A New Route to Isomers of Icosaborane(26), $B_{20}H_{26}$. The Use of 115.5-MHz ^{11}B and ^{11}B-{^{1}H} Nuclear Magnetic Resonance Spectroscopy for the Comparison and Characterisation of Separated Isomers and the Identification of Three Further Icosaboranes as 1,2'-, 2,5'-, and 5,5'(or 5,7')-$(B_{10}H_{13})_2$

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Irradiation of crystalline $B_{10}H_{14}$ in the beam of a 3-MeV van der Graaf generator, followed by various chromatographic separations, has been developed as a new route to several individual isomers of the *conjuncto*-borane, $(B_{10}H_{13})_2$. The high-field (115.5-MHz) ^{11}B and ^{11}B-{^{1}H(broad-band noise)} n.m.r. spectra of the previously characterised icosaboranes 2,2'-, 2,6'-, 6,6'-, and 1,5'-$(B_{10}H_{13})_2$ have been recorded and assigned. Comparison with the spectra of three new isomers isolated from the u.v. photolysis of $B_{10}H_{14}$ in cyclohexane solution and from the high-energy electron bombardment of solid $B_{10}H_{14}$ has led to further structural characterisations: two of the new isomers are identified as 1,2'- and 2,5'-$(B_{10}H_{13})_2$ and the third is 5,5'-$(B_{10}H_{13})_2$ or its *meso*-diastereoisomer 5,7'-$(B_{10}H_{13})_2$. Analytical high-pressure liquid chromatography has been used to compare the isomeric composition of mixtures of icosaboranes produced by the above routes and by the catalytic thermolysis of $B_{10}H_{14}$, and the results permit further discussion on possible mechanisms of formation of bi(*nido*-decaboranyl). The melting points of individual isomers have been determined as follows: 1,2' 139—142; 1,5' 114—115; 2,2' 178—179; 2,5' 109—111; 2,6' 154—155; 5,5'(or 5,7') 97—98; and 6,6'-$(B_{10}H_{13})_2$ 198—199 °C.

ICOSABORANE(26) is the largest of the structurally characterised boranes.[1,2] It has the bi(*nido*-decaboranyl) structure, $(B_{10}H_{13})_2$,[3-6] and may exist as eleven distinct geometric isomers.[2] These are enumerated in Figure 1 to facilitate subsequent detailed discussion. It is of interest to synthesise, isolate, and identify these various isomers both for the development of their chemistry and for an understanding of the various processes by which they are produced. Isomers already identified and structurally characterised are 6,6'-$(B_{10}H_{13})_2$,[3] 2,2'-$(B_{10}H_{13})_2$,[4] 2,6'-$(B_{10}H_{13})_2$,[5] and 1,5'-$(B_{10}H_{13})_2$.[6] Here we report a novel additional route for the synthesis of icosaborane(26) isomers together with further work on the isolation and characterisation of isomers produced by the various synthetic routes now available. The high-field (115.5-MHz) ^{11}B and ^{11}B-{^{1}H(broad-band noise)} n.m.r. spectra of the four previously characterised isomers permit a ready assignment of the resonance positions for the boron atoms involved in the inter-cluster linkages and indicate that these boron atoms are associated with a deshielding of up to *ca.* 12 p.p.m. as compared to the corresponding ^{11}B resonances in *nido*-decaborane itself. This diagnostic then permits the structural characterisation of three further separated isomers. Two of the new isomers thus identified are 1,2'- and 2,5'-$(B_{10}H_{13})_2$ and the third is 5,5'-$(B_{10}H_{13})_2$ or its *meso*-diastereoisomer 5,7'-$(B_{10}H_{13})_2$. In addition, high-pressure liquid chromatography (h.p.l.c.) has been used to make a semi-quantitative comparison of the mixtures of icosaborane isomers produced by the various preparative routes and this permits further mechanistic discussion of the mode of formation of $B_{20}H_{26}$ from $B_{10}H_{14}$.

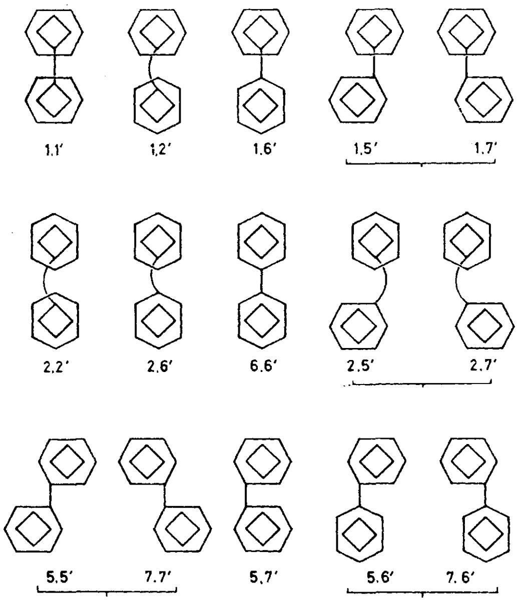

FIGURE 1 Schematic representation of the eleven geometric isomers of $(B_{10}H_{13})_2$ using the conventional numbering system of the decaborane(14) cluster (see ref. 2). The positions 5,7 (and 8,10) are chiral and intercluster bonding involving these positions leads to enantiomeric pairs as shown. The 5,7' isomer is the unique *meso*-diastereoisomer of the 5,5'- and 7,7'-$(B_{10}H_{13})_2$ enantiomeric pair

RESULTS AND DISCUSSION

Previous work from these laboratories has shown that the controlled thermolysis (with or without appropriate catalysts) and the u.v. photolysis of *nido*-decaborane, $B_{10}H_{14}$, all result in the production of mixtures of isomers of bi(*nido*-decaboranyl), $(B_{10}H_{13})_2$, as does the reaction of the decaboranyl Grignard reagent with 6-chloro-*nido*-decaborane.[2-5] We have identified 2,2'-$(B_{10}H_{13})_2$ as a component of the photolysis product mixture, 2,6'- and 6,6'-$(B_{10}H_{13})_2$ as components of the thermolysis product mixtures,[5] and have reasonably presumed that the 5,6' and 6,6' isomers are the major

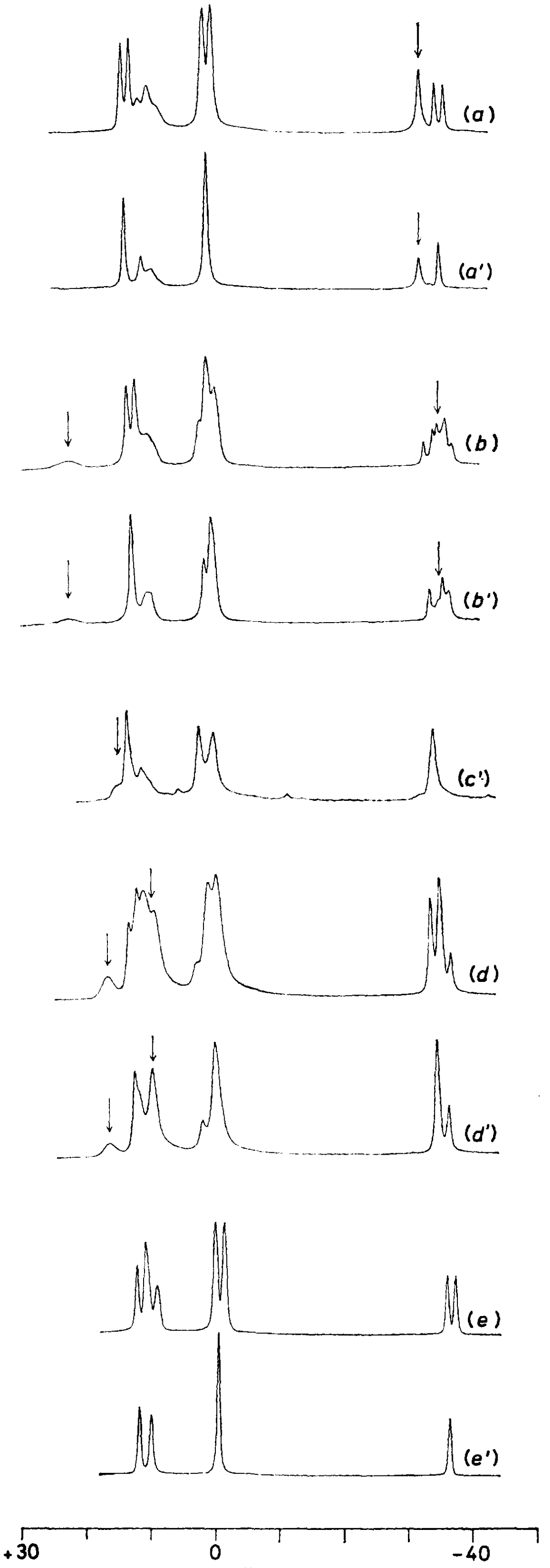

FIGURE 2 115.5-MHz ^{11}B n.m.r. spectra of the previously known isomers of $(B_{10}H_{13})_2$ in $C_6D_5CD_3$ solution: (*a*,*a*′), 2,2′-$(B_{10}H_{13})_2$; (*b*,*b*′), 2,6′-$(B_{10}H_{13})_2$; (*c*′), 6,6′-$(B_{10}H_{13})_2$; and (*d*,*d*′) 1,5′-$(B_{10}H_{13})_2$. Spectra (*e*,*e*′) are of $B_{10}H_{14}$ for comparison.

products from the Grignard reaction;[2] this last conclusion is reinforced by the more recently reported stereospecific synthesis of isomers of bi(*nido*-pentaboranyl), $(B_5H_8)_2$, using a similar route.[7] Recently, it has also been reported that the ^{60}Co γ-radiolysis of solid $B_{10}H_{14}$ also yields a mixture of isomers of $B_{20}H_{26}$, of which 1,5′-$(B_{10}H_{13})_2$ was found to be the major component.[6]

We have now developed an additional route to several icosaborane isomers, namely the high-energy electron radiolysis of solid $B_{10}H_{14}$ using the (nominal) 3-MeV beam of a van der Graaf generator. The product mixture consists principally of $B_{20}H_{26}$ isomers and unchanged decaborane. The unreacted decaborane can be removed by sublimation; column chromatography together with fractional crystallisation of the residue then readily yields the major isomer component of $B_{20}H_{26}$ as a colourless crystalline solid. Unit-cell parameters as determined by *X*-ray analysis were identical to those reported[6] for 1,5′-$(B_{10}H_{13})_2$ which thus establishes the identity of the compound. In addition, we have now subjected a sample of $B_{10}H_{14}$ to weak ^{60}Co γ-irradiation over an extended period: the h.p.l.c. trace of the $B_{20}H_{26}$ isomer mixture thus produced was essentially identical to that of the product of the van der Graaf electron irradiation experiments which implies an identical or closely related mechanism. This is reasonable as in both cases the reaction presumably occurs *via* secondary ionisation arising from the incident radiation; the predominance of the 1,5′ isomer in the product mixture may well result from the proximity of these positions as closest intermolecular contacts in the $B_{10}H_{14}$ crystal lattice.[8]

Using column chromatography and fractional crystallisation, we have now also been able to isolate, although somewhat less easily, three further pure isomers of $B_{20}H_{26}$ from the above reactions, two from the u.v. photolysis and one from the electron radiolysis. Although these were either in insufficient quantity or otherwise unsuitable for single-crystal *X*-ray diffraction analysis, we have nevertheless been able to determine their structure by means of ^{11}B and ^{11}B-{^{1}H} n.m.r. spectroscopy at relatively high field strengths.

The 115.5-MHz ^{11}B and ^{11}B-{^{1}H(broad-band noise)} spectra of the known 2,2′-, 2,6′-, 6,6′-, and 1,5′-$(B_{10}H_{13})_2$ isomers are given in Figure 2, traces (*a*)—(*d*) respectively. In the ^{11}B n.m.r. spectrum of a $(B_{10}H_{13})_2$ isomer each ^{11}B resonance will exhibit a doublet splitting of *ca.* 150 Hz arising from $^1J(^{11}B-^1H)$, except for those nuclei associated with the *conjuncto* B–B intercluster linkage which have no terminal H atoms associated with them and will therefore show no such splitting. For the 2,2′, 2,6′, and 6,6′ isomers these *conjuncto* boron resonances

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Unprimed traces (*a*), (*b*), (*d*), (*e*) refer to the normal ^{11}B spectra, primed traces (*a*′), (*b*′), (*c*′), (*d*′), (*e*′) to the ^{11}B-{^{1}H(broad-band noise)} spectra. Trace (*c*′) was obtained from an impure sample; the principal impurity was $B_{10}H_{14}$ and (*c*′) is the result of the subtraction of a spectrum of $B_{10}H_{14}$ (*e*′) from the original spectrum. Arrows denote positions of 'singlet' resonances for atoms in the B–B intercluster linkages are readily identifiable and indicate that the formation of a bi(*nido*-decaboranyl) *conjuncto* linkage results in a deshielding of up to *ca.* 12 p.p.m. for the atoms involved in the B–B intercluster bond, as compared to unsubstituted *nido*-decaborane itself. For the 1,5′ isomer the unsplit resonance associated with B(1) may be readily discerned, but that for B(5′) is not resolved. However, integration and inspection of the lineshapes at $\delta(^{11}B)$ *ca.* +10 p.p.m. shows that this resonance is at $\delta(^{11}B)$ +9.5 p.p.m. which again corresponds to a decrease in shielding upon *conjuncto* B–B bond formation, in this case of about 10 p.p.m.

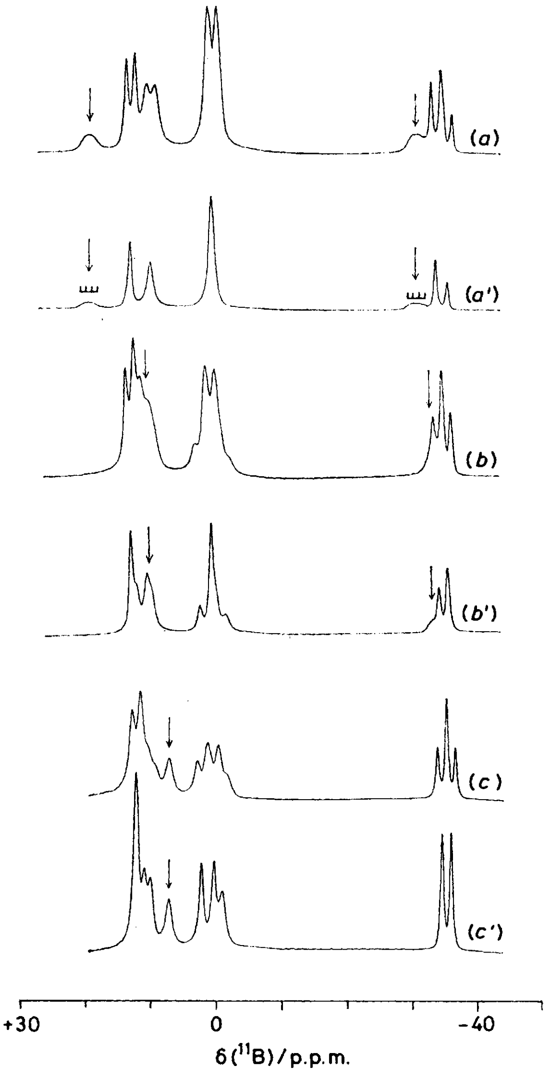

FIGURE 3 115.5-MHz ^{11}B n.m.r. spectra of (*a*,*a*′), 1,2′-$(B_{10}H_{13})_2$; (*b*,*b*′), 2,5′-$(B_{10}H_{13})_2$; and (*c*,*c*′), 5,5′(or 5,7′)-$(B_{10}H_{13})_2$. Unprimed traces (*a*), (*b*), (*c*) are the normal ^{11}B spectra, primed traces (*a*′), (*b*′), (*c*′) are spectra with $\{^1H$(broad-band noise)$\}$ decoupling. Arrows as in Figure 2

The 115.5-MHz ^{11}B and ^{11}B-$\{^1H\}$ spectra for the three previously unknown isomers are given in Figure 3. The traces (*a*,*a*′) for the first of the photolysis products show that the two *nido*-decaboranyl groups are different and that one is 2-substituted. The second *conjuncto* boron atom has a resonance at $\delta(^{11}B)$ +19.0 p.p.m. which we ascribe to 1-substitution; this implies that the isomer is 1,2′-$(B_{10}H_{13})_2$ and that there is a *conjuncto* substituent deshielding effect of *ca.* 7 p.p.m. for the B(1) nucleus in this case. In the absence of other evidence, other possibilities would be (*i*) the 2,6′ isomer, but this is known [Figure 2, traces (*b*,*b*′)], or (*ii*) the 2,5′ isomer, although this would imply a much larger *conjuncto* shift of *ca.* −20 p.p.m. and in any event is the formulation ascribed to the second new photolysis isomer [Figure 3, traces (*b*,*b*′)]. For this second new photolysis isomer the spectra again indicate different *nido*-decaboranyl groups and 2-substitution, but the other unsplit resonance for the second *conjuncto* boron atom is not separately resolved. Integration and the line shape, however, suggest that this resonance occurs at $\delta(^{11}B)$ *ca.* +10 p.p.m. and this is therefore ascribed to a B(5) atom with a *conjuncto* deshielding effect of *ca.* 10 p.p.m.; this isomer is therefore 2,5′-$(B_{10}H_{13})_2$. The simplicity of the spectra [Figure 3, traces (*c*,*c*′)] for the third new isomer, *i.e.* that isolated from the product of electron radiolysis, indicates a symmetrical compound with identical *nido*-decaboranyl groups. The two resonances of equal intensity (2 : 2) in the B(2,4) region at $\delta(^{11}B)$ −34.4 and −35.8 p.p.m., both split by one-bond coupling to ^1H, indicate that the *conjuncto* position is 1 or 5 (7), and that it is indeed B(5) (or 7) is confirmed by the unsplit resonance of intensity 2 at $\delta(^{11}B)$ +7.2 p.p.m. which is readily ascribed to B(5) (or 7) with a *conjuncto* deshielding effect of *ca.* 7.5 p.p.m. This n.m.r. evidence however cannot distinguish whether this is 5,5′-$(B_{10}H_{13})_2$ (which will in fact be the 5,5′/7,7′ racemate) or the geometrically distinct 5,7′ diastereoisomer (see Figure 1). The cleanness of the ^{11}B spectra indicates that the crystalline sample as isolated was not a mixture of all three isomers. This also tends to be confirmed by the cleanness of the 100-MHz ^1H-$\{^{11}B$(broad-band noise)$\}$ spectra in aromatic solvents, in which subtle effects due to changing anisotropic and other factors are expected to be more noticeable.[5,9,10] In particular, the two quartet resonance patterns expected for $^1H(6)$ and $^1H(9)$ arising from the couplings [5] $^2J(^1H-^1H)$ are nicely apparent (Figure 4) which we believe would probably not be the case if the sample were a mixture of the 5,5′/7,7′ and 5,7′ species.

For purposes of historical comparison, it is convenient at this point to relate these new isomers to the numbering system adopted in our initial work [2] on this system which was based on the order of t.l.c. elution. The 5,5′(or 5,7′)-$(B_{10}H_{13})_2$ isomer would appear in the same region as ‘ isomer (1) ’ [which we now know [5] to be 2,2′-$(B_{10}H_{13})_2$], whereas the 2,5′- and 1,2′-$(B_{10}H_{13})_2$ isomers would constitute the bulk of ‘ isomer (2) ’ from the photolysis experiments; the 1,5′-$(B_{10}H_{13})_2$ isomer would also be coincident with ‘ isomer (2) ’ on this basis. However, in common with other workers,[11] we have now found that h.p.l.c. offers a better method of distinguishing these isomers (*e.g.* Figure 5), and the individual structural identification of seven isomers now enables more meaningful comparisons of different product mixtures to be made.

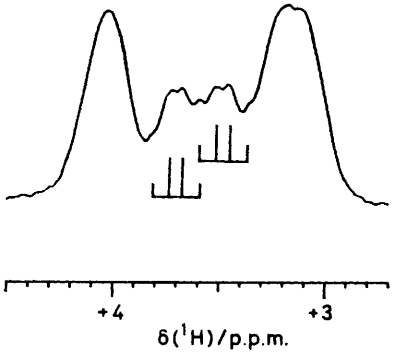

FIGURE 4 100-MHz ^1H-{^{11}B(broad-band noise)} n.m.r. spectrum of the $^1H(1,3)$, $^1H(6,9)$, and $^1H(5,7,8,10)$ resonances of the isolated crystalline sample of 5,5'(or 5,7')-$(B_{10}H_{13})_2$ in $C_6D_5CD_3$ solution at +21 °C. The quartet structures arise from couplings $^2J(^1H-^1H)$ to $^1H(2)$ or $^1H(4)$ (doublet splitting) and to ^1H-(bridge) (triplet splitting). The complete spectrum is $\delta[^1H(1,3)]$ +4.04, $\delta[^1H(6,9)]$ +3.72 and +3.51, $\delta[^1H(5,7,8,10)]$ +3.24, +3.14, and +3.07, $\delta[^1H(2,4)]$ +0.95 and +1.01, and $\delta[^1H$-(bridge)] −2.18 (intensity 1), and −2.60 (intensity 3) p.p.m. ($C_6D_5CD_3$ solution at +21 °C; assignments by selective ^1H-{^{11}B} spectroscopy)

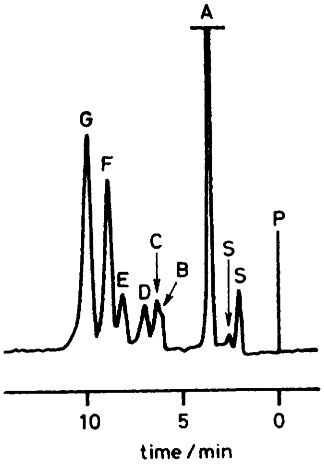

FIGURE 5 High-pressure liquid chromatogram of the hexane-soluble fraction of the product of thermolysis of $B_{10}H_{14}$ in toluene in the presence of tetrahydrothiophene, after filtration through a short silica gel column. Peaks; S, solvent and reaction by-products; P, point of injection; A, $B_{10}H_{14}$; B and C, 1,5'-$(B_{10}H_{13})_2$; D, 6,6'-$(B_{10}H_{13})_2$; E and F, two of the three as yet unidentified $B_{20}H_{26}$ isomers [1,1'-, 1,6'-, and 5,6'-$(B_{10}H_{13})_2$]; G, 1,6'-$(B_{10}H_{13})_2$

The individual retention times for the known isomers together with co-injection experiments readily led to the assignment of the h.p.l.c. peaks (Table 1). A problem arises with 1,2'-$(B_{10}H_{13})_2$ and 2,2'-$(B_{10}H_{13})_2$ which we have not yet been able to distinguish by h.p.l.c. under the (limited) conditions used so far. However, we have been able to obtain a partial separation of these two components by g.l.c. analysis and thus arrive at the estimates of their relative proportions given in Table 1, which were also in agreement with more qualitative estimations based on t.l.c. spot intensities. Another point is that, on a statistical basis, the 5,5'(or 5,7')-$(B_{10}H_{13})_2$ component that we have isolated and identified should be accompanied by an equal quantity of its diastereoisomer, but we have not been able to distinguish the separation of such a component in the h.p.l.c. traces which may suggest that the 5,5'/7,7' racemate and the 5,7'-$(B_{10}H_{13})_2$ diastereoisomer have effectively identical retention times. In any event these are not major products; in none of the product mixtures examined here did their proportion exceed *ca.* 3% and so the peak arising from the second diastereoisomer could also easily be obscured by one of the more abundant components. Of the other as yet unassigned icosaborane isomers,

TABLE 1

Approximate icosaborane(26) isomer ratios in various reaction-product mixtures

Compound[a]	M.p./°C	H.p.l.c.[b] Retention time/min	H.p.l.c.[b] k' value	T.l.c.[b] R_f value	G.l.c.[b] retention time/min	Mol % in product mixtures[c,d] U.v. photolysis	Mol % in product mixtures[c,d] Catalysed thermolysis	Mol % in product mixtures[c,d] 3-MeV e⁻ radiolysis
$B_{10}H_{13}(C_6H_{11})$	*e*	2.6	0.3	0.50	*e*	33		
$B_{10}H_{14}$	98—99	3.6	0.8	0.40	*e*	excess	excess	excess
2,2'-$(B_{10}H_{13})_2$	178—179	4.3	1.15	0.30	27.50	40		6
1,2'-$(B_{10}H_{13})_2$	139—142	4.3	1.15	0.25	28.25	19		
5,5' (and/or 5,7')-$(B_{10}H_{13})_2$	97—98	5.2	1.6	0.30	*e*		trace	3
1,5'-$(B_{10}H_{13})_2$	114—115	5.0	2.0	0.25	28.75	7	3	*ca.* 45
2,5'-$(B_{10}H_{13})_2$	109—111	6.3	2.15	0.25	28.75	34	6	⩽*ca.* 10
6,6'-$(B_{10}H_{13})_2$	198—199	6.8	2.4	*ca.* 0.1	*e*		9	4
Unknown $(B_{10}H_{13})_2$[f]	*e*	8.2	3.1	*ca.* 0.15	*e*		10	2
Unknown $(B_{10}H_{13})_2$[f]	*e*	8.9	3.45	*ca.* 0.15	*e*		28	22
2,6'-$(B_{10}H_{13})_2$	154—155	10.0	4.0	*ca.* 0.15	*e*		44	10
$(B_{10}H_{13})_2$-$B_{10}H_{12}$[g]	*e*	*e*	*e*	0.05, 0.03	*e*	present	*ca.* 20[g]	present

[a] The assignments are based on the retention times of pure known components. It is not known how many cyclohexyl $B_{10}H_{13}$ isomers may be contained within the cyclohexyldecaborane peak, whether the second 5,5'(5,7')-$(B_{10}H_{13})_2$ isomer is or is not coincident with the one isolated, or whether the third of the as yet unassigned 1,1'-, 1,6'-, 5,6'-$(B_{10}H_{13})_2$ triad is absent or is coincident with another peak. [b] For chromatographic conditions see Experimental section. [c] Based on total $(B_{10}H_{13})_2$ isomers = 100% and the assumption of identical h.p.l.c. u.v. detector response factors. [d] For reaction conditions see Experimental section. [e] Not determined in this work. [f] As yet unidentified, must be one of 1,1'-, 1,6'-, or 5,6'-$(B_{10}H_{13})_2$, presumably 1,6'- or 5,6'-$(B_{10}H_{13})_2$; see text. [g] See ref. 16.

namely 1,1′-, 1,6′-, and 5,6′-$(B_{10}H_{13})_2$, the two components (Table 1 and Figure 5) with h.p.l.c. retention times between those of 6,6′- and 2,6′-$(B_{10}H_{13})_2$ will correspond to two, although it cannot be said whether the third is absent or coincident with another component; obviously the isolation and identification of these remaining isomers would be useful here.

The relative amounts of the isomers from the photolysis, the tetrahydrothiophene-catalysed thermolysis, and the 3-MeV electron radiolysis preparations are also given in Table 1. These amounts are based on the assumption of identical response factors to a u.v. detector operating at 254 nm. There are limitations to this assumption since it is known that the u.v. absorptions vary somewhat among the various isomers,[3,6] but in the absence of sufficient quantities of pure compounds for calibration purposes the results nevertheless give a useful semi-quantitative guide.

The product from the electron radiolysis contains at least nine bi(*nido*-decaboranyl) isomers, with the 1,5′ predominating; these results are similar to those recently reported for the ^{60}Co γ-radiolysis of *nido*-decaborane, in which the detection of initially eight, and subsequently all eleven isomers was claimed,[11] but no further details were given. The production of a large number of isomers is perhaps to be expected from these two reaction processes which will not be particularly specific, presumably occurring *via* essentially random secondary ionisations arising from the incident radiation. The products may well reflect the proximity of suitable intermolecular positions in the solid decaborane lattice, modified somewhat by molecular libration in the radiation-perturbed lattice microenvironment.

The cleanest product mixture is obtained from the u.v. photolysis of $B_{10}H_{14}$ in cyclohexane solution; this produces predominantly 2,2′- and 2,5′-$(B_{10}H_{13})_2$ with smaller amounts of 1,2′- and 1,5′-$(B_{10}H_{13})_2$, although the possibility of minor amounts of the 1,1′ isomer cannot on present evidence be excluded. In addition, substantial amounts of cyclohexyldecaborane, $B_{10}H_{13}(C_6H_{11})$, are formed, of which the precise isomeric constitution has not yet been established, but which we at present believe to be predominantly 5-cyclohexyl-*nido*-decaborane.[12] A reasonable reaction scheme would involve an initial photolytic homolysis of a B–H bond to produce *nido*-decaboranyl and hydrogen radicals [equation (1)], with cyclohexyl and further decaboranyl radicals produced by abstraction from the solvent and decaborane [equations (2) and (3)]. If the $B_{10}H_{13}$ radicals produced by these processes are principally 2-, 5-, or 1-*nido*-decaboranyl then radical combination [equations (4) and (5)] would account for the products. However, on this basis the observed product ratios are puzzling: for example the contrast between the absence of the 5,5′-/7,7′- and 5,7′-$(B_{10}H_{13})_2$ isomers and the high incidence of the other *nido*-decaboran-5(and 7)-yl products. This therefore perhaps suggests considerable site selectivity, possibly together with some rapid sequential solvent cage processes among the reactions described by equations (1)—(5). In addition, further radical equilibration *via* processes such as (6) and (7) and hydroboration reactions[13,14] with any cyclohexene produced may also be of significance. We plan further experiments to investigate this system in more detail.

$$B_{10}H_{14} \xrightarrow{h\nu} B_{10}H_{13}^{\bullet} + H^{\bullet} \quad (1)$$

$$H^{\bullet} + B_{10}H_{14} \longrightarrow B_{10}H_{13}^{\bullet} + H_2 \quad (2)$$

$$H^{\bullet} + C_6H_{12} \longrightarrow C_6H_{11}^{\bullet} + H_2 \quad (3)$$

$$B_{10}H_{13}^{\bullet} + B_{10}H_{13}^{\bullet} \longrightarrow (B_{10}H_{13})_2 \quad (4)$$

$$B_{10}H_{13}^{\bullet} + C_6H_{11}^{\bullet} \longrightarrow B_{10}H_{13}(C_6H_{11}) \quad (5)$$

$$C_6H_{11}^{\bullet} + B_{10}H_{14} \longrightarrow C_6H_{12} + B_{10}H_{13}^{\bullet} \quad (6)$$

$$B_{10}H_{13}^{\bullet} + B_{10}H_{14} \longrightarrow B_{10}H_{14} + B_{10}H_{13}^{\bullet} \quad (7)$$

In the third preparative reaction, the 6,9-bis(tetrahydrothiophene)-*arachno*-decaborane-catalysed thermolysis of *nido*-decaborene in boiling toluene, the predominant product is 2,6′-$(B_{10}H_{13})_2$ together with substantial quantities of two unknown isomers which the general patterns of substituent distribution in the product mixture suggests will be the 1,6′ and the 5,6′ species; the 1,2′ and 2,2′ isomers (and probably also the 1,1′ compound) are absent and 1,5′- and 2,5′-$(B_{10}H_{13})_2$ are minor components. It therefore seems likely that some 90% of the icosaborane products from this route involve 6-substitution and therefore that they may arise *via* an initial dissociation[5] of the *arachno*-bis(ligand) decaborane catalyst [equation (8)].

$$arachno\text{-}B_{10}H_{12}L_2 \rightleftharpoons \text{‘ reactive ’ } nido\text{-}B_{10}H_{12}L + L \quad (8)$$

The ‘ reactive ’ isomer[13] of *nido*-$B_{10}H_{12}(SC_4H_8)$, *i.e.* 9-(tetrahydrothiophene)-*nido*-decaborane(12), has a vacant and therefore highly electrophilic orbital in the 6-position. The smaller amounts of products involving 5-*nido*-decaboranyl substitution may arise from reaction of the ‘ inert ’ 5-(tetrahydrothiophene)-*nido*-decaborane species,[13] or from reactions which may be related to the formation of this ‘ inert ’ isomer from the ‘ reactive ’ species.

Returning now to the ^{11}B n.m.r. spectra, the simplicity of the spectra and the resolution attained at 115.5 MHz (Figures 2 and 3) for the symmetrical 2,2′-, 5,5′(or 5,7′)-, and 6,6′-$(B_{10}H_{13})_2$ isomers and comparison with $B_{10}H_{14}$ readily leads to the assignments of the resonances among, and in some cases within, the groupings B(1,3), B(6,9), B(5,7,8,10), and B(2,4) (Table 2); the values for the 2,2′ and 6,6′ isomers are essentially in agreement with those estimated previously[3-5] by a combination of 32-MHz ^{11}B ‘ partially relaxed ’ spectroscopy and 100-MHz $^{1}H\text{-}\{^{11}B\}$ selective double resonance. Comparison with these assignments thence leads to the other assignments listed in Table 2 for the asymmetric 1,2′-, 1,5′-, 2,5′-, and 2,6′-$(B_{10}H_{13})_2$ isomers. The observed changes in chemical shifts compared to unsubstituted *nido*-decaborane are small and rarely exceed *ca.* 2 p.p.m., except for those nuclei directly involved in the *conjuncto* inter-cluster linkages. There is a general trend in deshielding compared to $B_{10}H_{14}$ upon bi(*nido*-

TABLE 2

Boron-11 n.m.r. chemical shifts obtained at 115.5 MHz, and their tentative assignments to bi(*nido*-decaboranyl) isomers [a]

<table>
<tr><th></th><th>(1,3)</th><th>(1′,3′)</th><th>(6,9)</th><th>(6′,9′)</th><th>(5,7,8,10)</th><th>(5′,7′,8′,10′)</th><th>(2,4)</th><th>(2′,4′)</th></tr>
<tr><td>$B_{10}H_{14}$</td><td>+11.7</td><td>+11.7</td><td>+9.8</td><td>+9.8</td><td>−0.4</td><td>−0.4</td><td>−36.4</td><td>−36.4</td></tr>
<tr><td>2,2′-$(B_{10}H_{13})_2$</td><td>+13.2</td><td>+13.2</td><td>+10.5</td><td>+10.5</td><td>+0.6 [b]</td><td>+0.6 [b]</td><td>−32.5(2)</td><td>−31.5(2′)</td></tr>
<tr><td></td><td></td><td></td><td>+8.9</td><td>+8.9</td><td></td><td></td><td>−35.6(4)</td><td>−35.6(4′)</td></tr>
<tr><td>6,6′-$(B_{10}H_{13})_2$</td><td>+11.8</td><td>+11.8</td><td>+14.9(6)</td><td>+14.9(6′)</td><td>+2.0(5,7)</td><td>+2.0(5′,7′)</td><td>−34.5</td><td>−34.5</td></tr>
<tr><td></td><td></td><td></td><td>+11.0(9)</td><td>+11.0(9′)</td><td>−0.2(8,10)</td><td>−0.2(8′,10′)</td><td></td><td></td></tr>
<tr><td>5,5′-$(B_{10}H_{13})_2$</td><td>+12.1</td><td>+12.1</td><td>+10.8</td><td>+10.8</td><td>+7.1(5)</td><td>+7.1(5′)</td><td>−34.5</td><td>−34.5</td></tr>
<tr><td></td><td></td><td></td><td>+10.0</td><td>+10.0</td><td>+2.0</td><td>+2.0</td><td>−36.0</td><td>−36.0</td></tr>
<tr><td></td><td></td><td></td><td></td><td></td><td>+0.2</td><td>+0.2</td><td></td><td></td></tr>
<tr><td></td><td></td><td></td><td></td><td></td><td>−1.0</td><td>−1.0</td><td></td><td></td></tr>
<tr><td>1,2′-$(B_{10}H_{13})_2$</td><td>+19.0(1) [c]</td><td></td><td colspan="2">+9.7</td><td colspan="2">+0.3</td><td>−34.0</td><td>−31.9(2′) [c]</td></tr>
<tr><td></td><td colspan="2">+12.7</td><td></td><td></td><td></td><td></td><td></td><td>−35.7(4′)</td></tr>
<tr><td>1,5′-$(B_{10}H_{13})_2$</td><td>+16.2(1)</td><td></td><td colspan="2">+9.6</td><td></td><td>+9.5(5′)</td><td>−34.4</td><td>−34.4</td></tr>
<tr><td></td><td colspan="2">+12.8</td><td></td><td></td><td></td><td>+1.8</td><td></td><td>−36.1</td></tr>
<tr><td></td><td colspan="2">+11.6</td><td></td><td></td><td colspan="2">−0.1</td><td></td><td></td></tr>
<tr><td>2,5′-$(B_{10}H_{13})_2$</td><td colspan="2">+12.0</td><td>+9.5</td><td></td><td>+0.4</td><td>+10.0(5′)</td><td>−33.4(2)</td><td>−34.4</td></tr>
<tr><td></td><td colspan="2">+12.8</td><td colspan="2">+10.3</td><td></td><td>+2.2</td><td>−35.7(4)</td><td>−35.7</td></tr>
<tr><td></td><td></td><td></td><td></td><td></td><td></td><td>−0.5</td><td></td><td></td></tr>
<tr><td></td><td></td><td></td><td></td><td></td><td></td><td>−1.7</td><td></td><td></td></tr>
<tr><td>2,6′-$(B_{10}H_{13})_2$</td><td colspan="2">+12.6</td><td></td><td>+22.5(6′)</td><td>+0.2</td><td>+1.3</td><td>−34.7(2)</td><td></td></tr>
<tr><td></td><td></td><td></td><td colspan="2">+10.4</td><td></td><td>−0.3</td><td colspan="2">−33.5</td></tr>
<tr><td></td><td></td><td></td><td colspan="2">+9.6</td><td></td><td></td><td colspan="2">−35.5</td></tr>
<tr><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td colspan="2">−36.5</td></tr>
</table>

[a] $\delta(^{11}B)$ in p.p.m. ±0.5 to low field (high frequency) of $Et_2O{\cdot}BF_3$. Dilute solutions in $C_6D_5CD_3$ at +30 °C. Where chemically different boron resonances are not resolved, the value of the conglomerate peak maximum is given. Individual specific assignments are given in parentheses after the chemical shift values where appropriate. [b] Possible differentiation in ' partial relaxation ' experiments into two resonances at $\delta(^{11}B) = +1.3$ and -0.1 p.p.m. [c] $^1J[^{11}B(1) - {}^{11}B(2')] = 105 \pm 10$ Hz resolved in spectrum.

decaboranyl) formation, and this occurs principally at the *conjuncto* positions (up to *ca.* 12 p.p.m.) or its nearest-neighbour positions (up to *ca.* 3 p.p.m.), with other minor changes which may also reflect antipodal effects, *etc.* These changes around the *conjuncto* positions may reflect a greater electron demand from a *conjuncto* B–B rather than a terminal B–H bond, but since the changes in ^{11}B shielding in these molecules will by dominated by changes in the so-called ' paramagnetic ' or excited-state term of general shielding expressions,[15] the implied changes in electron density and distribution will be rather small, probably of the order of 0.05 e^- at most for the *conjuncto* positions themselves, and *ca.* 0.01 e^- at the adjacent positions.

These shielding changes at the *conjuncto* positions are summarised in Table 3 and exhibit two interesting trends: it is apparent that the *substituted* apical (1,3 and 2,4) boron nuclei are affected least and the basal (6,9 and 5,7,8,10) ones affected most by a *conjuncto* bi(*nido*-decaboranyl) bond formation, but that the substituted apicals affect a *substituent* site most and the basals affect it least. The significance of this is not clear at present, but it indicates that there is some additional electronic interaction between the clusters, and that this may be related to the differences of up to 0.02 Å in the *conjuncto* B–B bi(*nido*-decaboranyl) bond lengths that have so far been measured.[5,6] However, it should be noted that the coupling constant $^1J[^{11}B(1)-{}^{11}B(2')]$ of *ca.* 105 Hz resolved for the *conjuncto* B–B bond in 1,2′-$(B_{10}H_{13})_2$ (Figure 3 and Table 2) is within the range expected for a normal two-electron two-centre B–B bond between atoms with approximately sp^3 hybridisation.

TABLE 3

Substituent chemical shifts $\Delta\sigma$ [a] (p.p.m.) of *nido*-decaboranyl substituted *nido*-decaborane, $(B_{10}H_{13})_2$

Position of substituent	1,3	6,9	5,7,8,10	2,4
Substituent				
1,3	*b*	*b*	−9.9	−5.4
6,9	*b*	−5.1	*b*	−1.7
5,7,8,10	−4.5	*b*	−7.6	−3.0
2,4	−7.3	−12.6	−10.4	−4.0

[a] Increase in *shielding* of a bi(*nido*-decarboranyl) *conjuncto* boron nucleus over that observed for *nido*-decaborane itself. [b] Data for 1,1′-, 1,6′-, and 5,6′-$(B_{10}H_{13})_2$ not available.

EXPERIMENTAL

General aspects of the experimental work were as described previously,[2,5] as were the thin layer chromatographic (t.l.c.) and column chromatographic techniques used. T.l.c. R_f values quoted are for plates made using silica gel (Merck, Typ 60 G) with hexane–benzene–acetic acid (75 : 24.5 : 0.5) as eluant. Gas-liquid chromatography (g.l.c.) was carried out on a Perkin-Elmer F30B instrument with a hot wire detector, using a Dexsil 300 (3% w/w on Chromosorb) column of dimensions 0.635 cm o.d. (outside diameter) × 2 m, with H_2 carrier at 45 cm^3 min^{-1}; retention times quoted are for isothermal conditions at 200 °C; samples were injected as concentrated solutions in C_6H_6. Analytical high-pressure liquid chromatography (h.p.l.c.) was carried out at ambient temperatures on a Waters Associate Gradient instrument, using a u.v. detector set at 254 nm, with a Shandon Hypersil 5-μm silica column of dimensions 4.2 mm × 250 mm and using hexane–ethyl acetate (95 : 5) as carrier at a flow-rate of 4 cm^3 min^{-1}; ideal sample size was *ca.* 0.01 cm^3 of *ca.* 5 mg cm^{-3} solutions in ethyl acetate. Crude reaction mixtures were generally filtered, in C_6H_6 solution, through a plug of silica gel (Merck, Typ 60, 0.063—0.200 mm mesh) before g.l.c. or h.p.l.c. analysis to remove sticky yellow components which were presumably polymeric species of high molecular weight. 115.5-MHz ^{11}B and ^{11}B-{^1H} n.m.r. spectra were recorded straightforwardly on $C_6D_5CD_3$ solutions at *ca.* +30 °C on a Bruker 360-MHz instrument, and

100-MHz ^1H-{^{11}B} spectroscopy was performed using a JEOL FX100 instrument using the procedures described adequately elsewhere.[3,5,10]

Photolysis of decaborane in cyclohexane solution, thermolysis in toluene solution in the presence of tetrahydrothiophene, together with the isolations of 2,2′-, 2,6′-, and 6,6′-$(B_{10}H_{13})_2$ were also essentially as described previously.[3,5] Electron- and γ-irradiation of solid decaborane, together with the isolation of 1,2′-, 1,5′-, 2,5′-, and 5,5′/7,7′(or 5,7′)-$(B_{10}H_{13})_2$ were as described below; for simplicity the descriptions presume the experimentally subsequent n.m.r. identification and h.p.l.c. comparison, as described in the Results and Discussion above, of the various isomers.

Van der Graaf 3-MeV *Electron Irradiation of* $B_{10}H_{14}$.—The best compromise between convenience of experimental technique and the optimum yield of $B_{20}H_{26}$ isomers per mole of $B_{10}H_{14}$ consumed was as follows. Samples of $B_{10}H_{14}$ (1 g, 8.2 mmol) were sealed under vacuum in Pyrex tubes (2 mm wall) of approximate dimensions 1.5 cm o.d. × 10 cm long. By shaking, the decaborane was distributed evenly along the tubes, which were then lain on a water-cooled 15 cm × 15 cm aluminium heat-sink perpendicular to the 3-MeV electron beam bath of a KS3000 van der Graaf generator. Irradiation times used were typically *ca.* 2.5 h in a beam current of 0.2 μA cm^{-2} (estimated dose *ca.* 400 Mrad) and cooling was by a stream of air at ambient temperature directed onto the sample tubes, although no major changes of product distribution with temperature were detected at temperatures below which an uncatalysed thermolytic reaction itself commences.[2] The tubes were then opened in air, the residue transferred, and the excess of decaborane (*ca.* 0.9 g per tube, 7.4 mmol, *ca.* 90% recovery) removed by sublimation. The yellow gummy residue was then taken up in C_6H_6 (20 cm^3), filtered through a small plug of silica gel (*ca.* 5 g), washed through with benzene (4 × 5 cm^3), and the liquids combined. Removal of the more volatile components under reduced pressure yielded a waxy pale yellow solid (*ca.* 50 mg) which consisted principally of icosaboranes together with some triacontaboranes[16] and further unchanged decaborane. This was then subjected to chromatographic separation and analysis as described more specifically below and in the Results and Discussion section above.

Cobalt-60 γ-*Irradiation of* $B_{10}H_{14}$.—Samples prepared as for the van der Graaf irradiation above were subjected to weak ^{60}Co γ-irradiation. After 3 months (estimated dose *ca.* 270 Mrad) the samples were opened and processed as above; h.p.l.c. analysis showed the same $B_{20}H_{26}$ product distribution as obtained for the van der Graaf irradiation, but with a somewhat smaller conversion (*ca.* 2%) as expected from the smaller radiation dose (estimated $G(B_{20}H_{26})$ *ca.* 0.3).

Isolation of $B_{20}H_{26}$ *Isomers from Particular Reaction Mixtures*.—(*a*) *From photolysis*. T.l.c. analysis of the combined products of some 20 photolytic preparations[5] (*ca.* 2 g) exhibited components at R_f 0.50, 0.40, 0.30, 0.25, and 0.15 in the estimated ratios 3 : 2 : 8 : 8 : 1. Column chromatography completely separated the components with R_f 0.50 and 0.40 which were cyclohexyldecaborane and decaborane respectively, but only partial separation of the components with R_f 0.30 and 0.25 occurred; these fractions were also monitored by g.l.c. analysis which indicated three components A, B, and C, with retention times: A 27.50 min (corresponding to t.l.c. component R_f 0.30), B 28.25 min (corresponding to t.l.c. component R_f 0.25), and C 28.75 min (also corresponding to t.l.c. component R_f 0.25). Earlier column fractions were pure in A and recrystallisation from cyclohexane ($\leqslant$3 cm^3) yielded 2,2′-$(B_{10}H_{13})_2$, m.p. 178—179 °C, as fine colourless needles (55 mg) of which an additional crop (125 mg) was obtained by fractional crystallisation of A,B,C mixtures rich in A. The mother liquors from these combined with the later fractions rich in C upon repeated fractional crystallisation from light petroleum (b.p. 60—80 °C) gave more 2,2′-$(B_{10}H_{13})_2$ as white needles (18 mg), pure C as white crystalline clumps (120 mg), and pure B as discrete white lumps (25 mg), all separated from each other by hand. Recrystallisation of B from n-pentane ($\leqslant$5 cm^3) gave 1,2′-$(B_{10}H_{13})_2$, m.p. 139—142 °C, as fine colourless blocks (20 mg), and of C from light petroleum (b.p. 60—80 °C, $\leqslant$8 cm^3) gave 2,5′-$(B_{10}H_{13})_2$, m.p. 109—111 °C, as white crystalline clumps (110 mg), together with some colourless needles. Recrystallisation of these needles from n-pentane ($\leqslant$3 cm^3) gave 1,5′-$(B_{10}H_{13})_2$, m.p. 114—116 °C (3 mg), identified as such by its *X*-ray unit-cell parameters [Found: a = 721(1), b = 1 540(3), c = 1 491(7) pm, β = 91.4(7)°. Literature:[6] a = 723.5(1), b = 1 545.3(4), c = 1 489.5(3) pm, β = 91.42(2)°].

(*b*) *From van der Graaf electron irradiation*. Removal of $B_{10}H_{14}$ by sublimation from the combined products from 20 reaction tubes (see above) yielded *ca.* 2 g of a yellow gummy residue; this was taken up in C_6H_6 (*ca.* 20 cm^3) and filtered through silica gel (*ca.* 5 g), washed through with more C_6H_6, and the liquids combined. T.l.c. analysis showed four principal components at R_f = 0.40, 0.30, 0.25, and 0.15 in approximate estimated ratio of 3 : 1 : 10 : 2 respectively, along with substantial amounts of the components with $R_f \leqslant$ *ca.* 0.05. Removal of the C_6H_6 under reduced pressure, followed by column chromatography, gave fractions which showed good separation between the more mobile components. The component at R_f = 0.40 was decaborane; the fractions of the component at R_f = 0.30 were combined, and repeated crystallisation from n-pentane ($\leqslant$*ca.* 2 cm^3) yielded 5,5′/7,7′(or 5,7′; see text)-$(B_{10}H_{13})_2$ as fine white needles (5 mg), m.p. 97—98 °C. The fractions containing the compound at R_f = 0.25 similarly yielded 1,5′-$(B_{10}H_{13})_2$ as fine colourless needles (210 mg), m.p. 114—115 °C (from pentane), again identified as such by the unit-cell parameters after recrystallisation from cyclohexane [Found: a = 721(1), b = 1 535(3), c = 1 493(3) pm, β = 91.3(1)°].

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REFERENCES

[1] N. N. Greenwood, J. D. Kennedy, and D. Taylorson, *J. Phys. Chem.*, 1978, **82**, 623.

[2] N. N. Greenwood, J. D. Kennedy, T. R. Spalding, and D. Taylorson, *J. Chem. Soc., Dalton Trans.*, 1979, 840.

[3] S. K. Boocock, N. N. Greenwood, J. D. Kennedy, and D. Taylorson, *J. Chem. Soc., Chem. Commun.*, 1979, 16.

[4] N. N. Greenwood, J. D. Kennedy, W. S. McDonald, D. Taylorson, and J. Staves, *J. Chem. Soc., Chem. Commun.*, 1979, 17.

[5] S. K. Boocock, N. N. Greenwood, J. D. Kennedy, W. S. McDonald, and J. Staves, *J. Chem. Soc., Dalton Trans.*, 1980, 790.

[6] J. W. Pinson, G. M. Brown, and L. L. Ingram, *Inorg. Chem.*, 1979, **18**, 1951.

[7] D. F. Gaines, M. W. Jorgenson, and M. A. Kulzick, *J. Chem. Soc., Chem. Commun.*, 1979, 380.

[8] A. Tippe and W. C. Hamilton, *Inorg. Chem.*, 1969, **8**, 464.

[9] T. Onak, W. Inman, H. Rosendo, E. W. Distefano, and J. Nurse, *J. Am. Chem. Soc.*, 1977, **99**, 6488.

[10] J. D. Kennedy and N. N. Greenwood, *Inorg. Chim. Acta*, 1980, **38**, 93.

[11] J. W. Pinson, R. L. Hatton, J. P. Holloman, L. L. Ingram, and G. M. Brown, *Abs. Am. Chem. Soc.—Chem. Soc. Jpn. Chem. Congr., Honolulu*, April 1979, abstract no. INOR 93; G. M. Brown, J. W. Pinson, and L. L. Ingram, *Abs. Am. Crystallogr. Assn. Winter Meeting, Hawaii*, March 1979, abstract no. PB 10; J. W. Pinson, R. L. Hatton, and J. P. Holloman, *Abs. 2nd Chem. Congr. N. Am. Continent, San Francisco* (*Las Vegas*), August 1980, abstract no. INOR 74.

[12] Unpublished work with M. J. Hails in this laboratory.

[13] E. I. Tolpin, E. Mizusawa, D. S. Becker, and J. Venzel, *Inorg. Chem.*, 1980, **19**, 1182.

[14] B. J. Meneghelli, M. Bower, N. Canter, and R. W. Rudolph, *J. Am. Chem. Soc.*, 1980, **102**, 4355.

[15] N. F. Ramsey, *Phys. Rev.*, 1950, **78**, 699; 1951, **83**, 540; 1952, **86**, 243.

[16] S. K. Boocock, N. N. Greenwood, and J. D. Kennedy, *J. Chem. Res.*, 1981, (*S*) 50.