

# Comparison of $\pi$ -Bond Strengths in M–E (M = B, Al, Ga; E = O, N, S) Compounds. Ab Initio Calculation of Rotational Barriers

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Results of ab initio calculations of the electronic structure of compounds of the type  $R_2MER'_x$  and  $R_2MEMR'_2$  with R = H, Me, M = Al, Ga, and E = O, N, S are reported at the Hartree–Fock level with split-valence, polarization basis sets for all atoms except hydrogen where a split-valence basis set is used. Full optimizations for the equilibrium geometry and partial optimization at constrained rotational transition states have been performed to evaluate the barriers to rotation as a measure of the  $\pi$  interactions in these compounds. We conclude that, although important for determining the final conformational equilibrium geometries,  $\pi$  interactions are weak in these compounds as the rotational barriers are smaller than that for ethylene by 1 or 2 orders of magnitude.

## Introduction

Multiple bonding involving the heavier main group elements has been one of the major research themes in main group chemistry over the last 2 decades. Most of the studies have concerned elements from the main groups IV<sup>1</sup> and V.<sup>2</sup> In contrast, investigation of multiple bonding of the neighboring group III elements (i.e. Al, Ga, In, or Tl) has received little attention until recently.<sup>3</sup> These elements differ from the later groups in that their most common valence state (i.e. 3) affords a coordinatively and electronically unsaturated metal center which normally results in a strong association tendency among their compounds.<sup>4</sup> If, however, the metal is sterically encumbered with large organic groups, unassociated compounds may be obtained in which the remaining p-orbital at the metal is available for  $\pi$ -bonding. Thus, if such a metal center is directly bonded to groups which contain one or more lone pairs, side-on  $\pi$ -overlap between a lone pair and the metal p-orbital becomes, in principle at least, possible. Simple examples of such compounds are  $R_2MER'_2$  (R and R' = alkyl or aryl, M = Al–Tl, E = N–Bi) and  $R_2MER'$  (R and R' = alkyl or aryl, M = Al–Tl, E = O–Te) and related species. Even though such compounds appear straightforward, it is surprising to note that almost all the well-characterized examples of unassociated species with M–E bonds have been published only within the past decade.<sup>3</sup> In addition, sufficient structural data are now available to show that the M–E bonds in such compounds are invariably shorter than the sum of the covalent radii of M and E, which suggests the existence of a  $\pi$ -bonding component. Observation of the short M–E bonds has given rise to controversy since several explanations for the shortening are possible. For example some authors take the view that the, often

dramatic, contraction (up to 0.3 Å) in the bond length is evidence for the existence of significant  $\pi$ -bonding and cite calculations that favor this viewpoint.<sup>5,6</sup> Others contend that the shortening in such bonds is mainly a result of their strong ionic character (owing to the electropositive nature of the metals) and that  $\pi$ -bonding plays a relatively minor role in the bond strength. Some computational results, mainly on M–E ring systems tend to support this viewpoint.<sup>7</sup> In an attempt to resolve these questions, calculations have been carried out on several M–E systems, and in this paper the results of these calculations, together with the rapidly increasing amounts of structural and spectroscopic data currently available, are considered in order to shed further light on the extent of  $\pi$ -bonding in various M–E compounds.

## Method

We have undertaken a series of ab initio electronic structure calculations further to explore the importance of  $\pi$ -interactions in compounds of formula  $R_2MER'_x$  and  $R_2MEMR'_2$  (R = H, CH<sub>3</sub>; M = Al, Ga; E = O, N, S). We adopt the size of the rotational barrier in these compounds as a simple and straightforward criterion for the extent of  $\pi$  interactions, but examine geometrical parameters as well. The compounds were chosen because the recent experimental reports<sup>8–17</sup> of compounds of this type readily allow comparisons of theoretical and experimental data. We have performed geometry optimizations for the minimum energy and for the assumed rotational barrier transition state structures at a variety of levels of sophistication of basis set and

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**Table 1.** Total and Relative Energies for H<sub>2</sub>AlOH and H<sub>2</sub>AlNH<sub>2</sub> with Varying Levels of ab Initio Theory and Basis Sets<sup>a</sup>

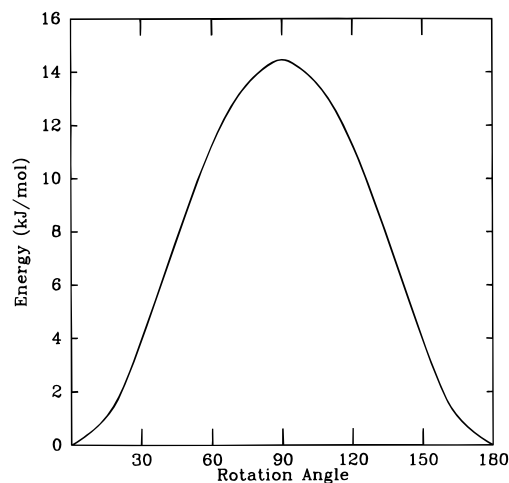
method	H <sub>2</sub> AlOH		H <sub>2</sub> AlNH <sub>2</sub>	
	tot. energy	barrier	tot. energy	barrier
RHF/STO-3G//RHF/STO-3G	-314.6166	28.02	-295.0986	56.36
RHF/6-31G//RHF/6-31G	-318.4964	0.0	-298.6576	46.68
RHF/6-31G**//RHF/6-31G*	-318.5421	14.58	-298.6961	46.85
RHF/6-31+G**//RHF/6-31+G**	-318.5580	9.98	-298.7119	45.48
MP2/6-31G**//MP2/6-31G*	-318.7776	18.58	-298.9163	54.90
CISD/6-31G**//MP2/6-31G*	-318.7776	17.50	-298.9229	53.07
CISD-sz crct//MP2/6-31G*	-318.7946	18.67	-298.9407	55.29

<sup>a</sup> The reported total energy is in hartrees for the calculated equilibrium geometry. The listed barriers are the energy difference between the partially optimized rotational transition state (constrained to stay at the rotational conformer of the transition state) and the fully optimized equilibrium geometry in kJ/mol.

treatment of electron correlation. We examine the trends across the series of compounds as an indicator of the extent of  $\pi$ -interactions in this general class of compounds. We have used the Gaussian series of programs<sup>18</sup> for most of the calculations. For molecules containing gallium, we have used the GAMESS programs.<sup>19</sup> To direct our efforts, we have used the compounds H<sub>2</sub>AlOH and H<sub>2</sub>AlNH<sub>2</sub> to evaluate basis set and methodology. The generally reliable and consistent restricted Hartree–Fock method using a split valence polarization basis set was then applied uniformly to the compounds H<sub>2</sub>AlOH, H<sub>2</sub>AlNH<sub>2</sub>, H<sub>2</sub>AlSH, (CH<sub>3</sub>)<sub>2</sub>AlOCH<sub>3</sub>, H<sub>2</sub>AlOAlH<sub>2</sub>, H<sub>2</sub>AlSAIH<sub>2</sub>, H<sub>2</sub>BOBH<sub>2</sub>, H<sub>2</sub>GaOH, H<sub>2</sub>GaSH, H<sub>2</sub>GaNh<sub>2</sub>, and H<sub>2</sub>GaOGaH<sub>2</sub>. We also did some preliminary calculations using a pseudopotential for gallium which proved to be somewhat problematical. For hydrogen, carbon, nitrogen, oxygen, aluminum, and sulfur we used the 6-31G\* basis set. For gallium we used the Binning and Curtiss<sup>20</sup> split valence basis augmented with a set of d-type polarization functions (exponent 0.141).

## Results and Discussion

Table 1 displays the total energies of the lowest energy molecular geometry and the rotational barrier for the molecules H<sub>2</sub>AlOH and H<sub>2</sub>AlNH<sub>2</sub>. We used these two molecules for careful exploration of the changes in calculated barriers with improvement of the basis set at the Hartree–Fock level of treatment beyond a split-valence polarization set and to increasing sophistication in the treatment of electron correlation. We wanted to pursue a study that gives a uniform quality of treatment to a large number of chemically different model compounds involving potential dative  $\pi$ -bonds and hoped that a Hartree–Fock treatment with a split-valence polarization basis set would give sufficiently reliable results that a qualitative conclusion about the order of magnitude difference in  $\pi$ -bond strength in these compounds could be reached. Of course in the absence of performing the more sophisticated calculations on all the compounds, we can not know the changes that may



**Figure 1.** Rotational barrier in H<sub>2</sub>AlOH calculated at the Hartree–Fock level with the 6-31G\* basis set. Calculations were performed at 15° increments of the dihedral angle, optimizing all other geometric parameters. The calculated relative energies were then interpolated by cubic splines to produce the continuous curve shown. The 2-fold barrier maximum occurs at 90°.

**Table 2.** Total and Relative Energies at the Hartree–Fock Level of Treatment with Split-Valence Polarization Basis Sets for the Compounds Listed<sup>a</sup>

compound	tot. energy	barrier
H <sub>2</sub> AlOH	-318.542 097	14.58
H <sub>2</sub> AlSH	-641.190 135	30.70
H <sub>2</sub> AlNH <sub>2</sub>	-298.696 090	46.85
(CH <sub>3</sub> ) <sub>2</sub> AlOCH <sub>3</sub>	-435.659 425	7.21
H <sub>2</sub> AlOAlH <sub>2</sub>	-561.083 957	3.94
H <sub>2</sub> AlSAIH <sub>2</sub>	-883.695 954	5.92
H <sub>2</sub> BOBH <sub>2</sub>	-126.620 005	30.45
H <sub>2</sub> GaOH	-1997.858 645	18.83
H <sub>2</sub> GaSH	-2320.497 753	35.33
H <sub>2</sub> GaNh <sub>2</sub>	-1978.013 278	53.76
H <sub>2</sub> GaOGaH <sub>2</sub>	-3919.697 812	3.89

<sup>a</sup> The total energy is given for the calculated equilibrium geometry in hartrees. The listed barrier values are the energy difference between the partially optimized rotational transition state (constrained to stay at the rotational conformer of the transition state) and the fully optimized equilibrium geometry in kJ/mol.

occur, but examination of H<sub>2</sub>AlOH and H<sub>2</sub>AlNH<sub>2</sub> in detail can give us some guide to what may be expected for the full set of compounds. The consistent level reported for the full set of compounds below can provide a tentative answer with significant chemical variety, albeit moderated by the range of differences in values found with increasing electronic structure sophistication for H<sub>2</sub>AlOH and H<sub>2</sub>AlNH<sub>2</sub>. We find from the data in Table 1 that the low rotational barrier for H<sub>2</sub>AlOH lies in the range of 10–30 kJ/mol, a factor of 3 variation across the different treatments. For H<sub>2</sub>AlNH<sub>2</sub> the range is 45–60 kJ/mol, a factor of 1.5 variation across the different treatments, despite the barrier being among the higher of any of the series of compounds considered. For both molecules the rather narrow range of variation of the calculated barrier upon improvement in the treatment of electron correlation is particularly important. For each molecule one of the highest two occupied molecular orbitals is characterizable largely as a lone-pair p-orbital on the electronegative element, while the LUMO is characterized as essentially an unoccupied p-orbital on aluminum. We shall examine these orbital natures in more detail below; however, one might expect that configurations involving excitation from the E lone pair to the empty Al p-orbital would improve the wave function's ability to depict bond disruption, differentially

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**Table 3.** Geometrical Parameters for the Equilibrium Minimum Energy Conformer and for the Rotational Barrier Conformer (Distances in Å and Angles in deg)

compound	min energy conformer			rotational barrier conformer		
	M–E dist	RME angle	MER' angle	M–E dist	RME angle	MER' angle
H <sub>2</sub> AlOH	1.6968	118.3	123.6	1.6805	119.4	144.1
Me <sub>2</sub> AlOMe	1.6964	119.0	137.3	1.6698	118.4	177.0
		117.0			119.3	
H <sub>2</sub> AlSH	2.1957	117.7	97.4	2.2286	119.5	95.9
H <sub>2</sub> AlNH <sub>2</sub>	1.7714	118.4	124.9	1.7944	121.3	125.4
H <sub>2</sub> AlOAlH <sub>2</sub>	1.6858	119.1		1.6866	119.3	
H <sub>2</sub> AlSAlH <sub>2</sub>	2.1517	118.1		2.1616	118.5	
H <sub>2</sub> GaOH	1.7865	118.4	119.1	1.7908	117.7	127.2
H <sub>2</sub> GaSH	2.2134	118.7	97.8	2.2579	118.6	95.3
H <sub>2</sub> GaNH <sub>2</sub>	1.8238	117.9	124.6	1.8551	120.2	124.8
H <sub>2</sub> GaOGaH <sub>2</sub>	1.7557	118.0		1.7574	118.2	
H <sub>2</sub> BOBH <sub>2</sub>	1.3299	119.1		1.3409	119.6	

lower the energy of the equilibrium geometry, and thereby contribute to an enhancement of  $\pi$ -bonding. Such terms would include the valence bond concept of negative hyperconjugation. We see from the results of the calculations involving electron correlation (MP and CISD) that this is clearly not a major effect in the description of the bonding of these compounds, that the single determinant treatment is already capturing the majority of the weak  $\pi$ -bonding and that there appears to be little extra forthcoming from wavefunction terms involving excitations that would further enhance  $\pi$ -character. The RHF calculation is adequately describing the barrier to rotation, and the numerical values found for the barrier are small. That the rotational barriers are small in these compounds is already evident in the computational literature in the work of Reed and Schleyer<sup>21</sup> and explicitly commented upon by Davy and Jaffrey.<sup>22</sup> Figure 1 displays the entire adiabatic rotational barrier for H<sub>2</sub>AlOH obtained with an RHF/6-31G\* treatment. The HAlOH dihedral angle was frozen at 15° increments from 0 to 90°, and all other geometric parameters were optimized. The barrier shape rises fairly steeply at small angles but does not achieve a high value.

Table 2 presents the systematic results we obtained for the calculated barriers at the Hartree–Fock level with split-valence-polarization basis sets. Optimizations were performed under the constraints of maintaining the dihedral angles R–M–E–R' at values of 0° for the equilibrium geometries and at 90° for the assumed rotational transition states. The total energies reported are for the equilibrium geometry and the barriers are the energy difference between these and the energy of the optimized transition state. The equilibrium geometries for the R<sub>2</sub>MER'<sub>x</sub> species are planar, while those of the H<sub>2</sub>MEMH<sub>2</sub> species have the two H<sub>2</sub>M planes at right angles to each other. Both of these geometries are to be expected if there is a  $\pi$ -interaction between Al and O in these molecules. The calculated barriers can be compared to the experimental value for the rotational barrier in ethylene of 272 kJ/mol as determined from the kinetics of isomerization of 1,2-dideuterioethylene,<sup>23</sup> to the barrier calculated for H<sub>2</sub>BNH<sub>2</sub> by McKee<sup>24</sup> of 134 kJ/mol, and to the barriers in H<sub>2</sub>BNH<sub>2</sub> and H<sub>2</sub>BPH<sub>2</sub> of 159 and 170 kJ/mol calculated by Allen *et al.*<sup>25–27</sup> Our calculated value of 47 kJ/mol for H<sub>2</sub>AlNH<sub>2</sub> is in good agreement with the value of 46 kJ/mol obtained by Davy and Jaffrey<sup>7</sup> with a DZP basis set and with that calculated by Müller of 40.7 kJ mol<sup>-1</sup> at the

MP2(fc)/6-31G\* level for (CH<sub>3</sub>)<sub>2</sub>AlNH<sub>2</sub> obtained in parallel with a matrix-isolation IR study of that compound.<sup>28</sup> The 1 or 2 orders of magnitude difference between the calculated values of the rotational barriers in these compounds and the barrier in ethylene implies that the  $\pi$ -interactions in these compounds are small and that the relatively short M–E bond distances are likely to originate from other aspects of the bonding. It should be noted however that the  $\pi$ -interactions are sufficient to give the expected ground state geometries, including the twisted terminal planes as in the allene structure for the H<sub>2</sub>MEMH<sub>2</sub> compounds.

Table 3 presents the calculated values of the essential geometrical parameters of these molecules in both the minimum energy and rotational barrier transition state conformers. The influence of the  $\pi$ -interactions is evident in the larger M–E distances for the rotational barrier conformers, where the  $\pi$  bond would be ineffectual, but the increases are only a few hundredths of an angstrom. Of particular interest are the aluminum alkoxides which show an exactly opposite effect. This is presumably associated with the larger AlOR' angle in the rotational barrier conformers. Rehybridization of the oxygen atom in the rotational transition state would permit maximization of the  $\pi$ -interaction and result in an enlargement of the AlOR' angle. While it is possible that recapture of the  $\pi$ -interaction in this fashion could account for a low rotational barrier in the oxygen-containing compounds, in view of the low barriers for all the others, it is a simpler explanation to conclude that  $\pi$ -interactions between aluminum or gallium with electronegative elements having available lone pairs is just inherently weak.

Most organometallic (and closely related) derivatives of aluminum have many of the physical properties that are normally associated with covalent compounds. Such compounds are often freely soluble in hydrocarbons (e.g. Al<sub>2</sub>Me<sub>6</sub>, Al{N(SiMe<sub>3</sub>)<sub>2</sub>}<sub>3</sub> or Al{O(i-Pr)}<sub>3</sub>) and can be distilled or sublimed under relatively mild conditions. This behavior effectively disguises the fact that bonding in these compounds often has quite a large polar component. Even in Al–C bonds the EN difference is 0.94 EN units<sup>29</sup> which, according to Pauling,<sup>30</sup> leads to a partial ionic character of 22%. For Al–O bonds the difference is 1.83 EN units which affords *ca.* 65% ionic character. Clearly, the often large polar component in bonding involving aluminum will have a very significant effect on orbital overlap. To place the polar component in the context of other compounds, it may be noted that the EN difference across the Al–O bond is greater than in Li–Br and Al–N has a greater EN difference than Li–I. It was against the background of such data and recent suggestions

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**Table 4.** Comparison of Theoretical and Experimental Values for Structural Parameters and Rotational Barriers

compound	M-E (Å)	barrier (kJ mol <sup>-1</sup> )
<i>t</i> -Bu <sub>2</sub> AlOMes* <sup>a</sup>	1.709 (av)	<30
<i>t</i> -Bu <sub>2</sub> AlOC <sub>6</sub> H <sub>2</sub> -2,6- <i>t</i> -Bu <sub>2</sub> -4-Me <sup>b</sup>	1.710(2)	<30
H <sub>2</sub> AlOH	1.6968	14.58
Me <sub>2</sub> AlOMe	1.6964	7.21
O[Al{CH(SiMe <sub>3</sub> ) <sub>2</sub> } <sub>2</sub> ] <sup>c</sup>	1.6877(4)	
O(AlH <sub>2</sub> ) <sub>2</sub>	1.6858	3.94
<i>t</i> -Bu <sub>2</sub> GaOC <sub>6</sub> H <sub>2</sub> -2,6- <i>t</i> -Bu <sub>2</sub> -4-Me <sup>b</sup>	1.821(3)	<30
<i>t</i> -Bu <sub>2</sub> GaOCPh <sub>3</sub> <sup>a</sup>	1.831(4)	
H <sub>2</sub> GaOH	1.7865	18.83
<i>t</i> -BuAl(SMes*) <sub>2</sub> <sup>d</sup>	2.196(2)	<25
Al(SMes*) <sub>3</sub> <sup>e</sup>	2.185(2)	
H <sub>2</sub> AlSH	2.1957	30.70
S[Al{CH(SiMe <sub>3</sub> ) <sub>2</sub> } <sub>2</sub> ] <sup>f</sup>	2.187(4)	
S(AlH <sub>2</sub> ) <sub>2</sub>	2.1517	5.92
Mes* <sub>2</sub> GaSMed <sup>d</sup>	2.271(2)	42
Ga(SMes*) <sub>3</sub> <sup>e</sup>	2.205(1)	
H <sub>2</sub> GaSH	2.2134	35.33
R <sub>2</sub> AlNR' <sub>2</sub> <sup>g,h</sup>	1.784(3)–1.879(4)	≤40–45
H <sub>2</sub> AlNH <sub>2</sub>	1.7714	46.85
R <sub>2</sub> GaNR' <sub>2</sub> <sup>h-j</sup>	1.832(10)–1.937(3)	40–45
H <sub>2</sub> GaNH <sub>2</sub>	1.8238	53.76

<sup>a</sup> Reference 10. <sup>b</sup> Reference 8. <sup>c</sup> Reference 17. <sup>d</sup> Reference 16. <sup>e</sup> Reference 9. <sup>f</sup> Reference 11. <sup>g</sup> Reference 12. <sup>h</sup> Reference 13. <sup>i</sup> Reference 14. <sup>j</sup> Reference 15.

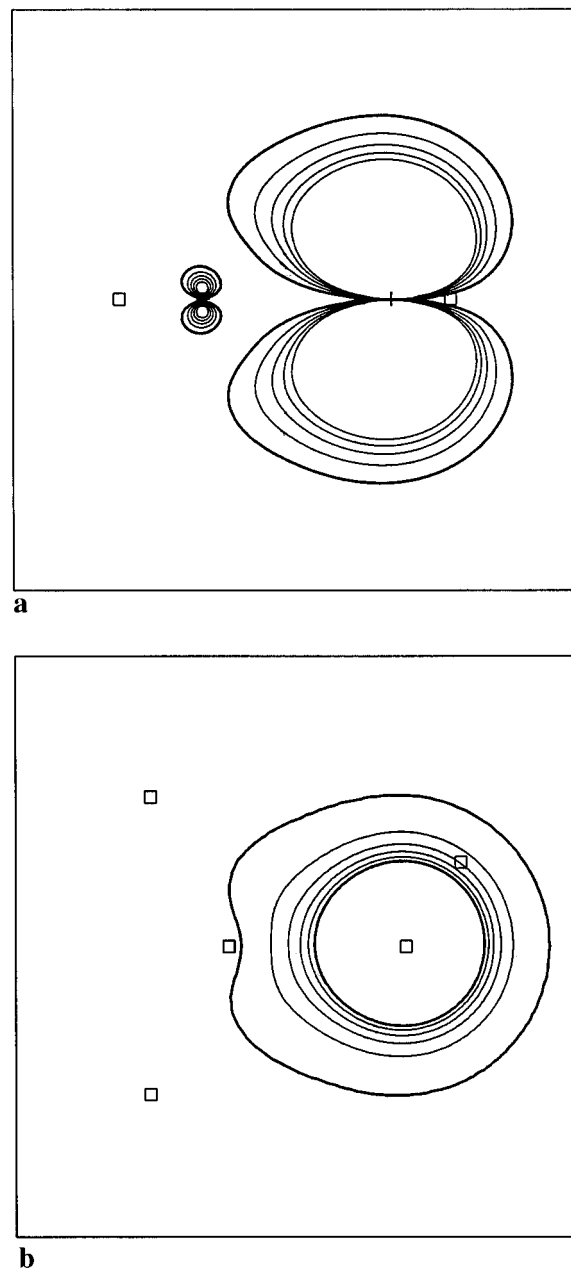
**Table 5.** Results Obtained Using Pseudopotentials for the Core Electrons of Gallium and a Split-Valence Polarization Basis Set for All Elements Except Hydrogen, Which Uses a Split-Valence Basis Set<sup>e</sup>

	H <sub>2</sub> GaOH	H <sub>2</sub> GaSH	H <sub>2</sub> GaNH <sub>2</sub>	H <sub>2</sub> GaOGaH <sub>2</sub>
energy <sup>a</sup>	-78.588503	-401.247963	-58.746940	-81.169470
barrier <sup>b</sup>	20.25	33.11	54.75	3.89
eq. Ga-E <sup>c</sup>	1.7392	2.2147	1.7937	1.7237
eq. HGaE <sup>d</sup>	119.1	118.7	118.5	118.6
eq. HEGa <sup>d</sup>	118.9	97.7	124.5	
ts. Ga-E <sup>c</sup>	1.7414	2.2581	1.8253	1.7258
ts. HGaE <sup>d</sup>	118.8	118.9	120.8	118.8
ts. HEGa <sup>d</sup>	126.2	95.2	124.8	

<sup>a</sup> hartrees. <sup>b</sup> kJ/mol. <sup>c</sup> Å. <sup>d</sup> deg. <sup>e</sup> Both equilibrium (eq.) and rotational transition state (ts.) geometries are presented.

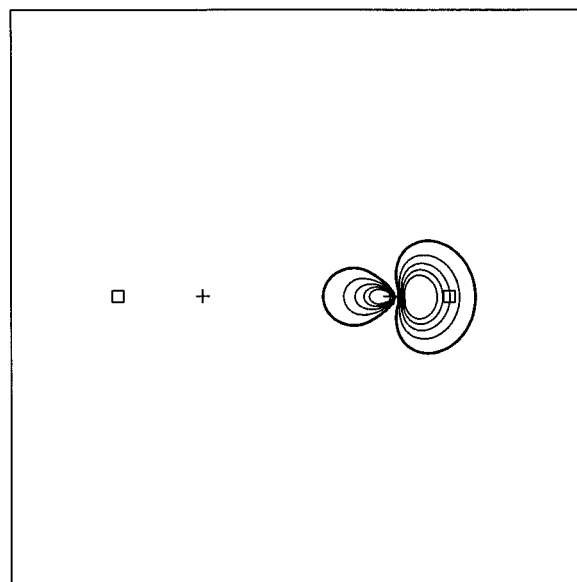
in the literature that short Al–O bonds were evidence for  $\pi$ -bonding that the calculations described were undertaken.

Comparison of the results of the calculations for the hypothetical compounds in this paper to the experimentally obtained data on the substituted analogues is presented in Table 4. It can be seen from Table 4 that, with the exception of the Ga–O compounds, there is very good agreement for the M–E bond lengths. Even for the Ga–O compounds the calculated Ga–O distance differs from that seen experimentally by only 0.04 Å. Generally speaking the experimental data afford M–E bond lengths that are marginally (0.01–0.02 Å) longer than the calculated distances. This elongation is to be expected in view of the very large substituents required to obtain unassociated molecules. Experimentally determined variable-temperature NMR rotational barriers are also in harmony with the computational data even where it was experimentally possible only to obtain estimates of the upper limit of such barriers. We must remark that in comparing the calculated barriers of the model compounds with some of the experimentally determined ones, we are ignoring the influence of substituent effects on the barrier to rotation. Because bulky substituents are necessary to synthesize these compounds, we can expect the calculated barriers of the model compounds to be generally smaller than those obtained experimentally if the substituent steric repulsions make an important contribution to the barriers. Given this

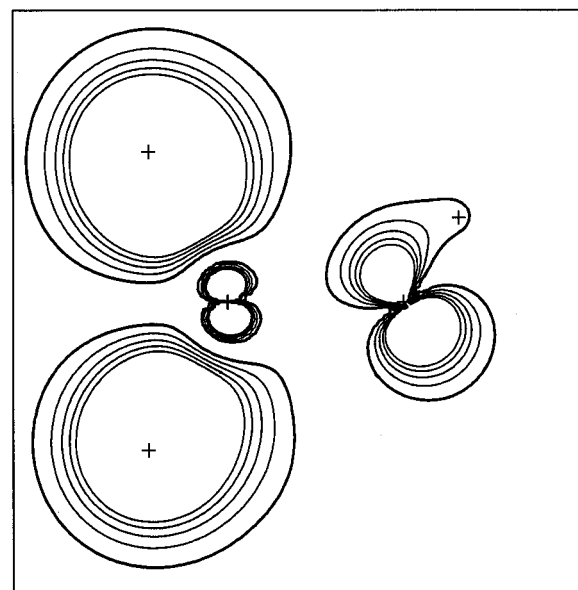


**Figure 2.** Electron probability contour diagram for the second-highest occupied molecular orbital (HOMO-1). (a) Contours are in the plane perpendicular to the molecular plane and containing the Al–O bond. Aluminum is to the left, and oxygen, to the right. Atom positions in the plane are indicated with crosses; the point in the plane where the perpendicular projection of the hydrogen atoms would lie is marked by a square. The outermost contour is at 0.01 electron per cubic angstrom and the increment between contours is 0.01 so that the maximum plotted contour is 0.05. (b) Contours of the second highest occupied molecular orbital of H<sub>2</sub>AlOH in a plane parallel to the molecular plane but elevated 1.0 bohr above it so that the nodal plane is avoided. Molecular orientation is as in part a and nuclear positions are marked in the same way. The outermost contour is at 0.002 electron per cubic angstrom with an increment between contours of 0.01 so that the maximum plotted contour is 0.052. The orbital's characterization as a lone-pair p-orbital on oxygen is clear.

caveat, it is notable that the experimental and theoretical data from the barriers in aluminum and gallium compounds are in excellent agreement. Unfortunately it was not possible to make an experimental distinction between the values obtained for the Al and Ga species for which a slightly higher barrier was predicted for the latter. No barriers were experimentally detected in the case of the Al–O and Ga–O molecules which is consistent with their calculated prediction of very low barriers.



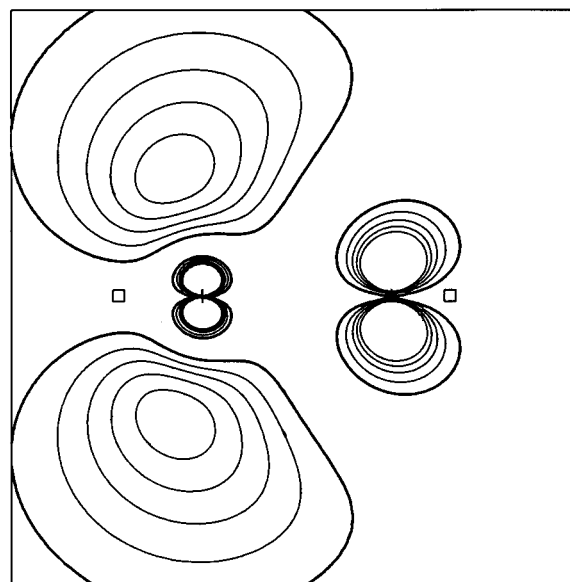
a



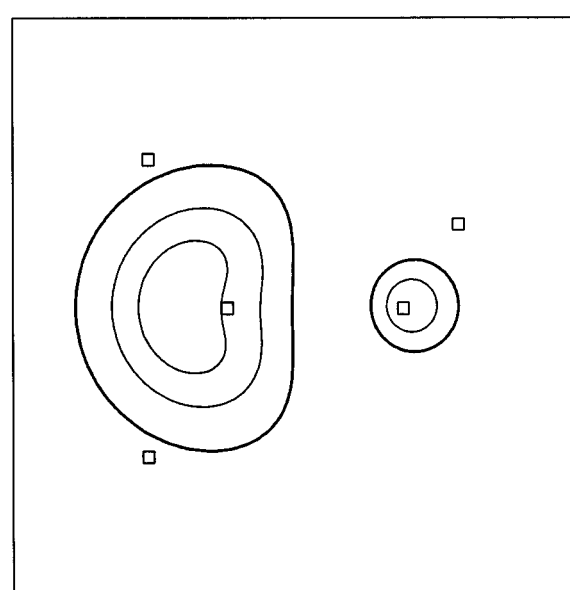
b

**Figure 3.** Electron probability contour diagram for the highest occupied molecular orbital. (a) Contours are plotted in the plane perpendicular to the molecular plane and containing the Al–O bond. Molecular orientation and nuclear position designations are as in Figure 2. The outermost contour is 0.01 electron per cubic angstrom and the increment between contours is 0.01 so that the highest contour plotted is 0.05. (b) Contours are plotted in the molecular plane. All nuclear positions are plotted with crosses. The outermost contour is 0.01 electron per cubic angstrom and the increment between contours is 0.01. The orbital character is not simply identifiable with portions of a Lewis structure but is contributing to the description of a second lone-pair on oxygen, aluminum to hydrogen bonding, and oxygen to hydrogen bonding.

An interesting feature of the Al–O data concerns the calculations on the allene analogue  $\text{H}_2\text{AlOAlH}_2$ . The lowest energy configuration for this molecule does indeed feature an allene-like structure in which the geometry at O is linear and the two Al coordination planes are perpendicular to each other, yet the rotational barrier is predicted to be less than  $4 \text{ kJ mol}^{-1}$ . The Al–O distance ( $1.6858 \text{ \AA}$ ) is practically identical to that reported for  $\text{O}[\text{Al}\{\text{CH}(\text{SiMe}_3)_2\}_2]_2$  which in contrast to  $\text{H}_2\text{AlOAlH}_2$  has parallel Al coordination planes. The computational data clearly imply the absence of appreciable Al–O  $\pi$ -bonding, and the low calculated barrier could easily be overcome by intermolecular



a



b

**Figure 4.** Electron probability contour diagram for the lowest unoccupied molecular orbital. Molecular orientation and nuclear position designations are as in Figure 2. (a) Contours are in the plane perpendicular to the molecular plane and containing the Al–O bond. (b) Contours are in a plane parallel with the molecular plane, but displaced from it by 1.5 bohr. The outermost contour in both is 0.01 electron per cubic angstrom with an increment of 0.01 between contours.

interactions in the substituted crystalline compound. Agreement between the calculated and experimental bond length data from the Al–S and Ga–S species is very good. It is also notable that Al–S and Ga–S rotational barriers are predicted to be significantly higher than the corresponding M–O compounds with a barrier as high as  $35.33 \text{ kJ mol}^{-1}$  being calculated for  $\text{H}_2\text{GaSH}$ . A variable-temperature NMR study of  $(\text{Mes}^*)_2\text{GaSMe}$  indicated a Ga–S rotation barrier of *ca.*  $42 \text{ kJ mol}^{-1}$  suggesting that the Al–S and Ga–S rotational barriers are indeed greater than the corresponding oxygen compounds.

We considered the use of pseudopotentials for the core electrons of gallium and explored the issue of ascertaining the appropriate level of basis set for the other atoms by doing calculations on  $\text{H}_2\text{AlOH}$  using the Hay–Wadt pseudopotentials and basis sets<sup>31</sup> for Al and 3-21G, 6-31G, and 6-31G\* basis sets on oxygen and hydrogen. For the latter we augmented the

Hay–Wadt basis with a set of d-polarization functions (exponent 0.325) on Al. We obtained results of 1.38, 0.22, and 13.98 kJ/mol for the barrier. Only with the polarization augmented split valence set do we have satisfactory agreement with the all electron calculations of the barrier for  $\text{H}_2\text{AlOH}$ . Table 5 presents the essential results that we obtained on the gallium-containing compounds when the Hay–Wadt pseudopotential and split valence basis set augmented with a set of d-type polarization functions (exponent 0.141) was used for the gallium atom and the 6-31G\* basis set was used for the other atoms. The majority of the results are qualitatively the same as for the all-electron calculations; however, the Ga–O distances are anomalously short compared with the all-electron calculations and compared with the experimental compounds of Table 4. Interestingly the rotational barriers calculated with the pseudopotentials mirror the results obtained by the all-electron calculations even for the Ga–O compounds, despite the shortening of the Ga–O distance.

Figures 2–4 display molecular orbital electron probability contour diagrams for the top two occupied orbitals and the lowest unoccupied orbital for the equilibrium geometry calculation of  $\text{H}_2\text{AlOH}$ . In all figures the aluminum atom is on the left and the oxygen atom is on the right. Nuclear positions are marked by squares if the position is a projection into the plane and crosses if the position lies in the plane. The planes in which the contours are depicted are chosen perpendicular to the molecular plane and containing the Al–O bond for each “a” part of Figures 2a–4a. The “b” parts of the figures depict the contours in planes chosen parallel to the molecular plane. The plane of Figure 2b is 1.0 bohr above the molecular plane, since the molecular plane is a nodal plane of this orbital; the plane of Figure 3b is the molecular plane, and the plane of Figure 4b is 1.5 bohr above the molecular plane, again since the molecular plane is a nodal plane for this orbital. The highest occupied

orbital, displayed in parts a and b of Figure 3, is not simply identifiable with the intuitive chemistry of a Lewis structure for the compound. It has elements of the in plane oxygen lone pair, the two Al–H bonds, and the O–H bond. It shows no closed contours encircling both the aluminum and oxygen centers. The orbital just lower in energy than this, however, displayed in parts a and b of Figure 2 is clearly identifiable with the oxygen lone pair in a p-orbital perpendicular to the molecular plane. Likewise the lowest unoccupied orbital, displayed in parts a and b of Figure 4 is identifiable with the unoccupied p-orbital on aluminum. In none of these figures do we see contours enclosing both the aluminum and oxygen atoms or appreciable shaping of the contours in the fashion of  $\pi$ -bond formation. There is some, albeit slight, pinching of the contours of the oxygen lone pair orbital in the direction of the aluminum center in Figure 2, which is evidently the orbital indicating a very weak  $\pi$ -bond.

## Conclusion

Ab initio electronic structure calculations on 11 compounds containing potential dative  $\pi$ -bonds have been performed to explore the strength of the  $\pi$ -bonding in these compounds. Using the rotational barrier as a measure of this interaction, we find the  $\pi$ -bonding to be 1 or 2 orders of magnitude smaller than the classic case of ethylene. For  $\text{H}_2\text{AlOH}$  and  $\text{H}_2\text{AlNH}_2$  the influence of electron correlation on the rotational barriers does not change the order of magnitude of the barrier. Therefore, at least for these two molecules, significant contributions to the  $\pi$ -bond from electron correlation effects such as negative hyperconjugation can be ruled out. Calculated bond lengths are in good agreement with the experimental values for substituted compounds of the same type. Examination of the higher occupied and the lowest unoccupied Hartree–Fock molecular orbitals reinforces the conclusion that there is little  $\pi$ -interaction in these compounds.

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