] In the present paper we report the results of more extensive studies on complexes of thioketocarbenes, the synthesis of analogous



$$\mathrm{R{-}\overset{\overset{|\underline{S}|}{\|}}{C}{-}\bar{C}{-}R} \longleftrightarrow \mathrm{R{-}\overset{\overset{|\bar{\underline{S}}|^{\ominus}}{|}}{C}{=}\overset{\oplus}{C}{-}R}$$

$\underline{1}$ $\underline{2}$

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[1] On leave of absence from Max Planck Institut für Kohlenforschung, Division of Radiation Chemistry, Mülheim/Ruhr, Germany.

[2] R. Huisgen, *Angew. Chem.*, **75**, 604, 741 (1963), and references cited therein.

[3] G. N. Schrauzer, H. N. Rabinowitz, J. K. Frank, and I. C. Paul, *J. Amer. Chem. Soc.*, **92**, 212 (1970).

[4] W. Kirmse and L. Horner, *Justus Liebigs Ann. Chem.*, **614**, 4 (1958).