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BONDING AND ROTATIONAL BARRIERS IN $H_2Al(\eta^2-C_5H_5)$ STUDIED BY AB INITIO MOLECULAR ORBITAL CALCULATIONS

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Summary

Ab initio molecular orbital calculations have been carried out on three conformations of the model compound $H_2Al(C_5H_5)$. The equilibrium conformation is found to be $H_2Al(\eta^2-C_5H_5)$ with the H(Al) atoms in the symmetry plane. The barrier to rotation of the cyclopentadienyl ring is 2.36 kcal mol^{-1} and the barrier to exchange of the H(Al) atoms 11.83 kcal mol^{-1}. The nature of the bonding is discussed.

Introduction

Dimethyl(cyclopentadienyl)aluminium, Me_2AlCp, has recently been studied by gas phase electron diffraction [1]. Under the experimental conditions the gas jet was found to contain monomeric species only, and models for the monomer containing η^1-Cp (σ-bonded) or η^5-Cp (symmetrically π-bonded) rings could be ruled out. The four models containing η^2-Cp or η^3-Cp (asymmetrically π-bonded) rings shown in Fig. 1 were then considered. Somewhat disappointingly it was found that each model could be brought into satisfactory agreement with the experimental intensity data. In each case the value obtained for the distance from the Al atom to the (approximate) five-fold symmetry axis of the ring (o—p in Fig. 1) was such as to place the Al atom directly above the edge of the ring; above the midpoint of the C_1—C_2 bond in models I and III, above C_1 in models II and IV. The values obtained for the perpendicular distances from the Al atom to the plane of the Cp ring (Al—p in Fig. 1) ranged from 2.05 to 2.20 Å.

Subsequently CNDO/2 molecular orbital calculations were carried out on all four models with the various structure parameters obtained by the least squares refinements. The calculations consistently pointed to model I as the

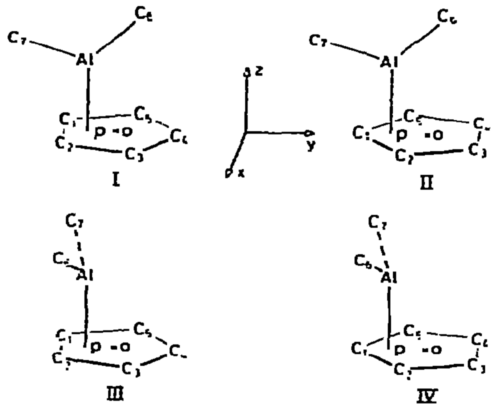

Fig. 1. The four models of Me$_2$AlCp with C_s symmetry compatible with the gas phase electron diffraction data [1].

equilibrium conformation, but indicated that the barrier to rotation of the Cp ring (via model III) is of the order of 5 kcal mol^{-1} or less, and that the barrier to exchange of the two non-equivalent Me groups (via model III) is between 10 and 20 kcal mol^{-1}.

The structure of model I obtained by least squares calculations on the electron diffraction data is shown in Fig. 2. It is probably best described as containing a η^2-Cp ring. A very similar arrangement has also recently been found for one of the Cp rings in Cp$_3$Ti by X-ray crystallography [2].

Me$_2$AlCp appears to be partly associated in freezing benzene [3]. The ^{1}H NMR spectrum of Me$_2$AlCp in this solvent [3,4] as well as in CCl$_4$ [5] at ambient temperatures consists of two singlets corresponding to the six Me protons and the five Cp protons respectively. Benzene and CCl$_4$ can hardly be regarded as non-interacting solvents, and it cannot be taken for granted that the structure of the monomer in these solvents is the same as in the gas phase. It should

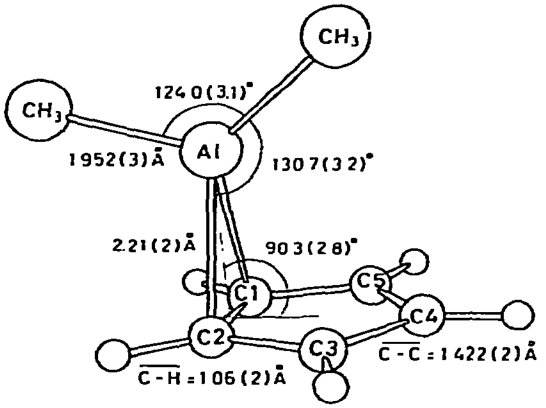

Fig. 2. Structure of model I of Me$_2$AlCp obtained by least squares refinement on the gas phase electron diffraction data [1].

nevertheless be noted that the simplicity of the ^1H NMR spectra is consistent with the low barrier to rotation of the Cp ring and the moderate barrier to exchange of the Me groups indicated by the approximate molecular orbital calculations on $Me_2Al(\eta^2\text{-}Cp)$.

In order to get more reliable information about the metal to ring bonding and the rotational barriers we have performed a series of ab initio molecular orbital calculations on the model compound H_2AlCp.

Computational details

The Al—H bond distance in H_2AlCp was put equal to 1.56 Å as found in H_3AlNMe_3 [6]. Calculations were first carried out on model I (C_s symmetry) with the bond distances and velence angles shown in Fig. 2. The Cp ring was assumed to have D_{5h} symmetry. Subsequently calculations were carried out on models in which the Cp ring had been rotated 36° about the five-fold symmetry axis (model II) and in which the H_2Al fragment had been rotated 90° about the line bisecting the H—Al—H angle (model III).

Calculations were carried out with the program MOLECULE [7] which solves the Roothaan—Hall equations for a Gaussian type basis. For Al we used a (13,9,1) basis contracted to ⟨6,4,1⟩ [8], for C a (9,5) basis contracted to ⟨4,2⟩ [9] and for H a (4) basis contracted to ⟨2⟩ [10]. A scale factor of 1.25 was used for the H basis set. The *d*-orbital exponent of Al was fixed at 0.30.

Results and discussion

The total energies obtained for the three models are listed in Table 1 along with the energies and approximate assignment of the highest occupied orbitals. Like the CNDO/2 calculations, the ab initio calculations point to model I as the

TABLE 1

TOTAL ENERGIES AND ORBITAL ENERGIES OF THE THREE MODELS OF H_2AlCp

		Model		
		I	II	III
E_{total}	(a.u.)	—435.23187	—435.22811	—435.21301
$E_{pot.\ nuc.}$	(a.u.)	260.24307	260.27195	260.25733
ΔE (kcal mol^{-1})		0.00	2.36	11.83
Orbital energies (a.u.)				
$17a'$	$e_{1y}\pi$	—0.322923	—0.323610	—0.330454
$16a'$	Al—H	—0.439886	—0.440826	—0.447568^a
$15a'$	Al—H	—0.492515	—0.492455	—0.493794
$14a'$	σ(C—H)	—0.534988	—0.529450	—0.531557
$13a'$	σ(C—H)	—0.563195	—0.564513	—0.562417
$12a'$	$a_1\pi$	—0.594952	—0.595217	—0.596906
$8''$	$e_{1x}\pi$	—0.326639	—0.323586	—0.304135
$7a''$	σ(C—H)	—0.530553	—0.534708	—0.526472
$6a''$	σ(C—H)	—0.564601	—0.563501	—0.557709

[a] This orbital has a'' symmetry for model III.

TABLE 2

GROSS ATOMIC POPULATIONS AND OVERLAP POPULATIONS OBTAINED FOR THE CALCULATED EQUILIBRIUM CONFORMATION OF H_2AlCp (MODEL I).

	MO					Total
	$12a'$ $(a_1\pi)$	$15a'$ (Al—H)	$16a'$ (Al—H)	$17a'$ $(e_{1y}\pi)$	$8a''$ $(e_{1x}\pi)$	
Gross atomic populations						
Al	0.635	0.562	0.753	0.128	0.174	12.381
H_6	0.180	0.303	0.623	0.008	0	1.123
H_7	0.147	0.360	0.532	0.104	0	1.160
AlH_2	0.962	1.224	1.908	0.240	0.174	14.663
$C_{1(2)}$	0.310	0.166	0.026	0.278	0.357	6.431
$C_{3(5)}$	0.149	0.149	0.007	0.179	0.554	6.299
C_4	0.096	0.142	0.023	0.844	0.001	6.320
Cp	1.038	0.776	0.092	1.760	1.826	35.337
Overlap populations						
Al—H_6	0.150	0.245	0.421	0.010	0	0.833
Al—H_7	0.127	0.290	0.365	0.034	0	0.828
Al—$C_{1(2)}$	0.082	−0.017	−0.015	0.112	0.061	0.290
Al—$C_{3(5)}$	0.031	−0.007	0.004	−0.057	0.042	0.007
Al—C_4	0.004	−0.004	0.008	−0.069	0.002	−0.070
Al—Cp	0.230	−0.052	−0.013	0.041	0.208	0.525
C_1—C_2	0.081	0.063	0.018	0.207	−0.306	0.746
C_2—C_3	0.056	0.055	−0.002	−0.154	0.311	1.041
C_3—C_4	0.032	0.049	0.002	0.249	−0.002	1.135

equilibrium conformation. The barrier to internal rotation of the Cp ring (via model II) is calculated as 2.36 kcal mol^{-1}, the barrier to exchange of the H atoms (via model III) as 11.83 kcal mol^{-1}. The corresponding numbers obtained by the CNDO/2 calculations on Me_2AlCp were 4.1 and 17.1 kcal mol^{-1} with an *sp* basis and 6.2 and 10.4 kcal mol^{-1} with *spd* basis [1].

The gross atomic and overlap populations obtained by population analysis of the Al—H and Al—Cp bonding orbitals of the equilibrium conformation are listed in Table 2, along with the total gross atomic and overlap populations.

The highest occupied molecular orbital of a'' symmetry, $8a''$, can be clearly identified as the e_{1x} π-orbital of the Cp ring, but it also contains a small contrigution from the Al $3p_x$ atomic orbital, the contribution from this molecular orbital to the electron density on Al is 0.174. The molecular orbital is consequently weakly bonding between Al and $C_{1(2)}$ and $C_{3(5)}$.

The highest molecular orbital of a' symmetry, $17a'$, is more complex. It can be roughly described as the e_{1y} π-orbital of the Cp ring mixed with the a_1 π-orbital in such a way as to increase the electron density on the C atoms that are the greatest distance from Al. But it also has a small contribution from the Al $3p_y$ and $3p_z$ atomic orbitals, the resulting hydrid p-orbital pointing roughly towards the center of the Cp ring. The contribution from the $17a'$ molecular orbital to the electron density on Al is 0.128. There appears to be bonding between Al and $C_{1(2)}$, but antibonding between Al and $C_{3(5)}$ and between Al and C_4. We shall return to this point below.

Then follow two molecular orbitals of a' symmetry. The highest of these is an almost completely localized Al—H bond orbital with large contributions from the Al $3p_y$ and $3p_z$ orbitals. On rotation of the H_2Al fragment to model III this orbital changes its symmetry to a''. The lowest Al—H bond orbital has a large contribution from the Al 3s atomic orbital and is to a considerable extent mixed with the a_1 π-orbital of the Cp ring. It is antibonding between the Al atom and the ring.

The energy of the a_1 π-orbital of the Cp ring lies below the energy of four of the σ C—H bond orbitals. The a_1 π-orbital has been mixed with the e_{1y} π-orbital in such a way as to increase the electron density on C_1 and C_2. The molecular orbital also contains a large contribution from the Al 3s orbital, the contribution from this molecular orbital to the electron density on Al being 0.635. The molecular orbital is consequently bonding Al and $C_{1(2)}$ and Al and $C_{3(5)}$.

The total overlap populations obtained indicate substantial bonding between Al and $C_{1(2)}$, negligible bonding between Al and $C_{3(5)}$ and a net antibonding effect (due largely to the $17a'$ orbital) between Al and C_4. The overlap populations therefore support the description of the compounds as $H_2Al(\eta^2\text{-Cp})$.

The overall bonding between the Al atom and the ring appears to be due to the interaction of the a_1 π-orbital with the 3s orbital of Al and of the e_{1x} π-orbital with the $3p_x$ orbital on Al. The interaction between the e_{1y} π-orbital and the atomic orbitals on Al results in bonding between Al and $C_{1(2)}$, but antibonding between Al and $C_{3(5)}$ and C_4. It seems reasonable to assume that this antibonding is due to the non-availability of the Al $3p_y$ orbital for bonding to the ring, and to assume that the resulting repulsion between Al and $C_{3(5)}$ and C_4 is responsible for the asymmetric structure of the π-complex.

The population analysis indicates that Al to Cp bonding is accompanied by a flow of 0.530 electrons from Al to Cp in the a' molecular orbitals and a back-donation of 0.194 electrons into the $3p_x$ and to a much smaller extent the $3d_{xy}$ and $3d_{xz}$ orbitals of Al. Similarly ab initio calculations on H_2AlOH [11] have indicated a transfer 0.478 electrons from Al to O in the σ-orbitals and a back-donation of 0.113 electrons into the $p\pi$ and $d\pi$ atomic orbitals of Al.

The resulting net charge on the Cp ring, —0.336, is intermediate between the net charges on the Cp rings in $HBe(\eta^5\text{-Cp})$ [12] and $H_3Si(\eta^1\text{-Cp})$ [13] obtained by ab initio molecular orbital calculations, —0.507 and —0.280 respectively. Since the H(Al) atoms also carry a negative charge, the calculated dipole moment is only 0.75 Debye.

The $3d$ orbitals of Al do not appear to be very important for the bonding in H_2AlCp. The total $3d$ orbital population is 0.249 which is not much greater than in AlH_3, 0.184 [11].

When the H_2Al fragment is rotated 90° to model III, the energies of the $12a'$ ($a_1\pi$) and $17a'$ ($e_{1y}\pi$) orbitals decrease slightly (see Table 1), while the energy of the $8a''$ ($e_{1x}\pi$) orbital increases by 0.025 a.u. (= 16 kcal mol^{-1}) and the contribution of this molecular orbital to the electron density on Al decreases from 0.174 to 0.071. It is clear that model III is less favorable than model I because conjugation between the e_{1x} π-orbital of the ring and the formally empty $3p$ orbital of Al has been broken.

Similarly comparison of the orbital energies for models I and II show that the energies of the $12a'$ ($a_1\pi$) and $17a'$ ($e_{1y}\pi$) orbitals decrease as the Cp ring is rotated, while the energy of the $8a''$ ($e_{1x}\pi$) orbital again increases, and the contribution from the latter MO to the electron density on Al decreases slightly from 0.176 to 0.168. Since the energy difference is small, the case is not entirely clear-cut, but it seems reasonable to assume that model I is favored because conjugation between the e_{1x} π-orbital of the Cp ring and the $3p_x$ orbital of Al is less effective in model II than in model I.

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