Theoret. chim. Acta (Berl.) 17, 1—14 (1970)

Commentationes

Methylaluminium Compounds

I. The Electronic Structure of Some Methylaluminium and Methylboron Hydrides

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Received July 25, 1969

The S.C.M.O. methods has been employed to study the valence electronic structures of some isomers of the methylboron and methylaluminium hydrides. Basis sets including $3s$, $3p$ and diffuse and contracted $3d$ orbitals were used for the aluminium atoms. For both boron and aluminium compounds hydrogen is energetically favoured over methyl as a bridging group. This stems mainly from the different nuclear repulsion energies of the isomers. Participation of the $3d$ orbitals is quite marked, particularly in the metal-metal cross-ring interactions.

Mittels der SCMO Methode wurde die Valenzelektronenstruktur einiger Isomere der Methylbor- und Methylaluminiumhydride untersucht. Die Basis enthielt für Aluminiumatome $3s$, $3p$ und kontrahierte und nicht kontrahierte $3d$ Zustände. Sowohl bei den Bor- als auch den Aluminiumverbindungen sind Wasserstoffatome als Brücke gegenüber Methylgruppen energetisch begünstigt. Das rührt hauptsächlich von den unterschiedlichen Kernabstoßungsenergien her. Die Beteiligung der $3d$ Orbitale ist deutlich, besonders in der (transannularen) Metall-Wechselwirkung.

La méthode S.C.M.O. a été utilisée pour étudier les structures électroniques de valence de certains isomères des hydrures de méthylbore et de méthylaluminium. Pour les atomes d'aluminium on a utilisé des bases contenant des orbitales $3s$, $3p$ et des orbitales $3d$ diffuses et contractées. Tant pour les composés du bore que ceux de l'aluminium l'hydrogène est favorisé énergétiquement par rapport au méthyl en tant que groupement de pont. Ceci provient essentiellement des différences d'énergie de répulsion nucléaire. La participation des orbitales $3d$ est nettement marquée, particulièrement dans les interactions métal-métal à travers le cycle.

1. Introduction

The electronic structures of organoaluminium compounds are of great interest because of their relationship to the technically important Ziegler and Ziegler-Natta [4] catalysts and also because of the problems posed by the nature of the bonding in such compounds. Thus polymerisation in such compounds can take place *via* bridging methyl [4] or phenyl [18] groups, or, when present, by hydrogen atoms [4]. The possibility of the vinyl group functioning as a bridge in organoaluminium compounds clearly also exists since there is good evidence for this in gallium compounds [21].

Since the corresponding compounds of boron are generally monomeric [4] it may be that the formally empty $3d$ orbitals of aluminium exert some influence on the ease of formation of dimeric species. Ways in which these orbitals could participate are *via* (i) cross-ring metal-metal bonding involving interactions of σ-, π-, and δ-type, (ii) the metal-bridge bonds.

It is also cogent to establish which type of group (methyl, hydrogen, phenyl, or vinyl) is most efficacious in functioning as a bridging moiety and, as a result, what the favoured geometry of the dimer is likely to be. Finally a comparison with the corresponding boron compounds is obviously cogent in order to try and discern the reasons for their different behaviour. We have therefore carried out all valency-electron self consistent field calculations on a series of model compounds. In this paper we discuss the methylaluminium hydrides and the methylboron hydrides. Subsequent papers will be concerned with the vinylaluminium and phenylaluminium compounds and with trimethylaluminium. Some of the present work on aluminium compounds has already been reported briefly [13] but a full discussion was not presented.

We conclude from our studies that in organoaluminium polymers containing methyl groups and hydrogen atoms the latter will usually function as bridging groups. When the methyl group is constrained to act as a bridge (as in Al_2Me_6) the eclipsed and staggered conformations of the six hydrogen atoms are closely similar in energy. The 3*d* orbitals participate in the bonding of aluminium compounds and the extent to which they do this will, in general, depend on the nature of the attached groups. Metal-metal bonding appears to be important in dimers and the 3*d* orbitals contribute significantly in such systems. In dimeric boron compounds the internuclear repulsion energy seems to be the most important factor which determines the nature of the bridging unit.

2. Calculational Methods

The structural parameters for the organoaluminium hydrides are given in Ref. [13]. Bond lengths and angles not included in that paper, *i.e.* for the methylboron hydrides, were taken to be the same as those in BMe_3 and B_2H_6 [12] and are listed in Table 1. A modified form of the Pople-Segal-Santry C.N.D.O. method [22] was used throughout. For the aluminium atoms we considered it appropriate to use basis sets including the 3*s*, 3*p*, and 3*d* orbitals although the latter are formally empty in the ground state of the atom. In the present work we have neglected both the 4*s* and 4*p* functions (which would, of course, appear in a complete expansion of the molecular orbitals of the molecule around one centre) since the transition energies to spectroscopic states involving these orbitals are rather greater than for those incorporating the 3*d* orbitals [19].

It must also be recognised that such concepts as "3*d*–3*d* bonding" resulting from the inclusion in a calculation of *atomic* 3*d* functions are, to some extent, artefacts. However we believe that if such results are to be valuable to chemists and are to be correlatable from case to case then the individuality of each molecule has to be sacrificed somewhat. Even in a unique one-centre expansion certain weighted terms would correspond in symmetry, energy, and nodal properties to atomic *d* orbital contributions to the molecule.

With respect to the one-centre Coulomb repulsion integrals, it was considered most satisfactory to incorporate into the S.C.F. equations separate integrals for

Table 1. *Bond lengths and angles for Methylboronhydrides*

	Bond lengths Å monomer	Bond lengths Å dimer
B–$C^{term.}$	1.61	1.61
B–C^{bridge}	—	1.54
B–$H^{term.}$	1.19	1.19
B–H^{bridge}	—	1.33
C–H	1.09	1.09
	Bond angles (deg.)	
$C^{term.}$–B–$C^{term.}$	—	125
$C^{term.}$–B–$H^{term.}$	120	—
$H^{term.}$–B–$H^{term.}$	120	122
C^{bridge}–B–C^{bridge}	—	110
H^{bridge}–B–H^{bridge}	—	97
H–C–H	109	109

all types of orbital (*s*, *p*, and *d*) even though this results in loss of invariance of the calculation to an orthogonal transformation of the orbital basis sets. This replacement of the "*s*-only" integrals is important because there is a significant numerical difference between the integrals γ_{ss}, γ_{pp}, and γ_{dd}, for a second row atom, particularly if the 3*d* radial function is diffuse. Test calculations on the NaF and NaCl molecules and chosen silicon compounds were performed in parallel to determine the effect of similarity transformations of the bases on the total energy. These studies will be reported separately [15] but it may be stated here that the change in total energy with basis modification was small. Comparative calculations, where the orbital basis set for a molecule remains unchanged, will not be affected.

The one-centre integrals involving 2*s*, 2*p*, 3*s*, 3*p*, and 3*d* orbitals were calculated purely theoretically [14] and the two centre type then obtained from these by a scaling procedure [20].

The starting Hamiltonian matrix elements were the negatives of the orbital ionisation potentials. These have previously been computed for the 3*s*, 3*p*, and 3*d* orbitals of second row atoms [14]. In the above paper several possible values were quoted for the latter. The first corresponds to a diffuse 3*d* orbital form which will be appropriate for a negative aluminium ion. However *in a compound* the nucleus of a central electropositive atom is likely to be directionally unshielded and so an electron in a 3*d* orbital may well experience essentially the same nuclear charge as does a valence 3*s* or 3*p* electron. This would then be described by a 3*d* wave function which was considerably contracted and could contribute significantly to the bonding.

There is at present no unanimity of view on this point. Craig *et. al.* [5] have shown that overlap integrals between π type orbitals can be quite large even with diffuse overlapping 3*d* functions and Craig *et. al.* [6, 7] further concluded that 3*d* orbitals could play a useful part in bonding if they were contracted under the influence of the electrostatic field of the ligands. Other workers however [8, 9]

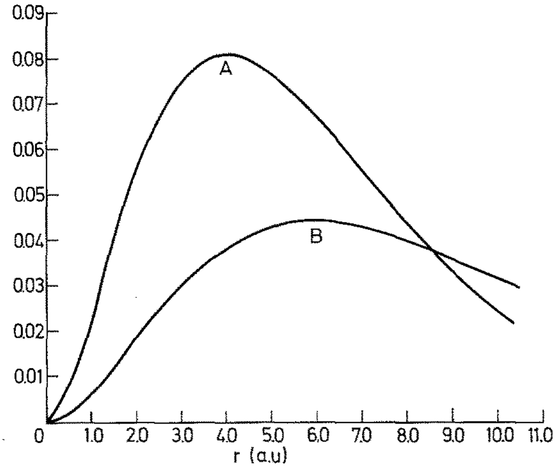


Fig. 1. Forms of (A) contracted and (B) diffuse 3*d* orbitals

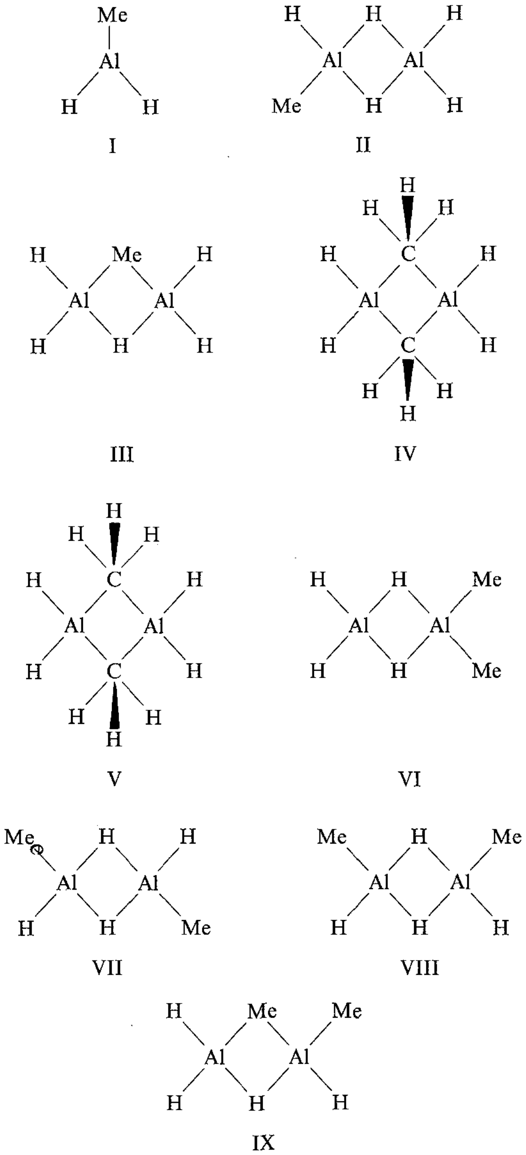
Table 2. *Input parameters* I_μ *and* $\gamma_{\mu\mu}$ *(eV)*

	Atom	I_μ	$\gamma_{\mu\mu}$
H	1*s*	13.06	20.40
C	2*s*	19.44	15.60
	2*p*	10.67	14.37
B	2*s*	14.05	12.33
	2*p*	8.30	10.85
Al	3*s*	11.32	9.25
	3*p*	5.97	6.60
	3*d* (Al^0)	1.86	3.76
	3*d* (Al^-)	0.75	2.51

have criticised this approach and have stated that it is not necessary to invoke *d* orbital participation to explain the bonding in phosphorus or sulphur compounds.

The best solution to the problem would be a variational calculation, superimposed on the basic S.C.F. scheme, in which the effective nuclear charge, Z^*, was considered to be a variable parameter unfixed by any physical considerations. The appropriate Z^* should then differ for every molecule. We are at present investigating this solution.

For the present purpose however we have adopted two separate Z^* values; these correspond to a 3*d* electron "seeing" either (*a*) an aluminium nucleus screened by thirteen electrons ($Z^* = 1.0$) or (*b*) by twelve electrons ($Z^* = 1.5$). The Burns [3] radial functions corresponding to these two orbitals are illustrated in Fig. 1. The maximum in the radial function is pulled in from 3.2 Å to 2.1 Å by the increased nuclear charge and the expectation value for the radial variable is 5.6 Å and 3.7 Å in the two cases. There is thus some contraction in the 3*d* function on increasing the charge by 0.5 units but the change is not dramatic. This will affect the values of the overlap integrals between the 3*d* and other orbitals. It is also of some significance that, even for the contracted *d* function, the expectation



I II III IV V VI VII VIII IX

Fig. 2. Organoaluminiumhydride isomers

value for the position of the *d* electron is *beyond* the nucleus of adjacent atoms. This implies that the *d* orbital should perhaps be contracted further still. However, at present there is no definite guide as to which of the above functions will more accurately represent the *d* orbital contribution in aluminium compounds and in this paper we will make a comparison of the two *i.e.* with $Z^* = 1.0$ and $Z^* = 1.5$ units. It is clear however that, for configurations lying between Al^0 and Al^-, the results of calculations should not be sensitive to this factor. A further set of calculations, which omitted the 3*d* orbitals, was also performed. For the boron compounds the basis sets included only the 2*s* and 2*p* atomic orbitals. Orbital input parameters for all the atoms are listed in Table 2.

The off-diagonal elements of the core matrix were obtained in the same way as in the paper by Greenwood, Perkins, and Wall [11]. Certain overlap integrals necessary for the calculation of these elements were not available in the literature. Master formulae for these are therefore quoted at the end of this paper. In deriving these the analytical form of orbital suggested by Burns [3] was employed. The calculations were all performed on the Newcastle University KDF9 and the Strathclyde University ICT 1905 computers.

It was necessary to restrict the size of the orbital basis set as far as possible in the calculations and so only one methyl group per aluminium atom was considered. The remainder of the substituents were then hydrogen atoms. Thus the series of systems included various isomers of $Al_2Me_2H_4$ and Al_2MeH_5 (Fig. 2).

It is unfortunate that none of the above compounds has yet been prepared. However, the problems posed by the bonding therein are the same as those which obtain in similar known bridged systems and the information and conclusions obtained in the present work are directly relevant to the latter.

3. Results and Discussion

Position of the Methyl Groups

Perhaps the most important point to establish in the dimeric compounds is whether the bridging moieties are more likely to be methyl groups or hydrogen atoms. Two associated features are (*a*) what positions the methyl groups would occupy if terminal (*b*) whether the methyl hydrogen atoms are staggered or eclipsed with respect to each other when the methyl group acts as a bridge.

Calculations were carried out including the 3*d* orbitals and a comparison between Models VI and VII shows immediately that, when the methyl groups occupy terminal positions and independently of the *d*-orbital exponent, the favoured conformation of the molecules is that in which they lie mutually *trans*. Curiously enough, the *gem*-dimethyl compound (VI) is more stable electronically than VII (i.e. the sum of its bonding and electronic repulsion energies is greater) but here the nuclear repulsion factor dominates and hence the *total* energy of the latter isomer is greater. If all the hydrogen atoms were replaced by chlorine (which has a large core charge) then the *gem*-dimethyl compound might well be the more stable of the two and indeed evidence for the formulation of $Al_2Me_2Cl_4$ as $Me_2Al^+ AlCl_4^-$ has been adduced [10]. We did not study the *cis* dimethyl isomer (VIII) but in this case internuclear repulsion would be greater than in the *trans* isomer without any obvious gain in its electronic bonding energy.

In models IV and V, when the methyl group is acting as a bridge (as it must in Al_2Me_6) the calculations show that the electronic and nuclear energies are mutually compensating so that similar total energies result for the staggered and eclipsed isomers. However, the relative stabilities of the two are sensitive to the extent of *d* orbital participation since this can only modify one energy factor i.e. the electronic energy. Thus, with a contracted *d* function, the eclipsed isomer is energetically favoured whilst with the diffuse *d* function the staggered form is of lower energy. We conclude therefore that the calculational method does not unequivocally establish the bridge geometry and the equilibrium between the two forms may well be labile.

Finally the relative efficacies of the methyl group and the hydrogen atom as bridging units may be compared. Calculations with both parameter sets on Models IV, V, and VII lead to the same conclusion i.e. that a hydrogen bridged dimer should be more stable. It is interesting that the methyl bridged isomer is *electronically* more stable but the juxtaposition of a methyl group to two aluminium atoms and a second methyl across a small ring increases the nuclear energy drastically and precludes this type of bridging if there is an alternative. This result may be extrapolated to the known trimer $Al_3Me_3H_6$ which appears to have a ring structure and in which, it is believed, hydrogen bridging exists [4]. Again the nuclear energy must be a greater destabilising force (which cannot be adequately compensated) when the methyl group is inserted between two aluminium atoms than when it occupies a terminal position.

For the compound Al_2MeH_5 (Models II, III) the same factors operate and it appears from the single calculation carried out using the diffuse 3*d* function that the stabilisation due to one bridging hydrogen atom is approximately one half that brought about by two. Model IX was not studied but, on the basis of the results for II and III, it would not be expected to be more stable than the *trans* form (VII). In the series $Al_2Me_{6-n}Cl_n$ the members in which n is odd are unknown. This has been explained [10] on the basis of disproportionation to the compound with n even and which contains the stable Me_2Al^+ unit. In the case of Al_2MeH_5 the products of disproportionation would be $Al_2Me_2H_4$ and Al_2H_6:

$$2\,Al_2MeH_5 \rightarrow Al_2Me_2H_4 + Al_2H_6\,.$$

If the calculated total energies of Al_2MeH_5, *gem*-dimethyl $Al_2Me_2H_4$ and Al_2H_6 [16] are put into this equation we find that the RHS is favoured energetically. This is support for Glick and Zwickel's [10] disproportionation argument.

Lowering of Ground-State Energy by d-orbital Mixing

All the features discussed above were also reproduced by calculations in which the *d* orbitals were ormitted. It is important, therefore, to try and assess to what extent these orbitals actually contribute to the molecular energy and this can be accomplished by comparing the energies of the isomers calculated with or without inclusion of the *d*-functions. It turns out that, firstly, participation of *d* orbitals in the dimer (VII) lowers the total energy of the system by 4–6 times the comparable stabilisation energy of the monomer (I). Although it is not strictly possible, in a molecular orbital calculation, to apportion the total energy out among the various bonding interactions, it does seem here that the cross-ring Al–Al bonding, which is not possible in a monomer, is an important stabilising factor. This is not surprising in view of the short Al–Al distance (0.04 Å greater than the covalent diameter of aluminium). Such Al–Al bonding was first suggested by Rundle *et al.* [17].

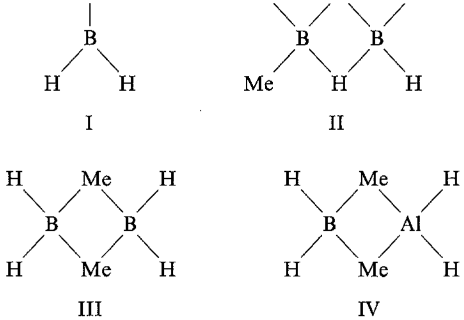
Another point of interest here is that the effective electronic environment of the aluminium atom has a marked effect on the lowering of energy by the *d* orbitals. Thus the change of configuration from Al^- to Al^0 brings about an increase of ~ 3.6 times in stabilisation energy for $AlMeH_2$ and of 4–5 times for the dimers. This means that *d*-orbital participation should be particularly strong when the aluminium atom is surrounded by electronegative ligands and so will affect the bonding much more in such cases. At present it is difficult to decide absolutely, particularly in a molecular situation, where the carbon atom should be placed on the scale. This emphasises the need for a variational S.C.F. procedure which minimises the total energy with respect to *d*-orbital participation.

Organoboron and Organoboron-Aluminium Compounds

Cross-ring B–B bonding is also possible in the analogous organoboron dimers although for such cases the atomic 3*s*, 3*p*, and 3*d* levels are energetically too remote to contribute effectively. Hence for there to be strong cross-ring bonds it would be necessary for the boron atoms to approach each other quite closely. Overlap of the contracted 2*s* and 2*p* orbitals would only then be effective. Hence if both methyl and hydrogen bridging were possible in a compound it would reasonably be expected that the latter would be favoured because the nuclear repulsion of two methyl groups in bridge positions would force the two boron atoms apart. This type of bridging seems therefore less likely to exist in boron than in aluminium compounds e.g. B_2Me_6 is likely to be less stable than Al_2Me_6.

In order to throw more light on this point and to compare the cross-ring bonding possible between the "normal" valence orbitals of the boron and aluminium atoms we calculated the electronic structures of $AlBMe_2H_4$ and some isomers of $BMeH_2$ (Fig. 3). In (III) the methyl hydrogen atoms were staggered with respect to each other (this configuration is most stable in the corresponding aluminium compounds when *d* orbitals are omitted).

Comparison of the energies for compounds II and III shows that the more stable isomer of the two *electronically* is that which has methyl bridging. However, the size of the four-membered boron-carbon ring necessary to achieve this stability brings together the methyl groups to such an extent that the nuclear energy dominates and hydrogen bridging is once more favoured. The difference between the stability of methyl and hydrogen bridging (as judged by the energies) is some four times greater here than in the comparable aluminium case and in this context the proportional is more significant than the absolute change. It



I II

III IV

Fig. 3. Organoboronhydride isomers

seems, therefore, that because of the nuclear energy factor, the chance of preparing dimeric boron compounds which contain methyl bridges is far less likely than it is for aluminium compounds.

Taking this reasoning further, if bridging between boron monomers is to be accomplished by *any* group (including those like $-NR_2$ which are classical σ donors) then the gain in stabilising electronic energy by the new dimer system must be considerable in order to offset the repulsive nuclear energy introduced by juxtaposing bulky groups within a small ring. Thus atoms like chlorine and bromine which are weak electron donors but which possess high effective nuclear charge are less likely to act as bridging entities between boron monomers than aluminium monomers because in the latter the interatomic distances at which bonding is maximised are considerably greater.

Since methyl groups are not favoured as a means of dimerising boron compounds then it is also interesting to speculate on the situation in the dimer of $BH_2 \cdot NH_2$. Here the $-NH_2$ groups in the dimer will produce a similar nuclear field to methyl groups and so unless the ring σ bonding between nitrogen and boron is strong, then this compound could be hydrogen bridged like diborane. The problem of dimerisation of boron compounds has not previously been considered in this light: past work [1] has concentrated on the properties of the monomers themselves (reorganisation energies, electron densities on the central atom etc.). A forthcoming publication will examine these points more closely by an *ab initio* study of the dimeric form of $BH_2 \cdot NH_2$ [2]. This should assess the relative importance of all the factors involved.

Since the boron and aluminium systems appear to differ so markedly in their quantitative features it is obviously of interest to study the intermediate compound containing both boron and aluminium. The compound $AlBMe_6$ has been synthesised from BMe_3 and Al_2Me_6 [23] and we therefore investigated the related (although unknown) hydride, $AlBMe_2H_4$, in which methyl bridging only was considered. The latter isomer was chosen so as to ascertain how the nuclear energy factor affects the bonding situation here. The geometry of this model was derived by combining that assumed for $Al_2Me_2H_4$ and $BMeH_2$. The calculations show that although the electronic energy of this compound would be less than of methyl-bridged $B_2Me_2H_4$, the nuclear repulsion energy is also much diminished (it is only a little greater than that of methyl-bridged $Al_2Me_2H_4$). The model $AlBMe_2H_4$ has, in fact, the lowest total energy of all three model compounds, a result which is consistent with the chemical evidence that the formation of the isolated known compound, $AlBMe_6$, is thermodynamically favoured over a mixture of BMe_3 and Al_2Me_6.

If the calculated total energies for the components (i.e., methyl-bridged $Al_2Me_2H_4$ and H-bridged $B_2Me_2H_4$) in the hypothetical reaction

$$Al_2Me_2H_4 + B_2Me_2H_4 \rightarrow 2\,AlBMe_2H_4$$

are inserted, then the right-hand side is energetically favoured over the left. The energy difference is not quoted here because it is not the true enthalpy of reaction; firstly, because it corresponds to the gas phase only; secondly, no vibrational, translational or rotational energy is included; thirdly, the C.N.D.O.S.C.F.

approximations render the theory too crude to reproduce heats of reaction quantitatively. It is, however, qualitatively consistent with chemical experience of a related system and moreover, the calculation could perhaps be developed further.

Charge Distribution

The electronic charge distribution for the isomeric aluminium compounds is reproduced in Table 3. This is obtained from the orbital density matrix for the molecule. In Tables 3 and 5 calculations (*a*) included a diffuse 3*d* function whilst calculations (*b*) incorporated *a* contracted orbital. Firstly, the overall electron distribution on the atoms is stable to variation in the *d* exponent: the diffuseness of the orbital thus has little effect. Secondly, the aluminium atom is quite strongly negatively charged, which is surprising in view of the nature of the attached groups. This observation confounds the usual assumptions of charge distribution in a bond based on diatomic electronegativities. The charge on aluminium is sufficiently marked that it should be detected by a technique sensitive to nuclear shielding and the ^{27}Al n.m.r. chemical shifts would therefore be of great interest. The only *individual* orbital populations appreciably altered by the change in *d* orbital exponent are those of the *d* orbitals themselves. These acquire considerable electron density almost completely at the expense of the 3*p* orbitals of the aluminium atom. In the dimers the populations of the *d* orbitals are much enhanced over those of the monomer with the same *d* orbital exponent. In the hydrogen bridged species the terminal carbon atoms are positive whilst the bridge hydrogens are negatively charged.

When methyl groups form the bridge (as must be the case in Al_2Me_6) there is also a strong drift of electrons to the aluminium atoms.

The bond order matrix illustrates several points. Firstly Al–Al cross-ring bonding exists and its most important contributors are the $3p_\sigma 3p_\sigma$ and $3p_\pi 3p_\pi$

Table 3. *Electronic charge densities for the Methylaluminium-hydride system*

	$AlMeH_2$		$Al_2Me_2H_4$ Bridged by hydrogen		$Al_2Me_2H_4$ Bridged by methyl groups	
	(*a*)	(*b*)	(*a*)	(*b*)	(*a*)	(*b*)
Al 3*s*	1.376	1.370	1.481	1.497	1.471	1.491
Al 3*p* (total)	1.739	1.695	1.803	1.726	1.761	1.667
Al 3*d* (total)	0.027	0.119	0.055	0.291	0.041	0.316
Total charge on Al	3.142	3.184	3.339	3.514	3.273	3.474
C^{bridge} 2*s*	—	—	—	—	1.582	1.577
C^{bridge} 2*p*	—	—	—	—	2.131	2.013
Total charge on C^b	—	—	—	—	3.713	3.590
H^{bridge} 1*s*	—	—	1.151	1.065	—	—
H on C^{bridge} 1*s*	—	—	—	—	1.117	1.104
$C^{term.}$ 2*s*	1.554	1.560	1.577	1.580	—	—
$C^{term.}$ 2*p*	2.107	2.060	2.012	1.955	—	—
Total charge on $C^{term.}$	3.661	3.620	3.589	3.535	—	—
H on $C^{term.}$	1.063	1.066	1.010	1.018	—	—
$H^{term.}$ 1*s*	1.004	0.998	0.889	0.831	0.830	0.811

components. The *d* orbitals do participate and add $3d_\pi 3d_\pi$, $3p_\pi 3p_\pi$, $3d_\sigma 3d_\sigma$, $3d3s$, $3p_\sigma 3d_\sigma$ and $3d_\delta 3d_\delta$ contributions. The proportionate increase in importance of these bond orders when the *d* function is contracted is very marked and leads to the view that $3d3d$ bonding is a factor which helps to account for the stability of this type of organoaluminium compound.

The $3d3s$ component is an important one but, curiously, neither $3d_\sigma 3p_\sigma$ nor $3d_\sigma 3d_\sigma$ overlap appear to matter. The $3d_\pi 3p_\pi$ and $3d_\pi 3d_\pi$ are also quite prominent features of the bonding. A $3d_\delta 3d_\delta$ contribution also appears but is weak because, of the two δ-type orbitals, the $d_{x^2-y^2}$ is involved in bonding to the bridge hydrogen atom whilst d_{xy} is virtually non-bonding.

The Al–H bridge bond is dominated mainly by $1s3p$ and $1s3s$ components which produce strong interactions. The d_{xz} orbital also takes part but only to a limited extent.

In summary, it appears that the role which the *d* orbitals play in the bridge ring is mainly confined to the metal-metal bond and is barely concerned with the bridging itself. This is consistent with chemical experience because B_2H_6 is stable yet the $3d$ orbitals would be expected to be of negligible importance here.

In the methyl-bridged isomer the mutual interactions of the $3p$ and $3s$ orbitals are similar to those occurring in the hydrogen-bridged isomer. Perhaps the chief difference lies in the $3d_{yz}3d_{yz}$ bond order.

a) Charge Distribution in Isomers of $B_2Me_2H_4$

In view of the above discussion it is of great interest to examine the electronic structure of the boron analogues. Table 4 reproduces both the electronic distributions in $B_2Me_2H_4$ with the two types of bridges.

The first striking feature of the results is that, independently of whether the methyl groups are terminal or bridging, the charge on the boron atom is small,

Table 4. *Electronic charge densities for the Methylboronhydride system*

	$B_2Me_2H_4$ Bridged by hydrogen	$B_2Me_2H_4$ Bridged by methyl groups
B^a $2s$	1.534	—
B^a $2p$ (total)	1.628	—
Total charge on B^a	3.162	—
B $2s$	1.458	1.539
B $2p$ (total)	1.489	1.581
Total charge on B	2.947	3.120
C^{bridge} $2s$	—	1.579
C^{bridge} $2p$ (total)	—	2.194
Total charge on C^{bridge}	—	3.773
H^{bridge} $1s$	1.243	—
H on C^{bridge} $1s$	—	1.126
$C^{term.}$ $2s$	1.546	—
$C^{term.}$ $2p$ (total)	2.110	—
Total charge on $C^{term.}$	3.656	—
H on $C^{term.}$ $1s$	1.018	—
$H^{term.}$ $1s$	0.992	0.864

[a] Boron bonded to terminal methyl groups.

i.e., the atom is virtually neutral. In this respect the compound differs markedly from its aluminium analogue. Hydrogen atoms situated in bridging positions or on the methyl bridge group are negatively charged. The latter charges have been a source of great difficulty even in calculations on diborane but a recent calculation by Kaufman [24] using Gaussian type atomic orbitals has shown the bridging hydrogen atoms to be slightly negatively charged. In both isomers of $B_2Me_2H_4$ the terminal hydrogen is positive.

In the B–H and B–C bridged systems, fairly substantial B–B bonding is present in both cases. The methyl bridged isomer possesses slightly greater bond orders which is consistent with the greater electronic energy of this model. The most important interaction is of p_σ-type with bond order 0.331 (H bridged) and 0.408 (Me bridged). Of the two p_π interactions one (*pypy*) is almost negligible. This orbital is virtually completely bonded to either the C 2*s* or to one of the terminal atoms.

The original suggestion [4] that methyl bridge bonding could be desribed by overlap between an "sp^3" hybrid of carbon and another hybrid of boron or aluminium is now seen to be inappropriate because only the 2*s* and two 2*p* orbitals on carbon (in the ring plane) take part in the bridge bonding: the other 2*p* orbital bonds only to the terminal hydrogen atoms (on carbon).

b) Charge Distribution in $AlBMe_2H_4$

Only the methyl bridged model of this compound was studied and the charge distribution in the ring is shown in Table 5. The Al–B, Al–C, and, B–C bonds are of great interest here because of the enhanced stability of this compound over its boron and aluminium analogues. The charge distribution in the Al–B pair exhibits a remarkable change when the more contracted *d* orbital is introduced on aluminium. This perturbation causes the polarity of this bond to be reversed from a situation approximately Al^0–$B^{-0.35}$ to one which is essentially $Al^{-0.22}$–$B^{-0.75}$. These charges are the same as those which obtain in the other boron and aluminium compounds studied in the present work. Again the carbon atom of the bridging methyl group is positively charged, as are also the four terminal hydrogen atoms.

Table 5. *Electronic charge densities for* $AlBMe_2H_4$

	(*a*)	(*b*)
Al 3*s*	1.447	1.459
Al 3*p* (total)	1.581	1.533
Al 3*d* (total)	0.043	0.229
Total charge on Al	3.071	3.221
B 2*s*	1.500	1.524
B 2*p* (total)	1.849	1.627
Total charge on B	3.349	3.151
C^{bridge} 2*s*	1.567	1.571
C^{bridge} 2*p* (total)	2.186	2.223
Total charge on C^{bridge}	3.753	3.794
H on C^{bridge} 1*s*	1.081	1.104
$H^{\text{term.}}$ on Al 1*s*	0.800	0.841
$H^{\text{term.}}$ on B 1*s*	0.994	0.866

We obtained the important bonding interactions in the Al–B, Al–C and B–C bonds (an increase of these quantities when the *d*-orbital exponent increases is shown). For the former the bond orders remain, overall, rather similar to those of the Al–Al bond in $Al_2Me_2H_4$. This is surprising because it might have been expected that cross-ring bond orders would diminish as a consequence of the markedly different radial functions for 3*d* and 2*s*, 2*p* orbitals. Furthermore, bond orders appear in the SCF total energy equation [22] as weighting factors which multiply the relevant *F* and *H* matrix elements, which are greater for boron than aluminium atoms. Hence the cross ring interaction energy will be greater in this ring than in $Al_2Me_2H_4$.

In the Al–C bridge bond the only two *d*-orbitals which interact with carbon at all appreciably are the d_{xz} and the $d_{x^2-y^2}$. These produce fairly large bond orders with the 2*s* and $2p_x$ (i.e. σ-type) orbitals of carbon respectively. Moreover these particular quantities increase markedly when a contracted *d* function is employed: the trend here is therefore similar to that previously noted. The B–C bonding pattern correlates closely with that in the methyl bridged isomer of $B_2Me_2H_4$ i.e. the *s* and the two 2*p* orbitals of carbon situated in the plane are responsible for essentially all the bridging.

In summary, the bonding in the rings of all these compounds appears to conform to a similar pattern. This includes both the "metal-metal" type and the M–C or M–H bridge bonds. The similarity is reflected in the closeness of the calculated electronic energies. However overall stability seems to be dominated by the nuclear repulsion energy, a factor which, in the Born-Oppenheimer approximation, is purely electrostatic.

One of us, (K.A.L.), wishes to thank S.R.C. for a maintenance grant.

Appendix

Master Formulae for Overlap Integrals

The choice of coordinate system and the definition of the *A* and *B* functions are identical with those of Mulliken.

$$S(1s3d) = \frac{p^5(1+t)^{\frac{3}{2}}(1-t)^{\frac{7}{2}}}{48\sqrt{2}}[3(A_2B_0 - A_0B_2)$$

$$+3(A_4B_2 - A_2B_4) - 4(A_3B_1 - A_1B_3) - A_4B_0 + A_0B_4],$$

$$S(3s3d) = \frac{p^7(1-t^2)^{\frac{7}{2}}}{144\sqrt{5}}[A_0(B_6 - 3B_4) + A_1(6B_5 - 6B_3)$$

$$+A_2(9B_4 - 3B_6) + A_3(6B_1 - 6B_5) + A_4(3B_0 - 9B_2)$$

$$+A_5(6B_3 - 6B_1) + A_6(3B_2 - B_0)],$$

$$S(3d3s) = \frac{p^7(1-t^2)^{\frac{7}{2}}}{144\sqrt{5}}[A_0(-B_6 + 3B_4) + A_1(6B_5 - 6B_3)$$

$$+A_2(-9B_4 + 3B_6) + A_3(6B_1 - 6B_5) + A_4(-3B_0 + 9B_2)$$

$$+A_5(6B_3 - 6B_1) + A_6(-3B_2 + B_0)].$$

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