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Rules for Generating Conformers and Their Relative Energies in *n*-Alkanes with a Heteroelement O or S: Ethers and Alcohols, or Sulfides and Thiols

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With the aid of density functional theory calculations, all conformers of several single-chain alcohols, thiols, ethers, and sulfides are investigated. Starting from earlier computational works on *n*-alkanes, we construct an extended set of general rules for predicting the number and occurrence of conformers in these oxygen- or sulfur-containing compounds. In alcohols and thiols, it is found that only the conformers generated by internal rotations in the $HXCH_2CH_2CH_2$ (X = O or S) top are distinctive from those in *n*-alkanes. In ethers and sulfides, the primary influence of the heteroelement also extends up to three internal rotations, but many more conformers are possible. However, a number of double gauche sequences are forbidden, and therefore, several conformers can be eliminated. These exclusions in particular make up a set of rules for eventually deducing all possible conformers. Furthermore, on the basis of only an exact calculation of these *gg* conformations in addition to single gauche conformers, it is possible to make an accurate estimate of the relative energy. This two-dimensional approximation scheme constitutes an effective tool for adequately describing the relative energies of all possible conformers at a minimal computational cost.

1. Introduction

In this article, we focus on the conformers of four types of single-chain molecules. We choose the heteroelements O and S for substitution of a CH_2 fragment in *n*-alkanes. The resulting compounds (ethers and alcohols or sulfides and thiols) are, like *n*-alkanes, also single-chain molecules, but their energetically most stable structure is not a priori an all-trans conformation. Furthermore, it is unclear what the geometries and relative energies of the different conformers are.

The considered molecules are omnipresent in (fine) chemistry and biochemistry,[6−15] and are tremendously economically important. For a thorough understanding of the (bio)chemical processes in which these molecules are involved, one needs an accurate description of the conformational flexibility. A microscopic evaluation of molecular properties mainly depends on the knowledge of the various conformers which can be formed, and in particular on their relative energies. This is essential, since it is far from certain that the active conformer always corresponds to the global minimum of the potential energy surface.

It is well-known that internal rotation about a single C−C bond generates a potential energy curve with three local minima: one trans (*t*) and two gauche (g_- and g_+) conformations.[1−5] Rotation about a single C−O or C−S bond produces a similar potential energy profile. An easy conclusion would be that there are 3^n conformers for any molecule having *n* such (C−C, C−O, or C−S) single bonds. This was shown not to be true for *n*-alkanes,[3−5] and in fact, 3^n presents only a lower bound for the actual number of possible conformers. However, for longer molecules with many internal rotations, this number of conformers grows exponentially, and it becomes almost impossible to locate and describe them all. For this reason, Tasi et al.[5] introduced a general set of rules for predicting the number and occurrence of conformers in *n*-alkanes. However, it has not been established whether these rules also apply for similar compounds, such as those of this study.

In this article, we therefore deduce an additional set of general rules for the occurrence of conformers in alcohols, thiols, ethers, and sulfides. Despite their apparent similarities (O and S are situated in the same column of Mendelev's table), the properties of oxygen- or sulfur-containing molecules may vary substantially, and the most important differences and analogies are highlighted. In addition, the relative energies of all conformers are rigorously determined, and an approximation scheme for making reasonable estimates for the relative energies without the need for explicit ab initio calculations on all conformers is suggested.

The introduction of general rules for determining the number and occurrence of conformers and the availability of a fast method for producing reliable energy estimates for these structures constitute an important step forward in tackling long chain alcohols and thiols or ethers and sulfides. The methodology presented in this paper can readily be extrapolated to examine other types of single-chain compounds.

2. Labeling Convention for Conformers

To unambiguously describe the different conformers, a convenient and consistent labeling system must be introduced. A first step is to specify the conformation of an individual internal rotation. In Figure 1a, typical potential energy variation is shown as a function of the dihedral angle controlling the internal rotation about a C−C bond (this figure does not apply for internal rotation of ending methyl tops). There are three minima corresponding to three conformations, labeled by the indices *t*, g_-, and g_+, corresponding to trans, gauche −, and gauche + orientations, respectively. Rotations about a C−O or

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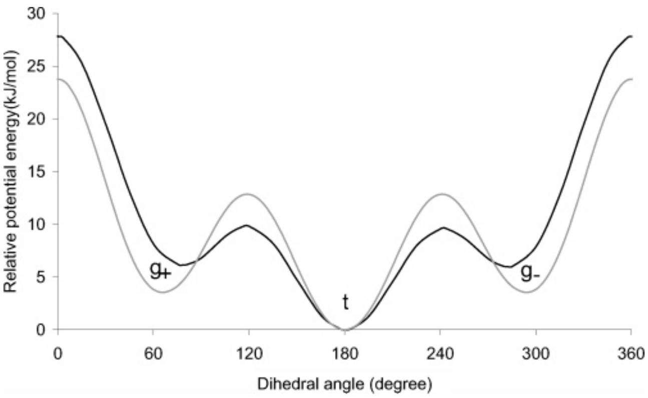

Figure 1. Example of typical potential energy profiles of internal rotation about a (C)C−C(C) bond (gray line) and a (C)C−O(C) bond (black line). The three minima are labeled. The reference of the (absolute) dihedral angle corresponds with the cis geometry.

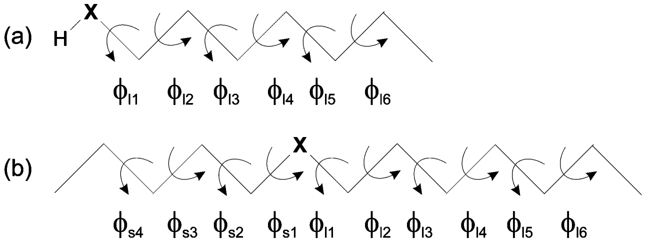

Figure 2. Illustration of labels used to identify specific internal rotations (with their dihedral angles) in (a) primary alcohols (X = O) and thiols (X = S) and (b) ethers (X = O) and sulfides (X = S).

C−S single bond generate similar potential energy profiles, and the minima are labeled in a similar way.

When multiple internal rotations within a molecule are considered, the individual conformation of each rotation has to be assigned. The appropriate labeling convention for a sequence of internal rotations in the molecules considered in this paper is illustrated in Figure 2. For alcohols and thiols (Figure 2a), the first internal rotation (with dihedral angle ϕ_{l1}) is about the C−X bond (X = O or S). The other rotations are labeled as ϕ_{lx} where x indicates the position of the C−C rotation axis with regard to the C−X bond. Also, the position of the hydroxyl top is written explicitly. For example, the $HOg_{+}tg_{-}t$ conformer of 1-pentanol (or $HSg_{+}tg_{-}t$ for 1-pentanethiol) is a shorthand notation for $\phi_{l1} = g_{+}$, $\phi_{l2} = t$, $\phi_{l3} = g_{-}$, and $\phi_{l4} = t$, where l4 indicates the ethyl torsion, l3 the propyl torsion, etc.

For ethers and sulfides, the same convention applies, but one has to distinguish between the two alkyl fragments (Figure 2b). The subscript l indicates that the rotation is situated in the longest alkyl top on the heteroelement, and the s refers to the shortest alkyl branch. The numbers refer to the position of the involved bond with respect to X: 1 specifies the rotation about the C−X bond, 2 the consecutive rotation, etc. In general, we refer to a conformer by specifying the individual conformations in the order ϕ_{smax} ... $\phi_{s1}X\phi_{l1}$ ... ϕ_{lmax} (for alcohols and thiols, there are no s internal rotations, making the above-defined nomenclature a special case of this more general definition), where X = O or S. For example, in ethyl propyl ether, $tOg_{-}g_{+}$ is the shorthand notation for $\phi_{s1} = t$, $\phi_{l1} = g_{-}$, and $\phi_{l2} = g_{+}$, while the same configuration in ethyl propyl sulfide is called $tSg_{-}g_{+}$.

We remark that all molecules in this work are subject to the symmetry operation σ_h which converts all gauche +/− orientations into its gauche −/+ mirror image. The trans conformations are not affected. For example, the above-mentioned $HOg_{+}tg_{-}t$ conformer of 1-pentanol is converted to $HOg_{-}tg_{+}t$. Similarly, the $tSg_{-}g_{+}$ conformer in ethyl propyl sulfide is converted into $tSg_{+}g_{-}$. As a result, all tabulated conformers, except the all-trans conformers, correspond to two mirror geometries with the same electronic energy.

3. Computational Details

Within the class of density functionals, it is well-known that the hybrid B3LYP and B3PW91 functionals[16] have proven to be a successful approach for obtaining accurate molecular structures, vibrational frequencies, heats of formation, and bond energies.[17−20] In particular, we have shown in ref 1 that the triple-ζ 6-311g** basis set in combination with the B3LYP functional produces reliable potential energy profiles for *n*-alkanes, and for this reason, we select this functional for the calculations in this work. Although the current set of molecules is very similar to *n*-alkanes (only one CH_2 fragment is replaced with an O or S atom), this level of theory (in particular, the basis set) cannot be used without further analysis. As oxygen and sulfur both have electron lone pairs and are hence likely to require a more extended basis set and diffuse functions, we have to select an appropriate basis set to be used in the B3LYP calculations. Moreover, S is a third-period element in Mendelev's table for which more polarization functions may be required, although the 6-311g** basis set (combined with MP2) was found to be more than adequate for dimethyl sulfoxide.[21] In this light, the 6-311+G(3df,2p) and 6-311++G(3df,3pd) basis sets will be employed. As these two larger basis sets are computationally very demanding, we also add the smaller 6-31+g* basis set to our basis set investigation. This basis set has the advantage over the 6-311g** basis set in that it includes a diffuse function, and in that it considerably reduces the computational time. The inclusion of a diffuse function is expected to improve the results considerably,[22] even more than the addition of polarization functions or improvement of the valence description.

For the transparency of the notation, we introduce the shorthand acronyms B1 for the 6-31+g* basis set, B2 for 6-311g**, B3 for 6-311+G(3df,2p), and B4 for 6-311++G(3df,3pd).

All calculations are performed with Gaussian98[23] and Gaussian03.[24]

We investigate the combination of the mentioned basis sets (B1−B4) with B3LYP, and also B3PW91 combined with the B1 and B4 basis sets, to select the appropriate DFT level of theory. These six approaches are used to evaluate the basis set dependence for 1-propanol, 1-propanethiol, methyl propyl ether, and methyl propyl sulfide which are model compounds for alcohols, thiols, ethers, and sulfides, respectively. For each of these molecules, all conformers are identified and the electronic energies obtained from full geometry optimizations on these conformers are compared with each other.

In addition to these molecules, also the conformers of methyl ethyl ether (MEE), methyl ethyl sulfide (MES), diethyl ether (DEE), and diethyl sulfide (DES) are calculated at different levels of theory. For these molecules, experimental data are available.

Each of the mentioned conformers in this article is found by performing full, unrestrained geometry optimizations. No potential energy scans or surfaces are employed. An initial set of conformer geometries was created, based on the possible conformations of a single internal rotation (gauche, trans, etc.). The set was then extended by additional sampling of the conformations of consecutive internal rotations. Finally, the initial geometries were optimized without any constraints.

TABLE 1: Relative Energies without ZPE (in kJ/mol) of the Various Conformers of the Model Compounds 1-Propanol, Methyl Propyl Ether, 1-Propanethiol, and Methyl Propyl Sulfide[a]

	B3LYP				B3PW91	
	B1	B2	B3	B4	B1	B4
1-propanol						
$HOg_{-}g_{-}/HOg_{+}g_{+}$	0.85	0.00	0.68	0.65	0.91	0.67
$HOg_{-}g_{+}/HOg_{+}g_{-}$	1.05	1.23	0.83	0.89	1.07	0.84
$HOtg_{-}/HOtg_{+}$	0.39	1.48	0.35	0.21	0.77	0.58
$HOg_{-}t/HOg_{+}t$	0.00	1.19	0.00	0.04	0.00	0.00
HOtt	0.19	2.44	0.11	0.00	0.43	0.22
methyl propyl ether						
$Og_{-}g_{-}/Og_{+}g_{+}$	6.70	6.07	6.35	6.45	6.46	6.34
Otg_{-}/Otg_{+}	0.19	0.00	0.02	0.03	0.29	0.15
$Og_{-}t/Og_{+}t$	6.33	7.50	6.22	6.30	6.10	6.16
Ott	0.00	1.38	0.00	0.00	0.00	0.00
1-propanethiol						
$HSg_{-}g_{-}/HSg_{+}g_{+}$	2.31	1.63	1.91	1.88	1.96	1.56
$HSg_{-}g_{+}/HSg_{+}g_{-}$	2.66	2.20	2.01	1.98	2.52	1.84
$HStg_{-}/HStg_{+}$	5.71	5.37	5.23	4.97	5.69	4.83
$HSg_{-}t/HSg_{+}t$	0.00	0.00	0.00	0.00	0.00	0.00
HStt	2.92	3.01	2.66	2.43	3.13	2.49
methyl propyl sulfide						
$Sg_{-}g_{-}/Sg_{+}g_{+}$	1.98	1.22	1.60	1.66	1.49	1.33
$Sg_{-}g_{+}/Sg_{+}g_{-}$	5.94	5.54	5.88	5.96	6.01	6.06
Stg_{-}/Stg_{+}	2.83	2.84	2.56	2.51	2.60	2.27
$Sg_{-}t/Sg_{+}t$	0.08	0.00	0.17	0.32	0.05	0.39
Stt	0.00	0.40	0.00	0.00	0.00	0.00

[a] The conformer with the lowest electronic energy is taken as a reference. The basis sets are defined as follows: B1 = 6-31+g*, B2 = 6-311g**, B3 = 6-311+G(3df,2p), and B4 = 6-311++G(3df,3pd).

Basis Set Dependence. As a primary task, the basis set dependence of the B3LYP (B3PW91) functional for alcohols, thiols, ethers, and sulfides is studied. One of the principal aims of this study is the selection of a cost-effective level of theory that still produces accurate results. For this reason, we apply only the B3LYP and B3PW91 functionals in the DFT calculations. We use two "small" basis sets (B1 and B2) and two more extended basis sets (B3 and B4). The latter basis sets are used to calculate the reference energy differences. The values predicted by the smaller B1 and B2 sets can then be compared with these reference values.

Four reference molecules are chosen to represent the different classes of molecules that are studied: 1-propanol (alcohols), methyl propyl ether (ethers), 1-propane thiol (thiols), and methyl propyl sulfide (sulfides). Each of these molecules shows two single bonds about which an internal rotation can generate different conformations, and forms the smallest compound of each class to have more than two energetically different conformers. In accordance with the labeling convention, these rotations are identified as ϕ_{l1} and ϕ_{l2}, each rotation covering three conformations (t, g_{-}, and g_{+}). Combination of these geometries leads to a total of nine conformers. Due to the σ_h symmetry, this number is reduced to five sets of energetically different conformers: *Xtt*, $Xg_{-}t/Xg_{+}t$, Xtg_{-}/Xtg_{+}, $Xg_{-}g_{-}/Xg_{+}g_{+}$, and finally $Xg_{-}g_{+}/Xg_{+}g_{-}$ [X = (H)O or (H)S]. The latter set of conformers is a result of the combination of gauche standings with different orientations. Only for methyl propyl ether could no such $Og_{-}g_{+}/Og_{+}g_{-}$ conformer be found.

Table 1 shows the relative energies of the different conformers of 1-propanol. The most stable conformer at each level of theory is the reference for the potential energy differences. Except for the B3LYP/6-311g**(B2) level, all other levels of theory attribute the global minimum to either the *HOtt* or *HOgt* conformer. The energy difference between these two types of conformers is quite small (0.4 kJ/mol at most). These differences are smaller than the expected accuracy of the B3LYP or B3PW91 functionals, and therefore, it is not possible to conclude from these data which geometry is the real global minimum. Moreover, with the inclusion of zero-point energies (Table 1 of the Supporting Information), the *HOtt* conformer becomes the lowest-energy conformer for all methods (except B3LYP/B2). The energies of the other conformers increase in the following order in all methods (except B3LYP/B2): $HOtg < HOg_{-}g_{-} < HOg_{-}g_{+}$ (with a maximal energy difference of ∼1 kJ/mol).

The B3LYP/6-311g**(B2) results show a slightly different pattern, but we should be careful in drawing conclusions as the energy discrepancies are on the order of 2 kJ/mol. Anyway, there are indications that B2 is not the most adequate basis set for describing these molecules. This is confirmed by the results predicted for methyl propyl ether (see Table 1). Within the same level of theory, basis sets B1, B3, and B4 give almost identical results, while the results obtained with the B3LYP/B2 method are deviating for the conformers with ϕ_{l2} in trans ($Og_{-}t/Og_{+}t$ and *Ott*).

For both molecules, the results with the B1 basis set show a very good quantitative agreement with those with the larger B3 and B4 basis sets. Additionally, the geometries of the conformers optimized with B1 are almost identical to the B3 and B4 geometries, while the B2 geometries are somewhat divergent.

We now discuss the relative energy values for the conformers of the sulfur compounds 1-propanethiol and methyl propyl sulfide (Table 1). In contrast with oxygen compounds, the influence of the selected basis set is rather limited, and the B2 set produces results that are comparable with the B1 values. As B1 is somewhat faster than B2, and because we wish to use the same level of theory for both oxygen and sulfur compounds, the B1 basis set still has a preferential status.

The above discussion supports the preference of basis set 6-31+g*(B1) to basis set 6-311g**(B2) for DFT/B3LYP calculations on the selected set of molecules, but a validation with experimental data is needed to draw final conclusions about the most suitable basis set.

The smallest alcohol of our set of molecules for which experimental data are available is ethanol. Several experimental papers have reported that the trans conformer in this molecule is slightly more stable than its gauche conformer. Depending on the experimental methods, the measured energy differences vary from 0.49 kJ/mol for microwave spectroscopy[25] to 1.31 kJ/mol for gas-phase Raman spectroscopy[26] and to 2.9 kJ/mol for overtone spectroscopy.[27] Also on the theoretical level, a lot of work has been done.[28] For example, a recent study of Weibel et al.[29] gives an interesting overview of several theoretical results on this trans−gauche energy difference. A correct theoretical prediction of the trans form as the most stable conformer is not uniformly obtained, and is very sensitive to the level of theory used. The assignation of the lowest-energy conformer can even change by inclusion of zero-point energy (ZPE). In this work, the B3LYP/6-31+g*(B1) results favor the trans conformer by 0.27 kJ/mol (no ZPE included). The predicted energy difference is rather small, but acceptable.

More recently, Takahashi et al.[30] performed a DFT calculation on the B3LYP/6-311++G(3df,3pd)(B4) level of theory, resulting in an energy difference of 0.41 kJ/mol in favor of the trans conformer in ethanol, with inclusion of ZPE. They also reported energy differences (including ZPE contributions) on the same level of theory between the conformers of 1-propanol. They predict that the all-trans conformer is the most stable conformer, followed by the *HOtg* and *HOgt* conformers with a maximal

TABLE 2: Relative Energies (in kJ/mol) of the Various Conformers of the Compounds Methyl Ethyl Ether, Methyl Ethyl Sulfide, Diethyl Ether, and Diethyl Sulfide Compared with Experiment[a]

	B3LYP					
	B1	B2	B3	B4	experiment	refs
methyl ethyl ether						
Og	6.48	6.14	6.35	6.48	4.6 → 6.3	31, 32
methyl ethyl sulfide						
Og	0.57	0.07	0.46	0.67	−0.8 → 1.5	31, 33
diethyl ether						
g_-Og_-/g_+Og_+	12.70	11.33	12.47	12.71		
g_-Og_+/g_+Og_-	16.21	15.49	16.04	16.27		
$tOg_-/tOg_+/g_-Ot/g_+Ot$	6.60	6.13	6.42	6.59	4.81	34
tOt	0.00	0.00	0.00	0.00	0.00	34
diethyl sulfide						
g_-Sg_-/g_+Sg_+	1.14	0.15	0.82	1.15	≈0	35
g_-Sg_+/g_+Sg_-	4.47	3.73	4.38	4.78	large	35
$tSg_-/tSg_+/g_-St/g_+St$	0.69	0.24	0.52	0.73	≈0	35
tSt	0.00	0.00	0.00	0.00	small	35

[a] The basis sets are defined as follows: B1 = 6-31+g*, B2 = 6−311g**, B3 = 6-311+G(3df,2p), and B4 = 6-311++G(3df,3pd).

energy difference of merely 0.25 kJ/mol. The HOg_-g_- and HOg_-g_+ geometries are 0.8 and 1.2 kJ/mol higher in energy, respectively, than the *HOtt* reference. These results almost coincide with the values reported in this work (see Table 1 of the Supporting Information), except for the B3LYP/B2 level of theory.

Other available experimental and/or ab initio data are very scarce, and are collected in Table 2. The agreement between experiment and the theoretical calculations is very satisfactory.

Finally, this basis set investigation allows us to conclude that the B3LYP/6-31+g*(B1) level is the best cost-effective level of theory for use in all further calculations.

4. Conformational Analysis

The different conformers of *n*-alkanes are reached by performing internal rotations about the C−C bonds apart from the methyl tops. Each rotational profile is characterized by three distinct potential energy minima (as shown in Figure 1, *t*, g_+, and g_-). Obviously, one could expect that a molecule with *n* such internal rotations would lead to 3^n conformers.

In several papers, the occurrence of conformers in *n*-alkanes was studied.[3−5] The most extensive study was performed by Tasi et al.[5] They reported the existence of distorted gauche standings *x*, for which the typical dihedral angle has a value of approximately ±85°, or 95° from trans, while normal gauche standings in *n*-alkanes have a dihedral of ±65°, or 115° from the trans conformation (Figure 3a). The combination of these five possible conformations leads to 5^n conformers. The actual number of conformers lies between 3^n and 5^n, since the distorted gauche conformations exist under only special circumstances. In particular, the *x*-gauche conformations are found in *n*-alkanes when two consecutive internal rotations reside in gauche standings of the opposite orientation. This g_-g_+ combination brings two carbon atoms close to each other, forcing the carbon backbone to relax. This relaxation was also observed by the authors for *n*-pentane and *n*-hexane[2,3] in their study of coupled internal rotations. On the two-dimensional potential energy profiles of consecutive internal rotations, two local minima were identified around the g_-g_+ geometry, corresponding to x_-g_+ and g_-x_+ conformers. The relative energy associated with these conformers was found to be considerably higher than those of the conformers with consecutive gauche standings of the same orientation (g_-g_-/g_+g_+).

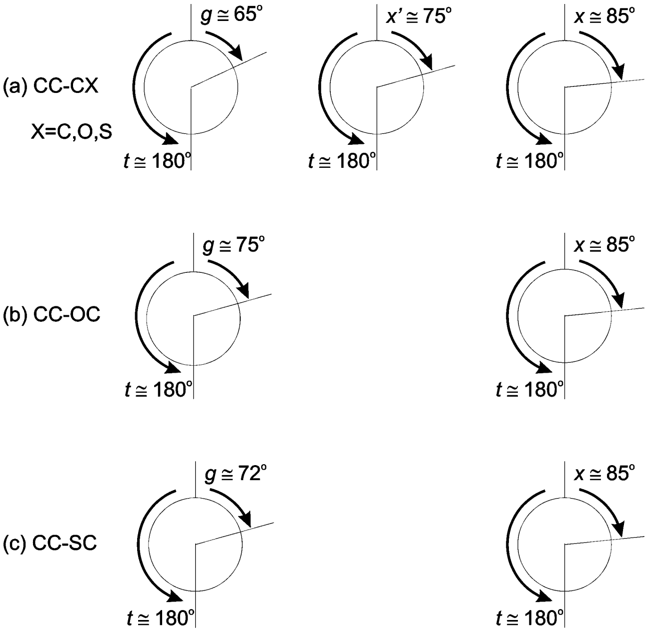

Figure 3. Newman projections of the typical dihedral angle values for gauche *g*, slightly distorted gauche *x*′, and distorted gauche *x* around a (a) C−C, (b) C−O, and (c) C−S single bond.

In this study, we evaluate the geometries of the conformers of alcohols, thiols, ethers, and sulfides. The possible interactions between consecutive internal rotations will be investigated, and the occurrence of distorted gauche conformations *x* will be examined. On the basis of these findings, we will introduce a complementary set of rules which allows the determination and structural identification of the total number of conformers in these compounds at a minimal computational expense. In addition, we also calculate the relative energies of the different conformers and compare these to the corresponding values in *n*-alkanes.

4.1. Alcohols. Since primary alcohols are *n*-alkanes in which a methyl top has been replaced with an OH group, similar conformations can be expected to occur, especially for rotations about bonds that are far from the hydroxy group. Table 3 displays the relative electronic energy of a selection of conformers from ethanol to 1-hexanol, determined at the B3LYP/6-31+g* level of theory. The conformers are arranged according to the labeling convention for the five rotations $\phi_{l1}-\phi_{l5}$, even when the involved primary alcohol has fewer than five internal rotations. For instance, the notation $HOg_+g_-(ttt)$ refers to the HOg_+g_-ttt conformer in 1-hexanol, HOg_+g_-tt in 1-pentanol, HOg_+g_-t in 1-butanol, and the HOg_+g_- conformer in 1-propanol. No energy value for ethanol is given, since only the ϕ_{l1} rotation is available in this molecule.

Table 3 is divided into two parts. The first part treats conformers with one or more gauche standings in the $\phi_{l1}-\phi_{l3}$ internal rotations, while the ϕ_{l4} and ϕ_{l5} dihedral angles remain in trans. The second part shows the conformers with one or more gauche conformations in the latter three $\phi_{l3}-\phi_{l5}$ rotations, now with ϕ_{l1} and ϕ_{l2} in trans. It is clear that these latter conformers have geometries and relative energy differences that are in accordance with those of alkane fragments (see ref 5). The relative energies of the *HOtttg*(*t*) and *HOttttg* conformers in 1-pentanol and 1-hexanol amount to almost 4 kJ/mol, which is approximately the typical value of 3.9 kJ/mol found in *n*-alkane conformers with one gauche standing (at the B3LYP/6-31+g* level of theory). Alcohol conformers with consecutive gauche standings of the same orientation in the $\phi_{l3}-\phi_{l5}$ part of

TABLE 3: Relative Energies (in kJ/mol) of Selected Conformers of Primary Alcohols (at the B3LYP/6-31+g* level of theory)[a]

$\phi_{l1}\phi_{l2}\phi_{l3}\phi_{l4}\phi_{l5}$	ethanol	1-propanol	1-butanol	1-pentanol	1-hexanol
$HOCH_2CH_2CH_2$ Functional Group Conformers					
$HOt(tttt)$	0.00	0.19	0.10	0.10	0.10
$HOg_{-}(tttt)$	0.27	0.00	0.00	0.00	0.00
$HOtg_{-}(ttt)$		0.39	0.00	0.13	0.08
$HOg_{-}g_{-}(ttt)$		0.85	0.61	0.76	0.76
$HOg_{+}g_{-}(ttt)$		1.05	0.80	0.75	0.71
$HOttg_{-}(tt)$			4.22	4.30	4.26
$HOg_{-}tg_{-}(tt)$			4.26	4.25	4.24
$HOg_{+}tg_{-}(tt)$			3.82	3.83	3.80
$HOtg_{-}g_{-}(tt)$			3.42	3.69	3.57
$HOg_{-}g_{-}g_{-}(tt)$			3.68	3.91	3.78
$HOg_{+}g_{-}g_{-}(tt)$			4.83	5.10	4.96
$HOtg_{-}x'_{+}(tt)$			7.00	6.95	7.08
$HOg_{-}g_{-}x'_{+}(tt)$			7.14	7.09	7.11
$HOg_{+}x_{-}g_{+}(tt)$			9.20	8.97	8.75
Alkane-like Conformers					
$HOtttg_{-}(t)$				4.01	3.92
$HOttg_{-}g_{-}(t)$				7.98	8.06
$HOttx_{-}g_{+}(t)$				13.66	13.43
$HOttg_{-}x_{+}(t)$				14.16	13.88
$HOttttg_{-}$					4.15
$HOttg_{-}tg_{-}$					8.16
$HOttg_{-}tg_{+}$					8.61
$HOtttg_{-}g_{-}$					7.52
$HOtttx_{-}g_{+}$					14.67
$HOtttg_{-}x_{+}$					14.69

[a] The conformer with the lowest binding energy is taken as a reference.

the molecule [$HOttg_{-}g_{-}(t)$ and $HOtttg_{-}g_{-}$] have an energy of ~8 kJ/mol, which is merely twice the energy value for the single gauche conformers. The energy of the $HOttg_{-}tg_{-}$ and $HOttg_{-}tg_{+}$ conformers is also in accordance with this summing rule. For a $g_{-}g_{+}$ sequence, steric hindrance comes into play. As in *n*-alkanes, this $g_{-}g_{+}$ geometry actually corresponds to a transition state between two energy minima, each with one distorted gauche conformation: $g_{-}g_{+} \rightarrow g_{-}x_{+}$ and $x_{-}g_{+}$. The energy of these conformers cannot be deduced by simply adding the energies of the conformers with only one gauche. The steric hindrance causes an energy increase, varying between 5.5 and 6.5 kJ/mol in excess of the earlier value of 8 kJ/mol. These additional energy values are close to the ab initio values in *n*-hexane.[3]

The conformers with one or more gauche standings in the $\phi_{l1}-\phi_{l3}$ part of the alcohol sequence seem to have a particular behavior, in contrast with the alkane-like behavior of the $\phi_{l3}-\phi_{l5}$ interactions. The all-trans conformer and the conformers with only one gauche for either ϕ_{l1} or ϕ_{l2} have approximately the same energy. For all alcohols, the reference conformer is $HOg(tttt)$, except for ethanol, where the all-trans conformer has the lowest energy. A $g_{-}g_{-}$ or $g_{+}g_{-}$ sequence for the ϕ_{l1} and ϕ_{l2} rotations results in a slightly higher energy value, but this still remains below 1 kJ/mol. Apparently, the ϕ_{l3} rotation, and its interaction with the other internal rotations in the $HOCH_2CH_2CH_2$ top, mainly determines the electronic energy. The $HOttg(tt)$ conformers have relative energies of 4.25 kJ/mol on average. These energies are not significantly altered by an additional gauche (g_{+} or g_{-}) standing in ϕ_{l1}. Hence, the interaction of the ϕ_{l3} and ϕ_{l1} internal rotations can be considered negligible. A small stabilization is observed for the $HOtg_{-}g_{-}(tt)$ and $HOg_{-}g_{-}g_{-}(tt)$ conformers. This interaction between ϕ_{l2} and ϕ_{l3} becomes more apparent when these internal rotations assume gauche conformations of the opposite orientation ($g_{-}g_{+}$). The relative energies become significantly higher than the $\phi_{l2}\phi_{l3} = g_{-}g_{-}$ conformers, due to the occurrence of a slightly distorted (x') or fully distorted (x) gauche conformation (Figure 3a). However, in this part of the alcohols, only one conformer is present around the $g_{-}g_{+}$ geometry, in contrast to the double minima typical for *n*-alkanes. Depending on the value of the ϕ_{l1} dihedral angle, their structures become $HOtg_{-}x'_{+}(tt)$, $HOg_{-}g_{-}x'_{+}(tt)$, and $HOg_{+}x_{-}g_{+}(tt)$. The latter conformer has the most distorted geometry ($\phi_{l2} = x$) and also has the highest relative energy (~9 kJ/mol). Still, this is significantly lower than the corresponding energy difference in *n*-alkanes.

The net result of these interactions is that the $HOCH_2CH_2CH_2$ top of primary alcohols does not obey the typical behavior of *n*-alkanes, as summarized by Tasi et al.[5] At the B3LYP/6-31+g* level of theory, the first 14 conformers in Table 3 are identified as being specific for the $\phi_{l1} \rightarrow \phi_{l3}$ internal rotations. Hence, they must be considered as an extension of Tasi's rules for primary alcohols, and an exact description of these alcohol conformers is required. However, the relative energies in Table 3 do not vary largely when the chain length is increased, as the geometries of the different conformers are practically not affected (Table 2 of the Supporting Information). We may therefore conclude that the 14 functional group conformers as given in Table 3 may serve as a suitable, valuable data set for the determination of all conformers in long primary alcohols.

4.2. Thiols. A similar analysis has been done for ethanethiol to 1-hexanethiol. As in alcohols, the influence of the SH end group only has a limited range. The conformers found by the three rotations in the $HSCH_2CH_2CH_2$ top ($\phi_{l1}-\phi_{l3}$) determine the specific functional group behavior of the thiol and are presented in Table 4 (with ϕ_{l4} and ϕ_{l5} both in trans). The conformers resulting from internal rotations further from the heteroelement exhibit typical alkane-like behavior. The results for these rotations are supplied in the Supporting Information (Table 3) and are not further discussed.

The most striking difference with alcohols is that the various thiol conformers are energetically more distinct from each other. The $HSg_{-}(tttt)$ conformer systematically has the lowest energy, and all other thiol conformers are at least 2 kJ/mol higher in energy. We have condensed all calculated data in Table 5, where relative energies are presented with reference to the $HSg_{-}tttt$ conformer as well as the $HStttt$ conformer. Each $\langle \Delta E \rangle$ value represents an averaged energy difference over all thiol conformers corresponding to a specific conformational class. The shorthand notation **g** can refer to either a g, an x, or an x' conformation. For example, the 14.74 kJ/mol energy difference of the $HSg_{\pm}\mathbf{g}_{-}\mathbf{g}_{+}tt$ conformational class with respect to the $HSg_{-}tttt$ reference is an average over the relative energies of the $HSg_{-}x'_{-}x'_{+}(tt)$, $HSg_{-}g_{-}x_{+}(tt)$, $HSg_{+}g_{-}x_{+}(tt)$, and $HSg_{+}x_{-}g_{+}(tt)$ conformers of 1-butanethiol, 1-pentanethiol, and 1-hexanethiol. Several main characteristics and rules applicable to thiol conformers can be extracted from this table in a transparent way:

(i) The energy increase due to a single gauche standing in one of the torsions ϕ_{li} when $i > 1$ is almost independent of the conformation for ϕ_{l1}. Only a small discrepancy of ~0.2 kJ/mol is noticed between the $HStg_{-}ttt$ (with respect to the $HStttt$ reference) and $HSg_{\pm}\mathbf{g}_{-}ttt$ conformational classes (with respect to the $HSg_{-}tttt$ reference). One easily concludes that the conformational interaction of ϕ_{l1} with the other torsional motions is rather small.

(ii) In general, the above rule is also valid when multiple gauche standings are present in the conformer. The average relative energies for the $HSg_{\pm}\mathbf{g}_{-}\mathbf{g}_{-}tt$ and $HSt\mathbf{g}_{-}\mathbf{g}_{-}tt$ conformational classes, for example, differ by only some 0.2 kJ/mol.

TABLE 4: Relative Energies (in kJ/mol) of Some Conformers in Primary Thiols (at the B3LYP/6-31+g* level of theory)

$\phi_{l1}\phi_{l2}\phi_{l3}\phi_{l4}\phi_{l5}$	ethanethiol	1-propanethiol	1-butanethiol	1-pentanethiol	1-hexanethiol
$HSt(tttt)$	2.37	2.92	2.75	2.72	2.72
$HSg_{-}(tttt)$	0.00	0.00	0.00	0.00	0.00
$HStg_{-}(ttt)$		5.71	5.44	5.51	5.46
$HSg_{-}g_{-}(ttt)$		2.31	2.44	2.53	2.53
$HSg_{+}g_{-}(ttt)$		2.66	2.65	2.66	2.62
$HSttg_{-}(tt)$			6.60	6.78	6.77
$HSg_{-}tg_{-}(tt)$			4.07	4.22	4.22
$HSg_{+}tg_{-}(tt)$			3.66	3.87	3.84
$HStg_{-}g_{-}(tt)$			8.35	8.57	8.50
$HSg_{-}g_{-}g_{-}(tt)$			5.51	5.76	5.64
$HSg_{+}g_{-}g_{-}(tt)$			6.14	6.43	6.28
$HStx'_{-}x'_{+}(tt)$			15.17	15.28	15.25
$HSg_{-}x'_{-}x'_{+}(tt)$			14.22		
$HSg_{-}g_{-}x_{+}(tt)$			14.16	13.96	13.96
$HSg_{+}g_{-}x_{+}(tt)$			15.48	14.97	15.11
$HSg_{+}x_{-}g_{+}(tt)$			15.33	15.14	15.10

TABLE 5: Schematic Overview of the Different Classes of Conformers in Thiols (at the B3LYP/6-31+g* level of theory)[a]

	$\langle \Delta E\rangle$				
reference	conformational class			alkane	reference
	HSg±g-ttt	*HSg±tg-tt*	*HSg±ttg-t*	*gttg-t*	
HSg-tttt	2.55	3.98	3.85	3.94	*gtttt*
HSttttt	2.75	3.99	3.84	3.96	*ttttt*
	HStg-ttt	*HSttg-tt*	*HStttg-t*	*tttg-t*	
	HSg±g-g-tt	*HSg±tg-g-t*	*HSg±ttg-g-*	*gttg-g-*	
HSg-tttt	5.96	7.83	7.61	7.80	*gtttt*
HSttttt	5.74	7.68	7.51	7.82	*ttttt*
	HStg-g-tt	*HSttg-g-t*	*HStttg-g-*	*tttg-g-*	
	HSg±g-g+tt	*HSg±tg-g+t*	*HSg±ttg-g+*	*gttg-g+*	
HSg-tttt	14.74	14.02	14.66	14.66	*gtttt*
HSttttt	12.50	14.00	14.61	14.65	*ttttt*
	HStg-g+tt	*HSttg-g+1*	*HStttg-g+*	*tttg-g+*	

[a] The energy differences $\langle \Delta E\rangle$ (in kJ/mol) with respect to the displayed reference conformer are average values over several thiols and over various gauche orientations in the same class. Corresponding energy differences are also given for alkanes.

Moreover, the energy of the $HSg_{-}g_{-}g_{-}(tt)$ and $HSg_{+}g_{-}g_{-}(tt)$ conformers in Table 4 is virtually independent of a g_{-} or g_{+} conformation for ϕ_{l1}. The only exception to this rule occurs for the $HSg_{\pm}\mathbf{g}_{-}\mathbf{g}_{+}tt$ conformational class, where notably higher average energy values are obtained in comparison with those of the $HSt\mathbf{g}_{-}\mathbf{g}_{+}tt$ class. Here, ϕ_{l1} does interact with ϕ_{l2} and influences the relative energy.

(iii) Sequences with two consecutive gauche standings of the opposite orientation in positions ϕ_{li} and ϕ_{li+1} when $i > 1$ cause large interactions (up to 15 kJ/mol) and give rise to double minima around the $g_{-}g_{+}$ maximum. So, starting from ϕ_{l2} and ϕ_{l3}, consecutive internal rotations interact. However, only for 1-butanethiol does this specific interaction result in four different conformations: $HSg_{-}x'_{-}x'_{+}(tt)$, $HSg_{-}g_{-}x_{+}(tt)$, $HSg_{+}g_{-}x_{+}(tt)$, and $HSg_{+}x_{-}g_{+}(tt)$ (Table 4). In 1-pentanethiol and 1-hexanethiol, the $HSg_{-}x'_{-}x'_{+}(tt)$ conformer does not occur.

(iv) The influence of the thiol functional group is virtually negligible from the ϕ_{l4} torsion on. This is suggested in the table as the average energies seem to converge to those found in *n*-alkanes.

The $HSCH_2CH_2CH_2$ top in thiols also does not meet the typical behavior of *n*-alkanes. This result is similar to that in alcohols, but here interaction effects between the internal rotations are more apparent, which gives rise to energetically distinct conformers. In all compounds, 15 conformers are identified that uniquely characterize the $\phi_{l1} \rightarrow \phi_{l3}$ internal rotations in the thiol functional group. In 1-butanethiol, one additional conformer is found ($HSg_{-}x'_{-}x'_{+}$).

4.3. Ethers. In this section, the different conformers in a series of eight ethers are discussed: methyl ethyl ether (MEE), methyl propyl ether (MPE), methyl butyl ether (MBE), methyl pentyl ether (MPeE), diethyl ether (DEE), ethyl propyl ether (EPE), ethyl butyl ether (EBE), and dipropyl ether (DPE).

Whereas in alcohols or thiols it was possible to list all conformers and their calculated energies, this would present an inefficient approach to examining ethers (or sulfides). Their functional group is not an end group, and the influence of the heteroelement can extend to both sides of the molecule. As a result, a considerably larger number of conformers must be studied. Ethyl butyl ether, for example, is characterized by four internal rotations and gives rise to at least 3^4 (81) conformers. A more functional approach is to subsequently examine conformers with one single, two consecutive, and three consecutive gauche conformations, and to deduce some general rules which apply to all possible ether conformers.

Additionally, we will evaluate two approximation schemes on the basis of their ability to produce reasonable estimates of the relative energy of a conformer, based on minimal conformational data.

4.3.1. Conformers with a Single Gauche. A summary of the results for the conformers with a single gauche conformation in ethers is given in Table 6. The table lists the energy differences relative to the all-trans conformer of the molecules along with absolute dihedral angles. A gauche conformation for a dihedral angle alongside the oxygen (ϕ_{l1} or ϕ_{s1}) results in an energy increase of ~6.5 kJ/mol for ethyl tops, and ~6.3 kJ/mol for longer alkyl chains. This is quite in contrast to *n*-alkanes, in which a single gauche conformation causes an energy increase of ~3.9 kJ/mol at the B3LYP/6-31+g*(B1) level of theory [at the B3LYP/6-311g**(B2) level of theory, this is 3.6 kJ/mol]. Furthermore, the corresponding dihedral angles of normal gauche conformations about the C−C−O−C dihedrals in ethers assume values in the range of 75−77° (Figure 3b). This is much larger than the typical dihedral angle of 65° in *n*-alkanes and rather resembles the *x*′-gauche angle of a C−C−C−C dihedral (Figure 3a). A gauche standing in the next neighboring internal rotation alongside the oxygen (ϕ_{l2} or ϕ_{s2}) causes a conformer almost as stable as the all-trans conformer, with dihedral angles of 64°. Note that this applies for ethers as well as alcohols, where the ϕ_{l2} single gauche conformer has the same energy as the all-trans conformer. Further from the oxygen, the values seem to "relax" to the *n*-alkane situation: angles of ~65° and relative energies of 4 kJ/mol for ϕ_{l3} and 3.8 kJ/mol for ϕ_{l4}.

TABLE 6: Conformers of Various Ethers and Sulfides with One Gauche[a]

conformer	MEE	MPE	MBE	MPeE	DEE	EPE	EBE	DPE	
gtOtttt								0.22	V_{s2}^{1D}
								63.7	ϕ_{s2}
tgOtttt					6.60	6.42	6.53	6.24	V_{s1}^{1D}
					75.3	*75.2*	*75.2*	*76.7*	ϕ_{s1}
ttOgttt	6.48	6.33	6.28	6.25	6.60	6.30	6.39	6.24	V_{l1}^{1D}
	74.8	*76.4*	*76.7*	*75.9*	*75.3*	*77.2*	*77.1*	*76.7*	ϕ_{l1}
ttOtgtt		0.19	−0.07	0.01		0.24	0.02	0.22	V_{l2}^{1D}
		63.6	*64.1*	*64.4*		*63.8*	*64.3*	*63.7*	ϕ_{l2}
ttOttgt			3.99	4.02			4.03		V_{l3}^{1D}
			66.0	*65.8*			*66.1*		ϕ_{l3}
ttOtttg				3.83					V_{l4}^{1D}
				65.2					ϕ_{l4}

conformer	MES	MPS	MBS	MPeS	DES	EPS	EBS	DPS	
gtSttt								2.75	V_{s2}^{1D}
								66.2	ϕ_{s2}
tgSttt					0.69	0.62	0.63	0.02	V_{s1}^{1D}
					72.3	*72.6*	*72.8*	*73.1*	ϕ_{s1}
ttSgttt	0.57	0.08	0.20	0.16	0.69	0.17	0.27	0.02	V_{l1}^{1D}
	70.0	*72.5*	*71.4*	*71.7*	*72.3*	*74.1*	*73.2*	*73.1*	ϕ_{l1}
ttStgtt		2.83	2.70	2.66		2.80	2.64	2.75	V_{l2}^{1D}
		65.9	*66.5*	*66.1*		*65.7*	*65.8*	*66.2*	ϕ_{l2}
ttSttgt			3.80	3.91			3.79		V_{l3}^{1D}
			65.4	*65.9*			*65.3*		ϕ_{l3}
ttStttg				3.80					V_{l4}^{1D}
				65.5					ϕ_{l4}

[a] Relative energies in kJ/mol and absolute dihedral angles in degrees (at the B3LYP/6-31+g* level of theory). The reference is the all-trans conformer.

In conclusion, the nearest (ϕ_{l1} and ϕ_{s1}) and next-nearest (ϕ_{l2} and ϕ_{s2}) internal rotations show a behavior which is distinctly different from that of *n*-alkanes. For rotations which are further distanced from the oxygen atom, the alkane-like behavior seems to be restored.

4.3.2. Two Consecutive Gauche Standings. All possible ether conformers with two consecutive gauche orientations are listed in Table 7. For each conformer, the energy (V_{AB}^{2D}) is given relative to the all-trans conformer. In addition, the two corresponding dihedral angles (ϕ_A and ϕ_B) are given. In the supposition of noninteracting internal rotations, it would be possible to make a rough guess of these relative energies and dihedral angles using the data of single gauche conformers (Table 6). This energy estimate corresponding to two consecutive gauche standings would then be

$$\Delta E_{AB}^{1D-est} = V_A^{1D}(\phi_A = g_A^{1D}) + V_B^{1D}(\phi_B = g_B^{1D}) \qquad (1)$$

where V_A^{1D} is the relative energy obtained in a one-dimensional approach corresponding to a gauche orientation in torsional angle ϕ_A. g_A^{1D} refers to the gauche angle in the single gauche conformer, and this dihedral generally differs from the corresponding angle in the conformer with two consecutive gauche orientations. In Table 7, the difference between both angles ($\Delta\phi_A$) is presented along with the one-dimensional energy guess (ΔE_{AB}^{1D-est}). However, it is clear from the previous discussions that the interaction between consecutive internal rotations is not negligible. This was thoroughly confirmed on *n*-alkanes in refs 3 and 5. Still, it is valuable to discuss double gauche conformers in terms of their differences with a one-dimensional approach.

TABLE 7: Conformers of Various Ethers and of EBS with Two Consecutive Gauche Standings[a]

(ϕ_A,ϕ_B)	conformer	molecule	V_{AB}^{2D}	ϕ_A	ϕ_B	ΔE_{AB}^{1D-est}	$\Delta\phi_A$	$\Delta\phi_B$
(ϕ_{s1},ϕ_{l1})	x_-Ox_-	DEE	12.70	86.0	86.0	13.20	10.7	10.7
		EPE	12.20	86.6	88.3	12.72	11.4	11.1
		EBE	12.24	86.6	87.4	12.92	11.4	10.3
		DPE	11.69	88.3	88.2	12.48	11.6	11.5
	x_-Ox_+	DEE	16.21	91.8	−91.8	13.20	16.5	16.5
		EPE	15.67	91.9	−92.3	12.72	16.7	15.1
		EBE	N/A	N/A	N/A	12.92	N/A	N/A
		DPE	N/A	N/A	N/A	12.48	N/A	N/A
(ϕ_{l1},ϕ_{l2})	Og_-g_-	MPE	6.70	75.3	59.1	6.52	−1.1	−4.5
		MBE	6.57	75.7	60.1	6.21	−1.0	−4.0
		MPeE	6.52	75.8	60.2	6.25	−0.1	−4.2
		EPE	6.90	75.2	59.3	6.54	−2.0	−4.5
		EBE	6.58	76.3	60.5	6.41	−0.8	−3.8
		DPE	6.75	74.9	58.7	6.46	−1.8	−5.0
(ϕ_{l2},ϕ_{l3})	Otg_-g_-	MBE	3.37	61.5	65.2	3.92	−2.6	−0.8
		MPeE	3.56	61.5	65.6	4.02	−2.9	−0.2
		EBE	3.37	61.5	64.6	4.04	−2.8	−1.5
	$Otg_-x'_+$	MBE	6.93	69.8	−74.8	3.92	5.7	8.8
		MPeE	6.82	69.6	−75.3	4.02	5.2	9.5
		EBE	7.19	69.9	−75.8	4.04	5.6	9.7
(ϕ_{l3},ϕ_{l4})	$Ottg_-g_-$	MPeE	7.74	64.0	61.8	7.85	−1.8	−3.4
	$Ottg_-x_+$	MPeE	13.81	65.7	−87.3	7.85	0.1	22.1
	$Ottx_-g_+$	MPeE	13.52	97.4	−63.7	7.85	31.6	−1.5
(ϕ_{s1},ϕ_{l1})	g_-Sg_-tt	EBS	0.96	72.4	73.0	0.91	−0.4	−0.2
	g_-Sx_+tt		3.94	73.3	−97.3	0.91	0.5	24.1
	x_-Sg_+tt		4.03	96.1	−74.4	0.91	23.3	1.2
(ϕ_{l1},ϕ_{l2})	tSg_-g_-t	EBS	2.21	76.3	67.1	2.91	3.1	1.3
	tSx_-g_+t		5.37	97.1	−66.2	2.91	23.9	0.4
(ϕ_{l2},ϕ_{l3})	$tStg_-g_-$	EBS	5.58	62.5	60.7	6.42	−3.3	−4.6
	$tStx'_-x'_+$		12.02	75.7	−76.4	6.42	9.9	11.1

[a] Relative energies are given in kJ/mol and absolute dihedral angles in degrees (at the B3LYP/6-31+g* level of theory). The reference is the all-trans conformer. N/A means that the conformer is not present. ΔE_{AB}^{1D-est} is defined in eq 1.

When the gauche standings take place at either side of the oxygen (*gOg*), $\Delta\phi$ angles can amount to ≥10°. This is mainly due to the strong interaction existing between the ϕ_{s1} and ϕ_{l1} torsions, manifesting in strongly distorted gauche positions ($\phi \approx 90°$). Those gauche positions with opposite orientations (x_-Ox_+) exhibit very shallow minima and give no evidence for a double minimum. They are only detected in smaller ethers DEE and EPE at the B3LYP/B1 level of theory. At the B3LYP/B2 level, this minimum is observed in only DEE. In addition, their relative energies are underestimated by some 3 kJ/mol in the one-dimensional approximation. The minima corresponding with equal orientation (x_-Ox_-) are more pronounced and occur in all investigated ethers. The relative energies are described well within the one-dimensional approach, but evidently, the gauche dihedral angles deviate substantially.

Conformers with two consecutive gauche standings alongside the oxygen (*Ogg*) occur only when both ϕ_{l1} and ϕ_{l2} assume equivalent gauche orientations. Their properties are rather well predicted in the one-dimensional approximation: ΔE_{AB}^{1D-est} closely resembles V_{AB}^{2D}, and $\Delta\phi_A$ and $\Delta\phi_B$ values are small.

When the two consecutive gauche standings are moved one torsion further (*Otgg*), the typical *n*-alkane-like pattern already begins to manifest. The Otg_-g_- conformers reveal dihedral angles that are very close to the typical undisturbed value of 65°. But, as in the preceding case, two consecutive gauche standings with the opposite orientation do not yet give rise to the double conformational minimum. Instead, only one $Otg_-x'_+$ conformer is found with a slightly distorted ϕ_{l3} gauche angle. A similar effect was observed in alcohols [e.g., the $HOtg_-x'_+(tt)$ type conformer in Table 3].

TABLE 8: Conformers of Various Ethers and of EBS with Three Consecutive Gauche Standings[a]

(ϕ_A,ϕ_B,ϕ_C)	conformer	molecule	V^{3D}_{ABC}	ϕ_A	ϕ_B	ϕ_C	ΔE^{1D-est}_{ABC}	ΔE^{2D-est}_{ABC}
$(\phi_{s1},\phi_{l1},\phi_{l2})$	$x_-Ox_-g_-$	EPE	12.83	86.4	87.7	61.7	12.96	12.80
		EBE	12.53	86.4	87.6	62.3	12.94	12.44
		DPE	12.32	88.0	87.4	61.5	12.70	12.20
$(\phi_{l1},\phi_{l2},\phi_{l3})$	$Og_-g_-g_-$	MBE	9.82	73.8	56.2	64.3	10.20	10.01
		MPeE	9.84	73.2	56.1	65.2	10.27	10.07
		EBE	9.87	74.9	56.6	63.9	10.43	9.94
	$Og_-g_-x'_+$	MBE	13.18	76.9	66.9	−74.0	10.20	13.57
		MPeE	12.90	76.2	66.1	−75.3	10.27	13.33
		EBE	13.37	77.8	68.1	−72.5	10.43	13.76
$(\phi_{l2},\phi_{l3},\phi_{l4})$	$Otg_-g_-g_-$	MPeE	7.31	60.7	63.3	63.1	7.85	7.28
	$Otx'_+g_-g_-$		10.14	73.5	−68.9	−62.9	7.85	10.54
	$Otx'_-g_+x_-$		17.53	78.8	−67.4	88.8	7.85	16.61
	$Otg_-x_-g_+$		14.17	65.3	93.6	−65.1	7.85	13.06
	$Otg_-g_-x_+$		14.49	59.7	62.9	−92.5	7.85	13.35
$(\phi_{s1},\phi_{l1},\phi_{l2})$	$g_-Sg_-g_-t$	EBS	2.89	73.3	75.2	66.3	3.58	2.77
	$g_+Sx_-g_-t$		5.40	−70.2	101.5	66.6	3.58	5.88
	$g_-Sx_-g_+t$		6.03	75.6	100.1	−67.1	3.58	6.06
$(\phi_{l1},\phi_{l2},\phi_{l3})$	$tSg_-g_-g_-$	EBS	5.57	72.9	62.4	63.9	6.70	5.15
	$tSx_+g_-g_-$		9.91	−98.7	66.8	66.3	6.70	8.31
	$tSx_-g_+x_-$		17.94	95.9	−68.4	90.5	6.70	14.75
	$tSg_-x_-g_+$		13.42	79.4	86.6	−67.4	6.70	11.59
	$tSg_-g_-x_+$		13.66	70.7	66.7	−88.8	6.70	11.59

[a] Relative energies in kJ/mol and absolute dihedral angles in degrees (at the B3LYP/6-31+g* level of theory). The reference is the all-trans conformer.

Finally, when the consecutive gauche conformations are farther from the oxygen (e.g., $\phi_{l3}\phi_{l4}$ in MPeE), the same behavior is revealed as in *n*-alkanes with the double $Ottg_-x_+$ and $Ottx_-g_+$ minima around the $Ottg_-g_+$ maximum.

4.3.3. Three Consecutive Gauche Standings. The number of ether conformers with three consecutive gauche conformations is rather limited (Table 8) as the restrictions on two consecutive gauches also seem to apply for three successive gauche standings. The g_-g_+ conformation never appears for the $\phi_{s1}\phi_{l1}$ and ϕ_{l1} and ϕ_{l2} dihedral angles. This implies that only the $x_-Ox_-g_-$ conformer is formed in the $\phi_{s1}-\phi_{l2}$ class and $Og_-g_-g_-$ and $Og_-g_-x'_+$ are formed in the $\phi_{l1}-\phi_{l3}$ class.

The influence of the oxygen on the conformers with three consecutive gauche standings weakens when they occur large distances from the oxygen (e.g., in the dihedral angles $\phi_{l2}-\phi_{l4}$). An *n*-alkane-like behavior makes its appearance in a more pronounced way. According to the Tasi rules,[5] one could expect six conformers: $g_-g_-g_-$, $x_+g_-g_-$, $g_+x_-g_-$, $x_-g_+x_-$, $g_-x_-g_+$, and $g_-g_-x_+$. However, this pattern is not entirely found according to the constraints reported in the previous paragraph, restricting the first two rotations (ϕ_{l2} and ϕ_{l3}) to reside in g_-g_-/g_+g_+ or x'_+g_-/x'_-g_+ double gauche conformations. This additional constraint reduces the total number of conformations of this class to five, as given in Table 8.

These findings enable us to propose an adjusted version of Tasi's rules which can be applied on ethers. Starting from the original rules suitable for *n*-alkanes, one can impose some additional constraints in the sense that when a particular double gauche sequence is not allowed in a conformer, it remains excluded in the structure of all other conformers with multiple gauche conformations. To illustrate with an example, from Table 7 it follows that some g_-g_+ sequences are not occurring. In the formation of conformers with three or more gauche standings, we can a priori eliminate all combinations having this particular g_-g_+ sequence.

Since the occurrence of a triple gauche conformer is mainly determined by the rules governing two consecutive gauche conformations, it is reasonable to assume that its energy could be better approximated by including energy effects of all *gg* conformations. In this two-dimensional approach, the relative energy is estimated as

$$\Delta E^{2D-est}_{ABC} = V^{2D}_{AB}(\phi_A = g^{2D}_A, \phi_B = g^{2D}_B) + V^{2D}_{BC}(\phi_B = g^{2D}_B, \phi_C = g^{2D}_C) - V^{1D}_B(\phi_B = g^{1D}_B) \quad (2)$$

which is merely an extrapolation of eq 1. This estimate is also given in Table 8 compared to the one-dimensional guess ΔE^{1D-est}_{ABC}. The calculated energy V^{3D}_{ABC} is given relative to the all-trans conformer.

The energies of the triple gauche conformers exhibit large variations, and they are not reproduced correctly by the one-dimensional scheme. Whenever a g_+ or x_+ conformation occurs, discrepancies are even enormous. The two-dimensional approach, on the other hand, is quite accurate. The difference between the exact and the two-dimensional prediction only exceeds 1 kJ/mol for the $Otg_-x_-g_+$ and $Otg_-g_-x_+$ conformers of MPeE. For all other conformers, the discrepancy is limited to 0.5 kJ/mol. The adequacy of the two-dimensional approximation in describing fully coupled three-dimensional features in *n*-alkanes has already been reported in ref 3. Energy estimates based on a one-dimensional scheme (ΔE^{1D-est}) are manifestly inadequate.

In summary, we have found a set of rules for deducing all conformers in ethers. These are based on the possible occurrence of double gauche sequences in these compounds. Starting from the general *n*-alkane rules of Tasi et al.,[5] one can eliminate several conformers on the basis of these *gg* combinations. In addition, a two-dimensional scheme has been proposed which is adequate for describing all possible conformers and their relative energies solely based on information for conformers with single and double gauche standings.

4.4. Sulfides. In view of the evident similarity between the two types of molecules, all sulfides are discussed in comparison with the ether properties. More specifically, methyl ethyl sulfide (MES), methyl propyl sulfide (MPS), methyl butyl sulfide (MBS), methyl pentyl sulfide (MPeS), diethyl sulfide (DES), ethyl propyl sulfide (EPS), ethyl butyl sulfide (EBS), and dipropyl sulfide (DPS) are considered. Only a selection of the results is presented in the paper, but all other results are available as Supporting Information (Tables 4 and 5).

The analogy between the conformers with a single gauche of both systems can be examined in Table 6. The energies of sulfide conformers with one gauche in either ϕ_{l1} or ϕ_{s1} is very close to the all-trans reference energy. In this respect, sulfides clearly differ from ethers, in which the ϕ_{l2} or ϕ_{s2} single gauche conformers closely match the all-trans energy. The ϕ_{l2} rotations in sulfides show the opposite behavior: the energy differences amount to 2.7 kJ/mol, with dihedral angles of 66°. A complete accordance between ethers and sulfides is only found for the ϕ_{l3} and ϕ_{l4} gauche conformers, for which the energies and dihedral angles actually converged to typical alkane values.

The discussion of conformers with two gauche dihedrals is limited to EBS (Table 7), since the other sulfides yield similar results. Some striking differences with ethers are observed. It appears that several sequences of gauche standings with the opposite orientation are not forbidden. For the $\phi_{s1}-\phi_{l1}$ interaction, there is even a doubling of conformers (x_-Sg_+tt and g_-Sx_+tt). This is analogous with the alkane situation, but here the dihedrals are substantially more distorted with angles of up to 97°. These conformers have 3 kJ/mol of additional energy as compared to the g_-Sg_-tt conformer.

There is only one conformer with opposite gauche orientations for the $\phi_{l1}-\phi_{l2}$ and $\phi_{l2}-\phi_{l3}$ interactions: tSx_-g_+t and $tStx'_-x'_+$, respectively. As from the $\phi_{l3}-\phi_{l4}$ interaction, the conformers have full alkane-like features. This is illustrated for MPeS in the Supporting Information (Table 4).

The one-dimensional energy estimates ΔE_{AB}^{1D-est} are only adequate for conformers with two consecutive gauche standings of equal orientation. In contrast, the ΔE_{AB}^{1D-est} values considerably underestimate the energy of the conformers with opposite gauche orientations, up to 6 kJ/mol for $tStx'_-x'_+$. This partial success and partial failure is also observed for ethers, for alcohols and thiols, and for *n*-alkanes.[3]

For the study of three consecutive gauche standings (Table 8), we also restrict the discussion to EBS. The number of conformers is definitely higher than in ethers, but still less than that predicted by Tasi's alkane rules. Furthermore, it is not possible to predict the occurrence of triple gauche conformers on the basis of the double gauche conformers. This also applies for the (ϕ_{l2},ϕ_{l3},ϕ_{l4}) conformers of MPeS (Table 5 of the Supporting Information).

By confronting the relative energies for these conformers with the predictions obtained in the one- and two-dimensional approaches, we confirmed that the ΔE_{AB}^{1D-est} energies do not describe the correct features. The ΔE_{ABC}^{2D-est} values on the other hand are very satisfactory, describing both stabilization effects ($g_-g_-g_-$) and additional energies for conformers with g_-g_+ sequences.

5. Overview of Conformational Rules

The revised Tasi rules (up to triple gauche) for ethers and sulfides are presented in Table 9. It is obvious that the region exposed to the specific influence of the heteroelement is $\phi_{s2} \rightarrow \phi_{l2}$. In other words, all double or triple consecutive gauche conformers involving one of these internal rotations do not obey Tasi's alkane rule.

The specific conformers of primary alcohols and thiols not obeying Tasi's law are presented in Tables 3 and 4.

6. Summary

In this work, we performed a conformational analysis of alcohols, thiols, ethers, and sulfides. Our main goal was to modify the general rules for the occurrence of conformers in *n*-alkanes deduced by Tasi et al.[5] for these systems. Essentially, this was accomplished by identifying that part of the molecule not obeying Tasi's law, and by analyzing all possible conformers in this part of the molecule.

TABLE 9: Overview of Alterations of Tasi's Rule for Alkane Conformers in Ethers and Sulfides[a]

Double Gauche Conformers

	$\phi_{s1}\phi_{l1}$	$\phi_{l1}\phi_{l2}$	$\phi_{l2}\phi_{l3}$	$\phi_{l3}\phi_{l4}$
Tasi	ethers			
g_-g_-	x_-Ox_-	Og_-g_-	Otg_-g_-	$Ottg_-g_-$
g_-x_+	(x_-Ox_+)		$Otg_-x'_+$	$Ottg_-x_+$
x_-g_+				$Ottx_-g_+$
Tasi	sulfides			
g_-g_-	g_-Sg_-	Sg_-g_-	Stg_-g_-	$Sttg_-g_-$
g_-x_+	g_-Sx_+		$Stx'_-x'_+$	$Sttg_-x_+$
x_-g_+	x_-Sg_+	Sx_-g_+		$Sttx_-g_+$

Triple Gauche Conformers

	$\phi_{s1}\phi_{l1}\phi_{l2}$	$\phi_{l1}\phi_{l2}\phi_{l3}$	$\phi_{l2}\phi_{l3}\phi_{l4}$
Tasi	ethers		
$g_-g_-g_-$	$x_-Ox_-g_-$	$Og_-g_-g_-$	$Otg_-g_-g_-$
$x_+g_-g_-$			$Otx'_+g_-g_-$
$x_-g_+x_-$			$Otx'_-g_+x_-$
$g_-g_-x_+$		$Og_-g_-x'_+$	$Otg_-g_-x_+$
$g_-x_-g_+$			$Otg_-x_-g_+$
Tasi	sulfides		
$g_-g_-g_-$	$g_-Sg_-g_-$	$Sg_-g_-g_-$	$Stg_-g_-g_-$
$g_+x_-g_-$	$g_+Sx_-g_-$		$Stx'_+x'_-g_-$
$x_+g_-g_-$	($x_+Sg_-g_-$)	$Sx_+g_-g_-$	
$x_-g_+x_-$		$Sx_-g_+g_-$	$Stx_-g_+x_-$
$g_-g_-x_+$		$Sg_-g_-x_+$	$Stg_-g_-x_+$
$g_-x_-g_+$	$g_-Sx_-g_+$	$Sg_-x_-g_+$	$Stg_-x_-g_+$
			$Stg_-x'_-x'_+$

[a] The conformers given in parentheses occur for the smallest molecules only, and are of no importance for the general behavior of (longer) ethers and sulfides.

For alcohols and thiols, it was found that the $HXCH_2CH_2CH_2$ (X = O or S) top is the part distinct from *n*-alkanes, while for ethers and sulfides, third-order rotations from the heteroelement ($\phi_{s3} \rightarrow \phi_{l3}$) have to be taken into consideration to sufficiently account for the effects of the oxygen or sulfur. The conformational structure and pattern of the hetero region differ in the four types of molecules.

The identification of this region of hetero influence ($\phi_{s3} \rightarrow \phi_{l3}$) enables us to make some assumptions for carbon chains with multiple heteroelements. It is clear that when these heteroatoms are separated by fewer than six bonds, both regions of influence are likely to interact and change the relative energy and geometry of the conformations in this area. When the heteroelements are separated by at least six bonds, a reduced mutual influence can be expected, although other intramolecular effects (e.g., hydrogen bonding, anomeric resonance) cannot be excluded. This will no doubt affect the predicted conformations.

Only thiols exhibit a distinct global minimum [$HSg(tttt)$]. All other conformers are at least 2 kJ/mol less bound. For the three other types of molecules, no strict rules can be proposed for the ground-state configuration. Many conformers are competing within an energy interval of 1 kJ/mol. An accurate description of molecular properties, even at low temperatures, requires a complete knowledge of all existing conformers. It is thus important to use a model that generates all low-energy conformers.

While for primary alcohols and thiols it is possible to reproduce all conformers specific to the functional group (14 and 15, respectively), this becomes more cumbersome for ethers and sulfides, because the heteroelement now affects two alkyl side chains. For this reason, we have focused on conformers with up to three consecutive gauche standings, and we have introduced rules that allow the successful identification of all conformers in the functional group region. Moreover, an exact calculation of conformers with two consecutive gauches, in addition to single gauche conformers, permits a reliable prediction of their relative energies. This reduces the calculation time considerably as only a fraction of the total number of conformers has to be determined explicitly. Furthermore, conformers with more than two gauche standings are considerably higher in electronic energy than single or double gauche structures. As a result, they are generally less important.

Generally, the contribution of each conformer to thermodynamic properties (e.g., enthalpies of formation) is proportional to the Boltzman factor $e^{-\beta\Delta E}$, where ΔE is the energy difference with the reference conformer.[36,37] Using the energy scheme introduced in this work, one is able to determine the importance of every conformer (at a given temperature) without the need of explicit calculations.

Our rules may thus serve as a fast method for selecting those conformers with associated energies below a given energy threshold, and therefore with a significant contribution to the desired property.

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Supporting Information Available: Relative energies of the five conformers of 1-propanol (Table 1), absolute dihedral angles of the different conformers in primary alcohols (Table 2), relative energies of selected alkane-like conformers of primary thiols (Table 3), relative energies of the double gauche conformers of sulfides (Table 4), and relative energies of the triple gauche conformers of sulfides (Table 5). This material is available free of charge via the Internet at http://pubs.acs.org.

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