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Molecular Orbital Study of the Bridge Bonding in an Electron Deficient Molecule $[(CH_3)_2ALH]_2$

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The electronic distribution in the AlH_2Al bridge of the dimethyl aluminium hybride dimer was computed through ab initio SCF calculation. Comparison with diborane shows an increased role of the ionic $Al^+H_2^{2-}Al^+$ structures with respect to the usual covalent three-center bonds.

Key words: Bridge bonding in an electron deficient molecule.

1. Introduction

Nature of bridge bonding in electron deficient compounds of boron have been the subject of many quantum mechanical calculations [1–3], but isoelectronic molecules containing heavier elements of group III have received less attention.

An intriguing feature of dimethyl aluminium dimer is the rather short Al—Al distance as determined by an electron diffraction study [4] (0.24 Å smaller than the distance in the metal). This paper reports a study of the bridge bonding in

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$[(CH_3)_2AlH]_2$ by means of SCF *ab initio* molecular orbital calculation; the resulting molecular wave function is analysed by means of population analysis, electron density maps and localized orbitals description.

2. Computational Details

The *ab initio* calculations were performed in basis of contracted gaussian functions. The aluminium and the carbon atoms are respectively described by (10s6p1d/4s3p1d) and (7s3p/2s1p) sets derived from Roos and Siegbahn [5]. Starting from a Slater exponent of 1.2 a STO 3G for methyl hydrogens and a STO 4/31G for bridge hydrogens were generated. Therefore, bridge atoms are described at a valence double-zeta level whereas the methyl groups are treated using minimal basis only.

The molecular geometry was taken from the electron diffraction study [4]. In order to investigate the possibility of deviation from the D_{2h} symmetry we have also considered a geometry in which the bridge hydrogen atoms were removed out of the original plane of the molecule (Fig. 1).

3. Results and Discussion

The atomic charges (Table 1) computed according to the Mulliken scheme [6] are of the same order than those obtained by SCF-MO calculations of some halogen bridged aluminium halides [7]. Thus, the SCF calculation leads to highly ionic Al—X—Al bonds in molecules of this type. The total electron density in the plane of the bridge as well as in the perpendicular mirror plane has been plotted in Fig. 2a. The density in the bridge plane may be compared with the analogous density for diborane (see Fig. 4 of reference [2]): we find significant differences. A decrease of covalent character of bridge bonding for the aluminium compound is

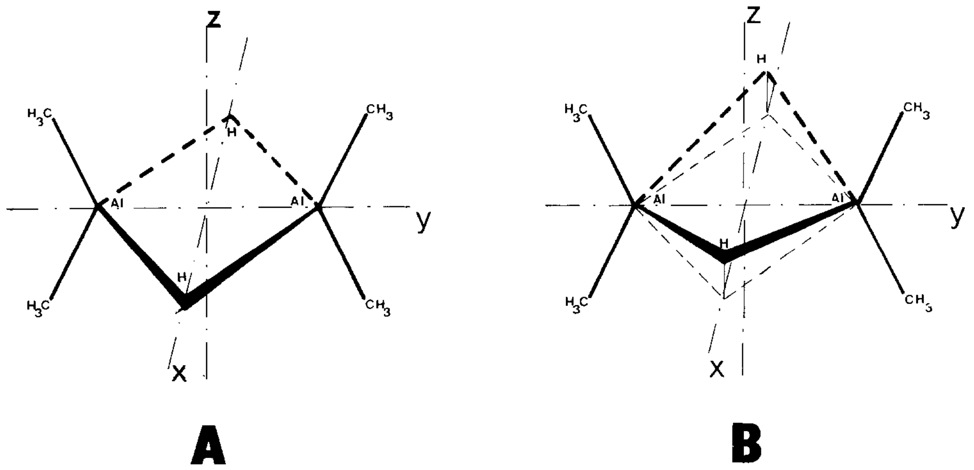

Fig. 1. Geometrical models A and B

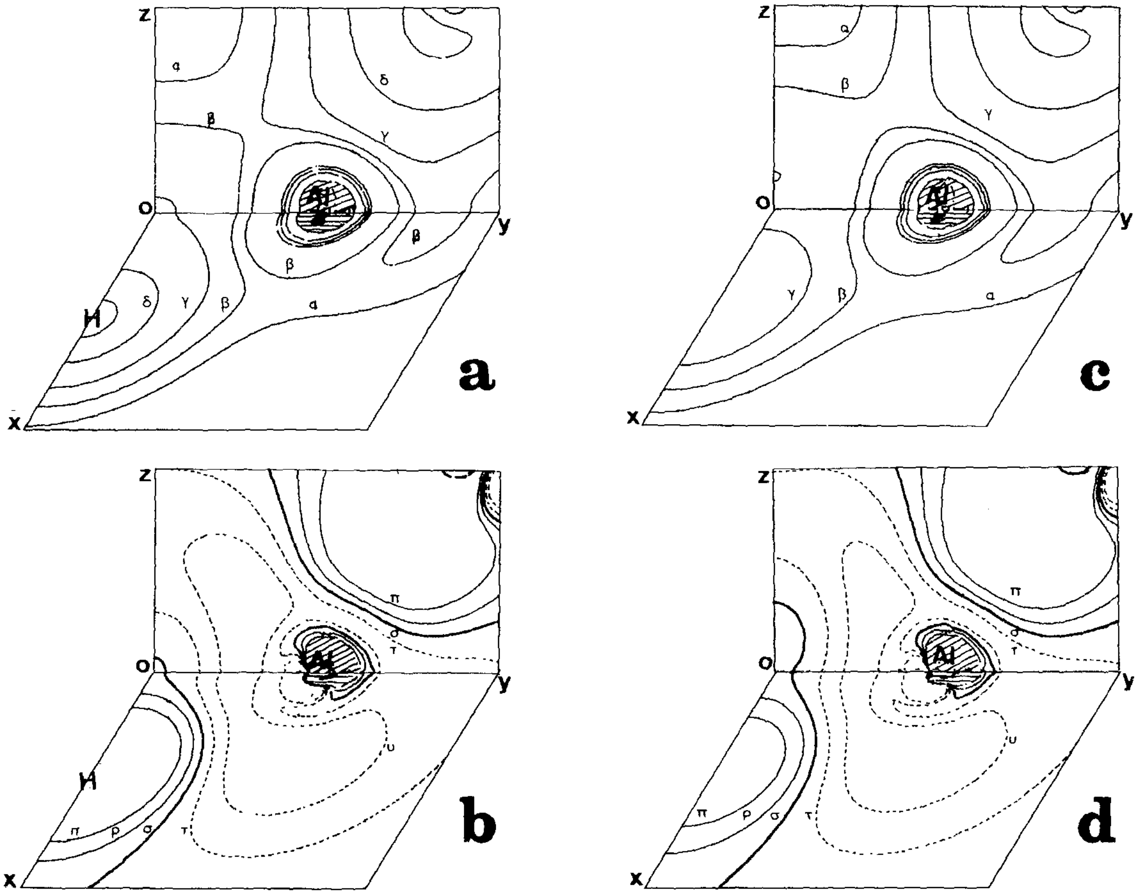

Fig. 2. Valence Electron density maps in the planes XOY and ZOY of Fig. 1 (first quadrant):
a Total density for model A
b Differential density for model A
c Total density for model B
d Differential density for model B
Contour levels (e. a.u.$^{-3}$) are: $\alpha = 0.01$, $\beta = 0.02$, $\gamma = 0.04$, $\delta = 0.1$, $\varepsilon = 0.25$, $\pi = 0.01$, $\rho = 0.004$, $\sigma = 0$, $\tau = -0.004$, $\mu = -0.008$; negative signs indicate a loss of electron

Table 1. Mulliken population analysis

	Model A (Fig. 1)	Model B (Fig. 1)
Al	+0.979	+0.856
C	−0.938	−0.936
$H^{av}_{CH_3}$	+0.178	+0.176
H_{bridge}	−0.168	−0.047
Al . . . Al	+0.340	+0.455
Al—C	+0.616	+0.609
Al . . . H_b	+0.404	+0.411
H_b . . . H_b	−0.139	−0.102

suggested by the deep valley in electron density which is placed between the aluminium and hydrogen atoms. The ionic character of the bond between the bridge atoms is demonstrated by the displacement of charges shown in the differential density map (Fig. 2b). The hydrogen bridge atoms carry negative charges as expected from population analysis. Moreover, the excess charge density is not spherically distributed around the proton but is distorted towards the other hydrogen atom of the bridge, suggesting a covalent interaction. This contrasts with the negative overlap population obtained (Table 1) for the H_bH_b interaction, but is compatible with the shape of the total electron density contours labelled β in Fig. 2a. On the opposite, the density maps do not suggest any covalent bond between the aluminium atoms, in contradiction with the Mulliken population analysis which leads to a positive overlap population for Al . . . Al, similar to those reported for B . . . B in diborane [1]. As a consistent remark, one may note that the density difference map displayed in Fig. 2d gives no indication for the formation of an aluminium-aluminium bond, when hydrogen bridge atoms are moved out of the original bridge plane. This is quite surprising since contours levels as well as atomic charges give evidence for the formation of a neutral H—H molecule keeping an electron pair shared between the two dimethyl aluminium groups in this case.

The arbitrariness of Mulliken analysis is emphasized by the results of Lappert et al. [7] who obtained a weak antibonding Al . . . Al interaction in the similar halogen bridged molecule $[Me_2AlCl]_2$. As pointed out by Mason and Mingos "we do not and cannot distinguish in general the cases where a metal-metal bond order is due to direct overlap or to appropriate bridge bonding" [8].

Localized descriptions have been widely used to rationalize the bridge bonding in diborane in term of three-center bonds [1–2]. Thus, it is of interest to investigate whether the quantitative differences obtained from global analysis of SCF wavefunctions have a counterpart in the localized description of bridge bonding or not. To this end, SCF localized MOs have been obtained which satisfy the Boys criterion [9]:

The bonding in the bridge is described by two three-center orbitals as first pointed out by Longuet-Higgins [10] but their covalent character is less noticeable than it

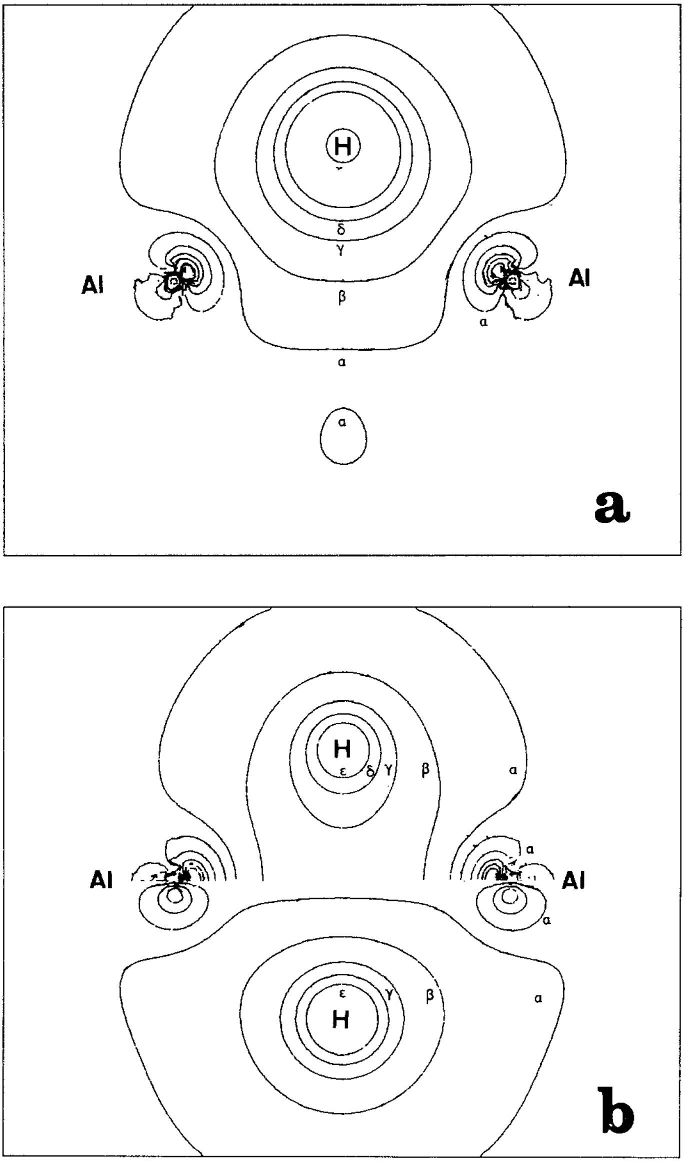

Fig. 3. Bridge electron density maps (plane XOY):
a three-center bond;
b four-center bond (upper: σ, down: π)
$\alpha = 0.015$; $\beta = 0.02$; $\gamma = 0.05$; $\delta = 0.075$; $\varepsilon = 0.1$; $\xi = 0.3$

is in diborane as shown by comparing our Fig. 3a with Fig. 5 and Fig. 6 of reference [2]. Since the Boys criterion acts by achieving the maximization of the distance between the centroids of charge of the orbitals, it favours "banana-type" bonds instead of equivalent $\sigma + \pi$ description [11]. The symmetric plus antisymmetric combination of the two three-center bonds gives symmetry adapted SCF localized orbitals which describe the bridge bond. The electron density of both localized symmetry adapted MOs is plotted in Fig. 3b. The orbital with σ symmetry closely resembles a H—H bond with electron density on an atom tending towards the other atom. The π-like orbital is mainly an H—H antibonding orbital as indicated by the shape of the electron density contours. At this point, it might be noticed from an energetic point of view that these two orbitals, being bonding and anti-bonding, lead to a nearly zero interaction between the two hydrogen atoms but result in a $\sigma+\pi$ bonding interaction for the two aluminium atoms and, consequently, give an account for the observed short aluminium–aluminium distance. It would be also noticed the above description of bridge bonding implies labile hydrogens; the energy difference (13 Kcal mole^{-1}) between the two calculated models A and B (Fig. 1) does not support this assumption. In fact, the ionic interactions between the hydrogen atoms and the aluminium atoms are predominant as we can see from a valence bond analysis of the SCF wave function. The SCF wave function can be written as

$$\phi = \mathscr{A}(R\Sigma^2\Pi^2) \qquad (1)$$

R is the remainder part of the wavefunction and

$$\Sigma = \alpha\sigma + \beta \mathrm{H} \qquad (2)$$

$$\Pi = \gamma\pi + \delta \mathrm{H}^* \qquad (3)$$

σ represents the Al—Al σ orbital whereas π represents the Al—Al π orbital, H and H* respectively label the H—H σ orbital and the antibonding H-H σ^* orbital. Notice that σ and H as well as π and H* can be supposed orthogonal.

The resulting predominant valence bond structures are reported in Fig. 4. The first one involves negative aluminium atoms and positive hydrogen atoms. On the basis of simple electronegativity argument we can predict a small weight for this structure. However, in the case of diborane, electronegativity argument does not apply and this representation of the Pitzer model [12] for bridge bonding has to be taken into account. The second one is an antibonding H—H structure and consequently would have also a small weight. The third one implies a π Al—Al bond without the more energetic σ bond and seems to be defavourised. The last one is the completely ionic structure involving positive aluminium atoms and negative hydrogen atoms which agrees with electronegativity trends and it has the greater weight in the SCF wave function due to a stabilizing electrostatic interaction. It is clear that only CI wave function can take into account a structure such as $\sigma^2\mathrm{H}^2$ in Fig. 4 which is expected to contribute to the bonding with a noticeable weight.

4. Conclusion

The SCF calculation on $[(\mathrm{CH_3})_2\mathrm{AlH}]_2$ shows basic similarities with diborane three-center bonds. However, a detailed analysis of charge distributions, as vizualized through Mulliken population, charge density maps and differential density maps, reveals a significantly more ionic bonding of the type $\mathrm{Al}^{+}{}^{\mathrm{H}^-}_{\mathrm{H}^-}\mathrm{Al}^{+}$ of

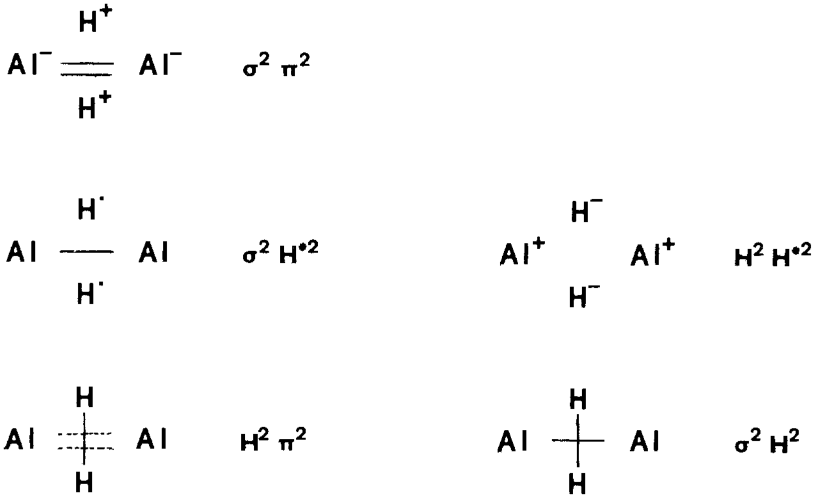

Fig. 4. Main valence-bond structures

the same amplitude as for the halogen bridged analogs. The localization procedure has been used to turn back to $\Sigma^2\Pi^2$ localized description of the Al... Al interaction. A qualitative discussion shows that the SCF approximation, neglecting possible Σ^4 structures, should overestimate the ionic component of the wave function. A CI study of this problem is undertaken.

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