The Chemistry of Isomeric Icosaboranes, $B_{20}H_{26}$. Molecular Structures and Physical Characterization of 2,2′-Bi(*nido*-decaboranyl) and 2,6 -Bi(*nido*-decaboranyl)

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The structures of the large neutral boranes 2,2′-bi(*nido*-decaboranyl), 2,2′-$(B_{10}H_{13})_2$, m.p. 178 °C, and 2,6′-bi(*nido*-decaboranyl), 2,6′-$(B_{10}H_{13})_2$, m.p. 154 °C, have been established by single-crystal *X*-ray diffraction. The 2,2′ isomer is tetragonal, space group $I4_1cd$, with a = 11.901(3), c = 23.135(4) Å, molecular symmetry C_2; the 2,6′ isomer is orthorhombic, space group *Pbca*, with a = 14.673(3), b = 19.765(4), and c = 11.580(3) Å. The intercluster B–B bond lengths are respectively 1.692(3) and 1.679(3) Å, and there is a lengthening of 0.015 Å of the adjacent cluster B–B distances when compared with the corresponding distances in decaborane(14) itself. The ^1H-{^{11}B} and ^{11}B n.m.r. behaviour of the two isomeric *conjuncto*-boranes has been investigated and the results for the 2,2′ isomer are discussed in some detail. Infrared and u.v. spectroscopic data are presented. The unambiguous determination of the structures permits a discussion of possible synthetic mechanisms.

ALTHOUGH the chemistry of the boron hydrides and their derivatives is a rapidly expanding and potentially enormous field, there are in fact relatively few well characterized neutral boranes. This is partly a consequence of the thermal instability and chemical reactivity of many boranes, particularly the lower ones, but is also due in part to the difficulty of discovering kinetically favourable synthetic routes. Of the 24 well characterized boranes five are simple *nido*-boranes, B_nH_{n+4} (B_2H_6,[1-5] B_5H_9,[1,6,7] B_6H_{10},[5,8,9] B_8H_{12},[10] and $B_{10}H_{14}$[1,11-13]) and six are simple *arachno*-boranes, B_nH_{n+6} (B_4H_{10},[1,2,13-15] B_5H_{11},[1,13,16] B_6H_{12},[17,18] B_8H_{14},[19] n-B_9H_{15},[20,21] and i-B_9H_{15}[22,23]). The remaining 13 boranes can be regarded as being structurally derived by the formal fusion of these simpler borane clusters and can be given the convenient generic description of *conjuncto*-boranes.

Amongst the boranes themselves four structural types of *conjuncto*-borane have been found, though further modes of linkage have been encountered in borane anions and other derivatives. The most common linkage is that in which two clusters share two boron atoms at a common edge, as in $B_{13}H_{19}$,[24-26] $B_{14}H_{18}$,[27,28] $B_{14}H_{20}$,[29] $B_{16}H_{20}$,[30,31] n-$B_{18}H_{22}$,[32,33] and i-$B_{18}H_{22}$.[34,35] Of the other boranes, $B_{20}H_{16}$[36,37] has a unique structure in which the formal face-to-face fusion of two *nido*-B_{10} clusters results in the four ' shared ' boron atoms having no attached H atoms of any kind. The third mode of linkage, found in $B_{14}H_{22}$ and $B_{15}H_{23}$,[38] can be thought of as a donor–acceptor complex (Lewis-base adduct) formed between two neutral borane fragments so as to give a new B–B–B three-centre two-electron bond. The fourth structural category comprises those *conjuncto*-boranes which consist of two smaller borane units linked by a single two-centre two-electron B–B bond: *e.g.* 2,2′-$(B_4H_9)_2$,[39-41] 1,1′-$(B_5H_8)_2$,[42] 1,2′-$(B_5H_8)_2$,[43] and 2,2′-$(B_5H_8)_2$.[41,43,44] We now report the detailed structures and physical properties of two further examples of this last class of compounds: 2,2′-$(B_{10}H_{13})_2$, for which preliminary data have been given,[45] and 2,6′-$(B_{10}H_{13})_2$. We have also previously established the identity of a further isomer, 6,6′-$(B_{10}H_{13})_2$, by means of n.m.r. spectroscopy,[46] and very recently a preliminary report of the structure of 1,5′-$(B_{10}H_{13})_2$ has appeared.[47] General synthetic routes to these and other isomers of $B_{20}H_{26}$ have been reported.[48] They are the largest neutral boranes yet to be fully characterized though we have also unequivocally identified triacontaborane(38), $B_{30}H_{38}$, by high-resolution mass spectrometry.

Decaborane(14), when photolysed or thermolysed under carefully defined conditions, yields a number of isomers of $B_{20}H_{26}$ which can be separated chromatographically [equations (1) and (2); the isomers are numbered as in ref. 48 throughout]. We have now

$$2B_{10}H_{14} \xrightarrow{h\nu} H_2 + B_{20}H_{26} \quad \text{(mainly isomers 1 and 2)} \tag{1}$$

$$2B_{10}H_{14} \xrightarrow[C_4H_8S]{\Delta/\text{catalyst}} H_2 + B_{20}H_{26} \quad \text{(mainly isomers 2, 4, and 7)} \tag{2}$$

obtained crystals of isomers 1 and 4 and have determined their structures by single-crystal *X*-ray diffraction experiments. In both cases the crystals were shown to be representative of the bulk samples by n.m.r. experiments.

EXPERIMENTAL

Preparation of Compounds.—(*a*) 2,2′-*Bi*(nido-*decaboranyl*), (*isomer* 1). This was prepared as described previously [45,48] from the u.v. photolysis of a solution of *nido*-decaborane in cyclohexane (*ca.* 0.05 mol dm^{-3}) and was isolated by column chromatography on untreated silica gel (100—200 mesh) with 85 : 15 light petroleum (b.p. 60—80 °C)–benzene as the eluting medium. Repeated crystallization from cyclohexane then gave colourless crystals, m.p. 177—178 °C. The crystals used for the *X*-ray diffraction experiments were obtained by recrystallization from diethyl ether and had the same m.p.

(*b*) 2,6′-*Bi*(nido-*decaboranyl*), (*isomer* 4). A solution of *nido*-decaborane (4 g, 32 mmol) and bis(tetrahydrothiophen)-*arachno*-decaborane $B_{10}H_{12}(SC_4H_8)_2$ (4 mg, *ca.* 0.05 mmol) in toluene (50 cm^3) was refluxed under dry nitrogen for 24 h. The more volatile components were then removed under reduced pressure, and the remaining *nido*-decaborane (3.2 g, 26 mmol) recovered by sublimation at *ca.* 60 °C (15 Pa). The waxy residue was chromatographed on untreated silica gel [70—230 mesh (ASTM), 120 g] using 75 : 25 light petroleum (b.p. 60—80 °C)–benzene as the eluting medium, the course of the chromatogram being followed by analytical t.l.c. Fractions containing *nido*-decaborane (0.4 g, 3 mmol), icosaborane(26) (isomer 2) (trace amounts), 2,6′-bi(*nido*-decaboranyl) (0.15 g, 0.6 mmol; *ca.* 40% yield based on amount of decaborane consumed), and impure 6,6′-bi-(*nido*-decaboranyl)[46] (*ca.* 0.02 g, 0.08 mmol) were collected. Removal of the more volatile components from the fractions containing 2,6′-$(B_{10}H_{13})_2$ yielded an oil which deposited a white solid on addition of pentane. Repeated recrystallization of this solid from cyclohexane resulted in colourless crystals, m.p. 154—154.5 °C, of which one was found suitable for *X*-ray diffraction experiments.

X-*Ray Structure Analyses.—Crystal data.* (isomer 1): 2,2′-$(B_{10}H_{13})_2$, $M = 242.41$, Tetragonal, $a = 11.901(3)$, $c = 23.135(4)$ Å, $U = 3\,304(1)$ Å^3, $Z = 8$, $D_c = 0.975$ g cm^{-3}, $F(000) = 1\,008$, space group $I4_1cd$, Mo-K_α radiation, graphite monochromatized, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 0.34 cm^{-1}. (isomer 4): 2,6′-$(B_{10}H_{13})_2$, $M = 242.41$, Orthorhombic, $a = 14.673(3)$, $b = 19.765(4)$, $c = 11.580(3)$ Å, $U = 3\,358(1)$ Å^3, $Z = 8$, $D_c = 0.959$ g cm^{-3}, $F(000) = 1\,008$, space group *Pbca*, Mo-K_α radiation, graphite monochromatized, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 0.33 cm^{-1}.

Structure Determination.—Measurements were made on a Syntex $P2_1$ diffractometer. For each isomer, cell dimensions were determined by least-squares treatment of the setting angles for 15 reflections having $35 < 2\theta < 40°$. For isomer 1 intensities of two octants of data in the range $5 < 2\theta < 50°$ were measured in the θ—2θ scan mode using scans from 1° below $K_{\alpha1}$ to 1° above $K_{\alpha2}$. Averaging of equivalent reflections gave a total of 755 independent reflections, and the 691 with $I > 3\sigma(I)$ were used in the subsequent structure refinement. For isomer 4 all independent reflections to $2\theta = 40°$ were measured, and of these 2 208 reflections the 1 475 with $I > 3\sigma(I)$ were used in the refinement. For both structures boron atoms were located using the MULTAN programs[49] and least-squares refinement with anisotropic temperature factors converged at $R = 0.12$ for isomer 1 and at $R = 0.15$ for isomer 4. The hydrogen atoms were then located from difference syntheses and further refinement of co-ordinates, anisotropic temperature factors for boron, and isotropic temperature factors for hydrogen converged to final R values of 0.036 and 0.045 respectively for isomers 1 and 4, with R' values of 0.045 and 0.053. Modified variances $\sigma^2(I) = \sigma^2_c(I) + (QI)^2$ were used, where $\sigma^2_c(I)$ is the variance derived from counting statistics, and least-squares weights were calculated from the corresponding expression $w^{-1} = \sigma^2(F) = \sigma^2_c(F) + \frac{1}{4}(QF)^2$; a value of $Q = 0.05$ was found to give satisfactory distributions of $\langle w\Delta^2\rangle$ *vs.* F_o for both structures. The final values of $[\Sigma w\Delta^2/(n-m)]^{\frac{1}{2}}$ were respectively 1.52 and 1.63. Atomic scattering factors were calculated from the analytical approximation and coefficients given in ref. 50, those for hydrogen being the contracted bonded-atom values.[51] The atomic co-ordinates and their estimated standard deviations are given in Table 1. Observed and calculated structure factors and thermal parameters are listed in Supplementary Publication No. SUP 22724 (18 pp).*

N.M.R. Spectroscopy.— 32-MHz ^{11}B and $^{11}B-\{^1H\}$ spectra, and 100-MHz ^1H and $^1H-\{^{11}B\}$ spectra were obtained for *ca.*

TABLE 1

Fractional co-ordinates with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
(*a*) 2,2′-$(B_{10}H_{13})_2$			
B(1)	0.154 73(12)	0.013 59(22)	0.061 43(14)
B(2)	0.064 69(18)	0.028 76(16)	0
B(3)	0.188 13(20)	−0.056 00(20)	−0.004 03(14)
B(4)	0.296 18(23)	−0.018 42(23)	0.044 88(17)
B(5)	0.105 69(22)	0.146 51(22)	0.043 67(16)
B(6)	0.090 96(21)	0.156 46(21)	−0.032 81(16)
B(7)	0.157 64(22)	0.034 32(23)	−0.060 88(15)
B(8)	0.311 15(23)	0.003 57(27)	−0.030 97(18)
B(9)	0.365 68(24)	0.098 63(27)	0.021 28(18)
B(10)	0.257 09(24)	0.114 81(24)	0.073 58(16)
H(1)	0.120 3(20)	−0.023 0(21)	0.100 2(10)
H(3)	0.180 5(23)	−0.143 0(22)	−0.015 3(11)
H(4)	0.341 2(24)	−0.081 1(25)	0.070 0(13)
H(5)	0.049 2(21)	0.191 9(21)	0.070 5(13)
H(6)	0.035 4(23)	0.215 8(22)	−0.054 8(12)
H(7)	0.144 7(20)	0.010 2(22)	−0.104 9(12)
H(8)	0.370 8(25)	−0.041 1(27)	−0.059 1(13)
H(9)	0.456 1(26)	0.124 0(25)	0.024 5(12)
H(10)	0.272 7(22)	0.151 5(24)	0.114 2(12)
H(56)	0.143 8(23)	0.209 4(21)	0.003 8(14)
H(67)	0.177 9(21)	0.135 6(20)	−0.062 7(10)
H(89)	0.338 1(25)	0.107 5(22)	−0.031 2(14)
H(910)	0.301 3(29)	0.174 4(27)	0.039 3(13)
(*b*) 2,6′-$(B_{10}H_{13})_2$			
B(1)	0.460 97(16)	0.375 50(11)	0.310 44(21)
B(2)	0.339 50(16)	0.376 37(11)	0.309 31(20)
B(3)	0.402 51(17)	0.392 99(12)	0.181 10(20)
B(4)	0.512 73(17)	0.426 95(12)	0.204 44(22)
B(5)	0.403 53(17)	0.415 79(12)	0.421 54(21)
B(6)	0.300 56(16)	0.451 17(12)	0.366 64(24)
B(7)	0.309 70(16)	0.444 33(12)	0.214 76(22)
B(8)	0.424 04(18)	0.477 33(14)	0.145 04(22)
B(9)	0.507 59(18)	0.510 58(12)	0.241 04(26)
B(10)	0.517 21(16)	0.449 17(13)	0.351 97(24)
B(1′)	0.267 72(17)	0.160 61(11)	0.382 92(20)
B(2′)	0.292 97(16)	0.242 98(11)	0.434 32(20)
B(3′)	0.187 56(17)	0.204 86(11)	0.468 21(19)
B(4′)	0.149 29(17)	0.145 09(11)	0.364 78(21)
B(5′)	0.317 71(16)	0.219 30(12)	0.289 94(20)
B(6′)	0.282 21(15)	0.303 61(11)	0.327 60(19)
B(7′)	0.189 59(16)	0.289 55(11)	0.425 20(19)
B(8′)	0.093 81(17)	0.224 22(12)	0.380 95(22)
B(9′)	0.108 05(17)	0.184 57(11)	0.244 36(23)
B(10′)	0.222 45(17)	0.154 61(11)	0.244 18(21)
H(1)	0.493 2(11)	0.327 5(9)	0.336 3(14)
H(3)	0.391 4(13)	0.359 4(10)	0.106 9(17)
H(4)	0.569 9(12)	0.409 3(9)	0.155 9(16)
H(5)	0.404 9(12)	0.397 1(10)	0.512 2(16)
H(6)	0.239 8(13)	0.459 6(10)	0.417 0(17)
H(7)	0.250 0(14)	0.448 1(10)	0.160 5(17)
H(8)	0.420 9(13)	0.496 5(10)	0.058 3(16)
H(9)	0.553 0(14)	0.551 0(10)	0.224 3(17)
H(10)	0.575 5(12)	0.448 2(10)	0.405 6(15)
H(56)	0.369 7(13)	0.472 8(9)	0.419 8(16)
H(67)	0.309 0(14)	0.494 1(10)	0.282 4(16)
H(89)	0.427 0(14)	0.527 8(10)	0.213 9(15)
H(910)	0.487 7(13)	0.509 7(9)	0.350 3(17)
H(1′)	0.311 8(11)	0.120 3(9)	0.409 6(15)
H(2′)	0.343 3(13)	0.249 6(10)	0.504 3(18)
H(3′)	0.170 2(12)	0.196 3(9)	0.558 3(16)
H(4′)	0.121 1(11)	0.096 4(9)	0.393 6(14)
H(5′)	0.384 1(12)	0.210 9(9)	0.252 1(17)
H(7′)	0.169 4(11)	0.332 7(9)	0.484 2(15)
H(8′)	0.027 3(13)	0.232 5(9)	0.414 6(16)
H(9′)	0.056 6(12)	0.170 2(9)	0.183 7(15)
H(10′)	0.241 0(13)	0.115 9(10)	0.180 5(15)
H(56′)	0.284 9(11)	0.267 6(8)	0.234 8(15)
H(67′)	0.194 3(10)	0.313 2(7)	0.325 4(12)
H(89′)	0.094 8(12)	0.244 7(9)	0.277 6(15)
H(910′)	0.182 8(12)	0.199 5(9)	0.186 8(15)

* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

0.5 mol dm^{-3} solutions in $CDCl_3$ and C_6D_6 at 21 °C using a JEOL FX-100 pulse (Fourier-transform) n.m.r. spectrometer. Chemical shifts δ are given in p.p.m. to high frequency (' low field ') of the reference standards which were $OEt_2{\cdot}BF_3$ and $SiMe_4$ for ^{11}B and ^1H respectively. Selective ^1H-{^{11}B} double-resonance experiments were straightforward and an illustrative example of the technique has been given elsewhere.[52] Longitudinal (quadrupolar) ^{11}B relaxation times T_1 were obtained by the null method using a 180°-τ-90° pulse sequence; the same sequence also provided the ' partially relaxed '[38,53,54] spectra. The null method was calibrated using the semi-logarithmic plot method over the range of T_1 values encountered using a solution of $B_{10}H_{14}$ in $CD_3C_6D_5$ at various temperatures. The 180° and 90° pulse widths for ^{11}B for all the samples examined were determined to be 32 and 16 μs respectively.

U.v. Spectra.—These were recorded on a Unicam SP 8000 spectrophotometer using *ca.* 2.4 × 10^{-4} mol dm^{-3} solutions in cyclohexane with a path length of 0.5 cm; 2,2'-$(B_{10}H_{13})_2$ (isomer 1) had maxima at 220 and 272 nm, with extinction coefficients ε of 2 760 and 5 015 respectively, and 2,6'-$(B_{10}H_{13})_2$ (isomer 4) had maxima at 233 and 272 nm, ε 5 300 and 5 890 dm^3 mol^{-1} cm^{-1} respectively.

Infrared Spectra.—These were recorded as KBr discs on a Perkin-Elmer 457 grating instrument; band maxima are quoted in cm^{-1} ± 5 cm^{-1} and were as follows. 2,2'-$(B_{10}H_{13})_2$. 2 580s, 2 540m, 2 510s, 1 940w, 1 870m, 1 550w, 1 510s, 1 455m, 1 380m, 1 100w, 1 040w, 1 000s, 995s, 965w, 945w, 925s, 915w (sh), 900m, 895w, 860m, 830s, 820m, 805m, 785s, 765s, 720/10s, 685w, 650m, 620m, 560w, 545w, 395m. 2,6'-$(B_{10}H_{13})_2$: 2 540s, 2 510s, 1 950m, 1 900m, 1 500s (br), 1 450s (br), 1 140w, 1 095m, 1 030w, 1 000s (br), 965m (sh), 955m, 920m, 900m, 870w (sh), 860m, 840m, 835m, 810m, 790m, 775m, 750w, 730w, 720m, 710m, 685m (sh), 680m, 655m, 645m, 620w, 595w, 560w, 520w, 490m, 460m, 440w, 405m, 385m. $B_{10}H_{14}$: 2 600s, 2 580s, 2 560s, 2 520s, 1 960w, 1 930w, 1880m, 1 550m, 1 510s, 1 460s, 1 350m, 1 100m, 1 030m, 1 000s, 960m, 940m, 920s, 900m, 850m, 810s, 760s, 740m, 720s, 650w, 620m, 450w, 440w, 390m. For the $(B_{10}H_{13})_2$ compounds there appeared to be bands in the 520—560 cm^{-1} region that may be associated with the *conjuncto* linkage.

DISCUSSION

The molecular structures of the two isomers are shown in Figures 1 and 2; isomer 1 (photolysis) is seen to be 2,2'-bi(*nido*-decaboranyl) and isomer 4 (thermolysis) is the 2,6' isomer. [Recently the crystal structure of another isomer, 1,5'-bi(*nido*-decaboranyl), has been briefly mentioned in a conference abstract,[47] but few details were given.] The framework B–B bond lengths are listed in Table 2. As the 2,2' isomer has crystallographic symmetry C_2, there are for the two isomers three independent $B_{10}H_{13}$ units and apart from those B–B distances involving a *conjuncto*-linked boron atom

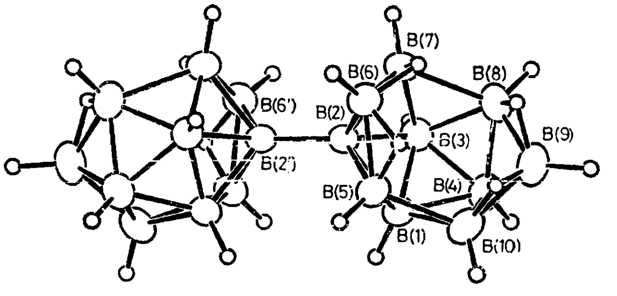

FIGURE 1 ORTEP drawing of the molecular structure of 2,2'-$(B_{10}H_{13})_2$. 50% Probability thermal ellipsoids are shown, with hydrogen atoms given artificial temperature factors of U_{iso} = 0.006 Å^2. In this isomer the primed atoms are related to the unprimed ones by a crystallographic two-fold axis

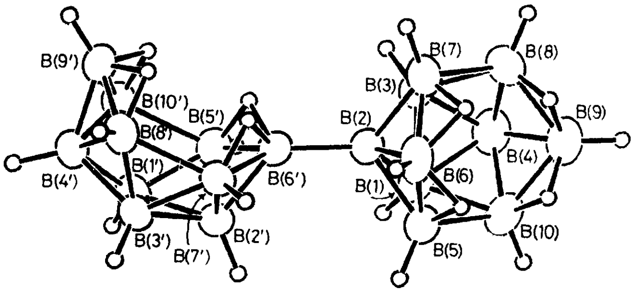

FIGURE 2 ORTEP drawing of the molecular structure of 2,6'-$(B_{10}H_{13})_2$. 50% Probability thermal ellipsoids are shown, with hydrogen atoms given artificial temperature factors of U_{iso} = 0.006 Å^2. In this isomer the primed and unprimed atoms are crystallographically independent

TABLE 2

Boron–boron distances (Å) and angles (°) in 2,2'-$(B_{10}H_{13})_2$ and 2,6'-$(B_{10}H_{13})_2$, with estimated standard deviations in parentheses

		2,6' isomer	
	2,2'isomer	2-substituted cluster	6'-substituted cluster
(*a*) Distances			
B(1)–B(2)	* 1.792(3)	* 1.782(3)	1.773(3)
B(1)–B(3)	1.773(4)	1.760(3)	1.767(3)
B(1)–B(4)	1.775(4)	1.766(3)	1.777(4)
B(1)–B(5)	1.742(4)	1.732(3)	1.744(3)
B(1)–B(10)	1.743(4)	1.741(3)	1.743(3)
B(2)–B(3)	* 1.792(3)	* 1.780(3)	1.765(3)
B(2)–B(5)	* 1.800(3)	* 1.783(3)	1.774(3)
B(2)–B(6)	* 1.733(3)	* 1.718(3)	* 1.729(3)
B(2)–B(7)	* 1.795(3)	* 1.787(3)	1.777(3)
B(3)–B(4)	1.775(4)	1.772(4)	1.774(3)
B(3)–B(7)	1.740(4)	1.742(3)	1.747(3)
B(3)–B(8)	1.748(4)	1.747(4)	1.749(3)
B(4)–B(8)	1.783(6)	1.777(4)	1.773(3)
B(4)–B(9)	1.716(4)	1.708(3)	1.709(3)
B(4)–B(10)	1.787(4)	1.765(4)	1.771(3)
B(5)–B(6)	1.782(5)	1.782(3)	* 1.800(3)
B(5)–B(10)	1.974(4)	1.966(3)	1.967(3)
B(6)–B(7)	1.785(4)	1.759(4)	* 1.789(3)
B(7)–B(8)	1.995(4)	1.973(4)	1.976(3)
B(8)–B(9)	1.782(5)	1.781(4)	1.778(4)
B(9)–B(10)	1.785(5)	1.773(4)	1.780(3)

B(2)–B(2') = * 1.692(3)

B(2)–B(6') = * 1.679(3)

(*b*) Angles in 2,2'-$(B_{10}H_{13})_2$

B(2')–B(2)–B(1)	120.5(1)	B(2')–B(2)–B(6)	121.5(1)
B(2')–B(2)–B(3)	121.5(1)	B(2')–B(2)–B(7)	125.5(1)
B(2')–B(2)–B(5)	124.5(1)		

(*c*) Angles in 2,6'-$(B_{10}H_{13})_2$

B(6')–B(2)–B(1)	119.4(1)	B(2)–B(6')–B(2')	129.7(2)
B(6')–B(2)–B(3)	121.6(2)	B(2)–B(6')–B(5')	128.1(1)
B(6')–B(2)–B(5)	123.1(2)	B(2)–B(6')–B(7')	126.4(1)
B(6')–B(2)–B(6)	121.4(2)	B(2)–B(6')–H(56')	110.6(7)
B(6')–B(2)–B(7)	126.8(2)	B(2)–B(6')–H(67')	111.7(7)

* Distances involving a *conjuncto*-linked boron atom are indicated with an asterisk.

the agreement between corresponding distances in independent clusters, and between chemically equivalent distances within a cluster, is good. The effect of the external B–B bond on the intracluster B–B distances is clearly shown however. The eight interatomic distances B(1)–B(2) and their equivalents average 1.772 Å when both borons are unsubstituted, but the four interatomic distances of this type carrying a *conjuncto*-linked boron atom average 1.787 Å. Similarly for B–B distances of the type B(2)–B(5) the averages are 1.776 and 1.791 Å, and for the B(5)–B(6) distance they are 1.780 and 1.795 Å. Thus in each case there is a lengthening of 0.015 Å in the intracluster B–B distances around the substituted boron atom. The external B–B bond lengths are 1.692(3) Å in the 2,2′ isomer and 1.679(3) Å in the 2,6′ isomer, compared with a value of 1.698(3) Å reported [47] for the 1,5′ isomer; these differences are on the borderline of significance, but may well show real differences between the substitution positions. The value reported for the intercluster bond in 1,1′-$(B_5H_8)_2$ was 1.74(6) Å.[42]

The B–H bond lengths are listed in Table 3. The terminal B–H bond lengths are in the range 1.05(3)—1.13(3) Å, whereas the B–H distances in B–H–B bridges are 1.19(3)—1.32(2) Å.

TABLE 3

Boron–hydrogen bond lengths (Å) in 2,2′-$(B_{10}H_{13})_2$ and 2,6′-$(B_{10}H_{13})_2$ with estimated standard deviations in parentheses

	2,2′ isomer	2,6′ isomer 2-substituted cluster	2,6′ isomer 6′-substituted cluster
B(1)–H(1)	1.08(3)	1.10(2)	1.07(2)
B(2)–H(2)			1.10(2)
B(3)–H(3)	1.08(3)	1.10(2)	1.09(2)
B(4)–H(4)	1.09(3)	1.07(2)	1.10(2)
B(5)–H(5)	1.07(3)	1.11(2)	1.08(2)
B(6)–H(6)	1.10(3)	1.08(2)	
B(7)–H(7)	1.07(3)	1.08(2)	1.13(2)
B(8)–H(8)	1.10(3)	1.08(2)	1.06(2)
B(9)–H(9)	1.13(3)	1.06(2)	1.07(2)
B(10)–H(10)	1.05(3)	1.06(2)	1.10(2)
B(5)–H(56)	1.28(3)	1.23(2)	1.25(2)
B(6)–H(56)	1.23(3)	1.26(2)	1.29(2)
B(6)–H(67)	1.27(3)	1.30(2)	1.30(2)
B(7)–H(67)	1.24(3)	1.26(2)	1.25(2)
B(8)–H(89)	1.28(3)	1.28(2)	1.26(2)
B(9)–H(89)	1.26(3)	1.27(2)	1.26(2)
B(9)–H(910)	1.26(3)	1.30(2)	1.32(2)
B(10)–H(910)	1.19(3)	1.27(2)	1.25(2)

The conformations of the two isomers may be defined with respect to an eclipsed conformation of C_{2v} symmetry for the 2,2′ isomer and of C_s symmetry for the 2,6′ isomer. The actual conformations are then defined by the torsion angles, 118° for B(6)–B(2)–B(2′)–B(6′) in the 2,2′ isomer and 92° for B(6)–B(2)–B(6′)–B(2′) in the 2,6′ isomer; these torsion angles represent the rotations from the eclipsed conformation about the B–B bond.

TABLE 4

Boron-11 and ^1H n.m.r. data for 2,2′-$(B_{10}H_{13})_2$ (isomer 1) in C_6D_6 solution at 23 °C

Position	$\delta(^{11}B)$/p.p.m.	$T_1(^{11}B)$/ms ($\pm$20%)	$^1J(^{11}B-^1H)$/Hz	$\delta(^1H)$/p.p.m.	$\delta(^1H)$ ($CDCl_3$, 23 °C)/p.p.m.	$\Delta\sigma$ [a]	$\Delta\sigma(B_{10}H_{14})$ [a]
1,3	14.0 ± 0.3	13.5	145 ± 10	4.09	3.67	−0.42	−0.40
6 9	*ca.* 11.1 [b]	b,c	*ca.* 170	3.46 3.51	3.80	*ca.* 0.3	0.39
5,7 8,10	0.9 ± 0.4	*ca.* 5.5 [c,d]	155 ± 15	3.17	3.13	−0.04	0.04
2	−31.6 ± 0.3	4.8				−0.44	−0.41
4	−34.5 ± 0.3	21.0	155 ± 10	1.15	0.67		
Bridging				−2.51 −2.66	1.98 2.10	0.53 0.56	0.69

[a] Shielding change $\Delta\sigma = [\delta(^1H)(CDCl_3) - \delta(^1H)(C_6D_6)]$/p.p.m. [b] Two resonances at $\delta(^{11}B)$ = 11.5 and 10.7 p.p.m. with $T_1(^{11}B)$ = 7.9 and 4.5 ms respectively distinguishable at 88 °C in $CD_3C_6D_5$ solution. [c] Mean values (see footnotes *b* and *d*). [d] Two resonances very close; apparent differentiation at 88 °C in $CD_3C_6D_5$ solution into (^{11}B) = 1.7 p.p.m. [$T_1(^{11}B)$ = 10.3 ms] and $\delta(^{11}B)$ = 0.1 p.p.m. (T_1 = 12.8 ms); however, we suspect that in this case the apparent differentiation may be an artefact.

The 32-MHz ^{11}B and ^{11}B-{^1H} n.m.r. spectra of 2,2′-$(B_{10}H_{13})_2$ and 2,6′-$(B_{10}H_{13})_2$ were very similar to those of $B_{10}H_{14}$ itself, exhibiting three groups of resonances around $\delta(^{11}B)$ = *ca.* 12, *ca.* 1, and *ca.* −33 p.p.m. It is known [41-44] that the ^{11}B shieldings of the boron atoms in a borane cluster bonded to a second borane residue by a two-electron two-centre bond are very similar to those in a cluster bonded instead to a terminal hydrogen atom but otherwise identical; analogy with $B_{10}H_{14}$ [55,56] therefore ascribes the three resonance groups above to the 1,3,6,9; 5,7,8,10; and 2,4 boron nuclei respectively.

The symmetrical 2,2′ isomer 1 should exhibit a 4 : 2 : 2 : 4 : 4 : 2 : 2 intensity pattern corresponding to B(1,3), B(6), B(9), B(5,7), B(8,10), B(2), and B(4) respectively. Of these, all should be doublets due to coupling with directly bonded hydrogen atoms, except for the singlet B(2) resonance which together with that for B(4) is therefore readily assigned (Table 4). ' Partially relaxed ' ^{11}B spectroscopy [44,52,53] at ambient temperatures differentiated the other resonances in Table 4, with the exception of the 5,7,8 and 10 resonances which were too close to be differentiated at 32 MHz, and the 6 and 9 resonances which required the narrower lines resulting from less efficient relaxation at higher temperatures for their resolution (Figure 3). The resonances in the 100-MHz ^1H-{^{11}B(broad band)} spectra (Table 4) were related to these ^{11}B resonances by selective ^1H-{^{11}B} experiments, partially overlapping resonances also being differentiated additionally by ' partially relaxed ' ^1H-{^{11}B(broad band)} spectroscopy. The ^1H assignments were confirmed by a comparison of their shielding changes on dissolution in aromatic solvents with those observed

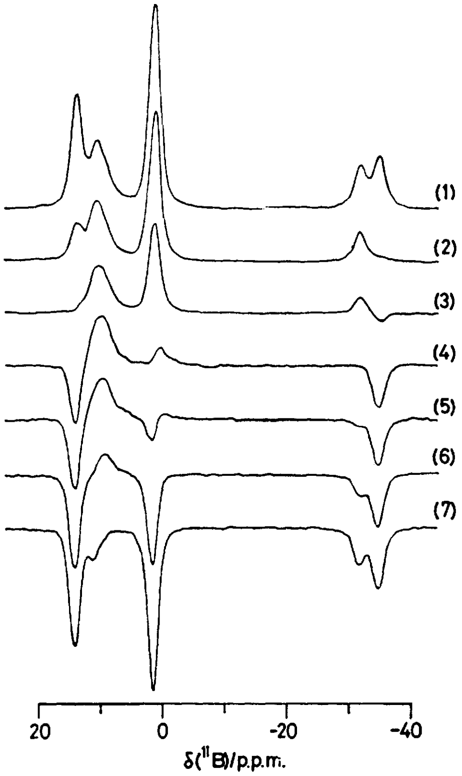

FIGURE 3 32-MHz ^{11}B-{^1H(broad band)} n.m.r. spectra of 2,2'-$(B_{10}H_{13})_2$ in $CD_3C_6D_5$ at 102 °C: (1) normal simple-pulse spectrum, (2)—(7) 'partially relaxed' spectra obtained using the 180°–τ–90° pulse sequence for various τ illustrating the successive nulling of resonances due to (2) B(4), (3) B(1,3), (4) B(5,7) and B(8,10), (5) B(2), (6) B(6), and (7) B(9)

for $B_{10}H_{14}$ itself, which thus also confirmed the assignment of the ^{11}B spectrum. Both ^1H and ^{11}B shieldings differed little from those of $B_{10}H_{14}$ which indicates that the perturbation of the electronic structure of the decaboranyl cluster by a decaboranyl substituent is small.

Of interest in these ^1H-{^{11}B} experiments on 2,2'-$(B_{10}H_{13})_2$ was the observation of fine structure in the 6 and 9 proton resonances which were shown by 'partially relaxed' spectroscopy under ^1H-{^{11}B(broad band)} conditions to consist of a triplet and a quartet (Figure 4). Consequent examination of the analogous 6,9 resonance in $B_{10}H_{14}$ showed that it was a symmetrical quartet with intensity ratios *ca.* 1 : 2 : 2 : 1 and with separations of 7.9 and 7.2 Hz for the outer and inner pairs of components respectively. In the 2,2' compound, the triplet is reasonably ascribed to the 6-proton, the additional splitting for the 9-proton resonance resulting from coupling to the single 4-proton with $^3J(^1H_t\text{–}B\text{–}B\text{–}^1H_t)$ = *ca.* 7.1 Hz, so that the two overlapping triplets appear as a quartet. The *ca.* 1 : 2 : 1 triplet structure probably arises from AX_2-type coupling to the two equivalent nearer bridging protons with $^2J(^1H_t\text{–}B\text{–}^1H_\mu)$ = *ca.* 8.2 Hz; that this splitting is due to coupling with the 1,3 or 5,7,8,10 terminal protons is discounted as this would result in noticeable second-order AB_2-type asymmetry, contrary to observation. Very few examples of resolved ^1H–^1H coupling are known in boranes and their derivatives, but the value of 8.2 Hz is similar to those observed for $^2J(^1H_t\text{–}B\text{–}^1H_\mu)$ in diborane (B_2H_6) and its derivatives (5.6—8.7 Hz),[57-59] although somewhat greater than those for *nido*-pentaborane (B_5H_9) and its derivatives (4.8—5.7 Hz).[60]

Of additional interest, and partly apparent from Figure 4, is that the longitudinal relaxation time T_1 of the 9 proton in the 2,2' compound is markedly shorter than that of the 6 and other terminal protons. It is shorter by a factor of *ca.* 2.1 at 21 °C in solvents such as C_6D_6 and $CDCl_3$ and by a somewhat smaller factor at higher temperatures, whereas in $B_{10}H_{14}$ the 6,9 protons have identical T_1's which differ by a factor of at most 1.3 from those for the other terminal protons. It may also be noted that the ^{11}B T_1 values of the 6 and 9 boron atoms in 2,2'-$(B_{10}H_{13})_2$ are also different (the factor is *ca.* 1.5 at 72 °C), although for ^{11}B there is greater variation in the T_1 values among all the skeletal environments (Table 4) and so for this and other reasons the differential behaviour may not be remarkable. We ascribe the shorter relaxation times for the nuclei in the 9 and 9' positions (and 2 and 2' positions) to rotational anisotropy. The principal molecular rotational axis and the principal intramolecular rotational axes lie close to the 2,2' boron atoms and their antipodal 9 and 9' ^{11}B and ^1H positions, whereas the other terminal protons are distributed around it at a distance of the order of 2 Å. Nuclei on the principal rotational axis of this rod-shaped molecule will experience greater effective rotational correlation times and consequently more efficient relaxation; the phenomenon is well characterized in the ^{13}C n.m.r. spectroscopy of rod-shaped hydrocarbons and their derivatives.[61,62]

The 2,6' isomer is a less symmetrical molecule and its consequently more complicated n.m.r. behaviour was more difficult to analyse at the field strengths available. At 32 MHz, none of the 14 different ^{11}B environments could be individually distinguished, even with the aid of

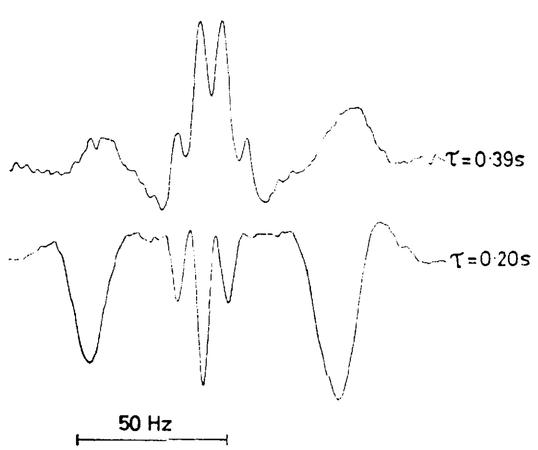

FIGURE 4 Line-narrowed 'partially relaxed' 100-MHz ^1H-{^{11}B (broad band)} n.m.r. spectra of the (1,3; 6,9; and 5,7,8,10) proton region of 2,2'-$(B_{10}H_{13})_2$ at 83 °C in $CD_3C_6D_5$ solution obtained using the 180°–τ–90° pulse sequence. The effective Y-gain is larger in the top trace

TABLE 5

Proton n.m.r. chemical shifts for 2,6′-$(B_{10}H_{13})_2$ (isomer 4) in C_6D_6 solution at 21 °C [a]

Position	δ(^{1}H)/p.p.m. 2-cluster	 6′-cluster	 $B_{10}H_{14}$
1,3	4.01	4.25	4.08
6	3.39 [b]	3.16 [c]	3.46
9	3.59 [b]		
5,7 8,10	3.14 [d] 3.37 [d]		3.09
2 4	1.10		1.06
Bridging	−2.67 −2.50 [d]	−2.18	−2.83

[a] Overlapping peaks differentiated by selective ^1H-{^{11}B} and by differential longitudinal relaxation behaviour; peaks assigned by selective ^1H-{^{11}B}, chemical shift and relaxation time analogy with 2,2′ and 6,6′ isomers, intensity comparisons, and aromatic solvent shifts. [b] Differentially assigned on basis of apparent triplet–quartet multiplicities as well as appreciably different T_1 values. [c] Assignment uncertain. [d] Resonances too close to be differentiated at 100 MHz.

'partially relaxed' spectroscopy and line-narrowing. The 100-MHz ^1H-{^{11}B(broad band)} spectra were somewhat better resolved, and comparison with the 2,2′ isomer (this work) and the 6,6′ isomer [46] together with selective ^1H-{^{11}B} and 'partial relaxation' experiments led to the ^1H assignments in Table 5 with only minor uncertainties noted in the table footnotes.

The identification of the three isomers 2,2′-, 2,6′-, and 6,6′-$(B_{10}H_{13})_2$ is critical in the preliminary postulation of mechanisms which may be involved in their formation. The 2,2′ compound is the major product from the u.v.-photolysis of $B_{10}H_{14}$,[45,48] and may be the result of initial excitation of the electrons in the highest-occupied molecular orbital of $B_{10}H_{14}$. This is principally associated with the boron atoms in the 2 and 5 positions,[63] and so other products from this reaction may therefore involve either or both of 2- and 5-substitution, although, as implied previously,[48] any equilibration of intermediate species could easily invalidate this prediction. The other two isomers that we have identified, 2,6′-$(B_{10}H_{13})_2$ and 6,6′-$(B_{10}H_{13})_2$, both arise from the thermolysis of decaborane in the presence of 6,9-bi(tetrahydrothiophen)decaborane.[46,48] These thioether–decaborane adducts are known to dissociate in solution [64] [equation (3)]. This dissociation would yield a decaboranyl species

$$B_{10}H_{12}L_2 \rightleftharpoons B_{10}H_{12}L + L \qquad (3)$$

with an electrophilic site in the 6 position which may therefore attack the electron-rich 2 position on $B_{10}H_{14}$ resulting in products with 2- and 6-substitution. However, in this case the implied ligand-hydrogen exchange remains unaccounted for, and again equilibration of intermediate species would interfere with this prediction. Obviously in both these reactions identification of the other products is important, and work on this is continuing.

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