Intra- and Intermolecular Hydrogen Bonds in Alkyl and Silyl Ethers: Experimental and Theoretical Analysis

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We have investigated the electronic impact of the R protecting group (TBS or PMB) in the conformational equilibrium of α-methyl substituted alcohols **1** (R = TBS) and **2** (R = PMB). The conformational analysis and ^1H NMR experiments for alcohols **1** and **2** reflect the tendency for the existence of hydrogen-bonded conformations. The intrinsic low basicity of silyl ethers does not affect the capacity of the oxygen attached to the silicon atom in forming intramolecular hydrogen bonds. We showed that the extents of the hydrogen bonds in silyl and alkyl ethers are determined by several properties, such as orbital interactions, lone pair hybridizations, and lone pair energies, and not just by the electronic occupancy of the donor atom. The populational analysis of NBO allowed understanding the intra- and intermolecular hydrogen bonds between the OH group and oxygen bonded to silicon as well as to alkyl ethers, concluding that there are distinct lone pair contributions.

Introduction

The silyl ether function plays a very important role in organic chemistry especially as silyl groups are widely used as protecting groups in multistep synthesis. Usually, silyl protecting groups on an oxygen prevent complexation of this oxygen with Lewis acids, due to their large size and the electron-deficient oxygen. This observed low oxygen basicity in silyl ethers, when compared to alkyl ethers, has been explained by delocalization of the nonbonding orbitals on oxygen into the empty orbitals on silicon.[1] In a very interesting theoretical study, Schreiber and co-workers showed that the common explanation for this lower basicity of silyl ethers, based on interactions of oxygen lone pairs with silicon 3d orbital and on steric effects, are not the most important factors.[1] In this work, the authors propose an alternative explanation, based on X-ray crystal structures and frontier orbital analysis. They observed a higher energy for $\pi(SiR_3)$ when compared to $\pi(CR_3)$ group orbitals and a poorer interaction of the $\pi(SiR_3)$ with oxygen lone pairs and, most importantly, an interaction of the oxygen lone pairs with the $\pi^*(SiR_3)$ group orbitals. The combination of these effects led to lower energies for the HOMO of silyl and disilyl ethers as well as to smaller oxygen coefficients when compared to alkyl ethers, which could explain the observed diminished basicity.[1]

In this context, several theoretical studies have been conducted to try to better understand the existence of hydrogen bonds in systems involving silyl ethers.[2,3] Blake and Jorgensen confirmed the low gas-phase basicity of silyl ethers when compared to alkyl ethers.[2] The recent theoretical studies published by Beckmann and Grabowsky[3] show that the strength of hydrogen bonds in systems like $CH_3SiO{-}H{-}O(X)(Y)$ involving silanol and alkyl ethers ($X = Y = CH_3$), alkyl silyl ethers ($X = CH_3$, $Y = SiH_3$) and disiloxanes ($X = Y = SiH_3$), are higher with the more basic oxygen, in accordance with the results of both Schreiber and Jorgensen.[1,2] The authors[3] investigated the magnitude of hydrogen bonds in these systems computationally by employing DFT methods using Bader's atoms in molecules (AIM) and Weinhold's natural bond orbital (NBO) analyses as well as by calculating the Complex Energy (E_{add}) and delocalization energy ($E_{LPn \rightarrow \sigma(O-H)^*}$).[3] The hydrogen-bonding energies become lower as a silicon group is added to the structure.

The possibility of involvement of hydrogen bonds in transition states could lead to different reaction pathways and influence the overall diastereoselectivity of some processes. In 2006, Paton and Goodman published very interesting theoretical studies to understand the origins of the 1,5-*anti* asymmetric induction in boron-mediated aldol reactions of methyl ketones.[4] They concluded that the boron-mediated aldol reactions of methyl ketones proceed *via* boat-like transition states (Figure 1). For boron enolates with a β-alkoxy substituent, it is proposed that a stabilizing formyl hydrogen bond (GO−H, where G = benzyl, *p*-methoxybenzyl, methyl, and other alkyl groups) favors the 1,5-*anti* aldol adduct by minimizing steric interactions between the β-alkyl group and one of the ligands on boron (Figure 1). Due to the lower intrinsic basicity of the oxygen, silyl protecting groups (when G = silicon protecting group) prevent this formyl hydrogen bonding and probably this is the reason for the low selectivity observed with silicon protecting groups at the β-oxygen. The magnitude of this hydrogen bonding has been established by natural bond orbital (NBO) analysis.[4]

^1H NMR and ^{13}C NMR spectroscopy are very useful tools to study substituent effects on the electronic environment of a given carbon, as well as to determine the relative stereochemistry in acyclic molecules, especially by analysis of the coupling constants (*J*) in the corresponding ^1H NMR spectra.[5] In the case of β-hydroxy ketones, it is possible to assign the relative stereochemistry by ^1H NMR analysis, as these compounds, by adopting an internal hydrogen-bonded conformation, exhibit magnetically distinct NMR environments. This makes it extremely important to understand the factors that influence the hydrogen bond formation, especially in an intramolecular sense.

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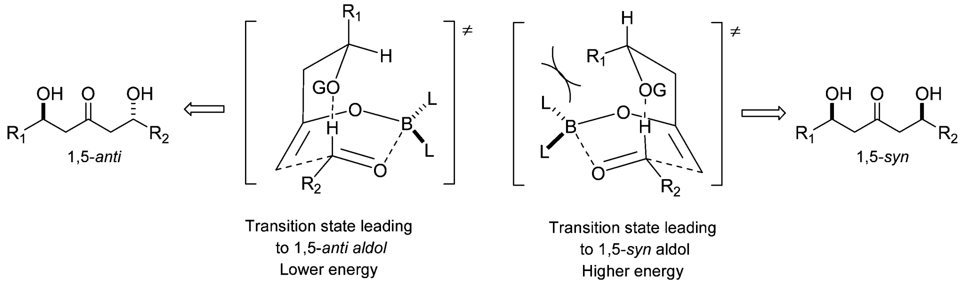
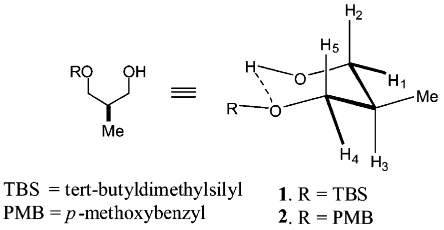


Figure 1. Transition state models showing the formyl hydrogen bond in boron-mediated aldol reactions.[4]

SCHEME 1



In this work, we intend to evaluate the electronic impact of the R protecting group (TBS or PMB) in the conformational equilibrium of α-methyl substituted alcohols **1** (R = TBS) and **2** (R = PMB) (Scheme 1). It is our intention to determine the extent of hydrogen bonding between the OH function and the oxygen of the OR group.

Computational Details

All structures were fully optimized through the Gaussian03 program,[6] applying the B3LYP hybrid functional[7] and 6-311+G(2d,p) basis sets used for molecules containing heteroatoms.[8] The potential energy surfaces (PES) were built by applying HF/3-21g. Electronic structures of compounds **1** (R = TBS) and **2** (R = PMB) were studied using Weinhold natural bond orbital (NBO 5.0) analysis.[9] The NBO analysis transforms the canonical delocalized DFT Kohn−Sham MO, into localized orbitals, which are closely tied to chemical bonding concepts. Filled NBO describe the hypothetical strictly localized Lewis structure. NBO analysis allows for specific lone pairs to antibonding orbital delocalizations to be quantified, from which a detailed picture of their contribution to the energetics of different conformations can be obtained. The interactions between filled and vacant orbitals represent the deviation of the molecule from the Lewis structure and can be used as a measure of delocalization.[10] The NBO energies were calculated at the B3LYP/6-311+G(2d,p) level using the geometries optimized at the B3LYP/6-311+G(2d,p) level. These delocalization energies are the stabilizing energies calculated by second-order perturbation theory analysis.[10]

Experimental Section

The ^{1}H NMR spectra for alcohols **1** and **2** were recorded in a spectrometer equipped with 5 mm gradient probe operating at 499.89 MHz. Measurements were carried out at a probe temperature of 25 °C using solutions of *ca.* 10 mg cm^{-3} in $CDCl_3$ and in CD_3CN; all spectra were reported using solvent as an internal standard ($CDCl_3$ at 7.25 ppm and CD_3CN at 1.94 ppm). Typical conditions for ^{1}H NMR spectra were: 16 transients, spectral width 10 000 Hz with 32 k data points, giving an acquisition time of 3.28 s and zero filled to 128 k to give a digital resolution of 0.15 Hz/point.

TABLE 1: $^2J_{HH}$, $^3J_{HH}$, and $^4J_{HH}$ NMR Coupling Constants (Hz) and Proton Chemical Shifts (ppm) for Alcohols 1 and 2 in $CDCl_3$ and CD_3CN as Solvents[a]

		alcohol **1** (R = TBS)		alcohol **2** (R = PMB)	
solvent	atom	δ	J	δ	J
$CDCl_3$	H_1	3.63	$J_{H_1H_4} = 0.8$; $J_{H_1H_3} = 4.4$; $J_{H_1H_2} = 9.9$	3.63	$J_{H_1H_4} = 0.6$; $J_{H_1H_3} = 4.7$; $J_{H_1H_2} = 10.7$
	H_2	3.59	$J_{H_2H_3} = 8.0$; $J_{H_2H_1} = 9.9$	3.57	$J_{H_2H_3} = 7.0$; $J_{H_2H_1} = 10.7$
	H_4	3.72	$J_{H_4H_1} = 0.8$; $J_{H_4H_3} = 4.2$; $J_{H_4H_5} = 10.7$	3.53	$J_{H_4H_1} = 0.6$; $J_{H_4H_3} = 4.6$; $J_{H_4H_5} = 9.1$
	H_5	3.53	$J_{H_5H_3} = 7.4$; $J_{H_5H_4} = 10.7$	3.39	$J_{H_5H_3} = 8.1$; $J_{H_5H_4} = 9.1$
CD_3CN	H_1	3.38	$J_{H_1OH} = J_{H_1H_3} = 5.7$; $J_{H_1H_2} = 10.5$	3.45	$J_{H_1OH} = 5.3$; $J_{H_1H_3} = 6.3$; $J_{H_1H_2} = 10.6$
	H_2	3.45	$J_{H_2OH} = 5.2$; $J_{H_2H_3} = 6.5$; $J_{H_2H_1} = 10.5$	3.38	$J_{H_2OH} = J_{H_2H_3} = 5.9$; $J_{H_2H_1} = 10.6$
	H_4	3.53	$J_{H_4H_3} = 5.7$; $J_{H_4H_5} = 9.9$	3.40	$J_{H_4H_3} = 6.4$; $J_{H_4H_5} = 9.1$
	H_5	3.56	$J_{H_5H_3} = 6.3$; $J_{H_5H_4} = 9.9$	3.33	$J_{H_5H_3} = 5.9$; $J_{H_5H_4} = 9.1$

[a] The attribution of the ^{1}H NMR spectrum of compound **2** in $CDCl_3$ was assigned by HMBC and HSQC 2D NMR experiments. The attribution of the ^{1}H NMR spectrum for compound **1** was made by comparison with compound **2**.

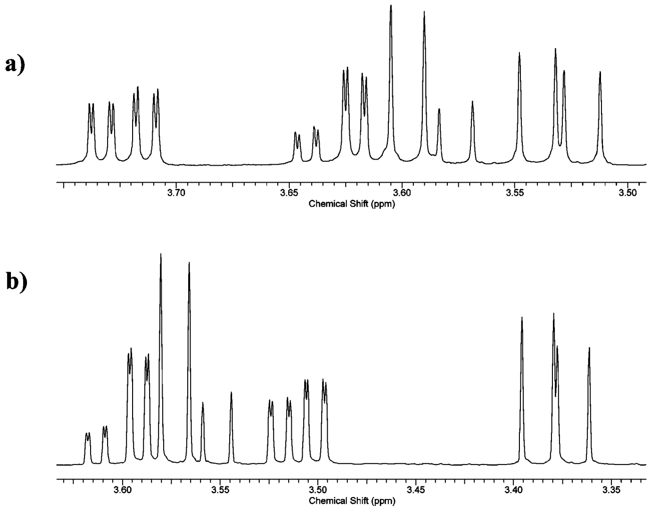
Alcohols **1** and **2** were easily prepared according to methods described in the literature.[11]

Results and Discussion

The ^{1}H NMR spectra for compounds **1** and **2** are first order and the coupling constants (*J*) and chemical shifts (*δ*) are directly measured from the spectra. Pertinent ^{1}H NMR data for compounds **1** and **2** appear in Table 1. In addition, Scheme 2 shows portions of the ^{1}H NMR spectra related to hydrogens H_1, H_2, H_4, and H_5 for alcohol **1** (3.50−3.75 ppm) and for alcohol **2** (3.35−3.65 ppm) in $CDCl_3$.

The predominance of hydrogen-bonded conformations should be reflected in different vicinal coupling constants.[12] In fact, very strong experimental evidence for the existence of intramolecular hydrogen bonds in alcohols **1** and **2** comes from the observed coupling constants in the ^{1}H NMR spectra measured in $CDCl_3$ (Schemes 1 and 2 and Table 1). For alcohol **1** (R = TBS), the coupling constants between H_5/H_3 and H_2/H_3 are 7.4 and 8.0 Hz, respectively, showing a *trans*-diaxial orientation between these two hydrogens. For H_4/H_3 and H_1/H_3 the coupling constants are 4.2 and 4.4 Hz, respectively, and are related to an axial−equatorial orientation. For alcohol **2**, the coupling constants between H_5/H_3 and H_2/H_3 are 8.1 and 7.0 Hz, showing again a *trans*-diaxial relationship between these hydrogens. In the case of H_4/H_3 and H_1/H_3, the coupling constants are 4.6

SCHEME 2: Partial ^{1}H NMR Spectra in $CDCl_3$ for Compounds (a) 1 and (b) 2



and 4.7 Hz, respectively, from an axial−equatorial orientation. As long as these conformational preferences apply, H_1/H_2 and H_4/H_5 are in different (average) chemical environments, giving rise to characteristic signals. In addition, both **1** (R = TBS) and **2** (R = PMB) exhibit a characteristic long-range coupling constants ($^4J_{H1H4}$) with values 0.8 and 0.6 Hz, respectively (Scheme 1). We believe that in the case of both **1** and **2** this is due to the illustrated hydrogen bonding between the hydroxyl group and the oxygen of the OR group (for both R = TBS and PMB), forming a chairlike six member ring, as illustrated in Scheme 1, which is probably the most stable chairlike conformer, with the methyl group in a pseudo-equatorial position. Both chemical shifts and coupling constants vary with NMR solvent and in CD_3CN we did not observe the long distance coupling constants, as the signals collapsed into broad resonances, as expected for a more polar solvent, capable of hydrogen bond formation.

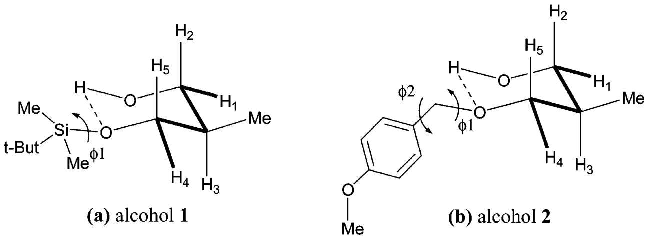
For both **1** and **2**, the NMR spectra at low temperatures (0 to −20 °C) showed that decreasing the temperature, an increase in the $^4J_{H-H}$ coupling constant was observed (from 0.8 Hz at 0 °C to 1.12 Hz at −20 °C). We have also observed an increase in$^3J_{Hax-Hax}$ coupling constant for **1** and **2** (from 8.0 Hz at 0 °C to 8.7 Hz at −20 °C). These observations are again consistent with the existence of intramolecular hydrogen bonding conformations.

Analysis of IR spectra for compounds **1** and **2** were performed under two different concentrations in $CHCl_3$ (0.03 and 0.06 mol L^{-1}) and corroborated the NMR measurements. For both **1** and **2** we have observed two distinct absorptions, one around 3650 cm^{-1} (very weak) due to the free OH group and a second one centered at 3500 cm^{-1} (very strong), related to the intramolecular hydrogen-bonded OH group. There is no evidence of intermolecular hydrogen-bonding due to the absence of IR stretching around 3400−3300 cm^{-1}.

To the best of our knowledge, there is no evidence in the literature to support such notion of a β-OTBS capable of internal chelation or hydrogen bonding in six-member rings. On the other hand, Hoffmann and co-workers suggested the existence of intramolecular hydrogen bonding in β-hydroxy silyl ethers leading to five-member rings and its implication in determining the relative stereochemistry of *syn* and *anti* isomers based on the ^{1}H NMR chemical shift of the OH proton.[13]

All of these earlier observations are consistent with alcohols **1** and **2** adopting the internally hydrogen bonded conformation indicated in Scheme 1. On the basis of these results, we believe that the low basicity of silyl ethers does not have an influence on the capacity of the oxygen attached to the silicon atom for forming intramolecular hydrogen bonds.

SCHEME 3: Dihedral Angles ϕ_1 and ϕ_2 Used To Perform the PES for Alcohols 1 and 2



(a) alcohol **1** **(b)** alcohol **2**

Hydrogen Bond and NBO Analysis[13,14]

Potential energy surfaces (PES) for alcohols **1** and **2** were performed to obtain their most stable conformations (Scheme 3).

For alcohol **1** the PES (Figure 2a) was performed varying the dihedral angle ϕ_1 (Scheme 3a), and for alcohol **2** two dihedral angles ϕ_1 and ϕ_2 (Scheme 3b) were used to perform the PES (Figure 2b). The geometry, energies, and NBO calculations were performed for the minima in PES with energy smaller than 1.5 kcal mol^{-1}, which were considered as stable conformations.

The hyperconjugative interaction between $LP_O \rightarrow \sigma^*_{O-H}$ has been assigned as the major contribution to hydrogen bond interaction obtained from NBO analysis.[10,14,15] The geometries for the most stable conformers of alcohols **1** and **2** were optimized and their structures are shown in Figure 3. From these structures we obtained the distance between the oxygen and hydrogen atoms involved in hydrogen bond interaction. For alcohol **1** the distance is 1.984 Å, and for alcohol **2** the distance is 1.992 Å (Figure 3). As can be observed, the hydrogen bond interaction (distance) for alcohol **1** is shorter than for alcohol **2**, which was not expected due to the presence of silicon attached to the oxygen in compound **1**.

The delocalization energy associated with the hydrogen bond interaction ($LP_O \rightarrow \sigma^*_{OH}$) obtained from NBO analysis is higher for alcohol **1** when compared with alcohol **2**, with values of 4.92 and 4.56 kcal/mol^{-1}, respectively.

These values from geometry optimization and NBO analysis are in good agreement; the shorter distance (1.984 Å) for hydrogen bond interaction presents the higher delocalization energy (4.92 kcal mol^{-1}) for alcohol **1**. However, we expected an opposite behavior due to the lower oxygen basicity of silyl ether in comparison with alcohol **2**, containing a PMB protecting group.[1,2]

To determine if the unexpected magnitude of hydrogen bond interaction observed for alcohols **1** and **2** is due to repulsive or attractive stereo-electronic interactions caused by the oxygen protecting group in the six-membered ring system, geometries, energies and NBO analyses for compounds **3** (R = SiH_3) and **4** (R = CH_3) (Figure 4) and for complexes between methanol and some molecules, such as $[CH_3OH-O(CH_3)R]$ (R = CH_3, SiH_3, TMS, and *tert*-butyl), were performed at the B3LYP/6-311+g(2d,p) level. The results are listed in Table 2.

As can be observed from Table 2, the delocalization energies for intermolecular hydrogen bond ($E_{LPO \rightarrow \sigma^*OH}$) are higher for complexes **5**−**8** in comparison with the intramolecular hydrogen bond in cyclic compounds **1**−**4**, which was expected due to

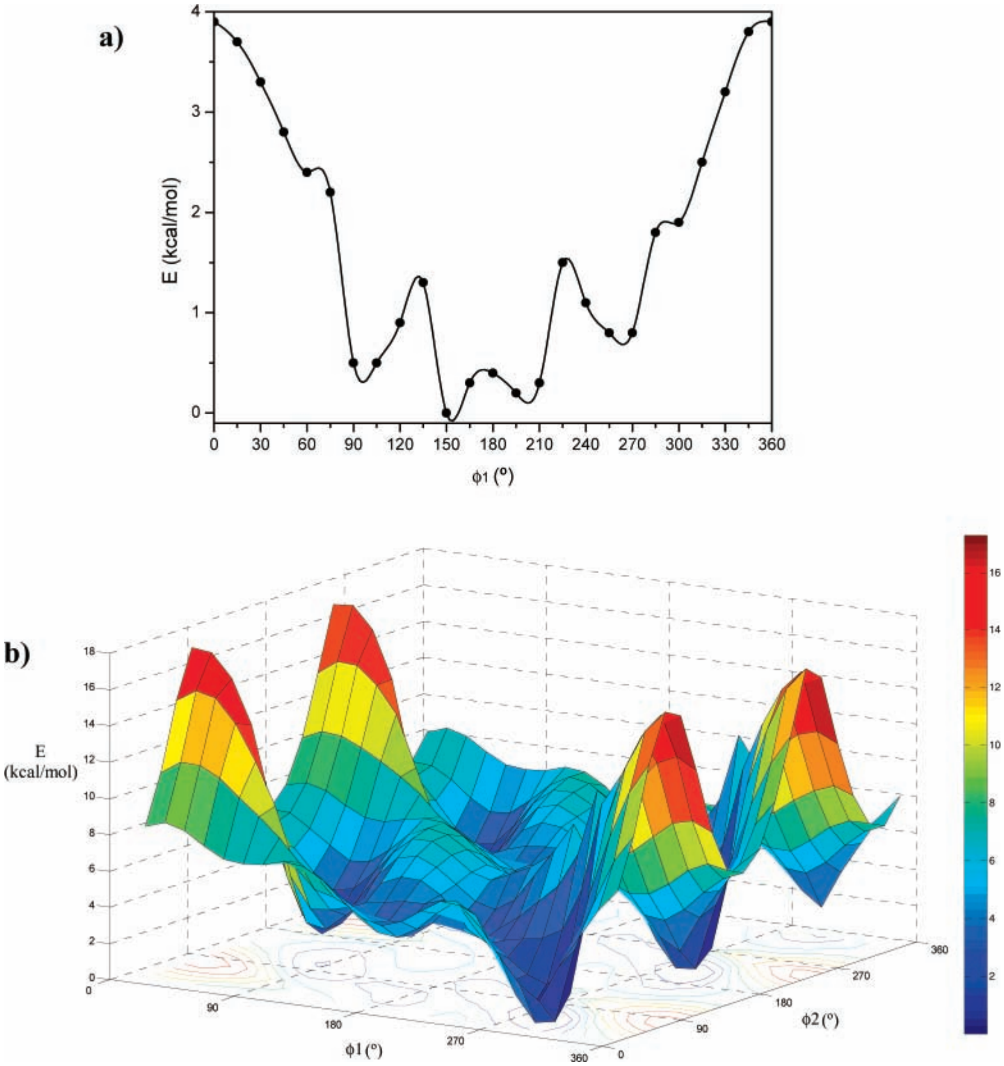
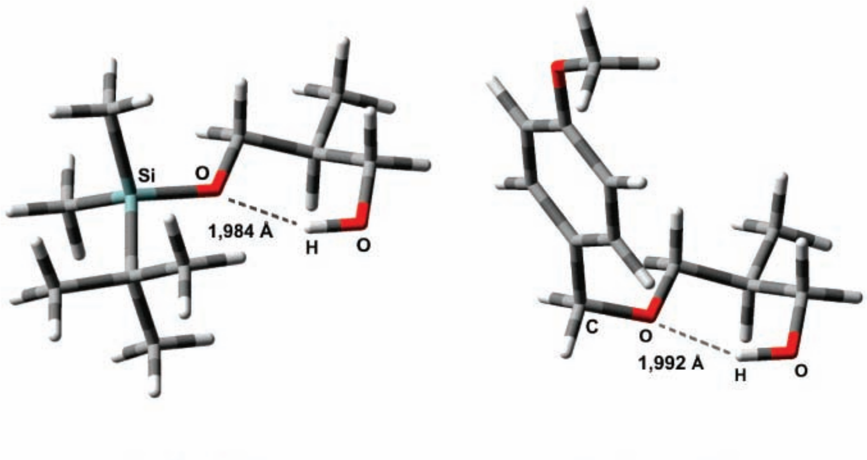


Figure 2. Potential energy surface for the alcohols studied: (a) alcohol **1** and (b) alcohol **2**.



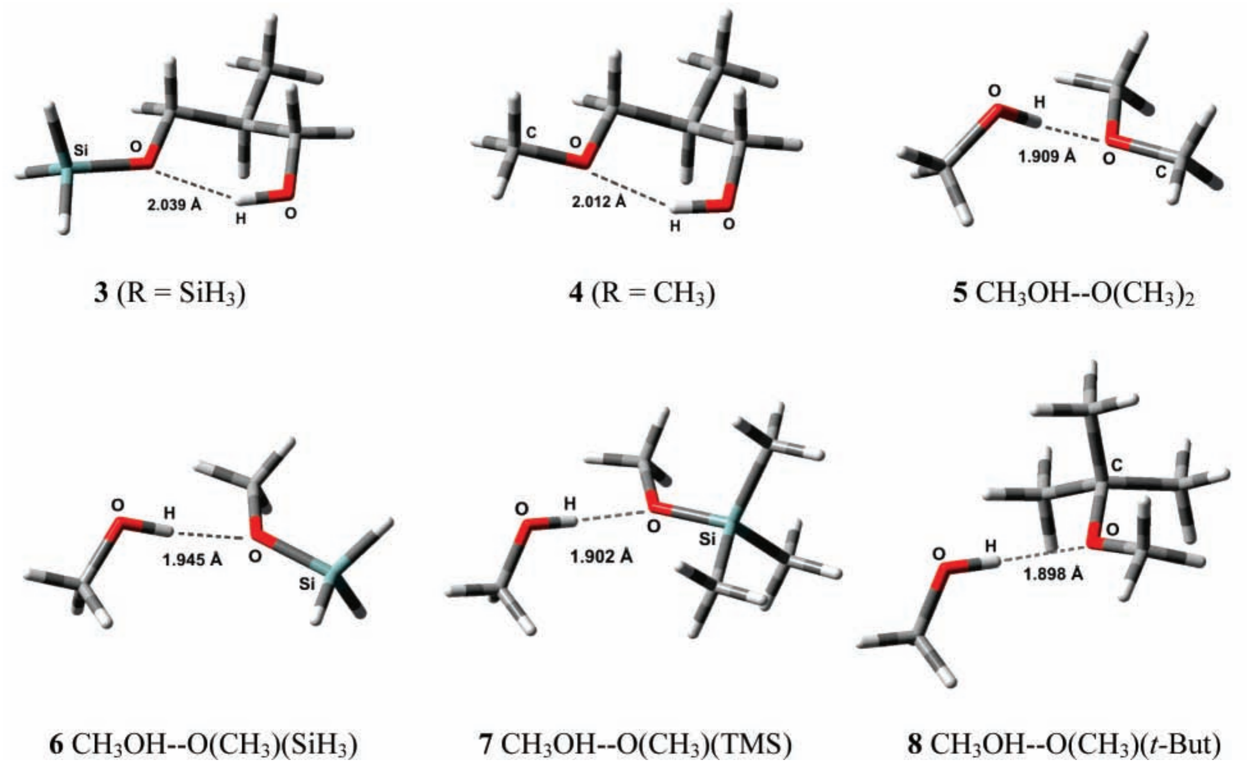
1 (R = TBS) **2** (R = PMB)

Figure 3. Optimized structure at the B3LYP/6-311+g(2d,p) level for the most stable conformers for alcohols **1** and **2**.

the better superposition between the orbitals involved in the intermolecular hydrogen bond for complex structures.[16]

As can be observed from Table 2, the delocalization energy between $LP_O \rightarrow \sigma^*_{O-H}$ is smaller, 3.67 and 6.37 kcal mol^{-1}, for compounds **3** and **6**, respectively, containing the SiH_3 group. However, for compounds containing a substituted silicon atom, such as TBS (alcohol **1**) and TMS (complex **7**) we observed that the delocalization energy $LP_O \rightarrow \sigma^*_{O-H}$ increases to 4.92 and 8.18 kcal mol^{-1} for alcohol **1** and complex **7**, respectively, when compared to alcohol **3** and complex **6**. For complex **8** (R = *tert*-butyl) the $LP_O \rightarrow \sigma^*_{O-H}$ energy is similar (8.63 kcal mol^{-1}) to that observed for complex **7**.

The distance (O−H···O) between the oxygen lone pair and the hydrogen from the O−H bond follows the same trend (Table



3 (R = SiH_3) **4** (R = CH_3) **5** CH_3OH--$O(CH_3)_2$

6 CH_3OH--$O(CH_3)(SiH_3)$ **7** CH_3OH--$O(CH_3)$(TMS) **8** CH_3OH--$O(CH_3)$(*t*-But)

Figure 4. Optimized geometries at the B3LYP/6-311+g(2d,p) level for compounds **3** and **4** and for complexes **5**−**8**.

TABLE 2: Delocalization Energies[a] ($LP_O \rightarrow \sigma^*_{O-H}$), Occupancies, and % of s Character for Lone Pairs (LP), Occupancies of σ^*_{O-H} from NBO Analysis, Distances,[b] and Angles[c] for Hydrogen Bond Interactions in Structures 1−8

parameters	1	2	3	4	5	6	7	8
$LP_{O1} \rightarrow \sigma^*_{O-H}$	4.26	3.17	3.26	2.79	3.71	6.04	6.64	3.13
$LP_{O2} \rightarrow \sigma^*_{O-H}$	0.66	1.39	0.41	1.47	4.42	0.33	1.54	5.50
$LP_{O} \rightarrow \sigma^*_{O-H}$	4.92	4.56	3.67	4.26	8.13	6.37	8.18	8.63
occup (LP_{O1})	1.9409	1.9603	1.9491	1.9627	1.9603	1.9445	1.9384	1.9540
occup (LP_{O2})	1.9157	1.9238	1.9147	1.9230	1.9204	1.9160	1.9161	1.9241
occup σ^*_{OH}	0.0183	0.0186	0.0146	0.0178	0.0256	0.0191	0.0230	0.0281
% s LP_{O1}	28.59	42.04	32.49	42.33	41.38	32.84	30.00	37.37
% s LP_{O2}	0.16	0.68	0.03	0.53	2.10	0.11	0.85	4.22
R_{OH-O}	1.984	1.992	2.039	2.012	1.909	1.945	1.902	1.898
$\angle O-H\cdots O$	141.3	139.5	137.9	138.2	176.8	168.0	173.8	175.3
$\angle_{R-O-C}$	123.7	114.3	122.1	113.1	112.8	121.8	123.5	117.9
d_{R-O}	1.679	1.430	1.661	1.416	1.420	1.663	1.680	1.456

[a] Energies in kcal mol^{-1}. [b] Distances in Å. [c] Angles in degree.

2) observed for local energy. For alcohol **1** and complex **7**, the distances are shorter, 1.984 and 1.902 Å, respectively, than for alcohol **3** and complex **6**, 1.992 and 1.945 Å. A large variation for the hydrogen bond distance for complexes **5**−**8**, was observed (Table 2), due to the better approximation between molecules to form the intermolecular hydrogen bond interaction when compared to alcohols **1**−**4**.

For alcohols **2** and **4**, as well as for complexes **5** and **8** the delocalization energies for the hydrogen bond interactions are: 4.45, 4.26, 8.13, and 8.63 kcal mol^{-1}, respectively. In these cases, we have observed that increasing the size of the substituent on the carbon atom (**2** and **8**) causes the delocalization energy for hydrogen bond interactions to increase. Thus, it is possible to represent a series (**8** > **7** > **5** > **6**) of decreasing delocalization energies for intermolecular hydrogen bond interactions and, in the same way, a series (**1** > **2** > **4** > **3**) of decreasing delocalization energies for intramolecular hydrogen bond interactions. These two series are consistent with the series (CH_3OY; Y = *tert*-But ≈ TMS > CH_3SiH_2 > CH_3CH_2 > CH_3 ≈ SiH_3) observed by Jorgensen and co-workers[2] for proton affinity in substituted silyl ethers and in substituted alkyl ethers. For both silyl and alkyl the magnitudes of proton affinities are equal. A similar series was obtained by Pitt et al.[17] for basicity in the gas phase.

We have also observed (Table 2) that an oxygen bonded to silicon presents a small electronic occupancy for oxygen lone pairs (LP_O) due to higher donation to the σ^*_{Si-R} antibonding orbital ($LP_O \rightarrow \sigma^*_{Si-R}$). These results are in close correlation with those observed by Schreiber and co-workers,[1] who showed that the presence of a silicon atom increases the electronic delocalization of oxygen and the oxygen lone pairs present a secondary character in HOMO and HOMO−1 orbitals, being the most important coefficient for this orbital observed in Si−X bonds where X = H and C.[1]

From NBO analysis (Table 3), it can be observed that donations from the oxygen lone pairs to the σ^*_{X-R} antibonding orbital ($LP_O \rightarrow \sigma^*_{X-R}$), where X = Si or C, are larger for compounds containing silicon (**1**, **3**, **6**, and **7**), in agreement with the previous observations. The energies for σ^*_{Si-R} antibonding orbitals are smaller than for σ^*_{C-R} (R = H or C), permitting the delocalization of oxygen lone pairs for compounds containing silicon to be larger.

TABLE 3: Total Delocalization Energies (kcal mol^{-1}) from Oxygen Lone Pairs to σ^*_{X-R} (X = Si or C) Antibonding Orbitals in Protected Alcohols 1−4 and Complexes 5−8

	1	2	3	4	5	6	7	8
$LP_{O1} \rightarrow \sigma^*_{X-R}$	5.51	4.49	4.56	3.38	3.92	4.44	5.17	4.01
$LP_{O2} \rightarrow \sigma^*_{X-R}$	11.60	10.50	12.20	12.17	11.25	12.12	11.65	9.27
total $LP_O \rightarrow \sigma^*_{X-R}$	17.11	14.99	16.76	16.05	15.17	16.56	16.82	13.28

The contributions of LP_{O1} to intramolecular hydrogen bonds ($LP_{O1} \rightarrow \sigma^*_{H-O}$) are larger for alcohols **1**−**4** and complexes **6** and **7** when compared to the contribution of LP_{O2} (Table 2). For complexes **5** and **8** the contributions to intramolecular hydrogen bond interaction are almost equal for LP_{O1} and LP_{O2}. However, for interactions between oxygen lone pairs and σ^*_{X-R} from the protected group, the most important contributions involve LP_{O2} that are much larger than those involved with LP_{O1} (Table 3).

As can be observed from Table 2, as the donation of the LP_O increases, their occupancy and s character diminish because, for the delocalization interaction to occur, a correct symmetry between the lone pair and σ^*_{H-O} is necessary, leading the LP_{O1} to increase its p character. This behavior was verified for alcohols **1** and **3**, and complexes **6** and **7** containing silicon. For these compounds the s character for LP_{O1} orbitals are around 28−32% and for **2**, **4**, **5**, and **8**, containing carbon, they are around 37−42%.

Conclusions

The conformational analysis and ^{1}H NMR experiments for alcohols **1** and **2** reflect the tendency for the existence of hydrogen-bonded conformations. The intrinsic low basicity of silyl ethers[1,2] does not affect the capacity of the oxygen attached to the silicon atom in forming intramolecular hydrogen bonds.

We showed that the extents of the hydrogen bonds in silyl and alkyl ethers are determined by several properties, such as orbital interactions, lone pair hybridizations, and lone pair energies, and not just by the electronic occupancy of the donor atom.[1,2,4] The populational analysis of NBO allowed understanding the intra- and intermolecular hydrogen bonds between the OH group and oxygen bonded to silicon as well as to alkyl ethers, concluding that there are distinct lone pair contributions.

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