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Ab initio study of the conformational equilibrium of trimethylene cyclic sulfite

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ABSTRACT: *Ab initio* calculations, in the frame of MO theory, were carried out on both most stable (chair) conformers of trimethylene cyclic sulfite. Optimized geometries derived at the HF/6–31G* level reveal that both conformers possess a rigid chair conformation with the S=O group located either axially (conformer I) or equatorially (conformer II). Energy calculations at the MP2/6–311++G**//HF/6–31G* level indicates that conformer I is ca 4.6 kcal mol^{-1} more stable than II. The I $\rightleftharpoons$ II interconversion was studied in the gas phase at different temperatures and in solutions of low- and high-polarity solvents. The calculations reveal that in the gas phase and in solutions of low-polarity solvents the conversion of I into II does not occur. In medium-high-polarity solvents, such as acetonitrile and dimethyl sulfoxide, II is present at ca 12%.

KEYWORDS: trimethylene cyclic sulfite; conformation; *ab initio* calculations

INTRODUCTION

It is well known that six-membered rings can exist in either chair (C) or boat (B) conformations. The chair to boat interconversion requires the molecule to pass through various flexible forms.[1,2] Pritchard and co-workers[3,4] isolated both geometric isomers of *meso*-2,4-pentanediol cyclic sulfite and found that the stretching S=O occurs at 1190 cm^{-1} for an axial orientation of this group, whereas in the equatorial isomer such stretching is at ca 1230 cm^{-1}. Thermal equilibration at 200 °C for 15 min converted conformer **II** (S=O equatorial) almost completely into **I** (S=O axial). Overberger *et al.*[5] reported that heating **I** for 12 h at 160 °C or 1 h. at 200 °C does not reveal the presence of **II**. These results indicate that for the **I** $\rightleftharpoons$ **II** interconversion $\Delta G > 4.4$ kcal mol^{-1} (1 kcal = 4.184 kJ).[6]

Arbouzov,[7] using a vectorial method, calculated dipole moments of 1.8 and 4.9 D for conformers **I** and **II** of trimethylenecyclic sulfite (TCS), respectively. Since these values are far away from the experimental value of 3.60 D, it has been suggested (1) that in solution TCS could exist as a mixture of both conformers. However, if the **I** $\Leftrightarrow$ **II** interconversion existed, then significant changes in both the dipole moment and the S=O stretching modes should be observed. The experimental μ values in low-polarity solvents (CCl_4, C_6H_6, C_6H_{12}) and ν(S=O) vary very little and just one band at ca 1190 cm^{-1} was detected in all cases. This implies that the calculated dipole moments are not the correct ones and that **I** (S=O group axial) would be the most stable species both in the gas phase and in solution. On the other hand, if the calculated dipole moments[7] are correct, then it is unclear why TCS shows an average μvalue between 1.8 and 4.9 D. If isomer **I** is the only species present in low-polarity solvents then the experimental μvalue would be close to 1.8 D. We believe that most probably the theoretical μ values have been erroneously calculated and that the experimental values shows large deviations from the real value. In this work, we studied theoretically the **I** $\rightleftharpoons$ **II** 'equilibrium' both in the gas phase and in solutions of various solvents in order to determine whether such equilibrium exists or not, to calculate well-based dipole moments for both conformers and to explain the reported values. Since 2,4-pentanediol cyclic sulfite, a closely related compound, isomerizes at room temperature and at 120 °C, we also studied the effect of temperature on the **I** $\rightleftharpoons$ **II** equilibrium.

COMPUTATIONAL METHODS

The geometries of conformers **I** and **II** were first optimized at AM1 level of theory. The AM1 geometries were further optimized at the HF/6–31G* level using the Gaussian 94 series of programs.[8] Frequency and IR intensities predicted at the equilibrium geometries

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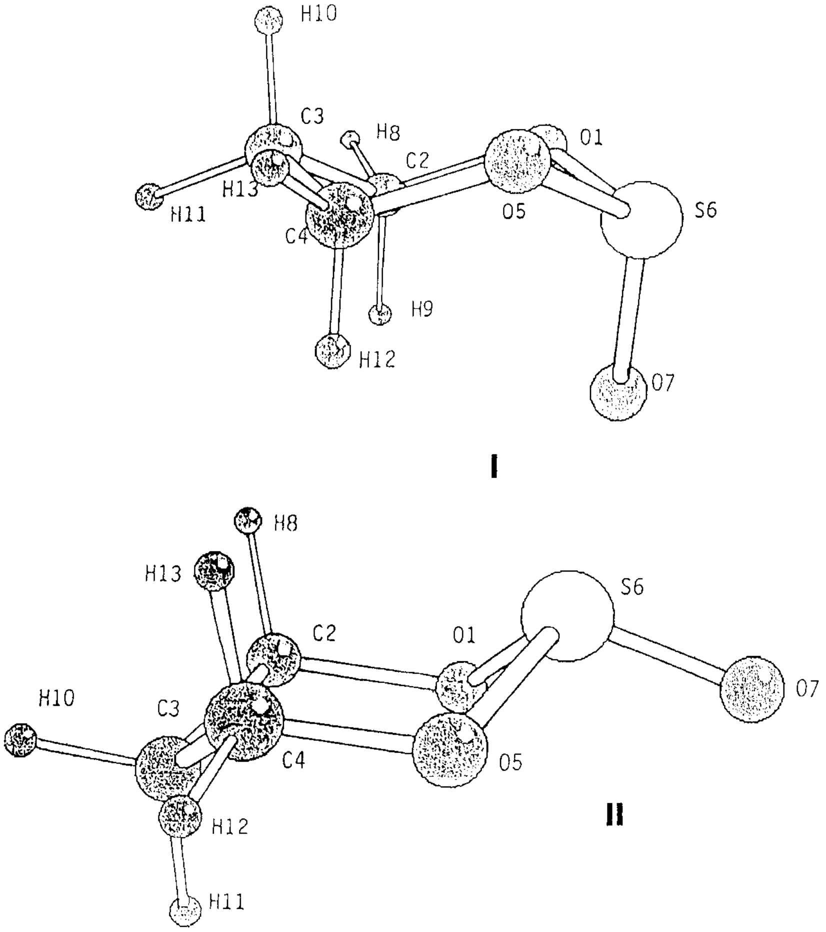

Figure 1. Optimized geometries and atom numbering for conformers **I** and **II** of TCS

produced all real values and hence both structures are local minima. Energy calculations were carried out using basis sets with polarization and diffuse functions on both heavy and hydrogen atoms at the MP2 level to include electron correlation. The calculated energies were corrected for zero-point vibrational energies (*ZPE*). To obtain the free energies of isomerization, enthalpies were calculated by adding *ZPE* and thermal corrections to the relative energies calculated at MP2/6–311++G** level. The ΔG values were obtained, as usual, from $\Delta G = \Delta H - \mathrm{T}\Delta S$. To estimate the solute–solvent effect, we used the SCRF polarized continuum method (PCM)[9] as modified by Wiberg and co-workers.[10,11] This method (IPCM) calculates the electric field analytically and the cavity is defined upon an isosurface of the total electron density. Thus, the cavity is uniquely derived form the electronic environment and just the isosurface level, i.e. the charge density ($0.0004 - 0.001e/B^3$), needs to be specified. The solvent effect in IPCM is derived from the surface potentials and the dielectric continuum interactions. This is equivalent to going to infinite order in the electric moments. To apply the IPCM method to modelate the solvent, the gas-phase molecular geometries were used since the structural parameters change very little on going from the gas phase to solution and hence no large effects on the solvation free energies are expected.[12,13] The free energies in solution (G°_{soln}) were calculated from $G^\circ_{\mathrm{soln}} = \Delta G_{\mathrm{gas}} + \Delta G^\circ_{\mathrm{s}}$, the second term being the free energy of solvation. The dielectric constants for the solvents were 36.64 and 46.7 for CH_3CN and DMSO, respectively.

To study the effect of temperature on the $\mathbf{I} \rightleftharpoons \mathbf{II}$ equilibrium, thermodynamic properties were calculated at 298, 348, 398, 448 and 498 K.

RESULTS AND DISCUSSION

Figure 1 shows the optimized geometries of conformers **I** and **II** of TCS and the atom numbering used in Table 1. From Table 1, it can be inferred that the bond distances involving the ring atoms are similar in both conformers. In fact, the C—C, C—O and O—S bond lengths are ca 1.52, 1.43 and 1.60 Å, respectively, characteristic of simple bonds. The sulfur–exocyclic oxygen distance is a typical of an S═O double bond.

The equatorial carbon–hydrogen bond lengths are ca 1.08 Å whereas the axial bond lengths vary from 1.081 to

Table 1. Structural parameters for conformers **I** and **II** of TCS[a]

Parameter	I	II
O1— C2	1.4317	1.4238
C2— C3	1.5235	1.5225
C3— C4	1.5236	1.5225
C4— O5	1.4316	1.4239
O5— S6	1.6074	1.6158
O1— S6	1.6071	1.6159
S6— O7	1.4427	1.4271
C2— H8	1.0789 eq	1.0868 ax
C2— H9	1.0810 ax	1.0787 eq
C3— H10	1.0846	1.0860
C3— H11	1.0860	1.0834
C4— H12	1.0810 ax	1.0787 eq
C4— H13	1.0789 eq	1.0868 ax
<C2C3C4	110.82	110.00
<C3C4O5	109.68	110.05
<C4O5S6	116.79	115.21
<O5S6O7	106.90	105.61
<O1C2H8	105.07	109.52
<O1C2H9	108.90	105.54
<C2C3H10	109.20	109.90
<C2C3H11	109.75	109.30
<C3C4H12	111.91	112.20
<C3C4H13	111.89	110.01
<O1C2C3C4	−54.60	54.42
<C2C3C4O5	54.60	−55.42
<C3C4O5S6	−61.90	63.48
<C4O5S6O7	−51.58	−169.09
<C4C3C2O8	−170.82	−66.13
<C4C3C2H9	66.39	172.51
<O1C2C3H10	65.73	−176.46
<O1C2C3H11	−175.97	−64.70
<C2C3C4H12	−66.38	−172.62
<C2C3C4H13	170.79	66.03

[a] Bond distances in Å and angles and degrees.

Table 2. Calculated energies[a,b] and dipole moments[c] for isomers **I** and **II** of TCS in the gas phase

Parameter	I	II
E(HF/6–31G*)	−739.123784	−739.112709
E(MP2/6–31G*)	−740.180782	−740.170887
E(MP2/6–311G*)	−740.349154	−740.339309
E(MP2/6–311G**)	−740.393515	−740.383803
E(MP2/6–311+G**)	−740.412406	−740.404365
E(MP2/6–311++G**)	−740.413049	−740.405126
ZPE	67.757	67.458
$H-H_0$	3.611	3.710
S	77.105	77.837
μ^c	3.87	6.57
Relative values (kcal mol^{-1}):		
E(HF/6–31G*)	6.95	
E(MP2/6–31G*)	6.20	
E(MP2/1–311G*)	6.18	
E(MP2/6–311G**)	6.09	
E(MP2/6–311+G**)	5.05	
E(MP2/6–311++G**)	4.97	
$\Delta(ZPE)$	−0.30	
$\Delta(H-H_0)$	0.10	
ΔH	4.77	
$T\Delta S$	0.22	
ΔG^d	4.55	

[a] Based on HF/6–31G* geometries.
[b] *E* in hartree, *ZPE*, $H-H_0$, ΔE, $T\Delta$S and $T\Delta S$ in kcal mol^{-1}; *S* in cal mol^{-1} K^{-1}.
[c] MP2/6–311++G** values, in debye.
[d] Based on ΔE calculated at the MP2/6–311++G** level.

1.087 Å. The internal bond angles are also very similar in both conformers, whereas the dihedral angles are characteristic of each conformation. Although there are no structure determination data, the derived structural parameters for **I** and **II** are in the range found for other sulfur-containing heterocyclic compounds.[14] In addition, it has been found that geometries calculated at the HF/6–31G* level are consistently in good agreement with the experimental data[15,16] and that optimized geometries are relatively unaffected by inclusion of polarization functions on hydrogen atoms, unless they are involved in hydrogen bonding.

The *ab initio* energy calculations and the thermodynamics for the $\mathbf{I} \rightleftharpoons \mathbf{II}$ equilibrium in the gas phase are given in Table 2. In order to establish an appropriate level of theory, we calculated the gas-phase energies using different basis sets. From Table 2, it can be inferred that electron correlation has a significant effect on the energies of conformers **I** and **II**. The same effect is observed when large basis sets are used, in particular if diffuse functions on the heavy atoms are included. At the MP2/6–311+G** level, the effect of including diffuse functions on hydrogen atoms seems to be small; nevertheless, the relative energies used to derived the free energy of isomerization (ΔG) were those obtained at the highest level of theory. At this level the free energy of isomerization for the $\mathbf{I} \rightleftharpoons \mathbf{II}$ equilibrium is ca 4.6 kcal mol^{-1} in the gas phase, in keeping with the experimental estimate of $\Delta G > 4.4$ kcal mol^{-1}.[6] We are aware that the calculated free energy change ΔG is good within 2 kcal mol^{-1}, but since we are dealing with differences between two very similar structures, the errors are most probably canceled out. Accordingly, conformer **I** must be the only species present in the gas phase and hence the value of 1.8 D must be in error as the experiment yielded a value of 3.60 D. The errors in the calculated dipole moments are most probably due to the S—O—C, O—C—C and O—S—O angles (110, 109 and 108°, respectively) used in the calculation of μ. In fact, the optimized geometries of **I** and **II** show values of ca 116, 110 and 97°, respectively. Our calculated μ values are 3.87 D for **I** and 6.57 D for **II**. These values greatly differ from the Arbouzov values[1] but agree well with the value for conformer **I** detected as the only species in the gas phase and in low-polarity solvents.

To study the solvent effect on the $\mathbf{I} \rightleftharpoons \mathbf{II}$ equilibrium, the IPCM self-consistent reaction field (SCRF) was used. Since the structural parameters change very little on going from the gas phase to solution, one can expect not to observe large changes in the solvation energies.

Table 3. Free energies of solvation and in solution of CH_3CN and DMSO for isomers **I** and **II** of TCS

Isomer	Gas phase	CH_3CN IPCM energies[a]	DMSO IPCM energies[a]
I	−739.123784	−739.133263	−739.133353
II	−739.112709	−739.127479	−739.127627
Free energies of solvation (ΔG°_s)[b]			
I		−5.95	−6.00
II		−9.27	−9.36
Free energies in solution (G°_{soln})[c]			
I		−5.95	−6.00
II		−4.72	−4.81
Relative values (ΔG°_{soln})		1.23	1.19

[a] Energies in hartree.

[b] $\Delta G^\circ_s = \Delta E(\text{soln.} - \text{gas})$.

[c] $G^\circ_{soln} = \Delta G^\circ_{gas} + \Delta G^\circ_s$.

[d] Relative values in kcal mol^{-1}; $\Delta G^\circ_{soln} = G^\circ_{soln}(\mathbf{II}) - G^\circ_{soln}(\mathbf{I})$.

Accordingly, the gas-phase molecular geometries at the HF/6–31G* level were used. Table 3 gives the total energies in solution for conformers **I** and **II**, free energies of solvation (ΔG°_s), free energies in solution (G°_{soln}) and the relative ΔG°_{soln} values. In medium-polarity solvents such as acetonitrile ($\epsilon = 36.63$) and dimethyl sulfoxide ($\epsilon = 46.7$), the ΔG°_{soln} values are 1.23 and 1.19 kcal mol^{-1}, respectively. These results implies that in these solvents conformer **II** becomes important as its concentration is ca 12%. At this concentration the dipole moment for the mixture of **I** and **II** should be ca 4.50 D. The IPCM results indicate that despite the difference of ca 10 D in the dielectric constants of CH_3CN and DMSO, conformers **I** and **II** possess similar free energies of solvation in both solvents, although conformer **II** is slightly better solvated than **I**. It is worth noting that using Onsager's SCRF at $l = 1$, i.e. the multipolar expansion being truncated at the dipole term, the results are very similar to those found with the IPCM method. This implies that the electric moments of higher order do not contribute significantly.

Hellier *et al.*[1] assigned the axial S═O stretching vibrational mode to a band at 1190 cm^{-1}, whereas the equatorial ν(S═O) shows up at 1230 cm^{-1}. The room temperature IR spectra of 2,4-pentanediol cyclic sulfite dissolved in perchlorethylene or in the neat liquid reveal a strong peak at 1190 cm^{-1} and a weak shoulder at 1230 cm^{-1}. At 120 °C, the band due to the axial S═O group decreases by ca 10%, whereas that at 1230 cm^{-1} increases its intensity, implying that the conversion $\mathbf{I} \rightleftharpoons \mathbf{II}$ takes place at this temperature. The IR bands due to the ν(S═O) modes of TCS conformers in several solvents are given in Table 4. According to Table 4, in the IR spectra of TCS in the gas phase and in CCl_4 and CS_2 solutions, just one band at ca 1190 cm^{-1} should be detected. In polar solvents, such as acetonitrile and dimethyl sulfoxide, a shoulder at ca 1230 cm^{-1} is also observed. From the experimental point of view, it would interesting to study the temperature effect on the IR spectra of TCS and see whether this compound behaves as 2,4-pentanediol cyclic sulfite.

Table 4. Calculated S═O stretching modes[a] (cm^{-1}) in TCS conformers **I** and **II** in various solvents

Solvent	ϵ	I	II	Experimental[b]
Gas	1.00	1180	1230	
CS_2	2.64	1179	1230	1190
CCl_4	2.24	1179	1230	1190
CH_3CN	36.64	1177	1231	1190
DMSO[c]	46.70	1177	1230	

[a] Frequencies scaled by 0.8929.

[b] From Ref. 1.

[c] DMSO = dimethyl sulfoxide.

Pritchard and Vollmer[3] converted **II** almost completely into **I** by heating at 200 °C, whereas Overberger *et al.*[5] failed to convert **I** into **II** by heating at the same temperature for 1 h. Table 5 shows the free energy changes of isomerization at temperatures ranging from 25 to 225 °C. From this table it can be inferred that in the studied range of temperatures $\Delta G \geq 4.4$ kcal mol^{-1}, in good agreement with the experimental observations. Therefore, in the above range of temperatures conformer **I** is the only species present in the gas phase.

CONCLUSIONS

From the present study we can conclude that: (1) conformer **I** is the only species present in the gas phase and in low-polarity solvents; (2) conversion of **I** into **II** takes place in polar solvents, the concentration of the latter being ca 12% in acetonitrile and dimethyl sulfoxide; (3) the reported IR spectra of TCS in CH_3CN and DMSO needs to be reinvestigated in order to see whether the band at 1230 cm^{-1} is observed; (4) in the range 25–225 °C temperature has no effect on the $\mathbf{I} \rightleftharpoons \mathbf{II}$ equilibrium since $\Delta G \geq 4.4$ kcal mol^{-1}; and (5) the experimental dipole moments in solution are also to be redetermined, since a μ of 3.25 D is not consistent with

Table 5. Thermodynamics[a] for the $\mathbf{I} \rightleftharpoons \mathbf{II}$ equilibrium at different temperatures (K)

	I					II				
Parameter	298	348	398	448	498	298	348	398	448	498
$H - H_0$	3.661	4.760	6.079	7.561	9.193	3.711	4.873	6.204	7.692	9.329
S	77.105	80.966	84.772	88.509	92.171	77.837	81.744	85.579	89.334	93.006
Relative values (kcal mol^{-1})										
ΔE	4.97	4.97	4.97	4.97	4.97					
ΔZPE	−0.30	−0.30	−0.30	−0.30	−0.30					
$\Delta(H - H_0)$	0.05	0.11	0.13	0.13	0.14					
$T\Delta S$	0.22	0.27	0.32	0.37	0.42					
ΔG^b	4.50	4.51	4.48	4.43	4.39					

[a] $H - H_0$ in kcal mol^{-1} and S in cal K^{-1} mol^{-1}.
[b] Based on ΔE calculated at the MP2/6–311++G** level.

the theoretical values; the values reported by Arbouzov are too approximate to be used as criterion for the $\mathbf{I} \rightleftharpoons \mathbf{II}$ equilibrium to exist.

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