Chemical and Electrochemical Substitution of Monocarbon Carboranes; Rationalisation of Experimental Behaviour of Derivatives of $[nido\text{-}7\text{-}CB_{10}H_{13}]^-$ and $[closo\text{-}1\text{-}CB_{11}H_{12}]^-$ †

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Controlled substitution of the monocarboranes $[nido\text{-}7\text{-}CB_{10}H_{13}]^-$, $nido\text{-}7\text{-}Me_3N\text{-}7\text{-}CB_{10}H_{12}$, and $closo\text{-}1\text{-}Me_3N\text{-}1\text{-}CB_{11}H_{11}$ has been achieved by chemical and electrochemical means. The position of boron substitution in $7\text{-}Me_3N\text{-}7\text{-}CB_{10}H_{12}$ derivatives depends on the experimental method. Chloride substitution at B(4) was achieved by electrophilic (electrochemical) methods, whereas HCl–$AlCl_3$ resulted in substitution at B(9). Substitution at B(8) was obtained through a *nido-closo-nido* sequence of oxidation and ligand addition. The compounds were structurally characterised by ^{11}B–^{11}B correlation n.m.r. spectroscopy. The experimental data were correlated with AM1 calculations.

Substitution chemistry of the monocarbon carborane species derived from $[nido\text{-}7\text{-}CB_{10}H_{13}]^-$, (**1**), and $[closo\text{-}1\text{-}CB_{11}H_{12}]^-$, (**2**), has been of interest since these species were first described through insertion reactions of RNC or CN^- substituents in derivatives of $B_{10}H_{14}$.[1,2] Although substituted derivatives of (**1**) and (**3**) are numerous, there are many compounds in which the positions of the substituents have not been established unambiguously.[1,3–5] Derivatives with substituents at C(7)[6] or in a bridge site[7] had unequivocal structures.

$$B_{10}H_{14} + RNC \longrightarrow 7\text{-}RH_2N\text{-}7\text{-}CB_{10}H_{12} \qquad (1)$$

$$[6\text{-}(NC)B_{10}H_{13}]^{2-} \xrightarrow[\text{(ii) OH}^-,\ Me_2SO_4]{\text{(i) H}^+} \underset{(\mathbf{3})}{7\text{-}Me_3N\text{-}7\text{-}CB_{10}H_{12}} \qquad (2)$$

$$\underset{(\mathbf{3})}{7\text{-}Me_3N\text{-}7\text{-}CB_{10}H_{12}} \xrightarrow[\text{or NaH}]{\text{Na, NH}_3} \underset{(\mathbf{1})}{[7\text{-}CB_{10}H_{13}]^-} \qquad (3)$$

Compounds of type (**2**), originally prepared by the disproportionation reaction (4), or by the borane insertion reactions (5) and (6),[1b,e,f,8,9] have also yielded a variety of substituted derivatives. Substituted derivatives of (**2**) and its zwitterionic analogues (**4**) and (**5**) have included compounds with substituents at C(1);[1e,10] electrophilic substitution occurred preferentially in the order B(12) > B(7)—B(11) > B(2)—B(6) by halogenation[10] or deuteriation.[9]

$$2Cs[7\text{-}CB_{10}H_{13}] \longrightarrow Cs[1\text{-}CB_9H_{10}] + Cs[1\text{-}CB_{11}H_{12}] + 2H_2 \qquad (4)$$

$$Cs[7\text{-}CB_{10}H_{13}] \xrightarrow{Et_3N\cdot BH_3} Cs[1\text{-}CB_{11}H_{12}] \qquad (5)$$

$$7\text{-}Me_3N\text{-}7\text{-}CB_{10}H_{12} \xrightarrow[\text{(ii) HCl}]{\text{(i) }Et_3N\cdot BH_3} \underset{(\mathbf{4})}{1\text{-}Me_2HN\text{-}1\text{-}CB_{11}H_{11}} \qquad (6a)$$

$$(\mathbf{4}) \xrightarrow{Me_2SO_4} \underset{(\mathbf{5})}{1\text{-}Me_3N\text{-}1\text{-}CB_{11}H_{11}} \qquad (6b)$$

In this work we have examined substitution reactions by chemical and electrochemical methods, and have prepared a number of new boron-substituted carboranes. We have established unambiguously the structures of these and a number of known derivatives through two-dimensional ^{11}B–^{11}B n.m.r. spectra. We have correlated the experimental behaviour with AM1 calculations.

The AM1 calculations have advantages over other methods in that the computational time involved for relatively complex species is short (compared with, for example, *ab initio* methods with high-quality basis sets).[11–14] The earlier MNDO method has been used recently to interpret u.v. photoelectron spectroscopic measurements on icosahedral dicarbaboranes.[15] Some of the weaknesses of the MNDO methods include a failure to reproduce hydrogen bonds, energies that are too positive in crowded molecules, and a tendency to overestimate repulsions between atoms which are separated approximately by their van der Waals distances. Some of these difficulties may be obviated by the AM1 method, and since it has been recently parametrised for B,[14] calculations have been carried out using these parameters. These results are most valid when applied to a series of compounds on a comparative basis. They are not intended to be considered as 'stand-alone' calculations on individual compounds.

Experimental

Reagents and Starting Materials.—Solvents were dried by standard methods [CH_2Cl_2, CaH_2, tetrahydrofuran (thf), sodium–benzophenone]. Hydrochloric acid and acetic acid were of analytical grade and were used as supplied. The compounds $7\text{-}Me_3N\text{-}7\text{-}CB_{10}H_{12}$,[1f] $1\text{-}Me_2HN\text{-}1\text{-}CB_{11}H_{11}$,[1f] $1\text{-}Me_3N\text{-}1\text{-}CB_{11}H_{11}$,[1f] $9\text{-}HO_2C\text{-}7\text{-}Me_3N\text{-}7\text{-}CB_{10}H_{11}$,[1e] $9\text{-}OC\text{-}7\text{-}Me_3N\text{-}7\text{-}CB_{10}H_{10}$,[1e] and $[N(PPh_3)_2]Cl$[16] were prepared by the published methods.

Electrochemical Syntheses.—Preliminary studies of electrochemical substitution were carried out in a two-compartment cell separated by Nafion ion-exchange membrane. Platinum electrodes were used, and the potential of the anode was controlled by a potentiostat (E.G. & G, Ltd., Model 273) and referenced to Ag–AgCl. Bulk electrochemical reactions were performed under a nitrogen atmosphere in an undivided cell using a two-phase system. The anodic reaction occurred in the dichloromethane phase, which contained the phase-transfer reagent $[N(PPh_3)_2]Cl$. The cathodic reaction occurred in the aqueous phase containing hydrochloric acid. A total charge of 2

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† *Non-S.I. units employed:* cal = 4.184 J, eV ≈ 1.60×10^{-19} J.

electron equivalents was applied at low constant current using a Weir 2000 digital power supply.

N.M.R. Spectra.—These were recorded on Bruker WM 250 and WH 360 spectrometers (^{1}H, 250 and 360; ^{11}B, 80.2 and 115.5 MHz) on solutions in CD_3CN. Chemical shifts are quoted as positive to high frequency of the reference standards $SiMe_4$ or $Et_2O{\cdot}BF_3$.

Mass Spectra.—These were recorded on an A.E.I. MS9 spectrometer.

Electrochemical Preparation of 4-Cl-7-Me_3N-7-$CB_{10}H_{11}$ (**6**).—Compound (**3**) (0.38 g, 2.0 mmol) and [N(PPh_3)$_2$]Cl (1.2 g, 2.0 mmol) were placed in the cell together with CH_2Cl_2 (80 cm^3) and concentrated aqueous HCl (80 cm^3). After 386 C of charge had been passed, the CH_2Cl_2 layer was separated and solvent removed *in vacuo*. Thin-layer chromatographic (t.l.c.) analysis of the product on silica (eluant CH_2Cl_2) showed a major product (R_f 0.3) and traces of starting material (R_f 0.5). The phase-transfer electrolyte [N(PPh_3)$_2$]Cl and impurities were removed by column chromatography on SiO_2 to yield 4-Cl-7-Me_3N-7-$CB_{10}H_{11}$ (0.3 g, 67%) (Found: C, 21.3; H, 8.9; Cl, 15.7; N, 6.2. Calc. for $C_4H_{20}B_{10}ClN$: C, 21.3; H, 8.9; Cl, 15.8; N, 6.2%). The high-resolution mass spectrum showed a group of ions with a highest-mass cut-off at *m/z* 227 corresponding to the ion [$^{11}B_{10}{}^{12}C_4{}^1H_{18}{}^{14}N^{37}Cl$]$^+$ (loss of 2 H from the parent ion).

Electrochemical Chlorination of 1-Me_2HN-1-$CB_{11}H_{11}$ (**4**).—Owing to the low solubility of compound (**4**) in CH_2Cl_2, this reaction was performed in glacial acetic acid. Compound (**4**) (0.22 g, 1.0 mmol) was dissolved in acetic acid (50 cm^3) to which was added concentrated HCl (50 cm^3). After 2 electron equivalents of charge had been passed the acids were removed under vacuum to give the product 12-Cl-1-Me_2HN-1-$CB_{11}H_{10}$ (Found: C, 16.3; H, 7.6; Cl, 16.2; N, 6.3. Calc. for $C_3H_{17}B_{11}ClN$: C, 16.3; H, 7.7; Cl, 16.3; N, 6.3%). The mass spectrum showed ions at *m/z* 221 and 187 corresponding to [$^{12}C_3{}^1H_{17}{}^{14}N^{10}B_2{}^{11}B_9{}^{35}Cl$]$^+$ and [$^{12}C_3{}^1H_{18}{}^{14}N^{10}B_2{}^{11}B_9$]$^+$, and at *m/z* 235 and 200 corresponding to [$^{12}C_4{}^1H_{18}{}^{14}N^{10}B_3{}^{11}B_8{}^{37}Cl$]$^+$ and [$^{12}C_4{}^1H_{18}{}^{14}N^{10}B_2{}^{11}B_9$]$^+$.

Electrochemical Chlorination of 1-Me_3N-1-$CB_{11}H_{11}$ (**5**).—By the same method compound (**5**) (0.69 g, 3.0 mmol) was electrolysed to give the product 12-Cl-1-Me_3N-1-$CB_{11}H_{10}$ (Found: C, 20.4; H, 8.1; Cl, 15.2; N, 6.0, Calc. for $C_4H_{19}B_{11}ClN$: C, 20.4; H, 8.1; Cl, 15.1; N, 6.0%). The mass spectrum showed a group of ions with a mass cut-off at *m/z* 238 (molecular ion) and the ion at *m/z* 234 corresponded to [$^{12}C_4{}^1H_{19}{}^{14}N^{10}B_3{}^{11}B_8{}^{35}Cl$]$^+$.

Reaction of 4-Cl-7-Me_3N-7-$CB_{10}H_{11}$ (**6**) *with* $Et_3N{\cdot}BH_3$.—Compound (**6**) (0.6 g, 3.0 mmol) and $Et_3N{\cdot}BH_3$ (0.9 cm^3, 6.0 mmol) were heated at 200 °C for 5 h. The products were identified by their ^{1}H and ^{11}B n.m.r. spectra.

Preparation of 9-Cl-7-Me_3N-7-$CB_{10}H_{11}$ (**7**).—Compound (**3**) (0.5 g, 2.6 mmol) and anhydrous $AlCl_3$ (0.347 g, 2.6 mmol) were placed in a vessel (250 cm^3) fitted with a greaseless stopcock which was evacuated. Dry CS_2 was condensed in, and the mixture warmed to room temperature to form a suspension. Gaseous HCl (1.23 g, 33.8 mmol) was condensed in, the mixture warmed to 20 °C and stirred for 24 h. The evolved gas and solvent were removed *in vacuo*. T.l.c. analysis on SiO_2 showed two products; the major component (R_f 0.7) was separated from the minor component (R_f 0.58) by column chromatography on SiO_2 to yield 9-Cl-7-Me_3N-7-$CB_{10}H_{11}$ (0.32 g, 55%) (Found: C, 22.0; H, 9.4; Cl, 15.4; N, 6.2. $C_4H_{20}B_{10}ClN$ requires C, 21.3; H, 8.9; Cl, 15.7; N, 6.2%). The mass spectrum showed a group of ions with a mass cut-off at *m/z* 227, corresponding to the ion [$^{11}B_{10}{}^{12}C_4{}^1H_{18}{}^{14}N^{37}Cl$]$^+$. The minor component was an isomer mixture, although probably predominantly 6,9-Cl_2-7-Me_3N-7-$CB_{10}H_{10}$ (Found: C, 20.8; H, 7.3; Cl, 22.8; N, 5.1. $C_4H_{19}B_{10}Cl_2N$ requires C, 18.5; H, 7.3; Cl, 27.3; N, 5.4%).

Preparation of 9-Cl-1,4,5,6,10-D_5-7-Me_3N-7-$CB_{10}H_6$ (**8**).—A reaction was carried out under similar conditions to that for compound (**7**) except that DCl was used. T.l.c. gave components with similar R_f values and yields [Found: C, 21.4; H(D), 8.6; Cl, 15.4; N, 6.0. $C_4H_{15}B_{10}ClD_5N$ requires C, 20.8; H(D). 10.9; Cl, 15.4; N, 6.1%]. The positions of deuteriation were obtained from the ^{11}B n.m.r. spectra. The mass spectra showed a cut-off at *m/z* 230, corresponding to loss of D_2 from the parent ion. The minor component was similar to that from the previous reaction.

Preparation of [NMe_4][8-HO-7-$CB_{10}H_{12}$] (**9**).—Compound (**3**) (0.5 g, 2.6 mmol) and sodium hydride (2.1 g, 87.5 mmol) (washed with dry Et_2O) were refluxed in dry thf for 24 h. The cooled solution was filtered in a nitrogen-filled glove-box. Solvent was removed *in vacuo*. The ^{11}B n.m.r. spectrum, at this stage, showed the boron product to be [2-$CB_{10}H_{11}$]$^-$. Addition of water and precipitation with NMe_4Cl gave a quantitative yield of the *product* (t.l.c. on SiO_2 eluted with 25% MeCN–75% CH_2Cl_2 showed a single component, R_f 0.4). The product was identified by its ^{11}B n.m.r. spectrum (Found: C, 26.8; H, 11.3; N, 6.1. $C_5H_{25}B_{10}NO$ requires C, 26.9; H, 11.3; N, 6.3%).

Preparation of 8-Et_3N-7-Me_3N-7-$CB_{10}H_{10}$ (**10**).—To a solution of compound (**3**) (0.25 g, 1.31 mmol) in dry thf (25 cm^3) was added NEt_3 (0.55 cm^3, 3.93 mmol) and a solution in thf of Tl($OCOCF_3$)$_3$ (0.71 g, 1.31 mmol). The dark red-brown mixture was refluxed for 24 h, cooled, filtered, and solvent removed *in vacuo*. T.l.c. (SiO_2, CH_2Cl_2) showed one major component (R_f 0.5) and several minor impurities; the *product* was separated by column chromatography on SiO_2 using CH_2Cl_2, to yield 0.15 g (40%) (Found: C, 40.9; H, 11.4; N, 9.8. $C_{10}H_{34}B_{10}N_2$ requires C, 41.3; H, 11.8; N, 9.6%). The mass spectrum showed no molecular ion. A group of ions with mass cut-off at *m/z* 191 corresponded to [$Me_3NCB_{10}H_{10}$]$^+$

Calculations.—The AM1[13,14] calculations were performed using the MOPAC program (version 2*, Quantum Chemistry Program Exchange no. 455) supplied by Dr. J. J. P. Stewart on a DEC Vax model 11/785 computer system. Symmetry constraints were not applied, and full geometry optimisations were obtained. Bond indices were printed for some compounds. Graphic presentation of input parameters, optimised geometries, and charge distributions was achieved by means of the INTERCHEM program (Dr. P. Bladon, Interprobe Chemical Services).

Results and Discussion

Preparations.—The monocarborane derivative 7-Me_3N-7-$CB_{10}H_{12}$ (**3**), whose correlation spectroscopy (COSY) ^{11}B–^{11}B n.m.r. spectrum is shown in Figure 1, can be chlorinated electrochemically using an undivided cell, provided that anodic and cathodic reactions are separated in a two-phase system. This was conveniently achieved by using solutions of the carborane in dichloromethane which contained a phase-transfer chloride {[N(PPh_3)$_2$]Cl} for the anodic reaction. The cathodic reaction was allowed to occur in the aqueous phase (concentrated HCl). The major product of the anodic chlorination was 4-Cl-7-Me_3N-7-$CB_{10}H_{11}$ (**6**) (Figure 2), and

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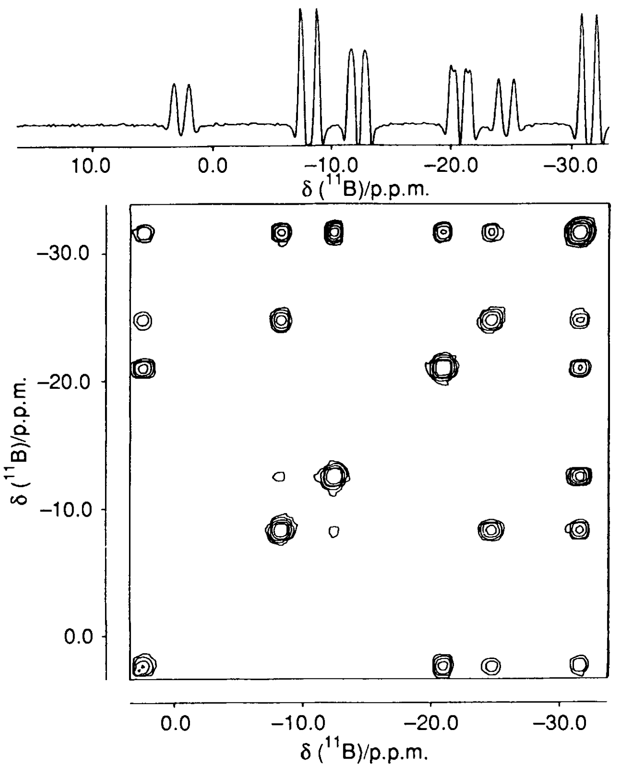
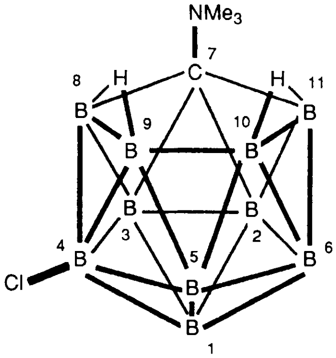


Figure 1. 115.5-MHz ^{11}B and COSY n.m.r. spectra of 7-Me_3N-7-$CB_{10}H_{12}$



B = B–H except for B(4)

Figure 2. Structure of 4-Cl-7-Me_3N-7-$CB_{10}H_{11}$

its structure was unambiguously established by ^{11}B–^{11}B COSY n.m.r. spectroscopy (Figure 3).

$$\underset{(3)}{7\text{-}Me_3N\text{-}7\text{-}CB_{10}H_{12}} + 2Cl^- \longrightarrow \underset{(6)}{4\text{-}Cl\text{-}7\text{-}Me_3N\text{-}7\text{-}CB_{10}H_{11}} + HCl + 2e^- \quad (7)$$

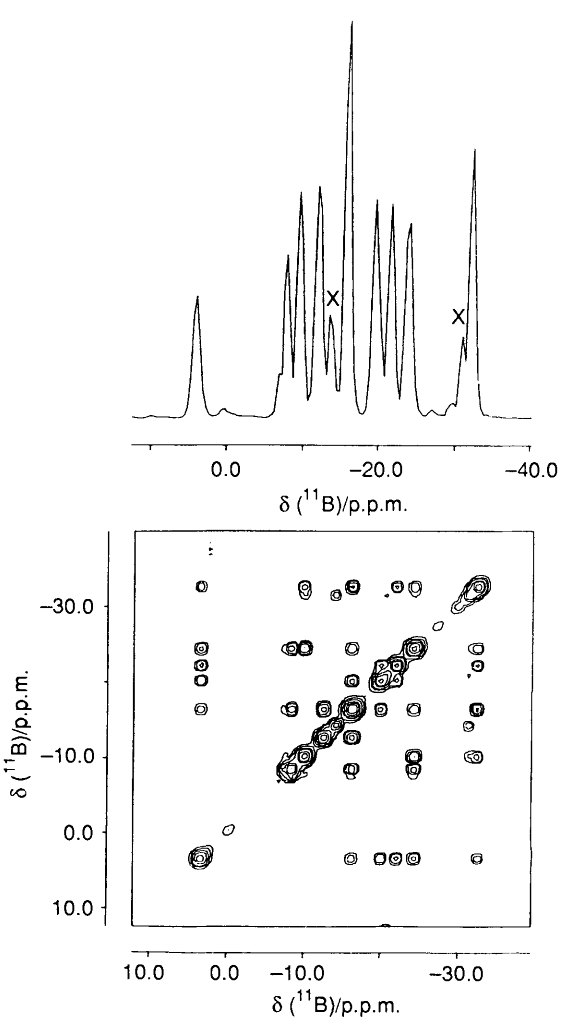
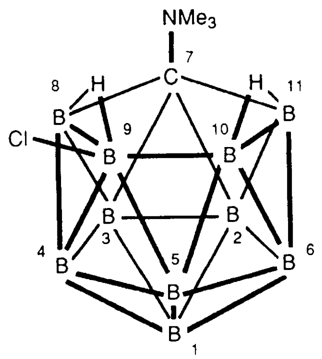


Figure 3. 115.5-MHz ^{11}B-{^1H} and COSY n.m.r. spectra of 4-Cl-7-Me_3N-7-$CB_{10}H_{11}$ (x = impurity)

Several substitution reactions of 7-Me_3N-7-$CB_{10}H_{12}$ under Friedel–Crafts conditions have been examined. When (3) was treated with HCl in the presence of $AlCl_3$, electrophilic-induced nucleophilic chlorination occurred to yield 9-Cl-7-Me_3N-7-$CB_{10}H_{11}$ (7) (Figure 4) as the major product, with a minor component of the disubstituted species, 6,9-Cl_2-7-Me_3N-7-$CB_{10}H_{10}$. The position of substitution in (7) was again unequivocally established by ^{11}B–^{11}B COSY n.m.r. spectroscopy (Figure 5). When DCl in the presence of $AlCl_3$ was used, deuterium substitution occurred in addition to chlorination. Only the terminal positions 1,4,5,6, and 10 were deuteriated in (8), the other terminal and bridge sites remaining protonated, and a similar dichlorinated by-product was also obtained. Friedel-Crafts alkylation (RCl,$AlCl_3$) led to a mixture of polyalkylated products which were not fully characterised.

Although it had been reported earlier that compound (1) was obtained from the reaction of (3) with sodium hydride, we have found that the reaction is significantly more complex, and the products depend on the conditions of the reaction. At low temperatures the initial product is the deprotonated species [7-Me_3N-7-$CB_{10}H_{11}$]$^-$, but after reflux and work-up the isolated products were [2-$CB_{10}H_{11}$]$^-$ and [8-HO-7-$CB_{10}H_{12}$]$^-$ (9), whose structure (Figure 6) was fully characterised by ^{11}B–^{11}B COSY n.m.r. spectroscopy (Figure 7). We also confirmed that the initial deprotonated product reacted with oxalyl chloride to yield 9(8?)-HO_2C-7-Me_3N-7-$CB_{10}H_{11}$, which was dehydrated to 9(8?)-OC-7-Me_3N-7-$CB_{10}H_{10}$. The COSY technique still resulted in some ambiguity in the position of substitution in these compounds.

Substitution at the 8 position was also achieved by an oxidation–ligand addition reaction of compound (3) by thallium trifluoroacetate in the presence of triethylamine, and the structure (Figure 8) confirmed by ^{11}B–^{11}B COSY n.m.r. spectroscopy (Figure 9).



B = B–H except for B(9)

Figure 4. Structure of 9-Cl-7-Me_3N-7-$CB_{10}H_{11}$

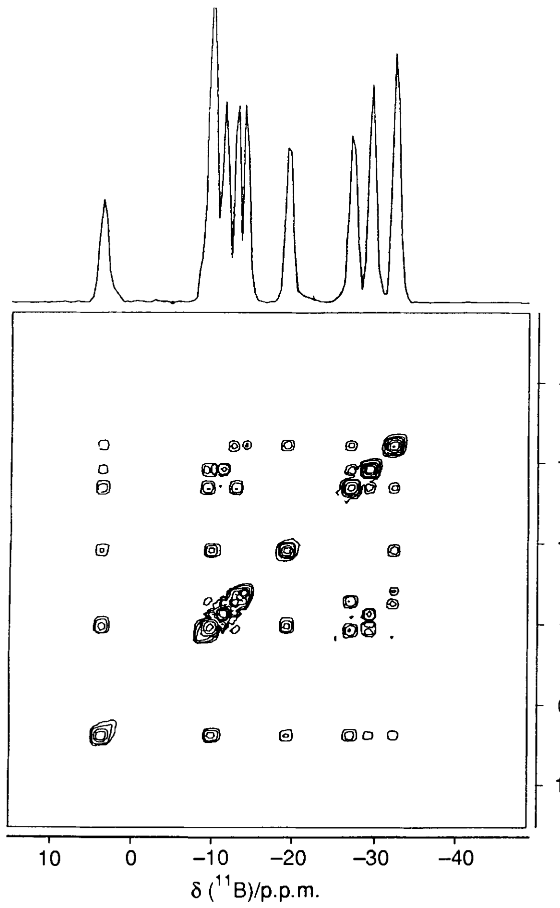
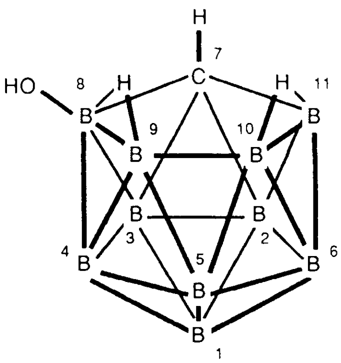


Figure 5. 115.5-MHz ^{11}B-{^1H} and COSY n.m.r. spectra of 9-Cl-7-Me_3N-7-$CB_{10}H_{11}$

$$7\text{-}Me_3N\text{-}7\text{-}CB_{10}H_{12} + Tl^{3+} + NEt_3 \longrightarrow \underset{\mathbf{(10)}}{8\text{-}Et_3N\text{-}7\text{-}Me_3N\text{-}7\text{-}CB_{10}H_{10}} + 2H^+ + Tl^+ \quad (8)$$

We have re-examined the preparation of compound (**4**) from (**3**) through its reaction with $Et_3N{\cdot}BH_3$.[1f,8] The ^1H and ^{11}B n.m.r. spectra of the reaction products indicated that the reaction was more complex than had been implied in earlier publications, and that demethylation of the NMe_3 group was accompanied by the formation of the $[NMeEt_3]^+$ cation [equation (9)].



B = B–H except for B(8)

Figure 6. Structure of $[8\text{-}HO\text{-}7\text{-}CB_{10}H_{12}]^-$

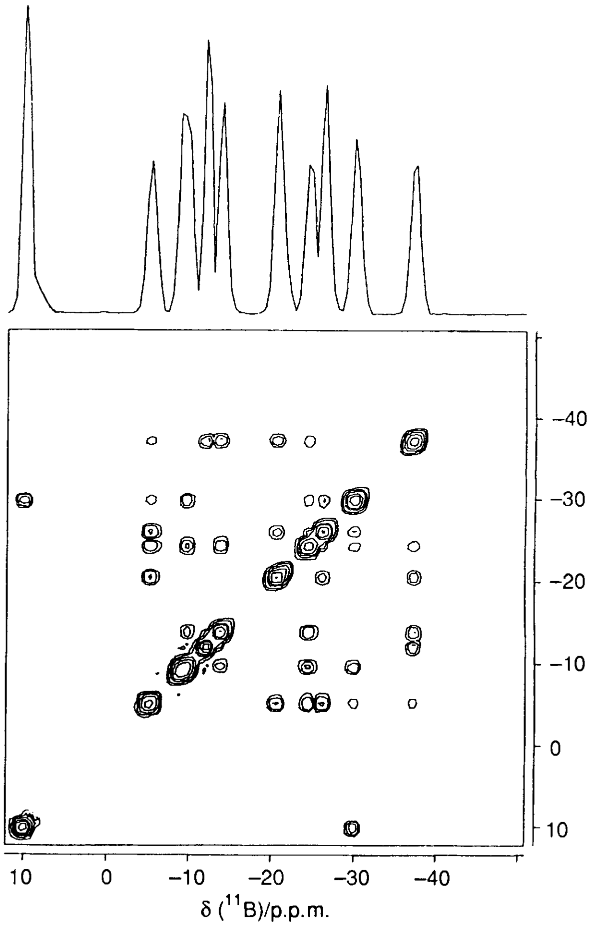
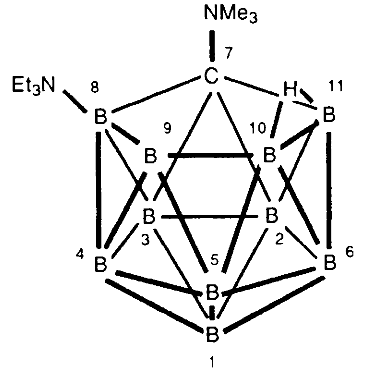


Figure 7. 115.5-MHz ^{11}B-{^1H} and COSY n.m.r. spectra of $[8\text{-}HO\text{-}7\text{-}CB_{10}H_{12}]^-$

$$7\text{-}Me_3N\text{-}7\text{-}CB_{10}H_{12} + Et_3N{\cdot}BH_3 \longrightarrow [NMeEt_3]^+[1\text{-}Me_2N\text{-}1\text{-}CB_{11}H_{11}]^- + 2H_2 \quad (9)$$

In an attempt to synthesise 7-Cl-substituted derivatives of (**4**) and (**5**), (**6**) was similarly treated with $Et_3N{\cdot}BH_3$. No chlorine-substituted *closo*-carboranes were isolated, and only products similar to those of reaction (9) were observed [equation (10)].

$$4\text{-}Cl\text{-}7\text{-}Me_3N\text{-}7\text{-}CB_{10}H_{11} + Et_3N{\cdot}BH_3 \longrightarrow [NMeEt_3]^+[1\text{-}Me_2N\text{-}1\text{-}CB_{11}H_{11}]^- + H_2 + HCl \quad (10)$$



B = B–H except for B(8)

Figure 8. Structure of 8-Et_3N-7-Me_3N-7-$CB_{10}H_{10}$

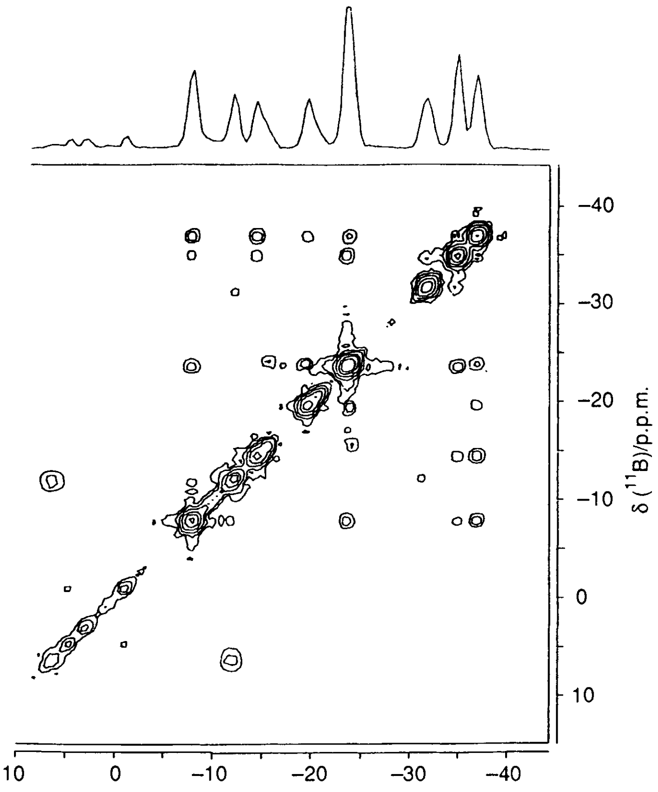


Figure 9. 115.5-MHz ^{11}B-{^{1}H} and COSY n.m.r. spectra of 8-Et_3N-7-Me_3N-7-$CB_{10}H_{10}$

Chlorination of compounds (**4**) and (**5**) was achieved electrochemically, to give 12-Cl-substituted products [equations (11) and (12)].

$$1\text{-}Me_3N\text{-}1\text{-}CB_{11}H_{11} + 2Cl^- \xrightarrow[-2e^-]{MeCO_2H} 12\text{-}Cl\text{-}1\text{-}Me_3N\text{-}1\text{-}CB_{11}H_{10} + HCl \quad (11)$$

$$1\text{-}Me_2HN\text{-}1\text{-}CB_{11}H_{11} \xrightarrow[MeCO_2H]{2Cl^-, -2e^-} 12\text{-}Cl\text{-}1\text{-}Me_2HN\text{-}1\text{-}CB_{11}H_{10}\ (\text{major}) + 12\text{-}Cl\text{-}1\text{-}Me_3N\text{-}1\text{-}CB_{11}H_{10}\ (\text{minor}) \quad (12)$$

Structural Characterisation by N.M.R. Spectroscopy.—The ^{11}B-{^{1}H} and ^{1}H-{^{11}B, selective} n.m.r. data for 7-Me_3N-7-$CB_{10}H_{12}$ and its substituted derivatives are presented in Table 1. The assignments, which are unambiguous for most of the compounds examined, are based on considerations of the COSY coupling correlations together with bridge-hydrogen locations. These were deduced from fine structure (on line narrowing) or broadening of ^{11}B resonances, or by decoupling specific boron environments in the ^{1}H-{^{11}B, selective} spectra. In the cases of 9-OC-7-Me_3N-7-$CB_{10}H_{10}$ and 9-HO_2C-7-Me_3N-7-C-$B_{10}H_{11}$ the data were not sufficiently good completely to remove all ambiguity, and it is just possible that the position of substitution was at B(8).

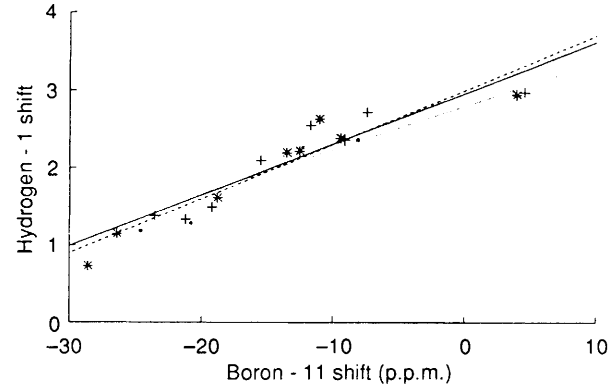


Figure 10. δ(^{11}B)–δ(^{1}H) correlations for 7-Me_3N-7-$CB_{10}H_{12}$ (□), 4-Cl-7-Me_3N-7-$CB_{10}H_{11}$ (+), and 9-Cl-7-Me_3N-7-$CB_{10}H_{11}$ (*)

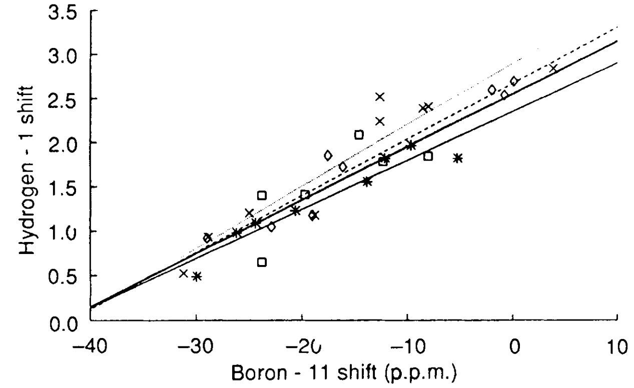


Figure 11. δ(^{11}B)–δ(^{1}H) correlations for [8-HO-7-$CB_{10}H_{12}$], (*), 8-Et_3N-7-Me_3N-7-$CB_{10}H_{10}$ (□), 9-HO_2C-7-Me_3N-7-$CB_{10}H_{11}$ (×), and 9-OC-7-Me_3N-7-$CB_{10}H_{10}$ (◇)

The ^{11}B–^{1}H chemical shift correlations are plotted in Figures 10 and 11. The slopes for the compounds (**3**), (**6**), (**7**), and (**11**) are close to 11.5, whereas the compounds with only one bridge hydrogen [(**10**) and (**12**)] or the anionic (**9**) have slopes up to near 18.5.

The ^{11}B and ^{1}H n.m.r. data for 1-Me_3N-1-$CB_{11}H_{11}$ and its derivatives are presented in Table 2. The assignment of their structures is straightforward, and is based on both literature assignments and COSY data.

AM1 *Calculations.*—Calculations were performed on a number of neutral and anionic derivatives of $[7\text{-}CB_{10}H_{13}]^-$ (**1**) and $[1\text{-}CB_{11}H_{12}]^-$ (**2**), in order to understand the factors governing the substitution in these systems. To simplify the calculations, the substituent at C(7) or C(1) was chosen to be NH_3 or $[NH_2]^-$.

Heats of formation and ionisation potentials. The heats of formation and ionisation potentials calculated by the AM1 method are presented in Table 3.

The heats of formation of the isomers 4-Cl-7-H_3N-7-$CB_{10}H_{11}$ and 9-Cl-7-H_3N-7-$CB_{10}H_{11}$ differed by less than 1 kcal mol^{-1}, consistent with the experimental preparation of both isomers of the 7-Me$_3$N species. However the heat of formation of 9-OC-7-H$_3$N-7-CB$_{10}$H$_{10}$ was 15 kcal mol^{-1} more stable than 8-OC-7-H$_3$N-7-CB$_{10}$H$_{10}$, thus providing further support for assigning the structure of the observed compound as 9-OC-7-Me$_3$N-7-CB$_{10}$H$_{10}$. Ionisation energies of C-substituted neutral species were all substantially larger than those of the anionic derivatives, and values in excess of 9 eV indicate substantial oxidative stability. Indeed, attempts to obtain electrochemical oxidation waves in cyclic voltammetric experiments were unsuccessful. However, the ionisation energy of the deprotonated species [7-H$_3$N-7-CB$_{10}$H$_{11}$]$^-$ is lower than that of [BH$_4$]$^-$,[17]

Table 1. N.m.r. data for derivatives of 7-Me$_3$N-7-CB$_{10}$H$_{12}$

Compound	Assignment	Rel. intensity	δ(^{11}B)[a]	δ(^{1}H)[b]
7-Me$_3$N-7-CB$_{10}$H$_{12}$	5	1 BH	2.6	2.50
	2, 3	2 BH	8.1	2.35
	8, 11	2 BH	−12.3	2.25
	9, 10	2 BH[c]	−20.8	1.28
	1	1 BH	−24.6	1.18
	4, 6	2 BH	−31.4	0.45
	Me$_3$N	9 H		3.12
	8–9, 10–11	2 BHB		−3.50
4-Cl-7-Me$_3$N-7-CB$_{10}$H$_{11}$	5	1 BH	4.5	2.96
	3	1 BH	−7.4	2.71
	2	1 BH	−9.1	2.35
	8	1 BH	−11.7	2.54
	4, 11	1 BCl, 1 BH	−15.5	2.09
	9	1 BH	−19.2	1.49
	10	1 BH	−21.2	1.33
	1	1 BH	−23.5	1.38
	6	1 BH	−31.6	0.52
	Me$_3$N	9 H		3.15
	8–9	1 BHB		−3.47
	10–11	1 BHB		−2.76
9-Cl-7-Me$_3$N-7-CB$_{10}$H$_{11}$	5	1 BH	3.9	2.93
	3, 9	1 BH, 1 BCl	−9.4	2.37
	8	1 BH	−11.0	2.62
	2	1 BH	−12.5	2.21
	11	1 BH	−13.5	2.19
	10	1 BH	−18.8	1.61
	1	1 BH	−26.4	1.14
	4	1 BH	−28.6	0.72
	6	9 H	−31.6	0.48
	Me$_3$N	1 BHB		3.14
	8–9	1 BHB		−1.54
	10–11			−3.08
9-Cl-1,4,5,6,10-D$_5$-7-Me$_3$N-7-CB$_{10}$H$_6$	5	1 BD	3.9	2.37
	3, 9	1 BH, 1 BCl	−9.4	2.62
	8	1 BH	−11.0	2.21
	2	1 BH	−12.5	2.19
	11	1 BH	−13.5	
	10	1 BD	−18.8	
	1	1 BD	−26.4	
	4	1 BD	−28.8	
	6	1 BD	−31.6	
	8–9	1 BHB		−1.5
	10–11	1 BHB		−3.1
[NMe$_4$]$^+$ [8-HO-7-CB$_{10}$H$_{12}$]$^-$	8	1 BOH	10.1	
	5	1 BH	−5.2	1.82
	3	1 BH	−9.6	1.96
	11	1 BH	−12.1	1.82
	2	1 BH	−13.8	1.55
	10	1 BH[c]	−20.6	1.23
	1	1 BH	−24.4	1.09
	9	1 BH[c]	−26.2	0.98
	4	1 BH	−30.0	0.49
	6	1 BH	−37.3	−0.06
	8–9	1 BHB		−1.78
	10–11	1 BHB		−3.58
	OH	1 H		2.25
	7-CH	1 H		1.40
	Me$_4$N$^+$	12 H		3.07

Table 1 (*continued*)

Compound	Assignment	Rel. intensity	$\delta(^{11}B)^a$	$\delta(^{1}H)^b$
$8\text{-}Et_3N\text{-}7\text{-}Me_3N\text{-}7\text{-}CB_{10}H_{10}$	8	1 BH	6.1	
	5	1 BH	−8.0	1.84
	3	1 BH	−12.3	1.78
	1	1 BH	−14.6	2.08
	2	1 BH	−19.7	1.41
	9	1 BH	−23.8	1.40
	11	1 BH	−23.8	0.65
	10	1 BH	−32.0	0.26
	4	1 BH	−35.1	0.11
	6	1 BH	−37.1	0.17
	10–11	1 BHB		−2.93
	Me_3N	9 H		2.98
	Et_3N	$9\ H(CH_3)^d$		1.25
	Et_3N	$6\ H(CH_2)^e$		3.15
$9\text{-}(HO_2C)\text{-}7\text{-}Me_3N\text{-}7\text{-}CB_{10}H_{11}$	5	1 BH	3.8	2.83
	2	1 BH	−8.0	2.40
	3	1 BH	−8.5	2.38
	8	1 BH	−12.6	2.51
	11	1 BH	−12.6	2.23
	9	$1\ BCO_2H$	−18.2	
	10	1 BH	−18.8	1.18
	1	1 BH	−25.0	1.20
	4	1 BH	−28.9	0.93
	6	1 BH	−31.3	0.52
	8–9	1 BHB		−2.56
	10–11	1 BHB		−3.30
$9\text{-}OC\text{-}7\text{-}Me_3N\text{-}7\text{-}CB_{10}H_{10}$	1	1 BH	0.1	2.69
	5	1 BH	−0.8	2.53
	8	$1\ BH^f$	−2.0	2.59
	2	1 BH	−16.1	1.72
	11	1 BH	−17.5	1.85
	3	1 BH	−19.0	1.18
	10	1 BH	−22.9	1.05
	4	1 BH	−29.0	0.92
	6	1 BH	−32.5	0.56
	9	1 BCO	−37.2	
	10–11	1 BHB		−2.10
$6,9\text{-}Cl_2\text{-}7\text{-}Me_3N\text{-}7\text{-}CB_{10}H_{10}$	5	1 BH	3.8	
	2	1 BH	−9.8	
	3–9	1 BH, 1 BCl	−11.5	
	8–11	2 BH	−14.3	
	6	1 BCl	−17.0	
	10	1 BH	−21.0	
	1	1 BH	−26.8	
	4	1 BH	−30.6	

[a] Chemical shifts (p.p.m.) positive to high frequency of the reference $Et_2O{\cdot}BF_3$, to ±0.2 p.p.m. obtained from $^{11}B\text{-}\{^1H\}$ n.m.r. measurements. [b] Chemical shifts ±0.05; B–H shifts obtained from $^1H\text{-}\{^{11}B$, selective$\}$ n.m.r. measurements. [c] Bridge-hydrogen coupling resolved in line-narrowed ^{11}B n.m.r. spectrum. [d] Triplet. [e] Complex multiplet, ABX_3, with further coupling to B(8). [f] Partly resolved ^{11}B–^{11}B coupling in $^{11}B\text{-}\{^1H\}$ n.m.r. spectrum.

Table 2. Boron-11 and ^1H n.m.r. data for $1\text{-}Me_3N\text{-}1\text{-}CB_{11}H_{11}$ and its derivatives *

Compound	B(12)	B(7)—B(11)	B(2)—B(6)
$1\text{-}Me_2HN\text{-}1\text{-}CB_{11}H_{11}$ (**4**)	−8.2 (1)	−13.6 (5)	−15.5 (5)
	[1.86]	[1.55]	[2.01]
$1\text{-}Me_3N\text{-}1\text{-}CB_{11}H_{11}$ (**5**)	−7.4 (1)	−13.6 (5)	−15.0 (5)
$[1\text{-}Me_2N\text{-}1\text{-}CB_{11}H_{11}]^-$	−13.1 (1)	−14.8 (10)	
	[1.36]	[1.36, 1.34, 1.90]	
$12\text{-}Cl\text{-}1\text{-}Me_3N\text{-}1\text{-}CB_{11}H_{10}$	5.3 (s) (1)	−13.2 (5)	−16.4 (5)

* $\delta(^{11}B)$/p.p.m. with relative intensities in parentheses and $\delta[^1H\text{–}^{11}B$, selective]/p.p.m. in square brackets.

and the implied ease of oxidation of $[7\text{-}Me_3N\text{-}7\text{-}CB_{10}H_{11}]^-$ correlates well with the products obtained on work-up from the reaction of NaH with $7\text{-}Me_3N\text{-}7\text{-}CB_{10}H_{12}$, namely $[2\text{-}CB_{10}H_{11}]^-$ and $[8\text{-}HO\text{-}7\text{-}CB_{10}H_{12}]^-$, which appear to have resulted from adventitious oxidation and hydrolysis of the deprotonated anion. Its low i.p. further suggests that the 7-Me_3N analogue is probably involved as an intermediate in the formation of $8\text{-}Et_3N\text{-}7\text{-}Me_3N\text{-}7\text{-}CB_{10}H_{10}$ [equations (13)—

(15)]. The other C-substituted *nido*-anionic derivatives, which are possible intermediates in the cluster-expansion reactions to *closo* derivatives, are significantly more stable to oxidation. The

$$7\text{-}Me_3N\text{-}7\text{-}CB_{10}H_{12} + NEt_3 \longrightarrow [7\text{-}Me_3N\text{-}7\text{-}CB_{10}H_{11}]^- + [NEt_3H]^+ \quad (13)$$

$$[7\text{-}Me_3N\text{-}7\text{-}CB_{10}H_{11}]^- + Tl^{3+} \longrightarrow 2\text{-}Me_3N\text{-}2\text{-}CB_{10}H_{10} + H^+ + Tl^+ \quad (14)$$

$$2\text{-}Me_3N\text{-}2\text{-}CB_{10}H_{10} + NEt_3 \longrightarrow 8\text{-}Et_3N\text{-}7\text{-}Me_3N\text{-}7\text{-}CB_{10}H_{10} \quad (15)$$

calculated ionisation potentials of $[7\text{-}CB_{10}H_{13}]^-$ and $[1\text{-}CB_{11}H_{12}]^-$ also correlate with experimental electrochemical or chemical oxidations of these anions.[18-20]

Table 3. Heats of formation (kcal mol^{-1}) and ionisation potentials (eV) calculated by the AM1 method

Compound	ΔH_f	I.P.
$[1\text{-}CB_{10}H_{13}]^-$	−128.70	5.37
$[8\text{-}HO\text{-}7\text{-}CB_{10}H_{12}]^-$	−220.84	5.05
$[7\text{-}H_3N\text{-}7\text{-}CB_{10}H_{11}]^-$	−103.58	3.31
$[7\text{-}H_2N\text{-}7\text{-}CB_{10}H_{12}]^-$	−125.38	5.04
$[4\text{-}Cl\text{-}7\text{-}H_2N\text{-}7\text{-}CB_{10}H_{11}]^-$	−176.32	5.20
$7\text{-}H_3N\text{-}7\text{-}CB_{10}H_{12}$	−59.54	9.38
$4\text{-}Cl\text{-}7\text{-}H_3N\text{-}7\text{-}CB_{10}H_{11}$	−107.04	9.07
$9\text{-}Cl\text{-}7\text{-}H_3N\text{-}7\text{-}CB_{10}H_{11}$	−107.15	8.98
$9\text{-}OC\text{-}7\text{-}H_3N\text{-}7\text{-}CB_{10}H_{10}$	−106.33	8.69
$8\text{-}OC\text{-}7\text{-}H_3N\text{-}7\text{-}CB_{10}H_{10}$	−91.00	8.28
$8\text{-}H_3N\text{-}7\text{-}H_3N\text{-}7\text{-}CB_{10}H_{10}$	−91.88	7.65
$[7\text{-}H_3N\text{-}7\text{-}CB_{10}H_{13}]^+$	113.78	14.10
$[1\text{-}CB_{11}H_{12}]^-$	−179.59	6.10
$[1\text{-}H_2N\text{-}1\text{-}CB_{11}H_{11}]^-$	−174.31	5.90
$[12\text{-}Cl\text{-}1\text{-}H_2N\text{-}1\text{-}CB_{11}H_{10}]^-$	−225.25	5.71
$1\text{-}H_3N\text{-}1\text{-}CB_{11}H_{11}$	−100.31	10.08
$12\text{-}Cl\text{-}1\text{-}H_3N\text{-}1\text{-}CB_{11}H_{10}$	−147.98	9.44

Optimised geometries. The AM1 method yielded cluster structures which were little distorted from the idealised icosahedron or icosahedral fragment, except for the carbonyl-substituted species. In these, the substituent appeared to induce substantial distortion from the idealised geometry. Furthermore the bridging hydrogen in the optimised structure of $8\text{-}OC\text{-}7\text{-}H_3N\text{-}7\text{-}CB_{10}H_{10}$ [Figure 12(*a*)] was displaced towards the centre of the open pentagonal face, and the distances indicated a structure between an *endo* environment at B(10) and bridging between B(9) and B(10). In the optimised structure of $9\text{-}OC\text{-}7\text{-}H_3N\text{-}7\text{-}CB_{10}H_{10}$ [Figure 12(*b*)] the bridge hydrogen environment was 'normal.' In conjunction with the n.m.r. data which show a 'normal' bridge hydrogen, the calculation gives further support to the conclusion of 9 substitution in $9\text{-}OC\text{-}7\text{-}Me_3N\text{-}7\text{-}CB_{10}H_{10}$.

Bond indices. Calculated bond indices in the compounds indicated substantial bonding between adjacent borons which exhibited COSY correlations. These are illustrated in Tables 4 and 5 [compounds (**7**) and (**9**)], and compare well with the experimental data in Figures 5 and 7. Thus it is for the first time that a rational explanation is available to account for the observation or otherwise of COSY correlations between adjacent boron atoms in cluster compounds; off-diagonal corre-

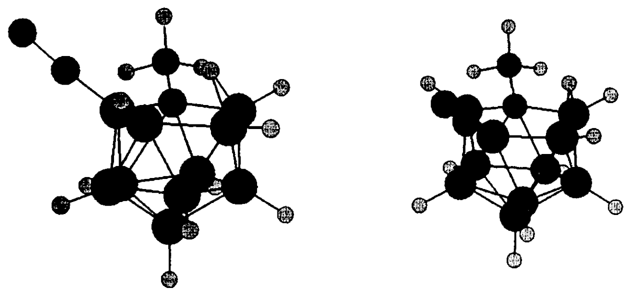

(*a*) (*b*)

Figure 12. AM1 Geometry-optimised structures of (*a*) $8\text{-}OC\text{-}7\text{-}H_3N\text{-}7\text{-}CB_{10}H_{10}$ and (*b*) $9\text{-}OC\text{-}7\text{-}H_3N\text{-}7\text{-}CB_{10}H_{10}$

Table 4. Boron–boron bond indices in $9\text{-}Cl\text{-}7\text{-}H_3N\text{-}7\text{-}CB_{10}H_{11}$

	5	3	9	8	2	11	10	1	4	6
5	*		0.43				0.40	0.53	0.47	0.46
3		*		0.29	0.44			0.54	0.56	
9	0.43		*	0.34			0.62		0.50	
8		0.29	0.34	*					0.58	
2		0.44			*	0.30		0.53		0.56
11					0.30	*	0.41			0.59
10	0.40		0.62			0.41	*			0.41
1	0.53	0.54			0.53			*	0.42	0.41
4	0.47	0.56	0.50	0.58				0.42	*	
6	0.46				0.56	0.59	0.41	0.41		*

Table 5. Boron–boron bond indices in $[8\text{-}HO\text{-}7\text{-}CB_{10}H_{12}]^-$

	8	5	3	11	2	10	1	9	4	6
8	*		0.26					0.26	0.65	
5		*				0.52	0.54	0.52	0.43	0.41
3	0.26		*		0.56		0.52		0.55	
11				*	0.30	0.39				0.58
2			0.56	0.30	*		0.46			0.58
10		0.52		0.39		*		0.45		0.52
1		0.54	0.52		0.46		*		0.45	0.46
9	0.26	0.52				0.45		*	0.49	
4	0.65	0.43	0.55				0.45	0.49	*	
6		0.41		0.58	0.58	0.52	0.46			*

Table 6. Atomic charges on the cluster atoms of derivatives of $[7\text{-}CB_{10}H_{13}]^-$

	Atom										
Compound	7	8	11	2	3	4	9	10	6	1	5
$[7\text{-}CB_{10}H_{13}]^-$	−0.39	0.02	0.02	−0.02	−0.02	−0.22	−0.18	−0.18	−0.22	−0.09	0.03
$[7\text{-}H_3N\text{-}7\text{-}CB_{10}H_{11}]^-$	−0.28	−0.19	−0.18	−0.14	−0.13	−0.02	−0.11	−0.12	−0.02	−0.13	−0.21
$[7\text{-}H_2N\text{-}7\text{-}CB_{10}H_{12}]^-$	−0.25	0.03	0.02	−0.05	−0.05	−0.22	−0.18	−0.18	−0.22	−0.08	0.03
$[4\text{-}Cl\text{-}7\text{-}H_2N\text{-}7\text{-}CB_{10}H_{11}]^-$	−0.25	0.02	0.02	−0.04	−0.06	−0.15	−0.18	−0.19	−0.22	−0.08	0.04
$[8\text{-}HO\text{-}7\text{-}CB_{10}H_{12}]^-$	−0.37	0.14	0.04	−0.02	−0.01	−0.27	−0.16	−0.15	−0.23	−0.06	0.01
$7\text{-}H_3N\text{-}7\text{-}CB_{10}H_{12}$	−0.45	−0.02	−0.01	−0.01	0.00	−0.20	−0.14	−0.16	−0.19	−0.05	0.05
$4\text{-}Cl\text{-}7\text{-}H_3N\text{-}7\text{-}CB_{10}H_{11}$	−0.44	−0.03	−0.02	0.02	−0.02	−0.14	−0.14	−0.16	−0.19	−0.06	0.06
$9\text{-}Cl\text{-}7\text{-}H_3N\text{-}7\text{-}CB_{10}H_{11}$	−0.45	−0.05	−0.00	−0.03	0.05	−0.25	−0.01	−0.18	−0.18	−0.06	0.06
$8\text{-}OC\text{-}7\text{-}H_3N\text{-}7\text{-}CB_{10}H_{10}$	−0.26	−0.46	−0.00	−0.21	0.08	−0.09	0.05	−0.22	−0.05	−0.02	−0.09
$9\text{-}OC\text{-}7\text{-}H_3N\text{-}7\text{-}CB_{10}H_{10}$	−0.38	−0.00	−0.06	0.03	−0.09	−0.05	−0.48	0.02	−0.22	−0.08	0.03
$8\text{-}H_3N\text{-}7\text{-}H_3N\text{-}7\text{-}CB_{10}H_{10}$	−0.40	−0.17	−0.07	0.02	−0.15	−0.17	−0.17	−0.07	−0.21	−0.06	0.02

lations in these COSY spectra are observed only where the bond index is greater than *ca.* 0.4 (some allowance should also be made for fast relaxing 'broad' resonances).

In $8\text{-}OC\text{-}7\text{-}H_3N\text{-}7\text{-}CB_{10}H_{10}$ the unique hydrogen showed a substantial bond index to B(10) (0.657) with a smaller but significant bond index to B(9) (0.130), again indicating a structure between *endo* and bridging. The corresponding hydrogen in $9\text{-}OC\text{-}7\text{-}H_3N\text{-}7\text{-}CB_{10}H_{10}$ was calculated to be bridging between B(10) and B(11), with bond indices of 0.398 and 0.478 respectively, in closer agreement with the n.m.r. data on compound (**12**).

Atom electron densities. The atomic charges at the cluster atoms are presented in Table 6. These show a substantial degree of correlation with the chemical shifts reported in Table 1, except for atoms whose shifts are clearly affected by factors other than electron density [*e.g.* B(1), ring currents]. The electron densities clearly indicate B(4, 6) as the sites most subject to electrophilic attack.

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