Table I. The 80.5 MHz ^{11}B NMR Spectra of $B_{10}H_{10}{}^{2-}$ Derivatives[a]

Compd	Rel intensity	Chemical shifts, δ^{b} (J_{B-H}, Hz)
$(CH_3)_4N[1\text{-}B_{10}H_9N_2]$	1:1:4:4	−22.0 (150), +13.4, +17.2 (130), +25.8 (140)
$1,6\text{-}N_2B_{10}H_8N(CH_3)_3$	1:1:1:2:2:2:1	−9.0 (140), +10.8, +17.9, +20.5 (140), +27.3 (120), +29.6 (120), +33.9 (140)
$[(CH_3)_4N_2][1\text{-}(1\text{-}Br\text{-}4N_2\text{-}C_6H_4)B_{10}Cl_9]$	1:9	−1.6, +8.5[e]
$(CH_3)_4N[1\text{-}C_5H_5NB_{10}H_9]$	1:1:8	−0.5, +2.5 (120), +31.3[c]
$1,10\text{-}N_2B_{10}H_8\text{-}NC_5H_5$	1:1:4:4	−25.6, +9.2, +17.2 (130), +22.4 (140)
$1,10\text{-}(CH_3)_2\text{-}SB_{10}H_8N_2$	1:1:4:4	−19.5, +4.1, +18.4 (130), +23.0 (130)
$1,10\text{-}N_2B_{10}H_8N(CH_3)_3$	1:1:4:4	−32.2, +8.4, +19.4 (130), +25.4 (130)
$CsB_{10}Cl_9N_2$[d]	1:1:8	−12.0, +2.4, +7.2[e]

[a] Obtained in CH_3CN solution except where noted. [b] Relative to $BF_3 \cdot O(C_2H_5)_2$. [c] Overlapping doublets. [d] Obtained in $(CH_3)_2SO$ solution. [e] Broad overlapping singlets.

1.3 g (36%) of $[(CH_3)_4N]_2[1\text{-}Br\text{-}4\text{-}N_2C_6H_4)B_{10}Cl_9]$. Anal. Calcd for $[(CH_3)_4N]_2[BrC_6H_4N_2B_{10}Cl_9]$: C, 22.14; H, 3.73; B, 14.23; N, 7.37; Cl, 42.01; Br, 10.52. Found: C, 22.60; H, 3.82; B, 13.69; N, 7.37; Cl, 41.95; Br, 10.69. The infrared spectrum contained peaks at 1640 (w), 1290 (w), 1150 (m), 1000 (s), 950 (s), 875 (m), 840 (m), and 715 (m) cm^{-1}.

The remainder of the ethanol from the filtrate was removed to yield 1.1 g of $(CH_3)_4NB_{10}H_xCl_{9-x}N_2$ which exhibited both a small peak at 2500 cm^{-1} due to B–H and a strong absorption at 2250 cm^{-1} due to the diazonium function. The mixture was chromatographed on a silica gel column to obtain fractions in which the 2500 cm^{-1} peak in the infrared spectrum was no longer apparent and then passed through a sodium form cation exchange column. Excess CsCl was added to the aqueous solution to obtain a low yield of the apparently impure mixed salt $Cs[1\text{-}N_2B_{10}Cl_9] \cdot CsCl$. Anal. Calcd for $CsB_{10}Cl_9N_2 \cdot CsCl$: Cs, 35.13; Cl, 46.87; B, 14.29; N, 3.70. Found: Cs, 33.48; Cl, 49.20; B, 12.58; N, 5.05; H, 0.0; C, 0.0. The infrared spectrum contained peaks at 2250 (s), 1140 (s), 1010 (s), and 825 (s) cm^{-1}.

Solutions of $[(CH_3)_4N]_2[1\text{-}(1\text{-}Br\text{-}4\text{-}N_2C_6H_4)B_{10}Cl_9]$ in CH_3CN were protonated changing the color from yellow to the dark red characteristic of the protonated dye. These solutions were refluxed over periods up to several weeks and only trace amounts of the diazonium function formed.

$(CH_3)_4N[1\text{-}C_5H_5NB_{10}H_9]$. In a 100 ml flask fitted with a reflux condenser and N_2 inlet were placed 3.1 g (14 mmol) of $(CH_3)_4N[1\text{-}B_{10}H_9N_2]$ and 50 ml of pyridine to give a clear solution. After several minutes at reflux a yellow precipitate had begun to form. After 3 hr at reflux the precipitate was separated by filtration and washed with acetone and diethyl ether giving 3.4 g (95%) of $(CH_3)_4N[1\text{-}C_5H_5NB_{10}H_9]$. Anal. Calcd for $(CH_3)_4N[C_5H_5NB_{10}H_9]$: C, 39.97; H, 9.69; B, 40.00; N, 10.35. Found: C, 39.82; H, 9.87; B, 40.23; N, 10.22. The infrared spectrum contained peaks at 2500 (s), 1630 (m), 1600 (m), 1540 (m), and 12.69 (m) cm^{-1}.

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Registry No. $(CH_3)_4N[1\text{-}B_{10}H_9N_2]$, 55913-46-7; $1,10\text{-}N_2B_{10}H_8N(CH_3)_3$, 55822-55-4; $1,10\text{-}N_2B_{10}H_8NC_5H_5$, 55822-56-5; $[(CH_3)_4N]_2[1\text{-}(1\text{-}Br\text{-}4\text{-}N_2C_6H_4)B_{10}Cl_9]$, 55904-73-9; $CsB_{10}Cl_9N_2$, 55886-11-8; $(CH_3)_4N[1\text{-}C_5H_5NB_{10}H_9]$, 55913-47-8; $K_2B_{10}H_{10}$, 12447-89-1; $(CH_3)_4N[1\text{-}B_{10}H_9N(CH_3)_3]$, 55904-74-0; $(CH_3)_4N[1\text{-}(1\text{-}Br\text{-}4\text{-}N_2C_6H_4)HB_{10}H_9]$, 55975-91-2; 2,4,6-tribromophenyldiazonium tetrafluoroborate, 4639-13-8; pyridine, 110-86-1.

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High-Resolution Boron-11 Nuclear Magnetic Resonance Spectroscopy.[1] V. Analysis of the Boron-11 Nuclear Magnetic Resonance Spectrum of Tetraborane(8)–Carbonyl at 32.1 MHz

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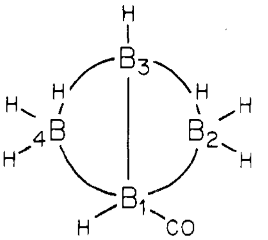
The boron-11 NMR spectrum of tetraborane(8)–carbonyl at 32.1 MHz has been interpreted in terms of the presence of two stereoisomers. This conclusion is based on the results of computer line-narrowed, proton-decoupled, and partially relaxed Fourier transform NMR spectra. The existence of isomers at −20° implies either isomers are formed during the synthesis and do not interconvert or isomer interconversion at −20° is slow with respect to the NMR chemical shift time scale.

Broad lines and overlapping resonances have previously made ^{11}B spectral interpretation and assignment of resonances arduous.[3] Utilization of techniques such as computer line-narrowing,[4,5] partially relaxed Fourier transform[6,7] NMR (PRFT), and complete proton decoupling[8,9] has made it possible to extract significantly more information from ^{11}B spectra recorded at any field strength. Because of our interest in the NMR parameters of low molecular weight boron hydrides and the structural implications of these data, we have applied the aforementioned methods in an attempt to elucidate the ^{11}B NMR spectrum of tetraborane(8)–carbonyl, $B_4H_8 \cdot CO$.

Tetraborane(8)–carbonyl was first synthesized[10] by Burg and Spielman in 1959 and several NMR investigations were subsequently reported.[11–13] The proton-coupled ^{11}B NMR spectrum consisted of two absorptions, a doublet at high shielding and a complex multiplet at lower shielding. The most shielded doublet was assigned to the substituted boron by comparison of the ^{11}B NMR spectrum of $B_4H_8{\cdot}CO$ with that of $B_4H_8{\cdot}PF_3$.[13] The complex multiplet to lower shielding was interpreted as resulting from the superposition of a doublet of relative area 1 and a triplet of relative area 2. Boron-11 and ^{1}H NMR spectral data are consistent with the structure for $B_4H_8{\cdot}CO$



Several other Lewis base adducts of B_4H_8 have been prepared.[11,14–16] In the ambient temperature ^{19}F NMR spectrum of $B_4H_8{\cdot}L$, where L = $PF_2N(CH_3)_2$, Centofanti et al.[15] observed two doublets, the temperature dependence of which led these workers to hypothesize the existence of endo and exo isomers. Furthermore, the interconversion of these isomers was slow on the NMR chemical shift time scale at ambient temperature. In the analogous adduct where L = F_2HP, however, resonance doubling was not observed which led to the further assumption that the $-NR_2$ portion of the base $F_2PN(CH_3)_2$ may be playing a specific role in isomer stabilization. For the related series of compounds $B_4H_8{\cdot}PF_2X$ (X = H, F, Cl, Br, I) isomers were again implicated by the temperature-dependent ^{19}F NMR spectra except for X = H. Isomers were rationalized as arising from restricted rotation around the boron–phosphorus bond and the lack of isomers for $B_4H_8{\cdot}PF_2H$ was interpreted as due to either free rotation around the B–P bond or the presence of a single rotamer. Independently, Leach et al.[17] have observed, in the 220-MHz ^{1}H NMR spectrum of tetraborane(10), chemical shift nonequivalence at ambient temperature of the protons of the $-BH_2$ fragments. Ring inversion (if it occurs at all) must therefore be slow on the NMR chemical shift time scale. From a single-crystal X-ray structure of $B_4H_8{\cdot}PF_2N(CH_3)_2$,[18] it was found that the integrity of the boron framework of B_4H_{10} is retained in the adduct. Since ring inversion in both of these structurally similar compounds is slow at ambient temperature, perhaps the role of the ligand in isomer stabilization is not as important as previously suggested. To this end, we chose to investigate $B_4H_8{\cdot}CO$ because of the similarity of its reported ^{11}B spectrum with that of $B_4H_8{\cdot}PF_2N(CH_3)_2$ and also because of the modest stereochemical requirements of the carbonyl group. In addition, we were interested in the value of $J_{B_1B_3}$ because of the bonding implications of this parameter.

Experimental Section

Tetraborane(8)–carbonyl was prepared from B_5H_{11} by the method of Spielman and Burg.[11] The ^{1}H and ^{11}B Fourier transform NMR spectra were obtained on a highly modified Varian Asociates XL-100-15 spectrometer.[19,20] Samples were run as 5% solutions in *n*-pentane at −20°. Partially relaxed Fourier transform (PRFT) NMR spectra were obtained by a standard 180°–τ–90° pulse sequence[6,7] and resolution-enhanced spectra were obtained by employing previously published methods.[4,5] Boron-11 chemical shifts were measured relative to the basal resonance of a trace amount of B_5H_9 impurity in the sample ($\delta(^{11}B_{base})$ + 12.5 ppm relative to $BF_3{\cdot}O(C_2H_5)_2$).[3,21]

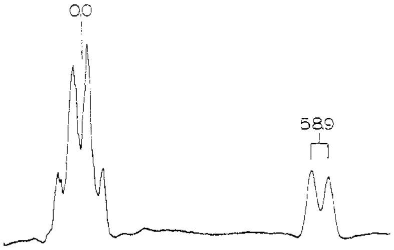


Figure 1. The 32.1-MHz ^{11}B NMR spectrum of tetraborane(8)–carbonyl in *n*-pentane solution at −20° ($J_{B_1H_t}$ = 129 Hz).

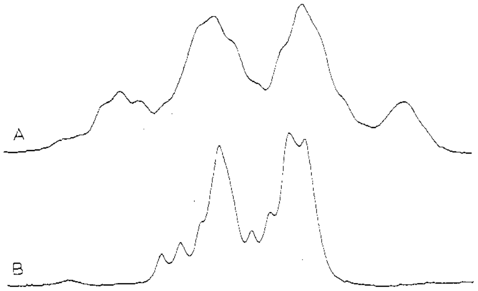


Figure 2. Expanded presentation of the deshielded resonance in the ^{11}B NMR spectrum of tetraborane(8)–carbonyl: (A) proton coupled; (B) proton decoupled.

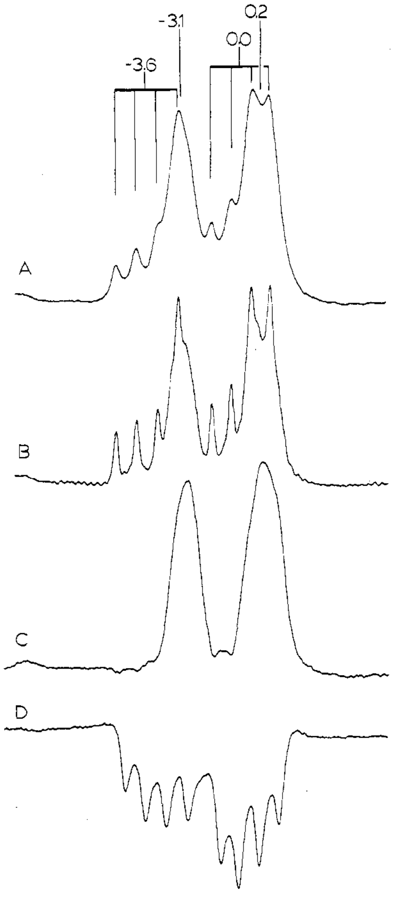


Figure 3. Expanded presentation of the deshielded resonance in the ^{11}B NMR spectrum of tetraborane(8)–carbonyl: (A) normal proton-decoupled spectrum. (B) line-narrowed proton-decoupled spectrum; (C) PRFT (τ 31 msec) proton-decoupled spectrum; (D) PRFT (τ 14 msec) proton-decoupled spectrum.

Results and Discussion

Presented in Figure 1 is the proton-coupled ^{11}B NMR spectrum of $B_4H_8{\cdot}CO$ obtained at 32.1 MHz. This spectrum is qualitatively the same as previously reported[13] for $B_4H_8{\cdot}CO$ at 19.3 MHz and is also quite similar to the 32.1-MHz ^{11}B NMR spectrum of $B_4H_8{\cdot}PF_2N(CH_3)_2$ reported by Centofanti et al.[15] Figure 2 is an expanded view of the deshielded multiplet. This portion of the spectrum has previously been interpreted as an overlapping doublet of relative area 1 (δ 2.1

ppm, $J_{BH} = 119$ Hz) and a triplet (δ 1.5 ppm, $J_{BH} = 127$ Hz) of relative area 2.[13] Under conditions of complete proton decoupling (Figure 2B), it becomes apparent that this interpretation is not sufficient to explain the resulting multiplicity of lines. Figure 3A and B shows the deshielded multiplet under conditions of complete proton decoupling. The utility of computer line narrowing is demonstrated in Figure 3B where at least 10 resonances can be distinguished. Proton-decoupled partially relaxed Fourier transform spectra (Figure 3C, D) indicate that this region is actually a composite of four resonances, two of which are singlets (τ 31 msec) and two of which are 1:1:1:1 quartets (τ 14 msec). Single-frequency ^1H bridge-decoupled PRFT NMR spectra obtained under similar conditions indicate that the boron atoms giving rise to the quartets have a single terminal proton associated with each ($\delta(B_3)$ 0.0 ppm, $J_{BH_t} = 120$ Hz; $\delta(B_{3'})$ 3.6 ppm, $J_{B_{3'}H_t} = 120$ Hz). Similarly, the boron atoms giving rise to the singlets have two terminal protons associated with each ($\delta(B_{2,4})$ 0.2 ppm, $J_{BH_t} = 132$ Hz; $\delta(B_{2',4'})$ −3.1 ppm, $J_{B'H_t} = 114$ Hz). Under conditions of complete proton decoupling and line narrowing in several solvents, the most shielded resonance remained a broad single line ($\nu_{1/2} \simeq 90$ Hz). No temperature dependence beyond expected changes in line width with T_2 is observed in the ^{11}B NMR spectrum between −94 and −20°. At temperatures above −20°, thermal decomposition of $B_4H_8{\cdot}CO$ prevented acquisition of meaningful data.

The quartets observed in the fully ^1H-decoupled spectra arise from ^{11}B–^{11}B coupling between B_1 and B_3 ($J_{B_1B_3} = 24$ Hz). This coupling most likely occurs through a two-center, two-electron bond in agreement with the structure presented above. Failure to resolve this coupling in the most shielded resonance (B_1) is presumably due to coincidental overlap of two nonequivalent quartets. Correlation of J_{BB} with the nature of the boron–boron bond[9,22] is under further investigation and results will be presented at a later time.

The above spectral results for $B_4H_8{\cdot}CO$ can best be interpreted in terms of an approximately 60:40 mixture of two isomers corresponding to endo and exo placement of the ligand with respect to the folded ring. An investigation of the variable-temperature 100-MHz ^1H NMR spectra of $B_4H_8{\cdot}CO$ with and without complete ^{11}B decoupling yielded no further information pertinent to the above conclusion. In view of the small chemical shift difference observed for endo and exo isomers in the 220-MHz ^1H NMR spectrum of B_4H_{10}, this result is not unexpected.

An obvious question at this point is: Why are isomers observed in the NMR experiment? The isomers may form by a nonstereospecific attack of CO on B_4H_8 during the synthesis of $B_4H_8{\cdot}CO$ to produce two static structures, or isomer interconversion must be slow with respect to the NMR time scale at −20°. At this time we have no evidence to distinguish between these alternatives. However, it should be pointed out that the related molecule $B_4H_8{\cdot}PF_2N(CH_3)_2$ has been shown[15] to undergo a reversible interconversion of isomers at elevated temperatures. It should also be noted that in the case of all $B_4H_8{\cdot}PF_2X$ compounds (except X = H) studied, the observation of isomers has been discussed[16] in terms of restricted rotation about the B–P coordinate bond. This obviously cannot be the case for $B_4H_8{\cdot}CO$. Futhermore, the failure of these $B_4H_8{\cdot}PF_2X$ isomers to interconvert rapidly at +40° necessitates a barrier to rotation about the B–P bond greater than 16 kcal/mol, a figure which would appear to be excessively large. Clearly the interesting class of $B_4H_8{\cdot}L$ compounds deserves further study.

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Registry No. $B_4H_8{\cdot}CO$, 12539-64-9; ^{11}B, 14798-13-1.

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