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CONFORMATIONAL ANALYSIS—XXI

^{1}H NMR CONFORMATIONAL STUDY OF ALKYL-SUBSTITUTED 2-OXO-1,3,2-DIOXATHIANES

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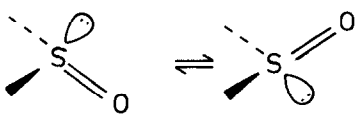
Abstract—2-Oxo-1,3,2-dioxathiane and all methyl- and several alkyl-substituted 2-oxo-1,3,2-dioxathianes were prepared for a ^{1}H NMR conformational study. The conformational energy of the axial S=O group in CCl_4, $-\Delta G^{\theta}_{50} = 14.8 \pm 0.3$ kJ mol^{-1}, was determined by chemical equilibration of the epimeric *cis*-4,6-dimethyl derivatives and it was found to decrease with the increasing solvent polarity. The conformational equilibria of alkyl-substituted derivatives were solved and the proportions of the conformers estimated using ^{1}H NMR chemical shifts, vicinal coupling constants and in three cases also dipole moments. The configurational interactions in the C_4–C_5–C_6 moiety are close to the corresponding values of 1,3-dioxanes.

The stucture of 2-oxo-1,3,2-dioxathianes has been studied intensively by means of dipole moments,[1,2–4] infrared spectroscopy,[1,3,5–13] electron diffraction,[14] chemical equilibration,[15,16] ultrasonic absorption,[17,18] ^{1}H and ^{13}C NMR spectroscopy,[1,5–12,19–29] X-ray diffraction[30–34] and mass spectroscopy.[35] The parent compound has been shown to exist in a chair conformation, where the bonds are nearly ideally staggered and the exocyclic oxygen atom axially orientated.[1,3,10,23,31] The ring flattening influence of the long S–O bonds (160 pm)[30–34] is partially compensated by the rather small bond angles (*ca.* 100°)[30–34] at the sulphur atom. A characteristic, special feature of the sulphoxides is the higher barrier to atomic inversion, which makes the unsymmetrical pyramidal structure of the sulphur atom stable at room temperature.[36] If the S=O group is a part of a conformationally rigid structure the pyramidal inversion can, however, lead to equilibration of isomeric forms which are normally of a different thermodynamic stability.



An axial S=O group has been found to be 8–15 kJ mol^{-1} more stable than an equatorial S=O group[1,3,16,37,38] owing largely to the dipole-dipole interaction. Under normal circumstances the conformer with the maximum number of lone-pair orbitals antiperiplanar to the electronegative groups is the most stable one (Fig. 1).[32] The shortness (144 pm)[30–34] and relatively high bond energy (523 kJ mol^{-1})[39] of the S=O bond point to a significant degree of double bond character. Hence the ionic S^+–O representation is inadequate.

Even though the predominance of an axial S=O group in the 2-oxo-1,3,2-dioxathiane itself is well established there has been a substantial controversy as to the definite spatial structure of alkyl-substituted 2-oxo-1,3,2-dioxathianes, especially of the derivatives having a single substituent syn-axial to the S=O group. On the basis of dipole moments[2–4] and ^{1}H and ^{13}C NMR[5–11,20–25,27,28] it has often been suggested that compounds including a syn-axial SO, CH_3-interaction occur mostly if not exclusively in twist forms. The twist form has, however, been estimated to be about 31 kJ mol^{-1} less stable thermodynamically than the chair form with an equatorial S=O group.[1] This estimate is high enough to suggest that even syn-axially substituted compounds adopt a chair conformation. This is strongly supported by the observation that all 2,2,4,4-tetramethyl-substituted 1,3-dioxanes do still exist in chair forms.[40]

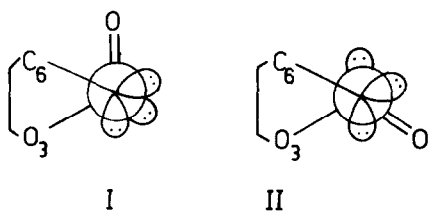


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Fig. 1. Newman projections along the O_1–S bond of the axial (I) and equatorial (II) conformers of 2-oxo-1,3,2-dioxathiane.

Since many of the earlier results have been conflicting and the number of studied compounds limited it seemed tempting and appropriate to synthesize 2-oxo-1,3,2-dioxathiane and all methyl- and several other alkyl-substituted derivatives in order to carry out a thorough and definite structural analysis of this interesting ring system using ^{1}H NMR spectroscopy and chemical equilibration as the tools.

EXPERIMENTAL

2-Oxo-1,3,2-dioxathianes were prepared by known methods.[1,2,9] When *cis*-4, *cis*-5- and *cis*-4, *trans*-5-dimethyl derivatives (**10** and **11**, respectively) were prepared the amount of pyridine was ten times the amount of the diol. The yields varied

generally from 60 to 75%. The characterization of the products was performed by gas chromatography and ^{1}H NMR spectra.

The starting materials, ethyl 3-hydroxyalkanoates and 1,3-alkanediols, were prepared by methods described earlier.[56,57]

GLC analyses were performed with a Perkin Elmer F11 gas chromatograph using columns containing 10% Carobowax 20 M and 5% XE-60 on Chromosorb G (60/80 mesh). The stereoisomers were separated by distillation or by using a Perkin Elmer F 21 preparative gas chromatograph equipped with the columns containing 10% Carbowax 20 M or XE-60 on Chromosorb G (60/80 mesh).

^{1}H NMR spectra were recorded with a Jeol PMX-60 spectrometer at 303 K using 10% (v/v) CCl_4-solutions and TMS as internal standard. The spectra were generally analysable on a first order basis (Tables 1–6). In the case of the *cis*-4-methyl-*r*-2-oxo (**3**) and *cis*-4, *trans*-6-dimethyl-*r*-2-oxo (**14**) derivatives the spectra were analysed by a computer (DEC-10, LAME program). The spectra of the 2-oxo-1,3,2-dioxathiane (**1**), *trans*-4-methyl (**2**), 4,4-dimethyl (**6**), *cis*-4, *cis*-5-dimethyl (**10**) and *cis*-4,*trans*-5-*dimethyl* (**11**) derivatives were recorded at the University of Helsinki with a 100 MHz Jeol PFT-100 spectrometer. The spectra of the 4-methyl derivatives were recorded also at the University of Paul Sabatier in Toulouse, France, with a 250 MHz Cameca apparatus using $CDCl_3$ and C_6D_6 solutions. The spectra of 4,4,6-trimethyl derivatives (**17** and **18**) were recorded at the State University of Gent in Belgium with a 300 MHz Varian HR-300 apparatus (solvent $CDCl_3$). Finally the spectra of *trans*- and *cis*-4-isopropyl (**45** and **46**) and *trans*-4-*tert-butyl* (**47**) derivatives were recorded at the University of Nottingham in England with a 250 MHz Bruker appartus (solvent $CDCl_3$). The reported coupling constants are considered to be accurate within 0.1–0.3 Hz, ^{1}H chemical shifts within 0.02 ppm (Tables 1–6).

The dipole moments $\mu = 4.95$ D for **3**, $\mu = 4.19$ D for **14** and $\mu = 3.99$ D for **6** were determined conventionally in CCl_4-solution.

The samples for chemical equilibration were prepared by sealing a mixture consisting of 50 μl of the substrate, 10 μl of trifluoroacetic acid and 500 μl of CCl_4 or CH_3OH in glass vials. The vials were then kept at *ca* 352 K for 2–10 days. In case of the epimeric *cis*-4,6-dimethyl (**12** and **13**), *cis*-4, *trans*-5, *trans*-6- and *cis*-4, *cis*-5, *trans*-6-trimethyl (**24** and **23**) and 4,4,6-trimethyl (**17** and **18**) derivatives the equilibrium states were approached from both directions. When the equilibrium reactions had proceeded to completion a sample of the mixture was quenched with sodium methoxide, filtrated and analysed by gas chromatography using columns containing 5% Carbowax 20 M and/or 10% XE-60 on Chromosorb G. The relative amounts of epimers were then determined from the corresponding peak areas by graphical methods. Corrections for the response ratios were not made since their influence would have been small when compared with other sources of probable errors (e.g. the accuracy in peak area measurements; the standard error of the mean for $\Delta G^{\#}$-values is $\pm 0.2 - 0.3$ kJ mol^{-1}). In general the analysis of the equilibrium mixtures turned out to be difficult because of the partial decomposition.

RESULTS AND DISCUSSION

2-Oxo-1,3,2-dioxathianes are very suitable for ^{1}H NMR studies since the chemical shifts of H-4 and H-6 differ remarkably from those of H-5. Axial H-4 and H-6 generally resonate in a lower field than the corresponding equatorial protons. When the S=O group is axially orientated the axial protons resonate in the region of 4.8–5.2 ppm and the equatorial protons in the region of 3.5–3.9 ppm (both in CCl_4). The chemical shift difference has been interpreted as being due to the electric field effect and magnetic anisotropy effect of the S=O bond.[23] The shielding cone of the S=O bond is assumed to be similar to that of a triple bond –C≡C– (Fig. 2).[10] H-4 and H-6 lie within the deshielding region and the axial protons are exposed to maximum deshielding. For the compounds having an equatorial S=O group the chemical shift difference between axial and equatorial H-4 and H-6 is small. The effect of the S=O group orientation is easily seen in the chemical shifts of axial H-4 and H-6 (5.01 ppm vs 4.48; Table 1) of **12** and **13**. The equatorial 5-alkyl groups shield the axial 4/6-protons, but the phenyl substituent at position 5 has a deshielding influence. On the other hand 5-alkyl or 5-phenyl substituents have very little influence on the equatorial H-4 and H-6. The equatorial 4-methyl or -phenyl group deshields the axial proton at the same carbon whereas isopropyl and tert-butyl substituents have a shielding influence.

Table 1. ^{1}H chemical shifts of the protons of 2-oxo-1,3,2-dioxathiane and its methyl-substituted derivatives (ppm from TMS, solvent CCl_4)

Substitution		4e-H	4a-H	5e-H	5a-H	6e-H	6a-H
1		3.75	4.90	1.63	2.55	3.75	4.90
2	r-2-t-4		5.02	1.77	2.03	3.83	4.92
3[a,c]	r-2-c-4	4.61		1.74	1.80	4.37	4.42
4	r-2-c-5	3.75	4.51		2.50	3.75	4.51
5	r-2-t-5	3.49	4.99	1.83		3.49	4.99
6[a]	4,4			1.82	2.26	3.89	4.88
7	5,5	3.33	4.54			3.33	4.54
8	r-2-t-4,c-5		4.67		2.19	3.63	4.42
9	r-2-t-4,t-5		5.24	1.60		3.61	5.08
10[a]	r-2-c-4,c-5	4.45			—[b]	4.01	4.40
11[a]	r-2-c-4,t-5	4.00		—[b]		3.81	4.36
12	r-2-t-4,t-6		5.01	1.76	1.78		5.01
13	r-2-c-4,c-6		4.48	1.72	1.78		4.48
14[a]	r-2-c-4,t-6	4.41		1.94	2.09		5.04
15	r-2-4,4,c-5				2.33	3.54	4.55
16[a]	r-2-4,4,t-5			—[b]		3.70	4.66
17	r-2-4,4,t-6			1.63	1.93		5.10
18	r-2-4,4,c-6			1.70	2.57		4.46
19	r-2-t-4,5,5		4.84			3.26	4.52
20[a]	r-2-c-4,5,5	4.13				3.75	4.09
21	r-2-t-4,c-5,t-6		4.64		1.80		4.64
22	r-2-t-4,t-5,t-6		5.18	1.48			5.18
23[a]	r-2-c-4,c-5,t-6	4.28			2.20		4.72
24[a]	r-2-c-4,t-5,t-6	3.98		1.82			5.11
25[a]	4,4,5,5					3.29	4.77
26	4,4,6,6			1.93	2.64		
27	r-2-4,4,c-5,t-6				2.65		4.82
28	r-2-4,4,t-5,t-6			2.06			5.38
29	r-2-4,4,t-5,c-6				2.10		4.18
30	r-2-4,4,c-5,c-6			—[b]			4.70
31	r-2-t-4,5,5,t-6		4.87				4.87
32[d]	r-2-c-4,5,5,c-6		—				—
33[a]	r-2-c-4,5,5,t-6	3.91					4.84
34	r-2-4,4,5,5,t-6						5.18
35	r-2-4,4,5,5,c-6						4.71
36	r-2-4,4,t-5,6,6				3.16		
37	r-2-4,4,c-5,6,6			2.20			

[a]Not conformationally homogeneous.
[b]Not measured due to overlapping lines.
[c]250 MHz values in $CDCl_3$.
[d]This isomer was not isolated.

Fig. 2. A shielding cone for the axial S=O bond.

The axial 5-proton is less shielded than the corresponding equatorial proton. The chemical shift

Table 2. ^{1}H chemical shifts of the methyl protons of methyl-substituted 2-oxo-1,3,2-dioxathianes (ppm from TMS, solvent CCl_4)

Substitution		4e-Me	4a-Me	5e-Me	5a-Me	6e-Me	6a-Me
2	r-2-t-4	1.27					
3[a]	r-2-c-4		1.36[b]				
4	r-2-c-5			0.84			
5	r-2-t-5				1.40		
6[a]	4,4	1.33	1.67				
7	5,5			0.86	1.29		
8	r-2-t-4,c-5	1.29		0.87			
9	r-2-t-4,t-5	1.25			1.21		
10[a]	r-2-c-4,c-5		1.45	0.96			
11[a]	r-2-c-4,t-5		1.49		1.00		
12	r-2-t-4,t-6	1.25				1.25	
13	r-2-c-4,c-6	1.38				1.38	
14[a]	r-2-c-4,t-6		1.60			1.36	
15	r-2-4,4,c-5	1.31	1.60	0.88			
16[a]	r-2-4-4,t-5	1.28	1.63		1.09		
17	r-2-4,4,t-6	1.29	1.71			1.33	
18	r-2-4,4,c-6	1.47	1.50			1.43	
19	r-2-t-4,5,5	1.17		0.83	1.17		
20[a]	r-2-c-4,5,5		1.35	0.98	1.04		
21	r-2-t-4,c-5,t-6	1.28		0.92		1.28	
22	r-2-t-4,t-5,t-6	1.27			1.03	1.27	
23[a]	r-2-c-4,c-5,t-6		1.53	0.93		1.34	
24[a]	r-2-c-4,t-5,t-6		1.61		1.10	1.30	
25[a]	4,4,5,5	1.25	1.69	0.88	1.22		
26	4,4,6,6	1.46	1.53			1.46	1.53
27	r-2-4,4,c-5,t-6	1.31	1.61	0.89		1.32	
28	r-2-4,4,t-5,t-6	1.26	1.79		1.20	1.31	
29	r-2-4,4,t-5,c-6	1.36	1.49	0.93		1.45	
30	r-2-4,4,c-5,c-6	1.33	1.69		1.10	1.30	
31	r-2-t-4,5,5,t-6	1.18		0.84	1.02	1.18	
32[c]	r-2-c-4,5,5,c-6	—		—	—	—	
33[a]	r-2-c-4,5,5,t-6		1.45	0.88	1.05	1.25	
34	r-2-4,4,5,5,t-6	1.21	1.70	0.83	1.12	1.24	
35	r-2-4,4,5,5,c-6	1.33	1.61	0.81	1.14	1.28	
36	r-2-4,4,t-5,6,6	1.39	1.50	1.03		1.39	1.50
37	r-2-4,4,c-5,6,6	1.36	1.69		1.04	1.36	1.69
38	4,4,5,5,6,6	1.48	1.66	1.11	1.21	1.48	1.66

[a]Not conformationally homogeneous.
[b]250 MHz value in $CDCl_3$.
[c]This isomer was not isolated.

difference between these protons, 0.9 ppm, in the 2-oxo-1,3,2-dioxathiane itself is nearly the same as that in 1,3-dioxanes.[41,42] This situation has been explained by interaction between 1,3-oxygens and equatorial 5-proton.[10] Apparently the influence of the S=O group is small and the chemical shifts of H-5 for the compounds with an equatorial S=O group do indeed indicate that the orientation of the S=O group has no marked effect.

The methyl protons in the position 4/6 resonate in a lower field than those in position 5, furthermore the axial methyl protons generally resonate in a lower field than the corresponding equatorial protons. When going from S=O-axial to S=O-equatorial compounds the resonance of the equatorial 4/6-methyls shifts lowfield and the resonance of the axial 4/6-methyls upfield. The orientation of the S=O group does not have any systematic effect on the chemical shifts of 5-methyls. The substitution of the axial 4/6-proton by a methyl group deshields the equatorial methyl group in the same position, but on the other hand it has no significant influence on the methyl groups at the other carbons.

In the conformationally homegeneous derivatives the vicinal coupling constants ^3J are within the following ranges: J_{aa} 10.3–12.8 Hz, J_{ae} 2.1–3.0 Hz, J_{ea} 3.4–4.6 Hz and J_{ee} 1.5–2.2 Hz (Tables 4 and 6). Since the equatorial 5-proton is antiperiplanar to the ring oxygens the couplings J_{ae} and J_{ee} are small. For the same reason J_{ea} is greater than the other gauche-couplings.[20,43]

Methyl substituents in positions 4/6 and 5 have a special perturbation effect on the chair conformation of some 4,5-dimethyl and 4,5,6-trimethyl derivatives since van der Waals interaction decreases along with the flattening of the $C_{4,5,6}$-moiety. The dihedral angle between the axial protons, especially the angle H_4–C_4–C_5–H_5 gets smaller and as a consequence the coupling J_{aa} decreases. This can but partly explain the small J_{aa}-couplings in **8** and **21** (Table 4). A more important reason for this decrease is, however, the effect of the methyl substitution itself on the coupling constants. In cyclic systems the J_{aa}-coupling generally decreases by 1–1.5 Hz when the equatorial protons are substituted by methyl groups. This does not necessarily reflect stereochemical

Table 3. ^{1}H chemical shifts of isopropyl, tert-butyl and phenyl substituted 2-oxo-1,3,2-dioxathianes (ppm from TMS, solvent CCl_4)

Substitution		4e-H	4a-H	5e-H	5a-H	6e-H	6a-H	C-CH_3	C$\underline{H}$-CH_3	$C_6\underline{H}_5$
39	r-2-c-5-isoPr	3.82	4.57		2.08	3.82	4.57	0.95	2.04	
40[a]	r-2-t-5-isoPr	3.72	4.85	1.32		3.72	4.85	1.07	2.08	
41	r-2-c-5-t-Bu	3.85	4.69		2.15	3.85	4.69	0.97		
42[a]	r-2-t-5-t-Bu	3.95	4.67	1.69		3.95	4.67	1.05		
43	r-2-c-5-Ph	3.68	4.81		3.47	3.68	4.81			7.01
44[a]	r-2-t-5-Ph	3.90	5.03	2.90		3.90	5.03			7.01
45	r-2-t-4-isoPr		4.60	1.58	2.02	3.83	4.86	0.95	1.70	
			4.69	1.67	2.22	3.93	4.96	0.93	1.77[b]	
								0.95		
46[a,b]	r-2-c-4-isoPr	4.19		1.73	2.02	4.48	4.39	0.94	1.95[b]	
								1.02		
47	r-2-t-4-t-Bu		4.55	1.64	2.09	3.83	4.88	0.94		
			4.64	1.64	2.25	3.94	4.96	0.93[b]		
48[a]	r-2-c-4-t-Bu	4.03		2.25	2.25	4.33	4.33	0.98[c]		
49	r-2-t-4-Ph		5.85	1.82	2.25	3.80	4.97			7.23
50	r-2-t-4-t-Bu,-c-4-Me			1.50	2.57	3.83	5.00	0.94(t-Bu) 1.66(Me)		

[a]Not conformationally homogeneous.
[b]250 MHz values in $CDCl_3$.
[c]Degenerated spectra.

Table 4. Vicinal coupling constants of 2-oxo-1,3,2-dioxathiane and its methyl-substituted derivatives (Hz, solvent CCl_4).

Substitution		J_{4a5a}	J_{4e5e}	J_{4a5e}	J_{4e5a}	J_{6a5a}	J_{6e5e}	J_{6a5e}	J_{6e5a}
1	—	12.1	1.8	2.5	4.2	12.1	1.8	2.5	4.2
2[b]	r-2-t-4	11.6		2.6		12.6	2.0	2.6	4.4
3[a,c]	r-2-c-4	10.1		3.3		10.5	3.2	3.5	5.0
4	r-2-c-5	11.4			4.1	11.4			4.1
5	r-2-t-5		2.0	2.5			2.0	2.5	
6[a,b]	4,4					10.3	4.0	3.3	4.2
8	r-2-t-4,c-5	10.3				11.5			4.6
9	r-2-t-4,t-5			2.4			1.5	2.4	
10[a,b]	r-2-c-4,c-5				3.8	6.5			3.6
11[a,b]	r-2-c-4,t-5	8.5				9.3			4.6
12	r-2-t-4,t-6	11.6		2.4		11.6		2.4	
13	r-2-c-4,c-5	11.5		2.2		11.5		2.2	
14[a]	r-2-c-4,t-6		5.1		5.5	9.2			4.3
15	r-2-4,4,c-5					11.6			3.4
16[a]	r-2-4,4,t-5					7.0			4.0
17[c]	r-2-4,4,t-6					11.8		2.8	
18[c]	r-2-4,4,c-6					12.0		2.8	
21	r-2-t-4,c-5,t-6	10.3				10.3			
22	r-2-t-4,t-5,t-6			2.1				2.1	
23[a]	r-2-c-4,c-5,t-6				5.0	9.5			
24[a]	r-2-c-4,t-5,t-6		4.6					3.5	
27	r-2-4,4,c-5,t-6					10.5			
28	r-2-4,4,t-5,t-6							2.0	
29	r-2-4,4,t-5,c-6					10.6			
30	r-2-4,4,c-5,c-6							2.0	

[a]Not conformationally homogeneous.
[b]100 MHz values in CCl_4 (for 3 J_{4a5a} = 10.6, J_{4a5e} = 2.7, J_{6a5a} = 11.9, J_{6e5e} = 3.1, J_{6a5e} = 2.6 and J_{6e5a} = 4.2 Hz in C_6D_6).
[c]250 MHz values in $CDCl_3$.

changes but may be due to a change in Karplus constants.[44,45] In **22** the methyl substituents increase the steric crowding in the $C_{4,5,6}$-moiety. Thus the angle between axial and equatorial protons increases and the J_{ae}-coupling decreases. The repulsive interaction between the axial 5-methyl and ring oxygens causes the flattening of the ring in **9**. Hence the J_{ee}-coupling (1.5 Hz) is smaller than the value for the unsubstituted ring (1.8 Hz) even though the J_{ae}-coupling is of the same magnitude.

The ring geometry can be clarified by calculating the R-values and torsional angles ψ from Lambert-Buys equation[46,47,48] for the derivatives having a $-CH_2-CH_2-$ fragment (Table 7). According to these values the ring has an ideal chair conformation with the protons almost perfectly staggered. X-Ray studies[30–34] have on an average given a value of 59° and earlier R-value calculations[49] a value of 58° for the torsional angle, both in good agreement with the present results.

The geminal coupling constants ($-J_{gem}$) for the 4/6 protons are in the region of 10.9–12.5 Hz and for the 5-protons in the region of 13.8–14.5 Hz. The dependence of the geminal couplings on the ring geometry can be explained by comparing the values with the corresponding couplings of 1,3-dioxanes (Fig. 3). The more negative the value of $^2J_{44}$ the larger the geminal angle and the lower the ability of the sulphite group to remove electrons inductively as compared to the oxygen atoms of 1,3-dioxanes.[20] The value of $^2J_{55}$ becomes more negative due to an increase in the geminal angle, not due to changes in electronegativity. The orientation of the electrons at the β-substituent is known to cause changes in the geminal coupling constants,[50] but this effect is

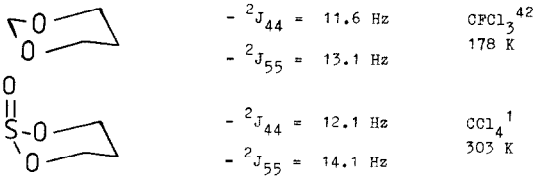


Fig. 3. The values of corresponding geminal coupling constants in 1,3-dioxane and 2-oxo-1,3,2-dioxathiane.

assumed to be similar in 1,3-dioxanes and 2-oxo-1,3,2-dioxathianes.

The observed methyl-proton couplings for the 4/6- and 5-methyl groups are fairly similar and both between 6.0 and 7.4 Hz. When the derivatives with similar substitution are compared the methyl-proton couplings of the axial substituent are often larger than those of the equatorial substituent, even though no systematic trend can be found.

Conformational equilibria from chemical shifts and coupling constants

The conformational equilibria can be solved and the mole fractions of the conformers (x_a and x_e) calculated from the model values using eqn (1)

$$J_{obs} = J_{aa} \cdot x_a + J_{ee} \cdot x_e \text{ or } \delta_{obs} = \delta_a \cdot x_a + \delta_e \cdot x_e. \quad (1)$$

The model values of the coupling constants and chemical shifts are taken either from anancomeric model compounds, for example 4-tert-butyl derivatives, or by direct observation of these parameters at low temperatures

Table 5. Geminal and methyl-proton coupling constants of 2-oxo-1,3,2-dioxathiane and its methyl-substituted derivatives (Hz, solvent CCl_4)

Substitution		$-^2J_{44(66)}$	$-^2J_{55}$	$J_{4\text{-Me,H}}$	$J_{5\text{-Me,H}}$	$J_{6\text{-Me,H}}$
1		12.1	14.1			
2[d]	r-2-t-4	11.8	13.8	6.3		
3[a,b]	r-2-c-4	12.0	14.5	6.5		
4	r-2-c-5	11.8		6.8	6.8	
5	r-2-t-5	11.3		7.0	7.0	
6[a,d]	4,4	11.8	14.1			
7	5,5	10.9				
8	r-2-t-4,c-5	11.4		6.0	6.6	
9	r-2-t-4,t-5	11.4		6.0	6.6	
10[d]	r-2-c-4,c-5	11.7		6.8	6.6	
11[d]	r-2-c-4,t-5	12.0		6.4	6.8	
12	r-2-t-4,t-6		14.1	6.4		6.4
13	r-2-c-4,c-6		14.1	6.3		6.3
14[a]	r-2-c-4,t-6		13.9	6.9		6.3
15	r-2-4,4,c-5	11.5			6.7	
16[a]	r-2-4,4,t-5	11.3			6.8	
17	r-2-4,4,t-6		14.0			6.0
18	r-2-4,4,c-6		14.4			6.0
19	r-2-t-4,5,5	11.0		6.6		
20[a]	r-2-c-4,5,5	11.8		6.3		
21	r-2-t-4,c-5,t-6			6.4	6.8	6.4
22	r-2-t-4,t-5,t-6			6.9	6.4	6.9
23[a]	r-2-c-4,c-5,t-6			7.1	7.1	6.5
24[a]	r-2-c-4,t-5,t-6			6.7	6.9	6.5
25	4,4,5,5	11.5				
26	4,4,6,6		14.5			
27	r-2-4,4,c-5,t-6				6.8	6.4
28	r-2-4,4,t-5,t,6				6.9	6.5
29	r-2-4,4,t-5,c-6				6.9	6.4
30	r-2-4,4,c-5,c-6				7.0	6.3
31	r-2-t-4,5,5,t-6			6.9		6.9
32[c]	r-2-c-4,5,5,c-6			—		—
33[a]	r-2-c-4,5,5,t-6			7.2		6.9
34	r-2-4,4,5,5,t-6					6.5
35	r-2-4,4,5,5,c-6					6.5
36	r-2-4,4,t-5,t-6				7.1	
37	r-2-4,4,c-5,6,6				7.3	

[a]Not conformationally homogeneous.
[b]250 MHz values in $CDCl_3$
[c]This isomer was not isolated.
[d]100 MHz values in CCl_4.

Table 6. Coupling constants of isopropyl, tert-butyl and phenyl substituted 2-oxo-1,3,2-dioxathianes (Hz, solvent CCl_4)

Substitution		J_{4a5a}	J_{4e5e}	J_{4a5e}	J_{4e5a}	J_{6a5a}	J_{6e5e}	J_{6a5e}	J_{6e5a}	$-^2J_{44}$	$-^2J_{55}$	$J_{Me,H}$
39	r-2-c-5-isoPr	11.8			4.3	11.8			4.3	11.7		6.0
40[a]	r-2-t-5-isoPr		2.8	2.7			2.8	2.7		11.4		6.2
41	r-2-c-5-t-Bu	11.8			4.3	11.8			4.3	11.8		
42[a]	r-2-t-5-t-Bu		4.4	4.8			4.4	4.8		11.4		
43	r-2-c-5-Ph	11.4			4.2	11.4			4.2	11.2		
44[a]	r-2-t-5-Ph		4.0	4.0			4.0	4.0		11.2		
45	r-2-t-4-isoPr	11.4		2.8		12.3	2.1	3.0	4.4	11.4	14.0	6.7
		11.9		2.3		12.9	2.0	2.4	4.7	11.4	14.1	6.7, 6.9[b]
46[a]	r-2-c-4-isoPr	11.0		2.8		10.8	3.0	5.2	3.4	12.2	14.1	6.9, 7.0[b]
47	*r-2-t-4-Bu*	11.4		2.5		12.4	2.1	2.6	4.4	11.3	14.1	
		12.1		2.3		12.8	2.0	2.4	4.7	11.4	14.0[b]	
48[a]	r-2-c-4-t-Bu	10.8		3.5		—[c]	—[c]	—[c]	—[c]	—[c]	—[c]	
49	r-2-t-4-Ph	11.0		2.6		12.4	1.8	2.6	4.3	11.4	13.9	
50	r-2-t-4-t-Bu,-c-4-Me					12.0	2.2	2.3	4.6	12.0	14.0	

[a]Not conformationally homogeneous
[b]250 MHz values in $CDCl_3$.
[c]Degenerated spectra

Table 7. Calculated R-values and torsional angles ψ for derivatives having a $-CH_2-CH_2-$ fragment

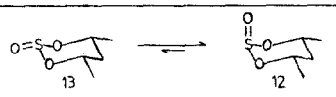
Substitution		R	ψ/degrees
1		2.07	57
2	r-2-trans-4-Me	2.00	57
3	r-2-cis-4-Me	1.70	54
6	4,4-diMe	1.90	56
45	r-2-trans-4-isoPr	1.95	57
47	r-2-trans-4-t-Bu	2.07	57
49	r-2-trans-4-Ph	2.06	57
50	r-2-trans-4-t-Bu,-cis-4-Me	2.09	57
			av. = 57

where ring inversion is slow, with extrapolation of these values to the temperature range of interest.[46,51] In the case of 2-oxo-1,3,2-dioxathianes the use of chemical shifts is difficult, especially since the derivatives with an axial 4/6-methyl exist in a conformational equilibrium. Furthermore, the magnitude of the chemical shifts depends on the orientation of the S=O group. The values for 1,3-dioxanes are not suitable models either because of the somewhat deviating ring geometry or different electronegativities of the heterocyclic portions.

Dipole moments can also be used[52] to estimate the relative amounts of the conformers. Since it is the molar polarization (P) not the dipole moment (μ) which is the additive parameter and since $P \propto \mu^2$ the corresponding equation[52] must be written

$$\mu^2_{obs} = \mu_a^2 \cdot x_a + \mu_e^2 \cdot x_e. \qquad (2)$$

Table 8. Chemical equilibria studied



		Method
352 K (CCl_4)	$K = 159 \pm 10$*	
	$-\Delta G^\ominus = 14.8 \pm 0.3$ kJ mol^{-1}	CE
352 K (CH_3OH)	$K = 26 \pm 4$*	
	$-\Delta G^\ominus = 9.5 \pm 0.4$ kJ mol^{-1}	CE

353 K (CCl_4)	$K = 1.8 \pm 0.1$*	
	$-\Delta G^\ominus = 1.6 \pm 0.2$ kJ mol^{-1}	CE

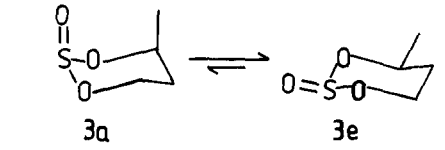
352 K (CCl_4)	$K = 8.6 \pm 0.5$*	
	$-\Delta G^\ominus = 6.3 \pm 0.2$ kJ mol^{-1}	CE
423 K (g)	$-\Delta H^\ominus = 6.9 \pm 2.0$ kJ mol^{-1}	ΔAP[M–HSO_3^-][35]
	$\Delta S^\ominus \sim 0$	

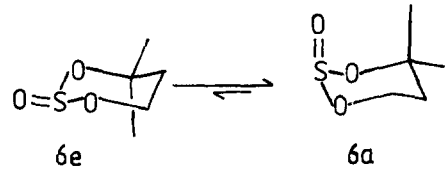
*Standard error of mean.

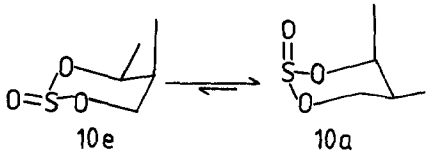
Table 9. Calculated conformer populations (%), equilibrium constants and standard Gibbs' energy differences for the equilibria studied (solvent CCl_4, 303 K)

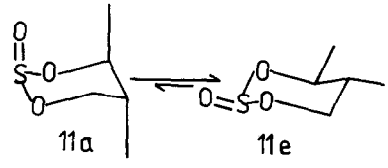
Equilibrium		K	$-\Delta G^\circ$/kJ mol^{-1}	Method
3	2a4a⇌2e4e			
	16 84	5.2 ± 1.0	4.2 ± 0.6	NMR
	22 78	3.5 ± 0.6	3.2 ± 0.5	DM
6	2e4e4a ⇌2a4a4e			
	19 81	4.3 ± 0.9	3.7 ± 0.6	NMR
	23 77	3.3 ± 0.6	3.0 ± 0.4	DM
10	2e4e5a⇌2a4a5e			
	45 55	1.2 ± 0.2	0.5 ± 0.3	NMR
11	2a4a5a⇌2e4e5e			
	22 78	3.5 ± 0.8	3.2 ± 0.5	NMR
14	2e4e6a⇌2a4a6e			
	30 70	2.3 ± 0.4	2.1 ± 0.4	NMR
	33 67	2.0 ± 0.3	1.7 ± 0.3	DM
16	2a4a4e5a ⇌2e4e4a5e			
	48 52	1.1 ± 0.1	0.2 ± 0.2	NMR
20	2e4e5e5a⇌2a4a5a5e			
	49 51	1.05 ± 0.1	0.1 ± 0.2	NMR
23	2e4e5a6a⇌2a4a5e6e			
	13 87	6.7 ± 1.3	4.8 ± 0.6	NMR
24	2e4e5e6a ⇌2a4a5a6e			
	32 68	2.1 ± 0.3	1.9 ± 0.3	NMR
33	2e4e5e5a6a ⇌2a4a5a5e6e			
	21 79	3.8 ± 0.9	3.4 ± 0.5	NMR
40	5-isoPr: 2e5e ⇌2a5a			
	8 92	11.5 ± 3.0	6.2 ± 0.5	NMR
42	5-t-Bu: 2e5e ⇌2a5a			
	25 75	3.0 ± 0.5	2.8 ± 0.5	NMR
44	5-Ph: 2e5e ⇌2a5a			
	21 79	3.8 ± 0.8	3.4 ± 0.5	NMR
46	4-isoPr:2a4a ⇌ 2e4e			NMR
	12 88	7.3 ± 1.5	5.0 ± 0.8	
48	4-t-Bu:2a4a ⇌ 2e4e	6.7 ± 1.3	4.8 ± 0.6	NMR
	13 87			

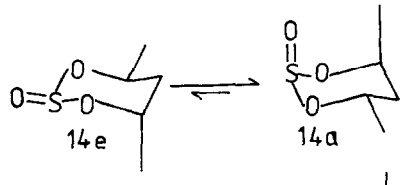
In the following the conformational equilibria will be considered in detail.

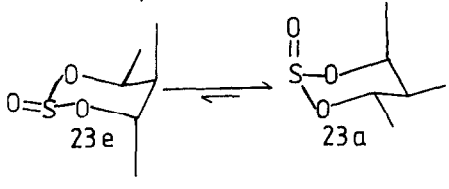












Cis-4-methyl-*r*-2-oxo-1,3,2-dioxathiane (**3**) exists as a mixture of two chair forms **3a** and **3e**. If the coupling constants of *trans*-4-methyl derivative (**2**) are accepted as model values (Table 4) the following proportions can be evaluated for the axial conformer.

$J_{obs}(CDCl_3)$	x_a	$J_{obs}(C_6D_6)$	x_a
10.5(6a5a)	0.20	11.9(6a5a)	0.07
10.1(4a5a)	0.16	10.6(4a5a)	0.10
3.2(6e5e)	0.12	3.1(6e5e)	0.10
Av.	0.16 ± 0.03	Av.	0.09 ± 0.01

The dipole moment of this isomer is 4.95 D in CCl_4. Using this value and the values 3.35 and 5.31 D for the S=O-axial and S=O-equatorial models,[25] respectively, equation (2) gives $x_{3e} = 0.22$.

From the values of the vicinal coupling constants (10.3 and 4.0 Hz) of 4,4-dimethyl-2-oxo-1,3,2-dioxathiane (**6**) we can estimate the proportion of **6a** to be 0.82 using the model values (Table 6) taken from the anancomeric 4-methyl-4-tert-butyl derivative (**50**). On the other hand, since J_{ee} varies from 1.5 to 2.2 Hz only we can select $J_{ee} = 1.8 \pm$ Hz and use equations (3)

$$10.3 = J_{aa} \cdot x_{6a} + 1.8 \cdot (1 - x_{6a})$$

$$4.0 = 1.8 \cdot x_{6a} + J_{aa} \cdot (1 - x_{6a}) \quad (3)$$

to estimate $J_{aa} = 12.5$ Hz and $x_{6a} = 0.80$.

The dipole moment for this derivative is 3.99 D in CCl_4. Using this value and the model values 3.51 D (reported for **12**) and 5.31 D for the axial and equatorial S=O group[25] the value 0.77 is derived for x_{6a}.

Using the observed coupling constants of *cis*-4, *cis*-5-dimethyl- (**10**) and *cis*-4, *trans*-5-dimethyl-*r*-2-oxo-1,3,2-dioxathiane (**11**) and the model values obtained from **4**, **8** and **5** (Table 4) the conformer populations are evaluated at $x_{10a} = 0.55$ and $x_{11a} = 0.22$ (for both J_{6a5a} and J_{4a5a}).

In several reports *cis*-4, *trans*-6-dimethyl-*r*-2-oxo-1,3,2-dioxathiane (**14**) has been claimed to exist in a twist form.[2,4,25,26,28] If we consider the methyl couplings on a first order basis the spectrum is of the ABRX-type where the coupling between R and X is near zero (Table 4). On the basis of the estimated ΔH^a_{CT}-value[1] and the values of the vicinal coupling constants this isomer is a mixture of two interconverting chair forms **14a** and **14e**. The model values $J_{aa} = 11.9 \pm 0.3$ Hz (the average of the J_{aa} of **17** and **18**) and $J_{ee} = 2.0 \pm 0.3$ Hz (**2**) give the mole fractions $x_{14a} = 0.72$ for $J_{obs} = 9.2$ and 0.69 for $J_{obs} = 5.1$. From eqns (4)

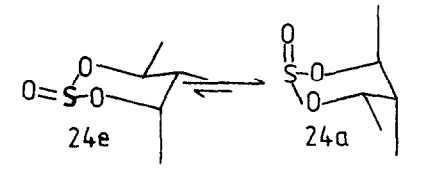
$$9.2 = J_{aa} \cdot x_{14a} + J_{ee} \cdot (1 - x_{14a})$$

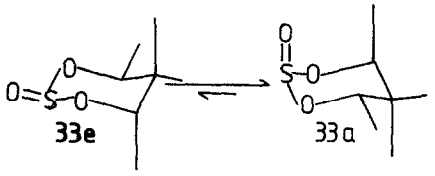
$$5.1 = J_{ee} \cdot x_{14a} + J_{aa} \cdot (1 - x_{14a})$$

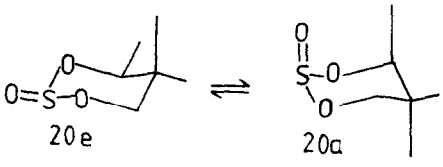
by substituting $J_{ee} = 2.0$ Hz the value of J_{aa} will be 12.3 Hz and that of x_{14a} 0.70.

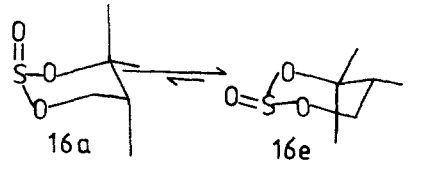
The dipole moment of this isomer is 4.19 D. Using this value and the model values 3.51 D (for S=O-axial and 5.31 D (for S = O-equatorial) the mole fraction of **14a** is estimated to be 0.67 in close agreement with the NMR results.

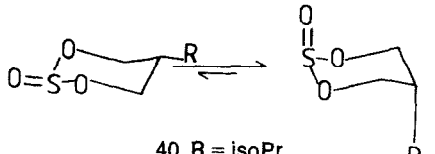
In the case of *cis*-4, *cis*-5, *trans*-6-trimethyl-(**23**) and *cis*-4, *trans*-5, -*trans*-6-trimethyl-*r*-2-oxo-1,3,2-dioxathiane (**24**) the model value for J_{aa} is rather difficult to estimate. In 1,3-dioxanes the axial 4- or 6-methyl increases this coupling about 0.8 Hz as compared to the isomer with the equatorial methyl.[46] The lower limit in the present case must be near the value 10.3 Hz observed for **21** and the upper limit in the range of 10.6–11.0 Hz. Using the value 10.6 ± 0.3 Hz of **27** or **29** (Table 4) for J_{aa} and 1.8 ± 0.3 Hz for J_{ee} the calculated mole fractions for **23a** and **24a** are 0.87 and 0.68. From IR results[8] **24** has been concluded to be a 69 : 31 mixture of chair and twist forms. If the IR absorption at 1230 cm^{-1} is attributed to the conformer **24e** with an equatorial S=O group and not to twist form[8] this result is in good agreement with the present one. The coupling constants calculated at 198 K (10.2 and 5.3 Hz for **23**, and 4.0 and 2.9 Hz for **24**) are close to the experimental values (10.5 and 5.2 Hz; 4 and 3 Hz, respectively) presented earlier.[8] Our conclusion is that non-chair conformations make a negligible contribution to the conformational states of **23** and **24**.



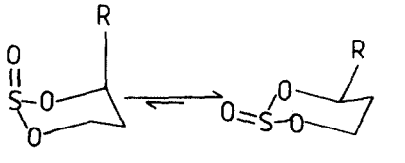








40 R = isoPr
42 R = t-Bu
44 R = Ph



46 R = isoPr
48 R = t-Bu

Cis-4,5,5, *trans*-6-tetramethyl-*r*-2-oxo-1,3,2-dioxathiane (**33**) has no vicinal protons. Hence the mole fractions must be estimated using the chemical shifts of the 4/6-methyl protons. By assuming that the chemical shift of the equatorial 4/6-methyl is 1.18 ppm (see **31**) and that the shielding effect of the axial and equatorial methyl groups in the conformer having an equatorial S = O group cancel each other out the chemical shift of the axial methyl group becomes equal to 1.52 ppm and the mole fraction of **33a** equal to 0.79.

The chemical shifts of the 6-proton and 5-methyl protons for *cis*-4,5,5-trimethyl-*r*-2-oxo-1,3,2-dioxathiane (**20**) differ markedly from those for isomer **19** (Tables 1 and 2) which indicates that **20** is a mixture of chair forms. Using the value 1.52 ppm calculated above for **33** for the chemical shift of the axial 4-methyl and the value 1.17 ppm obtained from **19** for the chemical shift of the equatorial methyl the observed chemical shift, $\delta = 1.35$ ppm, gives the value 0.51 for x_{20a}.

4,4, *trans*-5-trimethyl-*r*-2-oxo-1,3,2-dioxathiane (**16**) is also a mixture of chair forms. Using $J_{aa} = 11.6 \pm 0.3$ Hz (**8**) and $J_{ee} = 2.0 \pm 0.3$ Hz (**5**) as models the mole fraction of **16a** will be 0.48.

Using the values of J_{aa} and J_{ee} determined for **41** and **5** as models *trans*-5-isopropyl- (**40**) and *trans*-5-tert-butyl-*r*-2-oxo-1,3,2-dioxathianes (**42**) would include 8 and 25% of the diequatorial chair forms, respectively.

Similarly *cis*-4-*isopropyl*-(**46**) and *cis*-4-tert-butyl-*r*-2-oxo-1,3,2-dioxathianes (**48**) would include 88 and 87% of the diequatorial form as concluded from the values of J_{aa} and J_{ee} of **47** (Table 6).

Conformational equilibria from chemical equilibration studies

Chemical equilibration does not require the determination of the total energy content of a compound but the energy change between two different states, i.e. two isomers. The standard Gibbs energy difference $-\Delta G^\theta = 14.8$ kJ mol^{-1} for the equilibrium between epimeric *cis*-4,6-dimethyl derivatives (**12** and **13**) in CCl_4 (Table 8) represents the conformational preference of an axial S=O group. This value is in agreement with earlier results ($-\Delta G^\theta_{SO} = 8 - 15$ kJ mol^{-1})[3,16,37,38] even though it seems to represent the upper limit of this energy. Intramolecular dipolar forces are responsible for the preference of the axial S = O group. These dipolar forces are affected by a change in the solvent polarity (in methanol $-\Delta G^\theta_{SO} = 9.5$ kJ mol^{-1}). The situation closely resembles the behaviour of anomeric substituents in related carboheterocycles. Generally, the standard Gibbs free energy differences increase with a decreasing solvent polarity.[15,16] A highly polar molecule like *cis*-4, *cis*-6-dimethyl derivative (**13**) is stabilized as compared to a less polar molecule like *trans*-4, *trans*-6-dimethyl derivative (**12**) in a dielectric medium. Since the intramolecular interaction increases with the permittivity of the medium the apparent energy content of the more polar molecule decreases relative to the less polar molecule.[15,16]

CONCLUSIONS

The standard Gibbs energy differences so obtained can be used to estimate the magnitude of the non-bonding interactions. Using the derived conformational energies (Table 9) and assuming that $\Delta S^\theta = 0$(i.e. $\Delta G^\theta = \Delta H^\theta$) the eqns (5)–(13) can be written

$$-\Delta G^\theta_{SO} = \Delta G^\theta(\text{2a4a-SO,Me}) + \Delta G^\theta(\text{4a6a-Me,H}) = 3.6 \quad (5)$$

$$-\Delta G^\theta_{SO} + \Delta G^\theta(\text{2a4a-SO,Me}) - \Delta G^\theta(\text{2e4a-SO,Me}) = -2.9 \quad (6)$$

$$-\Delta G^\theta_{SO} + \Delta G^\theta(\text{2a4a-SO,Me}) + \Delta G^\theta(\text{4a6a-Me,H}) - \Delta G^\theta(\text{5a-Me}) + \Delta G^\theta(\text{4a5e-Me,Me}) - \Delta G^\theta(\text{4e5a-Me,Me}) = -0.5 \quad (7)$$

$$-\Delta G^\theta_{SO} + \Delta G^\theta(\text{2a4a-SO,Me}) + \Delta G^\theta(\text{4a6a-Me,H}) + \Delta G^\theta(\text{5a-Me}) - \Delta G^\theta(\text{4e5e-Me,Me}) = 3.2 \quad (8)$$

$$-\Delta G^\theta_{SO} + \Delta G^\theta(\text{2a4a-SO,Me}) - \Delta G^\theta(\text{2e4a-SO,Me}) - \Delta G^\theta(\text{5a-Me}) + \Delta G^\theta(\text{4e5e-Me,Me}) + \Delta G^\theta(\text{4a5e-Me,Me}) - \Delta G^\theta(\text{4e5a-Me,Me}) = -4.8 \quad (9)$$

$$-\Delta G^{\circ}_{SO} + \Delta G^{\circ}(2a4a\text{-}SO,Me) - \Delta G^{\circ}(2e4a\text{-}SO,Me) + \Delta G^{\circ}(5a\text{-}Me) - \Delta G^{\circ}(4e5e\text{-}Me,Me) - \Delta G^{\circ}(4a5e\text{-}Me,Me) + \Delta G^{\circ}(4e5a\text{-}Me,Me) = -2.0 \quad (10)$$

$$-\Delta G^{\circ}_{SO} + \Delta G^{\circ}(2a4a\text{-}SO,Me) + \Delta G^{\circ}(4a6a\text{-}Me,H) - \Delta G^{\circ}(4e5e\text{-}Me,Me) + \Delta G^{\circ}(4a5e\text{-}Me,Me) - \Delta G^{\circ}(4e5a\text{-}Me,Me) = -0.1 \quad (11)$$

$$-\Delta G^{\circ}_{SO} + \Delta G^{\circ}(2a4a\text{-}SO,Me) - \Delta G^{\circ}(2e4a\text{-}SO,Me) + \Delta G^{\circ}(5a\text{-}Me) - \Delta G^{\circ}(4e5e\text{-}Me,Me) - \Delta G^{\circ}(4a5e\text{-}Me,Me) + \Delta G^{\circ}(4e5a\text{-}Me,Me) = 0.2 \quad (12)$$

$$\Delta G^{\circ}(4e5e\text{-}Me,Me) + \Delta G^{\circ}(4a5e\text{-}Me,Me) - \Delta G^{\circ}(5a\text{-}Me) - \Delta G^{\circ}(4e5a\text{-}Me,Me) = -0.8 \quad (13)$$

where ΔG°_{SO} = the conformational energy of the axial S=O group; ΔG°(2a4a-SO,Me) = the interaction between the axial S=O group and an axial 4-methyl; ΔG°(2e4a-SO,Me) = the conformational energy of the axial 4-methyl in the conformer having an equatorial S=O group; ΔG°(4e5e-Me,Me) = the gauche interaction energy between equatorial 4- and 5-methyl groups; ΔG°(4a5e-Me,Me) = the gauche interaction energy between the axial 4-methyl and the equatorial 5-methyl; ΔG°(4e5a-Me,Me) = the gauche interaction energy between the equatorial 4-methyl and the axial 5-methyl; ΔG°(4a6a-Me,H) = the interaction energy between the syn-axial 4-methyl and 6-proton; ΔG°(5a-Me) = the interaction energy between the axial 5-methyl and 1,3-oxygen atoms (or better the lone pair orbitals).

The numerical value of eqn (5) is the average of the energies from the NMR and dipole moment calculations, that of eqn (6) is the average of the conformational energies for the equilibria **6e** ⇌ **6a**, **14e** ⇌ **14a** and **33e** ⇌ **33a** and that of eqn (13) is from the chemical equilibration of **23** and **24** (a four-component equilibrium [**24e**⇌**24a**]⇌[**23e**⇌**23a**]. Doing the above group of equations gives the following solution:

$-\Delta G^{\circ}_{SO} + \Delta G^{\circ}(2a4a\text{-}SO,Me) = -0.1$ kJ mol^{-1}

$\Delta G^{\circ}(2e4a\text{-}SO,Me) = 2.8$ kJ mol^{-1}

$\Delta G^{\circ}(4e5e\text{-}Me,Me) = 2.9$ kJ mol^{-1}

$\Delta G^{\circ}(5a\text{-}Me) = 3.3$ kJ mol^{-1}

$\Delta G^{\circ}(4a5e\text{-}Me,Me) - \Delta G^{\circ}(4e5a\text{-}Me,Me) = -0.8$ kJ mol^{-1}.

ΔG°(4a6a-Me,H) is assumed to be 3.8 kJ mol^{-1}, the value reported for 1,3-dioxanes.[53] The above results are of the expected magnitude taking into account the suspected error limit of ± 1 kJ mol^{-1} (for comparison ΔG°(4e5e-Me,Me) = 1.5 kJ mol^{-1} and ΔG°(5a-Me) = 3.6 kJ mol^{-1} for 1,3-dioxane).[54,55]

The results show that the stablizing effect of the axial S=O group is almost equal to the destablizing effect of the 2a4a-SO,Me-interaction. If the value 14.8 kJ mol^{-1} derived by chemical equilibration is given for the conformational energy of the S=O group the value of the 2a4a-SO,Me-interaction will be 14.7 kJ mol^{-1}. A value $-\Delta G^{\circ}$ = 2.9 kJ mol^{-1}, reported earlier for the conformational energy of the axial 5-methyl group (the equilibrium studied was 2a5a⇌2a5e)[15] is in good agreement with the present result.

The configurational interaction energies can be used to estimate the anancomerism of the compounds, or in the case of conformational equilibria, the proportions of the conformers. Thus *trans*-5-methyl derivative (**5**) exists mainly and 5,5-di-methyl derivative (**7**) exclusively in a chair conformation with an axial S=O group. 4,4,5,5-tetramethyl derivative **25** includes 76% of the S=O-axial conformer.

To conclude, 2-oxo-1,3,2-dioxanthiane exists in a chair conformation with the S=O group axially orientated. Substituted 2-oxo-1,3,2-dioxathianes exist preferentially in a chair conformation with an axial or equatorial S=O group or as a mixture of two chair forms. Equatorial substituents increase the anancomerism of the ring. The interaction between equatorial 4- and 5-methyl groups flattens the $C_{4,5,6}$-fragment of the ring in 4,5-dimethyl and 4,5,6-trimethylderivatives. An axial methyl group in position 4 or 6 does not force the ring to a twist conformation but moves the chair-chair equilibrium towards the conformer with an equatorial S=O group. This effect is more obvious with larger alkyl groups such as isopropyl and tert-butyl. The interaction between axial 4- and 6-methyl groups of 4,4,6,6-tetramethyl derivatives may deform the ring. The NMR parameters, however, resemble those of a chair form and the magnitude of the deformation is difficult to estimate. In 4,4, *cis*-6-trimethyl-*r*-2-oxo-1,3,2-dioxathiane which is a chair form the chemical shifts of the axial and equatorial 4-methyl are nearly identical. Thus similar chemical shifts do not necessarily mean isoclinal methyls but may rather be due to the effect of the equatorial S=O group and geminal substitution pattern on the equatorial methyl. Our results show no evidence of twist forms.

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