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Structure of Triamidoaluminum Complexes: A Theoretical ab Initio/IMOMM Study

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The electronic structure of three-coordinated complexes of aluminum $Al(NR_2)_3$ has been studied through theoretical calculations. In the unsubstituted system $Al(NH_2)_3$, ab initio calculations (MP2/6-31G(d,p) level) show that the optimal geometry results from a conrotatory motion of the three amido substituents starting from the fully conjugated planar species. The energy difference between these two structures is found to be small (less than 0.5 kcal/mol). In methylated species $Al(NMe_2)_3$, steric effects become important and the planar geometry is destabilized. The conrotatory geometry corresponds to the absolute minimum and is located 14.2 kcal/mol below the planar structure (MP2/6-31G(d,p) level). Several coupled motions of the amido substituents have been computed and have been found to stabilize the system with respect to the fully conjugated structure. A rough estimate of the steric repulsion is calculated by comparison between the unsubstituted and methylated species. Finally, the real molecules $Al[N(SiMe_3)_2]_3$ and $Al(N^iPr_2)_3$ have been studied through a coupled quantum mechanics/molecular mechanics method. In accordance with the experimental data, it is found that the conrotatory minimum is the absolute minimum in the R = $SiMe_3$ case whereas a less symmetrical minimum is found in the R = ^iPr case. In this last minimum, an amido group is almost deconjugated and the two other groups move in a conrotatory manner. The different behavior of these two systems may originate from the quasi-spherical shape of the $SiMe_3$ group, which leads to unavoidable steric repulsion.

Introduction

Electronic structures of molecules may be dramatically affected by the presence of π-donor substituents when compared to hydrogen or alkyl-substituted systems. A prototypal example of monofaced π-donor is the amido radical NR_2, which is widely used in organic, inorganic, and organometallic chemistry. For instance, tetrakis(dimethylamino)ethylene, $(Me_2N)_2C{=}C(NMe_2)_2$, exhibits a rather surprising structure in which the four amino planes rotate by about 55° with respect to the ethylenic plane.[1] In addition, the rotations of the four amido groups occur in a conrotatory manner. We have shown by theoretical calculations that this surprising geometry results from a balance between electronic and steric effects.[2] Analogous conclusions have been reached by Alvarez and co-workers in a recent study of inorganic species, $M(NR_2)_3$ (M = V ... Ni; R = H or SiH_3).[3] In these systems, the orientations of the amido groups again depend on a combination of steric and electronic effects.

In this paper the geometry and the electronic structure of three-coordinated aluminum compounds $Al(NR_2)_3$[4] are studied with the help of theoretical calculations. When R = $SiMe_3$, X-ray analysis shows that the NR_2 coordination planes are rotated by the same angle (50°) with respect to the aluminum coordination plane.[5] The overall symmetry of the AlN_3Si_6 skeleton is actually D_3. When trimethylsilyl substituents are replaced by isopropyl groups, the observed geometry becomes less symmetric:[6] two isopropyl groups rotate in conrotatory manner by about 37° with respect to the aluminum coordination plane, whereas the third group strongly deconjugates, its rotation angle being close to 75°. We decided to undertake theoretical calculations on $Al(NR_2)_3$ systems in order to understand the origin of the difference between the observed geometries of these two compounds. From a purely electronic point of view, a previous study[7] on boron systems has shown that the geometrical preference in $B(NH_2)_3$ results from a balance between maximization of B−N π conjugation and minimization of the nitrogen lone pair repulsions. From a steric point of view, since $SiMe_3$ or ^iPr groups are rather bulky, the nature of these substituents must be explicitly taken into account in order to understand their different behavior.

We will therefore study at first unsubstituted $Al(NH_2)_3$ compound at an ab initio level in order to get information on almost a purely electronic preference, steric effects being expected to be negligible in this system. Steric effects will be gradually introduced by calculations on a methylated derivative ($Al(NMe_2)_3$). Then, the experimentally synthesized molecules will be explicitly calculated with the help of a coupled quantum mechanics/molecular mechanics method (see next section).

Theoretical Methods

For unsubstituted and methylated species, calculations have been undertaken first at the SCF level with the Gaussian 94 set of programs.[8] The 6-31G(d,p) basis set has been used throughout. All extrema have been reoptimized and characterized at the MP2/6-31G(d,p) level. To check the convergence of our calculations, we have reoptimized the

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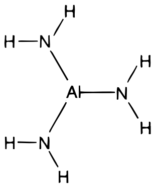
various extrema for the unsubstituted species with larger basis sets (correlated consistent cc-pVTZ basis set) and with more extended configuration interaction methods (MP4). Such refinements of the calculation method do not lead to substantial changes in the results (see below), and we will present results obtained at the MP2/6-31G-(d,p) level.

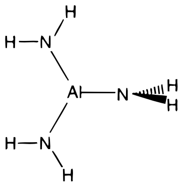
For real molecules (i.e. $Al[N(SiMe_3)_2]_3$ and $Al(N^iPr_2)_3$), the integrated molecular orbital/molecular mechanics (IMOMM) algorithm has been used.[9] In this method, a part of the molecule is calculated at the ab initio level and the rest of the molecule at a molecular mechanics level. It allows one to take into account the steric effects of the substituents without being prohibitively time and memory consuming. In our calculations, the quantic core will comprise the aluminum, the three nitrogen, and the six atoms (silicon or carbon) directly bound to nitrogen atoms. Since these calculations are rather time-consuming, we have restricted ourselves to SCF/6-31G(d,p) for the quantic core. The results obtained at the SCF and MP2 levels are shown to be almost the same in the case of unsubstituted species (see below).

Results

(A) Unsubstituted System $Al(NH_2)_3$. (1) Idealized Structures. Four limiting geometries have been computed. In the first (**1**), the three amido groups are located in the AlN_3 coordination plane and the three 2p nitrogen lone pairs conjugate with 3p Al central atom vacant orbital. In the three other geometries, one (**2**), two (**3**), or three (**4**) NH_2 groups are perpendicular to the aluminum coordination plane.



1



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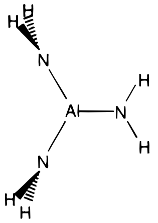

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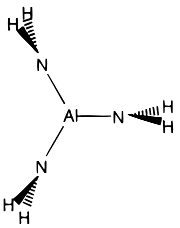

4

Partial optimizations have been performed on these four structures: the NH_2 groups have been constrained to be planar and their dihedral angles with the AlN_3 coordination plane are kept frozen to 0 or 90°. The relative energies and the main geometrical parameters are given in Table 1 at both the SCF and MP2 levels. As expected, the fully conjugated structure **1** is the most stable, the total deconjugation (**1** → **4**) costing more than 26 kcal/mol (MP2 level). A deconjugation consequence is also observed by the lengthening of the Al−N bond length from 1.79 Å (**1**) to 1.81 Å (**4**) at the MP2 level. Similar trends are found for structures **2** and **3**. It should be noted that deconjugation of only one pair (**1** → **2**) is a rather easy process (ΔE = 3.0 kcal/mol), the required energy being less than a third of that needed for full deconjugation (about 8.8 kcal/mol).

Table 1. Relative Energies (in kcal/mol) and Bond Distances (in Å) at the SCF Level (MP2 Level)[a]

struct	ΔE	$Al-N_{conj}$[a]	$Al-N_{deconj}$[a]
1	0 (0)[b]	1.778 (1.788)	
2	3.7 (3.0)	1.776 (1.786)	1.791 (1.800)
3	11.5 (10.7)	1.772 (1.782)	1.795 (1.804)
4	25.7 (26.3)		1.801 (1.810)

[a] The subscript conj or deconj refers to the NH_2 moieties which are conjugated or deconjugated with the aluminum atom, respectively. [b] Absolute energy: −408.841 49 au (−409.388 97 au).

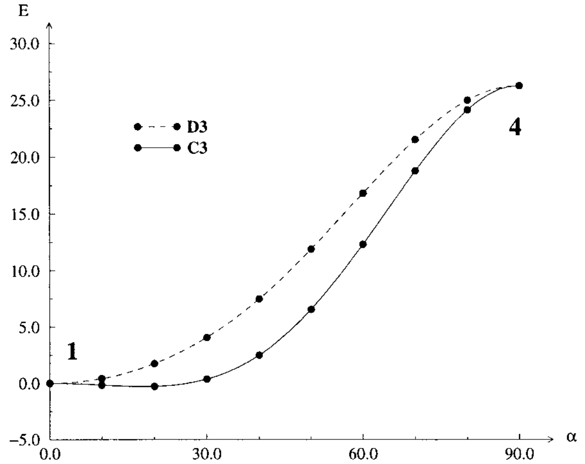

Figure 1. Energy curves associated with the **C3** and **D3** motions at the MP2 level.

Finally, one should note that SCF and MP2 calculations give very similar results: the relative energies are the same within 1 kcal/mol and the bond lengths within 0.01 Å. On the other hand, our results are very close to those recently published.[10]

(2) Amido Substituent Coupled Motions. We have first verified that the rotation of one conjugated group is destabilizing, whatever the starting structure (i.e. **1** → **2**; **2** → **3**; **3** → **4**) and that no intermediate minimum appears on the rotational energy curves.

When one consider the coupled rotations of the three amido groups, only two motions may occur from the fully conjugated structure **1**. In the first, all the amido groups rotate in a conrotatory manner (**C3**), and in the second, only one pair of amido groups rotate in a conrotatory manner (**D3**). The results are given in Figure 1 (MP2 level).

As found for the $B(NH_2)_3$[7] system, the conrotatory **C3** motion is found to be more favorable than the **D3** motion for each value of the rotation angle (Figure 1). This point has been already analyzed[7] and should originate from the weakening of the amido lone pair repulsion. A shallow minimum is found on the **C3**

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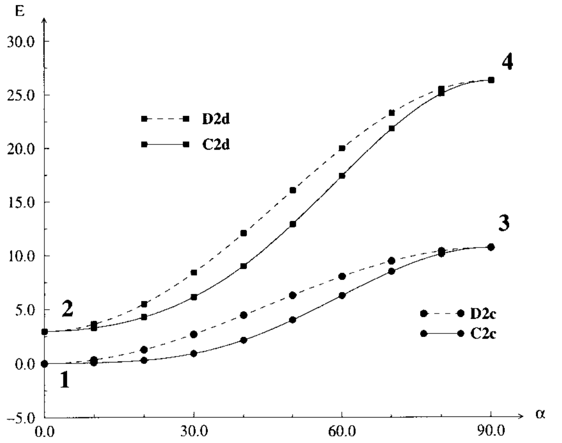
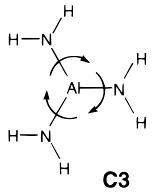
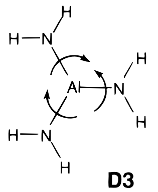


Figure 2. Energy curves associated with the various motions at the MP2 level.



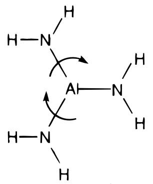
C3



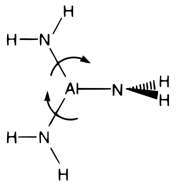
D3

energy curve at the MP2 level ($\Delta E = -0.3$ kcal/mol) for a rotational angle of 18.3°. No minimum is found on the **D3** energy curve (Figure 1).

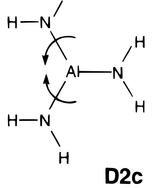
When only two amido groups are allowed to rotate, two motions (conrotatory **C2** and disrotatory **D2**) are found for coupled deconjugations. These two motions have been computed from the fully conjugated structure **1** (**C2c** and **D2c**) and from **2** in which one amido group is deconjugated (**C2d** and **D2d**). Note that the experimentally observed structure of $Al(N^iPr_2)_3$ seems to derive from the **C2d** motion.



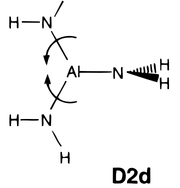
C2c



C2d



D2c



D2d

The four energy curves associated with these motions are given in Figure 2 (MP2 level). As in the preceding case, the conrotatory motions are always found to be more favorable than the corresponding disrotatory motions, for each value of the rotational angle and whatever the starting structure (**1** or **2**). No intermediate minimum is found within these four rotational energy curves.

(3) Full Optimization (MP2 Level). Starting from the preceding five structures considered (**1**−**4** and the **C3** minimum (**5**)), the pyramidalization angles of all the amido groups have been first optimized. Only structures **3** and **4** are stabilized by pyramidalization of the deconjugated amido groups by 1.1 and 2.9 kcal/mol, respectively.

Table 2. Relative Energies (in kcal/mol) at Various Levels of Calculation[a]

struct	SCF	MP2/6-31G(d,p)	MP2/cc-pVTZ	MP4/6-31G(d,p)
1[a]	0	0	0	0
2	3.7	3.0	3.8	3.0
3	11.5	10.7	11.7	10.7
4	25.7	26.3	26.4	26.5
5	−0.01	−0.3	−0.06	−0.3

[a] Absolute energy: −408.841 49 au (SCF), −409.388 97 au (MP2/6-31G(d,p)), −409.687 79 au (MP2/cc-pVTZ), −409.433 94 au (MP4/6-31G(d,p)).

Full optimization of the different minima leads to only one minimum: all the structures collapse to the **C3** minimum, **5**, in which no pyramidalization occurs. Its stabilization with respect to **1** is equal to 0.3 kcal/mol, and the optimized rotation angle is equal to 18.3°.

(4) Check of the Computational Method. We have tested our level of calculations by increasing the basis set and the configuration interaction method. The results are given in Tables 2 and 3. Geometry reoptimizations have been performed with the larger basis set (cc-pVTZ) and at the MP4 level.

From Table 2, it can be seen that the relative energies are rather insensitive to the level of calculation. The maximal change in these relative energies is less than 1 kcal/mol with increasing basis set or increasing configuration interaction method. Similar results are found for the geometrical parameters whose variations are about 0.01 Å with the calculation level (Table 3). The only noticeable variation is that of the optimized rotational angle in structure **5**. These changes (within the different computational level) are probably due to the flatness of the potential energy surface associated with this motion. In the following, we will present our results at the MP2/6-31G(d,p) level which is a good compromise between accuracy and calculation cost. It should be also noted that SCF calculations give reliable results in this study (see Tables 2 and 3).

(B) Methylated System $Al(NMe_2)_3$. (1) Idealized Structures. As in the unsubstituted case, four limiting structures have been optimized. To distinguish these structures from the unsubstituted ones, a prime (′) will be added to the number of the structure. Results (MP2 level of calculation) are given in Table 4.

Surprisingly, the fully conjugated structure **1′** is no longer the most stable one: structures **2′** and **3′** are found to be lower in energy by 8.9 and 2.8 kcal/mol, respectively (Table 4). Clearly, steric effects, which may be considered as negligible in unsubstituted species, are at work in methylated species and compete with electronic effects. They should be maximal in the planar structure **1′** where methyl groups are the closest. This point is illustrated by the lengthening of the Al−N bond: from 1.79 to 1.82 Å in **1** and **1′**, respectively (Tables 1 and 4). From the energy results in Tables 1 and 4, a rough estimate of steric repulsion can be calculated under two reasonable assumptions. We will suppose that (i) electronic effects are the same in hydrogenated and methylated compounds and (ii) steric effects between amido groups are almost zero in the fully deconjugated system **4′** which will be taken as the reference. Then, energy difference between **4′** and **1′** may be expressed as the electronic energy difference (which is the same as that between **4** and **1**, i.e., 26.3 kcal/mol) diminished by the steric repulsion which essentially occurs in **1′**. It gives a steric effect which is equal to the difference between relative energies of **4′** and **4**, i.e., 12.3 kcal/mol. Similar reasoning gives a steric repulsion equal to 0.4 and −1.2 kcal/mol in **2′** and **3′**, respectively. The small negative value (−1.2 kcal/mol) found in **3′** indicates that steric

Table 3. Optimized Distances (in Å) for the Conjugated (Deconjugated) Al−N Bonds in Structures **1**−**4** at the Various Levels of Calculation[a]

struct	SCF	MP2/6-31G(d,p)	MP2/cc-pVTZ	MP4/6-31G(d,p)
1	1.778 (-)	1.788 (-)	1.783 (-)	1.789
2	1.776 (1.791)	1.786 (1.800)	1.780 (1.792)	1.786 (1.801)
3	1.772 (1.795)	1.782 (1.804)	1.777 (1.795)	1.783 (1.805)
4	- (1.801)	- (1.810)	- (1.800)	- (1.811)
5	1.778 (8.7°)	1.788 (18.3°)	1.782 (12.8°)	1.788 (18.3°)

[a] For structure **5**, only one value is found; the optimized rotational angle is given in parentheses.

Table 4. Relative Energies (in kcal/mol) and Bond Distances (in Å) for the Four Idealized Geometries of the Methylated Species (MP2 Level)

struct	ΔE	Al−N_{conj}	Al−N_{deconj}
1′	0.0[a]	1.823	
2′	−8.9	1.800	1.810
3′	−2.8	1.793	1.810
4′	14.0		1.817

[a] Absolute energy: −644.297 03 au.

Table 5. Relatives Energies (ΔE, in kcal/mol), Rotation Angle (α in deg), Bond Distances (in Å), and Steric Repulsion (ΔE_{ste}, in kcal/mol) at the MP2 Level[a]

struct	ΔE	α	Al−N_1	Al−N_2	Al−N_3	ΔE_{ste}
C3	−14.2[a]	28.1	1.797	1.797	1.797	−2.0
C2c	−11.5	34.7	1.801	1.800	1.800	−0.6
C2d	−8.9	19.4	1.888	1.798	1.798	−0.8
D2c	−7.8	41.0	1.801	1.808	1.808	−0.1
D2d	−8.9	0.0	1.810	1.800	1.800	0.4
D3	−6.6	27.7	1.811	1.809	1.809	2.3

[a] The origin of the energies is that of the fully conjugated structure **1′** (see Table 4).

effects are even smaller in this structure than in **4′**. This result seems reasonable since no amido groups are coplanar in this structure. The small value found in **2′** (0.4 kcal/mol) is more surprising since two amido substituents are actually coplanar in this geometry. This low value probably comes from the opening of the N−Al−N angle between the conjugated amido substituents; it increases to 128.8°, a value significantly larger than in other geometries. Such a relaxation allows noticeable diminution of the steric repulsion in **2′**.

As a conclusion, it is worth noticing that electronic and steric effects are of the same magnitude and may indeed compete in methylated species; full deconjugation ($\mathbf{1} \rightarrow \mathbf{4}$) costs 26.3 kcal/mol, and steric repulsion has been estimated to be equal to 12.3 kcal/mol in **1′**. As a consequence, it can be expected that any motion which diminishes steric effect and does not suppress conjugation should be favorable.

(2) Rotations of the Amido Groups. We have first calculated the energetic curves associated with the deconjugation of only one amido group from structures **1′**, **2′**, and **3′**. Contrarily to the unsubstituted case, deconjugation of only one group in **1′** is stabilizing because of the strong steric effects in this structure. We found a 9.0 kcal/mol stabilization for a rotation angle (α) equal to 50.6°. Starting from structures **2′** and **3′**, no stabilization is found by deconjugating one amido substituent probably because steric repulsion is very small in both structures **2′** and **3′** (see above).

The six coupled motions (**C2c**; **D2c**; **C2d**; **D2d**; **C3**; **D3**) described in the preceding section have been computed. In each case (except for the **D2d** motion), a minimum is found. The stabilization energies and the main geometrical parameters are given in Table 5. In the **D2d** motion case, no stabilization from **2′** is found and the parameters given in Table 5 are those of the idealized structure **2′**. The steric repulsion (ΔE_{ste}) has been also calculated in the way described before; we have constrained the rotational angle to its optimized value in the methylated system and reoptimized the unsubstituted structure. The difference between the relative energies of the unsubstituted and methylated structures is then a rough estimate of the steric repulsion in the different extrema.

The largest stabilization is found for the **C3** motion ($\Delta E = -14.2$ kcal/mol) for a rotation angle of 28.1°. Examination of the estimates of the steric effect (ΔE_{ste}) shows that this quantity is small in each case (from −2.0 to 2.3 kcal/mol), indicating that all these motions (excepted **D2d**) allow a drastic lowering of the steric repulsion. It should also be noted that the largest reductions of the steric repulsion (from −0.6 to −2.0 kcal/mol) occur for conrotatory motions which are therefore the most favored on steric grounds.

(3) Full Optimizations. Starting from the 11 above constrained minima (four idealized structures plus the six constrained minima depicted in Table 5 plus the minimum resulting from the rotation of one amido substituent from **1′**), we obtained only one extremum (**5′**) resulting from the **C3** motion whose characteristics are given in Table 5. It should be noted that this structure is favored on both electronic grounds (see above paragraph) and on steric grounds: we indeed found that steric repulsion is 2.0 kcal/mol smaller than in the structure **4′** in which such repulsion was expected to be small. In this structure the steric repulsion is calculated to be the smallest with respect to other optimized constrained structures.

(C) Experimentally Synthesized Molecules ($\mathbf{Al(NR_2)_3}$; $\mathbf{R = SiMe_3}$ and $\mathbf{R = {}^iPr}$). From the above results, it can be concluded that steric effects are of dramatic importance, even in methylated systems where such a repulsion is not expected to be dominant. As a consequence, the nature of the substituents must be explicitly taken into account in order to understand the differences between $Al[N(SiMe_3)_2]_3$ and $Al(N^iPr_2)_3$. Since ab initio calculations are not tractable on such systems, we performed coupled molecular mechanics/molecular orbital calculations (IMOMM algorithm; see Theoretical Methods). Briefly, a part of the molecule (AlN_3Si_6 and AlN_3C_6) is described at the ab initio level (i.e. a quantic core comprising 10 atoms) and the rest of the molecule at a molecular mechanic level which essentially accounts for steric effects. During the optimization process, the bonds connecting the two subspaces (quantic and classic) are kept frozen to their averaged experimental values (Si−C =1.90 Å and C−C = 1.535 Å). Consequently the calculation of the full Hessian matrix is meaningless and the optimized extrema have not been characterized.[11]

(1) Idealized Structures. Computations on idealized structures have been carried out only for sake of comparison with hydrogenated or methylated structures. Although all planar $Al(NR_2)_3$ structures, with R being a bulky substituent, dramatically

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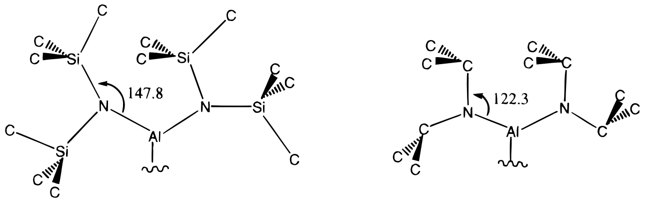
(11) We are aware that, in a more recent version of the Gaussian package, a new algorithm (ONIOM) is proposed which allows the calculation of the Hessian matrix. We did not use this version since the force fields used within this algorithm are less adapted to the molecules under study.

Table 6. Relatives Energies (in kcal/mol) of the Idealized Structures of $Al(NR_2)_3$[a]

struct	ΔE ($R = SiMe_3$)	ΔE ($R = {}^iPr$)
1	0^a	0^b
2	−81.6	−19.3
3	−115.0	−19.9
4	−102.7	−9.0

[a] Absolute energy: −2149.242 64 au. [b] Absolute energy: −642.892 63 au.

Chart 1



suffer large steric repulsions, these calculations allow a rough estimate of steric effects which will be discussed later. Numerous conformations are possible with such polyatomic substituents (see below), and we will give only the results corresponding to the most stable conformations. The relative energies are given in Table 6.

Comparing steric repulsion values for $R = SiMe_3$ and $R = {}^iPr$ shows that steric repulsions in conjugated geometries are much greater in the former case ($\Delta E = 128.4$ kcal/mol)[12] than in the latter ($\Delta E = 34.7$ kcal/mol). This point is important and may be explained by considering the relative geometries of two adjacent NR_2 groups (Chart 1).

Because of the quasi-spherical geometry of the $SiMe_3$ groups, steric repulsion cannot be avoided in structure **1**. On the opposite, isopropyl groups may orientate in such a manner that steric repulsion is strongly diminished in **1** (Chart 1). This is illustrated by the noticeable opening of the Al−N−Si angle (147.8°) in $SiMe_3$ case whereas a nearly trigonal angle (122.3°) is found for the isopropyl substituent. Consequently, steric repulsion is unavoidable with $SiMe_3$ groups whereas it may be reduced when $R = {}^iPr$.

(2) R = SiMe₃. As in the methylated system, we have first verified that rotation of only one amino group is stabilizing in each case. It is very large for **1** ($\Delta E = 83.0$ kcal/mol, $\alpha = 82.4°$), smaller in **2** ($\Delta E = 33.7$ kcal/mol, $\alpha = 85.5°$), and almost 0 ($\Delta E = 0.4$ kcal/mol, $\alpha = 5.2°$) in **3**, indicating the relative strength of steric repulsions in these conformations. As expected from the above results, reduction of the steric repulsion is a dominant factor in this molecule. As in methylated systems, we have optimized constrained structures resulting from coupled rotations of the amido groups. The results are given in Table 7.

Among the six constrained minima, the largest stabilization is found for a conrotatory motion of the three amido groups (**C3** minimum, Table 7). A 11.4 kcal/mol weaker stabilization is found for the **C2d** motion in which one group is deconjugated and the two other amido substituents move in a conrotatory manner. Note that this structure resembles the experimentally observed geometry in the $Al(N^iPr_2)_3$ complex. Other constrained minima are located much higher in energy (more than 19 kcal/mol above the absolute minimum; see Table 7).

Table 7. Relative Energies (ΔE, in kcal/mol), Rotation Angle (α in deg), and Bond Distances (in Å) of the Optimized Constrained Minima of $Al[N(SiMe_3)_2]_3$[a]

struct	ΔE	α	$Al-N_1$	$Al-N_2$	$Al-N_3$
C3	0^a	48.1	1.827	1.827	1.827
C2d	11.4	46.7	1.830	1.830	1.839
C2c	19.2	72.6	1.832	1.841	1.847
D2c	20.6	92.9	1.845	1.845	1.828
D3	31.6	67.0	1.855	1.848	1.853
D2d	34.1	62.1	1.844	1.850	1.860

[a] The origin of the energies is that of the lowest structure (**C3**), which is located 133.5 kcal/mol under the idealized structure **1** (absolute energy: −2149.455 44 au).

Table 8. Optimized Parameters and Relative Energies of the Two Minima Obtained for $Al[N(SiMe_3)_2]_3$[a]

	α_1	α_2	α_3	$Al-N_1$	$Al-N_2$	$Al-N_3$	ΔE
C3	48.1	48.1	48.1	1.827	1.827	1.827	0
C2	48.9	48.7	66.1	1.826	1.825	1.835	2.6
expt	50(1)	50(1)	50(1)	1.78(2)	1.78(2)	1.78(2)	

[a] Bond lengths are in Å, angles in deg, and relative energies in kcal/mol. The experimental data are from ref 5.

Full optimization of the 13 constrained minima (four idealized structures plus three resulting from the motion of only one amido substituent from idealized structures plus the six constrained minima depicted in Table 7) leads to only two minima which are the **C3** minimum and a **C2** minimum whose geometry is close to that of the constrained **C2d** minimum. The optimized geometrical parameters and the relative energies are given in Table 8 together with the experimental data.

The results given in Table 8 indicate that reduction of the steric effects may be achieved by two motions, leading to two minima, **C3** and **C2**. The rotations of the amido groups are close to that experimentally observed in the $R = SiMe_3$ and $R = {}^iPr$ cases, respectively. The theoretical absolute minimum is however found for the **C3** motion in the $R = SiMe_3$ case, in accordance with the experimental determination. The optimized parameters of the **C3** minimum are in rather good agreement with the experimental data:[6] the α rotational angle found is close to the X-ray determination value (48.3° vs 50°). A poorer agreement is found for the Al−N bond length: 1.827 vs 1.78 Å. Note however that the theoretical value lies within the experimental indetermination.

(3) R = ⁱPr. The study of this molecule is much more complicated than in the preceding case since numerous conformers may be considered depending on the relative orientation of the isopropyl groups. Large steric effects may be generated when bulky substituents are in an eclipsed position; for instance, three symmetrical conformers of the idealized structure **1** have been optimized (Chart 2). Their relative energies are in the range 0−80 kcal/mol depending on the nature of the eclipsing groups; when two methyl groups are close together, steric repulsion is large and the conformer is strongly destabilized.

From the results obtained for **1**, we have calculated between 3 and 10 conformers for each idealized structure in which steric repulsion is expected to be small. The results for the lowest energy structures have been presented in Table 6 and allow a rough estimate of the steric repulsion in this species. Exploration of the whole PES is much more complicated since prediction of the highly destabilized structures by steric effects is hardly predictable in rotated geometries. We therefore decided to explore this PES by starting from all the possible conformers[13] of the most sterically congested structure **1**. In addition, structures derived from the minima **1**−**5** have been considered.

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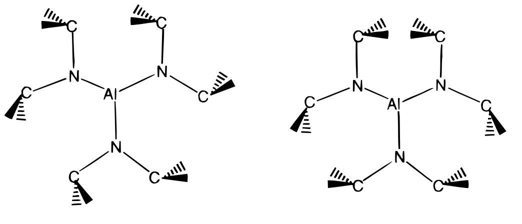
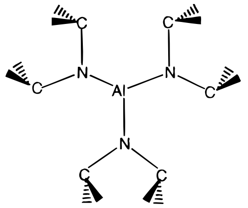
(12) Calculation of the steric effect has been done as presented above. The result obtained in the $Al[N(SiMe_3)_2]_3$ case should be taken with some care because silicon electronic effects are expected to be rather different from the hydrogen ones due to its low electronegativity. However, the large value obtained should not be dramatically reduced by more accurate calculations.

Chart 2



ΔE = 0 kcal/mol ΔE = 8.3 kcal/mol



ΔE = 80.3 kcal/mol

Table 9. Optimized Parameters and Relative Energies of the Absolute Minimum **C2** and of the Four Conrotatory Minima **C3** Obtained for Al(N^{i}Pr$_2$)$_3$[a]

	α_1	α_2	α_3	Al−N$_1$	Al−N$_2$	Al−N$_3$	Δ*E*
expt	36.6	75.5	38.3	1.791	1.801	1.794	
C2	36.8	66.8	36.7	1.802	1.806	1.802	0[b]
C3(1)	46.8	46.3	46.2	1.802	1.802	1.802	2.3
C3(2)	54.6	54.6	54.5	1.806	1.806	1.806	2.6
C3(3)	51.4	51.4	51.5	1.809	1.809	1.809	3.2
C3(4)	37.2	37.2	37.2	1.795	1.795	1.795	3.6

[a] Bond lengths are in Å, angles in deg, and relative energies in kcal/mol. Experimental data are from ref 6. [b] Absolute energy: −642.933 73 au.

Optimization of these different conformers leads to 35 different minima whose relative energies are in the range 0−7 kcal/mol. Description of these different minima would be rather fastidious, and we therefore will principally focus on the lowest energy structure (**C2**). This structure is very near that resulting from a **C2d** motion; one amino group is strongly deconjugated ($\alpha = 66.8°$) while the two other amino groups rotate in a quasi-conrotatory manner ($\alpha = 36.7−36.8°$). The main geometrical parameters together with the experimentally determined ones are given in Table 9 (two first entries). Comparison of the theoretical and experimental parameters shows a rather good agreement: two angles are almost the same (36.8° vs 36.6° and 36.7° vs 38.3°; Table 9) while a difference of about 10° is found for the third one (that of the "deconjugated" amido group). Similarly, good accordance is found for the calculated bond lengths; the differences between experimental and calculated values are less than 0.01 Å, and the bond distances ordering is the same in both determination (i.e. the longest distance is associated with the largest rotational angle).

Higher in energy are found the other conformers in the range 1.3−7 kcal/mol. Two points deserve some comments: (i) Within 7 kcal/mol 35 different conformers have been found which illustrates well the complexity of the PES. The average energy separation between two of them is therefore less than 0.2 kcal/mol. Since the closest conformer in energy is located 1.3 kcal/mol above the absolute minimum, this latter may be viewed as separated from the other conformers. (ii) Among the 35 conformers, four of them are geometrically close to the conrotatory conformer found in the preceding case (**C3(1)**−**C3(4)**). Their energetic and geometrical characteristics are reported in Table 9. The basic difference between these four conformers is the relative orientation of the isopropyl groups. It leads to substantial differences in the optimal rotation angle values (from 37.2° to 54.6°; see Table 9).

In conclusion, when R = ^{i}Pr, we found that the absolute minimum roughly results from a **C2d** motion and the lowest **C3** structure (which is the optimal structure in the R = SiMe$_3$ case) is no longer the absolute minimum and is located 2.3 kcal/mol above.

Conclusions

The geometry of Al(NR$_2$)$_3$ compounds results from a balance between electronic and steric effects. Study of the unsubstituted species Al(NH$_2$)$_3$ shows that electronic preference does not firmly impose only one geometry: fully conjugated structure **1** and conrotatory optimum **5** are almost isoenergetical. In addition, the study of coupled rotation indicates that substantial rotations of two amido groups (up to 60°) may lead to only weak destabilizations (less than 5 kcal/mol; see Figures 1 and 2). When hydrogen atoms are replaced by bulky substituents R, steric effects become important. Our results show that when R is quasi-spherical (R = SiMe$_3$), the optimal way to avoid steric repulsion is the conrotatory motion of the three amido groups. When R is anisotropic (R = ^{i}Pr), steric repulsion may be partly avoided by a particular orientation of the substituents. The optimal geometry of the complex then results from a subtle balance between steric and electronic effects, and multiple minima are found on the PES.

The following point concerns the comparison between calculated and experimentally determined Al−N bond lengths: the agreement is rather good on the R = ^{i}Pr case (see Table 9) while it is less satisfactorily in the R = SiMe$_3$ case (1.828 vs 1.78 Å; Table 8). This discrepancy may originate from our level of calculations, the SiMe$_3$ substituent being partly described at a molecular mechanics level. However a better agreement is found with recent determination of Al−N bond lengths in other tricoordinated aluminum compounds R$_1$R$_2$Al−N(SiMe$_3$)$_2$. Crystal determinations give the following values: Al−N = 1.807 Å (R$_1$ = Mes; R$_2$ = N(SiMe$_3$));[6] Al−N = 1.819 Å (R$_1$ = Mes; R$_2$ = H).[14] These values are in reasonable agreement with our calculated value (1.827 Å).

Finally, it is worthwhile to emphasize the ability of the IMOMM algorithm to account for subtle differences in such systems. In the two cases under study, two minima (**C3** and **C2**) have been found to be close in energy. In agreement with the available experimental data, we have found that the absolute minimum is **C3** when R = SiMe$_3$ and **C2** when R = ^{i}Pr, although their energy differences are less than 3 kcal/mol in both cases.

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(13) The study has been restricted to conformers in which the central hydrogen of isopropyl groups lie in the NC$_2$ plane. In addition, a small rotation angle (5°) has been imposed on the amido groups from **1** in order to lower the overall symmetry.

(14) Wehmschulte, R. J.; Power, P. P. *Inorg. Chem.* **1998**, *37*, 2106.