Chemistry of the S=O Bond. Part 11.† *trans,trans*-4,6-Di-t-butyl-*trans*-5-methyl-1,3,2-dioxathiane 2-Oxide and *cis,cis*-4,6-Di-t-butyl-*cis*-5-methyl-1,3,2-dioxathiane 2-Oxide, Synthesis and Crystal Structure Determination

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Reduction by $LiAlH_4$ of 2,2,4,6,6-pentamethylheptane-3,5-dione gives a mixture of diastereoisomeric diols, which upon cyclisation with thionyl chloride yields a mixture of isomeric 4,6-di-t-butyl-5-methyl-1,3,2-dioxathiane 2-oxide. From the distribution of the latter mixture, a small, but distinct stereoselectivity of the dione reduction is inferred, which in turn suggests a preference of the reacting dione for an extended conformation.

Single crystal X-ray determinations have been performed on the two title compounds (components of the cyclic sulphite mixture) to establish their structure, conformation and geometry. The geometries are compared with currently available population averages of cyclic sulphites. The high substitution present in the title compounds does not show in the C–O–S(O)–O–C region of the ring, but reveals itself markedly in the C(4)–C(6) region and in the substituents.

The title compounds were studied because their synthesis can serve as an indirect probe of the stereoselectivity of the $LiAlH_4$ reduction of 2,2,4,6,6-pentamethylheptane-3,5-dione, and their structure can serve as a direct probe of the influence of steric crowding upon the geometry of a 1,3,2-dioxathiane 2-oxide ring. The prochiral dione may be reduced, at least in principle, to four diastereomeric diols. Figure 1 shows each of these diols in the conformation, which is best suited to give a cyclic ester, together with the 1,3,2-dioxathiane 2-oxides which could be produced upon reaction with thionyl chloride. One notes that each cyclisation may give rise to two different compounds: one with the pyramidal S=O group pointing upwards (axial in Figure 1) and one with the S=O group pointing downwards (equatorial in Figure 1). Finally, each of the six different compounds may exist as an equilibrium mixture of conformations, as exemplified by the *trans*, *cis*-4,6-di-t-butyl-5-*trans*-methyl derivative (Figure 1, bottom). The strong preference of a t-butyl group for the equatorial position, however, allows us to predict the preferred conformation with confidence; the results are presented in Table 1. A knowledge of all possible compounds and their conformations should suggest the stereoselectivity of the $LiAlH_4$ mediated dione reduction from the distribution of the 1,3,2-dioxathiane 2-oxide derivatives formed.

Single crystals of the two title compounds could be grown, permitting their *X*-ray structure determination. Since the geometry of the unperturbed 1,3,2-dioxathiane 2-oxide ring is reasonably well known,[1] a direct comparison with the geometry of the title compounds should reveal the effects of steric crowding.

Table 1. Preferred conformation expected for the 1,3,2-dioxathiane 2-oxide derivatives.

Compound	Conformation[a]
4-*trans*, 5-*cis*, 6-*trans*	CA
4-*cis*, 5-*trans*, 6-*cis*	CE
4-*trans*, 5-*trans*, 6-*trans*	CA
4-*cis*, 5-*cis*, 6-*cis*	CE
4-*cis*, 5-*cis*, 6-*trans*	TBT
4-*trans*, 5-*trans*, 6-*cis*	TBT

[a] CA: chair form with axial S=O; CE: chair form with equatorial S=O; TBA: boat form with S in bow sprit position and pseudo-axial S=O; TBE: boat form with S in bow sprit position and pseudo-equatorial S=O; TBT: any other (twist) boat form.

Synthesis and Distribution of the Isomers of the 4,6-*Di-t-butyl-*5-*methyl-*1,3,2-*dioxathiane* 2-*Oxides*.—The isomeric mixture was prepared in a three-stage synthesis involving the preparation of 2,2,4,6,6-pentamethylheptane-3,5-dione and its subsequent reduction to 2,2,4,6,6-pentamethylheptane-3,5-diol, followed by cyclisation with thionyl chloride.

The diketone (10 g, 0.05 mol) was prepared from 2,2,6,6-tetramethylheptane-3,5-dione (Aldrich) according to the procedure of Elguero, Gonzalez, and Jacquier[2] and was reduced with lithium aluminium hydride (1 g, 0.26 mol) in diethyl ether at 0 °C to give the diol (9.5 g, 0.047 mol; 95%). Following the standard procedure,[3] the diol (7.5 g, 0.037 mol) and pyridine (7.5 cm^3, 0.095 mol), dissolved in benzene (200 cm^3), were reacted with thionyl chloride (3.0 cm^3, 0.04 mol) to yield the crude sulphite (6.6 g, 0.026 mol; 72%). The crude sulphite was purified by h.p.l.c. using a semi-preparative column packed with Nucleosil 50–55 μm. The mobile phase of 4% ethyl acetate–96% light petroleum (60–80 °C) separated three products with retention times in the range 5–12 min, eluted at a rate of 6 cm^3 min^{-1}. The products were labelled as isomers A, B, and C (50:15:35%) in order of elution. In each case their purity was greater than 96% by h.p.l.c. (Found: C, 58.1; H, 9.8; S, 13.0. $C_{12}H_{24}O_3S$ requires: C, 58.02; H, 9.74; S, 12.91%).

The i.r. spectrum of isomer B (Nujol mull) showed ν 1 198 cm^{-1} (S=O). This proves[1] that B has the CA conformation (Table 1), requiring only a distinction to be made between the 4-*trans*, 5-*trans*, 6-*trans*- and the 4-*trans*, 5-*cis*, 6-*trans* isomers. For the 5-*trans* compound, in which the three endocyclic hydrogen atoms are on one side of the ring (Figure 1), an A_2B

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† For Part 10, see ref. 7.

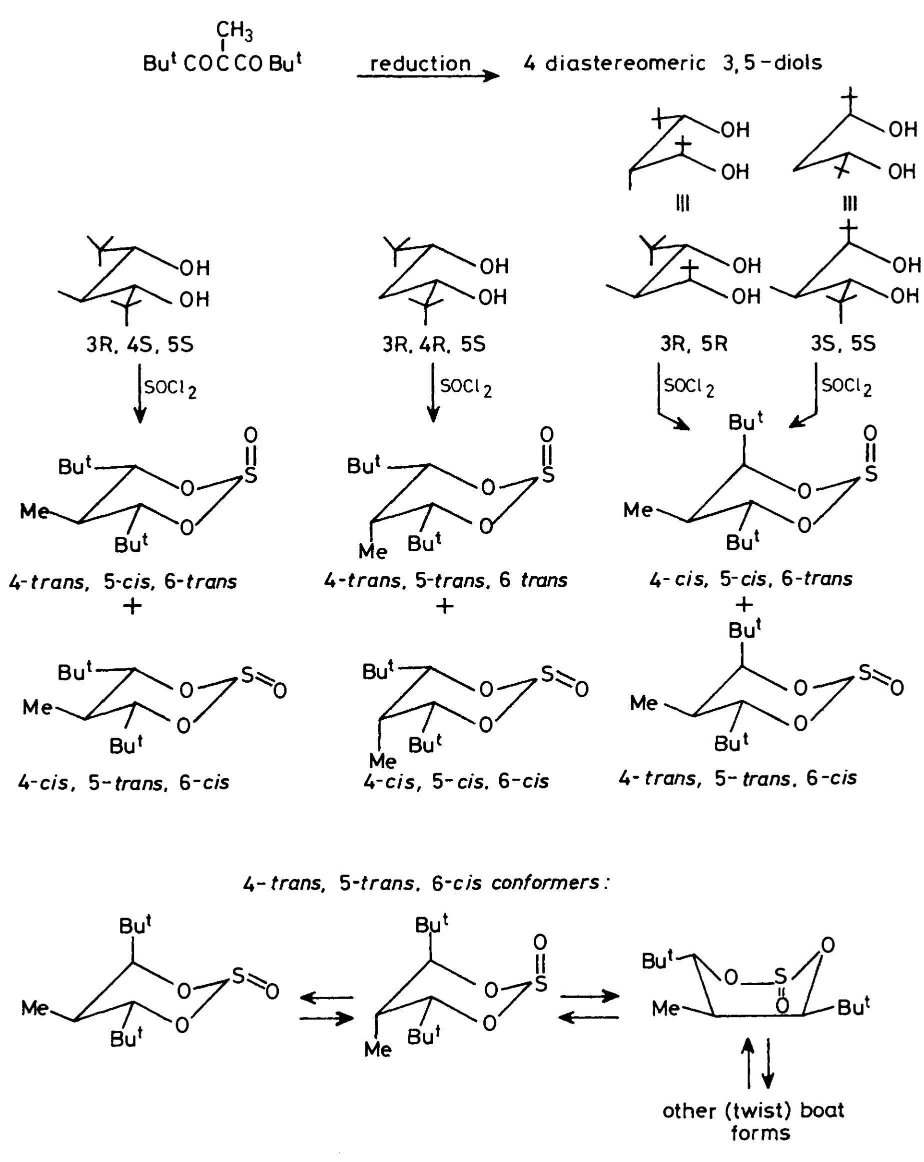

Figure 1. Stereochemical relation between stereo isomeric 2,2,4,6,6-pentamethylheptane-3,5-diols and isomeric 4,6-di-t-butyl-5-methyl-1,3,2-dioxathiane 2-oxides.

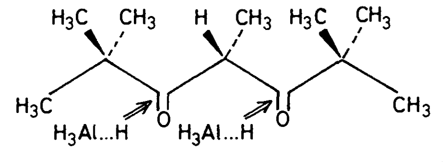

Figure 2. Suggested transition state for the $LiAlH_4$ reduction of 2,2,4,6,6-pentamethylheptane-3,5-dione.

spectrum with $J(AB) \approx 2.5$ Hz should be found, whereas for the 5-*cis* compound, in which the H(5) atom is staggered with respect to the other hydrogen atoms, an A_2B spectrum with $J(AB) \approx 11.5$ Hz is expected. The spectrum of B($CDCl_3$) showed ring hydrogen atoms at δ 4.31 and 2.20 (relative to TMS) with $J(AB) = 3.23$ Hz. Similar reasoning can be applied to isomer C. The i.r. spectrum (Nujol mull) shows ν 1 230 cm^{-1} (S=O), proving that isomer C has the CE conformation. The distinction has to be made between the 4-*cis*, 5-*cis*, 6-*cis* and the 4-*cis*, 5-*trans*, 6-*cis* compounds. Now, the 5-*cis* compound has the three endocyclic hydrogen atoms on one side of the ring, whereas in the 5-*trans* compound the H(5) atom is staggered. Thus a spectrum with $J(AB) \approx 2.2$ Hz for 5-*cis* and $J(AB) \approx 11.5$ Hz for 5-*trans* is expected. The experimental spectrum of C($CDCl_3$) revealed ring hydrogen atoms at δ 3.98 and 2.01 (relative to TMS) with $J(AB) = 1.73$ Hz.

Finally, the i.r. spectrum of isomer A (neat) shows a broad band centred at 1 212 cm^{-1} (S=O), proving[1] that A has a TBT conformation (Table 1). It has been argued,[1] however, that TBT represents in fact a fairly large section of the pseudorotation path and thus a range of possible 4(H)–C–C–5(H) and 6(H)–C–C–5(H) torsion angles. Then it becomes impossible to discriminate, from $J(AB)$ coupling constants, between 4-*cis*, 5-*cis*, 6-*trans* and 4-*trans*, 5-*trans*, 6-*cis*. In conclusion we arrive at the following assignments.

Isomer B. 4,6-*trans*, *trans*-Di-t-butyl-5-*trans*-methyl-1,3,2-dioxathiane 2-oxide, m.p. 65 °C, relative abundance 15%.

Isomer C. 4,6-*cis*, *cis*-Di-t-butyl-5-*cis*-methyl-1,3,2-dioxathiane 2-oxide, m.p. 117 °C, relative abundance 35%.

Isomer A. Either a mixture or one of the isomers 4-*cis*, 6-*trans*-di-t-butyl-5-*cis*-methyl- and 4-*trans*, 6-*cis*-di-t-butyl-5-*trans*-methyl-1,3,2-dioxathiane 2-oxide, liquid, relative abundance 50%.

Isomer(s) A is (are) formed (Figure 1) from either one of the enantiomeric 3*R*,5*R*/3*S*,5*S* diol pairs, while B and C both arise

Table 2. Crystallographic details of isomers B and C.

	B	C
M.p./°C	65	117
Molecular weight ($C_{12}H_{24}O_3S$)	248.39	248.39
Crystal size/mm	0.2 × 0.2 × 0.25	0.2 × 0.15 × 0.2
μ (Mo-K_α/mm^{-1})	0.210	0.199
Space group	*Pnam*	$P2_1/c$
Cell dimensions a/Å	7.195(4)	6.476(1)
b/Å	10.097(2)	18.943(3)
c/Å	19.514(3)	12.232(3)
β/°	90.00	103.95(2)
V/Å^3	1 417	1 456
Z	4	4
Density calc./Mg m^{-3}	1.164	1.024
Max. Bragg angle/°	27	27
h range	$0 \leqslant h \leqslant 9$	$0 \leqslant h \leqslant 10$
k range	$0 \leqslant k \leqslant 12$	$0 \leqslant k \leqslant 24$
l range	$0 \leqslant l \leqslant 24$	$-15 \leqslant l \leqslant 15$
Number of reflections measured	1 817	3 169
Number of reflections with $I > 3\sigma(I)$	752	2 171
Number of variables in least-squares	116	242
R [R_w]	0.046 [0.046]	0.043 [0.041]
Max. noise in final difference Fourier map/e A^{-3}	0.3	0.2
Max. shift/e.s.d. in last cycle of LS refinement	0.4	0.06

Table 3. Fractional positional parameters for: (*a*) isomer C, *cis*-5-methyl-*cis*, *cis*-4,6-di-t-butyl-1,3,2-dioxathiane 2-oxide and (*b*) isomer B, *trans*-5-methyl-*trans*, *trans*-4,6-di-t-butyl-1,3-2-dioxathiane 2-oxide. The e.s.d.s given in parentheses refer to the last significant digit.

(*a*) *cis*-5-Methyl-*cis*, *cis*-4,6-di-t-butyl-1,3,2-dioxathiane 2-oxide (CE).

	x	y	z
S(2)	0.556 8(1)	0.239 1(1)	0.810 1(1)
O(1)	0.435 4(2)	0.312 3(1)	0.771 9(1)
O(2)	0.570 5(2)	0.234 8(1)	0.929 0(1)
O(3)	0.368 8(2)	0.184 8(1)	0.755 4(1)
C(4)	0.290 2(3)	0.192 3(1)	0.632 5(1)
C(5)	0.181 2(3)	0.264 5(1)	0.609 5(1)
C(6)	0.357 3(3)	0.319 9(1)	0.648 9(1)
C(7)	0.170 2(3)	0.123 7(1)	0.589 6(2)
C(8)	0.341 9(4)	0.433 3(1)	0.090 8(2)
C(9)	0.023 6(4)	0.402 2(1)	0.160 6(2)
C(10)	0.046 3(4)	0.365 0(1)	0.967 8(2)
C(11)	−0.012 1(3)	0.273 9(1)	0.657 2(2)
C(12)	0.318 7(3)	0.398 6(1)	0.623 9(2)
C(13)	0.465 2(4)	0.566 4(1)	0.362 2(2)
C(14)	0.201 0(4)	0.436 9(1)	0.702 5(2)
C(15)	0.192 5(4)	0.406 7(1)	0.501 2(2)

(*b*) *trans*-5-Methyl-*trans*, *trans*-4,6-di-t-butyl-1,3,2-dioxathiane 2-oxide (CA).

	x	y	z
S(2)	0.376 0(2)	0.544 2(1)	0.2500
O(2)	0.386 8(5)	0.686 8(3)	0.2500
O(3)	0.499 3(3)	0.491 7(2)	0.187 1(1)
C(4)	0.697 6(4)	0.531 8(3)	0.187 2(2)
C(5)	0.792 1(6)	0.470 6(4)	0.2500
C(7)	0.769 4(5)	0.505 7(3)	0.114 6(2)
C(8)	0.689 3(6)	0.612 5(4)	0.067 6(2)
C(9)	0.720 0(6)	0.370 8(4)	0.084 9(2)
C(10)	0.982 2(5)	0.522 2(4)	0.115 7(2)
C(11)	0.800 5(7)	0.320 7(5)	0.2500

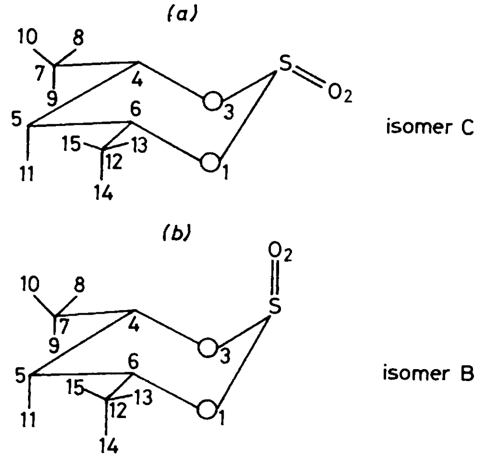

Figure 3. Structural formula of the isomers with atomic numbering scheme.

from the same diastereoisomer, *i.e.* (3*R*,4*R*,5*S*)-2,2,4,6,6-pentamethylheptane-3,5-diol. Its mirror image, the (3*R*,4*S*,5*S*)-configuration, proves to be absent in the diol mixture, because otherwise it would certainly have produced the corresponding, stable cyclic sulphites. Thus, comparison of a completely non-stereospecific reduction, leading to 25% (3*R*,4*R*,5*S*), 25% (3*R*,4*S*,5*S*), and 50% (3*R*,5*R*/3*S*,5*S*), with the observed 50% (3*R*,4*R*,5*S*), 0% (3*R*,4*S*,5*S*), and 50% (3*R*,5*R*/3*S*,5*S*), shows a small, but distinct stereoselectivity. Note that the formation of the (3*R*,4*R*,5*S*)-diol follows Cram's rule (incoming hydrides preferentially attack C=O groups on their least-hindered side). This, in turn, suggests a preference of the reacting dione for the extended conformation (see Figure 2).

X-*Ray Determination*.—Crystals suitable for *X*-ray single crystal determinations were grown for the isomers B and C by slow evaporation of an ethereal solution. All *X*-ray experiments were performed on an Enraf-Nonius CAD4 diffractometer using Mo-radiation with a graphite monochromator (λ = 0.710 69 Å). For both isomers cell dimensions were deduced from angular settings of 25 high-order reflections ($8° \leqslant \theta \leqslant 15°$) and intensity data recorded at room temperature up to a Bragg angle of 27°. Three intensity control reflections, measured every 2 h, showed no significant change for the monoclinic isomer C during the data collection, but a loss of 25% of the original intensity for the rhombic isomer B. The latter data set was corrected for the observed decay. In

Table 4. Geometry of the title compound and comparison with (*a*) Bond lengths/Å, (*b*) bond angles/°, and (*c*) torsion angles/°, the average geometry of the CA and CE forms (Petit *et al.*[1]) with e.s.d.s in parentheses. To facilitate comparison the crystallographically dependent values of isomer B have also been added.

		(*cis*, *cis*, *cis*-CE)-isomer C	Average CE chair	(*trans*, *trans*, *trans*-CA)-isomer B	Average CA chair
(*a*)	S(2)=O(2)	1.438(1)	1.441	1.442(3)	1.447
	S(2)–O(1)	1.607(1)		1.604	
	S(2)–O(3)	1.610(1)	1.617	1.604(2)	1.611
	O(1)–C(6)	1.475(1)		1.483	
	O(3)–C(4)	1.473(1)	1.470	1.483(2)	1.475
	C(6)–C(5)	1.540(1)		1.531	
	C(4)–C(5)	1.534(1)	1.515	1.531(3)	1.526
	C(4)–C(7)	1.540(1)		1.532(3)	
	C(7)–C(8)	1.547(2)		1.528(4)	
	C(7)–C(9)	1.515(2)		1.523(5)	
	C(7)–C(10)	1.527(2)		1.541(4)	
	C(5)–C(11)	1.514(1)		1.514(5)	
	C(6)–C(12)	1.531(1)		1.532	
	C(12)–C(13)	1.521(2)		1.528	
	C(12)–C(14)	1.544(2)		1.523	
	C(12)–C(15)	1.534(2)		1.541	
(*b*)	O(1)–S(2)=O(2)	104.41(5)	103.9	107.4(1)	107.8
	O(3)–S(2)=O(2)	103.93(5)		107.4	
	O(1)–S(2)–O(3)	99.33(3)	98.2	99.9(1)	99.5
	S(2)–O(1)–C(6)	113.84(6)		116.1	
	S(2)–O(3)–C(4)	113.79(6)	112.8	116.1(2)	117.8
	O(1)–C(6)–C(5)	107.43(7)		108.6	
	O(3)–C(4)–C(5)	107.69(7)	109.7	108.6(3)	109.2
	C(4)–C(5)–C(6)	106.07(7)	112.4	106.3(3)	111.6
	O(1)–C(6)–C(12)	107.32(7)		106.0	
	C(5)–C(6)–C(12)	121.90(8)		121.4	
	C(6)–C(12)–C(13)	107.5(1)		107.9	
	C(6)–C(12)–C(14)	114.6(1)		115.3	
	C(6)–C(12)–C(15)	108.4(1)		107.7	
	C(13)–C(12)–C(14)	107.7(1)		108.4	
	C(13)–C(12)–C(15)	108.9(1)		108.0	
	C(14)–C(12)–C(15)	109.6(1)		109.5	
	O(3)–C(4)–C(7)	106.82(7)		106.0(2)	
	C(5)–C(4)–C(7)	121.17(8)		121.4(3)	
	C(4)–C(7)–C(8)	106.5(2)		107.9(3)	
	C(4)–C(7)–C(9)	114.3(2)		115.3(3)	
	C(4)–C(7)–C(10)	108.6(1)		107.7(3)	
	C(8)–C(7)–C(9)	106.5(1)		108.4(3)	
	C(8)–C(7)–C(10)	108.3(1)		108.0(3)	
	C(9)–C(7)–C(10)	110.5(1)		109.5(3)	
	C(4)–C(5)–C(11)	114.9(1)		114.9(2)	
	C(6)–C(5)–C(11)	114.7(1)		114.9	
(*c*)	O(3)–S(2)–O(1)–C(6)	−58.9(1)	−63.5	−54.1(2)	−54.0
	O(1)–S(2)–O(3)–C(4)	58.7(1)	63.5	54.1	54.0
	S(2)–O(3)–C(4)–C(5)	−66.6(2)	−62.8	−64.0	−59.3
	S(2)–O(1)–C(6)–C(5)	66.7(2)	62.8	64.0(2)	59.3
	O(1)–C(6)–C(5)–C(4)	−65.0(2)	−54.4	−63.6(2)	−56.2
	O(3)–C(4)–C(5)–C(6)	65.1(2)	54.4	63.6	56.2
	O(2)–S(2)–O(1)–C(6)	−166.0(1)		57.8(3)	
	O(2)–S(2)–O(3)–C(4)	166.2(1)		−57.8	
	O(1)–C(6)–C(5)–C(11)	62.9(2)		64.6(3)	
	C(12)–C(6)–C(5)–C(11)	−61.4(2)		−58.5(3)	
	O(3)–C(4)–C(5)–C(11)	−62.8(2)		−64.6	
	C(7)–C(4)–C(5)–C(11)	60.5(2)		58.5	
	C(13)–C(12)–C(6)–O(1)	74.7(2)		73.7(3)	
	C(13)–C(12)–C(6)–C(5)	−161.0(2)		−162.0(3)	
	C(14)–C(12)–C(6)–O(1)	−45.0(2)		−47.5(3)	
	C(14)–C(12)–C(6)–C(5)	79.3(2)		76.8(3)	
	C(15)–C(12)–C(6)–O(1)	−167.8(2)		−170.0(3)	
	C(15)–C(12)–C(6)–C(5)	−43.5(2)		−45.8(3)	
	C(8)–C(7)–C(4)–O(3)	−75.6(2)		−73.7	
	C(8)–C(7)–C(4)–C(5)	160.8(2)		162.0	
	C(9)–C(7)–C(4)–O(3)	44.2(2)		47.5	
	C(9)–C(7)–C(4)–C(5)	−79.4(2)		−76.8	
	C(10)–C(7)–C(4)–O(3)	168.0(2)		170.0	
	C(10)–C(7)–C(4)–C(5)	44.4(2)		45.8	

neither case were the intensities corrected for absorption, because of the small size of the crystals. Further experimental details are given in Table 2. The space group $P2_1/c$ of isomer C was inferred from systematically absent reflections and confirmed by the centric distribution of E-values. The most likely E-map, evaluated using MULTAN,[4] showed the non-hydrogen atom positions. A subsequent series of least-squares calculations and difference Fourier maps revealed all hydrogen atoms. Least-squares refinements were performed on Structure factors (F), and each individual reflection was given a weight based on counting statistics. Non-hydrogen atoms were refined anisotropically and hydrogen atoms isotropically to $R_w = 0.41$. No extinction correction was applied. Refined parameters* are given in Table 3(*a*) and the atomic numbering scheme in Figure 3(*a*).

Systematically absent reflections of isomer B are in line with space groups *P*nam and *P*na2_1. The non-centric E-distribution seemed to favour the latter, but this choice did not lead to a refinable structural model. In *P*nam, however, the structure, solved by MULTAN, refined smoothly. We note that, in this space group with $Z = 4$, the molecule is in a special position. It is situated such that a crystallographic mirror plane passes through S(2), O(2), and C(5). With the H-atoms located at the expected positions and their isotropic temperature parameters fixed at $B = 4.0$ A^2, the non-hydrogen atoms were refined anisotropically. As before, least-squares calculations were performed on structure factors, with individually weighted reflections. No extinction correction was applied. The weighted *R*-factor converged to $R_w = 0.046$. Refined parameters* are given in Table 3(*b*) and the atomic numbering scheme in Figure 3(*b*).

Atomic scattering factors were taken from International Tables for *X*-Ray Crystallography[5] and all computer calculations performed with an Enraf-Nonius CAD4-SDP.[6]

Discussion of Geometry and Influence of Steric Crowding.—The *X*-ray determinations confirm the interpretation of the i.r. and n.m.r. spectra: isomer B has a dioxathiane ring in the chair form with an axially oriented S=O group (CA form), one axial methyl, and two equatorial t-butyl substituents. Isomer C has a dioxathiane ring in the chair form with an equatorially oriented S=O group (CE form) and the other substituents oriented as in isomer B. The observed conformations are depicted in Figure 3.

Bond distances, valence angles, and selected torsion angles are shown in Table 4. We also include in Table 4 the current population average of distances and angles for CA and CE sulphites, published by Petit *et al.*[1] We use these values as reference for the unperturbed 1,3,2-dioxathiane 2-oxide ring in its CA and CE forms. A comparison with the actual values for the title compounds shows that high substitution leaves the C–O–S(O)–O–C part of the dioxathiane ring of both isomers largely unchanged. The only exceptions are the torsion angles O(3)–S(2)–O(1)–C(6) and O(1)–S(2)–O(3)–C(4) of isomer C. In contrast the C(4)–C(6) region of the ring is seriously affected by the demands of the substituents. Steric hindrance between the alkyl groups is relieved partly by pushing the methyl group at C(5) downward and partly by opening some exocyclic valence and torsion angles. The downward push of the methyl group is revealed in the increase of the puckering at the C(5) side of the ring. The relevant torsion angles O(1)–C(6)–C(5)–C(4) and O(3)–C(4)–C(5)–C(6) are enlarged by about 10° and the valence angle C(4)–C(5)–C(6) is decreased from *ca.* 112° to *ca.* 106°. At the exocyclic side of the ring one notes the large increase to 121° of the angles C(5)–C(4)–C(7) and C(5)–C(6)–C(12), as well as a rotation over 15° of the t-butyl groups along C(4)–C(7) and C(6)–C(12). In this way the downward oriented groups C(9) and C(14) rotate towards O(3) and O(1) and away from the hindering C(11) atom. Furthermore, the valence angles C(4)–C(5)–C(11), C(6)–C(5)–C(11), C(6)–C(12)–C(14), and C(4)–C(7)–C(9) open to about 115°, again relieving strain in the most hindered region, the downwards pointing methyl groups C(9), C(11), and C(14).

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References

1 G. H. Petit, P. Van Nuffel, C. Van Alsenoy, A. T. H. Lenstra, and H. J. Geise, *J. Am. Chem. Soc.*, 1984, **106**, 6899.

2 J. E. Elguero, E. Gonzalez, and R. Jacquier, *Bull. Soc. Chim. Fr.*, 1968, 707.

3 C. H. Green and D. G. Hellier, *J. Chem. Soc., Perkin Trans. 2*, 1972, 458.

4 G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. A*, 1971, **27**, 368.

5 International Tables for *X*-Ray Crystallography, vol. 4, Kynoch Press, Birmingham, 1974. (Present distributor D. Reidel, Dordrecht).

6 B. A. Frenz, The Enraf-Nonius CAD4 Structure Determination Package in 'Computing in Crystallography,' eds. H. Schenk, R. Olthof-Hazekamp, H. Van Koningsveld, and G. C. Bassi, Delft University Press, 1978, p. 64.

7 D. G. Hellier and H. G. Liddy, *Magn. Reson. Rev.*, 1988, **26**, 671.

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