^{1}H Nuclear Magnetic Resonance Study of the Small *Closo*-Carboranes 1,5-Dicarba-*closo*-pentaborane(5), Carba-*closo*-hexaborane(7), 1,2-Dicarba-*closo*-hexaborane(6), 1,6-Dicarba-*closo*-hexaborane(6), and 2,4-Dicarba-*closo*-heptaborane(7)

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Boron-11 decoupled proton n.m.r. spectra and data are reported for the *closo*-carboranes 1,5-$C_2B_3H_5$, CB_5H_7, 1,2-$C_2B_4H_6$, 1,6-$C_2B_4H_6$, and 2,4-$C_2B_5H_7$. The ^{1}H n.m.r. results are in agreement with the structural assignments for these carboranes and are compatible with previously obtained boron-11 n.m.r. results. Fine structure, attributed to homonuclear long-range coupling, is observed in the decoupled spectrum of each of these closed polyhedral compounds. The largest long-range proton–proton spin coupling (10—12 Hz) is found between *trans* situated nuclei in 1,5-$C_2B_3H_5$, CB_5H_7, and in 1,2-$C_2B_4H_6$. An estimate of orbital hybridization in $C_2B_3H_5$ from $^{11}B^{13}C$, $H^{13}C$, and $H^{11}B$ coupling data indicates that most of the cage-orbital *s*-character is to be found in the C–B bonds and very little in the B–B bonds. Unambiguous chemical shift assignments are made for all the proton resonances except for the 2,3 and 4,5 positions of CB_5H_7.

MICROWAVE studies have confirmed four of the five polyhedral structures (Figures 1—5) previously assigned to the small carboranes 2,4-$C_2B_5H_7$,[1a,b] 1,2-$C_2B_4H_6$,[2] CB_5H_7, 1,6-$C_2B_4H_6$,[3] and 1,5-$C_2B_3H_5$.[4] Because dipole moments are lacking in the parent compounds of the latter two cages, they were examined as chloro- and methyl derivatives, respectively.

Only nearest-neighbour B–H coupling has been observed in the previously reported boron-11 and undecoupled proton n.m.r. spectra [1b,5-9] of these parent *closo*-carboranes. Longer range coupling has, however, been cited for several of the boron hydrides, B_2H_6,[10,11] B_4H_{10},[12] and B_5H_9.[13,14] This encouraged us to look for long-range spin interactions in the parent carboranes. Such information could be useful in confirming the previously assigned structures and may eventually be useful in deciding the extent of delocalized cage bonding in the *closo*-carboranes.

EXPERIMENTAL

Materials.—Both 1,5-$C_2B_3H_5$ and CB_5H_7 were prepared from methylpentaboranes using flash vacuum thermolysis techniques.[8] A sample of ^{13}C-enriched (90%) $C_2B_3H_5$ was prepared from 1,2-$(^{13}CH_3)_2B_5H_7$ by a procedure analogous to that outlined for the isotopically normal compound.[8] Several batches of 1,2-$C_2B_4H_6$, prepared earlier,[5,15] were combined and gas chromatographed to a purity of >99%. Both 1,6-$C_2B_4H_6$ and 2,4-$C_2B_5H_7$ were gifts from R. E. Williams and J. F. Ditter.

Nuclear Magnetic Resonance.—The n.m.r. spectra were obtained from liquid samples sealed in 3 or 5 mm thick wall n.m.r. tubes under vacuum. Tetramethylsilane (τ 10·0) was used as internal reference in assigning chemical shifts as well as providing a lock signal for the decoupling experiments.

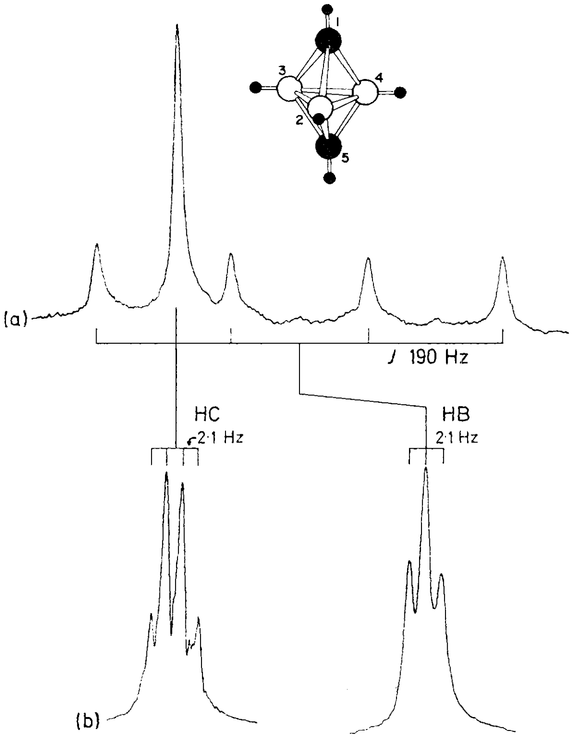

FIGURE 1 ^{1}H N.m.r. of 1,5-$C_2B_3H_5$, (a) undecoupled, (b) boron-11 decoupled

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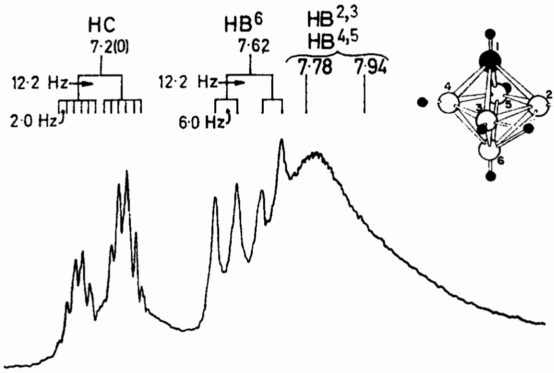

FIGURE 2 ^{1}H N.m.r. of CB_5H_7, boron-11 decoupled with frequency focused at B^6; the bridge hydrogen is a single broad resonance appearing at much higher field than the depicted spectrum

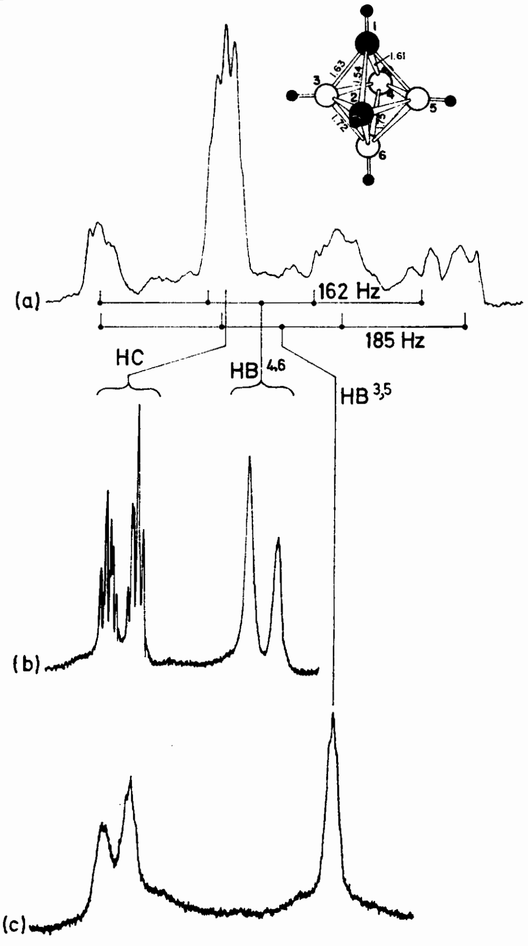

FIGURE 3 ^{1}H N.m.r. of 1,2-$C_2B_4H_6$, (a) undecoupled, (b) boron-11 decoupled with frequency focused at 4,6-positions, (c) boron-11 decoupled with frequency focused at 3,5-positions

The ^{1}H (100·0 MHz) n.m.r. spectra (Figures 1—6) were recorded using a Varian HA100 spectrometer operating at ambient temperatures. Boron-11 decoupled spectra were obtained with a Nuclear Magnetic Resonance Specialities HD-60 spin decoupler attachment, modified for use with HA 100. The radiation frequency (*ca.* 32·1 MHz) was controlled by a Hewlett–Packard 200 CD wide range oscillator. Another 200 CD oscillator drives a pseudo-random binary noise generator whose output is used to phase shift the radiation frequency. This signal amplified by an Electronic Navigation Industries 320L RF power amplifier is then applied to the HA 100 probe which has been double tuned for decoupling.

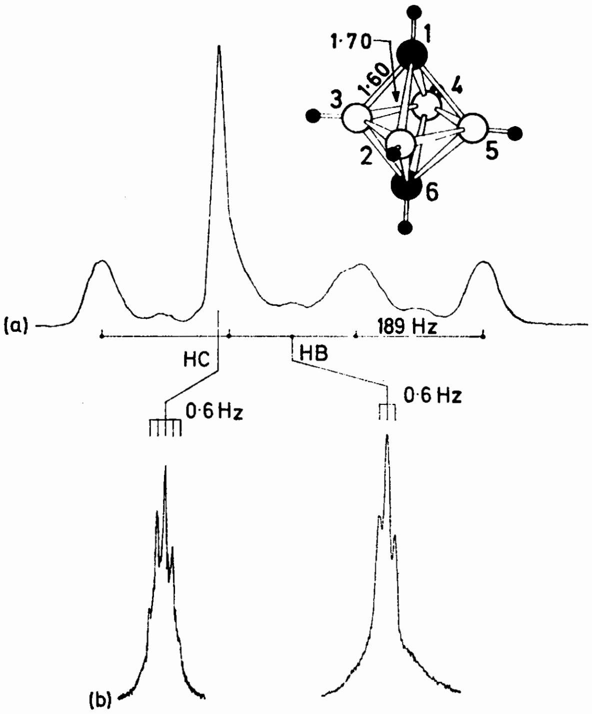

FIGURE 4 ^{1}H N.m.r. of 1,6-$C_2B_4H_6$, (a) undecoupled, (b) boron-11 decoupled

RESULTS

The experimental results of the boron-11 decoupled ^{1}H n.m.r. are in agreement with the assigned structures and symmetry requirements of all the *closo*-carboranes studied in this work. Assignment of the resonances, Table 1, were

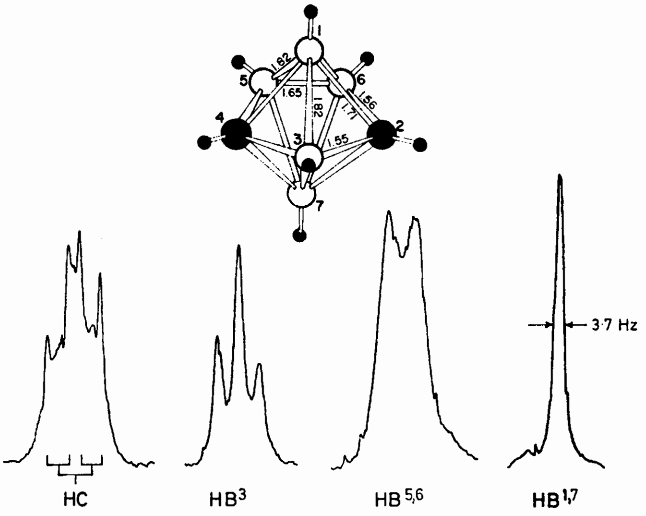

FIGURE 5 ^{1}H N.m.r. of 2,4-$C_2B_5H_7$, boron-11 decoupled with frequency focused for best resolution of individual resonances made by taking into consideration (a) available boron-11 n.m.r. data,[6-9] (b) relative area ratios of the various resonances, and (c) coupling patterns. In all the undecoupled spectra a somewhat broad singlet is observed for the carbon-attached protons and a 1 : 1 : 1 : 1 broadened quartet (J 169—190 Hz) for the boron-11 attached terminal protons;[16] however, boron-11 white noise decoupling produces fine structure which is described in some detail below.

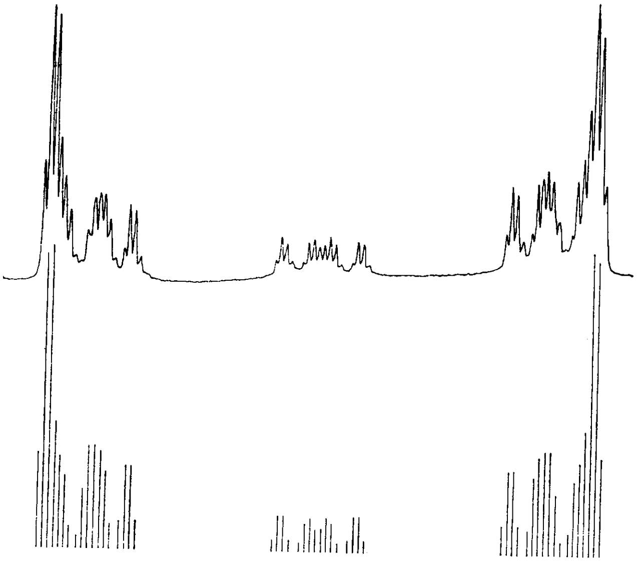

FIGURE 6 ^1H N.m.r. pattern for carbon-attached hydrogen of $^{13}C_2B_3H_5$ (90% ^{13}C-enriched) with boron-11 decoupling. Beneath the observed spectrum is the calculated pattern

1,5-*Dicarba*-closo-*pentaborane*(5).—The undecoupled ^1H spectrum for the isotopically normal $C_2B_3H_5$, Figure 1(a), shows a single ^{11}BH (1 : 1 : 1 : 1) quartet and a C–H singlet. In the ^{11}B decoupled proton spectrum, Figure 1(b), a 1 : 2 : 1 triplet and a 1 : 3 : 3 : 1 quartet having identical coupling constants are observed. These patterns are expected for coupling between the three magnetically equivalent B*H* protons and the two equivalent C*H* protons.

TABLE 1

^1H N.m.r. data

Compound	τ *	$J(HCBH)$/Hz	$J(H^{11}B)$/Hz
1,5-$C_2B_3H_5$	4·50 HC	2·1 (1—2)	189
	6·17 HB		
CB_5H_7	7·20 HC	12·2 (1—6)	
	7·62 HB^6	6·0 (6-μ)	178 ± 20 (all)
	7·78 $HB^{2,3}$	2·0 (1,2,3,4,5,μ)	
	7·94 $HB^{4,5}$		
	13·90 $H\mu$		
1,2-$C_2B_4H_6$	7·40 HC	11·0 (1—6)	185 (3,5)
	8·18 $HB^{3,5}$	1·5 (1—3,4,5)	162 (4,6)
	7·89 $HB^{4,6}$		
1,6-$C_2B_4H_6$	7·00 HC	0·6 (1—2,3,4,5)	184
	8·20 HB		
2,4-$C_2B_5H_7$	4·55 HC	8·6 (2—6)	179 (1,7)
	5·17 HB^3	6·7 (2,3)	182 (3)
	6·64 $HB^{5,6}$		169 (5,6)
	10·69 $HB^{1,7}$		

* Relative to tetramethylsilane (τ = 10·00).

The undecoupled ^1H and ^{11}B patterns for $^{13}C_2B_3H_5$ are almost identical to that of the isotopically normal compound except for the HC_{cage} region in the ^1H spectrum. White noise ^{11}B irradiation of the proton spectrum, Figure 6, gave a sharpened spectrum from which the coupling values cited in Table 2 are derived.

TABLE 2

Coupling constants for $^{13}C_2B_3H_5$

Group	J/Hz	J_{cu}*
$H^{13}C$	192	27·5
$HC^{13}C$	19·7	2·52
$HCCH$	10·8	0·346
$HCBH$	2·1	0·067
$H^{11}B$	189	18·88
$^{13}C^{11}B$	*ca.* 18	*ca.* 7·15
$HC^{11}B$	*ca.* 2—4	*ca.* 0·3
$HB^{11}B$	*ca.* 3—5	*ca.* 0·4
$^{13}C^{13}C$	15·0	7·6

* Obtained by dividing J/Hz by the product of the gyromagnetic ratios of the two coupled nuclei. $\gamma(^1H) = 5{\cdot}5854$, $\gamma(^{13}C) = 1{\cdot}4043$, $\gamma(^{11}B) = 1{\cdot}792$ (magnetic moments expressed in nuclear magnetons and spin angular in units of $h/2\pi$).

Both members of the ^{11}BH doublet in the undecoupled boron-11 n.m.r. spectrum and the proton-decoupled resonance pattern of this same boron exhibit a triplet structure (Figure 7) in the ^{13}C-enriched compound that is not seen in $C_2B_3H_5$ with isotopes distributed normally. This triplet (J *ca.* 18 Hz) is assigned to $^{13}C^{11}B$ coupling. The ^{13}C chemical shift was observed at δ +69 relative to CS_2.

Carba-closo-*hexaborane*(7).—By irradiating boron (6), the terminally attached proton is resolved into a doublet of J 12·2 Hz, Figure 2. Each member of the doublet is also split into a smaller doublet of 6 Hz, and the entire pattern overlaps with partially decoupled $H^{2,3,4,5}$ resonances. The doublet of 12·2 Hz is assigned to coupling with *H*C which, in turn, is also seen as a doublet, 12·2 Hz with fine structure, in the downfield region. The 6·0 Hz doublet is the result

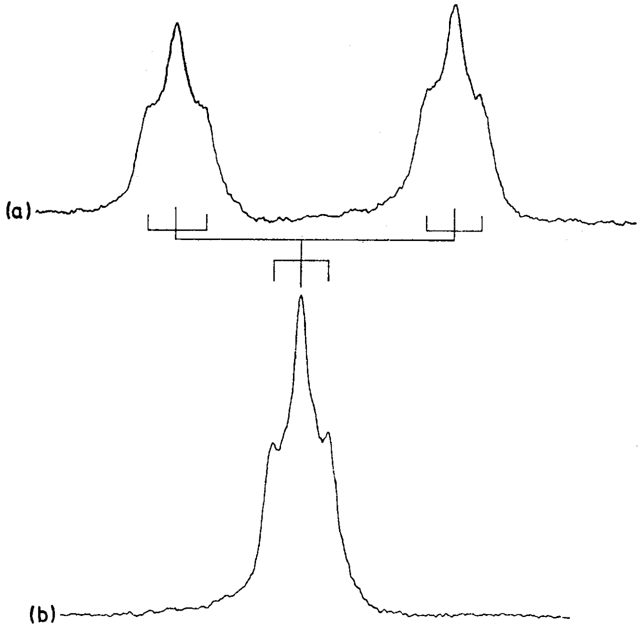

FIGURE 7 $C_2B_3H_5$ boron n.m.r. spectra; (a) ^{13}C enriched, (a) undecoupled; (b) ^{13}C enriched, proton decoupled

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[16] Naturally occurring boron consists of 81% ^{11}B ($I = 3/2$; magnetogyric ratio, 1366 G^{-1} Hz) and 19% ^{10}B ($I = 3$; magnetogyric ratio 457·5 G^{-1} Hz). The quartets assigned to the ^{11}B-attached hydrogens in the ^1H spectrum are usually well defined, whereas the smaller septets of the ^{10}B-attached hydrogens are buried under the labyrinth of all other resonances.

of coupling to the bridge hydrogen; for, if it were coupled to either of the terminal hydrogens, $HB^{2,3}$ and/or $HB^{4,5}$, one would expect at least a triplet. In the low field region, the *H*C doublet exhibits a multiplet structure which undoubtedly represents weak coupling to the four protons on the basal region, $H^{2,3}$, $H^{4,5}$, and perhaps the bridge hydrogen. Attempts were made to irradiate $B^{2,3;\,4,5}$ so that fine structures for the resonances of the attached terminal protons might be observed. Unfortunately, only broad signals are obtained. This is possibly due to long range heteronuclear coupling between B^6 and $H^{2,3;\,4,5}$ combined with both terminal–bridge HH and strong *trans* terminal–terminal HH coupling.

A calculated spectrum [17] for the carbon-attached hydrogens using the coupling values in Table 1 is in good agreement with the observed pattern.

1,2-*Dicarba*-closo-*hexaborane*(6).—Since there are two kinds of *H*B's and one kind of *H*C in this octahedral carborane, one expects two quartets and a singlet in this undecoupled spectrum. Figure 3(a) shows the undecoupled spectrum in which the two quartets overlap, while Figures 3(b) and (c) show the decoupled spectra in which the low and high field borons are irradiated, respectively. A long range homonuclear coupling (11 Hz) is observed as a set of doublets in Figure 3(b) which is assigned to the *trans* coupling between HC^2 and H^4. Each member of the *H*C doublet is further coupled to the remaining *H*B's to give the observed multiplet. The $H^{3,5}$ resonance appears as a poorly resolved multiplet interpreted as either a triplet with coupling to $HC^{1,2}$ or to $HB^{4,6}$, or as a quintet, the result of nearly equal coupling between $H^{3,5}$ and the remainder of the protons. From the coupling patterns the lower field *H*B resonance can be unambiguously assigned to $H^{4,6}$; for, only the mutual coupling of either H^4, or H^6, to *H*C can give the observed set of doublets.

1,6-*Dicarba*-closo-*hexaborane*(6).—Expectedly, the undecoupled spectrum, Figure 4(a), exhibits only one $H^{11}B$ quartet and one *H*C singlet. Upon decoupling the boron atoms long-range coupling between the two different kinds of protons is observed, Figure 4(b); the *H*C's are coupled to the four *H*B's giving a quintet with *J* 0·60 c.p.s., whereas the *H*B's are coupled to the two *H*C's giving a triplet with the same coupling constant. This coupling constant is the smallest observable long range (*i.e.* greater than one-bond) splitting among those carboranes which have been studied. The two resonances are rather susceptible to saturation effects which accounts for the minor deviation from mirror symmetry in the observed multiplets. Sweeping the signals in the opposite direction reverses the effect.

2,4-*Dicarba*-closo-*heptaborane*(7).—This compound exhibits a complicated undecoupled spectrum with three sets of overlapping *H*B quartets. Figure 5 shows the decoupled spectrum. The $H^{1,7}$ resonance is a sharp single peak of half-height width 3·7 Hz, indicating that the apical protons are not strongly coupled to the equatorial belt of hydrogens. H^3 is split into a triplet, *J* 6·7 Hz, by the two carbon-attached hydrogens. The carbon attached proton (2) or (4) is coupled to H^6 or H^5, *J* 8·6 Hz, and then split further by H^3, *J* 6·6 Hz.

DISCUSSION

All the ^1H n.m.r. resonances for $1,5-C_2B_3H_5$, CB_5H_7, $1,2-C_2B_4H_6$, $1,6-C_2B_4H_6$, and $2,4-C_2B_5H_7$ except for $H^{2,3}$ and $H^{4,5}$ of CB_5H_7 are unambiguously assigned in this study. Although the *H*C and *H*B chemical shift ranges τ 4·5—7·5 and τ 5·1—10·7, respectively, for this series are rather wide, it is noted that all the carbon- and boron-attached hydrogens of the octahedral carboranes (CB_5H_7, 1,2- and $1,6-C_2B_4H_6$) fall in the relatively narrow ranges of τ 7·2—7·5 and 7·6—8·2, respectively. From this it is tempting to predict that narrow chemical shift ranges will be found for hydrogens with similar environments in the isoelectronic cage isomers of other closed polyhedral carboranes.

Long-range Coupling.—From the results of the present decoupling study, it is clear that the broadness of the undecoupled *H*C and *H*B peaks can be largely attributed to multiple long-range coupling rather than quadrupole effects of the cage boron atoms. Observable three-bond coupling, *J*(HCBH), varies from 0·6 to 8·0 Hz in the small carboranes. The largest long-range proton–proton coupling, 10—12 Hz, is observed in $1,5-C_2B_3H_5$, CB_5H_7, and $1,2-C_2B_4H_6$, and is attributed to *trans* coupling between *H*C and *H*B hydrogens located on opposite vertices of a polyhedral framework.[18] A detailed analysis of the ^{13}CH pattern (Figure 6) of $^{13}C_2B_3H_5$ also reveals a significant long range $HC\ ^{13}C$ coupling. This is apparent when comparing coupling constants in terms of nuclear-independent units,[19] $J_{(c.u.)}$, which are independent of the magnetic properties of the nuclei involved and are characteristic only of the intervening electronic structure (Table 2). Ignoring the *trans* *HCCH* and $HC\,^{13}C$ values, it is seen that the remaining internuclear-coupling constants fall in the expected order based solely on the number of bonds between each pair, *e.g.* $H^{13}C$, $H^{11}B$, $^{13}C^{11}B$, $^{13}C^{13}C > HB^{11}B$, $HC^{11}B >$ *HCBH*. But both constants for *HCCH* and $HC^{13}C$ are significantly larger than comparison values in this trend.

Other studies have shown a *trans* effect in the boron-11 n.m.r. chemical shifts of CB_5H_7 [8] and $2,4-C_2B_5H_7$ [20] but *trans* coupling has not heretofore been observed for the *closo*-carboranes. Such strong long-range coupling observed in the polyhedral *closo*-carboranes may eventually shed light on the extent of cage electron delocalization or the extent of direct *trans*-cage bonding which could help to transmit spin information across the cage.

Coupling and Hybridization.—Application of the relationship [21] given in equation (1) to the ^{11}BH coupling

$$\%s\text{-orbital} = 0{\cdot}31[J(\mathrm{BH})] \qquad (1)$$

found for the carboranes indicates that all the borons are approximately *sp* hybridized (Table 3). There is

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[17] Using computer program LAOCN3 cited in 'Computer Programs for Chemistry,' vol. 1, D. F. Detar, Benjamin, New York, 1968.

[18] A separate n.m.r. study on $1-Me-1,2-C_2B_4H_5$ carried out by J. Spielman, E. Wan, and T. Onak (unpublished results) further supports the assignment of the large *trans*-coupling in the parent $1,2-C_2B_4H_6$.

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about 5% greater *s*-character in the B–H bonds neighbouring two carbon atoms than those neighbouring one carbon. This is consistent with the higher electronegativity of carbon relative to boron which increases the *p*-orbital contribution of neighbouring borons toward the cage B–C bonds, and thus effectively increasing the *s*-orbital contribution of boron toward the terminal B–H bond.

TABLE 3

%*s*-Orbital character of B in the B–H bond

Carboranes	%*s*
1,5-$C_2B_3H_5$	57
CB_5H_7	53 ± 6 B (all)
1,2-$C_2B_4H_6$	48·6 $B^{4,6}$
	55·5 $B^{3,5}$
1,6-$C_2B_4H_6$	55·2
2,4-$C_2B_5H_7$	53·7 $B^{1,7}$
	54·6 B^{3}
	50·7 $B^{5,6}$

By applying both equations (1) and (2) to the ^{13}CH

$$\%s(^{13}\mathrm{CH}) = (0{\cdot}20)\ [J(^{13}\mathrm{CH})]\ \text{(ref. 22)} \qquad (2)$$

and ^{11}BH coupling constants (Table 2) found for $C_2B_3H_5$, the hybrid orbitals contributed by the cage atoms to each of their terminal bonds have 39 and 59% *s*-orbital content, respectively. From the first value it can be concluded that the three carbon orbitals directed toward the three skeletal boron atoms contain 20 %s-orbital character each. However, the analogous situation for boron is more complex because each boron can contribute three cage orbitals but each is bonded to four cage atoms; also, the pair of bonds directed toward the apically situated carbon atoms are obviously not equivalent to those directed toward the equatorial borons.

Propitiously, a relationship between *s*-orbital content in a ^{13}C^{11}B bond and $J(^{13}\mathrm{C}^{11}\mathrm{B})$ has been developed, equation (3), which allows a reasonable prediction to be

$$(\%s,\ ^{11}\mathrm{B})(\%s,\ ^{13}\mathrm{C}) = (21)[J(^{13}\mathrm{C}^{11}\mathrm{B})] \qquad (3)$$

made concerning the hybrid contribution by each atom.[23] From the observed $J(^{13}\mathrm{C}^{11}\mathrm{B})$ of *ca.* 18 Hz and the above determined 20 %*s*-orbital character for the carbon cage orbital it is found [equation (3)] that each boron orbital contributing to C–B bonding has *ca.* 19% *s*-orbital content. This leaves a residual 1—2% *s*-contribution, *i.e.* 1/2[(100 − 59) − 2(19)], to each of the equatorial B–B bonds. With such low *s*-orbital content in the B–B bonds it is satisfying to find that this bond distance is found to be rather long (1·85+ Å).[24]

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