The Vibrational Spectra of the Carboranes. Part II.[1] 4,5-Dicarba-*nido* hexaborane(8) and its *C*-Methyl Derivatives

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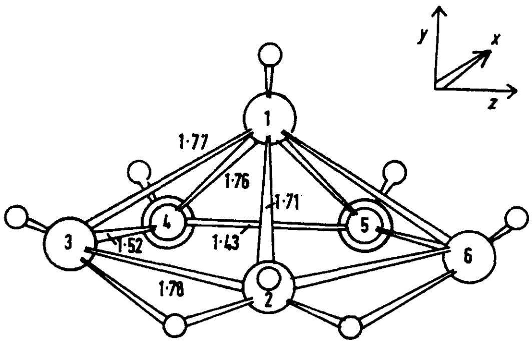
The Raman spectra of 4,5-$C_2B_4H_8$, $C_2B_4H_7Me$, and $C_2B_4H_6Me_2$ are presented, together with qualitative intensities and states of polarisation. Vibrational assignments are given for $C_2B_4H_8$ using both Raman and remeasured i.r data and the results of published i.r. deuteriation studies, and comparative assignments are given for the methylated derivatives. The vibrational frequencies are partially correlated with the bonding in the polyhedral framework, and compared with data for the small *closo*-carboranes.

IN Part I,[1] we presented i.r. and Raman data for the three small *closo*-carboranes, $C_2B_3H_5$, 1,6-$C_2B_4H_6$, and $C_2B_5H_7$, and we were able to give almost complete assignments for these molecules. These data have provided much information on the interactions within the polyhedral frameworks. We now present the results of a comparative study on the *nido*-carborane 4,5-$C_2B_4H_8$ (Figure) and its *C*-methyl derivatives.



4,5-dicarba-*nido*-hexaborane(8)

The structures of $C_2B_4H_8$ and $C_2B_4H_6Me_2$ have been the subject of an *X*-ray investigation,[2] and the charge distributions on various atoms have been calculated.[3] The B_3C_2 basal skeleton is almost planar and the carbon atoms are essentially sp^2 hybridised with a very short C–C distance of 1·43 Å. I.r. data on $C_2B_4H_8$ and its bridge-, *C*- and *B*-deuteriated derivatives have been published.[4,5] Low-resolution i.r. data have been given for the *C*-methyl derivatives,[6] but no Raman data have been published previously.

EXPERIMENTAL

$C_2B_4H_8$, $C_2B_4H_7Me$, and $C_2B_4H_6Me_2$ were prepared by the low-temperature, high-pressure reactions of B_5H_9 with C_2H_2, C_2HMe, and C_2Me_2 respectively,[7,8] and were purified by g.l.c. I.r. spectra were recorded on gaseous and liquid samples using a Perkin-Elmer 457 spectrophotometer. Liquid-phase Raman spectra were recorded on the same

TABLE 1

The vibrational spectra of liquid 4,5-dicarba-*nido* hexaborane(8)

Raman (cm^{-1})	Infrared (cm^{-1})	Notes [a]	Assignment
180w, p?			$\nu_{20?}$
443m, p	444w	A	ν_{19}
448wsh,* p			
586m, p?	586vw		ν_{17}
600w, ?			$\nu_{35?}$
607wsh, dp	605w		ν_{33}
637m, p	637m		ν_{18} overlap
644msh,* p	643m *		
656sh, dp	655sh		ν_{34}
666wsh,* dp	666m *		
	670sh		?
735m, dp	732s	*A*	ν_{32}
747sh,* dp?	743msh *		
784w, p	782vw	*C*	ν_{14}
	822,wsh		?
837w, dp	837m	*B*	ν_{29}
854vw, p?			ν_{13}
867wsh, p	865m	*C*	ν_{16}
889vs, p	889wsh		ν_{10}
905sh, dp	900m	*A*	ν_{31}
	910wsh *		
958w, p	957s	*C*?	ν_8
987w, dp	985vw		ν_{26}
	1022w	*B*	ν_{30}
1034s, p	1033m	*A*	ν_9, ν_{28}
1052sh, dp?			$\nu_{25?}$
1070vs, p	1068s	*A*	ν_{15}
1081msh,* p	1080msh *		
1106m, p			ν_7
1112m, p	1111?vwsh		ν_{12}
	1305wsh		?
1324vw, dp	1322w,b		ν_{27}
	1348w	*A*	ν_{11}
	1460w		$\nu_{13} + \nu_{33?}$
	1510vs	*B*	ν_{24}
	1590w	*B*	ν_{23}
	1825vw		$\nu_8 + \nu_{16?}$
1843w, p	1840wsh		$\nu_8 + \nu_{10}$
1885w, p	1882m	*B*	ν_6
1899w, p	1900wsh?		$2 \times \nu_{8?}$
1934m, p	1936w	*B*	ν_5
1975w, p	1976vwsh?		$\nu_{10} + \nu_{15}$
2480?			?
2592m, p			ν_3, ν_4
2604b,msh, dp	2610vs	*A*	ν_{22}
2624m, p	2630vssh		ν_2
3032sh, dp	3032m	*A*	ν_{21}
3044m, p	3040m		ν_1

[a] A, B, C Gas-phase band contours.

* $C_2{}^{10}B^{11}B_3H_8$ Component.

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[1] Part I, R. W. Jotham and D. J. Reynolds, *J. Chem. Soc.* (*A*), 1971, 3181.

[2] F. P. Boer, W. Streib, and W. N. Lipscomb, *Inorg. Chem.*, 1964, **3**, 1666.

[3] W. E. Streib, F. P. Boer, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, 1963, **85**, 2331.

[4] J. Spielman, R. Warren, G. Dunks, J. Scott, and T. Onak, *Inorg. Chem.*, 1968, **7**, 216.

[5] T. Onak and G. Dunks, *Inorg. Chem.*, 1966, **5**, 439.

[6] R. N. Grimes, C. L. Bramlett, and R. L. Vance, *Inorg. Chem.*, 1968, **7**, 1066.

[7] T. Onak, R. P. Drake, and G. B. Dunks, *Inorg. Chem.*, 1964, **3**, 1686.

[8] J. Ditter, *Inorg. Chem.*, 1968, **7**, 1748.

samples enclosed in smoothly blown Pyrex tubes as previously described.[1] Many of the repeatedly purified samples of $C_2B_4H_6Me_2$ apparently contained traces of an insoluble impurity which scattered the argon-ion incident beam (488 nm) excessively, and we eventually used a He–Ne source for this compound as it seemed likely that the troublesome impurity was a photolysis product. The Raman data for this compound consequently show a poorer resolution than the data for $C_2B_4H_8$ and $C_2B_4H_7Me$ (± 2 cm^{-1} for the stronger bands).

TABLE 2

The vibrational spectra of liquid 4(5)-methyl-4,5-dicarba-*nido*-hexaborane(8)

Raman (cm^{-1})	Infrared (cm^{-1})	Notes	Assignments
226vw, p			ν_{30}
320vw, dp			?
449w, dp	451vw		ν_{45}
470s, p			ν_{29}
563ms, dp?			ν_{27}
593wm, dp			?
613w, dp	614w		ν_{42}
653w, dp	654m	*A*	ν_{32}
	665wsh		?
671s, dp	673w	*C*	ν_{44}
680msh,* dp			
732m, dp	730m	*A*	ν_{41}
741m, dp	740wsh		ν_{43}
751m,* dp	750w *		
769m, p	770w	*C*	ν_{24}
773wsh, dp	775wsh		ν_{31}
786m, p			ν_{28}
797wsh?, dp?			?
840m, p	840m	*C*?	ν_{23}
853wsh, dp	847wsh		ν_{38}
	873w		ν_{40}
881vs, p	880w		ν_{13}
886w, dp			ν_{20}
901s, p	901m		ν_{26}
908m,* p	910wsh *		
	964s		ν_{21}
975w, dp	976s	*A*?	ν_{37}
990ms, p?	988m		ν_{11}
1035w, dp	1037w	*C*	ν_{39}
1062wm, dp?			ν_{36}
1079vs, p	1080m	*B*	ν_{25}
1099wm, p	1100vw		ν_{12}
1160vs, p	1160w	*B*	ν_{10}
1183wsh, dp?			?
	1255vw		ν_{14}
1307vw, dp	1301m,b	*B*	ν_{15}
1378vw, p?	1376m		ν_{17}
1384w, dp	1383m	*B*	$\nu_{32} + \nu_{41}$??
1447w, dp	1445s,b	*B*	ν_{18}, ν_{19}
1492?vw, ?	1485s,b	*A*	ν_{35}
1870vw, dp			$\nu_{25} + \nu_{28}$?
1901w,b, p?	1895m,b	*B*	ν_9
1936m,b, p?	1928m,b	*B*	ν_8
1984vw,b, p?			$2 \times \nu_{11}$?
	2290?vw		?
2588m, p			ν_6, ν_7
2600m, dp	2595vs	*A*	ν_{33}
2618s, p	2615vs,sh		ν_5
2736?vw			?
2871m, p	2865m	*A*	$2 \times \nu_{18}$, $2 \times \nu_{19}$
2929vs, p	2915s	*B*	ν_2
	2955s	*C*	ν_3
2970w, dp	2975msh		ν_4
3019s, p	3014m	*B*	ν_1
3065vw, p			$\nu_9 + \nu_{10}$?

RESULTS

Vibrational spectra of liquid $C_2B_4H_8$, $C_2B_4H_7Me$, and $C_2B_4H_6Me_2$ are given in Tables 1—3 together with relative intensities, Raman polarisation data, the gas-phase i.r. contours, and the assignments. The i.r. data agree closely with published data but generally show a better resolution.[5,6] The few clear-cut cases of ^{10}B satellite bands are indicated. Copies of the Raman spectra of $C_2B_4H_8$, $C_2B_4H_7Me$, and $C_2B_4H_6Me_2$ are in Supplementary Publication No. SUP 20285 (5 pp.).*

TABLE 3

Vibrational spectra of liquid 4,5-dimethyl-4,5-dicarba-*nido*-hexaborane(8)

Raman (cm^{-1})	Infrared (cm^{-1})	Notes	Assignments
260vw, p?			ν_{27}
[illegible], dp	480vw		ν_{52}
5[illegible]ms, dp	563vw		ν_{51}
580sh,* dp	580vw		
624w, dp			ν_{49}
661?vw	659m	*A*	ν_{54}
682w, p?	681vw		ν_{29}
	688vw		ν_{53}
	721w	*C*?	ν_{50}
727vs, p	727wsh		ν_{25}
753sh, dp	753m	*C*	ν_{48}
	765w		ν_{28}
786w, p			ν_{21}
	796w	*B*	ν_{20}?
	805vw		ν_{45}?
847m, p	847m	*A*	ν_{12}
857sh,* p?	857wsh *		
885w, p	885vw		ν_{23}
898vwsh			ν_{17}, ν_{42}?
	904m	*B*	ν_{47}
	953vw		ν_{18}
996vw	966msh		ν_{43}
	970m	*B*	ν_{10}
995w, dp	994w,b	*B*?	ν_{37}
1054vw, p?			ν_{11}
1067w, dp	1064vw	*B*	ν_{36}
1098vw, p?			ν_{22}
1168ms, p	1170vw,b	*B*	ν_9
1222vw, p?			ν_{13}
	1265vw,b		ν_{38}
	1373m	*A*	ν_{39}
1381w,b, p			ν_{14}
	1420wsh		ν_{15}, ν_{40}, ν_{16}, ν_{41}
1447w,b, dp	1440s		
	1456s	*A*?	ν_{35}
	1462s		?
	1476s	*A*	ν_{34}
	1888w,b		ν_8
	1910w,b		$2 \times \nu_{43}$?
1932w,b, p	1931m,b	*B*	ν_7
	1980w,b	*B*	$\nu_9 + \nu_{25}$?
	2480vw		?
2578m, p	2578vs	*A*	ν_5, ν_6
2600msh, dp	2600vs	*A*	ν_{33}
2609s, p?			ν_4
2869w, p	2864m	*B*?	$2 \times (\nu_{15}, \nu_{16}, \nu_{40}, \nu_{41})$
2927s, p	2922s	*A*	ν_1, ν_{30}
2960sh, dp	2954s	*C*?	ν_2, ν_{31}
	2980m	*A*	ν_3, ν_{32}
	3125?vw		?

Molecular Geometry and Symmetry Co-ordinates.—4,5-$C_2B_4H_8$ (Figure) is an asymmetric-top molecule with a single mirror plane (σ_{xy}). The structure does, however, approximate to a pentagonal pyramid so that the axis of greatest inertia, I_c, almost passes through the apical boron atom, B^1. For $C_2B_4H_8$, $I_A \simeq I_B$ but for $C_2B_4H_6Me_2$,

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* Copies can be obtained from the National Lending Library, see Notice to Authors No. 7, *J. Chem. Soc.* (*A*), Issue No. 20, 1970.

$I_B = I_Z$. We regard the methylated carboranes as cases of local C_{3v} symmetry (CH_3) combined with local C_s symmetry ($C_2B_4H_6$). Thus in the case of $C_2B_4H_7Me$ it is possible to distinguish between essentially polarised and depolarised Raman bands just as in the true C_s cases and to interpolate the assignments accordingly.

ASSIGNMENTS

Symmetry species, vibrations, and their approximate descriptions are given in Table 4 for all three compounds. Where a vibration has not been assigned, an estimated frequency is given in parentheses. The assignments of the methylated compounds are based on comparison with the $C_2B_4H_8$ assignments and the established values for the methyl halides [9] and the methyldiboranes.[10]

(*a*) $C_2B_4H_8$.—The A' and A'' modes are allocated to those Raman bands which are polarised and depolarised respectively. I.r. and Raman co-incidence is observed for nearly all of the modes, and the gas-phase i.r. band structures provide a guide to several key assignments. Finally the comparative i.r. data on $C_2B_4H_8$, $C_2D_2B_4H_6$, μ_2-$C_2H_2B_4D_2H_4$, 2,3,6-$C_2H_2B_4D_3H$, and $C_2H_2B_4D_6$ are used to distinguish between the essentially cage and B–H deformation modes which overlap extensively in the 700—1100 cm^{-1} region.

The A' and A'' C–H stretching modes are assigned to the bands at 3042 and 3032 cm^{-1} respectively. In the B–H stretching region of all three compounds three Raman peaks are observed, a central depolarised shoulder flanked by two medium strength polarised bands. The most intense of the corresponding i.r. bands, with a type A contour, corresponds to the depolarised shoulder, and is assigned to the asymmetric B–H equatorial stretching mode. In order to distinguish the three B–H stretching modes of type A' we utilise the positive correlation between ν_{B-H} and J_{B-H} which was established in Part I of this series for a wide range of boron hydrides and carboranes.[1] The n.m.r. coupling constants are 178, 157, and 159 Hz for the apical, equatorial, and axial boron atoms of $C_2B_4H_8$ respectively.[11] Therefore we attribute the band at 2624 cm^{-1} to the B–H apical stretching mode of $C_2B_4H_8$. Considerable mixing, and ' repulsion ', may be expected for the A' B–H axial and B–H equatorial stretching modes which might otherwise be almost isoergic ($J_{B^2-H} \simeq J_{B^3-H}$), but we note that the topological relationship between the B–H axial and B–H equatorial groups is the same as that between the C–H groups so that the repulsion is unlikely to exceed 10 cm^{-1}, *i.e.* the coupling observed between the C–H stretching modes. We therefore assign the band at 2592 cm^{-1} to the overlapping totally symmetric B–H axial and B–H equatorial stretching modes.

The separation between symmetric and asymmetric B–H bridge-stretching modes is commonly *ca.* 400 cm^{-1}; furthermore, Fermi resonance involving the totally symmetric peaks in the 1900 cm^{-1} region is often very marked.[10] The B–H$_\mu$ stretching modes of $C_2B_4H_8$ give very broad peaks, but the broad band near 1900 cm^{-1} is readily seen to incorporate several non-fundamentals. We assign the two strongest components at 1936 and 1882 cm^{-1} to the two B–H$_\mu$ stretching modes of A' symmetry. As in the case of the methyldiboranes,[10] the asymmetric B–H$_\mu$ stretching modes give extremely weak Raman bands but very strong i.r. bands. The two fundamentals of A'' symmetry are assigned to the bands at 1510 and 1590 cm^{-1}.

The i.r. bands near 1340 cm^{-1} disappear on *C*-deuteriation.[4] They may therefore be attributed confidently to the two in-plane C–H deformations (throughout this discussion ' plane ' refers to the basal plane). The Raman band at 1324 cm^{-1} is probably depolarised, and this band is therefore assigned to the A'' mode. The i.r. band at 1348 cm^{-1} has a type A contour in the gas-phase; it is assigned to the totally symmetric in-plane C–H deformation.

The two medium-strength Raman bands at 1112 and 1106 cm^{-1} are attributed to the totally symmetric C–H out-of-plane deformation and the C–C cage-stretching mode respectively. The ambiguity is resolved solely on the presence of an i.r. counterpart to the 1112 cm^{-1} band, as the C–C stretch should involve a very small dipole moment change. The strong i.r. band at 1068 cm^{-1} has a type A contour in the gas-phase and is shifted on deuteriation of the basal boron atoms.[5] The corresponding Raman band is very strong and polarised, and ^{10}B satellites are prominent in both spectra. These bands are assigned to the B–H equatorial in-plane deformation of type A'.

The medium-strength i.r. band at 1033 cm^{-1} has a type A contour in the gas-phase, and appears to be shifted on *C*-deuteriation.[4] It has a strong Raman counterpart and assignment of the latter to a C–H deformation mode is excluded on the grounds that these C–H deformation modes give rise to very low intensity Raman bands in the case of the small *closo*-carboranes.[1] We therefore conclude that the C–H out-of-plane deformation mode of type A'' and the B–C stretching mode of type A' almost coincide at 1034 cm^{-1} and give rise to the bulk of the i.r. and Raman intensity respectively. The depolarised shoulder in the Raman spectrum at 1052 cm^{-1} is attributed tentatively to the asymmetric B–C stretching mode. The coupling between the B–C vibrations appears to be small but the situation is complicated by the coupling to the B–B and C–C stretching modes.

The weak i.r. band at 1022 cm^{-1} has a type B contour. Its fate on deuteriation is uncertain since this band was not distinguished from that at 1033 cm^{-1} in the published data.[4,5] It is ascribed to the in-plane B–H axial deformation (A''), but it should be borne in mind that the coupling between this mode and the A'' B–H equatorial in-plane deformation will be fairly large.

The very weak i.r. band at 985 cm^{-1} corresponds to a weak depolarised Raman band at 987 cm^{-1}. These bands are tentatively assigned to the B–B stretching mode of type A''. The strong i.r. band at 957 cm^{-1} has a very strong, sharp Q branch in the gas-phase. It is little affected by *C*- or *B*-deuteriation,[4,5] and the weak corresponding Raman band is polarised. This band is therefore firmly assigned to the apex-basal-plane stretching mode of the framework, termed the O–B apex stretch, of type A'. The medium i.r. band at 900 cm^{-1} has a ^{10}B satellite and a type A contour. The corresponding Raman feature is depolarised and the i.r. band is shifted on deuteriation of the basal boron atoms. These bands are attributed to the asymmetric B–H equatorial in-plane deformation.

The very strong polarised Raman band at 889 cm^{-1} is assigned to the B–B stretch of type A'. The medium

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[9] G. Herzberg, ' Infra-red and Raman Spectra of Polyatomic Molecules,' Van Nostrand, 1945.

[10] J. H. Carpenter, W. J. Jones, R. W. Jotham, and L. H. Long, *Spectrochim. Acta*, 1970, **26***A*, 1199; 1971, **27***A*, 1721.

[11] R. E. Williams, *Progr. Boron Chem.*, 1970, **2**, 37.

TABLE 4

The vibrational modes of $C_2B_4H_8$, $C_2B_4H_7Me$, and $C_2B_4H_6Me_2$

Species	Approximate description	$C_2B_4H_8$		$MeC_2B_4H_7$		$Me_2C_2B_4H_6$	
		Running No.	Frequency (cm^{-1})	Running No.	Frequency (cm^{-1})	Running No.	Frequency (cm^{-1})
A′(*A*)	C–H stretch (carborane)	1	3042	1	3017		
	C–H stretch sym. (Me)			2	2929	1	2925
	C–H stretch asym. (Me)			3	2955	2	2954
	C–H stretch asym. (Me)			4	2975	3	2980
	B–H stretch (apex)	2	2624	5	2617	4	2609
	B–H stretch (axial)	3	2592	6	2588	5	2578
	B–H stretch sym. (equatorial)	4	2592	7	2588	6	2578
	B–H_μ stretch sym.	5	1936	8	1932	7	1931
	B–H_μ stretch sym.	6	1882	9	1898	8	1888
	C–C stretch	7	1106	10	1160	9	1169
	O–B stretch (apex)	8	958	11	990	10	970
	B–C stretch sym.	9	1034	12	1099	11	1054
	B–B stretch sym.	10	889	13	881	12	847
	C–CH_3 stretch			14	1255?	13	1222
	C–H def. (i.p.)	11	1348	15	1303		
	C–H def. (o.o.p.)	12	1112	16	(1070)		
	CH_3 def. sym.			17	1376	14	1381
	CH_3 def. asym.			18	1446	15	1420
	CH_3 def. asym.			19	1446	16	1443
	CH_3 rock			20	886	17	(900)
	CH_3 rock			21	964	18	953
	CH_3 torsional			22	(100)	19	(100)
	B–H apex def.	13	854	23	840	20	796?
	B–H axial def. (o.o.p.)	14	784	24	770	21	786
	B–H equatorial def. (i.p.)	15	1069	25	1079	22	1098?
	B–H equatorial def. (o.o.p.)	16	866	26	901	23	885
	B–H_μ def.	17	586	27	563	24	(570)
	Cage def.	18	637	28	786	25	727
	Cage def.	19	443	29	470	26	(450)
	Cage def.	20	180?	30	226	27	260?
	C–Me def. (i.p.)			31	774?	28	765
	C–Me def. (o.o.p.)			32	654?	29	682
A″(*A*)	C–H stretch (carborane)	21	3032				
	C–H stretch sym. (Me)					30	2925
	C–H stretch asym. (Me)					31	2954
	C–H stretch asym. (Me)					32	2980
	B–H stretch asym. (equatorial)	22	2610	33	2595	33	2600
	B–H_μ stretch asym.	23	1590	34	(1530)	34	1476
	B–H_μ stretch asym.	24	1510	35	1488	35	1456
	B–C stretch asym.	25	1052?	36	1062	36	1066
	B–B stretch asym.	26	986?	37	976	37	995
	C–Me stretch					38	1265
	C–H def. (i.p.)	27	1323				
	C–H def. (o.o.p.)	28	1033?				
	CH_3 def. sym.					39	1373
	CH_3 def. asym.					40	1420
	CH_3 def. asym.					41	1443
	CH_3 rock					42	(900)
	CH_3 rock					43	966
	CH_3 torsional					44	(100)
	B–H apex def.	29	837	38	850	45	805?
	B–H axial def. (i.p.)	30	1022	39	1036	46	(1030)
	B–H equatorial def. (i.p.)	31	902	40	873	47	904
	B–H equatorial def. (o.o.p.)	32	734	41	731	48	753
	B–H_μ def.	33	606	42	613	49	624
	Cage def.	34	656	43	741	50	721
	Cage def.	35	600	44	672	51	565
	Cage def.	36	(400)	45	450	52	480
	C–Me def. (i.p.)					53	688
	C–Me def. (o.o.p.)					54	659

The apical, axial, and equatorial boron atoms are those numbered **1**, **2**, **3**(**6**) respectively in the Figure, sym. = symmetric, asym. = asymmetric, def. = deformation, O = origin, i.p. = in-plane (*i.e.* the *basal* plane not the mirror plane), o.o.p. = out-of-plane, μ = bridge, ? = uncertain, estimated data in brackets.

strength i.r. band at 865 cm^{-1} has a type *C* contour and a polarised Raman counterpart. As there are several nearby i.r. bands of similar intensity, the fate of this band on deuteriation is uncertain. We tentatively assign this band to the totally symmetric B–H equatorial out-of-plane deformation. The i.r. band at 837 cm^{-1} is shifted on deuteriation of the apical boron atom,[5] and its Raman counterpart is depolarised. Accordingly, we attribute this band to the B–H apical deformation of type *A''*. We would expect the *A'* counterpart to be of almost the same energy so the probably polarised Raman band at 854 cm^{-1} is the natural assignment for this mode.

The strong i.r. band at 732 cm^{-1} has a type *A* contour in the gas-phase and a depolarised Raman counterpart. Each band has a ^{10}B satellite. The i.r. band is shifted on deuteriation of the basal boron atoms,[5] and these bands are therefore attributed to the B–H equatorial deformation of type *A''*. One terminal B–H deformation remains to be assigned, namely the B–H axial out-of-plane deformation (*A'*). The weak polarised Raman band at 784 cm^{-1} has an i.r. counterpart with a type *C* contour and is therefore ascribed to this mode.

The deuteriation studies do not extend beyond 600 cm^{-1},[4,5] and it is therefore difficult to distinguish the B–H bridge deformation modes from the cage deformation modes. The group of overlapping bands in the 630—670 cm^{-1} region are not shifted on bridge deuteriation however, and so we assign these to cage deformations.

The Raman band at 586 cm^{-1} is of uncertain polarisation despite its medium intensity, but this seems to be the most likely candidate for the totally symmetric B–H bridge deformation mode.

Many of the above assignments are necessarily tentative; a few other assignments of a similar nature are given in Table 4.

(b) *Carborane Modes of* $MeC_2B_4H_7$ *and* $Me_2C_2B_4H_6$.—The stronger and more characteristically shaped bands of these molecules can be fairly confidently assigned by comparison with the $C_2B_4H_8$ spectra. Average values of in- and out-of-phase modes of the C–H groups of $C_2B_4H_8$ formed the basis of comparison with the corresponding modes of $MeC_2B_4H_7$. Conversely, the assignment of the weaker features is very tentative and, in the 800—1200 cm^{-1} region, it is complicated by the presence of internal rocking vibrations of the methyl groups. Essentially polarised and depolarised Raman bands can be distinguished even in the case of $MeC_2B_4H_7$, and these polarisation data again proved to be of great value in the assignments for the methylated compounds. These are listed in Tables 2—4, and we shall not discuss the comparative assignments further. In a few cases we have been able to list in Table 4 estimated frequencies only.

The very weak i.r. band at 1255 cm^{-1} is assigned to the C–CH_3 stretching mode of $MeC_2B_4H_7$. In the case of $Me_2C_2B_4H_6$ the in- and out-of-phase C–Me stretching modes are assigned to the weak Raman and i.r. bands at 1222 and 1265 cm^{-1} respectively. The C–CH_3 deformation modes were expected to absorb in the 600—800 cm^{-1} region, and so the assignments are necessarily tentative.

(c) *Internal Vibrations of the Methyl Groups of* $MeC_2B_4H_7$ *and* $Me_2C_2B_4H_6$.—If the methylated carboranes are regarded as pseudo-CH_3X compounds, a number of the internal vibrations are readily assigned. Coupling between the two methyl groups of $Me_2C_2B_4H_6$ was not readily observed. Accordingly we have frequently assigned the same energy to the corresponding *A'* and *A''* modes.

The radial C–H deformation motions of methyl groups give rise to one symmetric and two asymmetric methyl deformation modes, which are commonly observed in the 1350 and 1440 cm^{-1} regions respectively.[9,10] The two asymmetric deformation modes gave rise to broad peaks in these compounds and could not be separated for $MeC_2B_4H_7$. The *A'* and *A''* symmetric methyl deformations of $Me_2C_2B_4H_6$ are assigned to bands at 1381 and 1373 cm^{-1} respectively, because in this case the maxima of the polarised Raman band and the i.r. band do not coincide. Two of the four asymmetric methyl deformations could be distinguished at 1420 and 1443 cm^{-1}. In both methylcarboranes there appears to be overlap between these modes and one of the asymmetric B–H stretching vibrations.

The tangential motions of the C–H groups give rise to one torsional mode and two rocking (or wagging) modes. In many methyl compounds the torsional mode functions as an internal rotation and it is generally observed, if at all, at low energy. The rocking vibrations of alkanes and other methyl compounds involve motion of a peripheral nature, which motion is much influenced by Van der Waals interactions with neighbouring groups. Accordingly, these modes are typically observed over the wide range 800—1200 cm^{-1} even in the series of methyldiboranes.[9,10,12] Assignment of the rocking modes of $Me_2C_2B_4H_7$ and $Me_2C_2B_4H_6$ is necessarily very tentative in these circumstances.

No hindrance to free internal rotation of the methyl groups would be expected for these compounds, and we have therefore arbitrarily estimated values of 100 cm^{-1} for all of the torsional modes.

DISCUSSION

In view of the tentative nature of many of the assignments, we restrict our discussion to the firm assignments and to the broad trends in the other modes.

Vibrations of the Methyl Groups of $MeC_2B_4H_7$ *and* $Me_2C_2B_4H_6$.—The C–H stretching and C–H deformation frequencies of these two compounds are very similar and differ little from the corresponding values found for the methyldiboranes and the alkanes.[10,12] The C–CH_3 stretching modes are found at a relatively high energy (1250 cm^{-1}) by comparison with the C–C stretching mode of the carborane itself. Other assignments are too tentative for detailed comment.

C–H *Stretching and Deformation Modes of* $C_2B_4H_8$ *and* $MeC_2B_4H_7$.—The average C–H stretching frequency of $C_2B_4H_8$ is 3037 cm^{-1}, whereas that of the methylated compound is 3017 cm^{-1}. These values, although much higher than those associated with alkanes, are *ca.* 100 cm^{-1} below the values observed for the small *closo*-carboranes.[1] They reflect the moderately high electronegativity of the *nido*-carborane nucleus which, on this basis, appears to have much in common with an aromatic nucleus. There is indeed a formal requirement for an *sp*^{2} hybridisation of the carbon atoms,[3] and Onak and his co-workers have proposed that

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[12] L. J. Bellamy, 'The Infra-red Spectra of Complex Molecules,' Methuen, 1958.

aromatic-type ring-currents may be magnetically induced in the basal plane.[13] The C–H stretching frequency of $MeC_2B_4H_7$ is considerably lower (20 cm^{-1}) than the average value for $C_2B_4H_8$, reflecting the reduced electronegativity of the framework of the alkylated compound. The coupling between the C–H stretching modes of $C_2B_4H_8$ is interesting because in the *closo*-carboranes the symmetric C–H stretching mode is at lower energy than the asymmetric mode.[1] As with B–H stretching modes of 1,6-$C_2B_4H_6$,[1] it is apparent that adjacent M–H groups couple so that the in-phase motion has the higher energy, whereas M–H groups separated by another such group couple more weakly in the opposite sense. An interesting alternation is suggested, because M–H groups on the same atom M tend to couple so that the in-phase stretching motion vibrates at lowest frequency.

The C–H deformation frequencies are rather similar (1000—1350 cm^{-1}) to the values associated with hydrocarbons. The in-plane deformations are assigned to bands at higher energy than the out-of-plane modes because the former motions require the reduction of angles in the fairly congested basal plane, whereas the latter are relatively free from restoring forces. The C–H deformation modes of the *closo*-carboranes are also assigned to bands in the region of 1200 cm^{-1}.[1]

B–H *Terminal Stretching and Deformation Modes*.—The average $B-H_t$ stretching frequencies for $C_2B_4H_8$, $MeC_2B_4H_7$, and $Me_2C_2B_4H_6$ are 2604, 2596, and 2591 cm^{-1} respectively. These values may be correlated with an increasing electron density in the nucleus as a result of methylation and the consequent reduced electronegativity of the framework. The average values of the B–H stretching modes of $C_2B_3H_5$, 1,6-$C_2B_4H_6$, and $C_2B_5H_7$ are over 40 cm^{-1} higher, whereas the values for neutral boranes tend to be rather lower than those of the *nido*-carboranes.[1]

The $B-H_t$ deformation modes span a wide range of frequencies (700—1100 cm^{-1}) which is, nevertheless, rather similar to that found for the *closo*-carboranes and for typical boranes and their alkyl derivatives.[1,10] The apical deformation modes could be separated from the basal counterparts with the aid of the data on deuteriated $C_2B_4H_8$; their relatively low energy by comparison with the latter is of interest, since it is clear that the apical B–H bond is the strongest of the B–H terminal bonds. These relatively ready apical deformations presumably result from the lack of congestion at the apex itself.

B–H *Bridge Stretching and Deformation Modes*.—The symmetric $B-H_\mu$ stretching modes of $C_2B_4H_8$, $MeC_2B_4H_7$, and $Me_2C_2B_4H_6$ are observed at very similar energies (1933 and 1890 cm^{-1}), but it is impossible to comment meaningfully on the actual observed values because of the extensive Fermi resonance in this region. Conversely, the frequency of the strongest (i.r.) corresponding asymmetric mode falls steadily from 1510 through 1488 to 1456 cm^{-1} on successive methylation, and therefore these bands reflect the same trend in the electronegativity of the framework as the C–H and $B-H_t$ stretching modes. Interestingly, both the symmetric and the asymmetric $B-H_\mu$ stretching modes of diborane and the methyldiboranes are observed at a higher frequency than their counterparts in the *nido*-carboranes, whereas the terminal B–H stretching modes vibrate at a lower energy than those of the carboranes. It would therefore appear that the bridging hydrogen atoms of the *nido*-carboranes are relatively weakly bonded. The observed $B-H_\mu$ stretching frequencies of the *nido*-carboranes are, however, similar to those of B_5H_9.[14]

Rather little is known about bridge deformation modes of boranes or carboranes; it is clear from the present work that these are probably found below 650 cm^{-1} for $C_2B_4H_8$ and its *C*-methyl derivatives, but firm assignments will probably require a Raman study of bridge-deuteriated $C_2B_4H_6D_2$.

Cage Stretching and Deformation Modes.—The C–C stretching modes of $C_2B_4H_8$, $MeC_2B_4H_7$, and $Me_2C_2B_4H_6$ are observed at 1106, 1160, and 1169 cm^{-1} respectively. (This is the highest frequency assigned to a cage molecule.) This is a relatively low energy for a C–C bond stretch and must reflect the low bond order in the electron-deficient system. The donation of electron-density by the methyl groups into the framework tends to increase this bond order and hence the C–C stretching frequency. Despite the low formal bond-order, the C–C bond of $C_2B_4H_8$ is very short (1·43 Å),[2] indeed rather like a typical aromatic C–C bond. It is of interest to note that, whereas the C–H stretching frequencies of $C_2B_4H_8$ and benzene are similar, the C–C stretching frequencies are very different indeed.[12] The B–C and B–B stretching modes of the *nido*-carboranes are assigned to bands in the region 850—1100 cm^{-1}. Conversely, several of the corresponding modes of the *closo*-carboranes are observed in the region 1100—1200 cm^{-1}.[1] The framework of the *closo*-carboranes appears to be significantly more strongly bound than that of the *nido*-carboranes we have studied, quite apart from considerations of the relative flexibility of cage and basket structures.

A remarkable feature of the spectra of the *closo*-carboranes is that, because of the very rigid structures, all the cage modes are observed in the region 450—850 cm^{-1}.[1] From Table 4 it is apparent that some of the cage deformation modes of the *nido*-carboranes are observed at lower energy but, nevertheless, many of these deformations occur in this same relatively high-energy region. It seems that the puckering of the basal plane can give rise to low energy modes but that the upper part of the pentagonal pyramid itself is also a fairly rigid system.

CONCLUSION

The vibrational assignments indicate that the *nido*-carboranes studied are not only more flexible than the

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[13] D. Marynick and T. Onak, *J. Chem. Soc.* (*A*), 1969, 1797.

[14] H. J. Hrostowski and G. C. Pimental, *J. Amer. Chem. Soc.*, 1954, **76**, 998.

closo-carboranes, but also are intermediate between the *closo*-carboranes and the boranes themselves in electronic character. Thus the framework bonding in $C_2B_4H_8$ is not as strong as that in the small *closo*-carboranes while the M–H stretching frequencies are lower because the open framework is not such a strong electron attracting system as one of the *closo*-carborane cages. It is evident that, even if some of the assignments are tentative, a valuable guide to the bonding in polyhedral frameworks may be obtained from an assignment of the principal cage vibrations, and it is relevant to comment that, in the case of boron polyhedra, these modes tend to be amongst the strongest Raman bands but are not very prominent in the i.r. spectra.

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