"Mechanism of isomerization in dithietane-1,3-dioxide"

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cis and *trans* conformations in 3-substituted thietane-1-oxide

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Abstract

For a series of 3-substituted-thietane-1-oxide (3-R-TOX) derivatives (R = chloro, methyl, ethyl, acetate, *t*-buthyl, phenyl and *p*-chlorophenyl), the *cis* ⇔ *trans* isomerization reactions have been theoretically studied in the frame of molecular orbital theory. Optimized geometries have been obtained at HF/6-31G** level, whereas the energetics and thermodynamics were calculated with basis sets that include polarization, diffuse functions and electron correlation at the second-order Møller–Plesset perturbation theory. The size and nature of the substituent seems to exert no influence on the structure of the thietane-1-oxide ring. Gas phase thermodynamics predict the *cis* isomers to be the preferred structure in these compounds as a result of the H10···O9 non-bonded interaction. The exception to this trend are the chloro and acetate derivatives where a 14 and 46% of the *trans* isomer, respectively, is predicted. In CCl_4 solution, the isomerization reaction would take place in large extent. The calculated ^{1}H-NMR chemical shifts correlate well with the experimental data and demonstrate that the β-protons (H10) are magnetically sensible enough to allow the *cis* and *trans* isomeric forms to be distinguished. The β-protons chemical shifts calculated in CCl_4 do not differ appreciably from the gas phase values. The ^{17}O-NMR signals have also been derived and the potentiality of this nucleus to be used to assign the preferred geometry as well as to follow the isomerization reaction, in this kind of compounds is pointed out. The present work also indicates that the S=O stretching mode can be used to assign either a *cis* or *trans* conformation in these species, though this vibrational mode is strongly coupled with some ring and H–C–H angle deformation modes.

Keywords: Substituted thietane-oxide; Isomerization *cis*/*trans*; NMR calculations

1. Introduction

Although substituted sulfines were known as stable compounds, the parent sulfine (CH_2SO) was first detected by mass spectrometry by Block et al. [1] in 1976 in a study of flash vacuum pyrolysis of thietane-1-oxide (TOX) and dithietane-1-oxide. In fact, both compounds start to decompose in the gas phase to yield sulfine at ca. 600 and 300 °C, respectively. In previous papers [2,3], the *cis* conformation preference for some chloro, methyl, ethyl and *t*-buthyl derivatives of thietane-1-oxide, were reported. The thermodynamics for the *cis* to *trans* interconversion reaction show that the *cis* isomeric form predominates over the *trans* regardless the size of the substituent on C3. For the chloro derivatives, the *trans* isomer would be in ca. 14–16% concentration, whereas in the other derivatives the *trans* form concentration is negligible (ca. 1%). It was also found that that the 1,3 repulsive interactions and the repulsion between H_β···sulfur lone-pair of electrons do not determine the preferential conformation in these compounds. In fact, the H_β···O9 non-bonded interaction seems to be an important factor in favoring the *cis* geometry over the *trans*. The *cis* ⇔ *trans* isomerization reaction in the 3-chloro and 3-methyl thietane-1-oxides would take place via a quasi-planar transition state and an activation energy (E_a) of ca. 45 kcal/mol was predicted [3]. In the present work, the 3-chloro, 3-methyl, 3-ethyl and 3-*t*-buthyl thietane-1-oxide series has been extended to include some other substituents. Thus, acetate, phenyl and chlorophenyl derivatives for which ^{1}H-NMR experimental data is available [4] have been added. The aim of this work is to study whether the previous *cis* preference can be reversed with bulkier substituents and also to see if the theoretical H_β (H10 in Fig. 1) signals would allow to distinguish between *cis* and *trans* conformations.

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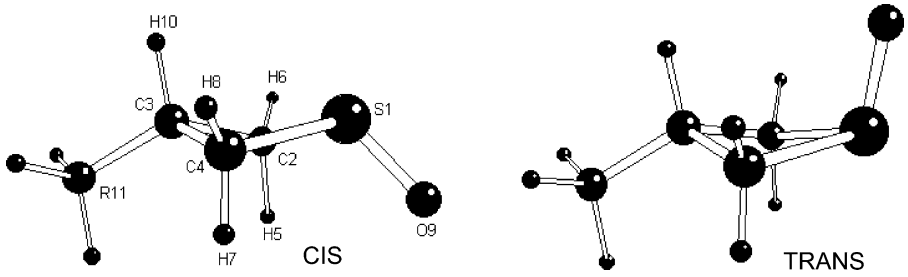

Fig. 1. Optimized geometries of *cis* and *trans* 3-methyl-thietane-1-oxide and atom numbering used in Table 1.

Although, Johnson and Siegl [4] reported that isomers could be separated by elution from a silica gel column, overlap of the H_α and H_β of the NMR signals lead to the assignment of a given geometry to be not so straightforward. Since the S=O bond exerts a significant deshielding effect on H_β, the *trans* form would exhibit a larger chemical shift than the *cis* one. A difference of ca. 0.8–1.1 ppm has been proposed [4].

2. Computational methods

Geometry optimization for all species were carried out at HF/6-31G** and B3LYP/6-31G** levels. For some species, the optimized geometries were also calculated at the MP2/6-31G** level. In all cases, GAUSSIAN 03 series of programs were used [5]. The initial geometries were that reported previously [2,3]. The energies derived at the MP2/6-31G**//HF/6-31G** and MP2/6-31G**//MP2/6-31G** were compared in order to determine whether or not the geometries need to be calculated at a correlated level to obtain accurate energies. ΔE(*cis–trans*) values of ca. 0.08 and 0.02 kcal/mol were found for 3-chloro and 3-acetate derivatives. These values clearly indicate that optimization at correlated level is not necessary. In fact, the largest differences in bond distances calculated at correlate and uncorrelated levels are ca. 0.03 Å whereas the bond angle largest variation is ca. 1.1° for both *cis* and *trans* isomeric forms. Frequency and IR intensities were predicted at the equilibrium geometries (HF/6-31G**) yielding all real frequencies so that all calculated structures are local minima. Energy calculations were carried out using a flexible basis set like 6-311+G** that includes both polarization and diffuse functions. Electron correlation at the second-order Møller Plesset theory in the frozen core approximation was also included. Attempts to explore higher order Møller Plesset and QCISD using the same basis set failed due to our limited computational facilities. The calculated energies were corrected for zero point vibrational energies and enthalpies and free energy changes of isomerization were obtained from the corresponding sums of electronic and thermal enthalpies and free energies, respectively. The solute–solvent interactions were taken into account by using the polarized continuum method (PCM) [6–11] for which its capacity to reproduce solvation energies [12] leads us to conclude that PCM behaves well in most cases but fails in others. The failure occurs mainly with solvents other than water. To apply PCM, the gas phase geometries were taken since very small changes in the geometrical parameters are observed in going from the gas phase to the solution (Table 1). In fact, optimization of all structures at HF/6-31G** level in CCl_4 show that bond distances largest variation is ca. 0.006 Å, whereas bond angles varies ca. 0.07°. Free energies in solution (G^0_{SOLN}) were calculated from $G^0_{SOLN} = \Delta G^0_{GAS} + \Delta G^0_S$ where the later term is the PCM solvation energy that includes both electrostatic and non-electrostatic contributions. The concentration of each species was estimated from the corresponding ΔG^0_{SOLN} value.

To obtain the theoretical ^1H and ^{17}O chemical shifts (δ), the B3LYP/6-31G** geometries were obtained for all compounds studied here as well as the equilibrium geometry for the molecules used as standards. The magnetic shielding tensors were calculated at HF/6-311+G**//B3LYP/6-31G** level of theory [13] using the Gauge-Independent Atomic Orbital (GIAO) method [14,15]. Chemical shifts were derived with respect to the NMR isotropic magnetic shielding tensors (in ppm) from the corresponding standard tensors (TMS = 32.1 ppm for ^1H and H_2O = 321.0 ppm for ^{17}O).

3. Results and discussion

3.1. Molecular structures

Thietane is a non-planar four-membered ring containing a sulfur atom that can be easily oxidized to thietane-1-oxide (TOX). Accordingly, TOX can be considered as a cyclic sulfoxide whose 3-substituted derivatives can exit in the *cis* or *trans* isomeric forms. The *cis* form is that possessing the C3 substituent (R = Cl–, Me–, Et–, Acet–, *t*-but–, phen–, *p*-Cl-phen–) *cis* to the oxygen atom bonded to sulfur. In this configuration the H_β-proton (H10) is *cis* to the electron pair on sulfur. In the *trans* isomer, oxygen is *trans* to R and the H_β is also *trans* to the lone pair. Fig. 1 shows the *trans* and *cis* isomers optimized structures for 3-methyl-TOX as well as the numbering used in Table 1. From Table 1, it can be inferred that despite de differences in the size and nature of

Table 1
Selected structural parameters for some 3-substituted-thietane-1-oxide (TOX)

	Acetate		*t*-Buthyl		Phenyl		*p*-Cl-phenyl	
	cis	*trans*	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*
Bond distances (Å)								
S1–C2	1.822(−1)	1.826(−1)	1.817(−2)	1.824(−2)	1.817(−2)	1−823(−1)	1.817(−1)	1.823(−1)
C2–C3	1.537(0)	1.536(0)	1.544(1)	1.545(0)	1.544(0)	1.544(0)	1.543(1)	1.544(0)
S1–09	1.476(0)	1.484(4)	1.479(5)	1.485(5)	1.478(5)	1.484(5)	1.477(5)	1.484(4)
C3–R11	1.401(2)	1.400(0)	1.544(0)	1.542(0)	1.513(0)	1.512(0)	1.513(0)	1.512(0)
C2–H5,7	1.083(0)	1.084(0)	1.083(0)	1.084(0)	1.084(0)	1.084(0)	1.084(0)	1.084(0)
C4–H6,8	1.081(0)	1.081(0)	1.081(0)	1.081(0)	1.081(0)	1.081(0)	1.081(0)	1.081(0)
C3–H10	1.082(−1)	1.079(0)	1.087(0)	1.084(0)	1.087(0)	1.085(0)	1.087(0)	1.084(1)
C2···C4	2.249(2)	2.246(2)	2.247(2)	2.252(1)	2.245(1)	2.248(1)	2.245(2)	2.248(1)
S1···C3	2.390(−1)	2.398(1)	2.384(3)	2.417(0)	2.386(−3)	2.419(0)	2.386(−2)	2.417(0)
R11···H10[a]	2.055(1)	2.063(0)	2.132(1)	2.138(0)	2.127(1)	2.134(0)	2.125(1)	2.133(−1)
Bond angles (deg)								
C3C2S1	90.3(0)	90.6(1)	90.0(−1)	91.3(1)	90.1(−1)	91.5(0)	90.1(−1)	91.4(0)
C4C3C2	94.3(1)	94.2(1)	93.4(0)	93.6(0)	93.3(0)	93.5(0)	93.3(1)	93.5(0)
C2S1C4	76.3(1)	75.9(1)	76.4(1)	76.2(2)	76.3(1)	76.1(1)	76.3(1)	76.1(1)
O9S1C2	112.4(−1)	107.1(2)	112.8(0)	107.9(0)	112.9(0)	107.8(1)	112.8(0)	107.7(1)
RC3C2	116.2(−2)	116.2(1)	119.9(−1)	120.2(0)	118.2(−1)	118.3(0)	118.2(−1)	118.3(0)
H5,7CH6,8	111.0(0)	111.1(1)	110.4(1)	110.1(1)	110.6(1)	110.5(−1)	110.7(0)	110.5(−1)
H10C3C2	111.7(2)	110.9(0)	107.7(1)	106.9(0)	108.7(0)	108.0(1)	108.0(0)	108.0(1)
H10C3R11	111.1(0)	112.0(−2)	107.0(1)	107.8(−1)	108.6(1)	109.4(0)	108.6(0)	109.4(−1)
S1C4C3C2	23.6(−4)	23.4(0)	25.7(1)	22.2(−4)	25.6(0)	22.0(3)	25.6(−1)	22.2(3)
O9S1C2C3	129.1(0)	−84.1(7)	131.6(2)	−85.5(4)	131.6(1)	−85.6(−3)	131.5(0)	−85.3(4)
H10C3C2S1	91.2(6)	90.2(1)	84.1(0)	86.6(6)	85.4(0)	88.2(4)	85.5(1)	88.0(4)
RC3C2S1	139.9(5)	140.4(2)	153.3(0)	150.4(6)	150.2(−1)	146.0(−4)	150.2(−2)	147.2(6)
Φ[b]	30.6	30.3	33.6	28.7	33.4	28.4	33.3	28.7

Deviations (in the third and first figures for bond distances and angles, respectively) of gas phase values with respect to the CCl4 solution are given in parentheses.

[a] R11···H10 values are (*cis*/*trans*) = Cl (2.325/2.337); Me(2.143/2.148); Et(2.126/2.132).

[b] Puckering angle.

the substituents on C3, the ring bond distances remain fairly constants at ca. 1.83, 1.54, 1.48 and 1.08 Å for C–S, C–C, C–O and C–H, respectively. For *cis* and *trans* isomers the S=O bond length is ca. 1.48 Å, i.e. a typical value for a sulfoxide group [16–18]. The C–S–C and C–C–C bond angles quite constant throughout this series of compounds. Table 1 also shows that these angles are ca. 76 and 93°, respectively. The *trans* to *cis* differences in these angles are just ca. 0.2°. On the other hand, the C–C–S angles are slightly different (ca. 1.4°) for *cis* and *trans* form. This angle increases almost constantly in 1.4° for the *trans* isomers. In the chloro and acetate derivatives, the difference in these angles is just 0.3°. The dihedral angles confirm that the ring is quite regular. The torsional angle O9S1C3H10 is either 0 (*trans*) or 180° (*cis*) in all cases. The substituent on C3 is also aligned with the plane passing along the atoms defining the above-mentioned dihedral. The torsional O9S1C3R11 is either 0 (*cis*) or 180° (*trans*) except in the acetate derivatives for which the substituent is tilted ca. 5° to the right. In both, *cis* and *trans* isomers of 3-acetate-TOX, the substituent is not symmetrically placed with respect to the thietane ring. The displacement of ca. 5° can be explained by the minimization of the lone-pair on O11 and the bonding pair (on C3–H10) repulsive interactions. If this effect takes place, the lone-pair is forced to lie in the plane C3O11C12C13. In fact, when R = acetate the H10···R11 non-bonded distance (H10···O11 in this case) is clearly the shortest distance throughout the series of compounds studied here (Table 1), whereas the H10C3R11 angles are the largest along the series. In all cases, the plane containing the methylene groups bisects the dihedral 180–ϕ where ϕ is the puckering angle as defined in Ref. [19]. From Table 1, it can also be inferred that the *cis* isomeric form is more puckered (by ca. 5°) than the corresponding *trans* form. The puckering angles correlate well with the S1···C3 non-bonded distances. It can be inferred that the longer the S1···C3 distance the smaller the puckering angle. Accordingly, this distance and the dihedral S1C4C3C2 give an approximate idea of the puckering of these species.

Assuming that the Hβ···S1 approximately corresponds to the distance between H10 and the lone pair on sulfur, it can be seen that in the *trans* isomeric forms is just ca. 0.05 Å larger than in *cis* ones. This result is consistent with the conclusions found previously [2,3] for the chloro, methyl and ethyl derivatives and can be considered to be an unimportant factor in the determination of the conformational preference in these species. It is believed that the Hβ···O9 non-bonded interaction determines the *cis* geometry to be the preferred. In fact, in the *cis* forms this distance is ca. 4.1 Å, whereas in the *trans* a value of ca. 2.9 Å was calculated.

The above reasoning is consistent with the experimental fact that all the derivatives studied here can be separated by elution chromatography, though the *trans* concentration is rather low. On the other hand, samples prepared with variable [*cis*]/[*trans*] ratio dissolved in HCl/dioxane always produce a 5/1 *cis* to *trans* proportions at room temperature [20]. Accordingly, the experimental results clearly show that the *cis* conformation is preferred over the *trans* one.

3.2. Energetics and thermodynamics

The present work deals with the study of the stability of the isomeric species 3-substituted-TOX both in the gas phase and in carbon tetrachloride solution. In this sense it would be interesting to see to what extension the *cis* ⇔ *trans* isomerization reaction takes place when a bulk substituent is present and thereby to find out whether theoretical methods support the experimental data [4,20]. Detailed ab initio calculations, using a flexible basis set that includes both polarization and diffuse functions, have been carried out. This basis set, namely 6-311+G**, is necessary for a good description of the energetic of these systems. In fact, at least for the smaller substituents [2,3], on can see that inclusion of electron correlation stabilize all systems by ca. 500 kcal/mol, whereas the use of a larger basis set like 6-311G** a net gain in stabilization of ca. 80 kcal/mol, with respect to the 6-31G**, is obtained. Inclusion of diffuse function just on the heavy atoms produces an additional gain of ca. 8 kcal/mol, whereas diffuse functions on the hydrogens render just a modest stabilization of ca. 0.5 kcal/mol. Accordingly, the MP2/6-311+G** level has been considered to be as good as the more computationally expensive MP2/6-311++G** to predict the thermodynamic properties of the *cis* ⇔ *trans* isomerization reaction. All calculations have been performed at the MP2/6-311+G**// HF/6-31G** level. Table 2 gives the thermodynamics of the isomerization reaction for the compounds reported here. From the thermodynamics given in Ref. [2] for the chloro, methyl and ethyl derivatives of TOX (Table 2), it can be inferred that, at this level of theory, the *trans* isomer in 3-chloro-TOX would be in ca. 14% concentration and that in the 3-methyl and 3-ethyl-TOX would be just ca. 2% in the gas phase. A special case is the 3-acetate-TOX species since the *cis* and *trans* concentrations would be similar (46% *trans*), whereas the 3-*t*-buthyl, 3-phenyl and 3-*p*-chlorophenyl derivatives seem to exist mainly in the *cis* form. The *trans* concentration in these species is just 1.1% for the former and ca. 0.8% for the two later. These results are consistent with the experimental fact that the *cis* isomeric form is the most stable species, regardless the size and nature of the substituent on C3. However, it is worthwhile to point out that a ΔG_S^0 of ca. 2.5 kcal/mol for the isomerization reactions in these species, is not a very large difference to prevent the independent existence of both isomers. In fact, as it has been mentioned above the isomers have been actually separated by elution chromatography from silica gel [4].

3.3. Solvent effect

To study the effect of the solvent on the isomerization reactions of TOX derivatives, the free energy of solvation (ΔG_S^0) for all species studied here was calculated using the polarized continuum method (PCM) [6–11]. The calculation of (ΔG_S^0) has been carried out on the gas phase geometries. From Table 1 it can be inferred that the structures of all species in carbon tetrachloride ($\varepsilon = 2.228$) solution are almost the same to that found in the gas phase. In fact,

Table 2
Gas phase energetics and dipole moments for the *cis* and *trans* isomers for the 3-substituted derivatives of thietane-1-oxide (TOX)

Energy[a]	R = acetate		R = *t*-buthyl		R = phenyl		R = *p*-chlorophenyl	
	cis	*trans*	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*
HF/6-31G**	−816.02916	−816.02945	−745.54598	−745.54185	−818.94857	−818.94529	−1277.84612	−1277.84296
HF/6-311+G**	−816.15336	−816.15419	−745.63704	−745.63341	−819.05516	−819.05229	−1277.97813	−1277.97535
MP2/6-311+G**	−817.60882	−817.60855	−747.04602	−747.04139	−820.66319	−820.65923	−1279.72308	−1279.71925
ZPE	0.14001	0.13998	0.21425	0.21396	0.18112	0.18094	0.17107	0.17089
H_{CORR}	0.14987	0.149874	0.22501	0.22482	0.19102	0.19088	0.18214	0.18200
G_{CORR}	0.10473	0.10459	0.17936	0.17895	0.14448	0.14509	0.13226	0.13294
S[b]	95.007	95.299	96.082	96.533	87.951	96.380	104.970	103.243
μ (D)	5.80	0.94	5.54	5.28	5.26	5.00	3.97	3.08
E_o+ZPE	−817.46881	−817.46857	−746.83177	−746.82743	−820.48207	−820.47829	−1279.55201	−1279.54836
E_0+H_{CORR}	−817.45900	−817.45868	−746.82102	−746.81657	−820.47217	−820.46835	−1279.54094	−1279.53725
E_0+G_{CORR}	−817.50409	−817.50396	−746.86667	−746.86244	−820.51871	−820.51414	−1279.59082	−1279.58631
$\Delta H^{0(c))}$	0.201		2.792		2.397		2.314	
$\Delta G^{0(c))}$	0.082		2.654		2.868		2.830	
% trans	46.5		1.1		0.8		0.8	

[a] All energies in Hartrees.
[b] S in cal k mol^{-1}.
[c] in kcal/mol.

Table 3
Free energies of solvation and in solution (kcal/mol) for 3-substituted-TOX in carbon tetrachloride ($\varepsilon = 2.228$)

Substituent	$\Delta G_s^0(cis)$	ΔG_s^0 (*trans*)	ΔG_{SOLN}^0 (*cis*)	ΔG_{SOLN}^0 (*trans*)	ΔG_{SOLN}^0	*%trans*
Chloro	−1.05	−0.90	0.01	0.16	0.15	44
Methyl	0.02	0.07	2.39	2.44	0.05	48
Ethyl	0.43	0.45	3.07	3.09	0.02	49
Acetate	2.45	2.91	2.54	3.00	0.46	31
t-Buthyl	2.01	2.10	4.65	4.75	0.10	46
Phenyl	2.50	2.55	5.36	5.41	0.05	42
Cl-phenyl	2.65	2.70	5.48	5.53	0.05	42

$G_{SOLN}^0 = \Delta G_{GAS}^0 + \Delta G_S^0$.

variations in the third and first figures were found for the bond lengths and angles, respectively. Table 3 shows the free energies of solvation for each pair of *cis*/*trans* isomeric forms, the free energies in solutions (ΔG_{SOLN}^0) and the relative ΔG_{SOLN}^0 values and *%trans* concentration. The ΔG_S^0 values show that solvent exerts a strong effect on the stabilization of the *trans* form. The *%trans* is ca. 45% in most cases studied here. The decrease of the *trans* concentration in the 3-acetate derivative (by ca. 15%) is most likely due to the large difference in the free energies of solvation (ΔG_S^0). In fact, PCM predicts a ΔG_S^0 of ca. 2.91 kcal/mol for the *trans* isomer, whereas a value of 2.45 kcal/mol has been calculated for the *trans* form. However, the *cis* isomer is still being the most important species mainly due to its larger intrinsic stability compared with the *trans* isomer. It is worth noting that for the acetate isomeric forms, the calculated dipole moments are 5.80 and 0.94 D for the *cis* and *trans*, respectively. This is the largest difference in μ (ca. 4.90 D) derived for the isomers of all species considered in the present work.

3.4. NMR spectra

Johnson and Siegl [4] have assigned a *cis* or *trans* conformation to the 3-chloro, 3-acetate, 3-*t*-buthyl, 3-phenyl and 3-*p*-chlorophenyl derivatives of TOX, using a method based on the ^{1}H-NMR chemical shifts (δ) of the β (H10)-ring protons. In most cases, the assignment is not straitforward as the H_β signals are either buried into the H_α multiplet or the signals need to be extracted from the α-deuterated TOX derivatives. In other cases, the H_β signal is abroad one and the δ values used to assign the conformation or to determine the difference $\Delta[\delta_{trans}-\delta_{cis}]$ were taken from the center of gravity of the multiplet. Johnson and Siegl have concluded that due to similarity of the spectra shown by these species a change in the geometry of them it is unlikely that could occur and that the *cis* conformation is the preferred one. In the present work, the ^{1}H-NMR chemical shifts for the β-protons (H_β) of all the TOX derivatives, have been calculated and compared with the values reported in literature [4] (Table 4). To calculate the NMR properties, the equilibrium geometries derived at B3LYP/6-31G** were used, whereas the GIAO magnetic shielding tensors were obtained at HF/6-311+G** level [13,15]. Since the reported experimental shielding constants are shifts relative to a standard compound, usually tetramethylsilane (TMS), its geometry and NMR properties were also calculated at the levels indicated above. Values of 32.1 and 194.1 ppm for ^{1}H and ^{13}C have been obtained, respectively. From Table 4 it can be inferred that the predicted δ values are in good agreement with the experimental data and that the *cis* isomers would possess a δ ca. 3.3 ppm, whereas for the *trans* forms a δ of ca. 5.3 ppm is predicted.

The δ_{trans}–δ_{cis} difference is ca. 2 ppm in each case. Exceptions to these trends are the δ values predicted for the alkyl derivatives of TOX, i.e. methyl, ethyl and *t*-buthyl-TOX species where δ ca. 1.6 and 3.9 ppm are calculated for the *cis* and *trans* isomers, respectively. The different behavior between the alkyl and the acetate, phenyl and *p*-chlorophenyl substituents would imply that the former groups exhibit an enhanced shielding effect on the β-protons [21]. In this sense the inductive effect of the alkyl groups looks to be stronger than the resonance effect to release electrons from R to the ring and thereby to the β-protons.

^{17}O is a nucleus possessing a nuclear spin $I = 5/2$, a very low natural abundance (0.036%) and an appreciable electric

Table 4
Gas phase and carbon tetrachloride calculated and experimental ^{1}H-NMR shifts of β-protons of 3-substituted-TOX

Species	Gas phase	CCl_4 soln	Experimental[a]
cis-3-Cl	3.5	3.8	[b]
trans-3-Cl	5.4	5.5	5.4[c]
cis-3-methyl	1.7	1.4	
trans-3-methyl	3.9	3.5	
cis-3-ethyl	1.8	1.5	
trans-3-ethyl	4.1	3.7	
cis-3-acetate	3.6	3.7	4.9[c]
trans-3-acetate	5.4	5.5	5.8[c]
cis-3-*t*-buthyl	1.3	1.4	1.9
trans-3-*t*-buthyl	3.7	3.7	3.1
cis-3-phenyl	3.2	3.2	3.6[c]
trans-3-phenyl	5.3	5.3	4.4[c]
cis-3-*p*-chlorophenyl	3.1	3.2	3.2
trans-3-*p*-chlorophenyl	5.3	5.3	4.3

Chemical shifts in ppm downfield from TMS.
[a] Experimental data from Ref. [3].
[b] Peak burried into the H_α multiplet.
[c] Average value. Center of gravity of multiplet taken to determine δ.

quadrupole moment and thereby one can expect that NMR signals to be difficult to observe [22] However, the availability of enriched samples, FT instrumentation and some special techniques such as solid state magic angle spinning (MAS) [23] led to a powerful method to study among others the isomerization reactions involving oxygen-containing species. In fact, ^{17}O chemical shifts are very sensitive to the stereochemistry of the molecule under study [24–26]. In the present work, the ^{17}O-chemical shifts relative to water (321.0 ppm) have also been calculated for all *cis* and *trans* isomers (Table 5). Due to the large difference in the chemical shifts predicted for the *cis* and *trans* forms, they are proposed as a good method to assign the conformation of these species. In those cases that either a complete separation of the isomers fails or the H_β-NMR signal overlap extensively with the α-proton signals, the difference of ca. 49 ppm between *cis* and *trans* forms would allow to readily infer the conformation.

3.5. Infrared spectra

Thietane-1-oxide can be seen as a cyclic sulfoxide in which the S=O stretching mode shows up at ca. 1050 cm^{-1} [27,28]. In fact, from Ref. [3] it can be seen that the *cis* isomers of chloro and alkyl substituents this vibrational mode appears at ca. 1056–1080 cm^{-1}, whereas in the *trans* ones shows up at ca. 1040–1050 cm^{-1}. In cyclic six-membered [17,27] sulfites the S=O stretching mode occurs in the range 1195–1215 cm^{-1}, whereas in five-membered rings a band at ca. 1215 cm^{-1} has been attributed to this vibrations. In four-membered cyclic sulfoxides and an intense and characteristic band should appear in the range 1020–1080 cm^{-1} if TOX derivatives are to behave as typical sulfoxide [26,28]. The *cis* isomers would show a band at ca. 1050–1075 cm^{-1} that is predicted to be the most intense of their spectra. This band shifts ca. 20 cm^{-1} to lower frequencies in the *trans* forms (1035–1045 cm^{-1}). The good agreement between the calculated and the range for the S=O stretching mode to be observed [27] indicates that the TOX derivatives behave as cyclic sulfoxides. Animation [29] and analysis of the atomic cartesian displacements show that the S=O stretching is strongly coupled to a ring deformation mode and in some cases also to a H–C–H bending. From Table 6, it can be inferred that this mode is to be observed in the range of 1050–1080 cm^{-1} in the *cis* isomeric forms, whereas a band in the range of 1035–1050 cm^{-1} would characterizes a *trans* derivatives. According to these frequency ranges, IR spectroscopy could also be used to assign the geometry of these species.

Table 5
Calculated ^{17}O-chemical shifts[a] (ppm) for the *cis* and *trans* isomeric forms of 3-substituted-thietane-1-oxide

Species	δ(gas phase)	δ(CCl_4 soln)	Δδ(*cis*–*trans*)
cis-3-Cl	44.7	35.6	40.7 (gas)
trans-3Cl	4.0	−3.1	38.7 (soln)
cis-3-methyl	54.3	26.7	45.4
trans-3-methyl	8.9	−14.5	41.2
cis-3-ethyl	52.5	25.1	48.6
trans-3-ethyl	3.9	−18.5	43.6
cis-3-acetate	31.0	22.7	33.8
trans-3-acetate	−2.8	−9.2	31.9
cis-3-*t*-buthyl	51.0	40.6	48.2
trans-3-*t*-buthyl	2.8	−5.4	46.0
cis-3-phenyl	54.3	43.8	40.1
trans-3-phenyl	14.2	5.5	38.3
cis-3-*p*-chloro-phenyl	55.5	45.0	40.6
trans-3-*p*-chloro-phenyl	14.9	6.2	38.8

[a] Chemical shifts relative to water.

Table 6
Predicted ν(S=O) infrared bands (cm^{-1})

Derivative	*cis*	*trans*
Chloro	1056(157)	1049(158)
Methyl	1080(121)	1035(91)
Ethyl	1078(75)	1050(115)
Acetate	1048(224)	1039(80)
t-Buthyl	1059(149)	1047(124)
Phenyl	1054(185)	1042(155)
p-Chlorophenyl	1055(203)	1043(161)

IR intensities in parentheses; units = KM/mole.

4. Conclusions

From the results outlined above some interesting conclusions can be drawn:

(1) In 3-substituted thietane-1-oxide, the *cis* conformation is preferred over the *trans* one.
(2) The size of the substituent on C3 has no effect on the geometry of the four-membered thietane-1-oxide ring, in the gas phase and carbon tetrachloride solution.
(3) The 3-chloro and 3-acetate-TOX systems show significant concentrations of the *trans* isomer in the gas phase.
(4) In CCl_4 solution, the *cis*/*trans* concentration ratio is quite close to 1, pointing out a marked effect of the solvent on the interconversion reaction.
(5) The calculated gas phase ^1H-NMR chemical shifts for the β-protons, show a good agreement with the experimental data and thereby the method proposed in Ref. [4], is appropriated to assign the conformation of these species.
(6) The solvent (CCl_4) does not affect significantly the predicted gas phase chemical shifts.
(7) ^{17}O-NMR chemical shifts seem to be a promising method to predict the conformation of molecular systems studied here. The large difference between the corresponding signals for the *cis* and *trans* isomers indicates that the assignments would be straightforward. Experimental work is called for.

The predicted S=O stretching mode for the *cis* and *trans* isomers, suggests that IR can be applied to distinguish between these conformations. The frequency at which this mode shows up depends on the geometry of the S=O group.

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