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Theoretical Investigation of Aluminum–Oxygen π-Bonding in 3- and 4-Coordinate Aluminum Alkoxides

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Abstract: A number of monomeric 3- and 4-coordinate aluminum aryloxides have been observed to exhibit unusually short Al–O bonds and very obtuse Al–O–C angles. We have explored the bonding in models for these complexes using ab initio molecular orbital theory. Both the shortening of the Al–O bonds and the large Al–O–C angles are attributed to π-symmetry interactions between the oxygen lone pair and the empty aluminum p-orbital in the 3-coordinate compounds, a not unexpected result for group III elements. The equally large angles in the 4-coordinate complexes are attributed to donation from oxygen into the σ^* donor–acceptor orbital.

We have observed that certain 4-coordinate aryloxide compounds of aluminum exhibit unusually obtuse Al–O–C angles.[2,3] The Al–O–C angles in these aryloxides range from 140.6 to 164.5°, far larger than the 110–130° range expected. In addition, the Al–O bond angles in these cases are significantly shorter than expected. The observed aryloxide Al–O distances in these compounds range between 1.740 Å in $AlMe_2BHTpy$ (py = pyridine, BHT = 2,6-di-*tert*-butyl-4-methylphenoxide) and 1.702 Å in $Al(DIP)_3py$ (DIP = 2,6-diisopropylphenoxide). The typical Al–O single-bond distance is usually considered to be 1.8–2.0 Å. 3-Coordinate aryloxides of aluminum have also been isolated, and these are similarly distorted.[4]

Shortening of bonds between group III elements and those, such as fluorine and oxygen, that have lone pairs is not unexpected.[5] Relatively short B–F bonds are observed in BF_3 and have been attributed to donation from the fluorine lone pairs into the unoccupied boron p. The large electronegativity difference between boron and fluorine (2.0 on the Pauling scale) results in a significant ionic component to the bonding, and this also contributes to a shorter than expected B–F linkage. Similar effects are observed both experimentally and theoretically in the alkoxides of boron.[5,6] Therefore, the observation of short Al–O bonds in these systems is not in and of itself surprising.

In contrast, the extremely large Al–O–C angles are not an expected feature. The simple 3-coordinate alkoxides of boron do not exhibit the unusually large B–O–C angles that we have observed in the corresponding aluminum complexes. Obtuse M–O–C angles are common among transition-metal complexes where they are attributed to interaction of both oxygen lone pairs with empty d-orbitals on the metal center. While the participation of the 3d-orbitals for aluminum could conceivably be invoked, their energy relative to the valence molecular orbitals on the aryloxide ligands is such that it is most unlikely they could be the source of such significant structural change. The 3-coordinate oxides have access to only a single vacant aluminum p, and even this orbital is formally occupied in the 4-coordinate compounds by the lone pair of the Lewis base. Since the oxides considered here are bulky, steric effects could provide a reasonable explanation for the enlarged angles, especially in the case of the 4-coordinate complexes.

Our work indicates the source of the distortions in *both* the 3- and the 4-coordinate structures is electronic—not steric. We report here an ab initio molecular orbital study of the bonding between aluminum and oxygen in simple aluminum alkoxides.

Methods

Ab initio all electron molecular orbital (MO) calculations were performed using the GAUSSIAN 82[7] and GAUSSIAN 86[8] suite of programs. Optimized structures were determined at the Hartree–Fock level with the 3-21G(*) basis set.[9] We have previously found the HF/3-21G(*) model to give good descriptions of the structures of organoaluminum compounds,[10] in comparison to both available experimental data and larger basis sets, such as 6-31G*.[11] Our earlier work also indicated that including electron correlation in the model using MP2/6-31G* did not significantly alter the predicted geometries of 3-coordinate aluminum compounds.

Since the Al–O bond in the complexes under consideration is potentially quite ionic, we determined optimum structures for AlH_2OH and AlH_2OCH_3 at the HF/6-31+G*[12] level. In both cases, the Al–O bond length is found to be approximately 0.04 Å longer than that from 3-21G(*). The bond angles are smaller than those garnered from 3-21G(*) by 17 and 36°, respectively. Since we are seeking in this work not the prediction of structure, but rather a qualitative explanation for observed structural features, we do not feel the application of the larger basis set is warranted.

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Table I. HF/3-21G(*) Structural Parameters for Aluminum Alkoxides AlH_2OR and $AlH_2OR\cdots PH_3$ (R = H, CH_3)

molecule	pt gp	parameter[a]	HF/3-21G(*)
AlH_2OH[b]	C_s	r(Al–O)	1.665
		∠(HO–Al)	144.5
		r(Al–H_c)	1.589
		r(Al–H_{tr})	1.581
		r(OH)	0.953
		∠(H_c–Al–O)	120.4
		∠(H_{tr}–Al–O)	117.3
AlH_2OCH_3[b,c]	C_s	r(Al–O)	1.649
		∠(C–O–Al)	176.2
		r(Al–H_c)	1.587
		r(Al–H_{tr})	1.586
		r(O–C)	1.408
		r(C–H_{ip})	1.084
		r(C–H_{op})	1.084
		∠(H_c–Al–O)	119.5
		∠(H_{tr}–Al–O)	119.3
		∠(H_{ip}–C–O)	110.9
		∠(H_{op}–C–H_{op})	108.1
$AlH_2OH\cdots PH_3$[d]	C_1	r(Al–O)	1.690
		∠(H–O–Al)	136.5
		r(Al–H)	1.599
		r(O–H)	0.955
		r(P–H_{tr})	1.393
		r(P–H_g)	1.394
		r(Al–P)	2.659
		∠(H–Al–H)	120.0
		∠(H–P–H)	98.9
		∠(P–Al–O)	103.2
$AlH_2OCH_3\cdots PH_3$[c,d]	C_1	r(Al–O)	1.665
		∠(C–O–Al)	175.5
		r(Al–H)	1.599
		r(O–C)	1.403
		r(C–H_{ip})	1.086
		r(C–H_{op})	1.085
		r(P–H_g)	1.394
		r(P–H_{tr})	1.393
		r(Al–P)	2.679
		∠(H–Al–H)	118.6
		∠(H_{ip}–C–O)	110.9
		∠(H_{op}–C–H_{op})	108.0
		∠(H–P–H)	98.9
		∠(P–Al–O)	103.3

[a] Parameters in angstroms and degrees. [b] Subscripts c and tr refer to the cis and trans orientation of the Al–H bond to the OH bond about the Al–O bond, respectively. [c] Subscripts ip and op refer to the in-plane and out-of-plane orientations of the C–H bond to the Al–H bonds about the Al–O bond, respectively. [d] Subscripts tr and g refer, respectively, to the trans and gauche orientation of the P–H bonds relative to the Al–O bond about the Al–P bond.

In accord with the work of others,[13] we have found previously[10] that donor–acceptor complexes, such as the 4-coordinate complexes considered here, were not treated as well as their component monomers using Hartree–Fock models. Neither large basis sets nor those that included diffuse functions resulted in noticeable improvement over the structural descriptions from small split-valence basis sets such as 3-21G(*). However, in all cases, the only significant differences between the Hartree–Fock structures and those from MP2, or experiment, were in the lengths of the donor–acceptor bonds. Both bond lengths and angles for the remaining parameters of each complex were generally close to experimental values.

Atomic charges were determined by fitting point charges centered on the atoms to the molecular electrostatic potential function. A modified version of CHELP[14] was used. A total of between 500 and 550 points was used for each fit, chosen to be outside the van der Waals envelope of each molecule.[15] The average root mean square (rms) deviation of the electrostatic potential from the monopole fit was less than 1 kcal/mol. Increasing the number of points led to a reduction in the rms deviation without significantly affecting the charges.

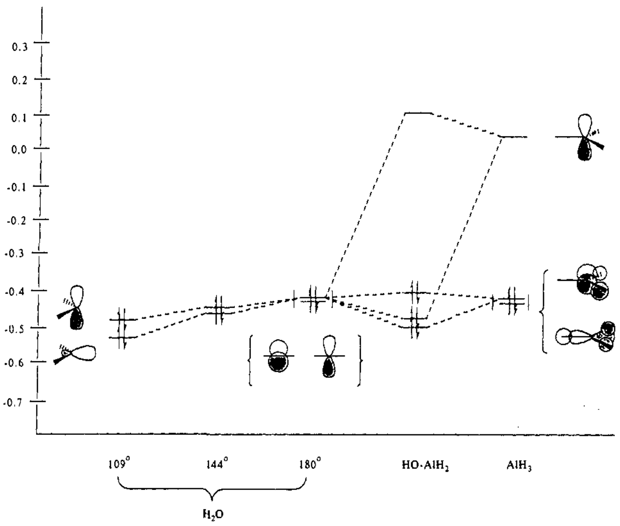


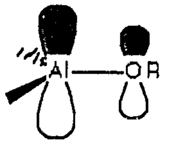
Figure 1. MO interaction diagram for AlO bonding in $HOAlH_2$. Orbital energies are in atomic units and drawn from HF/3-21G(*) calculations. Lone-pair energies are shown for water at H–O–H angles of 109, 144 (the optimal Al–O–H angle in $HOAlH_2$ at HF/3-21G(*)), and 180°.

In order to explore the intrinsic nature of the Al–O interaction and to reduce the time required for calculations, we chose to model the systems of interest as $H_2Al(OR)\cdots PH_3$ (R = H, CH_3). The free H_2AlOR compounds were also examined in order to determine the effect of the Lewis base on the Al–O bond. The geometries of the molecules examined in this work are collected in the table. In general, they appear to be not unreasonable in comparison with available experimental data and previous theoretical work.[8] Structures were confirmed as corresponding to minima on the potential energy surface by normal-mode analyses. No restrictions were placed on the Al–O–R angles. Imposed symmetry constraints are as noted in Table I.

Results and Discussion

Bonding in the 3-Coordinate Complexes. To ascertain whether the Lewis base played a significant role in this deformation, optimal geometries of free AlH_2OH and AlH_2OCH_3 were determined. Both structures exhibit the expected short Al–O bonds, 1.665 and 1.649 Å, respectively. The large Al–O–C angles (144.5 and 176.2°) observed experimentally in the 3-coordinate aryloxides are also reproduced in these systems. This strongly suggests that steric factors alone are not responsible for the angular distortions. It should be further noted that smaller angles are observed in the sterically similar aryloxides $Me_2ClSiBHT$ and Me_3SiBHT, 140.0 and 139.4°, respectively.[16] (The Si–O–C distortion in these complexes has been attributed to electron donation to the phenyl ring from the oxygen and not to a π-type interaction with silicon.)

The short Al–O distances in the 3-coordinate complexes are consistent with the expected π-bonding interaction between the Al empty p and an oxygen lone pair, i.e.



Note that while this explains the anomalous Al–O distances, it does not at first glance account for the unusually large angles. Nor does it appear to apply to the 4-coordinate complexes, since

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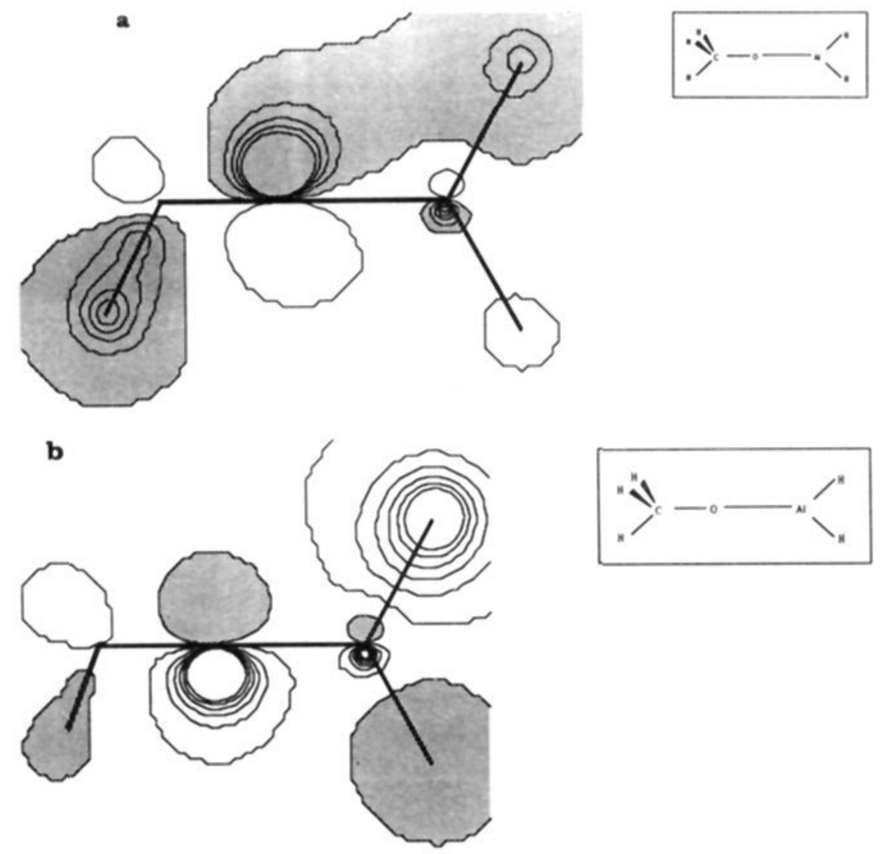
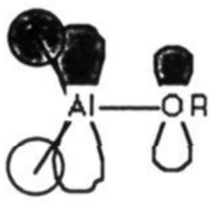


Figure 2. Cross section of electron density taken in the COAl plane for the MO corresponding to the (a) bonding and (b) antibonding combination of the oxygen in-plane lone pair and the π fragment orbital on AlH_2 in CH_3OAlH_2. light areas are regions of positive phase, and shaded regions, of negative phase.

these do not have an empty p-orbital.

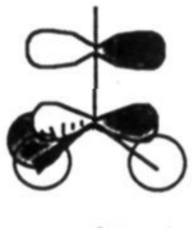
In order to explore the interaction between aluminum and oxygen in simple aluminum alkoxides, we first constructed semiquantitative MO diagrams for HO + AlX_2 (based on the energy levels for H_2O and AlH_3 at the same level) at a variety of H–O–Al angles. In doing so, (Figure 1), we noted that straightening of the H–O–Al angles raises the energy of the out-of-plane oxygen lone pair (hereafter designated O (1p,oop)). This increases the interaction between the empty aluminum p and O(1p,oop), as the energy of the bonding combination of Al(p) and O(1p,oop) attests. This MO is 0.02 au more stable when the Al–O–H angle is linear than when it is at its optimal value of 144°. This is the source of the Al–O bond shortening. As the Al–O–R angle straightens, however, a 4e$^-$ *destabilizing* interaction



between the AlH_2 π and the in-plane oxygen lone pair (O(1p,ip)) becomes symmetry allowed. This interaction is also at a maximum in the linear configuration. The final angle is a result of the balance between maximizing the stabilization of the O(1p,oop) and minimizing the destabilization of O(1p,ip). The occupied π-symmetry aluminum–oxygen MOs are shown in Figure 2.

We have previously suggested[2] that the observed short Al–O distance *and* the large Al–O–C angles in 4-coordiate aluminum aryloxides could be accounted for by the donation from the O lone pairs into π^*-symmetry orbitals on the AlX_2Y fragment, i.e.

and



We see no evidence for interaction between O(1p,ip) and the π^* on AlH_2, but this is not unexpected, since our calculations show the π^* to lie between 0.15 and 0.20 au *above* the empty p.

The substitution of methyl for hydrogen results in a nearly linear arrangement of aluminum, oxygen, and carbon. This ultimately can be traced to the π-donating capabilities of the CH_3 group. As the MO diagram sketched in Figure 3 indicates, in the linear configuration the CH_2 π splits the O(1p,ip). The resulting bonding combination is roughly 0.15 au above the AlH_2 π. In the hydroxide system, the analogous O(1p,ip) orbital is virtually equal in energy to the AlH_2 π. Thus, the energetic importance of the 4e– destabilizing interaction is significantly reduced in the methoxide compound. The splitting between the bonding and antibonding combinations is 0.05 au in methoxide, as compared to 0.10 au in hydroxide. A similar trend can be observed in $ROCH_2^+$, where the C–O–R angle is larger for R = CH_3 than R = H by 10°.[17]

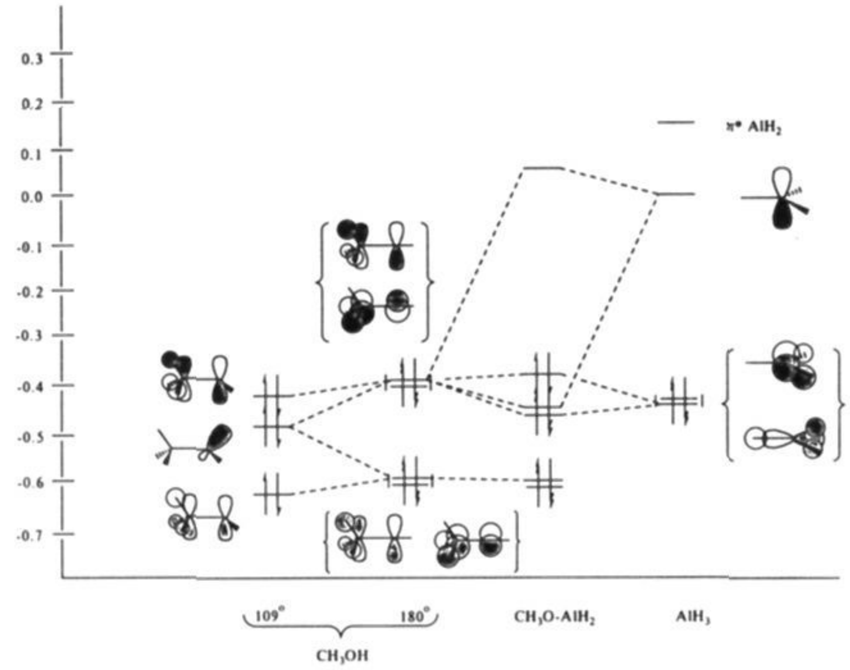


Figure 3. MO interaction diagram for AlO bonding in CH_3OAlH_2. Orbital energies are in atomic units and drawn from HF/3-21G(*) calculations. Lone-pair energies are shown for methanol at H–O–C angles of 109 and 180°.

If the opening of the Al–O–C angle in aluminum oxides is a function of the π-donating capabilities of the R group of which the α-C is a part, then using an electron-withdrawing group should result in a more acute angle. We therefore synthesized the perfluorinated phenoxide complex. X-ray crystallography revealed an Al–O–C angle of 128°, more than 20° smaller than the average angle in the BHT complexes.[18]

Bonding in the 4-Coordinate Complexes. Optimization of $H_2Al(OR)\cdots PH_3$ revealed a slightly longer Al–O distance than in the corresponding 3-coordinate complexes. In the hydroxide, the Al–O bond length is 0.024 Å longer and in the methoxide, 0.016 Å longer. This is in accord with experimental results where the average Al–O distance in the 3-coordinate $AlMe(BHT)_2$ is 1.686 Å[4] compared to 1.719 Å in a series of 4-coordinate compounds.[3]

In neither AlH_2OH nor AlH_2OCH_3 do we observe any significant change in the Al–O–R bond angles relative to their 3-coordinate counterparts. Again, experimental work is in agreement; the observed Al–O–R angles in the 3-coordinate $AlMe(BHT)_2$ are virtually unaffected by the complexation of pyridine.[3]

The addition of a Lewis base to either the hydroxide or methoxide compound should effectively thwart the interaction of the Al(p) with the O(1p,oop). What then is the source of the angular distortions in the 4-coordinate complexes?

The σ^* aluminum–Lewis base orbital is energetically accessible, though it lies some 0.05 au above the empty aluminum p, as Figure 4 shows. Since the addition of a Lewis base does not result in significant pyramidalization of the AlL_2OR fragment (in both the hydroxide and methoxide complexes, the Al is shifted by less than 0.2 Å out of the HHO plane; see Figure 5), the σ^* AlP-orbital

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[17] Carnegie-Mellon Quantum Chemistry Archive, c. 1983, Carnegie-Mellon University. Francl, M. M. Unpublished work.

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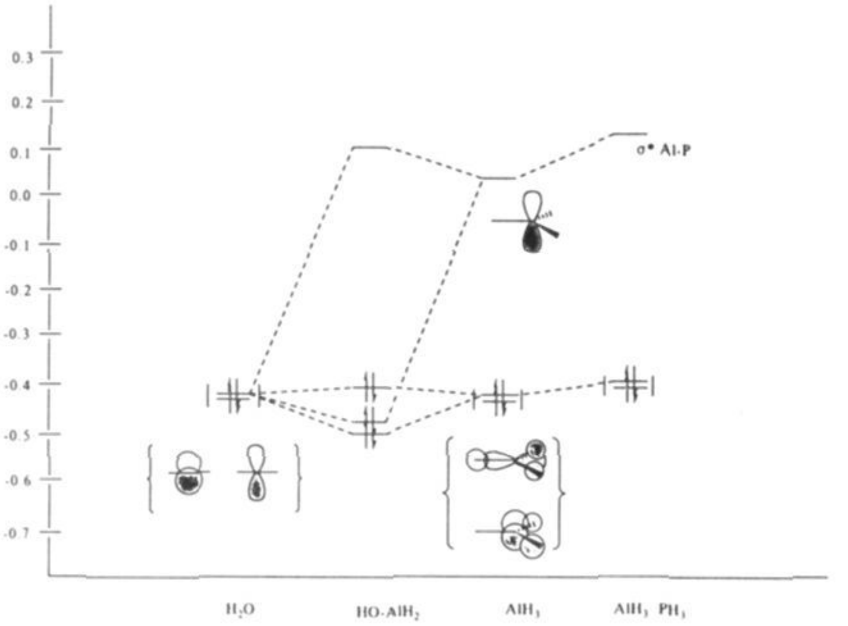


Figure 4. MO interaction diagram for AlO bonding in $HOAlH_2$, energy of the σ^* AlP orbital and the π AlH_2 orbital shown for comparison. Orbital energies are in atomic units and drawn from HF/3-21G(*) calculations.

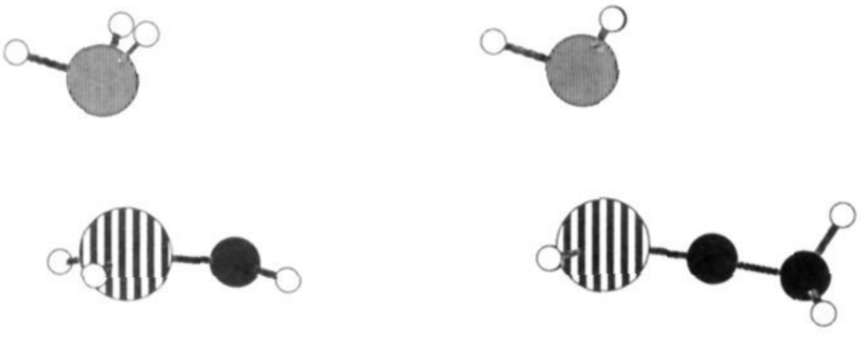
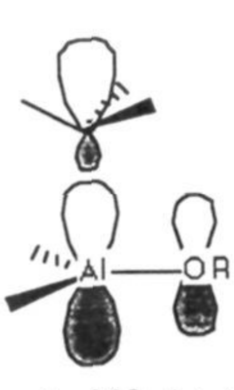


Figure 5. HF/3-21G(*)-optimized structures of AlH_2OH and AlH_2OCH_3 complexes with PH_3.

is also geometrically positioned for overlap with the oxygen lone pairs, i.e.



As can been seen from the MO plots in Figure 6, the resulting interaction mimics the stabilizing interaction in the 3-coordinate complexes. Donation from the oxygen will not be as facile as in the 3-coordinate systems, due to competition from the Lewis base. Thus, one would expect a longer Al–O bond than in the corresponding free molecule and a tighter Al–O–R angle. In the H_2AlOH complex with phosphine the Al–O bond is longer, as noted above, and the Al–O–H angle is found to be slightly smaller, 137° compared to 144°. The tightening of the Al–O–C angle is less pronounced in the 4-coordinate methoxide complex with phosphine, which closes relative to the free H_2AlOCH_3 by less than 1°. The aluminum–oxygen bond distance in $H_2AlOCH_3\cdots PH_3$ is longer by 0.016 Å with respect to the corresponding 3-coordinate molecule. One would also expect the Al–P linkage to be lengthened relative to the simple Lewis acid–base complex due to donation into an antibonding orbital. We find this to be the case; the Al–P bond is approximately 0.1 Å longer in the alkoxide complexes than in $H_3Al\cdots PH_3$.

Charge Analysis. The charges on the oxygen in AlH_2OH, AlH_2OCH_3, $AlH_2OH\cdots PH_3$, and $AlH_2OCH_3\cdots PH_3$ at the HF/3-21G() level are shown in Table II, along with the corresponding AlO bond lengths. For comparison, the charge on oxygen in methanol at the same level is −0.705.[14] The values found for the charges on oxygen in AlH_2OH and $AlH_2OCH_3\cdots PH_3$ are comparable to that in methanol, suggesting that the bonding is polar covalent, rather than ionic. The low charge (−0.127) found on the oxygen in AlH_2OCH_3 is also indicative of a covalent linkage. Note also that the negative charge on oxygen in these aluminum complexes increases with increasing bond length. This is the reverse of what would be expected for strongly ionic compounds, where increasing charge should lead to tighter bonds and shorter bond lengths, and further supports our contention that the geometrical distortions in aluminum alkoxides are the result of covalent interactions.

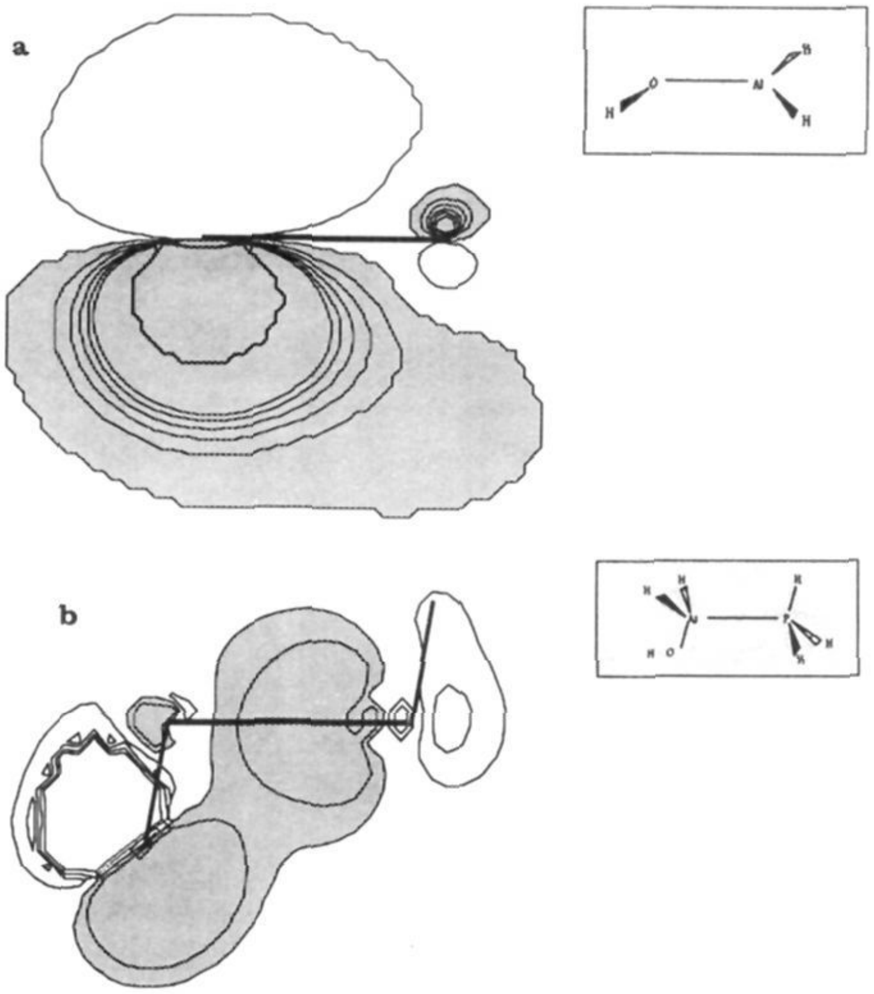


Figure 6. Cross section of electron density taken in the plane perpendicular to the HOAl plane for the MO corresponding to the bonding combination of the oxygen out-of-plane lone pair and the (a) empty p on aluminum in $HOAlH_2$ and (b) Al–P σ^* in $HOAlH_2\cdots PH_3$. Light areas are regions of positive phase, and shaded regions, of negative phase.

Table II. HF/3-21G(*) Bond Lengths in 3- and 4-Coordinate Aluminum Alkoxides Compared to Net Charges on Oxygen

molecule	r(Al–O)[a]	q(O)[b]
AlH_2OCH_3	1.649	−0.127
AlH_2OH	1.665	−0.828
$AlH_2OCH_3\cdots PH_3$	1.665	−0.854
$AlH_2OH\cdots PH_3$	1.690	−1.2275

[a] Bond lengths in angstroms. [b] Charges in fractions of an electron.

Conclusion

We find that π-symmetry interactions between the oxygen lone pairs and the aluminum accounts for the observed short Al–O distance in *both* 3-coordinate and 4-coordinate aluminum oxides. The unusually obtuse Al–O–R angles are also a result of these π-interactions, since increasing this angle makes the oxygen lone pairs energetically more accessible. A vacant p-orbital is the acceptor in the 3-coordinate complexes, while the Lewis acid–base *σ-orbital* serves the same purpose in the 4-coordinate complexes. In both cases, the analysis is complicated by an additional 4e$^-$ π-type interaction between the in-plane oxygen lone pair and the π AlL_2 fragment, which increases with the increasing Al–O–R angle. The degree to which this interaction is important is quite sensitive to the energies of the oxygen lone pairs; thus, substituent effects are expected to play a significant role in determining the Al–O–R angles in aluminum alkoxides.

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Supplementary Material Available: Listing of full Cartesian coordinates and total energies for all optimized structures included in this paper (1 page). Ordering information is given on any current masthead page.

Vibrational Circular Dichroism in Methylthiirane: Ab Initio Localized Molecular Orbital Predictions and Experimental Measurements

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Abstract: Vibrational circular dichroism (VCD) spectra for both enantiomers of methylthiirane were measured in CCl_4 and CS_2 solutions, and also in the vapor phase. The first ab initio localized molecular orbital (LMO) predictions of vibrational circular dichroism were carried out. The LMO-VCD predictions were found to be in satisfactory agreement with the experimental observations.

1. Introduction

Theoretical models[1,2] for understanding the vibrational circular dichroism (VCD) phenomenon have played a major role in the development of VCD spectroscopy. After the first measurements of VCD by Holzwarth and co-workers[3] and by Nafie, Keiderling, and Stephens[4] several groups[5] have contributed to the theoretical and experimental details. VCD spectroscopy has now come to a stage where excellent quality VCD spectra can be recorded and exact theoretical formulations are available. The implementation of these theoretical formulations, however is plagued by practical problems as described below.

VCD intensity for a given vibrational transition is determined by the product of electric and magnetic dipole transition moments. While the evaluation of electric dipole transition moments, which also determine the vibrational absorption intensities, is very well-known, special care is required in formulating the magnetic dipole transition moment, because the electronic contribution to this transition moment vanishes if one confines the formulation to the uncorrected Born-oppenheimer (BO) wave function (vide infra). Currently there are three distinct approaches to the quantum mechanical evaluation of magnetic dipole transition moments. The first approach referred to as localized molecular orbital (LMO) formulation was due to Walnut and Nafie.[6] In this approach they corrected the BO wave function to incorporate the correlation between nuclear and electronic velocities, which is necessary to retrieve the vanishing electronic contribution to the magnetic dipole transition moments. This initially leads to an expression that involves the summation over all excited electronic states. This sum, however, was reduced to a product of vibronic gauge function and ground electronic wave function. This vibronic gauge function was specified by a differential equation and solved for a set of elliptical and Gaussian orbitals that depend on the nuclear displacements. The rocking motion of these elliptical orbitals can contribute to the magnetic dipole transition moment, and this contribution is difficult to evaluate in general. Nevertheless, it was argued[6] that this contribution represents only 15% (approximately) of the total magnetic dipole transition moment and therefore can be ignored. If the orbitals are spherical, the rocking contributions to the magnetic dipole transition moment are identically zero. In the absence of spherical orbitals, one could localize the molecular orbitals to minimize this rocking contribution.

An alternate, but less rigorous, approach to LMO-VCD formulation was also advanced by Nafie and Walnut,[7] along with the rigorous approach of Walnut and Nafie. A more general account of LMO-VCD approach, along with calculational results, was presented by Nafie and Polavarapu.[8] The calculations reported to date[8,9] employed CNDO wave functions[10] whose quality is not reliable enough to seriously judge the reliability, or otherwise, of LMO-VCD predictions.

An exact quantum mechanical approach, which we refer to as the magnetic field perturbative (MFP) method, for the magnetic dipole transition moment is now well-documented.[11-15] In this MFP approach also one starts with a corrected BO wave function which leads to an expression that involves the summation over excited electronic states. In contrast to the approach of Walnut and Nafie, it was shown that this sum-over excited states expression for magnetic dipole transition moment can be replaced by the overlap of nuclear displacement derivative with the magnetic field derivative of the same ground electronic state wave function.

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