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Validity of Infrared Criteria in the Assignment of Conformations to Substituted 1,3,2-Dioxathiane 2-Oxides. Crystal Structure of 4,4-Dimethyl-6,6-diphenyl-1,3,2-dioxathiane 2-Oxide at 110 K

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Abstract: 4,4-Dimethyl-6,6-diphenyl-1,3,2-dioxathiane 2-oxide crystallizes in the monoclinic space group $C2/c$, $Z = 8$, with $a = 17.239$ (10) Å, $b = 9.771$ (10) Å, $c = 18.390$ (8) Å, $\beta = 107.74$ (4)° at 110 K. The X-ray determination converged to $R = 0.032$ and showed the sulfite ring to have a boat-like conformation. Infrared spectroscopy in solution as well as in the solid state interpreted according to accepted criteria indicated, however, the sulfite ring to be in the chair form with axial S═O. The reasons for the discrepancy between the observed conformation and the IR criteria commonly used to assign conformations to sulfites are discussed together with a comparison of the geometries of 13 other substituted 1,3,2-dioxathiane 2-oxides. It is shown that the anomeric effect provides the basis to rationalize detailed geometries as well as S═O stretching frequencies observed in all cases.

Introduction

In the last 2 decades the conformations of substituted cyclic sulfites have been the subject of vigorous research. Spectral data provided the basis upon which configurational and conformational assignments rest. Notably Hellier et al.[1,2] and Maroni et al.[3,4] investigated by IR and NMR techniques a wide range of 1,3,2-dioxathiane 2-oxides, often substituted at the 4,6, and/or 5 position. These authors pointed out that six-membered ring sulfites can be divided into three distinct classes, characterized by the orientation of the S═O bond and the shape of the ring; i.e., they mark out sulfites in the classes:

CA: the rigid chair conformation with the S=O bond pointing in the axial direction
CE: the rigid chair conformation with the S=O bond pointing in the equatorial direction
TB: the (twist) boat conformation

The main criterion typifying a particular sulfite is the position of the strong IR band corresponding to the S═O stretching frequency at 1180–1200 cm^{-1} (class CA), at 1230–1245 cm^{-1} (class CE), or at 1210–1220 cm^{-1} (class TB).

At this point two remarks are in order. First one wonders why a very flexible system as the twist boat form should lead to the smallest range of S═O frequencies. Second, the translation of a single physical property into an unequivocal assignment of conformation is still difficult, making independent verification by X-ray investigations advisable. For example, IR spectroscopy in solution as well as in the solid state put 4,4-dimethyl-6,6-diphenyl-1,3,2-dioxathiane 2-oxide (Figure 1; abbreviated as MPDO) into class CA. However, the X-ray analysis to be reported here proved MPDO to belong to class TB. Although in other cases for which X-ray geometries were available the IR criteria had predicted the correct conformation, its failure in the present case induced us to search for an explanation and possibly to extend the limits of the criteria. We compared the geometrical details of 13 1,3,2-dioxanthiane 2-oxides and found in the anomeric effect the structural basis for their differences. The anomeric effect allows for a detailed description of conformations and geometries as well as for S═O stretching frequencies in six-membered ring sulfites in function of substitution.

Experimental Section

MPDO was prepared[2] following a standard procedure in which 1,1-diphenyl-3-methylbutane-1,3-diol was reacted with thionyl chloride in pyridine; mp 98 °C. In passing we note that under similar conditions 1,1-diphenylpropane-1,3-diol did not produce a cyclic sulfite but a five-membered ring sulfone, 3,3-diphenyl-1,2-oxathiane 2,2-dioxide, the crystal structure of which was reported previously.[5]

Table I. Experimental Details and Crystallographic Data of MPDO

empirical formula	$C_{17}H_{18}O_3S$
molecular weight	302.1
space group	$C2/c$
cell dimensions (110 K)	$a = 17.239$ (10) Å
	$b = 9.771$ (10) Å
	$c = 18.390$ (8) Å
	$\beta = 107.74$ (4)°
	$Z = 8$
V	2950 (2) Å^3
$F(000)$	1280
d(calcd)	1.361 Mg m^{-3}
μ(Mo Kα)	2.27 cm^{-1}
crystal dimensions	0.2 × 0.15 × 0.3 mm
no. of reflections recorded	3235
no. reflections in LS	2147 with $I > 2\sigma(I)$
R_w value[a]	0.032
R value[b]	0.034

[a] $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$. [b] $R = \{\sum(|F_o| - |F_c|)^2/\sum|F_o|^2\}^{1/2}$.

Colorless single crystals of MPDO were obtained from a mixture of diethyl ether and petroleum ether (50:50) by slow evaporation at −30 °C. IR spectra (Figure 2) in $CHCl_3$ solution and in a KBr disk were recorded on a Perkin-Elmer 580, while the Raman spectrum of a single crystal was taken on a Coderg PHO. The strong band near 1190 cm^{-1} should indicate a CA conformation. Since the spectra are almost identical we conclude that MPDO has the same conformation in solution as in the solid state. X-ray intensities were collected on an Enraf-Nonius CAD4 diffractometer using Zr-filtered Mo radiation (λ 0.71073 Å) up to $\theta \leq 30°$. A pure ω scan was applied, the scan angle given by 0.9 + 0.35 tan θ. Cell dimensions were determined by least-squares on angle settings of 25 reflections. All measurements were performed at 110 K. Past experiences had taught us that sulfite crystals often suffer from slow sublimation.[6-9] The process is reflected by a steady decline in intensity

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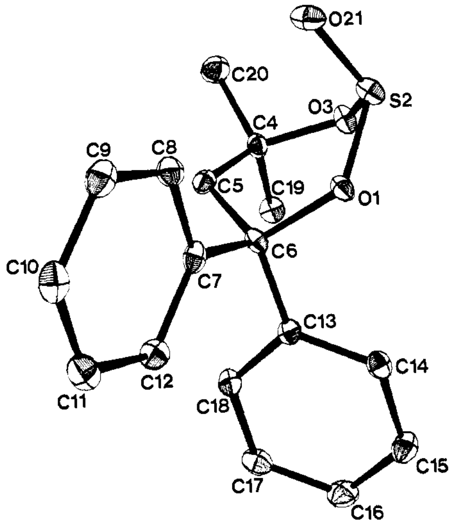

Figure 1. Structure and conformation of the title compound with numbering of the atoms.

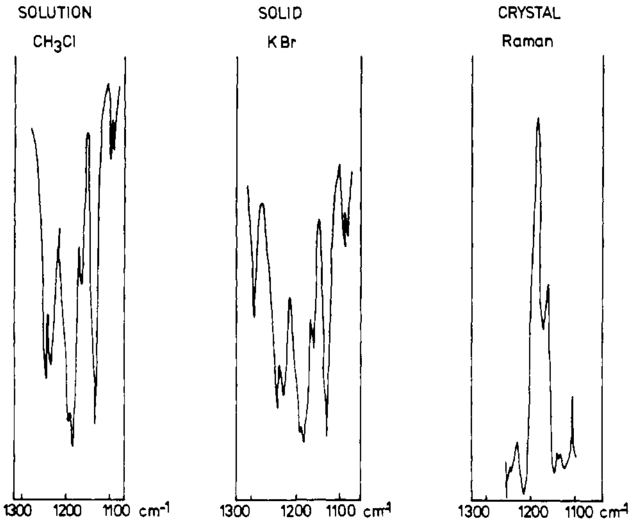

Figure 2. IR and Raman spectra of MPDO in the range 1100–1300 cm^{-1}.

of standard reflections. Therefore, we decided to measure at low temperature rather than to correct a set of room-temperature data afterwards. At 110 K no drift in intensity was noted, indicating that sublimation damage was absent.

Of the 3235 independent reflections recorded, 2147 were significanly ($I > 2\sigma(I)$) above the background. In view of the small size of the crystal (0.2 × 0.15 × 0.3 mm) and the low value of the linear absorption coefficient (μ = 2.27 cm^{-1}), no absorption correction was made. Further details of the crystallographic procedures are given in Table I.

Systematic extinctions leave a choice between the acentric space group Cc (Z = 4) and the centric one $C2/c$ (Z = 8). The latter was chosen because the Wilson statistics preferred the centric space group and because the density calculated for Z = 8 (see Table I) fits to densities normally encountered in substituted 1,3,2-dioxathiane 2-oxides.

A series of Patterson and (difference) Fourier calculations yielded the positions of all atoms, including H atoms. During the refinement by the Gauss-Seidel[10] semiblock-diagonal least-squares method the 2147 observed reflections were given individual weights based on counting statistics. H positions were refined, but their isotropic temperature parameter was kept fixed at B = 1.8 Å^2. No extinction correction was made. The weighted R value converged to 0.032.

The final difference electron density function showed no maxima above the level of 0.6 e Å^{-3}. Refined structural parameters are listed in

Table II. Positional Parameters in Fractions of the Cell Edges with Esd's in Parentheses[a]

	x	y	z	B_{iso}
O(1)	0.32934 (8)	0.0603 (2)	−0.18595 (8)	1.29
S(2)	0.41652 (3)	0.06963 (8)	−0.12079 (3)	1.62
O(3)	0.40187 (9)	−0.0371 (2)	−0.06087 (8)	1.49
C(4)	0.3001 (1)	−0.1813 (3)	−0.0841 (1)	1.27
C(5)	0.3422 (1)	−0.1894 (3)	−0.1711 (1)	1.18
C(6)	0.2865 (1)	−0.0711 (3)	−0.2099 (1)	1.14
C(7)	0.2719 (1)	−0.0763 (3)	−0.2964 (1)	1.92
C(8)	0.3375 (1)	−0.0573 (3)	−0.3247 (1)	1.36
C(9)	0.3277 (1)	−0.0658 (3)	−0.4020 (1)	1.62
C(10)	0.2523 (1)	−0.0935 (3)	−0.4525 (1)	1.67
C(11)	0.1863 (1)	−0.1122 (3)	−0.4262 (1)	1.67
C(12)	0.1957 (1)	−0.1026 (3)	−0.3483 (1)	1.39
C(13)	0.2075 (1)	−0.0638 (3)	−0.1888 (1)	1.16
C(14)	0.1616 (1)	−0.1821 (3)	−0.1912 (1)	1.46
C(15)	0.0890 (1)	−0.1774 (3)	−0.1734 (1)	1.54
C(16)	0.0610 (1)	−0.0548 (3)	−0.1541 (1)	1.82
C(17)	0.1057 (1)	0.0621 (3)	−0.1524 (1)	1.81
C(18)	0.1787 (1)	0.0578 (3)	−0.1696 (1)	1.35
C(19)	0.3231 (1)	−0.2211 (3)	−0.0394 (1)	1.60
C(20)	0.4378 (1)	−0.2644 (3)	−0.0589 (1)	1.99
O(21)	0.4773 (1)	0.0156 (2)	−0.1525 (1)	1.93

[a] Isotropic temperature parameters were calculated according to Lipson and Cochran[26] [$B_{iso} = 8\pi^2(U^{\circ}_{11}U^{\circ}_{22}U^{\circ}_{33})^{1/3}$], assuming equal volume of the 50% probability region. All anisotropic thermal parameters were physically acceptable.

Table III. Valence Angles (deg) with Their Estimated Standard Deviations in Parentheses

O1–S2–O21	107.8 (1)	O3–S2–O21	109.1 (1)
O1–S2–O3	99.7 (1)	C6–C5–C4	117.0 (1)
S2–O1–C6	122.5 (1)	S2–O3–C4	120.1 (1)
O1–C6–C5	109.4 (1)	O3–C4–C5	109.7 (1)
O3–C4–C19	103.7 (1)	O3–C4–C20	107.3 (1)
C5–C4–C19	114.4 (1)	C5–C4–C20	110.4 (1)
C19–C4–C20	110.9 (1)	C7–C6–C13	112.8 (1)
O1–C6–C7	104.3 (1)	O1–C6–C13	106.6 (1)
C5–C6–C7	109.9 (1)	C5–C6–C13	113.4 (1)
C8–C7–C12	118.2 (1)	C9–C8–C7	121.1 (2)
C10–C9–C8	120.1 (2)	C11–C10–C9	120.1 (2)
C12–C11–C10	120.1 (2)	C7–C12–C11	120.4 (2)
C6–C7–C8	119.1 (1)	C6–C7–C12	122.6 (1)
C6–C13–C14	119.6 (2)	C6–C13–C18	121.7 (2)
C13–C18–C17	120.5 (2)	C18–C17–C16	120.7 (2)
C17–C16–C15	119.5 (2)	C16–C15–C14	120.0 (2)
C15–C14–C13	120.6 (2)	C14–C13–C18	118.7 (1)

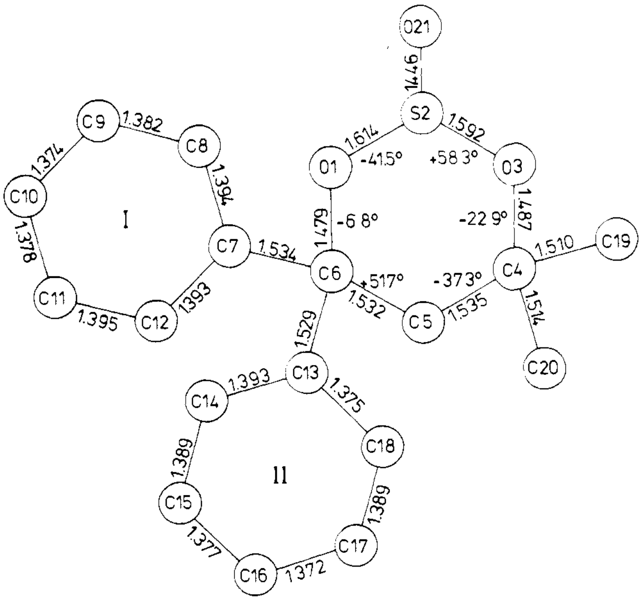

Figure 3. Bond distances (Å) with esd's of 0.002 Å and endocyclic torsion angles (°) with esd's of about 0.4° for the title compound.

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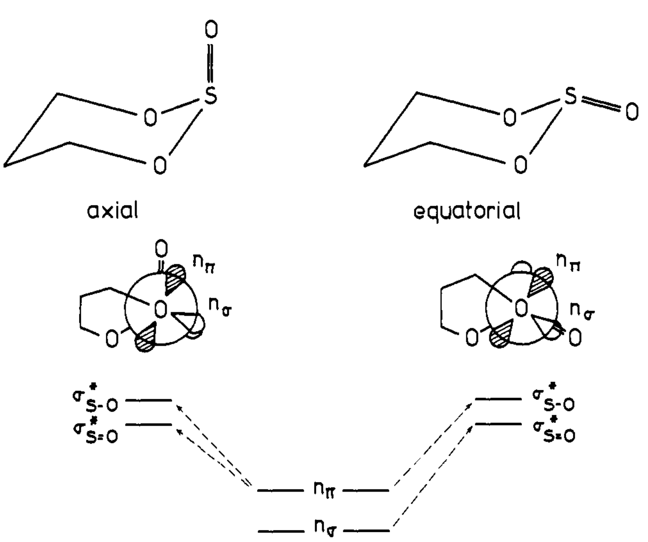

Figure 4. Main stabilizing orbital interactions occurring in 1,3,2-dioxathiane 2-oxides, shown by Newman projections along an S—O bond.

Table II. Bond distances and endocyclic torsion angles are given in Figure 3, valence angles in Table III. CH bond lengths average 0.97 (1) Å, while mean bond angles are CCH(phenyl) = 119.8 (6)°, CCH(other) = 109.1 (8)° and HCH = 109 (1)°. None of the bond lengths or valence angles deviates from the value normally occurring in sulfite rings. As could be expected, both phenyl rings are planar within experimental error. In contrast, however, to the chair conformation with axial S=O that was expected on the basis of the IR spectra (solution and solid state), the six-membered sulfite ring of MPDO is in an almost true boat conformation with the S=O bond in the axial direction. This can be seen from the distribution of torsion angles (Figure 3) as well as from the ORTEP picture (Figure 1).

Comparison of Geometries of 1,3,2-Dioxathiane 2-Oxides and the Anomeric Effect

Table IV gives geometrical details of 13 six-membered ring sulfites grouped according to their conformational classes. Differences in the numbering scheme of the atoms by the various authors could introduce a bias. Therefore, averages according to local C_s symmetry in the sulfite ring are presented for classes CA and CE. The experimental values had shown that within the error limits the rings have C_s symmetry regardless of the substituents. For class TB the averaging is not always permitted and the actual values are given. General mean values for the classes CA and CE are given in Table V. Such averaging for class TB does not seem justified considering the large differences between the members in the class. Part of the differences are connected to the fact that the compounds are at different positions on the pseudorotation path.

The experimental differences of the geometrical parameters in CA and CE can be reproduced qualitatively by theoretical calculations. The chair conformations with axial and equatorial S=O were simulated by optimizing the geometry of two conformations of H_2SO_3 in which the torsion angle τ (S—O) was fixed at the experimental value found in the cyclic sulfites, but all other parameters were allowed to relax freely. The ab initio gradient method of Pulay[11,12] and Pulay's program TEXAS[13] were used. A 3-3-21G basis set[14] with polarization functions was chosen for sulfur and a 3-21G set[15] for oxygen and hydrogen. The results are also given in Table V.

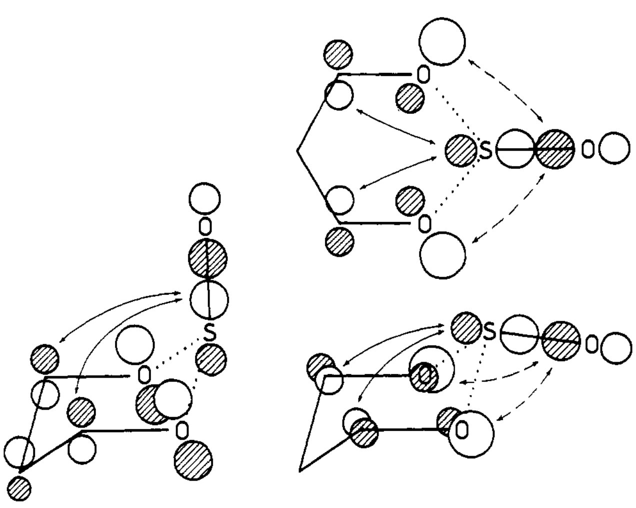

Figure 5. Orientation of interacting orbitals in 1,3,2-dioxathiane 2-oxides in class CA (left) and CE (right) viewed from the side (middle) and from above (top). Secondary negative, antibonding overlap between n_π(O) and σ^*(S=O) in CA and n_σ(O)–σ^*(S=O) in CE is indicated by solid arrows. Another antibonding, secondary overlap between n_σ(O) and σ^*(S=O) in CE is indicated by broken arrows.

Main interactions occurring in cyclic sulfites are shown in Figure 4. The concept of CMO's leading to a π- and a σ-type lone pair on each ring oxygen atom is used. The n_π(O) orbital is energetical higher than the n_σ(O) orbital. As a result the two-electron stabilization from interactions between n_π(O) and an adjacent antibonding orbital σ^*(S=O) and σ^*(S—O) will be larger than the stabilization from interaction between n_σ(O) and an adjacent antibonding orbital. This explains why six-membered ring sulfites with axial S=O are more stable than those with equatorial S=O.

Torsion angles are certainly the most sensitive parameters to visualize differences between the classes. In CA the most important interaction is n_π(O)–σ^*(S=O); the overlap in these interactions increases when the torsion angle τ(S—O) decreases. One sees from Figure 4 that in CE the stabilization is caused for an important part by the n_π(O)–σ^*(S—O) interactions, which increase with increasing torsion angle τ(S—O). As a result in class CA one finds τ(S—O) $< 60°$, whereas the class CE one finds τ(S—O) $> 60°$.

Valence angles are the next parameter sensitive to a different orientation of the S = O bond. First, we note that the valence angles around S are significantly smaller than expected for a normal sp^3 configuration. Two possible explanations can be given. The presence of an electron-rich S=O and a rather large lone pair on S could cause a decrease of valence angles around S. In contrast to this explanation based on sterical considerations (VSEPR—theory of Gillespie[16]), another explanation based on maximization of attractive forces can be given. From the Newman projections in Figure 4 and the orientation of the interacting orbitals in Figure 5 it can be deduced that the primary overlap (i.e., overlap between orbitals on bonded atoms;[17] here n_π(O)–σ^*(S=O) in CA and n_σ(O)–σ^*(S=O) in CE) increases when the torsion angle τ(S—O) is adapted, but also when the valence angles O=S—O and O—S—O are decreased. Second, we observe that the valence angles O=S—O and S—O—C in class CA are larger than those in class CE. This can partly be explained by the fact that the variations of torsion angles and valence angles in six-membered rings are coupled. The larger SOC angle can, therefore, be connected to the flattening of the ring in class CA. The variation of the exocyclic O=S—O angle, however, is *not* coupled to the overall geometry of the ring and can, thus, not be explained from variations in torsion angles. It can be explained from the interactions presented in Figure 5. In addition to the bonding primary overlap (n_σ(O) – σ^*(S=O) in CE and n_π(O)–σ^*(S=O) in CA), there exists a negative, antibonding overlap between the σ^*(S=O) orbitals on sulfur and the tailing orbitals of the n_π(O)

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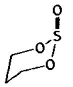
Table IV. Comparison of 1,3,2-Dioxathiane 2-Oxide Geometries Grouped According to Their Conformations[a]

	class CA								class CE				class TB		
	DCDO	DOTO	ADTA	HFS_1	$MNDO_1$	$PMDO_a$	$PMDO_b$	TBDO	DMDO	TMDO	$MNDO_{2a}$	$MNDO_{2b}$	HFS_2	CBDO	MPDO
S2=O	1.442	1.45	1.434	1.448	1.456	1.452	1.447	1.443	1.440	1.446	1.436	1.443	1.476	1.439	1.446
S2—O1	1.623	1.60	1.623	1.622	1.617	1.599	1.600	1.603	1.603	1.610	1.625	1.630	1.598	1.605	1.614
S2—O3													1.626	1.616	1.592
O1—C6	1.462	1.46	1.493	1.486	1.458	1.487	1.488	1.470	1.482	1.484	1.462	1.453	1.521	1.467	1.479
O3—C4													1.464	1.479	1.487
C4—C5	1.523	1.52	1.526	1.520	1.515	1.547	1.548	1.512	1.513	1.514	1.519	1.514	1.525	1.551	1.535
C6—C5													1.515	1.524	1.532
O1—S2—O3	97.8	100	99.1	101.2	98.7	99.9	99.9	99.4	99.1	98.9	97.4	97.5	99.6	97.5	99.7
S2—O3—C4	116.2	116	115.0	118.2	115.5	122.7	122.7	116.0	113.2	113.9	111.4	112.6	120.6	115.6	120.1
S2—O1—C6													118.5	116.5	122.5
C4—C5—C6	110.6	110	107.1	111.4	110.7	117.2	116.9	109.0	113.9	115.6	110.4	109.6	111.1	111.2	117.0
O3—C4—C5	108.7	109	109.5	109.2	110.5	108.7	107.8	110.0	109.1	108.0	110.5	111.3	108.7	106.8	109.7
O1—C6—C5													112.6	106.2	109.4
O1—S2=O	107.8	107	107.6	107.6	106.8	109.1	109.0	107.8	104.7	103.6	103.8	103.4	107.3	109.8	109.1
O3—S2=O													108.0	102.2	107.8
τ(O1—S2)	57.8	56.0	56.2	48.7	57.8	49.9	49.8	55.7	63.3	63.1	65.2	62.5	60.0	−30.2	−41.5
τ(O3—S2)													−26.9	−42.6	58.3
τ(O3—C4)	62.8	61.6	64.2	57.3	61.4	51.9	53.0	62.1	61.4	61.0	64.6	64.1	−28.8	70.5	−22.9
τ(O1—C6)													−30.0	75.5	−6.8
τ(C4—C5)	58.3	60.4	62.0	58.8	55.4	46.7	49.4	58.8	53.4	53.8	55.0	55.3	65.1	−20.5	−37.3
τ(C6—C5)													−34.1	−43.7	51.7
Q	0.615	0.606	0.635	0.566	0.599	0.488	0.506	0.602	0.627	0.626	0.661	0.639	0.750	0.818	0.711
θ	2.7	4.5	3.4	11.7	4.9	3.2	0.8	0.7	10.2	10.4	11.9	9.4	90.2	91.5	94.9
ϕ													24.9	98.9	13.9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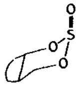
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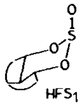
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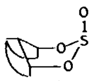
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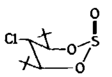
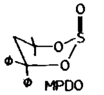
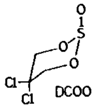


CBDO



MPDO



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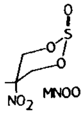
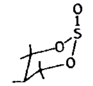
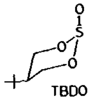
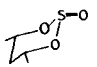
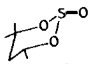


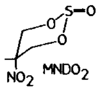
$MNOO_1$


PMDO


TBDO


DMDO


TMOO



$MNDO_2$

[a] Abbreviations used are: DCDO, 5,5′-dichloro-1,3,2-dioxathiane 2-oxide: J. W. L. Van Oyen, R. C. D. E. Hasekamp, G. C. Verschoor, and C. Romers, *Acta Crystallogr., Sect. B*, **24**, 1471 (1968). DOTO, 1,3,2-dioxathiane 2-oxide: C. Altona, H. J. Geise, and C. Romers, *Recl. Trav. Chim. Pays-Bas*, **85**, 1197 (1966). ADTA, 17β-acetoxy-2,4-dioxa-3-thia-5α-androstan-3-one: W. L. Duax, J. F. Griffin, and E. Wolff, *Cryst. Struct. Commun.* **5**, 279 (1976). HFS_1, dihydrofukinolidol sulfite, isomer **I**; A. Furusaki and T. Watanabe, *Bull. Chem. Soc. Jpn.* **45**, 2288 (1972). $MNDO_1$, *cis*-5-methyl-*trans*-5′-nitro-1,3,2-dioxathian 2-oxide: G. H. Petit, A. T. H. Lenstra, H. J. Geise, and P. Swepston, *Cryst. Struct. Commun.* **9**, 187 (1980). PMDO, *cis*-4,4,5,6,6-pentamethyl-1,3,2-dioxathiane 2-oxide, two crystallographically independent molecules (a and b): G. H. Petit, A. T. H. Lenstra, and H. J. Geise, *ibid.*, **11**, 867 (1982). TBDO, *cis*-5-*tert*-butyl-1,3,2-dioxathiane 2-oxide: P. Van Nuffel, G. H. Petit, H. J. Geise, and A. T. H. Lenstra, *Acta Crystallogr., Sect. B*, **36**, 1220 (1980). DMDO, *cis,cis*-4,6-dimethyl-1,3,2-dioxathian 2-oxide: G. H. Petit, A. T. H. Lenstra, and H. J. Geise, *Bull. Soc. Chim. Belg.*, **87**, 659 (1978). TMDO, *cis*-4,6,6-trimethyl-1,3,2-dioxathiane 2-oxide: G. H. Petit, A. T. H. Lenstra, and H. J. Geise, *ibid.*, **90**, 23 (1981). $MNDO_2$, *trans*-5-methyl-*cis*-5′-nitro-1,3,2-dioxathiane 2-oxide, two crystallographically independent molecules (a and b): G. H. Petit, A. T. H. Lenstra and H. J. Geise, *Cryst. Struct. Commun.*, **11**, 873 (1982). HFS_2, dihydrofukinolidol, isomer **II**: A. Furusaki and T. Watanabe, *Bull. Chem. Soc. Jpn*, **45**, 2288 (1972). CBDO, *trans*-5-chloro-*cis,trans*-4,6-di-*tert*-butyl-1,3,2-dioxathiane 2-oxide: A. C. Carbonelle, Y. Jeannin, and F. Robert, *Acta Crystallogr., Sect. B*, **34**, 1631 (1978). MPDO, 4,4-dimethyl-6,6-diphenyl-1,3,2-dioxathiane 2-oxide: this work.

Table V. Differences between Geometrical Parameters in Different Classes, Determined Experimentally in Six-Membered-Ring Sulfites and Simulated Theoretically in H_2SO_3

theoretical			experimental		
parameter	CA	CE	parameter	CA	CE
S=O	1.433	1.422	S=O	1.447	1.441
S—O	1.602	1.607	S—O	1.611	1.617
O—H	0.982	0.977	O—C	1.475	1.470
			C—C	1.526	1.515
O—S—O	98.2	98.2	O—S—O	99.5	98.2
S—O—H	119.1	118.5	S—O—C	117.8	112.8
			O—C—C	109.2	109.7
			C—C—C	111.6	112.4
O—S=O			O—S=O	107.8	103.9
τ(O—S)	54.0[a]	63.5[a]	τ(O—S)	54.0	63.5
			τ(O—C)	59.3	62.8
			τ(C—C)	56.2	54.4
$-E$ (hartree)	620.1107321	620.0917600			
ΔE (kcal/mol)	0.000	11.905			

[a] Not optimalized; the mean experimental value was used for this torsion angle.

CMO on the C atoms in the 4 and 6 position of the ring. This secondary overlap decreases when in class CA the O—S=O and S—O—C angles increase and when in class CE the S—O—C angles increase. Another, negative secondary overlap occurs in the n_σ(O)-σ^*(S=O) interaction in CE, between the orbitals of the endocyclic O atoms and those of the exocyclic S=O bond (Figure 5, broken arrows). This unfavorable overlap also decreases by increasing the O—S=O angle. Effects are expected to be larger in CA because n_π(O) -σ^*(S=O) is more important than n_σ(O) σ^*(S=O) in CE, the net result being that O=S—O (CA) > O=S—O (CE) and S—O—C (CA) > S—O—C (CE).

The O—S—O angle shows no significant difference between the classes. This is not surprising since the same $n_\pi - \sigma^*$(S—O) interaction is the dominant factor in both cases. The valence angles in the remaining OCCCO part of the ring are not directly influenced by the anomeric effect and therefore one does not expect variations in OCC and CCC angles among the classes. Indeed no systematic trends are observed in the OCC angles. The differences in individual CCC angles are probably due to effects of substituents. Systematic differences in bond lengths that discriminate between the classes are much more difficult to detect. Bonded distances are the most rigid parameters in a molecule; thus the effect of anomeric delocalization on bond lengths can be expected to be much smaller than on angles[18] and can easily be camouflaged by experimental uncertainties. One notes, however, that the small experimental differences are qualitatively reproduced by the theoretical calculations. The anomeric effect causes electrons from the n_π or n_σ oxygen lone pairs to flow into the antibonding σ^*(S=O) orbital, causing a lengthening of the S=O bond. Also other bond distances are influenced by the existence of n-σ^*(S=O) interactions. From Figure 5 one notes an increase of stabilizing primary overlap when shortening the S-O bonds. The unfavorable secondary overlap between S and the endocyclic C atoms in the 4 and 6 position decreases by enlarging the C-O bonds. Since stabilization by two-electron interactions is more important in class CA, one expects all bond effects cited to be more pronounced in CA. Although the differences between the bond lengths of the classes are small, they are all in the expected direction. One notes also that the CO bonds in 1,3,2-dioxathiane 2-oxides are significantly longer (1.473 ± 0.020 Å) than normally found in ethers and alcohols (1.43–1.44 Å). Similar elongations have also been observed in other anomeric systems, e.g., acetals,[18,19] phosphates,[20] and thiophosphates.[21]

Other meaningful observables in the comparison of ring geometries are the Cremer and Pople parameters,[22,23] viz., the ring-type parameter θ, the pseudorotation parameter ϕ, and the puckering parameter Q. Differences in valence and torsion angles between CA and CE also reflect themselves in the puckering parameter Q, which is larger in CE than in CA. Ring-type parameters θ are much larger in CE than in CA. Although an ideal 1,3,2-dioxathiane chair might not have $\theta = 0°$ or $\theta = 180°$,[24] it seems safe to say that CE forms deviate more from a perfect chair than CA forms. This deviation cannot be explained by the occurrence of substituents only. The most substituted compound (PMDO) in CA shows a small θ, and of the two compounds with identical substituents ($MNDO_1$ and $MNDO_2$) only the one with equatorial S=O has a large θ. Possibly the occurrence of an anomeric unfavorable equatorial S=O is attended with a deviation from the ideal chair form. The pseudorotation parameter ϕ is only meaningful in class TB, where it can be used to further subdivide class TB. The variation of forms met along the pseudorotation path as a function of ϕ is depicted in Figure 6. We see that the subdivision can be made into:

TBa: forms in the ϕ range 330-0-30° with an almost axial orientation of the S=O bond and maximum anomeric stabilization

TBe: forms in the ϕ range 150–180-210° with an almost equatorial orientation of the S=O bond and minimum anomeric stabilization

TBt: forms in the ϕ ranges 30-150° and 210-330° in which at best only one oxygen atom is in a position to give some anomeric stabilization
A description of S=O being axially or equatorially oriented is not meaningful

In conclusion, the conformation of 1,3,2-dioxathiane 2-oxides is primarily determined by the anomeric n_π(O) − σ^*(S=O) interaction. Spatial requirements of the orbitals are such that, in the absence of other effects, the chair form with axial S=O (class CA) is the most stable conformer. An increase in steric hindrance, such as in *cis,cis*-4,6-dimethyl-1,3,2-dioxanthiane 2-oixde causes a change to the chair form with equatorial S=O (class CE). If such a transition does not produce relief in steric strain, as for example in the present compound 4,4-dimethyl-6,6-diphenyl-1,3,2-dioxathiane 2-oxide, a (twist)-boat form occurs. The exact shape of the latter will be dictated by the properties of the substituents present at C(4), C(5), and C(6), but even then the anomeric effect drives the conformation toward a TBa conformation.

Validity of Conformational Criteria Based On Position of the S=O Stretching Frequency

The delocalization of oxygen lone pair electrons into the antibonding orbital of the S=O bond weakens the latter bond and

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[18] G. A. Jeffrey, J. A. Pople, J. S. Binkley, and S. Vishveshwara, *J. Am. Chem. Soc.*, **100**, 373 (1978).

[19] W. Van de Mieroop and A. T. H. Lenstra, *Cryst. Struct. Commun.*, 7, 577 (1978).

[20] P. Van Nuffel, A. T. H. Lenstra, and H. J. Geise, *Bull. Soc. Chim. Belg.*, **91**, 43 (1982).

[21] P. Van Nuffel, A. T. H. Lenstra, C. Van Alsenoy, H. J. Geise, and G. R. Van den Berg, *Acta Crystallogr., Sect. C*, **40**, 1263 (1984).

[22] J. Cremer and J. A. Pople, *J. Am. Chem. Soc.*, **97**, 1354 (1975).

[23] J. Cremer, *QCPE*, **11**, 288 (1975).

[24] G. H. Petit, J. Dillen, and H. J. Geise, *Acta Crystallogr., Sect. B*, **39**, 648 (1983).

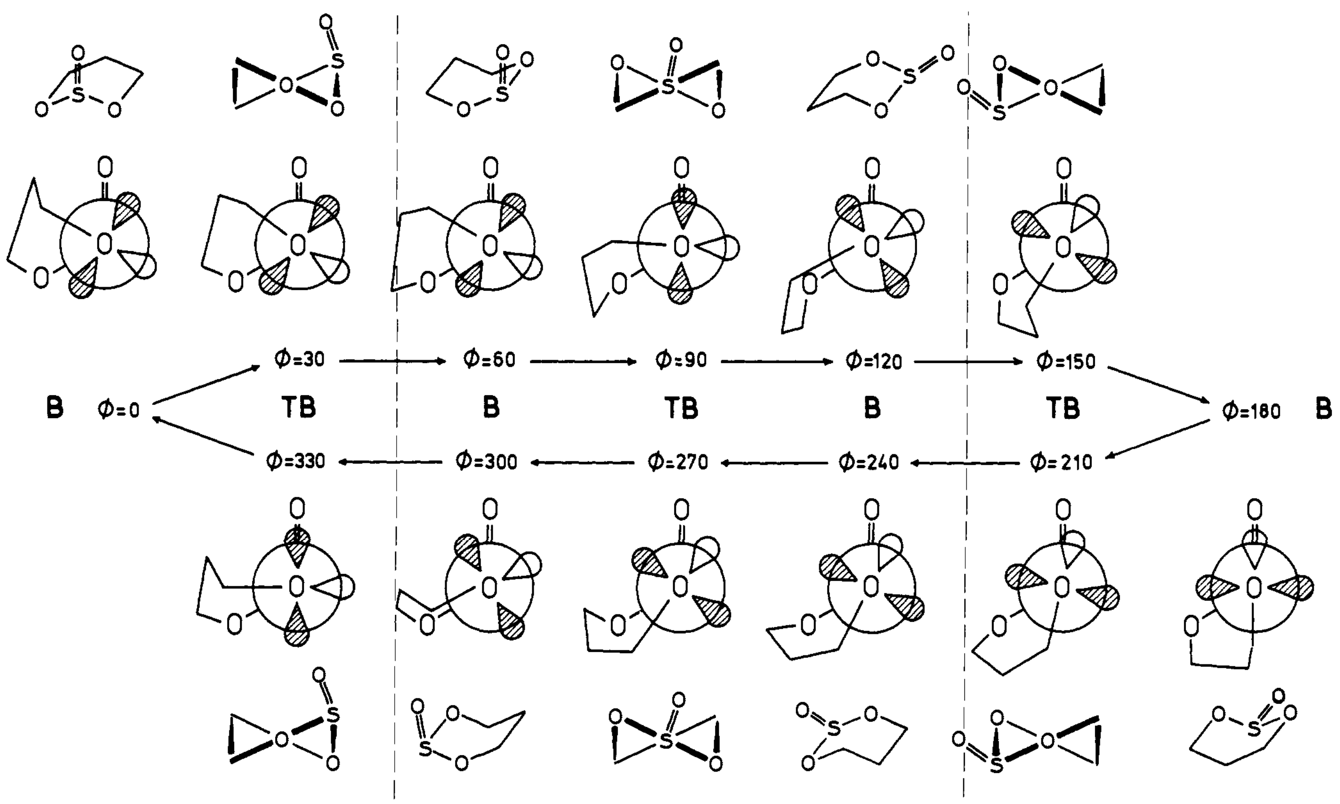

Figure 6. The boat-like forms of 1,3,2-dioxathiane 2-oxides met along the pseudorotation path in function of ϕ. Newman projections along O(3)-S(2) show inter alia the variation of the torsion angle C(4)-O(3)-S(2)-O(1). The Newman projection along S(1)-O(1) at a particular value of ϕ is equal to the one S(2)-O(3) at 360 - ϕ.

Table VI.[a] Relation between the Torsion Angle C—O—S=O and the S=O Stretching Frequency[2,4]

compd	class	τ(C—O—S=O)	ν(S=O), cm^{-1} [b]	
			CCl_4	CH_3CN
DCDO	CA	53.4	1208	1204.5 (1.25) 1192 (0.3)
DOTO	CA	55.7	1194	1186
TBDO	CA	56.6	1195.5 (1.8) 1186.5 (0.5)	1192.5 (1.0) 1184 (1.0)
PMDO	CA	64.4	1200	1192
DMDO	CE	171.2	1245.5 (1.55) 1230 (0.25)	1224.5
TMDO	CE	169.4	1234	1227
MPDO	TBa	54.4/72.3	1196	1190
CBDO	TBt	75.8/154.9	1229.5	1219

[a] See Table IV for abbreviations. [b] Relative intensities (if known) are given in parentheses.

decreases its stretching force constant. In class CA the delocalization is at a maximum and therefore ν(S=O) should be and is at its minimum (1180–1200 cm^{-1}). Reversed, ν(S=O) reaches its maximal value (1230–1245 cm^{-1}) in class CE, corresponding to a minimal anomeric effect.

The position of the S=O bond in the IR spectrum is a direct probe for the amount of anomeric delocalization. Figures 4 and 6 show that maximum overlap n_π(O)- σ^*(S=O) occurs when the torsion angle C—O—S=O approaches 90°. Of course, this value is not likely to be met in an actual structure because of the large ring strain involved. In Table VI we test whether there exists a correlation between C—O—S=O torsion angles observed in the solid state and ν(S=O) frequencies in solution. Although medium effects undoubtedly play an important role, it follows that ν(S=O) $\approx$ 1190 cm^{-1} corresponds to τ(C—O—S=O) $\approx$ 60° and ν(S=O) $\approx$ 1235 cm^{-1} corresponds to τ(C—O—S=O) $\approx$ 170°. The immediate consequence is that the ν(S=O) frequency of class TBa molecules must be very near the ν(S=O) of class CA molecules, rendering it impossible to discriminate between these two classes using the IR criterion. This explains why the IR criterion erroneously put MPDO in class CA, whereas it belongs to class TBa. In the case of HFS_1 and HFS_2 the spectra[25] were so close that no distinction could be based on the IR criterion. Again, HFS_1 and HFS_2 belong to class CA and TBa, respectively. So far no molecules belonging to class TBe have been found, but the position of their ν(S=O) band should be very close to the one of class CE (1230–1245 cm^{-1}). Only molecules belonging to class TBt can have ν(S—O) stretching bands distinguishable from those of classes CA and CE at an intermediate value of ν. The narrow limits observed (ν = 1215 ± 5 cm^{-1}) correspond thus with certain narrow portions of the pseudorotation pathway.

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Registry No. MPDO, 92241-57-1.

Supplementary Material Available: Table of positional and thermal parameters of 4,4-dimethyl-6,6-diphenyl-1,3,2-dioxathiane 2-oxide (2 pages). Ordering information is given on any current masthead page.

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