Group 3 Tetrahydroborates. Part 3.[1] The Molecular Structure of Methylaluminium Bis(tetrahydroborate) in the Gas Phase as determined by Electron Diffraction

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Gaseous methylaluminium bis(tetrahydroborate), $Al(BH_4)_2Me$, as studied by electron diffraction, appears to be monomeric with a planar $CAlB_2$ skeleton. The structure involves five-fold co-ordination of the aluminium atom, each of the tetrahydroborate groups functioning as a bidentate ligand; the planes containing the $Al(\mu\text{-}H)_2B$ units evidently depart from being normal to the plane of the $CAlB_2$ skeleton by *ca.* 5°, thereby reducing the symmetry of the $CAl(BH_4)_2$ moiety from C_{2v} to C_2. Other salient parameters (estimated standard deviations in parentheses) are: r_a(Al–C) 194.1(0.9), r_a(Al–B) 215.2(1.6), r_a(Al–H_b) 182.0(0.9), r_a(B–H_b) 124, r_a(B–H_t) 120 pm; B–Al–B 121.5(0.7), H_b–Al–H_b 70.3(0.4)° (t = terminal, b = bridging). The features of the structure are compared with those of other molecules in the series $Al(BH_4)_{3-n}Me_n$ (n = 0—3).

THE tetrahydroborate group is remarkable for the versatility of its ligation with respect to metal atoms which may entail triple,[2,3] double,[2,3] or even single[4] hydrogen bridges. On the other hand, the circumstances of this versatility are hard to assess as long as definitive structural information is available for only a handful of gaseous tetrahydroborate molecules; as long as the structural characterisation of a given molecule is mainly confined to just one phase; and as long as the dimensions of the co-ordinated tetrahydroborate group itself remain, for the most part, relatively poorly defined.[1] In our investigations of molecular species in which the tetrahydroborate group competes with ligands like H, CH_3, or NH_3 for co-ordination of an aluminium or gallium centre,[5,6] we have encountered several volatile tetrahydroborates which pose significant structural problems; these include the methylaluminium compounds $Al(BH_4)_{3-n}Me_n$ (n = 1 or 2)[1,5,7] and the gallium compounds $Ga(BH_4)Me_2$,[1,8] $Ga(BH_4)(H)Me$,[6] and $Ga(BH_4)_2H$.[5,9] To judge by its vapour density, methylaluminium bis(tetrahydroborate) vaporises as monomeric molecules the i.r. spectrum of which is consistent with the presence of bidentate tetrahydroborate groups.[5,7,10] Hence it resembles the tetrahydroborates $M(BH_4)Me_2$ (M = Al or Ga)[1,5,8] and $Al(BH_4)_3$,[11,12] but where these exhibit four- and six-fold co-ordination respectively, the molecular model $MeAl[(\mu\text{-}H)_2BH_2]_2$ deduced for methylaluminium bis(tetrahydroborate) implies five-fold co-ordination of the metal atom. Less obvious is the geometry of the central $CAlH_4$ unit; in fact, a range of possible conformations is open to the molecule depending on the orientation of the two $Al(\mu\text{-}H)_2B$ four-membered rings with respect to the $CAlB_2$ skeleton which is likely to be planar. To investigate the details of this unusual structure, we have measured the electron scattering pattern of gaseous methylaluminium bis(tetrahydroborate) by electron diffraction. The results reported here are analysed to determine the dimensions, amplitudes of vibration, and likely conformation of the molecule, thereby establishing further reference points for the structural characterisation of other molecules containing a metal atom linked to two tetrahydroborate groups, *e.g.* $Ga(BH_4)_2H$.[5,9]

EXPERIMENTAL

The synthesis and manipulation of methylaluminium bis(tetrahydroborate) were accomplished using a conventional high-vacuum line having stopcocks and ground-glass joints lubricated with Apiezon L grease. Aluminium(III) chloride was produced by direct interaction of the elements and purified by repeated vacuum sublimation. To prepare aluminium tris(tetrahydroborate) a mixture of aluminium(III) chloride and lithium tetrahydroborate (supplied by B.D.H. and recrystallized from diethyl ether immediately prior to use) was heated to *ca.* 100 °C;[13] to prepare trimethylaluminium an excess of the metal was heated with dimethylmercury.[14] Trimethylaluminium and aluminium tris(tetrahydroborate) in the proportions $AlMe_3 : Al(BH_4)_3 = 1 : 2$ were allowed to react together at room temperature for *ca.* 2 h to effect virtually quantitative redistribution in accordance with the equation.[5,7] Trap-to-

$$Al_2Me_6 + 4Al(BH_4)_3 \longrightarrow 6Al(BH_4)_2Me$$

trap distillation of the products gave samples of methylaluminium bis(tetrahydroborate) (m.p. −76 °C) judged to be pure by the criteria (i) of its vapour pressure and (ii) of the i.r. spectrum of its vapour.[5,7] Our experience is that gaseous methylaluminium bis(tetrahydroborate) at a pressure of 30 mmHg † undergoes minimal decomposition over a period of 2 weeks in clean glass apparatus at room temperature. The compound is extremely sensitive, however, to attack by traces of oxygen or moisture; accordingly the surfaces of any apparatus intended to contain the tetrahydroborate were first conditioned, *e.g.* by heating under high vacuum or by preliminary exposure to a sample of the vapour followed by pumping to waste of any volatile material.

Electron scattering patterns were recorded photographically on Kodak Electron Image plates using a Balzers KD.G2 gas-diffraction apparatus.[15] The sample was contained in an ampoule closed by a greaseless stopcock, access to the nozzle of the diffraction apparatus being gained *via* a greased metal–glass taper joint. Before each series

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† Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

of exposures, the ampoule was evacuated while the contents were held first at 77 K and then at 178 K to remove any hydrogen or diborane resulting from surface hydrolysis or oxidation. With the sample held at 228 K (corresponding to an equilibrium vapour pressure of *ca.* 10 mmHg) and the nozzle at room temperature (*ca.* 298 K), exposures were taken at nozzle-to-plate distances of 250, 500, and 1 000 mm, thereby affording a range of 10—300 nm^{-1} in the scattering variable s. The measurements were accumulated in digital form using a Joyce–Loebl automatic microdensitometer giving for its output 760 data points measured at equal intervals along each of eight diameters of a given plate. The electron wavelength used, 5.661 pm, was determined from the scattering pattern given by benzene vapour.

TABLE 1

Weighting functions, correlation parameters, and scale factors

Camera distance/mm	s/nm^{-1}	$s_{min.}/nm^{-1}$	sw_1/nm^{-1}	sw_2/nm^{-1}	$s_{max.}/nm^{-1}$	p/h	Scale factor, k *
250	4	68	100	260	304	0.364	0.732(24)
500	2	26	40	135	156	0.482	0.582(12)
1 000	1	10	23.5	67	76	0.482	0.621(12)

* Figures in parentheses are the estimated standard deviations of the last digits.

Calculations were performed on ICL 4-75 and 2970 computers at the Edinburgh Regional Computing Centre using the programs for data reduction [16] and least-squares refinement [17] previously described. The complex scattering factors listed by Schäfer *et al.*[18] were used throughout the calculations: molecular distances quoted correspond to r_a. The weighting functions used to set up the off-diagonal weight matrix, correlation parameters, and scale factors are given in Table 1.

STRUCTURE ANALYSIS

The i.r. spectrum of gaseous and matrix-isolated methylaluminium bis(tetrahydroborate) and the Raman spectrum of the liquid, taken in conjunction with the vapour density, prompt the belief that the predominant species in the vapour and liquid phases is of the form $MeAl[(\mu\text{-}H)_2BH_2]_2$. Conspicuous in the vibrational spectra are the features normally associated with doubly bridged tetrahydroborate groups; [2,3,10,12] by contrast, there are no signs attributable to the motions of either the terminal Al–H [19] or $-BH_2-H-BH_2-$ [20] unit required by a structure derived from the hypothetical borane B_3H_9 in its topologically most plausible form.[21] There is then a range of possible models for the framework of the molecule depending upon the precise configuration of the polyhedron defined by the five atoms directly co-ordinated to the metal centre, *i.e.* the carbon and four bridging hydrogen atoms. These models are bounded by two extremes corresponding respectively to the so-called ' prismatic ' (D_{3h}) and ' anti-prismatic ' (D_3) structures of aluminium tris(tetrahydroborate).[11] In the first model (I), on the lines of Figure 1, each of the two $Al(H_b)_2B$ groupings occupies a plane normal to that of the $CAl[B(H_t)_2]_2$ skeleton to complete a framework belonging to the C_{2v} symmetry group (t = terminal, b = bridging). The second model (II) preserves the planar heavy-atom skeleton $CAlB_2$ but allows the planes of the $Al(H_b)_2B$ groupings to rotate simultaneously about the Al · · · B axes through an angle θ so as to produce in the limit a $C(H_b)_4$ polyhedron approximating to a trigonal bipyramid (*i.e.* θ = 45°); with the carbon atom of the methyl group in an equatorial site, the framework of the molecule then conforms to C_2 symmetry. We have therefore adopted a structural model which includes as a variable the angle θ together with nine other independent parameters: these are the four internuclear distances Al–C, Al–B, C–H_m, and Al–H_b; a mean B–H distance and Δ(B–H), the difference between the B–H_b and B–H_t distances; and the three angles Al–C–H_m, B–Al–B, and H_t–B–H_t (H_m denotes the hydrogen of a methyl group).

The refinement calculations have focused first on model I with θ = 0°; only after refinement of the other parameters has a series of calculations been performed to study the effect of varying θ. No shrinkage corrections have been applied in any of our refinements. It is likely that some of the vibrations of the $CAl[(\mu\text{-}H)_2BH_2]_2$ skeleton have relatively large amplitudes liable to affect most of all the average values of long non-bonded distances or the shapes of their radial probability curves. Although the vibrational spectrum has been partially assigned in terms of the group vibrations appropriate to the molecule $Al(BH_4)_2Me$,[5] there is insufficient definitive information to provide a basis for assessing *a priori* the effects of shrinkage. There is no reason, however, to suppose that the results of our calculations will be significantly altered by due allowance for shrinkage, at least within the limits of error set by the estimated standard deviations. Such deviations as quoted take into account the effects of correlation, and have been augmented to allow for systematic errors in the electron wavelength, camera height, *etc.*

Most conspicuous in the radial-distribution curve $P(r)/r$ (Figure 2) is the peak located near 200 pm which depends on the lengths and amplitudes of vibration of the following distances in order of diminishing importance: Al–B, Al–C, and Al–H_b. Near 115 pm is another composite peak corresponding to the C–H_m, B–H_b, and B–H_t distances. The weak feature at *ca.* 260 pm originates in the non-bonded atom pairs Al · · · H_m, whereas the broad feature centred at *ca.* 350 pm originates mainly in the non-bonded atom pairs Al · · · H_t, B · · · C, and B · · · B; other non-bonded

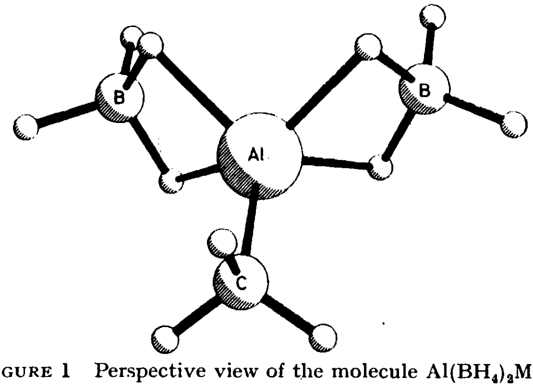

FIGURE 1 Perspective view of the molecule $Al(BH_4)_2Me$: structure corresponding to the optimum refinement

distances, *e.g.* B · · · H, C · · · H, and H · · · H, have also to be accommodated, not only near 350 pm, but also by the weak feature at *ca.* 460 pm. The absence of any major scattering caused by atom pairs separated by more than 400 pm contrasts with the radial-distribution curve for the Al_2Me_6 molecule,[22] and so bears out the implications of the vapour density and the vibrational spectrum that the vapour contains few, if any, aggregates of the type $[Al(BH_4)_2Me]_n$ where $n \geqslant 2$.

TABLE 2

Least-squares correlation matrix (×100) for the molecule $Al(BH_4)_2Me$

r_1	r_2	r_3	r_4	r_6	Angle 1	Angle 2	u_1	u_2	u_8	u_{10}	k_1	k_2	k_3	
100	96	38	86	85	−89	−73	−9	−13	−41	68	0	−7	−18	r_1
	100	83	91	91	−88	−82	−12	−13	−44	75	−2	−4	−15	r_2
		100	16	31	−42	−8	40	−26	0	−7	−25	−43	−43	r_3
			100	80	−81	−77	−16	−1	−43	76	11	8	−5	r_4
				100	−76	−82	−17	−25	−47	68	−28	−13	−14	r_6
					100	48	12	14	39	−63	−1	4	17	Angle 1
						100	15	10	41	−69	10	3	6	Angle 2
							100	35	24	−28	17	−7	−9	u_1
								100	15	−3	60	31	21	u_2
									100	−43	16	8	3	u_8
										100	1	11	5	u_{10}
											100	33	16	k_1
												100	22	k_2
													100	k_3

In our least-squares analysis, we have been able simultaneously to refine 11 parameters associated with the molecular model I. These comprise seven out of the nine independent geometric parameters previously defined [the five distances Al–C, Al–B, Al–H_b, B–H(average), and C–H_m, and the angles B–Al–B and Al–C–H_m], as well as the amplitudes of vibration allied to the distances Al–C and Al–B; the B · · · C and B · · · B amplitudes have been refined as a single parameter, as has a group of two-bond Al · · · H and C · · · H amplitudes. The refinement of the structure has proceeded with satisfactory convergence on the whole, despite the problems of correlation disclosed by the final least-squares correlation matrix (given in Table 2). Such correlation inevitably attends the overlapping of peaks in the radial-distribution curve. These circumstances likewise affect the definition of some of the amplitudes of vibration.

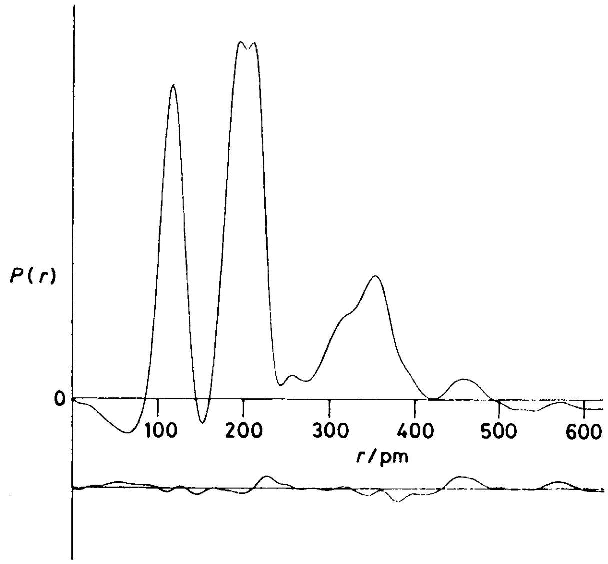

FIGURE 2 Observed and difference radial-distribution curves, $P(r)/r$, for methylaluminium bis(tetrahydroborate). Before Fourier inversion the data were multiplied by $s.\exp[(-0.000\,035\,s^2)/(z_{Al}-f_{Al})(z_B-f_B)]$

The geometrical parameters causing us the most trouble in the refinement have proved to be the two angles B–Al–B and H_t–B–H_t and Δ(B–H), the difference between the bridging and terminal B–H distances. After refining the rest of the parameters to reasonable values, we have performed two series of calculations to explore the dependence of the *R* factor on these parameters. Variations of Δ(B–H) in the range 2—10 pm give a minimum *R* factor at Δ(B–H) = *ca.* 4 pm with an estimated standard deviation of *ca.* 4 pm, whereas variations of the angle B–Al–B in the range 115—125° give a minimum *R* factor for an angle of 121.5°. With the angle H_t–B–H_t we have found that a slow refinement from the value of 116.2° favoured by B_2H_6 [23] and $Al(BH_4)_3$ [11] produces convergence towards a value of 116.0°, although the change can scarcely be regarded as significant in relation to the probable error limits. We have then fixed the values of these three parameters and investigated the effect of varying the $Al(\mu\text{-}H)_2B$ twist angle θ in the range 0—45°. The *R* factor passes through a minimum corresponding to a value of θ near 5°, representing no more than a slight departure from the C_{2v} symmetry of model I in a move towards the C_2 configuration of model II. Taking 5° as the starting point, the twist angle refines to a value of 4.8°, at which it has been held constant for the final stages of the calculations. The B–Al–B angle has been included in the final refinements.

With $Al(BH_4)_2Me$, as with $Al(BH_4)Me_2$ and $Ga(BH_4)Me_2$,[1] the relative poverty of detail afforded by the radial-distribution curve precludes the independent refinement of more than a comparatively small number of vibrational amplitudes. We have found though that variations of the vibrational amplitudes associated with some of the long non-bonded C · · · H_t and B · · · H_t' distances (where H_t' denotes a terminal hydrogen atom bound to the *second* boron atom) evoke marked changes in the *R* factor, while contributing but little to the radial-distribution curve. Unfortunately these parameters are not susceptible to stable refinement, and it has been necessary to fix the values so as to conform with those determined for related molecules, notably $M(BH_4)Me_2$ (M = Al or Ga) [1] and $Al(BH_4)_3$.[11] We have also appealed to the precedents set by related molecules [1,11,23] in fixing most of the other amplitudes which do not lend themselves to refinement.

The success of the refinement may be gauged by the difference (i) between the experimental radial-distribution curve and that simulated for the best model (Figure 2) and (ii) between the experimental and simulated molecular scattering (Figure 3). The structural details and vibrational amplitudes of the optimum refinement, corresponding to $R_G = 0.142$ ($R_D = 0.075$), are listed in Table 3, together with the estimated standard deviations.

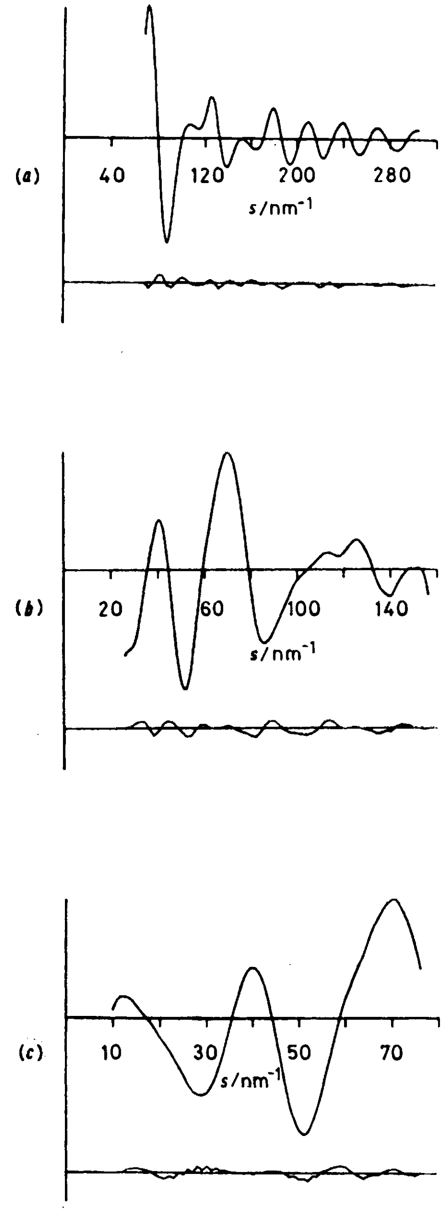

FIGURE 3 Experimental and final difference molecular-scattering intensities for methylaluminium bis(tetrahydroborate); nozzle-to-plate distances (*a*) 250, (*b*) 500, and (*c*) 1 000 mm

DISCUSSION

With the possible exception of beryllium bis(tetrahydroborate), the form of which in the gas phase is still a matter of contention,[24] methylaluminium bis(tetrahydroborate) is the only gaseous molecule containing two tetrahydroborate groups linked to a common metal atom for which structural details have been presented. In the event our analysis reveals for the $Al(BH_4)_2Me$ molecule dimensions which approximate closely, within the limits set by the standard deviations, to the corresponding dimensions of the $Al(BH_4)Me_2$ molecule,[1] with the difference that increased correlation has the effect of enlarging the error limits applicable to the methylaluminium compound. That the similarity extends to other molecules in the series $Al(BH_4)_{3-n}Me_n$ (n = 0—3) is exemplified by the Al–B distances in $Al(BH_4)_3$ (214.3 pm),[11] $Al(BH_4)_2Me$ (215.2 pm), and $Al(BH_4)Me_2$ (212.8 pm),[1] and by the Al–C distances in $AlMe_3$ (195.7 pm),[22] $Al(BH_4)Me_2$ (192.9 pm),[1] and $Al(BH_4)_2Me$ (194.1 pm). Again we note that the Al–B distance in methylaluminium bis(tetrahydroborate) is significantly shorter than that in the alumina-*nido*-carborane $Me_2AlB_9C_2H_{12}$ (230—234 pm),[25] where the aluminium atom is believed to be linked *via* a *single* hydrogen bridge to each of two adjacent boron atoms in the open pentagonal B_3C_2 face of an icosahedral $B_9C_2H_{12}$ fragment. As in other molecules of the type $Al(BH_4)_{3-n}Me_n$ (n = 0 or 2) [1,11] and in the tetrahydroborate species $Ga(BH_4)Me_2$,[1] $[Cu(BH_4)(PPh_3)_2]$,[26] and $Zr(BH_4)_4$,[27] the metal–boron distance approximates to the sum of the tetrahedral covalent radii of the relevant atoms (214 pm). This is consistent with the Raman [5,8,28] and photoelectron [29] spectra of such molecules in its intimation of appreciable metal–boron bonding.

TABLE 3

Molecular parameters [a] for methylaluminium bis(tetrahydroborate)

Parameter	Distance	Amplitude
(*a*) Independent distances and amplitudes/pm		
r_1(Al–C)	194.1 (0.9)	6.0 (0.5)
r_2(Al–B)	215.2 (1.6)	6.6 (0.4)
r_3(Al–H$_b$)	182.0 (0.9)	10.0 [b]
r_4(B–H) (average)	122.1 (0.9)	
$r_5\Delta$(B–H)	4.0 [c]	
r_6(C–H)	109.5 (1.5)	6.5 [b]
(*b*) Dependent distances and amplitudes/pm		
d_7(B · · · B)	375.6 (3.3)	13.9 [d]
d_8(B · · · C)	353.4 (3.7)	11.1 (0.7)
d_9[Al · · · H(methyl)]	253.5 (3.0)	13.6 [b]
d_{10}(Al · · · H$_t$)	296.7 (3.8)	17.6 (1.3)
d_{11}(B–H$_b$)	124.1 [c]	8.9 [b]
d_{12}(B–H$_t$)	120.1 [c]	7.5 [b]
(*c*) Independent angles/°		
1(Al–C–H)	110.1 (0.8)	
2(B–Al–B)	121.5 (0.7)	
3(H$_t$–B–H$_t$)	116.0 [c]	
4 θ, Al(μ-H)$_2$B twist	4.8 [c]	
(*d*) Dependent angle/°		
5(H$_b$–Al–H$_b$)	70.3 (0.4)	

[a] Figures in parentheses are the estimated standard deviations of the last digits, increased to allow for systematic errors. [b] Fixed. [c] See text. [d] Tied to u_8.

The internal dimensions of the methyl and tetrahydroborate groups in the $Al(BH_4)_2Me$ molecule do not differ significantly from those deduced in previous studies involving the other members of the series $Al(BH_4)_{3-n}Me_n$.[1,11,22] Thus, although it is difficult to define the precise dimensions of the bidentate tetrahydroborate group, the geometry is affected little, it appears, by the number of such groups simultaneously co-ordinated to the metal centre. The difference between the bridging and terminal B–H distances, $\Delta(B{-}H) = 4.0$ pm, may be relatively poorly defined, but we note that it is intermediate between the values of this parameter deduced for $Al(BH_4)Me_2$ (2.3 pm)[1] and $Al(BH_4)_3$ (8.7 pm).[11]

The influence of weak interactions between the closest $H_b \cdots H_b$ and $H_t \cdots H_t$ non-bonded atom pairs is probably reflected not only in the elongation of the Al–B distance from 212.8 to 215.2 pm and of the $Al{-}H_b$ distance from 177.0 to 182.0 pm attending substitution of a second tetrahydroborate for a methyl group in the $Al(BH_4)Me_2$ molecule,[1] but also in the slight twisting of the tetrahydroborate groups about the $Al \cdots B$ axes which appears to take place in the $Al(BH_4)_2Me$ molecule. In this respect, the $Al(BH_4)_2Me$ molecule is akin to $Al(BH_4)_3$, the electron-diffraction pattern of which gives grounds for invoking rotation of the BH_4 groups through an angle of *ca.* 17° relative to the ' prismatic ' (D_{3h}) conformation.[11] For neither molecule, however, does the deviation from the most symmetrical conformation lie beyond the reach of large-amplitude torsional motions of the $Al(\mu\text{-}H)_2BH_2$ groups; for $Al(BH_4)_2Me$, indeed, the deviation is described exactly by the a_2 torsion of the two BH_4 groups in a skeleton having C_{2v} symmetry. As long as shrinkage is neglected, therefore, it would be inappropriate to attach undue weight to estimates of the BH_4 twist angles. On the other hand, the conformation of the BH_4 groups may well assume greater prominence in the molecule hydridogallium bis(tetrahydroborate), $Ga(BH_4)_2H$, the i.r. spectrum of which points to C_2 rather than C_{2v} symmetry.[5,9]

In summary, the present study completes the survey by electron diffraction of the molecular geometry assumed by each molecule in the series $Al(BH_4)_{3-n}Me_n$ ($n = 0$—3).[1,11,22] It is clear that exchange of methyl for tetrahydroborate groups in molecules of this type induces but small changes in the dimensions and conformation of the other components. The results are thus consistent with the experience gained from the physical and chemical properties of compounds of the type $Al(BH_4)_{3-n}Me_n$ [5,7] in emphasising the similarity rather than the difference between the isoelectronic CH_3 and BH_4 ligands. In the circumstances, it is likely that non-bonded contacts are at least as influential in determining the finer structural details as are bonding interactions reflecting the dependence of the bonding molecular orbitals on the composition, polarization, and symmetry of the ligand environment.

We thank Professor D. W. J. Cruickshank for provision of experimental facilities and Mrs. V. Ulbrecht for practical assistance with the electron-diffraction measurements carried out at U.M.I.S.T.; the S.R.C. for the award of research studentships (to M. T. B., C. J. D., and P. D. P. T.); and Jesus College, Oxford for the award of a Graduate Scholarship (to P. D. P. T.).

[9/1621 *Received, 12th October*, 1979]

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