The Crystal Structure of Some 2-Oxo-1,3,2-dioxathiolanes

Gordon Lowe,*[a] Salvatore J. Salamone,[a] and Richard H. Jones[b]

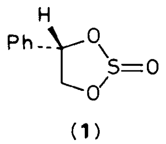
[a] *The Dyson Perrins Laboratory, Oxford University, South Parks Road, Oxford OX1 3QY, U.K.*
[b] *Chemical Crystallography Laboratory, Oxford University, 9 Parks Road, Oxford OX1 3PD, U.K.*

The *trans* diastereoisomers of 2-oxo-4(*S*)-phenyl-1,3,2-dioxathiolane and *meso*-2-oxo-4,5-diphenyl-1,3,2-dioxathiolane have been unambiguously identified by *X*-ray analysis; both adopt the half-chair conformation and differential endocyclic S–O bond lengths provide evidence for a stereoelectronic interaction with the S=O group.

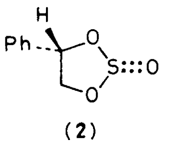
Because of the pyramidal nature of tri-co-ordinate sulphur in sulphite diesters, 2-oxo-4-phenyl-1,3,2-dioxathiolane exists as two diastereoisomers which have been prepared in their racemic form.[1] Our interest in the chiral diastereoisomers (**1**) and (**2**) arose from the possible use of this molecular framework for the synthesis of chiral [^{16}O,^{17}O,^{18}O] sulphate monoesters.[2]

2(*S*)-Phenylethane-1,2-diol (**3**) was prepared by reduction of (*S*)-mandelic acid with lithium aluminium hydride.[3] Treatment of the diol (**3**) with thionyl chloride gave a mixture of *trans*- and *cis*-2-oxo-4(*S*)-phenyl-1,3,2-dioxathiolane [(**1**) and (**2**) respectively; ratio 3:2] which were separated by flash chromatography.[4] Although the structure of the products could be assigned from their ^1H n.m.r. spectra† using the known electric field effect and diamagnetic anisotropy of the S=O group,[5,6] it was imperative for our subsequent studies that the configuration at sulphur was unambiguous. For this reason the *X*-ray structural analysis of the major diastereoisomer was undertaken. The conformation of the 2-oxo-1,3,2-dioxathiolane ring was also of interest since electron diffraction studies have led to conflicting conclusions, one suggesting that it is practically planar,[7] while the other that it adopts the half-chair conformation.[8] I.r. studies led to the conclusion that it exists in solution as an equilibrating pair of envelope conformations,[9] while from variable temperature ^1H n.m.r. studies the conclusion was drawn that the ring has an essentially fixed conformation with the S=O bond in the pseudo-axial conformation.[10] From subsequent ^1H and ^{13}C n.m.r. studies it was considered that the ring adopts the half-chair conformation.[11,12] Surprisingly, no *X*-ray analysis has been reported of an unfused 2-oxo-1,3,2-dioxathiolane.

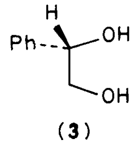
The major diastereoisomer of 2-oxo-4(*S*)-phenyl-1,3,2-dioxathiolane crystallised from ether–hexane, m.p. 73 °C, and its structure was determined by *X*-ray crystallography.



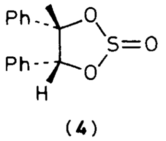
(**1**)



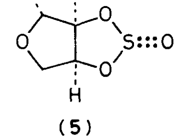
(**2**)



(**3**)



(**4**)



(**5**)

Crystal data: $C_8H_8O_3S$, M = 184.2, orthorhombic, space group $P2_12_12_1$, $a = 5.785(2)$, $b = 8.158(1)$, $c = 17.933(2)$ Å, U = 846 Å^3, Z = 4, D_c = 1.45 g cm^{-3}. Intensities of 1028 independent reflections ($4 < 2\theta < 150°$) were measured on a (CAD-4) diffractometer using graphite monochromated Cu-K_α radiation (λ = 1.5418 Å). The structure was solved by direct methods (MULTAN 80).[13] 826 Reflections [$I > 3\sigma(I)$] uncorrected for absorption [μ(Cu-K_α) = 30.2 cm^{-1}] were used in a full matrix least squares refinement, 'soft' constraints being applied to the C–H bonds.[14] The final R value is 0.059 (R_w = 0.068).‡

The *X*-ray structure (Figure 1) confirms the expectation based on the ^1H n.m.r. data that the major product is the *trans*-diastereoisomer (**1**). It further shows that the half-chair conformation is adopted with the S=O group and the phenyl group in pseudo-axial and pseudo-equatorial positions respectively. Although the envelope conformation of a 2-oxo-1,3,2-dioxathiolane (with sulphur as the flap) would allow lone electron pairs on both endocyclic oxygens to interact with the S=O group, this stereoelectronic stabilisation would be offset by the eclipsing of substituents at C(4) and C(5). The half-chair conformation not only releases these non-bonded interactions but also allows torsion in the O–C–C–O moiety to approach the gauche conformation which is known to be favoured in acyclic systems of the type $XCH_2{\cdot}CH_2X$ where X

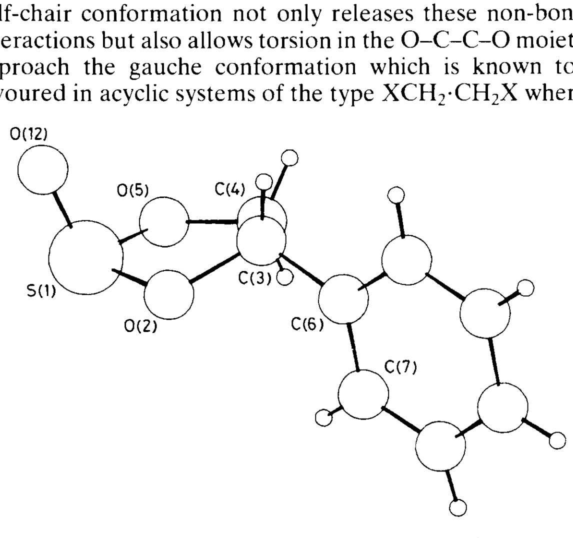


Figure 1. Crystal structure of *trans*-2-oxo-4(*S*)-phenyl-1,3,2-dioxathiolane (**1**). Selected bond lengths and angles are: S(1)–O(2) 1.600(3), O(2)–C(3) 1.472(5), C(3)–C(4) 1.510(7), C(4)–O(5) 1.406(7), S(1)–O(5) 1.634(5), S(1)–O(12) 1.431(4) Å; O(2)–S(1)–O(5) 93.6(2), O(1)–S(1)–O(12) 109.8(3), O(5)–S(1)–O(12) 105.5(3), S(1)–O(2)–C(3) 111.2(3), O(2)–C(3)–C(4) 103.2(4), O(2)–C(3)–C(6) 109.0(4), C(3)–C(4)–O(5) 107.8(5), C(4)--O(5)–S(1) 113.8(3)°.

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† The *trans*-isomer (**1**) as verified by *X*-ray analysis had m.p. 73 °C, $[\alpha]^{20}_D$ + 12.75° (1% $CHCl_3$), δ_H ($CDCl_3$) 7.53—7.35 (m, 5H, ph), 5.94 (br. t, 1H, *J ca.* 7 Hz, 4–H), 4.95 (dd, 1H, *J* 6.8, 8.4 Hz, 5–H_S), 4.21 (dd, 1H, *J* 7.5, 8.3 Hz, 5–H_R); ν_{max} (CCl_4) 1222 cm^{-1} (s). The *cis*-isomer (**2**) had m.p. 28—30 °C, $[\alpha]_D$ − 51.80° (1% $CHCl_3$), δ_H ($CDCl_3$) 7.61—7.36 (m, 5H, Ph), 5.42 (dd, 1H, *J* 6.6, 10.6 Hz, 4-H), 4.76 (dd, 1H, *J* 6.5, 9.2 Hz, 5–H_R), and 4.49 (dd, 1H, *J* 9.2, 10.5 Hz, 5–H_S); ν_{max} (CCl_4) 1215 cm^{-1} (s).

‡ The atomic co-ordinates are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

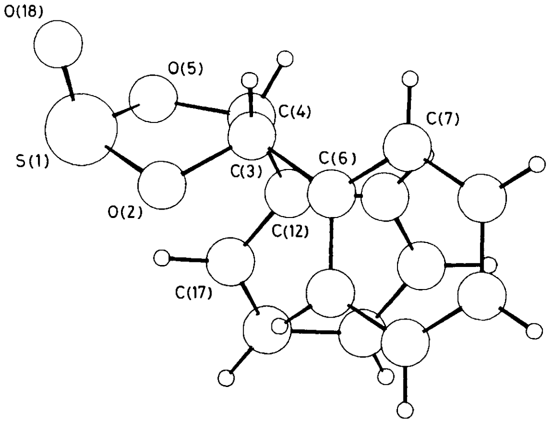

Figure 2. Crystal structure of *trans,meso*-2-oxo-4,5-diphenyl-1,3,2-dioxathiolane (**4**). Selected bond lengths and angles are: S(1)–O(2) 1.614(3), O(2)–C(3) 1.461(4), C(3)–C(4) 1.545(5), C(4)–O(5) 1.451(4), S(1)–O(5) 1.632(3), S(1)–O(18) 1.434(3) Å; O(2)–S(1)–O(5) 93.2(1), O(2)–S(1)–O(18) 109.3(2), O(5)–S(1)–O(18) 106.1(2), S(1)–O(2)–C(3) 108.6(2), O(2)–C(3)–C(4) 102.3(3), O(2)–C(3)–C(6) 110.4(3), C(3)–C(4)–O(5) 103.5(3), O(5)–C(4)–C(12) 110.7(3), C(4)–O(5)–S(1) 113.8(2)°.

are electronegative substituents.[15] It is also of interest to note that the length of the S–O(2) bond [1.600(3) Å] is considerably shorter than that of the S–O(5) bond [1.634(5) Å] providing evidence supporting the stereoelectronic interaction of the pseudo-axial lone electron pair on O(2) with the S=O group. It has recently been shown that for chemically equivalent but conformationally different C–O bonds the stereoelectronic effect results in a bond length difference of about 0.025 Å.[16]

The conformation of 2-oxo-1,3,2-dioxathianes (six-membered cyclic sulphites) have been studied by many physical methods[17] including *X*-ray crystallography[18,19] from which it is evident that the chair conformation is adopted with a strong preference for the S=O bond to take up an axial position. The endocyclic S–O bond lengths in trimethylene sulphite are 1.59 and 1.60 Å indicating that axial lone pairs on both endocyclic oxygens interact with the S=O bond, this generalised anomeric effect being the cause of the preferred axial orientation of the S=O bond.[20] These bond lengths do not differ (within experimental error) from the S–O(2) bond length in (**1**) suggesting that the pseudo-axial O(2) lone electron pair interacts favourably with the S=O group.

We were concerned, however, that the difference in bond length between the S–O(2) and S–O(5) bonds in (**1**) might in part be due to the effect of the phenyl substituent. For this reason *trans,meso*-2-oxo-4,5-diphenyl-1,3,2-dioxathiolane (**4**) was prepared,[21] and recrystallised from diethyl ether (4 times), m.p. 133 °C. Its structure was determined by *X*-ray crystallography.

Crystal data: $C_{14}H_{12}O_3S$, $M = 260.3$, monoclinic, space group $P2_1/c$, $a = 12.769(1)$, $b = 5.984(2)$, $c = 16.578(2)$ Å, $\beta = 101.60(1)°$, $U = 1241$ Å^3, $Z = 4$, $D_c = 1.39$ g cm^{-3}. Intensities of 2982 independent reflections ($4 \leqslant 2\theta \leqslant 150°$) were measured on a (CAD-4) diffractometer using graphite monochromated Cu-K_α radiation ($\lambda = 1.5418$ Å). The structure was solved by Patterson and Fourier techniques. 1654 Reflections [$I \geqslant 3\sigma(I)$] uncorrected for absorption [μ(Cu-K_α) = 22.4 cm^{-1}] were used in a full matrix least squares refinement, 'soft' constraints being applied to the C–H bonds.[14] The final R value is 0.060 ($R_w = 0.081$).‡

The *X*-ray structure (Figure 2) shows that *trans,meso*-2-oxo-4,5-diphenyl-1,3,2-dioxathiolane (**4**) also adopts the half-chair conformation. Not surprisingly the O–C–C–O dihedral angle of 35° is greater than in (**1**) (25°) since the interaction between the phenyl substituents would increase this angle. The same trend in the endocyclic S–O bond lengths is observed, although less marked; S–O(2) is 1.614(3) Å whereas S–O(5) is 1.632(3) Å, O(2) having the pseudo-axial lone pair approximately antiperiplanar to the S=O bond.

Of the two *X*-ray structural analyses of 2-oxo-1,3,2-dioxathiolanes previously reported (with R values of 18[22] and 3.6%[23]) only one, namely 2,5-anhydro-1-chloro-1-deoxy-L-ribitol 3,4-cyclic sulphite (**5**) was sufficiently refined to allow accurate bond lengths and angles to be measured.[23] The O–C–C–O dihedral angle in (**5**) (14.6°) is smaller than in (**1**) and (**4**) owing to ring fusion and the 2-oxo-1,3,2-dioxathiolane ring consequently adopts a slightly twisted envelope conformation. The endocyclic S–O bond lengths are 1.608(3) and 1.618(3) Å suggesting that the pseudo-axial lone electron pairs on both endocyclic oxygens interact with the S=O group, but because of the asymmetric substitution of the ring the stereoelectronic effect will not be the only factor affecting the bond lengths. The greater S=O bond length in (**5**) [1.445(4) Å] compared with (**1**) [1.431(4) Å] and (**4**) [1.434(3) Å] is consistent with the pseudo-axial lone electron pair of both endocyclic oxygen atoms interacting with the S=O group in this molecule.

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