Isomers of $B_{20}H_{26}$: Elucidation of the Structure of 6,6′-Bi(*nido*-decaboranyl) by ^{11}B-$\{^1H\}$ and ^1H-$\{^{11}B\}$ N.M.R. Spectroscopy

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Summary The structure of one of the $B_{20}H_{26}$ isomers formed by thermolysis of *nido*-decaborane in the presence of tetrahydrothiophen has been shown to be 6,6′-bi(*nido*-decaboranyl) by means of ^1H-$\{^{11}B\}$ n.m.r. spectroscopy in conjunction with 'partially relaxed' ^{11}B and ^{11}B-$\{^1H\}$ n.m.r. spectroscopy; it is the largest neutral borane yet characterised.

THE formulation of icosaborane(26), $B_{20}H_{26}$,[1] as bi(*nido*-decaboranyl), $(B_{10}H_{13})_2$, implies eleven geometric isomers. Five of these have been isolated but their spectroscopic similarity has so far prevented the determination of the positions of the linkages joining the two parts of the molecules.[2] We now report results which show that a further isomer (the 'seventh' isomer in ref. 2) has the linkage in the 6,6'-position (Figure).

TABLE. ^1H and ^{11}B N.m.r. parameters of 6,6'-bi(*nido*-decaboranyl); dilute solution in C_6D_6 at 25 °C unless otherwise indicated.

$\delta(^{11}B)$[a]	T_1/ms ($\pm 20\%$)	Relative intensity	$^1J(^{11}B-^1H)$/Hz	$\delta(^1H)$[a] ($\pm 0{\cdot}03$)	Relative intensity	$\delta(^1H)$ ($CDCl_3$ solvent)[a] ($\pm 0{\cdot}03$)	Assignment
$+15{\cdot}0 \pm 1{\cdot}0$	2·8	1	Singlet	—	—	—	6
$+13{\cdot}5 \pm 0{\cdot}3$	15·0	2	150 ± 10	+4·25	2	+3·92	1,3
$+11{\cdot}7 \pm 0{\cdot}3$	4·0	1	165 ± 20	+3·46	1	+3·84	9
$+2{\cdot}7 \pm 0{\cdot}3$	8·2	2	160 ± 20	+3·41	2	+3·29	8,10[b]
$+0{\cdot}9 \pm 0{\cdot}3$	6·2	2	155 ± 10	+3·16	2	+3·21	5,7[b]
$-33{\cdot}9 \pm 0{\cdot}2$	20·0	1	150 ± 5	+1·14[c]	2	+0·73	4[b]
$-34{\cdot}6 \pm 0{\cdot}2$	9·4	1	150 ± 5	+1·10[c]			2[b]
				−1·97	2	−1·76	Bridging
				−2·56	2	−1·92	

[a] In p.p.m. to high frequency (low field) of $BF_3{\cdot}Et_2O$ (^{11}B) and $SiMe_4$ (^1H). [b] Differentially assigned on the basis that ^{11}B nuclei with the smaller T_1 values are nearer the molecular centre. [c] Differentiation uncertain.

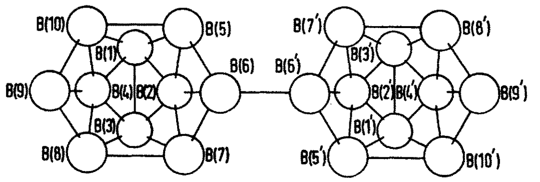

FIGURE. Schematic structure of 6,6'-bi(*nido*-decaboranyl); each of the boron atoms except those in the 6- and 6'-positions has a terminal hydrogen atom attached, and there are bridging hydrogen atoms between the 5,6; 6,7; 8,9; and 9,10 boron atoms on each cluster.

The heating of $B_{10}H_{14}$ in toluene at 110 °C for 24 h with $[CH_2]_4S$ as catalyst yielded three chromatographically separable $B_{20}H_{26}$ isomers. These were 2, 4, and the supposed 'seventh' isomer in the numbering system of ref. 2. The normal simple-pulse 32 MHz Fourier-transform ^{11}B and ^{11}B-{^1H(broad band)} n.m.r. spectra of this 'seventh' isomer were similar to those of $B_{10}H_{14}$.[2] However, experiments using the 180°–τ–90° pulse sequence[3] with values of τ between 1 and 200 ms differentiated seven ^{11}B resonances (Table). These were assigned among the three groupings 1,3,6,9; 5,7,8,10; and 2,4 based on the similarity of their chemical shifts with those[3] for $B_{10}H_{14}$. Their multiplicities and relative intensities suggested a symmetrical structure, and the singlet in the undecoupled spectra at $\delta = +15$ p.p.m. indicated either 1- or 6-substitution. The two resonances for the nuclei in the 2,4-positions therefore suggested the 6,6'-bi(*nido*-decaboranyl) structure, but the proximity and consequent overlap of some resonances made this conclusion tentative. Selective ^1H-{^{11}B} experiments however established the relationship between resonances in the ^1H and ^{11}B spectra shown in the Table; these results confirmed the structure as 6,6'-bi(*nido*-decaboranyl). In particular, the resonance at $\delta(^1H) = +3{\cdot}59$ p.p.m. was distinguished from that at $+3{\cdot}54$ (C_6D_6 solvent) and was ascribed to the 9,9'-protons on the basis that the solvent shift $\Delta\delta(^1H)$ of $+0{\cdot}27$ p.p.m. on the replacement of C_6D_6 as solvent by $CDCl_3$ was in the same sense and of the same order of magnitude ($+0{\cdot}26$ p.p.m.) as that observed for the 6,9-protons in $B_{10}H_{14}$.

The n.m.r. properties of the other $B_{20}H_{26}$ isomers so far isolated are in general more complex and have not yet yielded to analysis, although present evidence suggests that the isomer described here may be identical to an isomer prepared by a different route; *viz.* isomer 5 from the reaction of $B_{10}H_{13}MgI$ with 6-$ClB_{10}H_{13}$.

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