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AB INITIO MOLECULAR ORBITAL CALCULATIONS ON H_3AlOH_2, $(H_2AlOH)_2$, AND SOME RELATED SPECIES

ODD GROPEN* and RAGNAR JOHANSEN

Institute of Medical Biology, University of Tromsø, 9001 Tromsø (Norway)

ARNE HAALAND* and ODDVAR STOKKELAND

Department of Chemistry, University of Oslo, Blindern, Oslo 3 (Norway)

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Summary

Ab initio molecular orbital calculations have been carried out on H_3AlOH_2, $(H_2AlOH)_2$, and some related species, and the charge distribution and bonding are discussed on the basis of population analyses. It is found that the equilibrium conformation around the O atom in H_3AlOH and $(H_2AlOH)_2$ is intermediate between trigonal and tetrahedral. The energy minima are, however, very shallow. In H_3AlOH_2 the angle between the Al—O bond and the H_2O plane is 27°, in $(H_2AlOH)_2$ the angle between the two O—H bonds and the Al_2O_2 ring plane is 25°. The energy of a planar conformation of H_3AlOH_2 is 0.19 kcal mol^{-1}, the energy of a planar conformation of $(H_2AlOH)_2$ 0.35 kcal mol^{-1} above the equilibrium conformation. There is no indication for the formation of dative $p\pi$—$d\pi$ bonds between O and Al in the two molecules. It is suggested that the conformation adopted by analogous alkyl derivatives, $R_3AlOR'_2$ and $(R_2AlOR')_n$ is determined by intramolecular van der Waals repulsion.

Introduction

It has been known for several years that the three valencies of the oxygen atom in siloxy- or alkoxy-bridges between aluminium atoms tend to lie in one plane. The first example of such planar three-coordinate O atoms to be stablished by diffraction techniques was found in $(Me_2AlOSiMe_3)_2$ (Me = CH_3) [1]. Later examples include the siloxy-bridged $(Br_2AlOSiMe_3)_2$ [2] and the alkoxy-bridged species $(Me_2AlOMe)_3$ [3] and $(Me_2AlOCMe_3)_2$ [4]. Several authors have pointed out that the reason for this planarity may be the formation of dative $p\pi$—$d\pi$ bonds between O and Al, but recently one of us has suggested that the planarity results from repulsion between the large substituents on the O atom [5].

The only alane—ether complex whose structure has been determined is the 2/1 complex of Me_3Al with dioxane, which has been studied by X-ray crystallography [6]. In this case the ether O atom was found to be non-planar, the angle between the Al—O bond and the OC_2 plane of the ether being $\phi = 25.6°$. This value is intermediate between the angle expected for a tetrahedral ($\phi = 55°$) and a trigonal ($\phi = 0°$) O atom. It has been suggested, however, that in this case too dative $p\pi$—$d\pi$ O—Al bonding would stabilize a planar conformation around O, and that a complex like Me_3AlOMe_2 may be planar in the gas phase [7].

The present ab initio molecular orbital calculations on H_3AlOH_2, $(H_2AlOH)_2$, and related species were undertaken to gain insight into the nature of the Al—O bonds in these molecules; and in particular to investigate the equilibrium conformation of the O atoms and the possible formation of dative $p\pi$—$d\pi$ O—Al bonds.

Only very recently have we become aware of the determination of the crystal and molecular structure of the alkoxy-bridged compound $(Me_3COBeBrOEt_2)_2$ [8]. In this compound both the alkoxy and the ether O atoms are planar. Since $p\pi$—$d\pi$ O—Be bonding is precluded, it was concluded that steric interference was responsible for the planar conformations adopted. This view is in agreement with the results of the present study.

Basis

The calculations were carried out with the program MOLECULE [19] which involves the Roothan—Hall equations for a Gaussian-type basis. For Al we used a (13,9,1) basis contracted to <6,4,1> [10]. The d-orbital exponent was chosen as 0.30. For O we used a (9,5,1) basis contracted to <4,2,1> [11] with d-orbital exponent equal to 0.80, for H a (4) basis contracted to <2> [12] with a scaling factor of 1.25.

Calculations

H_3AlOH_2

The H_3AlO fragment was assumed to have C_{3v} symmetry, and the Al—H bond distance (1.56 Å) in this and all other species mentioned below as well as the H—Al—D (D = donor atom) angle (104.0°) were taken from the structure of H_3AlNMe_3 [13]. The O—H bond distance was put equal to 0.95 Å in this and all other species mentioned below.

The Al—O bond distance, the H—O—H valence angle and the angle ϕ between the Al—O bond and the plane of the water molecule (see Fig. 1) were varied to minimize the energy. All calculations except one was carried out on a model of C_s symmetry with the H_2O plane perpendicular to the symmetry plane as shown in Fig. 1.

First the angles H—O—H and ϕ were fixed in pairs as indicated at the head of Table 1, and calculations carried out for three values of the Al—O bond distance, 1.80, 1.90 and 2.10 Å. For each pair of H—O—H and ϕ the energy was regarded as a quadratic function of the Al—O distance, and the Al—O distance minimizing the energy were determined. The resulting distances are listed in the last line of Table 1. They are seen to be relatively insensitive to the values assum-

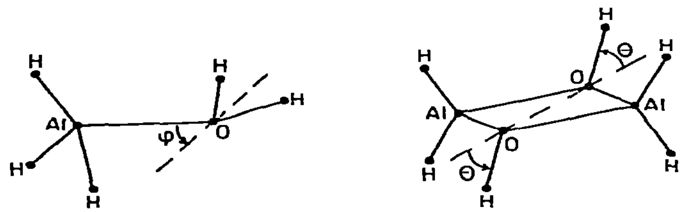

Fig. 1. Molecular models of H_3AlOH_2 and $(H_2AlOH)_2$.

ed for ∠H—O—H and ϕ, and since the lowest energies are obtained for ∠H—O—H = 110° and ϕ =40°, the equilibrium Al—O bond distance must be close to 2.02 Å.

Subsequently calculations were carried out with R(Al—O) 2.10 Å and ∠H—O—H and ϕ fixed in pars as indicated in Table 2, where the resulting energies are listed. For each value of ϕ the energy was assumed to be a quadratic function of ∠H—O—H, and the value of the valence angle minimizing the energy determined. These are listed in the last line of Table 2. They are seen to be relatively independent of ϕ and the average, 109.3°, must be close to the equilibrium angle.

Finally Al—O was fixed at 2.02 Å and ∠H—O—H at 109.3° and calculations carried out for the five values of ϕ listed in Table 3. The last energy listed is the result of a calculation on a model of C_s symmetry with the water molecule in the symmetry plane, i.e. where an O—H bond eclipses an Al—H bond. The lowest energy is obtained with ϕ = 25°. It was assumed that the energy can be expressed as a fourth degree polynominal of ϕ and the coefficients determined from the first five points in Table 3. The resulting energy curve is shown in Fig. 2. It has two minima, E = 0 at ϕ = 27°, and E = 0.17 kcal mol^{-1} at ϕ = −30°.

$(H_2AlOH)_2$

The Al—O bond distance (1.87 Å) and the Al—O—Al and H—Al—H valence angles (97.8° and 120.3° respectively) were taken from preliminary results in the structure determination of $(Me_2AlOCMe_3)_2$ by electron diffraction. They do not differ significantly from the final values [4]. Calculations were carried out on models of C_{2h} symmetry with the H_2Al planes perpendicular to the Al_2O_2

TABLE 1

CALCULATED ENERGIES FOR H_3AlOH_2 OBTAINED WITH DIFFERENT VALUES FOR R(Al—O), ∠H—O—H AND ϕ

The energies are given in kcal mol^{-1} in excess of the energy obtained with R(Al—O) = 2.02 Å, ∠H—O—H = 109.3° and ϕ = 25°, see Table 4.

R(Al—O) (Å)	∠H—O—H = 106° ϕ = 80°	∠H—O—H = 110° ϕ = 40°	∠H—O—H = 120° ϕ = 0°
1.80	13.90	5.60	6.65
1.90	8.56	1.50	2.78
2.10	5.83	0.58	2.22
R_{min} (Å)	2.05	2.02	2.01

TABLE 2

CALCULATED ENERGIES FOR H_3AlOH_2 OBTAINED FOR DIFFERENT VALUES OF ∠H—O—H AND ϕ WITH R(Al—O) = 2.10 Å

The energies are listed in kcal mol^{-1} in excess of the energy obtained with R(Al—O) = 2.02 Å, ∠H—O—H = 109.3° and ϕ = 25°, see Table 4.

∠H—O—H (deg)	ϕ = 0°	ϕ = 40°
106	0.92	0.64
110	0.62	0.58
120	2.22	2.78
∠H—O—H_{min} (deg)	110.2	108.4

ring plane (see Fig. 1). The angle θ between the O—H bonds and the ring plane were fixed at 0°, 20° and 40°. The lowest energy was obtained for θ = 20°, the energy obtained for θ = 0° being 0.31 kcal mol^{-1}, and the energy obtained for θ = 40° being 0.88 kcal mol^{-1} higher. It was assumed that $E(\theta) = a + b\theta^2 + d\theta^4$ and the coefficients determined. The resulting energy curve is shown in Fig. 2. The minimum energy, E_{min} = —0.04 kcal mol^{-1} is obtained for θ = ±25°.

*H_2AlOH**

The Al—O bond distance was fixed at 1.72 Å, that is somewhat shorter than the Al—O distance in Al_2O, 1.73 ± 0.01 Å, [14] and somewhat longer than the Al—O bond distance in $(C_{10}H_8NO)_2AlOAl(C_{10}H_8NO)_2$, 1.676(4) Å, [15]. The H—Al—H angle was fixed at 120°, the Al—O—H angle at the value (121.6°) obtained for the lowest energy conformation of H_3AlOH_2 (ϕ = 25°).

AlH_3

Calculations were carried out on a planar model of D_{3h} symmetry, and, in order to estimate the reorganization energy, on a model of C_{3v} symmetry with the same H—Al—H angle as in the complex H_3AlOH_2.

TABLE 3

CALCULATED ENERGIES FOR H_3AlOH_2 OBTAINED FOR DIFFERENT VALUES OF ϕ WITH R(Al—O) = 2.02 Å AND ∠H—O—H = 109.3°

The energies are given in kcal mol^{-1} in excess of the energy obtained with ϕ = 25°, see Table 4.

ϕ (deg)	E (kcal mol^{-1})
—40	0.23
0	0.19
25	0
40	0.15
80	6.20
0[a]	0.17

[a] H_2O molecule in the symmetry plane.

* A more thorough investigation of H_2AlOH including structure optimization has been initiated [26].

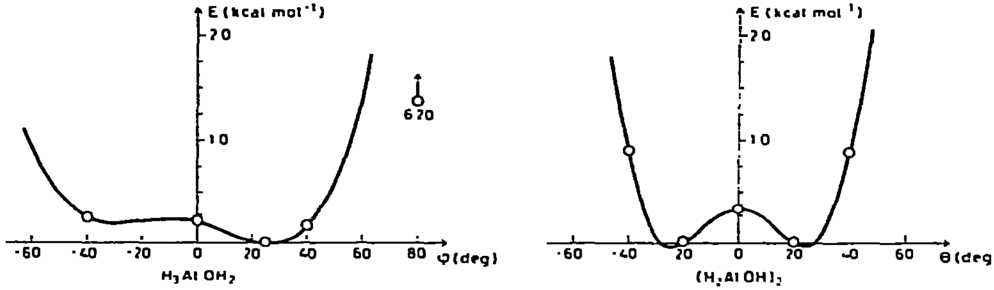

Fig. 2. Total energies of H_3AlOH_2 and $(H_2AlOH)_2$ as functions of the angles φ and θ. See Fig. 1.

AlH_4^-

Calculations were carried out on a model of T_d symmetry.

Al_2H_6

The Al—H (bridge) bond distance (1.676 Å) and the H_t—Al—H_t and Al—H_b—Al angles (118.5° and 102.6° respectively) were taken from the structure of $(Me_2AlH)_2$ as determined by electron diffraction [16].

Finally, calculations were carried out on H_2O with H—O—H = 104.45° [17] and on H_2 with a bond distance of 0.741 Å [18].

Results and discussion

The energies obtained by the calculations on the lowest energy conformations of H_3AlOH_2 and $(H_2AlOH)_2$ as well as the energies obtained by the calculations on H_2AlOH, AlH_3 (planar), AlH_4^-, Al_2H_6, H_2O and H_2 are listed in Table 4 along with some of the parameters obtained by the population analysis.

H_3AlOH_2

The energy of reaction 1 can be calculated from the energies listed in

$$AlH_3 + H_2O = H_3AlOH_2 \quad (1)$$

Table 4: $\Delta E_1 = -17.0$ kcal mol⁻¹. Since the present calculations do not include electron correlation, this number, as well as the reaction energies calculated below, must be regarded with some reservation. But since reaction 1 involves very little change of the charge distribution, one may hope that the omission is not serious. In any case, the calculated energy of the reaction is remarkably similar to the enthalpy of formation of the gaseous complex Me_3AlOMe_2 from its gaseous monomeric constituents: $\Delta H = -21.92 \pm 0.18$ kcal mol⁻¹ [19].

The reorganization energy of AlH_3 was calculated as 10.0 kcal mol⁻¹.

The calculated equilibrium Al—O bond distance (2.02 Å) is in good agreement with the Al—O distance found in the 2/1 complex of Me_3Al with dioxane, 2.02(2) Å [6].

The equilibrium conformation of H_3AlOH_2 is found to be one in which the O atom is nonplanar, the angle $\phi = 27°$. The energy minimum is however very shallow, see Fig. 2, the energy of a planar configuration being only 0.20 kcal mol⁻¹ higher, and only when ϕ becomes less than −50° or greater than +50° does the energy increase rapidly.

TABLE 4

ENERGIES, GROSS ATOMIC POPULATIONS, OVERLAP POPULATIONS, AND TOTAL *d*-ORBITAL POPULATIONS

	$(H_2AlOH)_2$ [a]	H_2AlOH	H_3AlOH_2 [b]	H_2O	AlH_3	Al_2H_6	$(AlH_4)^-$	H_2
Total energy	−637.25306	−318.57080	−319.69162	−76.03242	−243.63212	−487.30131	−244.22475	−1.126905
One-el. energy	−1331.96061	−545.58240	−564.57736	−123.16834	−366.12828	−833.15716	−381.23725	−2.49432
Two-el. energy	470.43288	175.32543	183.92022	37.88038	108.67379	267.44360	118.12704	0.65354
Nucl. repulsion	224.28371	51.67717	60.96552	9.25555	13.82237	78.41225	18.88546	0.71388
Gross atomic populations								
Al	12.052	12.151	12.439		12.457	12.447	12.731	
O	9.015	8.913	8.848	8.797				
H(Al)	1.200	1.186 [c]	1.228 [e]		1.181	1.253 [g]	1.317	
H(Al)	1.200	1.175 [d]	1.226 [f]			1.150 [h]		
H(O)	0.532	0.576	0.517	0.602				
Overlap populations								
Al—O	0.290	0.670	0.095					
Al···Al	−0.005					0.129		
O···O	−0.104							
Al—H(Al)	0.819	0.799 [c]	0.806 [e]		0.796	0.371 [g]	0.753	
Al—H(Al)	0.819	0.801 [d]	0.801 [f]			0.832 [h]		
O—H (O)	0.574	0.550	0.566	0.591				
Total d-orbital populations								
Al	0.212	0.208	0.193		0.184	0.254	0.174	
O	0.032	0.035	0.065	0.058				

[a] $\theta = 20^\circ$. [b] $R(Al—O) = 2.02$ Å, $\angle H—O—H = 109.3^\circ$ and $\phi = 25^\circ$. [c] *syn*. [d] *anti*. [e] In symmetry plane. [f] Not in symmetry plane. [g] Bridge. [h] Terminal.

Under these circumstances it seems reasonable to assume that the conformation actually adopted by a complex of a trialkylalane with an ether, $R_3AlOR'_2$, may be determined by steric interactions of the type Al···R' and R···R'. Al···R' repulsion would favor a planar, R···R' repulsion a nonplanar conformation with ϕ greater than zero. The fact that the calculated value for ϕ in $(H_2AlOH)_2$, 27°, is very similar to the value actually found in the crystalline complex $(Me_3Al)_2C_4H_8O_2$, ϕ = 26°, must be regarded as fortuitious.

The barrier to internal rotation about the Al—O bond in H_3AlOH_2, calculated as $V_s = E(\phi = -30°)-E(\phi = 27°)$ is less than 0.2 kcal mol^{-1}. Introduction of alkyl groups on Al or O would be expected to favor a staggered model and hence to increase the barrier.

The gross atomic populations listed in Table 5 indicate that the Al atom in H_3AlOH_2 carries a net positive charge of +0.56 and the O atom a net negative charge of —0.85, while the H(Al) atoms carry a negative charge and the H(O) atoms a positive charge. They further indicate that formation of the complex is accompanied by a transfer of —0.11 from donor to acceptor, and comparison with the gross atomic populations of AlH_3 and H_2O indicate that this charge is taken from the H(O) atoms and ends up on the H(Al) atoms while the net charge on Al and O remain virtually unchanged.

Similarly Mulliken population analysis of the molecular orbitals obtained by ab initio calculations on H_3BNH_3 [20] indicated that formation of the complex was accompanied by a transfer of —0.31 from donor to acceptor and that most of this charge was transferred from the H atoms of the donor to the H atoms of the acceptor. However, electron density difference maps indicate that charge was transferred from the proximity of the N nucleus to the region surrounding the B nucleus, and it was suggested that the partitioning used in the population analysis may be too coarse to reflect the real redistribution of charge.

The Al—O overlap population in H_3AlOH_2, 0.095, which is somewhat less than the B—N overlap population obtained for H_3BNH_3, 0.127, reflects the weakness of the dative bond.

Finally we wish to investigate whether there is a significant amount of dative $p\pi$—$d\pi$ bonding between O and Al, and since such bonding is believed to be favored by a planar conformation around O, we turn our attention to the planar model. For the model in which the water molecule is in the symmetry plane, the molecular orbital containing the $2p\pi$ lone pair of O is easily identified. It is found that for this molecular orbital the gross population in the O $2p\pi$ orbital is 1.976 electrons, while the population in the Al $3p\pi$ orbital (which normally would be considered to be unavailable for bonding to O) is 0.013 and in the Al $3d\pi$ 0.003 electrons. The Al—O overlap population due to the electrons in this molecular orbital is 0.025. In our view these numbers are sufficient to show that the dative π-bonding between O and Al is negligible, and that the slight π-bonding which may exist is of the $p\pi$—$p\pi$ rather than of the $p\pi$—$d\pi$ type.

H_2AlOH

The energy of reaction 2 is calculated as ΔE_2 = —9.5 kcal mol^{-1}.

$$H_3AlOH_2 = H_2AlOH + H_2 \quad (2)$$

The gross atomic populations in Table 4 show that the net charge on Al is +0.85 compared to +0.64 in AlH_3 and that the net charge on O is −0.91 compared to −0.80 in H_2O; clearly the Al—O bond is very polar.

The total Al—O overlap population, 0.670, is due to the formation of a σ-bond and a weak dative π-bond between Al and O. The molecular orbital containing the lone pair O $2p\pi$ electrons is easily identified and the Al—O overlap population due to the two electrons in this orbital is 0.156, i.e. considerably larger than the Al—O π overlap populations in H_3AlOH_2 or $(H_2AlOH)_2$ (see below). The gross population in the O $2p\pi$ orbital is 1.886 and in the Al $3p\pi$ and $3d\pi$ orbitals the populations are 0.079 and 0.034 respectively. In H_2AlOH then there appears to be a significant amount of dative π-bonding, but of the $p\pi$—$p\pi$ rather than the $p\pi$—$d\pi$ type.

$(H_2AlOH)_2$

The calculated energy of reaction 3 is E_3 = −58.6 kcal mol^{-1}. It would

$$2\ H_2AlOH = (H_2AlOH)_2 \qquad (3)$$

therefore seem to be this last step which provides the driving force for the formation of $(H_2AlOH)_2$ from AlH_3 and H_2O, reactions 1 + 2 + 3, and probably also for the reaction of trialkylalanes with alcohols to form associated dialkylaluminium alkoxides.

Since reaction 3 might be regarded as involving the formation of two dative Al—O bonds, it is perhaps surprising that the energy of reaction is so much larger than twice the energy of reaction 1, $2 \cdot \Delta E_1$ = −34.0 kcal mol^{-1}. The result is, however, in agreement with what is known about the strength of alkoxy bridges: even though the enthalpy of formation of Me_3AlNMe_3 from its gaseous monomeric constituents is 30.69 ± 0.29 kcal mol^{-1} [19, 21], i.e. nearly 10 kcal mol^{-1} higher than the enthalpy of formation of Me_3AlOMe_2, $(Me_2AlOMe)_3$ does not react with NMe_3 [22].

The equilibrium conformation of $(H_2AlOH)_2$ is found to be one in which two O atoms are nonplanar, the angle between the O—H bonds and the Al_2O_2 ring plane being 25°. The energy difference between this conformation and one with planar O atoms is however, only 0.35 kcal mol^{-1}, a difference so modest that the conformation of the O atom in compounds of the type $(R_2AlOR')_n$ may be determined by steric repulsions of the types Al···R′ and R···R′. In a dimer like $(Me_2AlOCMe_3)_2$ both repulsions would be at a minimum for a planar O atom*. In a trimer like $(Me_2AlOMe)_3$ Al···Me(O) interactions would favor a planar O atom, but Me(Al)···Me(O) interactions a non-planar. Since the O atom in the latter compound also is planar or nearly so, θ = 6.9(1.9)°, it would seem that Al···Me(O) repulsion dominates. Indeed, the Al···C(O) distance is only 2.81 Å.

While gross atomic populations indicated that formation of the complex H_3AlOH_2 was accompanied by a transfer of a charge of −0.11 from donor to acceptor, the association of H_2AlOH appears to be accompanied by a transfer

* CNDO/2 molecular orbital calculations on $(H_2AlOH)_2$ with (*sp*) basis [23] resulted in a non-planar equilibrium conformation with θ = 44°. But calculations on $(H_2AlOR)_2$ reduced θ to 21° for R = Me, to 19° for R = ethyl and to 13° for R = isopropyl.

of −0.06 from the acceptor part (AlH_2) to the donor part (OH). But if the association is assumed to proceed in two steps, the first being the breaking of the dative Al—O π bond and consequently involving a transfer of −0.11 from Al to O, the second step would involve a transfer of −0.05 from the donor part to the acceptor part.

The Al—O overlap population in $(H_2AlOH)_2$, 0.290, is somewhat less than the average of the Al—O overlap populations in H_3AlOH_2 and H_2AlOH, 0.383. But if the average is calculated using only the σ overlap population in H_2AlOH, it is reduced to 0.305, i.e. very similar to the overlap population in $(H_2AlOH)_2$. It is worth noting that both the O···O and Al···Al overlap populations are negative in contrast to the Al···Al overlap population in Al_2H_6 [5, 24]. Clearly there is no bonding ocross the ring.

Finally we turn our attention to the possibility of dative $p\pi$—$d\pi$ bonding in $(H_2AlOH)_2$, and again we investigate the planar conformation. The two molecular orbitals containing the lone pair $2p\pi$ electrons on O yield an Al—O overlap population of 0.059. The resulting gross population in the O $2p\pi$ orbital is 1.878, in the Al $3p\pi$ orbital (which again would not normally be thought to be available for bonding to O) 0.075 and in the two Al $3d\pi$ orbitals 0.019. Again we feel that these numbers are so small as to preclude any significant amount of dative $p\pi$—$d\pi$ bonding.

Inspection of the total *d*-orbital populations on Al listed in Table 5 show that it increases only very little in the sequence AlH_3, H_3AlOH_2, H_2AlOH, $(H_2AlOH)_2$. Inspection of the individual molecular orbitals for each species show that the Al *d* orbitals primarily occur in Al—H bonding orbitals. This indicates that they are best regarded as polarizing functions [25] rather than as orbitals that have chemical relevance.

We intend to return to a discussion of the bonding in Al_2H_6 in another context.

Conclusions

The calculated equilibrium conformation around O in H_3AlOH_2 and $(H_2AlOH)_2$ is intermediate between trigonal and tetrahedral: the angle ϕ between the Al—O bond and the H_2O plane in H_3AlOH_2 being 27°, and the angle between the O—H bonds and the Al_2O_2 ring plane in $(H_2AlOH)_2$ being 25°. The energy minima are however very shallow, in H_3AlOH_2 the energy difference between the equilibrium and a planar conformation about the O atom is only 0.19 kcal mol^{-1}. In $(H_2AlOH)_2$ the energy difference between the equilibrium and a planar configuration about both O atoms is 0.35 kcal mol^{-1}. There is no indication for the formation of dative $p\pi$—$d\pi$ bonds between O and Al in the two compounds.

It is suggested that conformation actually adopted by analogous alkyl derivatives $R_3AlOR'_2$ and $(R_2AlOR')_n$, is determined by intramolecular van der Waals repulsions Al···R' and R···R'.

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