Electronic and Geometrical Structures of Dialuminoxane, Diboroxane, and Their Sulfur Analogues: Ab Initio Study of H_2X-Y-XH_2 (X = Al, B; Y = O, S) Compounds

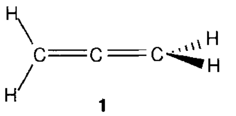
Laurent Boiteau, Isabelle Demachy, and François Volatron*

Abstract: The structures of H_2X-Y-XH_2 compounds (X = B, Al; Y = O, S) have been studied by means of ab initio calculations at the MP4/6-311G**//MP2/6-311G** level. The potential energy surface (PES) of the aluminoxane species H_2Al-O-AlH_2 is rather flat: the energy differences between the various located extrema are less than 1.5 kcal mol^{-1}, and this shows that the observed geometrical preference is not due to electronic factors. For the sulfur analogues H_2X-S-XH_2 (X = B, Al), three minima are located on the PES: a planar C_{2v} structure, a C_s structure in which one hydrogen atom bridges the two X atoms, and a C_{2v} structure with two bridging hydrogen atoms. For H_2Al-S-AlH_2, the C_s structure is the most stable, and the planar C_{2v} and the dibridged structures lie 3.2 and 6.7 kcal mol^{-1} higher, respectively. Qualitatively similar results are obtained for H_2B-S-BH_2: the C_s and planar C_{2v} structures are nearly isoenergetic, and the dibridged minimum lies 19.4 kcal mol^{-1} above the planar C_{2v} minimum. These results are rationalized by analyzing the ability of these systems to bend, depending on the nature (oxygen or sulfur) of the central Y atom. The conjugation in these species is also discussed, and calculations on model systems H_2X-YH (X = B, Al; Y = O, S) are presented.

Keywords
ab initio calculations · aluminum · boron · pi interactions · sulfur

Introduction

Here we address the electronic and geometrical structures of H_2X-Y-XH_2 species (X = B, Al; Y = O, S) by ab initio calculations. All these molecules have the same number of valence electrons as allene $H_2C{=}C{=}CH_2$. Therefore, a perpendicular D_{2d} arrangement, as found in $H_2C{=}C{=}CH_2$ (**1**), which maximizes the conjugation between the p orbitals of the XH_2 and Y fragments is expected to be most favorable.



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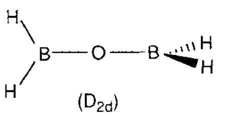
It has been shown that diboroxane systems (X = B; Y = O) can indeed adopt such a perpendicular geometry **2**.[1] However, an alternative structure of C_{2v} symmetry **3** lies almost at the same energy as **2**. It is characterized by a small B-O-B angle (123° at the MP2/6-311G** level) and the whole molecule is planar. These two minima can interconvert through a very weak energy barrier (1.2 kcal mol^{-1}); this indicates that the potential energy surface (PES) is rather flat between these two structures. Experimental data on substituted diboroxanes (R_2B-O-BR_2) confirm these findings: the experimentally determined geometries do not belong to the D_{2d} or C_{2v} symmetries, but are intermediate between the two. The smaller the B-O-B angle is, the smaller is the twist angle between the two BR_2 planes. An orbital analysis may explain the origin of the minimum-energy geometries for H_2B-O-BH_2. In the D_{2d} structure, each 2p oxygen lone pair is stabilized by conjugation with one empty boron 2p orbital. As a result, two two-center, two-electron stabilizing interactions are effective in this geometry. In the C_{2v} structure, the π oxygen lone pair is stabilized by conjugation with the vacant in-phase combination of the two boron 2p orbitals. The in-plane σ oxygen lone pair is stabilized by the rehybridization that occurs upon B-O-B bending. Two ways of stabilizing the two oxygen lone pairs are therefore available for this molecule. They are roughly equivalent, and the D_{2d} and C_{2v} structures are almost isoenergetical minima on the PES.



(D_{2d})

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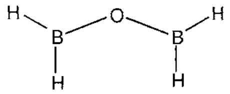
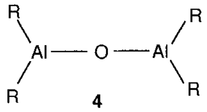


(C_{2v})

3

Recently,[2] Uhl et al. described a rather puzzling result: the structure of a dialuminoxane [R_2Al-O-AlR_2, R = $CH(SiMe_3)_2$] is planar, with a linear Al-O-Al arrangement **4** and a C_2Al-O-



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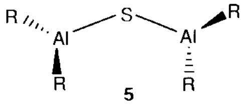

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AlC_2 skeleton of D_{2h} symmetry. This X-ray structure is clearly at odds with the theoretical results on H_2B-O-BH_2 mentioned above, provided that aluminum and boron behave similarly. This prompted us to undertake ab initio calculations on unsubstituted aluminoxane H_2Al-O-AlH_2 in order to understand the electronic differences between aluminum and boron that might explain the different geometrical preferences of dialuminoxane and diboroxane.

If the central oxygen atom is replaced by sulfur, the experimentally determined structure[3] is rather different [**5**, R = $CH(SiMe_3)_2$], although both atoms have the same number of valence electrons. In contrast with the linear Al-O-Al arrangement in R_2Al-O-AlR_2, the R_2Al-S-AlR_2 moiety is strongly bent (Al-S-Al = 117.5°), and the two aluminum coordination planes are rotated by 39.9° (average value) with respect to the Al-S-Al plane. Therefore, we studied the unsubstituted H_2Al-S-AlH_2 system and its boron analogue H_2B-S-BH_2. To our knowledge, no crystallographic data are available for the latter type of molecule.[4]

Methods of Calculation

The 6-311 G** basis set was used throughout. All geometries were optimized at the MP2 level by an analytical gradient method. The extrema were characterized by analytical frequency calculations at this level. The stationary points may be minima (Min, no imaginary frequency), transition states (TS, only one imaginary frequency), or *n*th order saddle points (*n*-SP, *n* imaginary frequencies). In the last case ($n > 1$), the stationary point has no chemical significance. The correlation energy was then calculated at the MP4 level on the geometries optimized at the MP2 level. Our best level of calculation is therefore MP4/6-311G**//MP2/6-311G**. The Gaussian 92 set of programs[5] was used.

Abstract in French: *Les structures géométriques et électroniques des composés H_2X-Y-XH_2 ($X = B, Al$; $Y = O, S$) ont été déterminées par des calculs ab initio à l'aide de la méthode MP4/6-311G**//MP2/6-311G**. La surface de potentiel associée au dialuminoxane H_2Al-O-AlH_2 est très plate: les trois extrema localisés (D_{2h}, D_{2d}, C_{2v}) diffèrent en énergie par moins de 1.5 kcalmole^{-1}. En conséquence, la préférence conformationnelle du dialuminoxane caractérisé expérimentalement (R_2Al-O-AlR_2 avec $R = CH(SiMe_3)_2$) n'est pratiquement pas gouvernée par des facteurs électroniques. Les composés soufrés H_2X-S-XH_2 ($X = B, Al$) présentent trois minima sur la surface de potentiel: un minimum plan C_{2v}, une structure C_s où un atome d'hydrogène est en pont entre deux atomes X et une structure C_{2v} possédant 2 hydrogènes pontant. Pour le système H_2Al-S-AlH_2, la structure C_s monopontée est la plus stable, les structures C_{2v} plane et bipontée se situant respectivement 3.2 et 6.7 kcalmole^{-1} au-dessus. Pour le système H_2B-S-BH_2, les structures C_s et C_{2v} planes sont pratiquement isoénergétiques et le minimum biponté est déstabilisé de 19.4 kcalmole^{-1} par rapport à la structure C_{2v} plane. Les stabilités relatives des différents extrema dépendent essentiellement de deux facteurs: d'une part de la facilité de fermeture de l'angle X-Y-X selon la nature de Y, et d'autre part de la stabilisation apportée par la conjugaison entre les paires libres de Y et les orbitales vacantes des fragments XH_2. Des calculs sur les sytèmes modèles H_2X–YH ($X = B, Al$; $Y = O, S$) sont également présentés et discutés.*

Results and Comparison with Experimental Data

H_2Al-O-AlH_2 (6): Three stationary points were located and characterized on the PES. They are of C_{2v}, D_{2h}, and D_{2d} symmetry, and no extrema of lower symmetry (C_s or C_2) were found. The D_{2d} structure is characterized as a minimum, the C_{2v} one as a transition state, and the D_{2h} one as a second-order saddle point. The energetical and geometrical characteristics of these extrema are given in Table 1.

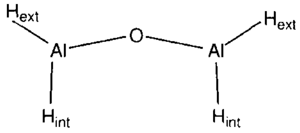

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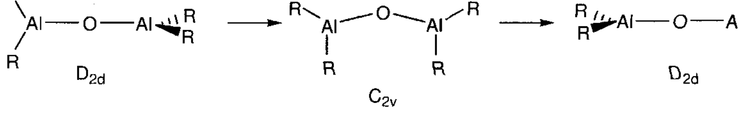
Table 1. Geometrical parameters (Å and °) and relative energies (kcal mol^{-1}) of the optimized extrema of the H_2Al-O-AlH_2 system (see **6** for the nomenclature of the atoms). The D_{2d} absolute energies (in a.u.) are −561.48028 (MP2) and −561.51819 (MP4/MP2).

	D_{2h}	D_{2d}	C_{2v}
Al–O	1.703	1.702	1.704
Al–H_{int}	1.572	1.572	1.572
Al–H_{ext}	–	–	1.571
Al-O-Al	180.0	180.0	169.9
O-Al-H_{int}	119.1	118.9	119.3
O-Al-H_{ext}	–		118.9
type	2-SP	min	TS
Δ*E*(MP2)	1.4	0.0	1.4
Δ*E* (MP4)	1.4	0.0	1.4

The three extrema are very close in energy (the energy difference is less than 1.5 kcal mol^{-1} at both MP2 and MP4/MP2 levels). Only the D_{2d} structure is a true minimum on the PES. The C_{2v} transition state allows the interconversion between two equivalent D_{2d} minima (Scheme 1): the transition vector associated with this TS mainly develops with the coupled rotation of the two AlH_2 groups. The Al-O-Al bending is marginal in this motion, since the C_{2v} extremum is weakly bent (Al-O-Al = 169.9°, Table 1). Following each of the two transition vectors from the D_{2h} second-order saddle point leads to the C_{2v} transition state or to the D_{2d} minimum.



Scheme 1. Interconversion between the two equivalent D_{2d} minima of R_2Al-O-AlR_2 via the C_{2v} transition state.

The results listed in Table 1 show that there is no electronic preference for a particular geometry in this species. In addition, the optimized geometrical parameters are nearly the same in each extremum; for instance, the difference between between the longest and the shortest Al–O bond lengths is only 0.002 Å

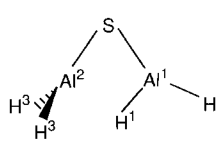
(Table 1). Consequently, it can be concluded that the PES is rather flat around these extrema. Steric effects or crystal packing forces are then likely to determine the geometry of the substituted dialuminoxane species. The experimental finding of Uhl et al.,[2] although unexpected, is thus not surprising in the light of our results. Finally, our structural parameters obtained for D_{2h} geometry agree well with those found by Uhl et al.: the aluminum atom is in an approximately planar trigonal environment, and the Al–O distance (1.688 Å) is slightly shorter than our calculated value (1.703 Å).

H_2B-O-BH_2: The results have been reported and analyzed elsewhere.[1] The C_{2v} and D_{2d} structures are almost isoenergetic minima on the PES. The D_{2h} structure is characterized as a second-order saddle point, and the two imaginary frequencies are associated with motions that lead to the C_{2v} or D_{2d} minima. For the sake of comparison, the geometrical and energetical results are listed in Table 2. On the whole they agree with the experimental data.[1]

Table 2. Geometrical parameters (Å and °) and relative energies (kcal mol^{-1}) of the optimized extrema of the H_2B-O-BH_2 system.

	D_{2h}	D_{2d}	C_{2v}
B–O	1.356	1.343	1.376
B–H_{int}	1.197	1.193	1.194
B–H_{ext}	–	–	1.191
B-O-B	180.0	180.0	123.0
O-B-H_{int}	119.4	118.5	120.1
O-B-H_{ext}	–	–	117.1
type	2-SP	min	min
ΔE (MP2)	11.3	0.8	0.0
ΔE (MP4)	11.3	0.6	0.0

H_2Al-S-AlH_2: Six extrema were located on the PES for this molecule. Three minima and three *n*th order saddle points were characterized. No attempt was made to locate the TS's for the interconversion between the minima. The optimized geometrical parameters and the relative energies of these extrema are given in Table 3. Two results strongly differ from those found in the preceeding cases: first, the D_{2d} geometry is no longer a minimum but a second-order saddle point, and second, two bridged minima (**7** and **8**) appear on the PES. The monobridged structure **7** is the absolute minimum.



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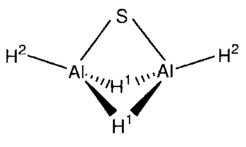

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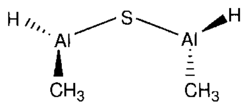
The planar C_{2v} structure is a real minimum on the PES, and its geometry can be compared to the experimental structure. The optimized Al–S bond length (2.178 Å) is a little shorter than the experimental value (2.187 Å) and, in agreement with the crystallographic structure, the Al environment is approximately trigonal planar. However, some discrepancies exist between the theoretical and experimental geometries.[3] First, the Al-S-Al angle (104.9°) is smaller than the experimental value (117.5°). Second, the Al coordination planes are rotated in the experimental structure (average twist angle: 39.9°), whereas our calculated structure is planar. Both these differences probably originate from the presence of bulky substituents [R = $CH(SiMe_3)_2$] on the aluminum atoms: minimization of steric repulsion should cause an opening of the Al-S-Al angle and rotation of the aluminum coordination planes. To investigate the influence of steric effects, we performed some additional geometry optimizations on dimethyl- and tetramethyl-substituted compounds **9** and **10** within the C_2 symmetry point group. In each case, we find an opening of the Al-S-Al angle [Al-S-Al = 108.0° (**9**) and 106.2° (**10**)] and a twist of the aluminum coordination planes (Tw) with respect to the Al-S-Al plane [Tw = 16.2° (**9**) and 24.4° (**10**)]. These values are intermediate between the optimized values in the unsubstituted system (Al-S-Al = 104.9°, Tw = 0, Table 3) and those experimentally determined in the substituted system (Al-S-Al = 117.5°, Tw = 39.9°). This shows that these two geometrical parameters strongly depend on steric effects, which are partly taken into account in **9** and **10**.[6] The optimized bond lengths are close to those observed experimentally [Al–S = 2.183 Å (**9**), 2.190 Å (**10**), 2.187 Å (exp.); Al–C = 1.957 Å (**9**); 1.959 Å (av. value in **10**); 1.93 Å (av. exp. value)].



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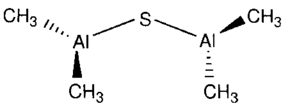

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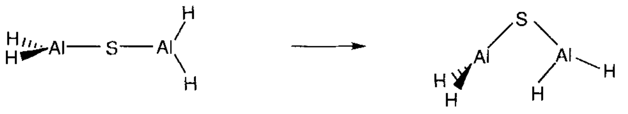
Table 3. Geometrical parameters (Å and °) and relative energies (kcal mol^{-1}) of the optimized extrema of H_2Al-S-AlH_2 system. The planar C_{2v} absolute energies (in a.u.) are −884.03611 (MP2) and −884.08478 (MP4/MP2).

	D_{2h}	D_{2d}	C_{2v} planar	C_{2v} butterfly	C_s monobridged	C_{2v} dibridged
S–Al1	2.149	2.145	2.178	2.178	2.105	2.211
S–Al2	–	–	–	–	2.285	–
Al1–H1	1.567	1.566	1.570	1.570	1.657	1.773
Al1–H2	–	–	1.568	–	1.556	1.555
Al2–H3	–	–	–	–	1.572	–
Al-S-Al	180.0	180.0	104.9	107.0	75.4	63.9
S-Al1-H1	118.3	117.8	120.1	119.1	99.6	90.6
S-Al1-H2	–	–	116.4	–	141.7	141.9
S-Al2-H3	–	–	–	–	115.9	–
Al1-S-Al2-H3		–	0.0	90.9	101.2	38.3
type	3-SP	2-SP	min	2-SP	min	min
ΔE (MP2)	14.0	12.2	0.0	7.6	−2.7	4.0
ΔE (MP4)	14.5	12.5	0.0	7.8	−3.2	3.5

Surprisingly, the D_{2d} geometry corresponds to a second-order saddle point located 12.5 kcal mol^{-1} above the C_{2v} structure, and not to a minimum as in the above oxygen systems. The two imaginary frequencies associated with this structure are degenerate and develop only on the Al-S-Al angle. The associated motions allow the stabilization to the C_s monobridged minimum **7**. Since the two H_2AlS planes are equivalent in D_{2d} geometry, the two vibrations corresponding to these motions are degenerate. One of them (the in-plane motion) is depicted in Scheme 2.



Scheme 2. In-plane motion of the D_{2d} geometry of $H_2Al\text{-}S\text{-}AlH_2$ to give the C_s monobridged minimum 7.

For the $H_2Al\text{-}S\text{-}AlH_2$ system, the absolute minimum belongs to the C_s point group and results from a large bending of the Al-S-Al angle away from D_{2d} geometry. The C_s minimum is 2.7 kcal mol^{-1} lower in energy than the C_{2v} minimum. We attribute this stability to the fact that one hydrogen atom of the in-plane AlH_2 group bridges the two aluminum atoms in this structure. The distance between the nonbonded atoms Al2 and H1 is indeed rather short (1.895 Å). This bridging interaction is also reflected by a 0.1 Å lengthening of the Al–H distance of the bridging hydrogen atom compared to that of the terminal one (Al1–H1 = 1.657 Å and Al1–H2 = 1.556 Å; see **7** and Table 3) and by a small S-Al-H1 angle (99.6° instead of 120° for trigonal coordination). This bridging interaction is probably the origin of the small valence angle at sulfur (Al-S-Al = 75.4°).

The dibridged structure **8** of C_{2v} symmetry is also a real minimum located 3.5 kcal mol^{-1} above the planar C_{2v} minimum. In this dibridged structure, the two hydrogen atoms are symmetrically bound to the aluminum atoms. The Al–H distance (1.773 Å) is longer than that found in the monobridged species; the valence angles are small due to the quasicyclic constraint (S-Al-H = 90.6° and Al-S-Al = 63.9°, Table 3). The terminal Al–H bond (1.555 Å) lies within the range of values found for the other geometries.

Neither of the two bridged structures **7** or **8** fits the experimental findings for these systems. This is not surprising since there are no hydrogen atoms directly bound to the aluminum atoms in the experimentally synthesized molecule. The carbon atoms bound to aluminum are probably less able than hydrogen to bridge the two aluminum atoms. This should explain why the experimental structure more closely resembles the planar C_{2v} structure (which is less than 3 kcal mol^{-1} higher in energy) than the bridged structures.

$H_2B\text{-}S\text{-}BH_2$: The results obtained for this species are listed in Table 4. They are very similar to those obtained for $H_2Al\text{-}S\text{-}AlH_2$: three minima and three nth order saddle points are found on the PES. The D_{2d} geometry is a second-order saddle point, and two bridged minima are found. In this case, the planar C_{2v} structure is the absolute minimum, and the monobridged minimum lies only 0.4 kcal mol^{-1} above it. Except for these two minima, the energetic ordering of the extrema is as for the aluminum species, although the energy differences are larger for boron compounds.

Discussion

The results obtained are almost independent of the calculation level. For each calculated structure, the energy ordering is the same at both MP2 and MP4/MP2 levels, and the relative energies are the same within 0.5 kcal mol^{-1}, except for the $H_2B\text{-}S\text{-}BH_2$ dibridged structure, for which the MP4/MP2 relative energy is 1.8 kcal mol^{-1} higher than the MP2 energy. This consistency of the results means that the computational level is adequate for these systems. Two features of these molecules are discussed in the following: bending and conjugation.

Bending in $H_2X\text{-}Y\text{-}XH_2$ species: The bending ability of these molecules is reflected in the $D_{2h} \rightarrow$ planar C_{2v} interconversion. The energy differences are reported in Table 5. In each case, this motion stabilizes the compound.

Table 5. Energy differences (in kcal mol^{-1}) between D_{2h} and C_{2v} structures and XYX bending angles (in °) in C_{2v} geometry for $H_2X\text{-}Y\text{-}XH_2$.

	$H_2B\text{-}O\text{-}BH_2$	$H_2Al\text{-}O\text{-}AlH_2$	$H_2Al\text{-}S\text{-}AlH_2$	$H_2B\text{-}S\text{-}BH_2$
$E(D_{2h}) - E(C_{2v})$	11.3	0.01	14.5	44.4
X-Y-X angle	123.0	169.9	104.9	102.4

Table 4. Geometrical parameters (Å and °) and relative energies (kcal mol^{-1}) of the optimized extrema of $H_2B\text{-}S\text{-}BH_2$ system. The planar C_{2v} absolute energies (in a.u.) are −449.57383 (MP2) and −449.62693 (MP4/MP2).

	D_{2h}	D_{2d}	C_{2v} planar	C_{2v} butterfly	C_s monobridged	C_{2v} dibridged
S–B1	1.807	1.760	1.802	1.843	1.703	1.871
S–B2	–	–	–	–	1.943	–
B1–H1	1.186	1.184	1.187	1.189	1.312	1.364
B1–H2	–	–	1.189	–	1.181	1.178
B2–H3	–	–	–	–	1.190	–
B-S-B	180.0	180.0	102.4	91.1	62.2	50.6
S-B1-H1	117.7	116.8	120.2	119.4	111.8	99.4
S-B1-H2	–	–	117.1	–	139.6	138.5
S-B2-H3	–	–	–	–	114.8	–
B1-S-B2-H3	–	–	0.0	91.0	105.7	42.6
type	3-SP	2-SP	min	2-SP	min	min
ΔE (MP2)	44.3	28.5	0.0	25.9	−0.3	17.3
ΔE (MP4)	44.4	28.2	0.0	26.1	0.4	19.1

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The calculated stabilization energy upon bending show two tendencies: a) it is larger for S than for O, and b) it is larger for boron than for aluminum compounds. Thus, it is approximately zero for $H_2Al\text{-}O\text{-}AlH_2$ and rather large for $H_2B\text{-}S\text{-}BH_2$ (44.3 kcal mol^{-1}). The greater ability of boron to form bent structures compared to aluminum compounds is difficult to explain. It may originate from the electronegativity difference between boron and aluminum or from the lengthening of Al–Y bonds with respect to B–Y bonds. Both these factors may play a role, and we did not find a satisfactory explanation for this difference.

The difference between sulfur and oxygen is more easily understood. The stabilization upon bending is due to the rehybridization of the central atom σ lone pair by mixing with the σ* orbital in the linear geometry (Figure 1). Since oxygen is more electronegative than sulfur, its lone pair is lower in energy. The energy gap to the antibonding orbital is then greater in the oxygen compounds than in the sulfur compounds. Thus the sulfur systems will be more bent than their oxygen analogues (Table 5). This difference between divalent sulfur and oxygen species is well known: for instance, H_2S is more strongly bent (H-S-H = 92.1°) than H_2O (H-O-H = 104.5°), and the same holds true for methylated compounds (C-S-C = 105° in Me_2S and C-O-C = 111° in Me_2O). The reluctance of sulfur to form linear structures is further illustrated by considering the $D_{2h} \rightarrow$ butterfly C_{2v} deformation (Scheme 3). For $H_2X\text{-}S\text{-}XH_2$, it stabilizes the compound by 6.7 kcal mol^{-1} (X = Al, Table 3) and 18.3 kcal mol^{-1} (X = B, Table 4), but is destabilizing in both oxygen-based systems.

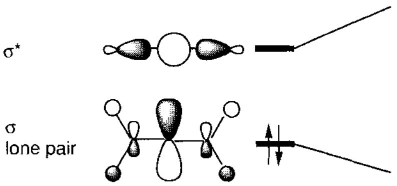

Figure 1. Schematic evolution of the in-plane Y lone pair of $H_2X\text{-}Y\text{-}XH_2$ species upon bending.

Scheme 3. The $D_{2h} \rightarrow$ butterfly C_{2v} deformation in $H_2X\text{-}S\text{-}XH_2$.

Starting from D_{2d} geometry leads to similar results: bending results in destabilization for oxygen as central atom, and stabilization for sulfur by 15.7 kcal mol^{-1} (X = Al, Table 3) and 27.8 kcal mol^{-1} (X = B, Table 4). As expected, the stabilization for this $D_{2d} \rightarrow C_s$ motion is greater than for the $D_{2h} \rightarrow$ butterfly C_{2v} deformation, since the lone pair is less strongly destabilized in the latter case.[1]

Conjugation in $H_2X\text{-}Y\text{-}XH_2$ species: The importance of conjugation between the Y lone pair and the vacant p orbital on the two XH_2 fragments is still under debate.[7, 8] According to Uhl et al.,[2] this conjugation should be the origin of the observed D_{2h} structure in $R_2Al\text{-}O\text{-}AlR_2$. In order to discuss whether this conjugation is at work in the studied systems, we shall focus first on the $D_{2h} \rightarrow D_{2d}$ interconversion. In the D_{2h} geometry, only the Y π lone pair is stabilized by conjugation with the two XH_2 vacant p orbitals, whereas both lone pairs are stabilized in the D_{2d} structure (Figure 2). The results for the various systems are summarized in Table 6.

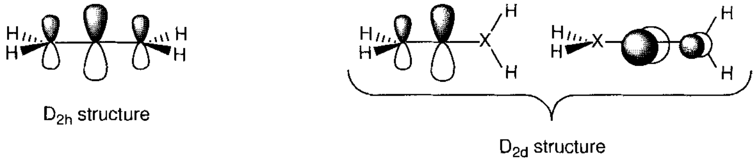

Figure 2. Stabilization of the lone pairs of Y in the D_{2h} and D_{2d} structures of $H_2X\text{-}Y\text{-}XH_2$.

Table 6. Energy differences (in kcal mol^{-1}) between the D_{2h} and D_{2d} structures for $H_2X\text{-}Y\text{-}XH_2$.

	$H_2B\text{-}O\text{-}BH_2$	$H_2Al\text{-}O\text{-}AlH_2$	$H_2Al\text{-}S\text{-}AlH_2$	$H_2B\text{-}S\text{-}BH_2$
$E(D_{2h}) - E(D_{2d})$	10.7	1.4	2.0	16.2

In each case, the D_{2d} structure is more stable than the D_{2h} structure; this indicates that the two conjugative interactions in D_{2d} geometry are more strongly stabilizing than the single interaction in the D_{2h} structure. As expected, the values are smaller than that found in allene (76 kcal mol^{-1}).[9] More important is the fact that this energy difference is significantly smaller for aluminum (1–2 kcal mol^{-1}) than for boron (> 10 kcal mol^{-1}). It can be concluded that the BH_2 fragment conjugates with oxygen or sulfur more strongly than the AlH_2 fragment. This difference in behavior may originate, at least in part, from the electronegativity difference [χ(Al) = 1.6 and χ(B) = 2.0 on Pauling's scale], which indicates that boron conjugates more efficiently than aluminum with electronegative atoms such as sulfur [χ(S) = 2.7] or oxygen [χ(O) = 3.2]. In addition, the aluminum 3p orbitals are more diffuse than the boron 2p orbitals, and this leads to poorer overlap with oxygen or sulfur orbitals. This last point has already been put forward to explain why second-row atoms form rather weak π bonds.[10] It can then be concluded that the energetic differences between the two geometries are noticeable only in the BH_2 case. For $H_2Al\text{-}Y\text{-}AlH_2$ (Y = O, S) systems, the rotational barrier is weak. As a consequence (see preceding section), the experimentally observed geometry of $R_2Al\text{-}O\text{-}AlR_2$ does not correspond to the lowest-energy geometry of the unsubstituted species.

Model systems study: In order to obtain a more detailed description of these conjugative interactions, we performed additional calculations on model systems $H_2X\text{-}YH$ (X = Al, B; Y = O, S). The calculation level is the same as before (optimization and characterization of the extrema at the MP2/6-311G** level and subsequent MP4/6-311G** calculation on the optimized geometries). In each case, a planar and a perpendicular structure were fully optimized. Regardless of the nature of the X and Y atoms, the planar and perpendicular structures are a minimum and a transition state, respectively. Therefore, the rotational barrier (planar → perpendicular) may be a good indication of the conjugation between X and Y atoms. The energetical results are given in Table 7.

Table 7. Rotational barrier (in kcalmol^{-1}) for H_2X–YH (X = Al, B; Y = O, S).

	H_2Al-OH	H_2B-OH	H_2Al-SH	H_2B-SH
ΔE (MP2)	3.6	16.9	7.6	20.5
ΔE (MP4/MP2)	3.9	17.1	7.8	20.6

As in the H_2X-Y-XH_2 study, both sets of results are nearly identical; the rotational barrier differs by less than 0.3 kcalmol^{-1} on changing the computational level. A weak rotational barrier (3.9 kcalmol^{-1}) is found for H_2Al–OH. It increases slightly to 7.8 kcalmol^{-1} for H_2Al–SH, and becomes significant in H_2B–OH (17.1 kcalmol^{-1}) and H_2B–SH (20.6 kcalmol^{-1}). These calculations confirm our results: conjugation increases in the order Al–O < Al–S < B–O < B–S (cf. Tables 6 and 7). It is weak when aluminum is involved, especially with oxygen, and becomes important for boron with both sulfur and oxygen. For boron compounds, our results agree well with those of Ashby and Sheshtawy,[11] who find slightly smaller rotational barriers for boron systems (14.3 and 18.0 kcalmol^{-1} for H_2B–OH and H_2B–SH, respectively, at the HF/6-31G* level). Previous calculations by Gropen et al.[12] gave very similar results for H_2B–SH (19.5 kcalmol^{-1}). Our results are also consistent with those of Zyubina and Charkin.[13] For aluminum compounds, our results agree well with those of Fink et al.,[8] who found rotational barriers of 3.5 and 7.3 kcalmol^{-1} for H_2Al–OH and H_2Al–SH, respectively. However, our conclusion of a small conjugation between Al and O is at variance with that of Barron et al.,[14] who found a substantial conjugation with oxygen in three- and four-coordinate aluminum compounds. In this case, the discrepancy may arise from the fact that the authors only discussed the geometrical features of some aluminoxy compounds.[15]

Conclusion

The geometrical and electronic structures of H_2X-Y-XH_2 (X = Al, B; Y = O, S) systems have been studied by means of ab initio calculations. The H_2Al-O-AlH_2 molecule has D_{2d} symmetry, and the energy difference to the D_{2h} structure is very small. When the central atom is sulfur, we find a strongly bent minimum in both cases (X = Al or B). In H_2Al-S-AlH_2, the absolute minimum is a hydrogen-bridged structure, which should be experimentally characterizable provided that at least one hydrogen is directly bound to the aluminum atom. Finally, calculations on model structures indicate that the rotational barrier is large in boron compounds and becomes weaker in H_2Al–SH. It is small in H_2Al–OH, a result that explains the very small energy difference between the D_{2h} and D_{2d} geometries in H_2Al-O-AlH_2.

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[1] F. Gatti, I. Demachy, N. Berthe-Gaujac, F. Volatron, *Chem. Phys. Lett.* **1995**, *70*, 2140.

[2] W. Uhl, M. Koch, W. Hiller, M. Heckel, *Angew. Chem.* **1995**, *107*, 1122; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 989.

[3] W. Uhl, A. Vester, W. Hiller, *J. Organomet. Chem.* **1993**, *443*, 9.

[4] H. Vahrenkamp, *J. Organomet. Chem.* **1971**, *28*, 167.

[5] Gaussian 92/DFT, Revision F.4, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. J. Johnson, M. W. Wong, J. B. Foresman, M. A. Robb, M. Head-Gordon, E. S. Reploge, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart, J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1993.

[6] In addition, these two parameters (Al-S-Al angle and Tw) are strongly coupled, and the associated PES is very flat: we found another minimum for **9** located 0.3 kcalmol^{-1} above our absolute minimum and corresponding to a larger angle at sulfur (Al-S-Al = 111.7°), whereas the rotation of the aluminum coordination planes is almost zero (Tw = 0.6°).

[7] See, for instance, M. A. Petrie, M. M. Olmstead, P. P. Power, *J. Am. Chem. Soc.* **1991**, *113*, 8704. R. J. Wehmschulte, K. Ruhlandt-Senge, P. P. Power, *Inorg. Chem.* **1995**, *34*, 2593.

[8] W. H. Fink, P. P. Power, T. L. Allen, *Inorg. Chem.* **1997**, *36*, 1431.

[9] R. Seeger, R. Krishnan, J. A. Pople, P. von R. Schleyer, *J. Am. Chem. Soc.* **1977**, *99*, 7103.

[10] W. Kutzelnigg, *Angew. Chem.* **1984**, *96*, 262; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 272.

[11] M. T. Ashby, N. A. Sheshtawy, *Organometallics* **1994**, *13*, 236.

[12] O. Gropen, E. Wisloff Nilssen, H. M. Seip, *J. Mol. Struct.* **1974**, *23*, 289.

[13] T. S. Zyubina, O. N. Charkin, *Russ. J. Inorg. Chem.* **1992**, *37*, 434.

[14] A. R. Barron, K. D. Dobbs, M. M. Francl, *J. Amer. Chem. Soc.* **1991**, *113*, 39.

[15] The geometrical consequences of conjugation and the relationship between conjugation and rotational barrier in these compounds need to be carefully analyzed and will be presented elsewhere: I. Demachy, F. Volatron, unpublished results