# 417. *Boron Hydride Derivatives. Part VII.* The Characterisation of Some Decaborane Derivatives of the Type,* $B_{10}H_{12}$,2M.

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Several derivatives of decaborane of the type $B_{10}H_{12}$,2M, where M is an electron-donor, have been prepared. Their infrared spectra and $^{11}B$ nuclear magnetic resonance spectra have been measured to decide whether they have the structural formula $B_{10}H_{12}$,2M or $[B_{10}H_{10}]^{2-}[MH]_2^{+}$. Reactions involving displacement of M by a second electron-donor have been studied.

Since Schaeffer's discovery[1] of the reaction of acetonitrile with decaborane to yield bisacetonitriledecaborane, $B_{10}H_{12}$,2MeCN, several other compounds of this type have been reported. They include derivatives from diethylcyanamide,[2] triphenylphosphine,[2] 2-isopropyl- and 5-2′-chloroethyl-2-methyl-tetrazole,[3] and triethylamine.[4,5] The last-named substance was shown by Hawthorne and Pitochelli[4,5] to give rise to two isomers, namely, an ionic derivative, $[B_{10}H_{10}]^{2-}[Et_3NH]_2^{+}$, and a covalent compound $B_{10}H_{12}$,2Et$_3$N. We have measured the infrared and $^{11}B$ nuclear magnetic resonance spectra of a number of these substances to decide whether they have ionic or covalent structures.

## Experimental

*Compounds Studied.*—Decaborane, purchased from the American Potash and Chemical Corporation, was recrystallised from hexane before use.

*Bisacetonitriledecaborane.* This was prepared by Schaeffer's method[1] from dry acetonitrile and decaborane and recrystallised from acetonitrile (Found: C, 22·9; H, 9·2; N, 13·8. Calc. for $C_4H_{18}B_{10}N_2$: C, 23·7; H, 9·0; N, 13·8%).

*Bis(diethylcyanamide)decaborane and bis(triphenylphosphine)decaborane.* These were prepared from decaborane and diethylcyanamide or triphenylphosphine by the methods of Hawthorne and Miller.[2] The diethylcyanamide compound was recrystallised from methylene chloride; the triphenylphosphine derivative was precipitated from chloroform by ether.

*Bistriethylaminedecaboranes.* These were prepared from bisacetonitriledecaborane and triethylamine in boiling benzene.[4] The hot benzene solution was filtered and the insoluble residue extracted with further quantities of hot benzene, which were added to the original filtrate, and the whole was concentrated. The covalent bistriethylaminedecaborane separated on cooling (Found: C, 44·3, 43·8; H, 11·6, 11·5; N, 9·6. Calc. for $C_{12}H_{42}B_{10}N_2$: C, 44·7; H, 13·1; N, 8·7%). The traces of benzene were removed from the insoluble ionic compound *in vacuo* (Found: C, 44·1; H, 12·9; N, 9·2%).

*Bis(dimethyl sulphide)decaborane.* The substance was prepared by refluxing decaborane (0·24 g., 0·02 mole) with dimethyl sulphide (0·30 g., 0·05 mole) in dry ether for 4 hr. The solution deposited colourless crystals of the *complex* overnight. These were filtered off, washed with ether, and dried *in vacuo*, and had m. p. 110° (decomp.) (Found: C, 19·4; H, 9·5. $C_4H_{24}B_{10}S_2$ requires C, 19·6; H, 9·9%).

*Bispyridinedecaborane.* Pyridine (0·17 g., 0·022 mole) in a small quantity of dry benzene was added to decaborane (0·12 g., 0·01 mole) in benzene, giving a yellow-red sticky precipitate. The whole was refluxed for 2 hr., then cooled. Hydrogen (20 ml.) was evolved (0·01 mole requires 22·4 ml.). The *product* was filtered off and on recrystallisation from hot dimethylformamide formed yellow crystals, m. p. 300° (decomp.) (Found: C, 43·0; H, 7·8; N, 10·0. $C_{10}H_{22}B_{10}N_2$ requires C, 43·1; H, 8·0; N, 10·1%).

*Bis(dimethylformamide)decaborane.* To decaborane (0·25 g., 0·02 mole) in benzene (5 ml.) dimethylformamide (0·30 g., 0·041 mole) was added. A suspension was formed after a few minutes' heating. The mixture was refluxed for 1 hr., 51·5 ml. of hydrogen being evolved

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* Part VI, Dunstan, Blay, and R. L. Williams, *J.*, 1960, 5016.

[1] Schaeffer, *J. Amer. Chem. Soc.*, 1957, **79**, 1006.

[2] Hawthorne and Pitochelli, *J. Amer. Chem. Soc.*, 1958, **80**, 6685.

[3] Fetter, *Chem. and Ind.*, 1959, 1548.

[4] Hawthorne and Pitochelli, *J. Amer. Chem. Soc.*, 1959, **81**, 5519.

[5] Lipscomb, Hawthorne, and Pitochelli, *J. Amer. Chem. Soc.*, 1959, **81**, 5834.

(0·02 mole requires 46·5m l.). After cooling, the suspension was filtered off, washed with benzene, then ether, and dried *in vacuo*. Dissolution in dimethylformamide, followed by precipitation with ether, did not alter the infrared spectrum of the *product* which had m. p. 162° (decomp.) (Found: C, 26·7; H, 10·4; N, 11·7. $\mathrm{C_6H_{26}B_{10}O_2N_2}$ requires C, 27·0; H, 9·8; N, 10·5%).

*Bis(dimethylacetamide)decaborane.* To decaborane (0·26 g., 0·21 mole) in benzene (5 ml.), dimethylacetamide (0·36 g., 0·41 mole) was added. The solution was heated. Gas evolution was rapid and two layers were formed. On cooling, the lower layer formed pale orange crystals of the *product*, m. p. 139° (decomp.) (Found: C, 31·4; H, 10·3; N, 9·8. $\mathrm{C_8H_{30}B_{10}O_2N_2}$ requires C, 32·6; H, 10·3; N, 9·5%).

*Bis-(2-bromopyridine)decaborane.* This *compound* was prepared by a similar method to bispyridinedecaborane (Found: C, 27·9; H, 4·8; N, 5·0. $\mathrm{C_{10}H_{20}B_{10}Br_2N_2}$ requires C, 27·5; H, 4·6; N. 6·4%).

*Spectra.*—The infrared spectra of the compounds were measured for Nujol and Fluorube mulls on a Grubb–Parsons GS2 double-beam grating spectrometer with a 2400 line/inch N.P.L. replica grating. The spectra of the corresponding donor substances were also measured as mulls, except for triphenylphosphine (solutions in $\mathrm{CCl_4}$ and $\mathrm{CS_2}$).

$\mathrm{Me_2S}$. 2986m, 2965m, 2915s, 2854m, 2833m, 1716w, 1431vs, 1308s, 1027s, 971ms, 903w, 740w, 690m.

$\mathrm{(Me_2S)_2,B_{10}H_{12}}$. 3025sh, 3015m, 2996w, 2923mw, 2527sh, 2504vs, 2493sh, 2457m, 1432mw, 1423s, 1412ms, 1328m, 1307w, 1086m, 1074sh, 1038m, 998vs, 976m, 965mw, 951mw, 936sh, 929m, 815vw, 795mw, 785sh, 761mw, 758mw, 678w, 643m.

MeCN. 3202w, 3164m, 3002ms, 2945ms, 2294mw, 2253s, 1715vw, 1439vs, 1414sh, 1374vs, 1224vw, 1039s, 918ms, 749m.

$\mathrm{(MeCN)_2,B_{10}H_{12}}$. 2981sh, 2974m, 2911mw, 2536sh, 2521vs, 2480m, 2328w, 1460m, 1404s, 1359w, 1353m, 1195w, 1124sh, 1119m, 1109sh, 1078mw, 1030m, 1017sh, 1002sh, 996s, 972m, 952sh, 948mw, 939mw, 930mw, 874w, 792ms, 777m, 747m, 680sh, 674m.

$\mathrm{Et_2N{\cdot}CN}$. 2980s, 2937m, 2880m, 2209vs, 1478sh, 1460sh, 1452s, 1400sh, 1383s, 1357m, 1325m, 1303mw, 1229s, 1179s, 1113sh, 1083s, 1071sh, 977w, 929w, 811sh, 796m, 713m.

$\mathrm{(Et_2N{\cdot}CN)_2,B_{10}H_{12}}$. 2976ms, 2936m, 2902mw, 2874w, 2534sh, 2511vs, 2492sh, 2479sh, 2461sh, 2302s, 1493m, 1384m, 1345w, 1304s, 1272sh, 1147sh, 1120m, 1110m, 1070mw, 1009sh, 994s, 970mw, 948w, 939w, 932w, 917w, 821m, 811sh, 789mw, 777w, 730mw, 717w, 704w.

$\mathrm{HCO{\cdot}NMe_2}$. 3072w, 2991sh, 2927m, 2856m, 2805sh, 2772w, 1674vs, 1500m, 1458sh, 1438m, 1404sh, 1396s, 1257m, 1151w, 1092s, 1063m, 865w.

$\mathrm{(HCO{\cdot}NMe_2)_2,B_{10}H_{12}}$. 3086w, 2986w, 2930w, 2861vw, 2820w, 2760w, 2523sh, 2503vs, 2473ms, 1672vs, 1484w, 1438w, 1428m, 1416sh, 1346s, 1248mw, 1138m, 1116mw, 1080w, 1060w, 1003ms, 992sh, 980sh, 909ms, 818ms, 792m, 751w, 723w.

$\mathrm{AcNMe_2}$. 3014w, 2930mw, 2872sh, 1643vs ($\mathrm{CCl_4}$ soln. 1658), 1548w, 1499m, 1445mw, 1412ms, 1395s, 1356w, 1265w, 1188mw, 1177sh, 1060w, 1035w, 1012m.

$\mathrm{(AcNMe_2)_2,B_{10}H_{12}}$. 3035vw, 2975vw, 2939w, 2873vw, 2856vw, 2522sh, 2494vs, 2451sh, 1618vs, 1495ms, 1431m, 1402ms, 1367w, 1260m, 1133m, 1120m, 1025w, 1011w, 988s, 969m, 890m, 819s, 735w, 721w, 674ms.

$\mathrm{Et_3N}$. 2970vs, 2933s, 2895mw, 2874m, 2797s, 2753sh, 2721sh, 2709sh, 1468m, 1449m, 1382s, 1371sh, 1357w, 1345w, 1334sh, 1309sh, 1293m, 1268sh, 1211sh, 1204s, 1145w, 1136w, 1094sh, 1085m, 1070s, 1058sh, 1047sh, 1019w, 998w, 919w, 901w, 800w, 781w, 743m, 736m.

$\mathrm{(Et_3N)_2,B_{10}H_{12}}$. 3009m, 3000m, 2987ms, 2967m, 2940m, 2885sh, 2821w, 2526s, 2502vs, 2490s, 2477ms, 1467s, 1438m, 1415w, 1390m, 1382s, 1365w, 1354w, 1343w, 1315vw, 1285vw, 1214m, 1192w, 1177vw, 1165w, 1147m, 1113vw, 1094w, 1082vw, 1068w, 1057vw, 1018s, 1010sh, 962w, 955w, 933vw, 910sh, 901mw, 893w, 833w, 813w, 780ms, 767ms, 753vw, 743w, 669w.

$\mathrm{(Et_3NH)^+{}_2PtCl_6{}^{2-}}$. 3085vs, 3008sh, 3003w, 2986w, 2979w, 2944vw, 2886vw, 2821vw, 2755vw, 1480w, 1468s, 1455ms, 1446m, 1431w, 1415m, 1396sh, 1391ms, 1388sh, 1360w, 1341vw, 1315vw, 1305vw, 1286w, 1268w, 1179sh, 1172w, 1162ms, 1091vw, 1064m, 1045w, 1012ms, 897w, 894sh 840m, 805mw, 775w, 729mw.

$\mathrm{(Et_3NH)^+{}_2,B_{10}H_{10}{}^{2-}}$. 3060s, 3015w, 2979w, 2955w, 2889vw, 2848vw, 2776vw, 2753vw, 2664vw, 2536m, 2494sh, 2465vs, 2447sh, 2410sh, 2353m, 1679w, 1614w, 1459ms, 1448s, 1405ms, 1362w, 1162m, 1076w, 1060w, 1034s, 1014sh, 928w, 894w, 844m, 792m, 777sh, 726w.

$\mathrm{Ph_3P}$. 3139w, 3070s, 3054s, 3030m, 3014m, 3000m, 2910vw, 1965sh, 1952w, 1891sh, 1881w, 1824sh, 1812w, 1773sh, 1758w, 1656w, 1585m, 1571sh, 1480s, 1433s, 1378w, 1325m, 1305m, 1278w, 1201w, 1181m, 1157w, 1119w, 1088ms, 1069m, 1027s, 999m, 984sh, 966vw, 914w, 846w, 741vs, 719w, 699sh, 693vs.

$(Ph_3P)_2,B_{10}H_{12}$. 3073sh, 3057w, 3022vw, 3005vw, 2950vw, 2924vw, 2859vw, 2540sh, 2519vs, 2472sh, 2431sh, 1973vw, 1901vw, 1814vw, 1746vw, 1668vw, 1588w, 1573w, 1482s, 1436s, 1343w, 1312w, 1186m, 1160m, 1120sh, 1101s, 1070m, 1062m, 1028m, 999m, 978m, 945m, 939sh, 925sh, 915m, 889mw, 847vw, 819vw, 801mw, 755sh, 743s, 722sh, 711s, 693vs.

$2\text{-}Br{\cdot}C_5H_4N$. 3130w, 3081sh, 3068sh, 3051s, 2990m, 2890w, 1602w, 1571s, 1560s, 1459sh, 1448s, 1414s, 1351w, 1282mw, 1239w, 1148m, 1117sh, 1106s, 1091w, 1077s, 1042ms, 1014w, 1003w, 987ms, 759vs, 724w, 700s.

$(Br{\cdot}C_5H_4N)_2,B_{10}H_{12}$. 3111vw, 3090vw, 3073vw, 3059vw, 3009vw, 2933vw, 2583m, 2570m, 2522sh, 2502vs, 2475ms, 1601m, 1554mw, 1509w, 1459s, 1425s, 1354vw, 1344vw, 1285m, 1225vw, 1170w, 1149w, 1118w, 1094m, 1083sh, 1071ms, 1048mw, 1011sh, 998s, 977m, 957w, 938sh, 933mw, 922w, 902w, 881vw, 858vw, 809vw, 791m, 784sh, 770s, 758sh, 730sh, 720m.

$C_5H_5N$. 3146vw, 3079m, 3053mw, 3032sh, 3026m, 3001mw, 2989sh, 2955w, 2932vw, 2910vw, 1989w, 1948sh, 1924w, 1873w, 1685vw, 1634w, 1599m, 1583sh, 1574sh, 1483m, 1438s, 1377w, 1356w, 1293vw, 1218m, 1147m, 1069m, 1031ms, 991ms, 940vw, 883vw, 747sh, 703vs.

$(C_5H_5N)_2,B_{10}H_{12}$. 3122sh, 3114sh, 3104vw, 3083sh, 3072vw, 3062sh, 3038vw, 2525sh, 2509vs, 2481s, 2461m, 1670w, 1623mw, 1614sh, 1574w, 1485m, 1458s, 1417w, 1354w, 1344mw, 1314vw, 1254mw, 1209m, 1162w, 1157sh, 1132m, 1121ms, 1095m, 1080sh, 1075m, 1058m, 1023sh, 1013sh, 999vs, 980m, 976m, 964vw, 955w, 941sh, 938m, 925sh, 903sh, 888vw, 871w, 867mw, 794m, 779s, 772ms, 759m, 747mw, 732w, 709m, 687vs.

$B_{10}H_{14}$. 2625sh, 2613ms, 2592sh, 2586vs, 2571vs, 2548sh, 2538s, 1970w, 1934mw, 1892m, 1557ms, 1514vs, 1467ms, 1103m, 1037m, 1007s, 971ms, 965ms, 959sh, 941sh, 938ms, 924sh, 921s, 902s, 862sh, 859s, 821sh, 814s, 774sh, 766s, 757w, 747m, 723vs, 709w, 700w, 693vw, 668vw 649w, 611ms.

$^{11}B$ nuclear magnetic resonance spectra were measured at 12 Mc./sec. with a Varian Associates V 4310 high-resolution spectrometer. Dimethylformamide was used as solvent for the compounds except that the dimethyl sulphide derivative was in methylene chloride, and the acetonitrile and dimethylacetamide compounds were in acetonitrile. After measurement, the solutes were recovered from solution by evaporation of the solvent or by precipitation with ether. Their infrared spectra showed that no reaction had taken place.

*Displacement Reactions.*—Some displacement reactions, $B_{10}H_{12}M_2 + 2M' \longrightarrow B_{10}H_{12}M'_2 +$ 2M, were studied.

(*a*) The original boron compound, identified by its infrared spectrum, was recovered after the following pairs had been heated together: bisdimethylformamidedecaborane–dimethyl sulphide, –acetonitrile, or –triethylamine (no solvent); bisdimethylacetamidedecaborane–dimethylformamide; bistriethylaminedecaborane(covalent)–pyridine; bispyridinedecaborane–triethyamine or –triphenylphosphine in dimethylformamide; bistriphenylphosphine–pyridine in dimethylformamide.

(*b*) Bis(dimethyl sulphide)decaborane was boiled in acetonitrile for a few minutes and the solvent removed. The infrared spectrum of the residue was identical with that of bisacetonitriledecaborane.

(*c*) Bisdimethylformamidedecaborane was heated with triethylamine in dimethylformamide, and the solute precipitated by ether. The infrared spectrum of the product showed it to be a mixture of the ionic and the covalent form of bistriethylaminedecaborane.

(*d*) Bisdimethylformamidedecaborane was heated in pyridine. On cooling, bispyridinedecaborane separated, its identity being confirmed by the spectrum.

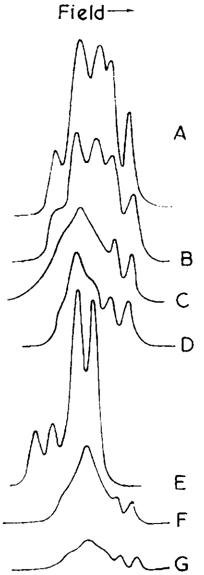
Attempts to make a bisdimethylnitrosaminedecaborane by direct reaction of dimethylnitrosamine with decaborane in benzene or by displacement from bis(dimethyl sulphide)decaborane or bisacetonitriledecaborane caused decomposition to hydroxylated compounds.

## DISCUSSION

*Nuclear Magnetic Resonance Spectra.*—Hawthorne *et al.*[4,5] converted the ionic bistriethylaminedecaborane $[Et_3NH]^+_2[B_{10}H_{10}]^{2-}$ into a tetramethylammonium salt and showed that the $^{11}B$ nuclear magnetic spectrum of this substance consisted of a low-field doublet of strength 1 and a high-field doublet of strength 4. The spectrum of the ionic bistriethylamine compound (Fig. 1) is identical with this and differs considerably from those of the other decaborane derivatives. The other derivatives therefore have covalently bonded structures in which the ligands donate electrons to the $B_{10}H_{12}$ unit.

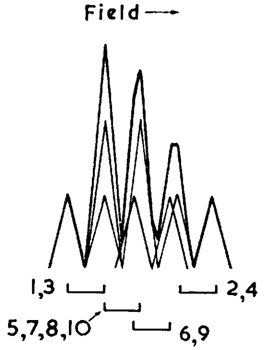
The structure of bisacetonitriledecaborane has been shown by Reddy and Lipscomb [6,7] to have the acetonitrile units attached at the 6,9-positions and to have positions 5 and 7 linked by bridge protons to positions 10 and 8, respectively (cf. I; the Y bonds represent three-centre bond approximations; there is, of course, no carbon atom at these junctions). The dispositions of the boron atoms are at the corners of two pentagonal pyramids sharing a common edge, as in decaborane. Accordingly, the $^{11}$B nuclear magnetic resonance spectrum will be made up of a number of doublets similar to those of decaborane.[8] If the major changes in charge on going from decaborane to the bis-derivative are restricted to an increase in electron density at the 6,9-positions, it would be expected that the 2,4-doublet would lie on the high-field side of the spectrum, the 5,7,8,10-doublet at a centre-field position, and the 1,3-doublet at low field, as with decaborane. The 6,9-doublet would be expected to shift towards higher field as in shifts observed for this doublet in decaboranes methylated at the 1-, 2-, 3-, and 4-positions.[9] A theoretical spectrum based on these assumptions (Fig. 2) shows satisfactory agreement with those observed, especially with the bis(dimethyl sulphide) and the bisacetonitrile compound.

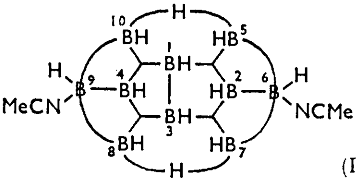
FIG. 1.



*The $^{11}$B nuclear magnetic resonance spectra of*:
(A) $(Me_2S)_2B_{10}H_{12}$; (B) $(MeCN)_2,B_{10}H_{12}$; (C) $(HCO{\cdot}NMe_2)_2,B_{10}H_{12}$; (D) $(AcNMe_2)_2,B_{10}H_{12}$; (E) $(Et_3NH)_2,B_{10}H_{10}$; (F) $(Et_3N)_2,B_{10}H_{12}$; (G) $(C_5H_5N)_2,B_{10}H_{12}$.

FIG. 2. *Theoretical spectrum for* $M_2B_{10}H_{12}$.





(I)

*Infrared Spectra.*—The spectra of the bis-derivatives of decaborane, $B_{10}H_{12}$,2M, together with those of the ligands, M, are shown in Fig. 3. Each spectrum falls into two

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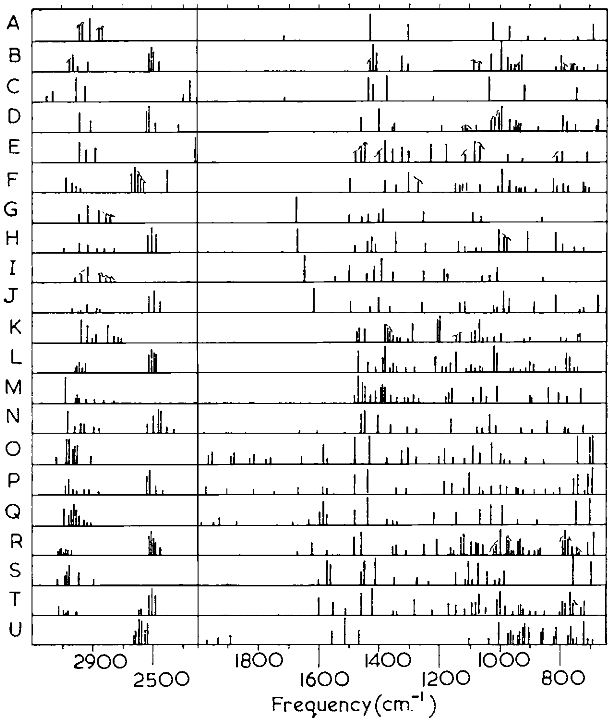
[6] Reddy and Lipscomb, *J. Amer. Chem. Soc.*, 1959, **81**, 754.
[7] Reddy and Lipscomb, *J. Chem. Phys.*, 1959, **31**, 610.
[8] R. E. Williams and Shapiro, *J. Chem. Phys.*, 1958, **29**, 677.
[9] R. L. Williams, Dunstan, and Blay, *J.*, 1960, 5006.

parts, that due to vibrations of the $B_{10}H_{12}$ unit, which is common to all the spectra, and that of the electron-donating unit, M. Thus all the spectra have a number of strong absorptions in the range 2520—2490 cm.$^{-1}$, due to the terminal B–H stretching vibrations, which are replaced by single peaks when solutions are measured. Decaborane behaves similarly, but its band centre lies at 2580 cm.$^{-1}$. The $[B_{10}H_{10}]^{2-}$ ion in the triethylammonium salt has its band centre at the much lower frequency of 2450 cm.$^{-1}$.

Apart from absorption of variable intensity near 930—900 cm.$^{-1}$, the only strong band common to all the spectra lies in the range 1015—990 cm.$^{-1}$, often with a weaker satellite of lower frequency. This band also occurs for decaborane, at 1007 cm.$^{-1}$, but for $[Et_3NH]^+{}_2[B_{10}H_{10}]^{2-}$ its position has risen to 1034 cm.$^{-1}$. The latter compound can, therefore, be distinguished from the $B_{10}H_{12}$,2M type by its lower B–H stretching frequency and the raised value of the band near 1000 cm.$^{-1}$.

FIG. 3.



*The infrared spectra of*:

(A) $Me_2S$; (B) $(Me_2S)_2,B_{10}H_{12}$; (C) MeCN; (D) $(MeCN)_2,B_{10}H_{12}$; (E) $Et_2N{\cdot}CN$; (F) $[Et_2N{\cdot}CN)_2,B_{10}H_{12}$; (G) $HCO{\cdot}NMe_2$; (H) $(HCO{\cdot}NMe_2)_2,B_{10}H_{12}$; (I) $AcNMe_2$; (J) $(AcNMe_2)_2,B_{10}H_{12}$; (K) $Et_3N$; (L) $(Et_3N)_2,B_{10}H_{12}$; (M) $(Et_3NH)^+{}_2PtCl_6{}^{2-}$; (N) $(Et_3NH)_2,B_{10}H_{10}$; (O) $Ph_3P$; (P) $(Ph_3P)_2,B_{10}H_{12}$; (Q) $C_5H_5N$; (R) $(C_5H_5N)_2,B_{10}H_{12}$; (S) 2-$BrC_5H_4N$; (T) $(BrC_5H_4N)_2,B_{10}H_{12}$; (U) $B_{10}H_{14}$.

The 1000 cm.$^{-1}$ band can be assigned to a terminal B–H deformation vibration since it persists in the spectrum of $B_{10}H_{10}D_4$, deuterated in the bridge positions by the method of Hawthorne and Miller.[10,11] On the other hand, this band is reduced in intensity in 2,4,5,7,8,10-hexadeuterodecaborane prepared by the action of deuterium chloride and

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[10] Hawthorne and Miller, *J. Amer. Chem. Soc.*, 1958, **80**, 754.

[11] Miller and Hawthorne, *J. Amer. Chem. Soc.*, 1959, **81**, 4501.

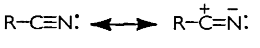
aluminium chloride on decaborane [12] and has disappeared completely from the spectrum [11] of $B_{10}D_{14}$.

The strong band at 1514 cm.$^{-1}$ in the decaborane spectrum, which is an alternative possibility for the B–H deformation vibration, by analogy with Hrostowski and Pimentel's assignment [13] for pentaborane-9, can be eliminated, since this band has disappeared from the spectrum of the bridge-deuterated $B_{10}H_{10}D_4$ and has been replaced by a strong band near 1160 cm.$^{-1}$ (ratio 1·30 : 1). Moreover, the $B_{10}H_{12}$,2M compounds differ only from decaborane in their hydrogen-bridge systems, and in none of them is there a strong band near 1500 cm.$^{-1}$.

The contribution, to the spectrum, of the ligand M differs from compound to compound and also differs from the spectrum of M in its unbonded state. It is therefore not possible to make detailed analyses except where M has a simple spectrum. Thus, in the case of dimethyl sulphide, bands are observed near 2980, 2915 (antisymm. $\nu$-$CH_3$) and 2840 (symm. $\nu$-$CH_3$), 1431 (antisymm. $\delta$-$CH_3$) and 1308 (symm. $\delta$-$CH_3$), 1027 and 971 ($CH_3$-rock), and 690 cm.$^{-1}$ ($\nu$-CS) [14]. On formation of the bis(dimethyl sulphide)decaborane most of these bands change slightly in frequency; *e.g.*, the antisymmetric and symmetric $\nu$-$CH_3$ vibrations increase to 3015 and 2923 cm.$^{-1}$. The methyl deformation vibrations split into several components but remain largely unaltered at 1423 and 1328 cm.$^{-1}$ respectively. Similarly, the methyl rocking vibrations can be identified with the bands at 1038 and 976 cm.$^{-1}$ and the C–S stretching vibration with that at 643 cm.$^{-1}$. The slight changes in the spectrum indicate a small change only in the electronic structure of the molecule and it is not surprising, therefore, that dimethyl sulphide is the most easily displaced ligand.

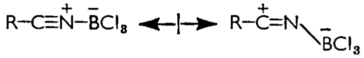
With the bisacetonitrile compound, it is possible to identify the bands at 2974 (antisymm. $\nu$-$CH_3$), 2911 (symm. $\nu$-$CH_3$), 2328 ($\nu$-C≡N), 1460 (antisymm. $\delta$-$CH_3$), 1404 (symm. $\delta$-$CH_3$), 1078 ($CH_3$-rock), and 948 cm.$^{-1}$ (possibly $\nu$-C–C) with the corresponding bands in acetonitrile [15] at 3002, 2945, 2252, 1439, 1376, 1040, and 919 cm.$^{-1}$. The most significant difference is the increase of the C≡N frequency by 75 cm.$^{-1}$ on complex formation. This change parallels that noted by Gerrard *et al.*[16] on formation of complexes of the type RCN,$BCl_3$. Because of the relative insensitivity of the frequency of the CN group to environmental changes,[17] the shift indicates a strong interaction between the group and the $B_{10}H_{12}$ unit.

Diethylcyanamide behaves in a similar manner to acetonitrile, but a vibrational assignment is not possible, except for a few bands, because of the complexity of the spectrum. The absence of a strong band at 2800 cm.$^{-1}$ indicates that the lone pair of electrons of the diethylamino-group is delocalised [18] and this is reflected by the lower CN frequency, namely, 2209 cm.$^{-1}$ compared with 2250 cm.$^{-1}$ for normal nitriles. On formation of the decaborane complex the CN frequency rises by 93 cm.$^{-1}$ to 2302 cm.$^{-1}$, which shows that the molecule is linked through the CN group rather than the nitrogen of the diethylamino-group. The lone pair of the latter remains delocalised since there is no strong absorption near 2800 cm.$^{-1}$.



$$R{-}C{\equiv}N\!: \longleftrightarrow R{-}\overset{+}{C}{=}\overset{-}{N}\!:$$

(I) (II)



$$R{-}C{\equiv}\overset{+}{N}{-}\overset{-}{B}Cl_3 \longleftrightarrow R{-}\overset{+}{C}{=}\overset{-}{N}{\diagdown}BCl_3$$

(III) (IV)

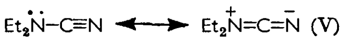
Gerrard *et al.*[16] explained the increase in CN frequency in their complexes by the absence of canonical form (IV) from the normal CN resonance because of its different geometry from form (III). However, it is unlikely that form (II) makes a significant contribution to

[12] Dupont and Hawthorne, *J. Amer. Chem. Soc.*, 1959, **81**, 4998.
[13] Hrostowski and Pimentel, *J. Amer. Chem. Soc.*, 1954, **76**, 998.
[14] Trotter and Thompson, *J.*, 1946, 486.
[15] Venkateswarlu, *J. Chem. Phys.*, 1951, **19**, 293.
[16] Gerrard, Lappert, Pyszora, and Wallis, *J.*, 1960, 2182.
[17] Mander and Thompson, *Trans. Faraday Soc.*, 1957, **53**, 1402.
[18] Hill and Meakins, *J.*, 1958, 760; Braunholtz, Ebsworth, Mann, and Sheppard, *J.*, 1958, 2780.

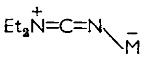
the nitrile structure, since the dipole moments of nitriles which were cited [19] as evidence for its existence can more reasonably be attributed [20] to the lone pair of electrons on the nitrogen. A comparison with the C≡C link, where no contribution from $\overset{+}{C}=\overset{-}{C}$ would be expected, confirms this: both bonds have very similar frequencies: [21] C≡C, 2260—2190 cm.$^{-1}$; C≡N, 2260—2240 cm.$^{-1}$.

Formation of the nitrile complex places a formal positive charge on the nitrogen (III). This would be expected [22] to reduce the covalent radius by about 0·02 Å, and this is confirmed on the structural analysis of the acetonitrile–boron trifluoride complex [23] (MeCN, $r_{CN}$ 1·16 Å; MeCN,$BF_3$, $r_{CN}$ 1·13 Å). The frequency increase corresponding to a bond-shortening of this size can be estimated from Badger's rule [24] to be approximately 150 cm.$^{-1}$, which compares with the observed shifts of 75—90 cm.$^{-1}$.

In the case of diethylcyanamide, the additional canonical form (V) makes a small contribution to the resonance structure, which is little altered in the complex. However,



$Et_2\ddot{N}{-}C{\equiv}N \longleftrightarrow Et_2\overset{+}{N}{=}C{=}\overset{-}{N}$ (V)



(VI)

a contribution from structure (VI) to the complex is not possible on steric grounds and the same mechanism as for acetonitrile applies to the frequency increase.

An alternative explanation, originally proposed [25] for the nitrile oxides, R·C≡N→O, is that the increase is due to coupling of the C≡N vibration with the N→M vibration. This is here very unlikely because of the wide separation of these two frequencies. Calculations for the linear system, C–N–M, on the basis that $\nu_{N-M}$ lies [26] near 700 cm.$^{-1}$, indicate a maximum increase of 30 cm.$^{-1}$ when the atomic mass of M is 11 (the frequency increase becomes smaller as the mass of M increases).

The spectrum of dimethylformamide is relatively simple and follows the pattern expected for a disubstituted amide [27] with amide I (CO) and amide III (CN) bands at 1674 and 1257 cm.$^{-1}$, and the methyl stretching, deformation, and rocking vibrations near 2900, 1450, and 1092 cm.$^{-1}$, respectively. The absence of a strong band at 2800 cm.$^{-1}$ shows that the lone pair of electrons on the nitrogen is delocalised. On formation of the bis-compound, most of the frequencies change but little, with the possible exception of the methyl rocking frequencies which rise to 1125 cm.$^{-1}$. The carbonyl frequency falls slightly to 1672 cm.$^{-1}$. Gerrard *et al.*[28] found that for nearly all of their amide complexes with boron trichloride and bromide there is a fall in the carbonyl frequency compared with that of the free amide in the liquid state or in methylene chloride solution. The two exceptions are the complexes of dimethylformamide and dimethylacetamide, which have slightly higher values. However, the carbonyl frequencies of disubstituted amides are very sensitive to solvent effects [29] and it is preferable to use the vapour or hexane-solution values for comparisons. These are 1716 and 1696 cm.$^{-1}$ for dimethylformamide and 1691 and 1675 cm.$^{-1}$ for the acetamide. On this basis, there is a considerable fall in the carbonyl frequencies both with the boron trihalide complexes and the bisdimethylformamide derivative compared with the free amide. This indicates that the carbonyl-oxygen atom is the point of attachment, since, unlike the position with the nitrile complexes, there are no geometrical objections to the contribution of form (VIII) and correspondingly no formal positive

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[19] Pauling, " Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, U.S.A., 1948, p. 75.

[20] Coulson, " Valence," Clarendon Press, Oxford, 1952, p. 209.

[21] Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen, London, 1958, pp. 58, 263.

[22] Ref. 19, p. 169.

[23] Hoard, Owen, Buzzell, and Salmon, *Acta Cryst.*, 1950, **3**, 130.

[24] Badger, *J. Chem. Phys.*, 1934, **2**, 128.

[25] Califano, Moccia, Scarpati, and Speroni, *J. Chem. Phys.*, 1957, **26**, 1777.

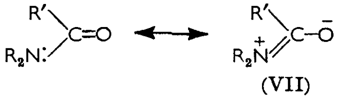
[26] Taylor and Cluff, *Nature*, 1958, **182**, 390.

[27] Ref. 21, p. 205.

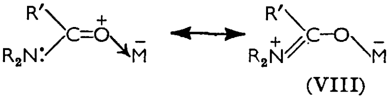
[28] Gerrard, Lappert, Pyszora, and Wallis, *J.*, 1960, 2144.

[29] Bellamy and R. L. Williams, *Trans. Faraday Soc.*, 1959, **55**, 14.

charge on the oxygen. Co-ordination through the dimethylamino-group, which would suppress form (VII), would be expected to raise the carbonyl frequency.



(VII)



(VIII)

The dimethylacetamide compound is similar to the formamide derivative. Most of the bands in the parent molecule appear with slight displacements in the spectrum of the bis-derivative, except for the carbonyl band, whose frequency falls to 1618 cm.$^{-1}$.

With both the dimethylformamide and the acetamide derivative, new strong bands appear in the spectrum near 890 and 819 cm.$^{-1}$. It is possible that these are associated with the boron–oxygen bond.

In the case of triethylamine, assignment is impossible because of the interactions which can take place between the various CH deformation vibrations and those due to the C–C and C–N stretching modes. However, there is a strong band at 2797 cm.$^{-1}$ in addition to the normal CH bands, which is characteristic of a lone pair of electrons on the nitrogen.[18] This band disappears from the spectrum of the covalent bistriethylaminedecaborane, confirming the formation of a co-ordinate link which is also shown by the appearance of strong bands at 1147 and 780 cm.$^{-1}$, both of which have been associated with N→B links.[30]

The spectrum of the ionic triethylamine derivative, $[Et_3NH]^+{}_2[B_{10}H_{10}]^{2-}$, is considerably simpler than that of the covalent compound and is characterised particularly by a strong band at 3060 cm.$^{-1}$, which can be assigned to the $NH^+$ stretching vibration. Hitherto, the $NH^+$ vibration of tertiary ammonium salts has been reported [31,32] to lie near 2740 cm.$^{-1}$ or lower, but in each case the salts are those of strong acids and the spectrum is complicated by very strong hydrogen bonding. With the chloroplatinate of triethylamine, hydrogen bonding is weaker and a strong band is found at 3085 cm.$^{-1}$. The remainder of the chloroplatinate spectrum also bears a strong similarity to that of the ionic decaborane compound, as Fig. 3 and the listed frequencies show.

The spectra of the three remaining compounds are less informative since the spectrum of each parent molecule is complex. With triphenylphosphine, the bands arise mainly from the phenyl groups, and frequency changes on complex formation will be slight because of relay through the phosphorus. This is borne out in practice. The parent and complex have similar spectra. However, it is noteworthy that the δ-BH band at 1000 cm.$^{-1}$ is abnormally weak.

The changes in the spectrum of pyridine on complex formation with boron trichloride have been fully discussed by Greenwood and Wade.[30] Similar changes take place with bispyridinedecaborane and it is possible to identify in the spectrum of the complex all the bands listed by Greenwood and Wade as due to the pyridine. These also lie at similar frequencies. In particular, the strong band at 1113 cm.$^{-1}$ associated with the formation of an N→B link is found as a strong doublet at 1121 cm.$^{-1}$ in bispyridinedecaborane.

2-Bromopyridine follows a similar pattern to pyridine. The ring stretching frequencies in the 1600—1400 cm.$^{-1}$ region are increased on complex formation, as are the out of plane CH deformations at 775—700 cm.$^{-1}$. The remainder of the spectrum is complex, but a new band appears near 1090 cm.$^{-1}$ in a similar way to those in pyridine–boron trichloride and bispyridinedecaborane.

*Displacement Reactions.*—The displacement reactions discussed in the Experimental section taken with those reported by Hawthorne and Pitochelli [4] make it possible to write the ligands in increasing bonding strengths, $Me_2S < MeCN < Et_2N{\cdot}CN < HCO{\cdot}NMe_2 = AcNMe_2 < Et_3N = C_5H_5N = Ph_3P$.

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[30] Greenwood and Wade, *J.*, 1960, 1130.

[31] Chenon and Sandorfy, *Canad. J. Chem.*, 1958, **36**, 1181; Brissette and Sandorfy, *ibid.*, 1960, **38**, 34.

[32] Bellanato and Barcello, *Anales real Soc. espan. Fís. Quím.*, 1956, **52**, *B*, 469.

Each of these substances will displace the ligand from the complex on its left provided a solution of the latter is used.

We thank Mr. A. C. Thomas (C.D.E.E., Porton) for analysing the samples, and Mr. G. Kidd (University College, London) for his co-operation in obtaining the nuclear magnetic resonance spectra.

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[*Received, December 7th,* 1960.]