2-Oxo-1,3,2-dioxathianes. II. Determination of the S=O Group Configuration by IR Spectroscopy

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The IR spectra of 2-oxo-1,3,2-dioxathiane and several alkyl-substituted 2-oxo-1,3,2-dioxathianes were recorded and used for the configurational assignment of the S=O group. A very strong absorption at *ca.* 1190 cm^{-1} is characteristic of an axial S=O group whereas a strong absorption at *ca.* 1240 cm^{-1} indicates an equatorial S=O group. The intermediate value, which earlier has been assigned to the S=O group of twist conformations, is more likely due to the mixed C–C(–H) stretch vibrations.

2-Oxo-1,3,2-dioxathiane has been shown to exist in a chair conformation with the S=O group axially oriented.[1-6] An axial S=O group has been found to be 8–15 kJ mol^{-1} more stable than an equatorial S=O group owing largely to the dipole–dipole

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interactions.[2,7-10] Substituted 2-oxo-1,3,2-dioxathianes exist preferentially in a chair conformation with the S=O group axially or equatorially oriented or as a mixture of two chair conformations.[7]

The configurational and conformational analysis with the aid of the IR spectra of 2-oxo-1,3,2-dioxathianes is concentrated in the use of the stretching vibration, $v(S=O)$, of the S=O bond. With the exception of this vibration band the positions of the main bands are less useful for the assignment of the ring conformation or configuration (Table 1).[3,11] The S=O stretching vibration has been shown to be sensitive to the environment of the S=O bond[12] and only very small changes in the S=O bond environment are needed to change the stretching frequencies by 0–50 cm^{-1}. The frequency ranges observed in this study for the stretching vibrations are fairly narrow: 1188–1200 cm^{-1} for axial S=O groups and 1238–1247 cm^{-1} for

Table 1. Group frequencies for 2-oxo-1,3,2-dioxathianes in the region of 1400–500 cm^{-1}.

Frequency range/cm^{-1}	Assignation of vibration
1400–1250	C–H vibration (CH$_2$-wag, as. CH$_3$-deformation, CH$_3$-rocking)
1250–1235	S=O stretch (an equatorial S=O group)
1235–1212	C–C(–H) stretch
1212–1200	CH$_3$ rock
1200–1185	S=O stretch (an axial S=O group)
1180–1100	C–H bend or deformation
1100–1060	C–O stretch
1050–1010	C–C stretch
970–900	Ring stretch
890–850	S–O–C stretch
750–670	S–O stretch (symm. and asymm.)
540–520	S=O deformation

Table 2. IR frequencies of 2-oxo-1,3,2-dioxathiane and its methyl-substituted derivatives observed in the region of $1300-1100$ cm^{-1} (values are in cm^{-1}, solvent CCl$_4$).

Compound		S=O(ax)	CH$_3$	C−C(−H)	S=O(eq)	C−H
1		1193 (vs)		1232 (m)		1250 (w)
2	2a4e	1193 (vs)		1225 (w)		
3[a]	2a4a⇌2e4e	1194 (w)		1225 (w)	1244 (s)	
	16 % 84 %					
4	2a5e	1194 (vs)	.	1227 (w)		1251 (w)
5	2a5a	1194 (vs)		1226 (w)		1250 (w)
6[a]	2e4e4a⇌2a4a4e	1195 (s)	1200 (vs)	1224 (w)	1244 (w)	1251 (m)
7	2a5a5e	1192 (vs)	1205 (s)	1220 (w)		1250 (w)
8	2a4e5e	1190 (vs)		1230 (w)		1250 (w)
9	2a4e5a	1190 (vs)		1230 (w)		
10[a,b]	2e4e5a⇌2a4a5e					
	45 % 55 %	1190 (s)			1240 (s)	
11[a,b]	2a4a5a⇌2e4e5e					
	22 % 78 %					
12	2a4e6e	1193 (vs)		1219 (w)		1260 (w)
13[c]	2e4e6e	1193 (vw)		1220 (w)	1241 (vs)	
14[a]	2e4e6a⇌2a4a6e	1197 (s)		1220 (w)	1243 (w)	
	30 % 70 %					
15	2a4a4e5e	1194 (s)	1206 (vs)	1227 (w)		
16[a]	2a4a4e5a⇌2e4e4a5e	1195 (s)	1206 (vs)	1225 (w)	1245 (m)	
	48 % 52 %			1232 (m)		
17[d]	2a4a4e6e	1189 (s)	1209 (vs)	1232 (m)		
18[e]	2e4a4e6e	1188 (w)	1207 (vs)		1238 (s)	
19	2a4e5a5e	1195 (vs)		1216 (m)		1250 (w)
20[a]	2e4e5e5a⇌2a4a5a5e	1194 (s)		1217 (m)	1247 (m)	1255 (w)
	49 % 51 %					
21	2a4e5e6e	1191 (s)		1216 (m)		
22	2a4e5a6e	1195 (s)		1218 (m)		1255 (w)
23[a]	2e4e5a6a⇌2a4a5e6e	1196 (s)		1219 (m)	1244 (w)	1255 (w)
	13 % 87 %					
24[a]	2e4e5e6a⇌2a4a5a6e	1195 (s)		1222 (m)	1244 (m)	1255 (w)
	32 % 68 %					
25[a]	2e4e4a5e5a⇌2a4a4e5a5e	1190 (s)	1206 (s)	1225 (m)	1242 (m)	1260 (w)
	24 % 76 %					
26[f]	2a4a4e6a6e	1200 (s)	1200 (s)	1225 (m)		1256 (w)
27[g]	2a4a4e5e6e					
28[g]	2a4a4e5a6e					
29[g]	2e4a4e5e6e	1190 (s)	1212 (s)	1230 (m)	1246 (m)	
30[g]	2e4a4e5a6e					
31	2a4e5a5e6e	1190 (s)	1202 (s)	1220 (m)		
32[h]	2e4e5a5e6e	−	−	−	−	
33[a]	2e4e5e5a6a⇌2a4a5a5e6e	1188 (s)	1200 (s)	1222 (m)	1245 (m)	
	21 % 79 %					
34	2a4a4e5a5e6e	1188 (s)	1205 (s)	1220 (w)		1255 (m)
35	2e4a4e5a5e6e		1205 (s)		1243 (m)	1250 (m)
36[i]	2e4a4e5e6a6e	1198 (s)	1202 (s)	1219 (w)	1243 (m)	1260 (m)
37[i]	2e4a4e5a6a6e					
38	2e4a4e5a5e6a6e		1203 (vs)	1220 (w)	1243 (s)	

[a] Not conformationally homogeneous; conformer population was determined by ^{1}H NMR spectroscopy using vicinal coupling constants and chemical shifts. [b] A mixture of isomers *10* and *11*. [c] Contains isomer *12* as impurity. [d] Contains isomer *18* as impurity. [e] Contains isomer *17* as impurity. [f] Exists in a more or less deformed chair conformation. [g] A mixture of isomers *27−30*. [h] Not measured. [i] A mixture of isomers *36* and *37;* isomer *37* exists in a deformed chair conformation.

equatorial S=O groups. The interaction between the axial lone-pair orbitals of the ring oxygen atoms and the anti-bonding orbitals of the axial S=O bond tend to weaken this bond thus rendering the vibration of the axial S=O bond to a lower wave number than the vibration of the equatorial S=O bond.[13]

Each 2-oxo-1,3,2-dioxathiane studied gives a characteristic IR spectrum, even though the spectra of isomeric derivatives are rather similar in the range of 1400−500 cm⁻¹ Since only the S=O stretching vibration clearly depends on the configuration, the following inspection is restricted to the S=O stretching vibration region of 1180−1260 cm⁻¹ (Tables 2 and 3).

The position of the very strong absorption due to an axial S=O group (range 1188−1200 cm⁻¹) shifts upon dilution to higher wave numbers in solvents of low polarity and to lower wave numbers in polar solvents. The change in the wave numbers in polar solvents. The change in the wave number is rather small, about 2−5 cm⁻¹ An increase in the polarity and solvating power of the solvent has been stated to increase the induced polarity of the axial S=O bond, to decrease the bond order and hence to lower the stretching frequency concerned.[3] 4,4- and 5,5-dimethyl-substituted derivatives have bands both in the region

of 1188−1200 cm⁻¹ and 1200−1212 cm⁻¹ The former is assigned to the S=O stretching and the latter to the methyl group vibrations, probably CH_3 rock.

A band in the region 1238−1247 cm⁻¹ indicates the presence of an equatorial S=O group. The position of this band shows little or no variation with the solvent or solute concentration. Intensity changes with the change of solvent and upon dilution usually reflect alterations in the position of the conformational equilibrium. The intensity of the absorption at the higher wave number greatly increases at the expense of that at the lower wave number in a polar medium. This supports a solvation mechanism where the polar medium favours polar conformers, here the conformer with an equatorial S=O group.[2,14]

The band in the region of 1216−1232 cm⁻¹ is probably due to C−C(−H) stretching vibrations[15,16] even though it has formerly been assigned to the S=O stretch of twist conformations.[2,13,17,18] It can be found as a sharp band or a shoulder of a band at 1200−1212 cm⁻¹ for almost all the compounds studied, even for the non-substituted ring which has shown to be in an S=O-axial chair conformation.[1−6] Changing the solvent from nonpolar to polar does not change the relative intensity of the band either although the twist form is

Table 3. IR frequencies of the S=O stretching vibration for isopropyl-, *tert*-butyl- and phenyl-substituted 2-oxo-1,3,2-dioxathianes (values are in cm⁻¹, solvent CCl_4).

Compound		S=O (ax)	S=O (eq)
39	2a5e-isoPr	1187 (vs)	
40[a]	2e5a-isoPr⇌2a5a-isoPr	1185 (s)	1247 (w)
	8 % 92 %		
41	2a5e-t-Bu	1185 (s)	
42[a]	2e5e-t-Bu⇌2a5a-t-Bu	1190 (s)	1240 (w)
	25 % 75 %		
43	2a5e-Ph	1185 (vs)	
44[a]	2e5e-Ph⇌2a5a-Ph	1185 (s)	1240 (w)
	21 % 79 %		
45	2a4e-isoPr	1185 (vs)	
46[a]	2a4a-isoPr⇌2e4e-isoPr		1200−1250 (vs)[b]
	12 % 88 %		
47	2a4e-t-Bu	1185 (vs)	
48[a]	2a4a-t-Bu⇌2e4e-t-Bu		1200−1250 (vs)[b]
	13 % 87 %		
49	2a4e-Ph	1185(s)	
50	2a4a-Me,4e-t-Bu	1185 (s)	

[a] Not conformationally homogeneous; conformer population was determined by ¹H NMR spectroscopy using vicinal coupling constants and chemical shifts. [b] A broad band.
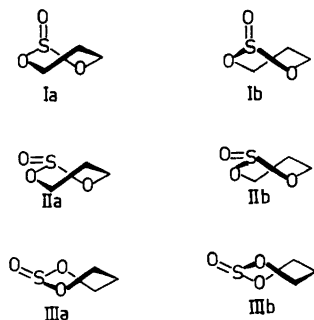
Fig. 1. Twist conformations of 2-oxo-1,3,2-dioxa-thiane.

Fig. 2. Possible conformations of 4,4,6,6-tetramethyl derivatives studied.

assumed to be more polar than the chair conformation with an axial $S=O$ group and the relative intensity of the band should increase.

2-Oxo-1,3,2-dioxathianes can, in principle, exist in three different twist forms: 2,5-, 1,4- and 3,6-twists (Fig. 1). When discussing the possible twist conformations for sterically crowded molecules one should remember that molecules which are so crowded as to be forced from a chair to a twist form may involve unfavourable interaction also in twist conformations. The axial orientation of the $S=O$ group is favoured and hence assumed to considerably increase also the stability of twist forms *Ia* and *Ib* as compared to other twist forms. A methyl group (and any other alkyl group) is more hindered in a pseudoaxial position than in a pseudoequatorial or isoclinal position and avoids this position whenever possible.[19,20] For vicinal substituents three possible *cis*-arrangements have energetic drawbacks: $\psi_e - \psi_a$ ($\psi =$ pseudo) and ψ_a-ic (ic = isoclinal) have an unfavourable pseudoaxial group and ψ_e-ic shows unfavourable torsional interaction. On the other hand, two conformations of trans-vicinal substituents may be energetically preferred: ψ_e-ψ_e with a dihedral angle of about 60° between the substituents and ψ_e-ic with a dihedral angle greater than 60°. In the light of this discussion and the calculated ΔH°_{CT}-value (the twist form has been estimated to be about 31 kJ mol^{-1} less stable thermodynamically than the chair form with an equatorial $S=O$)[7] it is easy to understand that an escape to a twist form does not necessarily relieve the steric compression in the polysubstituted derivatives.

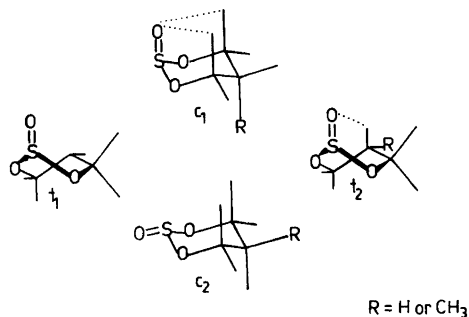4,4,6,6-Tetramethyl-substituted derivatives have a *syn*-axial interaction between 4- and 6-methyl groups, which could deform the ring. The deforma-tion cannot be deduced directly by IR spectroscopy since the most favourable twist form would have a purely axial $S=O$ group and would therefore give the normal $S=O$ stretching in the region of $1188 - 1200$ cm.$^{-1}$ The $S=O$ stretching absorptions 1200 cm^{-1} and 1198 cm^{-1} for 4,4,6,6-tetramethyl (*26*) and 4,4,6,6,*trans*-5-pentamethyl (*36*) derivatives, respectively, correspond to axial $S=O$ groups. Severe interaction between the axial 4- and 6-methyl groups and the axial $S=O$ group greatly disfavours the $S=O$-axial chair conformation (c_1 in Fig. 2). Evidently these derivatives exist in a more or less deformed twist conformation (t_1). On the other hand 4,4,6,6,*cis*-5-pentamethyl (*37*) and 4,4,5,5,6,6-hexa-methyl (*38*) derivatives exist in a $S=O$-equatorial chair conformation (c_2 in Fig. 2) since in these cases a twist conformation (t_2) cannot lead to a favourable relief of the steric interaction.

EXPERIMENTAL

The 2-oxo-1,3,2-dioxathianes studied were prepared earlier.[21] The characterization of the products was performed by gas chromatography and NMR spectra, and partly also by mass spectra. The isomers were separated by distillation or a preparative gas chromatograph using XE-60 and Carbowax 20 M columns.

The IR measurements were made on a Perkin Elmer 180 IR-spectrophotometer at 303 K using 4 % (w/v) CCl$_4$-solutions in a sealed AgCl cell of a fixed path length of 0.1 mm. The spectra for configurational assignment were recorded between $1400 - 400$ cm^{-1} on a linearly expanded, calibrated scale. The reported values are considered to be accurate within 0.5 cm^{-1}.

REFERENCES

1. Nikander, H., Lummaa, T. and Pihlaja, K. *Kem. Kemi 7* (1980) 29.
2. Van Woerden, H. F. and Havinga, E. *Recl. Trav. Chim. Pays-Bas 86* (1967) 341, 353.
3. Green, C. H. and Hellier, D. G. *J. Chem. Soc. Perkin Trans. 2* (1972) 458.
4. Albriktsen, P. *Acta Chem. Scand. A 29* (1975) 824.
5. Edmundson, R. S. *Tetrahedron Lett.* (1965) 1649.
6. Altona, C., Geise, H. J. and Romers, C. *Recl. Trav. Chim. Pays-Bas 85* (1966) 1197.
7. Nikander, H., Mukkala, V-M., Nurmi, T. and Pihlaja, K. *Org. Magn. Reson. 8* (1976) 375.
8. Van Woerden, H. F. and De Vries-Miedema, A. T. *Tetrahedron Lett.* (1971) 1687.
9. Hamblin, P. C., White, R. F. M., Eccleston, G. and Wyn-Jones, E. *Can J. Chem. 47* (1969) 2731.
10. Yuldasheva, L. K. and Arshinova, R. P. *Vopr. Stereokhim. 1* (1971) 57.
11. Hellier, D. G. and Webb, F. J. *J. Chem. Soc. Perkin Trans. 2* (1977) 612.
12. Gillespie, R. J. and Robinson, E. A. *Can. J. Chem. 41* (1963) 2074.
13. Petit, G., Lenstra, A. T. H., Van de Mieroop, W., Geise, H. J. and Hellier, D. G. *Recl. Trav. Chim. Pays-Bas 97* (1978) 202.
14. Van Woerden, H. F., Cerfontain, H., Green, C. H. and Reijerkerk, R. J. *Tetrahedron Lett.* (1968) 6107.
15. Remizov, A. B. *Zh. Prikl. Spectrosk. 14* (1971) 425.
16. Gren, A. I. *Vopr. Stereokhim. 2* (1972) 76.
17. Maroni, P. and Tisnes, P. *Bull. Soc. Chim. Fr.* (1972) 794.
18. Cazaux, L. and Maroni, P. *Bull. Soc. Chim. Fr.* (1972) 773, 780.
19. Hendrickson, J. B. *J. Am. Chem. Soc. 85* (1963) 4059.
20. Hendrickson, J. B. *J. Am. Chem. Soc. 89* (1967) 7036, 7043.
21. Virtanen, T. and Nikander, H. *To be published.*