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Methylaluminium Compounds

II. The Electronic Structure of Trimethylaluminium

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A study of the electronic structures of $AlMe_3$, and Al_2Me_6 has been made by the SCMO method. Basis sets including the 3*s*, 3*p* and 3*d* (diffuse and contracted) orbitals were employed for the aluminium atoms. The calculations included all valence electrons. The results are compared with those calculated for the methylaluminium hydrides.

Eine Untersuchung über die Elektronenstruktur von $AlMe_3$ und Al_2Me_6 wurde mit Hilfe der SCMO Methode durchgeführt. Dabei wurden Basissätze mit 3*s*-, 3*p*- und 3*d*-Funktionen (kontrahiert und nicht kontrahiert) für Aluminiumatome benutzt und alle Valenzelektronen in die Rechnung eingeschlossen. Die Resultate werden mit denen für Methylaluminiumhybride verglichen.

Emploi de la méthode S.C.M.O. pour l'étude de la structure électronique de $AlMe_3$ et Al_2Me_6. Les atomes d'aluminium sont traités avec des bases contenant les orbitales 3*s*, 3*p* et 3*d* (diffuses et contractées). Tous les électrons de valence sont introduits. Les résultats sont comparés avec ceux obtenus pour les hydrures de méthylaluminium.

1. Introduction

A recent paper [3] has dealt with the electronic structures of some methylaluminium and methylboron hydrides. These were calculated by the self-consistent molecular orbital method including all valence electrons [4, 5] and the results showed that, where there is a choice, the hydrogen atom rather than the methyl group will perform a bridging function between two aluminium atoms. We now present the results of similar calculations on compounds in which the methyl group is constrained to act as a bridge i.e. the fully methylated species $AlMe_3$ and Al_2Me_6. A previous calculation on the latter system has been carried out by the Extended Hückel method [1] but the conclusions resulting from this were only tentative.

Our method of calculation and input data for all the atoms concerned has been given previously [3, 4]. The calculations were carried out on the Strathclyde University ICT 1905, the Newcastle University KDF 9, and for the largest basis sets, the SRC Chilton Atlas Computers.

2. Results and Discussion

i) Lowering of Ground-State Energy by 3d Orbital Mixing

On inclusion of a diffuse 3*d* function the ground-state energies of $AlMe_3$ and Al_2Me_6 are lowered by 0.645 eV and 2.332 eV respectively. When the contracted function is employed the corresponding values are 3.818 eV and 11.095 eV. These quantities show an interesting interrelationship. Firstly the dimer is 3*d* stabilised by ~4 times that of the monomer and secondly, when the $3d$ functions are contracted, their energy contribution also increases by a factor of ~6.

The first effect stems from the fact that the $3d$ orbitals become involved in Al–Al bonding which is not possible in the monomer. Although it is *strictly* not allowable to partition the energy in the molecule nevertheless it is of interest to calculate roughly what proportion of the d bonding is attributable to the cross-ring bonds. Thus (taking the calculation with the diffuse $3d$ orbital as example) in the dimer there is an excess of 1.042 eV stabilisation energy over two monomer-molecules. If, further, the *mean* Al–Me d bonding energy in the monomer is one third of the total, i.e. 0.215 eV, and we suppose that this quantity can be transferred unaltered directly to the dimer system then the four terminal methyl groups account for 0.86 eV of the total energy decrease. This means that by far the greatest part of this energy (1.472 eV) can be associated with the four-membered bridge ring. This is a potent factor which helps to account for the dimerisation of electron-deficient compounds such as $AlMe_3$ through the medium of methyl bridges. In this context it is also interesting that the proportionate excess "dimer – twice monomer" d-stabilisation energy is greater for the fully methylated compound Al_2Me_6 than it is for the methylaluminium hydrides [3].

It is clear that contraction of the d-functions is a potent factor which can increase the contribution of these orbitals markedly and hence any ligand which tends to remove charge from the aluminium atom will render them more available. This conclusion was also reached by Craig and his co-workers from early work in the same area [2].

ii) Charge Distribution

The Table provides a breakdown of the atomic charges in the important areas of the molecule.

There is firstly a marked migration of electrons from the carbon atoms of the molecule to the aluminium atoms and the latter acquire a negative charge which is near unity. This drift, which is even more marked in Al_2Me_6 than in methylaluminium hydrides, is insensitive to the d orbital exponent, the chief effect of the latter being to alter the charge distribution between the aluminium orbitals. In this context, as would be expected, the population of the d set increases chiefly at the expense of the $3p$ orbitals.

The components of the Al–Al bond show that cross-ring bonding is appreciable and the d orbitals take a significant part in this. The interactions are not clearly separable into σ-, π-, and δ-type because the methyl groups destroy diatomic symmetry. However sufficient remains of these for their importance to be assessed. The main Al–Al bonding is brought about by a) $p-p$ interactions b) $p-d$ interactions of the π-type. When two d orbitals are involved again the bonding is mainly of π-type together with some δ-bonding; $d_\sigma d_\sigma$-bonding appears to be of little significance.

In the Al–C bridging bonds the σ and π components are again inseparable because the basis functions are not aligned correctly for a diatomic system. The point of interest here is a comparison of how much the d-orbitals take part in this as compared with the Al–Al bond. It can be seen that (with both $3d$ orbital

Table. *Charge densities for the trimethylaluminium system*

	$Al(CH_3)_3$			$Al_2(CH_3)_6$		
	Al 3*d* orbitals omitted	Al 3*d* orbitals included		Al 3*d* orbitals omitted	Al 3*d* orbitals included	
		(a)[a]	*(b)*[a]		*(a)*[a]	*(b)*[a]
Electron density on aluminium						
Al 3*s*	1.417	1,415	1.407	1.529	1.540	1.555
Total Al 3*p*	2.174	2.170	2.116	2.398	2.321	2.021
Total Al 3*d*	—	0.048	0.193	—	0.137	0.676
Total charge on Al	3.591	3.633	3.716	3.927	3.998	4.252
Electron density on bridging carbon						
C^b 2*s*	—	—	—	1.557	1.565	1.563
Total C^b 2*p*	—	—	—	2.069	2.016	1.907
Total charge on C^b	—	—	—	3.626	3.581	3.470
Electron density on terminal carbon						
C^t 2*s*	1.545	1.549	1.552	1.556	1.570	1.571
Total C^t 2*p*	2.058	2.035	2.019	1.986	1.952	1.899
Total charge on C^t	3.603	3.584	3.571	3.542	3.522	3.470
Electron density on hydrogen at C^b						
H 1*s*	—	—	—	1.104	1.110	1.097
Electron density on hydrogen at C^t						
H 1*s*	1.059	1.061	1.063	1.008	1.008	1.008

[a] In this Table, *(a)* denotes the calculation in which "diffuse" 3*d* orbitals were used whilst *(b)* refers to the calculation employing "contracted" 3*d* functions.

forms) *d* participation is very much more limited in the Al–C bond and suggests that the greater part of the *d* stabilisation energy of the system stems from the cross-ring Al–Al interactions.

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