π-Bond vs. Agostic Interaction in Three-Coordinated Alkoxy and Thiolate Derivatives of Aluminium, Boron and Cationic Carbon – An ab initio Study of H_2X–YR Systems (X = Al, B, C^+; Y = O, S; R = H, CH_3)

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Rotational barriers and π conjugation effects have been studied in H_2X–YR systems (X = Al, B; Y = O, S; R = H, CH_3) by means of ab initio calculations at the MP4/6–311G**//MP2/6–311G** level. In non-substituted systems H_2X–YH, it is shown that the rotational barrier depends on three factors: (i) π conjugation strength between the X vacant p orbital and the Y p-lone pair; (ii) the opening ability of the Y-valence angle and (iii) a possible direct interaction between X and the Y hydrogen substituent. The conjugation stabilization has been estimated through Valence Bond calculations and is found to decrease in the order BO (22.6 kcal/mol), BS (16.6 kcal/mol), AlO (10.2 kcal/mol), and AlS (8.1 kcal/mol). Study of the methylated systems confirm the results found in unsubstituted species. The most important feature is the location of a deconjugated secondary minimum for H_2B–SCH_3 species. An acute B–S–C angle (69.6°) is found, thus evidencing a direct H···B agostic interaction with a four-membered (BSCH) heterocycle. To further evidence our analysis, additional calculations have been performed on carbocationic species H_2C^+–YR (Y = O, S; R = H, CH_3) for which the H_2C^+ moiety is a strong π acceptor. As expected, the C^+–O and C^+–S conjugation are strong (about 60 kcal/mol). Only two minima have been located for the H_2C^+–OCH_3 species. In the sulfur case, the Potential Energy Surface (PES) is more complicated and six stationary points have been characterized. A strong agostic interaction is found for a secondary deconjugated minimum for which an hydrogen symmetrically bridges the two carbon atoms. A schematic energy profile connecting the various extrema is given for this cationic species.

Introduction

The question of π conjugation between Al and O in alkoxy derivative of aluminium has not received a definite answer until now although much theoretical and experimental work has been devoted to the problem. Following Brothers and Powell,[1] the conjugation in 3-coordinated species is expected to be weak: for instance, the rotational barrier around the Al−O bond has been shown to have an upper limit of 8 kcal/mol. In addition, the Al−O bond length in 3-coordinated species is found to decrease in the series $R_2Al{-}OR'$, $RAl(OR')_2$, $Al(OR')_3$, a trend which seems to be in contradiction with a strong π Al−O bonding. Different conclusions concerning the π Al−O bonding have been reached by Barron:[2] a noticeable π Al−O conjugation should be responsible for short Al−O bond lengths in 3-coordinated aluminium alkoxides. The lack of rotational barrier in these compounds is expected to have the same origin as in transition metal alkoxides where no rotational barrier is found although π-bonding in these complexes is not doubtful. In addition, similar π Al−O conjugation is also proposed in 4-coordinated alkoxy aluminium compounds.

Theoretical calculations by Barron, Dobbs and Francl[3] indicate that π Al−O conjugation in 3- and 4- coordinated systems may explain the geometrical distortions observed in these compounds. On the opposite, recent calculations by Fink, Power and Allen[4] give a low rotational barrier in both model compounds, $H_2Al{-}OH$ (3.5 kcal/mol) and $(CH_3)_2Al{-}OCH_3$ (1.7 kcal/mol). However, large geometric distortions in the deconjugated conformer do not allow a definite conclusion regarding the π bonding in these 3-coordinated aluminium alkoxides.

To shed some light on this problem, we have undertaken ab initio calculations on $H_2Al{-}OR$ model molecules (R = H, CH_3) in order to get a more detailed description of Al−O π bonding; the results are compared to those obtained when oxygen is replaced by sulfur. In order to calibrate our results, additional calculations where performed on boron systems $H_2B{-}YR$ (Y = O, S; R = H, CH_3) for which B−O B−S π conjugation is well etablished. These calculations are expected to check our previous conclusions for $H_2X{-}Y{-}XH_2$ species[5] (X = Al, B; Y = O, S) where it was found that X−Y π conjugation is a determining factor for understanding the geometrical structure of these compounds.

The results will be presented as follows: first, calculations on model species $H_2X{-}YH$ at a conventional MO level of theory will be followed by Valence-Bond (VB) calculations. Secondly, the effect of Y substitution by a methyl group will be studied. Finally, the conclusions drawn from these

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two sets of results will be checked with systems in which X is replaced by a strong π acceptor: C^+. Both model systems H_2C-YH^+ and $H_2X-YCH_3{}^+$ (Y = O, S) will be analyzed.

Method of Calculation

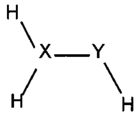
The 6−311G** basis set was used throughout the paper. All geometries were optimized at the MP2 level with the help of an analytical gradient method. Characterization of the extrema were made by analytical frequencies calculations at this level. The stationary points may be minima (Min, no imaginary frequency) or transition states (TS, only one imaginary frequency) or *n*-order saddle points (*n*-SP, *n* imaginary frequencies). In this last case ($n > 1$), the stationary point has no chemical significance. Subsequent calculation of the correlation energy was made at the MP4(SDTQ) level on the geometries optimized at the MP2 level. Our level of calculation is therefore MP4/6−311G**//MP2/6−311G**. In the simplest model systems (H_2X-YH) we have tested the influence of improving the correlation energy by optimizing the geometries at the MP4 level. The GAUSSIAN 92 set of programs[6] was used. Valence-Bond calculations were made with the help of the Turtle program.[7]

Results

A. Unsubstituted Systems

Energetical Analysis

For each system (referred as BS, BO, AlS and AlO in the following), three geometries [planar (**1**), perpendicular (**2**) and linear (**3**)] have been optimized and fully characterized by analytical frequencies calculations.



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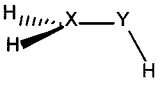

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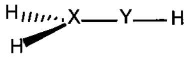

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All twelve structures are found to be stationary points on the various potential energy surfaces. In each case, the planar geometry is a real minimum while the perpendicular geometry is a transition state (TS, one imaginary frequency). Following the transition vector associated with the imaginary frequency leads to the planar minimum. The linear structure is found to be a second-order saddle point (2-SP, two imaginary frequencies) and the two associated transition vectors lead to the planar minimum or to the perpendicular transition state. The geometrical parameters of the optimized structures (MP2/6−311G** level) are given in Figure 1 and the corresponding relative energies in Table 1.

Figure 1. Geometrical optimized parameters of the H_2X-YH species (bonds in A and angles in degrees)

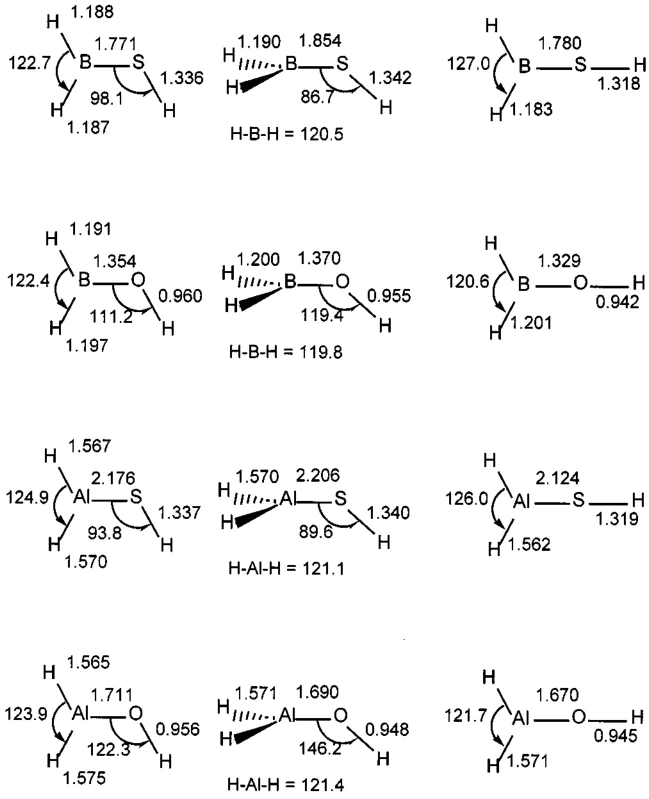


Table 1. Relative energies (in kcal/mol) of the three geometries for each species at the MP2/MP2 level of calculation.

	BS	BO	AlS	AlO
planar	0	0	0	0
perpendicular	20.5	16.9	7.6	3.6
linear	54.4	20.5	31.7	3.9

All the extrema have been recalculated at the MP4 level at the MP2 optimized geometries. The relative energies at the MP4/6−311G**//MP2/6−311G** level are given in Table 2.

Table 2. Relative energies (in kcal/mol) of the three geometries for each species at the MP4/MP2 level of calculation

	BS	BO	AlS	AlO
planar	0	0	0	0
perpendicular	20.6	17.1	7.8	3.9
linear	54.4	21.0	32.0	4.2

The results at MP2/MP2 and MP4/MP2 levels are very similar: improving the correlation energy calculation increases the energy differences by less than 0.5 kcal/mol. However, to be sure that improvement of the correlation energy calculation does not affect the optimized parameters, the planar and perpendicular geometries have been reoptimized at the MP4 level. The rotational barriers

[E(perp)−E(planar)] are exactly the same as that found at the MP4/MP2 level. In addition, the geometrical changes are less than 0.007 A for bond lengths and 1.5° for bond angles (except for the Al−O−H bond angle whose change is 3° in the perpendicular structure). Therefore, our calculation level can be considered as satisfactory. Note finally that our results agree well with those previously published: 18.0, 14.3, 7.3, and 3.5 kcal/mol for BS, BO,[8] AlS, and AlO[4] systems respectively. Similar values (19, 14, 8, and 4 kcal/mol) have been obtained by Zyubina and Charkin.[9]

The evolution of the rotational barrier should well illustrate the basic concept of conjugation in such compounds. In the planar structure, the vacant p orbital on aluminium or boron conjugates with the π-doubly occupied lone pair of sulfur or oxygen, leading to a 2-electron stabilization. A 90° rotation of the Y−H group destroy this conjugation and the rotational barrier could be a measure of the strength of the π X−Y bond. It is indeed found that the rotational barrier is very low when X and Y electronegativities are different (X = Al and Y = O) and becomes higher as the X and Y electronegativities become closer. As a result, the highest barrier is found when X = B and Y = S. In fact this interpretation of the barrier evolution is somewhat oversimplified as shown below.

Geometrical Analysis

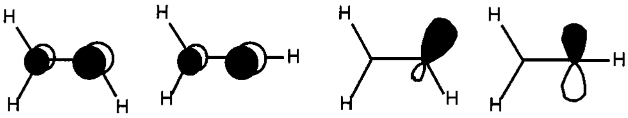
The X−Y bond lengths and X−Y−H angles for each system are reported in Table 3. To our knowledge only the unsubstituted H_2BOH species has been experimentally characterized (Microwave Spectrum).[10] Our optimized parameters (B−O = 1.354 A; O−H = 0.960 A; B−O−H = 111.2°; O−B−Hc = 120.9°; O−B−Ht = 116.7°; BHc = 1.197 A; BHt = 1.191 A) are in excellent agreement with the experimental ones (B−O = 1.352 A; O−H = 0.967 A; B−O−H = 112.0°; O−B−Hc = 121.8°; O−B−Ht = 117.2°, the B−H bond length being assumed to be 1.200 A).

Table 3. X−Y bond lengths (in Å) and X−Y−H bond angles (in degrees) in the various optimized extrema

X−Y Bond lengths	BS	BO	AlS	AlO
planar	1.771	1.354	2.176	1.711
perpendicular	1.854	1.370	2.206	1.690
linear	1.780	1.329	2.124	1.670
X−Y−H Bond angles				
planar	98.1	111.2	93.8	122.3
perpendicular	86.7	119.4	89.6	146.2

Let us first compare the X−Y bond lengths in planar and linear structures: in both structures π conjugation is at work between the p orbitals of X and Y (Scheme 1).

Scheme 1

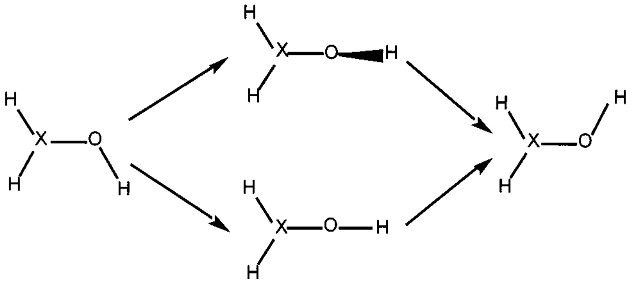


The main electronic difference between the two geometries comes from the interaction of the second Y lone pair with the H_2X moiety. The lone pair is expected to be strongly hybridized in the planar structure while it is a pure p orbital in the linear geometry (Scheme 1). In each case except H_2BSH, the X−Y bond length shortens from the planar to the linear geometry (Table 3). This shortening may come from a negative hyperconjugation interaction between this Y lone pair and the symmetry adapted H_2X antibonding orbitals (see below).

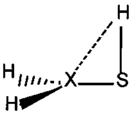
The geometrical evolutions from planar to perpendicular geometries are different for oxygen and sulfur systems and will be discussed separately. In *oxygen compounds*, the perpendicular structure is reminiscent of the linear geometry. The X−Y−H angle opens when going from the planar to the perpendicular geometries (by 8.2 and 23.9° in boron and aluminium cases respectively) which allows the dehybridization of the in-plane lone pair and therefore ensures a better conjugation with the p vacant orbital on the H_2X moiety. This effect is rather small in the boron compound and the BO bond length increases upon OH rotation (from 1.354 to 1.370 A). On the other hand, the Al−O−H angle dramatically increases by 23.9° upon rotation and that leads to a strong residual conjugation in the perpendicular geometry. This is illustrated by an Al−O bond length (1.690 A) which is intermediate between those of the planar (1.711 A) and linear (1.670 A) geometries. Consequently, the rotational barrier in H_2AlOH is not a measure of the π Al−O conjugation since a noticeable conjugation still remains in the perpendicular structure. A similar interaction (although attenuated) exists in H_2BOH, as previously pointed out by Ashby and Sheshtawy;[8] following these authors, the hydroxy group should be considered as a double-faced π-donor. Thus, the oxygen's ability to conjugate in both the planar and perpendicular geometries is further illustrated by the small energy differences between the perpendicular and linear geometries: it is 3.9 and only 0.3 kcal/mol for H_2BOH and H_2AlOH respectively (Table 2). These low values indicate that the energetical cost of dehybridization of the oxygen second lone pair is almost compensated by the additional conjugation interaction. This result gives an insight in the mechanism of aluminum alkoxides isomerization. Since the two (perpendicular and linear) structures are almost isoenergetic, this reaction may proceed by rotation or linearization of the alkoxide moiety (Scheme 2). As previously noted by Ashby,[8] the competition between the two mechanisms should be in favor the intermediacy of a perpendicular structure for H_2BOH because of the larger energy difference.

Fo the *sulfur derivatives*, linearization of the X−S−H arrangment costs much more energy (54.4 and 32.0 kcal/mol for H_2BSH and H_2AlSH respectively, Table 2). As a result, no dehybridization occurs in the perpendicular structure that is well illustrated by an X−S−H angle which is roughly equal to 90° in both planar and perpendicular geometries. The π residual conjugation is expected to be small in the rotated structure and, consequently, both Al−S and B−S bond lengths increase upon rotation (Table 3). A surprising

Scheme 2



point is the decrease of the X−S−H angle in the planar → perpendicular interconversion: this variation is small in H_2AlSH (4.2°) and becomes rather large (11.4°) in H_2BSH. It allows a shortening of the X···H distance (**4**) and we attribute this geometrical change (which is opposite to that found in oxygenated systems) to a direct interaction between the H_2X p vacant orbital and the hydrogen atom. Such interactions are well-known in organometallic chemistry and have been called "agostic" by Brookhart and Green.[11] Similar interactions will be analyzed in more details in the study of substituted species. Note that, following Ashby,[8] this angle decrease may be attributed to a relief of Pauli repulsion.



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π-Conjugation in H_2X-YH Species?

Since the rotational barrier cannot be a good measure of X−Y conjugation in these species, additional VB calculations have been performed on planar and linear structures at the MP2 optimized geometries. In a first step, the total energy is recalculated in a "normal" manner i.e. all the interaction are taken into account. In a second step, the π interaction in both geometries is set to zero by forbiding any delocalization of the π lone pair of the Y atom on the XH_2 moiety in both planar and linear geometries. The energy differences between the two sets of results give a reasonable estimation of the π interaction in those systems. (Note that a more accurate calculation of the conjugation interaction should require a full geometry reoptimization in the deconjugated species that is not possible with our VB program.) Similar calculations have been performed in the linear geometry by cancelling the delocalization of the in-plane Y p-lone pair in order to get a measure of the hyperconjugation (HC) with the XH_2 moiety. Finally, in the linear geometry, both conjugation and hyperconjugation have been cancelled. The results of these calculations are given in Table 4 for each system under study.

For each species the conjugation stabilizations are not identical for the planar and linear geometries since the X−Y bond lengths are not the same in both geometries (Table 3). However the two sets of values are rather close to each others and the results obtained in the planar geometry are expected to correctly reflect the stabilization due to conjugation in H_2X-YH species. The lowest value (8.1 kcal/mol) is found in the Al−S case, confirming that the π bonds are weak between two second-row atoms.[12] The X−Y conjugation is still weak in H_2Al-OH (10.2 kcal/mol) and becomes stronger in the boron compounds (16.6 and 22.6 kcal/mol for H_2B-SH and H_2B-OH respectively, Table 4). As expected the highest stabilization is found for H_2B-OH in which conjugation develops between two first-row atoms.

Table 4. Stabilization (in kcal/mol) due to conjugation (planar and linear structures) and to hyperconjugation (linear structure only)

	BS	BO	AlS	AlO
planar conjugation	16.6	22.6	8.1	10.2
linear conjugation	19.0	21.1	9.6	9.6
linear HC	7.0	7.9	6.0	6.6
linear conjugation + HC	27.0	30.6	16.6	17.3

In the four linear structures, the hyperconjugation of the in-plane Y lone pair with the H_2X moiety is found to be stabilizing and almost constant (between 6 and 8 kcal/mol) whatever the nature of the X and Y atoms. Finally, it is worth noting that the two contributions (conjugation and hyperconjugation) are fairly additive in the linear structure: adding the stabilization due to conjugation (entrie 2) and to hyperconjugation (entrie 3) in Table 4, gives (within about 2 kcal/mol) the total stabilization (entrie 4) obtained when both lone pairs are allowed to delocalize.

In Table 5 are brought together the values of conjugation stabilization (Table 4) and rotational barrier (energy difference between planar and perpendicular geometries, Table 2).

Table 5. Conjugation stabilization and rotational barrier for the various systems; all quantities are in kcal/mol.

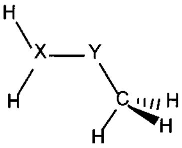
	BS	BO	AlS	AlO
planar conjugation	16.6	22.6	8.1	10.2
rotational barrier	20.6	17.1	7.8	3.9

The values are reasonably close in the sulfur-substituted systems but differ notably in the oxygenated cases. In these cases, the rotational barrier is systematically lower than the conjugation interaction (by 5.5 and 6.3 kcal/mol in boron and aluminium cases respectively) which indicates the reminiscent conjugation in the rotated structure as shown above. The two values notably differ in the H_2Al-OH case where the Al−O−H angle dramatically increases in the perpendicular geometry (Table 3).

B. Methyl-Substituted Systems

Energetical Analysis

Calculations on substituted systems H_2X-YCH_3 have been made in order to get more detailed informations on the various interactions in these species. As shown previously,[13] the eclipsed conformer (**5**) is the most stable in the planar geometry. Two rotamers have been fully optimized and characterized in the perpendicular geometry. In the first one (**6**), a CH methyl bond eclipses the X−Y bond while in the second one (**7**), the CH methyl bonds are staggered with respect to the X−Y bond. The energetical results are reported in Table 6 together with the characterization of the various structures. The rotational energy barriers in unsubstituted species have also been reported for sake of comparison.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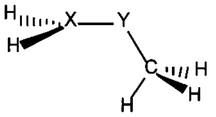
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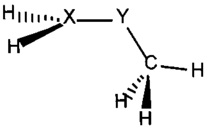
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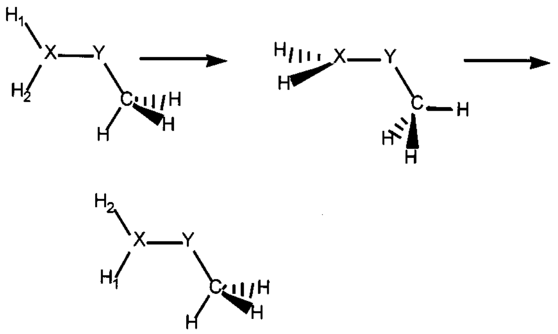
Table 6. Relative energies (in kcal/mol) at the MP4/MP2 level of the planar (**5**) and perpendicular (**6** and **7**) geometries in H_2X-YCH_3 species; the rotational barrier in unsubstituted species is also given for sake or comparison

	BS	BO	AlS	AlO
planar **5**	0 (Min)	0 (Min)	0 (Min)	0 (Min)
perpendicular **6**	22.2 (Min)	18.6 (2-SP)	9.2 (2-SP)	-[a]
perpendicular **7**	22.3 (TS)	17.2 (TS)	8.7 (TS)	3.0 (TS)
unsubst. R.B.	20.6	17.1	7.8	3.9

[a] No stationary point found, see text.

All the planar structures (**5**) are found to be real minima on the Potential Energy Surface (PES). Staggered perpendicular geometries (**7**) are found to be transition states (one imaginary frequency) and we have verified that they belong to the isomerization reaction path depicted in Scheme 3.

Scheme 3



The rotational barriers in the methylated species are therefore equal to the energies differences between structures **5** and **7**. They are found to be very close to that of the hydrogenated systems: for each molecule, the barrier in methylated and unsubstituted systems are the same within 1.7 kcal/mol (Table 6). It is worth to compare our calculated barriers on methyl-substituted species to those experimentally determined. In BS and BO cases, the theoretical values (22.3 and 17.2 kcal/mol) are larger than the experimental values (18.2−19.7 kcal/mol (BS)[14][15] and 11.2−13.9 kcal/mol (BO)[15][16]. The presence of bulky substituents may well be at the origin of this discrepancy since steric repulsion should be smaller in the perpendicular structure that lowers the rotational barrier. In aluminium compounds, there are few experimentally determined values: it is found to be less than 8 kcal/mol in Al−O case[17] and between 8 and 9 kcal/mol in AlS case.[18] (This last value is obtained in bisthiolate derivative of aluminium. To our knowledge, no data on monosubstituted compound are available). Both these values are in agreement with our theoretical values.

In the perpendicular geometries, the methyl group bonded to the Y atom does not seem to exhibit strong conformational preference: the energy differences between structures **6** (eclipsed) and **7** (staggered) are about 0.5 kcal/mol for BS, and AlS and increases up to 1.4 kcal/mol in H_2B-OCH_3 system. However these small energy differences originate from very different interaction as shown below. More puzzling, the characterization of this structure depends on the nature of X and Y atoms. In BO and AlS cases, the eclipsed geometries are 2-order saddle points as expected. The transition vector associated with one imaginary frequency essentially develops on the twist angle between H_2X and XYC planes and corresponds to the **6** → **5** motion. The second transition vector involves the in-block rotation of the methyl substituent and corresponds to the **6** → **7** motion. For Al−O, we did not find any stationary point corresponding to the eclipsed perpendicular conformer **6**. Optimization of this geometry leads to an opening of the Al−O−C angle beyond 180° and this structure collapses to the conformer **7** which is a transition state located 3.0 kcal/mol above the planar structure. More puzzling is the fact that in BS case, the eclipsed perpendicular structure is found to be a secondary minimum on the PES.

Geometrical Analysis

The main optimized geometrical parameters are given in Figure 2. For each structure, the X−Y bond length is slightly shorter than that found in the unsubstituted species: for instance, B−O = 1.345 A in H_2B-OCH_3 and 1.354 A in H_2B-OH for the planar structures. Our optimized parameters (X−Y and Y−C bond lengths and X−Y−C angles are in reasonable agreement (Table 7) with the experimental data available on monosubstituted compounds (except in Al−S case where only bis-thiolate derivative has been characterized). It should be noted that we find a large X−Y−C angle only in Al−O−C case, in accordance with the experimental data.

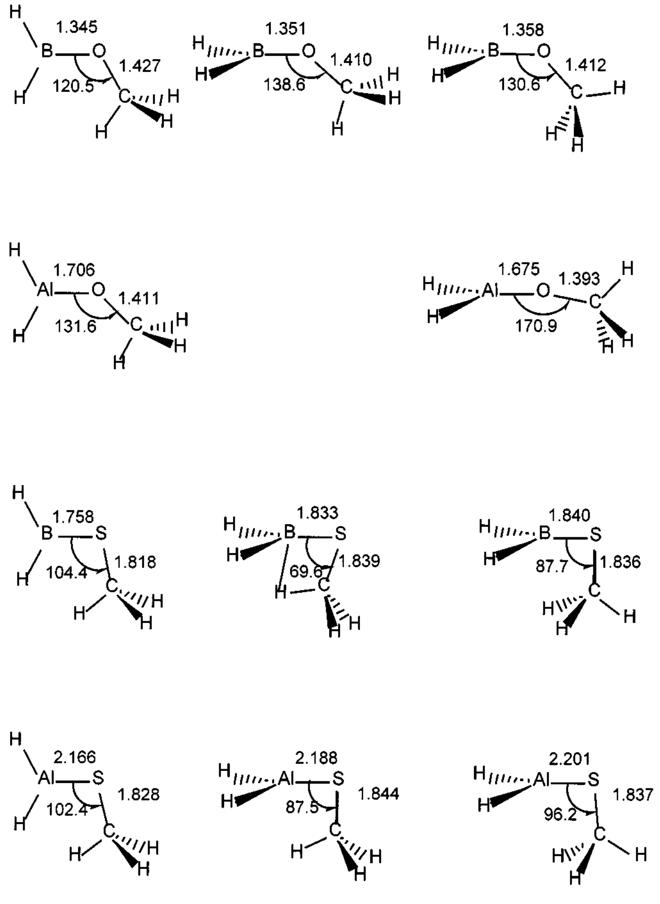
Partial deconjugation (**5** → **6** or **7**) leads in each case to a lengthening of the X−Y bond, except in $H_2Al-OCH_3$. In this case, the shortening of the Al−O bond length may be explained (as in the unsubstituted species) by the quasi-linear geometry of the rotated structure (Al−O−C = 170.9°, Figure 2).

Table 7. Comparison between theoretical and experimental parameters determined on monosubstituted species; bonds are in A and angles in degrees

B–S	S–C	B–S–C	ref.
1.758	1.818	104.4	this work
1.787	1.815	109.8	[8]
1.790	1.773	107.0	[19]
1.779	1.825	107.2	[20]
B–O	O–C	B–O–C	ref.
1.345	1.427	120.5	this work
1.352	1.438	123.6	[8]
1.361	1.421	124.4	[21]
Al–S	S–C	Al–S–C	ref.
2.166	1.828	102.4	this work
2.184–2.197	1.803–1.814	95.9–102.7	[18][a]
Al–O	O–C	Al–O–C	ref.
1.706	1.411	131.6	this work
1.709/1.710	–	129.4/135.2	[17]

[a] Bis-thiolate derivative.

Figure 2. Geometrical optimized parameters of the H_2X-YCH_3 species (bonds in A and angles in degrees)



In oxygenated compounds, the 90° rotation of the X–O–C plane relative to the H_2X plane leads to an opening of the oxygen valence angle as already noted in the unsubstituted species. In sulfur compounds, we find a smaller X–S–C angle in perpendicular **7** geometry than in the planar **5** one. The angular variations are in the same range as in unsubstituted species (6.2 vs. 4.2° in Al compounds and 16.7 vs. 11.4° in B compounds).

A dramatic change occurs in H_2B-SCH_3 perpendicular geometry **6**: the B-S-C angle is found to be very acute (69.6°), about 35° smaller than in the planar geometry. This very small sulfur valence angle may be attributed to a direct interaction between the eclipsing methyl hydrogen and the boron atom. A short distance (B···H = 1.764 A) is indeed found and is accompanied with a noticeable lengthening of the C–H bond (C–H = 1.12 A which may be compared to the standard value (1.09 A) found in H_2B-OCH_3). As a result of this stabilizing agostic interaction, the eclipsed geometry **6** is found to be a secondary minimum on the PES. A similar interaction – although attenuated – is found in $H_2Al-SCH_3$: the Al–S–C angle is small (87.5°) and the eclipsing C–H bond lengthens to 1.10 A. However, the Al···H distance remains large (2.50 A) and leads to a rather weak interaction. As a consequence, the eclipsed perpendicular structure **6** is a 2-order saddle point which may be stabilized by a 90° rotation of the methyl group (**6** → **7**). The difference between these two molecules ($H_2Al-SCH_3$ and H_2B-SCH_3) may be attributed to the lower π-acceptor ability of the aluminium relative to the boron due to its lower electronegativity.

In summary of the study of these methylated and hydrogenated systems, the rotational energy barrier in H_2X-YR (R = H, CH_3) depends on three factors: (i) the strength of π-conjugation between X and Y; (ii) the plasticity of the Y valence angle and (iii) possible agostic iteraction with the unsaturated H_2X moiety. Note that a similar direct interaction between the deficient central atom and a non bonded hydrogen has already been shown in aluminium[17][22][23] and gallium[18][22][24][25] derivatives. In order to check these conclusions, we have performed additional calculations on similar systems obtained by taking a strong π-acceptor X atom: C^+.

C. Carbocationic Systems

Unsubstituted Compounds

The unsubstituted cationic species H_2C-OH^+ and H_2C-SH^+ have been fully optimized in planar (**1**), perpendicular (**2**) and linear (**3**) geometries. The energetic results and main optimized parameters are given in Tables 8 and 9. Our optimized parameters are very close to that found by Suarez and Sordo[26] in their recent study of the H_2 elimination from these cations.

Table 8. Relative energies (in kcal/mol, MP4/MP2 level) and characterization of the various extrema for the H_2C-OH^+ and H_2C-SH^+ systems

	1 (planar)	**2** (perpendicular)	**3** (linear)
Y = O	0 (Min)	-[a]	25.4 (TS)
Y = S	0 (Min)	50.3 (Min)	76.3 (2-SP)

[a] No stationary point found.

Since the H_2C^+ moiety is a strong π-acceptor, a strong π conjugation is expected between the C^+ and the Y atoms. VB calculations of the same type as presented before indeed give a C^+-O π-bond strength of 59.5 kcal/mol (planar geo-

Table 9. Main optimized parameters of the two cations H_2C-OH^+ and H_2C-SH^+; bond lengths are in Å and angles in degrees

	CS	CO	COH	CSH
planar	1.617	1.354	114.1	98.0
perpendicular	1.680	–[a]	–[a]	50.3
linear	1.619	1.227		

[a] No stationary point found.

metry) and 57.3 kcal/mol (linear geometry). This π bond is therefore much stronger than that found between B and O (22.6 kcal/mol) or Al and O (10.2 kcal/mol). Similarly, the C^+-S π bond is calculated to be of 59.0 kcal/mol (planar) and 66.6 kcal/mol (linear);[27] as in the oxygen case, it is stronger than B–S (16.6 kcal/mol) or Al–S (8.1 kcal/mol) π bonds (Table 4).

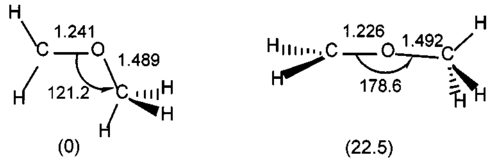
Rotation of the Y–H moiety about the C^+-Y bond destroys this strong conjugation that is energetically much unfavorable. Geometrical deformations therefore occur in order to diminish this energetical cost. In H_2C-OH^+, the C–O–H angle opens up to 180° and the dehybridization of the perpendicular lone pair allows a favorable π interaction. As a result, no stationary point corresponding to a perpendicular geometry is found. The linear structure is then the transition state allowing the isomerization of this species with a 25.4 kcal/mol activation energy (Table 8). In H_2C-SH^+, similar linearization of the C–S–H angle is too much expansive: the linear structure is located 76.3 kcal/mol above the planar geometry. It is a 2-order saddle point, the two transition vectors associated with the imaginary frequencies leading to the planar or perpendicular structures. However, a diminution of the C–S–H angle to 50.3° allows a noticeable interaction between the H atom and the cationic carbon. As a result, the S–H bond lengthens (from 1.346 Å in the planar geometry to 1.519 Å in the perpendicular structure) and the $C^+\cdots H$ distance is only 1.368 Å. This bridged structure is located 50.3 kcal/mol above the planar geometry and is found to be a real minimum (Table 8). We did not try to locate the transition state connecting these two minima. This has been previously done by Suarez and Sordo[26] who found the transition state only 0.2 kcal/mol above the secondary minimum.

Methylated Compounds

The potential energy surfaces associated with the methylated species $H_2C-OCH_3^+$ and $H_2C-SCH_3^+$ have also been investigated. The $H_2C-OCH_3^+$ cation behaves as its unsubstituted analog: the planar structure is found to be a real minimum and no stationary point corresponding to a perpendicular geometry has been found. A quasi-linear (C–O–C = 178.6°) transition state has been located 22.5 kcal/mol (MP4/MP2 level) above the minimum. The main geometrical parameters are depicted in Figure 3.

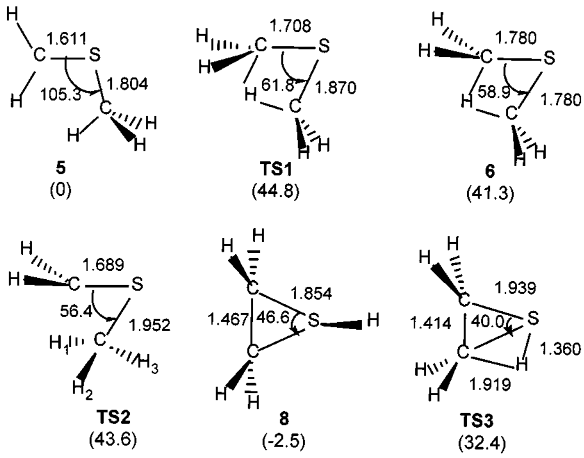
The PES associated with the $H_2C-SCH_3^+$ cation is more complicated. As in boron and aluminium systems, a planar (**5**) conformation and two perpendicular geometries (eclipsed **6** and staggered **7**) have been optimized.

Figure 3. Main geometrical parameters [Å,°] and relative energies (kcal/mol, MP4/MP2 level) of the optimized structures of $H_2C-OCH_3^+$



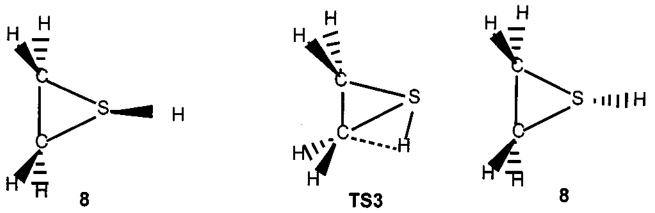
The planar structure **5** is a real minimum and we have verified that the conformation where a C–H bond eclipses the C–S bond is the most stable (by 0.6 kcal/mol with respect to the staggered conformation). The eclipsed perpendicular conformation **6** is also a real minimum located 41.3 kcal/mol above the planar geometry. In this structure, the $C^+\cdots H$ agostic interaction is strong and a C_{2v} geometry is found: the methyl hydrogen symmetrically bridges the two carbon atoms, both C–H distances being equal to 1.279 Å (Figure 4). The sulfur valence angle is acute (58.9°) and the two S–C bond are lengthened to 1.780 Å. The transition state connecting these two minima (**TS1**) has been located. Its geometry ressembles that of the secondary minimum **6** (Figure 4) and is located 3.5 kcal/mol above it.

Figure 4. Main geometrical parameters [Å,°] and relative energies (kcal/mol, MP4/MP2 level) of the optimized isomers of $H_2C-SCH_3^+$

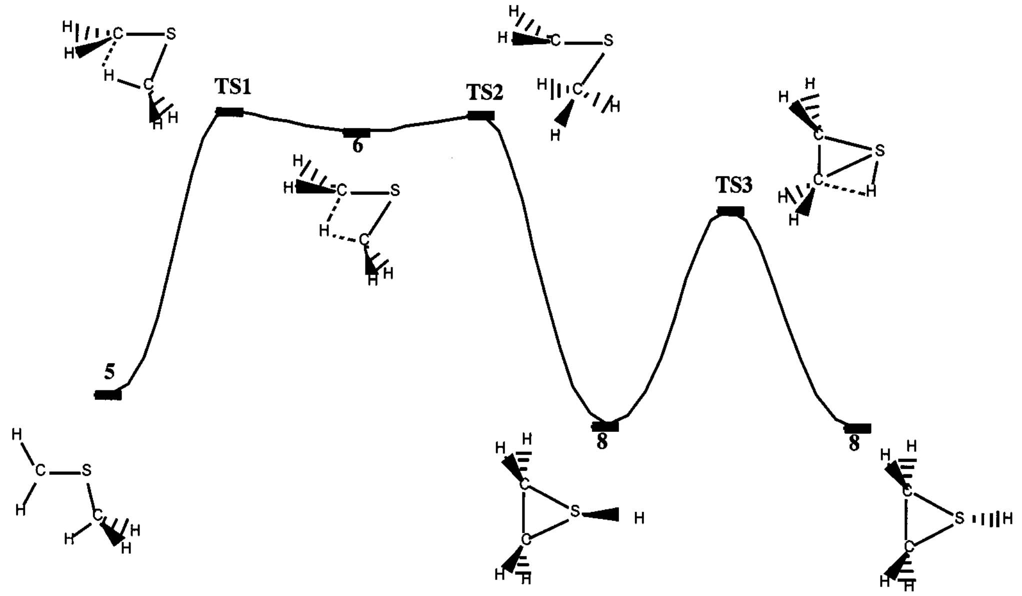


Optimization of the staggered conformation **7** leads to the location of two stationary points. Both of them are characterized to be transition states, **TS2** and **TS3**. The highest one, **TS2** is located 43.6 kcal/mol above the minimum **5**. It is of C_1 symmetry and its geometry is rather close to that of the secondary minimum **6** (C^+-S = 1.689

Scheme 4



Scheme 5



Å; C−S = 1.952 Å; C−S−C = 56.4°, Figure 4). Two C−H bonds of the methyl group are elongated ($C-H_2$ = 1.108 Å; $C-H_3$ = 1.104 Å). Following the transition vector associated with the imaginary frequency leads to a cyclic minimum which is the protonated thiooxirane **8**. This minimum is located 2.5 kcal/mol below the planar structure **5** (Figure 4). The structure **TS2** is therefore the transition state allowing the interconversion of the secondary minimum **6** into the protonated thiooxirane **8**. From a geometrical point of view, it should be noted that the migration of the hydrogen from carbon to sulfur is possible because the C_S symmetry plane has been removed in the **TS2** geometry. The second transition state (**TS3**) is of C_S symmetry and is located 32.4 kcal/mol above the minimum **5**. Formally, it is a conformer of the $H_2C-SCH_3^+$ cation, but severe distortions appear in this geometry: the C−C distance is very short (1.414 Å) indicating the presence of a C−C bond (Figure 4). In addition, the S−H (1.360 Å) and C−H (1.919 Å) distances indicate that a S−H bond is formed whereas a C−H bond is broken. With respect to the $H_2C-SCH_3^+$ cation, an hydrogen atom has moved from carbon to sulfur. The transition vector associated to the imaginary frequency almost only develops on the out-of-plane motion of the hydrogen atom bound to sulfur. This transition state is therefore thought to connect the two enantiomeric forms of the protonated thiooxirane (Scheme 4).

A schematic representation of the connection between these different extrema is given in Scheme 5.

Summary and Conclusion

Our theoretical study of H_2X-YR systems (X = Al, B, C^+; Y = O, S; R = H, CH_3) sheds some lights on π bonding in such compounds. π bonding is strong when X = C^+ (from 57 to 67 kcal/mol), intermediate for X = B (from 16 to 23 kcal/mol) and weak for X = Al (from 8 to 10 kcal/mol). The nature of the Y atom (Y = O or S) does not seem to strongly affect the strength of the X−Y π bond. The value of the rotational barrier is not a measure of the π conjugation because important geometrical deformations occur in the deconjugated perpendicular structure in order to compensate for -at least in part- the loss of the stabilization interaction. When Y = O, the X−O−R angle opens so that a X−O π conjugation still exists between the p(X) vacant orbital and the second oxygen lone pair which is partly dehybridized. The linearization of the X−O−R arrangment is more pronounced in methylated than in the unsubstituted systems. When Y = S, the opposite deformation is found, probably because of the reluctance of sulfur for obtuse valence angles. The X−S−R angle becomes more obtuse in the perpendicular geometry and a direct agostic interaction takes place between the X atom and the Y substituent R (R = H, CH_3). For R = H, as the π-acceptor capability of X increases, the X−S−H angle decreases [89.6° (Al); 86.7° (B); 50.3° (C^+)]. In methylated systems, the four-membered (X−S−C−H) ring seems to be particularly favorable and, provided that the agostic interaction is strong enough, the bridged structure is a secondary minimum on the PES (X = B, C^+). For X = C^+, this interaction is found to be rather strong and the bridging hydrogen is equally shared between the two carbon atoms.

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[27] We did not find any satisfactory explanation of the 7.6 kcal/mol difference between the two values of this π conjugation. However, it should be noted that in sulfur compounds, conjugation is always found to be larger in the linear geometry than in the planar geometry. The reverse tendency is found in oxygenated species.

[98053]