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AB INITIO CALCULATIONS ON THE BARRIER TO INTERNAL ROTATION AND π-BONDING IN HYDROXYALANE

O. GROPEN * and E. WISLØFF NILSSEN

Institute of Mathematical and Physical Sciences, Department of Chemistry, University of Tromsø, Tromsø (Norway)

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Summary

Ab initio calculations have shown that a partial π-bond is superimposed on the σ-bond between Al and O in the planar form of hydroxyalane. The barrier to internal rotation around the Al—O bond is calculated to be 4.35 kcal mol^{-1}, and energy analysis shows the barrier to be of the same type as that in similar boron compounds.

Introduction

A substantial degree of p_π—p_π bonding is thought to exist in many boron compounds and substantial π-bond orders have been found for the B—X bond in compounds of the type H_2BX, where X is NH_2, OH, F, PH_2, SH and Cl [1]. In contrast few, if any, compounds of aluminium are known to involve planar trigonal coordinated systems with possible p_π—p_π bonding. It has been suggested that the difference arises from the smaller overlap between the formally vacant p_z-orbital on aluminium and the p_z lone pair orbital on X [2].

If this is the case, the R_2AlX compounds should exhibit low barriers to internal rotation around the Al—X bond, and show rather small reorganisation energies when dimerisations occur, and a recent study of the dimerisation of H_2AlOH indicates a value of 58.6 kcal mol^{-1} for the dissociation of $(H_2AlOH)_2$ [3]. However, there has been no rigorous theoretical investigation of the ability of aluminium to form double bonds, and the magnitudes of any barriers are not known.

In order to throw light on the nature of the Al—X bonds in H_2AlX compounds, we have carried out ab initio calculations on H_2AlOH.

A secondary objective of the work is to analyse the barrier to internal rotation by a recently described method [1a], and to compare the results with those for H_2BSH and H_2BOH [4].

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* To whom correspondence should be addressed.

Computational details

The calculations were carried out with the program MOLECULE [5] which solves the Roothan—Hall equations for a Gaussian-type basis. The basis used was partly a (12, 9, 1/9, 5, 1/4) set contracted to double ζ [6], and partly a (10, 6, 1/7, 3/4) set contracted to double ζ [7]. For the *d*-orbital exponents the values 0.95 and 0.15 were used for oxygen and aluminium, respectively, whereas the hydrogen *s*-functions were multiplied by a factor of 1.25.

Results and discussion

(a) Barriers and geometry

Calculations were carried out for the planar and the orthogonal forms. In both cases 0.95 Å for the O—H bond length and 120 degrees for the angles around both the aluminium and oxygen atoms were assumed. The Al—H and Al—O bond lengths were optimized in the planar form using the smaller basis set. We also optimized the Al—O bond length in the planar form with the expanded basis set using the obtained value for the Al—H bond length. In that case the Al—O bond was only slightly decreased. This led us to optimize the Al—O bond in the twisted form using only the smaller basis set, whereas the Al—H bond length was given the same value as obtained for the planar form. Finally we made calculations in both planar and orthogonal forms with the expanded basis, and in both forms the values 1.593 and 1.704 Å were used for the Al—H and Al—O bond lengths, respectively.

In addition one calculation was performed on the planar form using the smaller basis and optimized geometry but with variation of the Al—O bond length from 1.704 to 1.87 Å [9]. This was done in order to consider the reorganization energy during a dimerisation. The results are presented in Tables 1 and 2.

The planar form is clearly the most stable. The calculated Al—H bond length of 1.593 Å in the planar form is only slightly longer than that in H_3AlNMe_3 (1.560 Å) [8]. The Al—O bond length is 0.16 Å shorter than in the dimer species [9], and 0.32 Å shorter than the calculated bond length in the ether complex [3]. This indicates that the Al—O bond is nearly a pure covalent single bond, and the rather small lengthening of this bond in the orthogonal form (0.01 Å) confirms this conclusion. The barriers to rigid internal rotation are calculated to be 4.56 and 4.35 kcal mol^{-1} with the small and expanded basis sets, respectively, and relaxation of the Al—O bond in the orthogonal form only changes the bar-

TABLE 1

OPTIMIZED GEOMETRY PARAMETERS. ALL VALUES IN ÅNGSTRØM

	Planar form		Orthogonal form
	Small basis	Expanded basis	Small basis
Al—H bond length	1.593	1.593 [a]	1.593 [a]
Al—O bond length	1.704	1.684	1.712

[a] Not optimized

TABLE 2

TOTAL ENERGIES AND ROTATIONAL BARRIERS

Total energy in the planar form calculated with the small basis and Al—H = 1.593, Al—O = 1.704:	—318.344 73 a.u.
Total energy in the planar form calculated with the extended basis and Al—H = 1.593, Al—O = 1.704:	—318.571 91 a.u.
Rigid rotational barrier with small basis (Al—O = 1.704, Al—H = 1.593)	4.56 kcal mol^{-1}
Rigid rotational barrier with expanded basis (Al—O = 1.704, Al—H = 1.593)	4.35 kcal mol^{-1}
Partly optimized rotational barrier with small basis (Al—O = 1.704, Al—H = 1.593 for the planar and Al—O = 1.712 for the orthogonal form)	4.51 kcal mol^{-1}

rier by 0.05 kcal mol^{-1}. This indicates that the rotational barrier is well described by the (10, 6, 1/7, 3/4) set using rigid rotation.

The barrier height is rather low compared to the calculated barriers for hydroxy- and mercapto-borane (16.4 and 19.5 kcal mol^{-1}) [1a,4], which is also reflected in the rather small perturbation of the Al—O bond during the rotation compared with that of the B—O bond in the boron compounds.

Increasing the Al—O bond length from 1.704 to 1.87 Å increased the total energy by 8.39 kcal mol^{-1}. This result, together with the small barrier, indicate that only a small amount of reorganisation energy is necessary for dimerisation.

(b) Population analysis

The results of the population analysis are given in Table 3 together with earlier results for H_2BSH [1a] and H_2BOH [4]. In the planar form we find a charge transfer from aluminium to oxygen in the σ-bonds and a back donation in the π-system. This is parallel to the results obtained for the H_2BSH and H_2BOH molecules, but H_2AlOH shows a smaller back donation. Similarly we find a slightly lower π-overlap population for the Al—O bond than for the B—S and B—O bonds.

During the rotation from the planar to the orthogonal form the population in the vacant p_z-orbital on aluminium is reduced from 0.15 to 0.09 electrons compared to 0.21 and 0.05 electrons for mercaptoborane and 0.21 and 0.12 electrons for hydroxyborane. This indicates that the variation in the multiple

TABLE 3

CALCULATED GROSS AND OVERLAP POPULATIONS IN PLANAR AND ORTHOGONAL FORMS FOR H_2AlOH COMPARED WITH RESULTS FOR H_2BSH AND H_2BOH

	H_2AlOH'		H_2BSH'		H_2BOH'	
	Planar	Orthogonal	Planar	Orthogonal	Planar	Orthogonal
Tot (Al, B)	12.19	12.16	4.90	4.83	4.76	4.67
Tot (O, S)	8.88	8.88	16.46	16.52	8.75	8.79
Tot (H')	0.55	0.56	0.77	0.77	0.53	0.53
3 p_z (Al, B)	0.15	0.09	0.21	0.05	0.21	0.12
Total overlap (Al, B—O, S)	0.71	0.72	0.62	0.54	0.72	0.70
π overlap (Al, B—O, S)	0.19		0.23		0.26	

bonding during the rotation is smaller than for the boron compounds, which may partly explain the lower barrier. Other noteworthy results are the negligibly small variations in the total gross charges and the small increase of the total overlap population between aluminium and oxygen. This seems to indicate that a weakening of the multiple bonding in the orthogonal form compared to the planar form is partly compensated by a strengthening of the σ-bonding. This is consistent with the very small variation in the Al—O bond length during the rotation and may also be a reason for the low barrier. The variation of the populations are however, of the same nature as in the H_2BSH molecule, and indicate the same type of barrier.

(c) Energy partioning

The differences between various energy terms for the two forms are given in Table 4. Since population analysis seems to indicate the same type of barrier in H_2AlOH as in H_2BSH we would expect to find this reflected in an analysis based on energy partioning.

Using the partioning proposed by Allen [10] we found both the rigid rotational barriers to be repulsive. On the other hand applying the electronic energies proposed by Clementi [11] for analysing the two barriers we find that the valence shell electronic energy tends to stabilize the planar form in H_2AlOH, while the inner shell electronic energies stabilize the planar form for the H_2BSH molecule.

In this paper we adopted another approach [1]. The difference in electronic energy between the planar and orthogonal form may be divided into two terms: (1) The change in the repulsion between valence electrons (VV). (2) The change in the "modified core attraction energy" (MCA). The modified core energy consists of the one-electron terms and the repulsion between valence shells and inner shells (VI) This partitioning is possible since the change in repulsion between the inner shells during the rotation is negligible. When the energy is divided in this way, the importance of the formally vacant p_z-orbital for the stabilization of the planar form is more clearly pronounced. The charge transfer of electrons from this orbital to the more electron-rich donor during the rotation increase as expected the repulsion between the valence electrons. The variation in the core-

TABLE 4

PARTITIONING OF THE ELECTRONIC ENERGY DIFFERENCES FOR H_2AlOH AND H_2BSH USING THE THREE MENTIONED METHODS, (For further comments see text; all values in kcal mol^{-1})

	H_2AlOH	H_2BSH
One-electron-term	−122.89	−5.30
VI	−131.67	−0.32
Modified core attraction energy	8.78	−4.98
VV	20.06	12.40
Nuclear repulsion term	−6.90	−2.99
Repulsive term	181.24	19.3
Attractive term	−160.37	−14.76
Electrons in shells	−42.01	8.36
Electrons in inner shells	70.22	−0.94
Barriers	21.94	4.56

interaction is negative for the aluminium compound, whereas it is positive for the sulphur compound. This energy contribution mainly depends on the formal core charge, atomic size and the bond distances B—O and Al—O. In the aluminium compound the charge transfer is from a large atom with a formal core charge of +3 to a small atom of formal charge +6 and the term is as expected negative. In the boron compound the charge transfer is from a small atom with a formal core charge of +3 to a large atom with a formal core charge of +6. In this case the sign and magnitude of the variation in MCA is not obvious, but taking into consideration the large bond distance (1.79 Å compared to 1.70 Å for the Al—O bond) the positive contribution is not unreasonable. We conclude that the barrier in both compounds arises from the need to break a partial double bond and force negative charge back to the donors.

We conclude that H_2AlOH is most stable in the planar form. The calculations indicate the existence of a π-bond superimposed on the σ-bond between Al and O in the planar form. The barrier to internal rotation around the Al—O bond is calculated to be 4.35 kcal mol^{-1} and the relaxation of the Al—O bond in the orthogonal form is negligible, and these results together indicate that conjugation is of minor importance in the aluminium compounds. From the energy analysis, however, we conclude that the barrier is of the same nature as that in the boron compounds.

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