

The Crystal Structures of 1,4-Ditosyl-1,4-Dioxabutane,
1,7-Ditosyl-1,4,7-Trioxaheptane and
1,10-Ditosyl-1,4,7,10-Tetraoxadecane at *ca.* $-130\text{ }^{\circ}\text{C}$

P. GROTH

Department of Chemistry, University of Oslo, N-0315 Oslo 3, Norway

Whereas 3-methoxypropyl tosylate can be distilled unchanged, the corresponding 2-methoxy-ethyl tosylate gives, under the same conditions, exclusively methyl tosylate.¹ Crystal structure determinations of the title compounds were carried out in order to find whether the conformation adopted by the $\text{TsOCH}_2\text{CH}_2\text{O}$ - unit might provide support for any one of several mechanistic proposals.¹

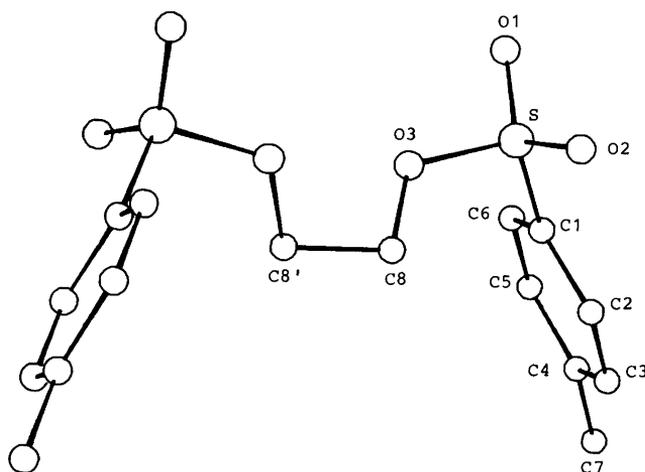


Fig. 1. Schematic drawing of (I) showing the numbering of atoms. The prime corresponds to symmetry operation $-x, y, 1\frac{1}{2}-z$.

Table 1. Crystallographic data for the molecules (I), (II) and (III).

Molecule	(I)	(II)	(III)
Space group	$C2/c$	$C2/c$	$P2_1/c$
$a(\text{\AA})$	10.572(2)	23.385(8)	8.351(3)
$b(\text{\AA})$	10.213(2)	5.442(3)	11.435(8)
$c(\text{\AA})$	15.704(4)	15.282(5)	11.112(9)
$\alpha(^{\circ})$	—	—	—
$\beta(^{\circ})$	90.02(2)	91.10(3)	93.12(8)
$\gamma(^{\circ})$	—	—	—
Z	4	4	2
$D_m(\text{g cm}^{-3})$	1.43	1.40	1.42
$D_x(\text{g cm}^{-3})$	1.45	1.41	1.44
Observed reflections	1378	1225	1075
$R(\%)$	3.1	4.5	8.7
$R_w(\%)$	3.8	4.3	8.6

Table 2. Final fractional coordinates with estimated standard deviations.

Atom	x	y	z
(I) S	.24886(4)	.14684(4)	.68636(2)
O1	.2442(1)	.2707(1)	.6446(1)
O2	.3088(1)	.1356(1)	.7672(1)
O3	.1045(1)	.1081(1)	.6963(1)
C1	.3091(1)	.0273(1)	.6175(1)
C2	.3678(2)	-.0828(2)	.6511(1)
C3	.4108(2)	-.1781(2)	.5958(1)
C4	.3980(1)	-.1654(2)	.5084(1)
C5	.3400(1)	-.0529(2)	.4763(1)
C6	.2953(1)	.0431(2)	.5300(1)
C7	.4452(2)	-.2698(2)	.4491(1)
C8	.0707(2)	-.0057(2)	.7470(1)
H2	.375(2)	-.096(2)	.708(1)
H3	.450(2)	-.254(2)	.615(1)
H5	.336(2)	-.040(2)	.419(1)
H6	.259(2)	.118(2)	.508(1)
H71	.385(3)	-.343(3)	.440(2)
H72	.468(3)	-.234(2)	.393(2)
H73	.525(3)	-.292(3)	.457(2)
H81	.112(2)	-.001(2)	.801(1)
H82	.100(2)	-.085(2)	.716(1)
(II) S	.61701(4)	.06129(17)	.06306(5)
O1	.6660(1)	.1539(4)	.1093(1)
O2	.5745(1)	.2279(4)	.0301(1)
O3	.5887(1)	-.1190(4)	.1304(1)
C1	.6388(1)	-.1317(6)	-.0216(2)
C2	.6202(1)	-.0872(7)	-.1068(2)
C3	.6393(1)	-.2357(7)	-.1729(2)
C4	.6763(1)	-.4312(7)	-.1564(2)
C5	.6942(1)	-.4711(7)	-.0702(2)
C6	.6759(1)	-.3238(6)	-.0032(2)
C7	.6967(2)	-.5938(9)	-.2284(3)
C8	.5336(1)	-.2278(8)	.1042(2)
C9	.5153(2)	-.3904(7)	.1770(2)
O4	.5000	-.2500	.2500
H2	.594(1)	.052(7)	-.119(2)
H3	.628(1)	-.204(6)	-.235(2)
H5	.721(1)	-.599(7)	-.057(2)
H6	.687(1)	-.349(7)	.055(2)
H81	.540(1)	-.316(6)	.048(2)
H82	.507(1)	-.094(6)	.093(2)
H91	.549(1)	-.511(6)	.194(2)
H92	.480(1)	-.490(6)	.158(2)
H71	.737(2)	-.620(9)	-.223(3)
H72	.689(2)	-.516(9)	-.286(3)
H73	.684(2)	-.725(10)	-.227(3)
(III) S	.3508(2)	.1786(2)	.6881(2)
O1	.3309(7)	.1259(5)	.8028(5)
O2	.4879(7)	.1491(5)	.6210(5)
O3	.3571(6)	.3140(5)	.7175(4)
O4	.1440(7)	.4999(5)	.6261(5)
C1	.1743(10)	.1630(8)	.5964(7)

C2	.1888(10)	.1380(8)	.4751(8)
C3	.0448(10)	.1298(8)	.4012(8)
C4	-.1014(10)	.1489(7)	.4455(8)
C5	-.1127(10)	.1721(9)	.5706(8)
C6	.0285(9)	.1787(9)	.6437(8)
C7	-.2519(12)	.1470(10)	.3652(11)
C8	.3963(10)	.3939(8)	.6218(7)
C9	.3127(10)	.5068(9)	.6406(8)
C10	.0891(12)	.4900(10)	.5007(8)
H2	.312(14)	.124(9)	.432(9)
H3	.061(8)	.104(5)	.322(6)
H5	-.211(7)	.180(5)	.600(4)
H6	.040(10)	.194(7)	.717(7)
H81	.367(7)	.354(5)	.542(5)
H82	.516(8)	.409(5)	.620(5)
H91	.347(9)	.557(6)	.583(7)
H92	.299(8)	.535(6)	.728(6)
H101	.082(12)	.411(8)	.449(8)
H102	.148(11)	.548(8)	.445(8)
H71	-.284(16)	.222(11)	.318(11)
H72	-.321(12)	.114(8)	.404(8)
H73	-.258(11)	.073(7)	.303(7)

Table 3. Bond distances and angles with estimated standard deviations.

	Distance	(Å)	Distance	(Å)	Angle	(°)	Angle	(°)
(I)	S-O1	1.426(1)	S-O2	1.423(1)	O1-S-O2	119.8(1)	O1-S-O3	103.5(1)
	S-O3	1.584(1)	S-C1	1.750(2)	O1-S-C1	110.3(1)	O2-S-O3	108.7(1)
	O3-C8	1.454(2)	C1-C2	1.388(2)	O2-S-C1	109.4(1)	O3-S-C1	103.7(1)
	C1-C6	1.392(2)	C2-C3	1.381(2)	S-O3-C8	119.4(1)	S-C1-C2	119.6(1)
	C3-C4	1.385(2)	C4-C5	1.396(3)	S-C1-C6	119.4(1)	C2-C1-C6	121.0(1)
	C4-C7	1.501(2)	C5-C6	1.377(2)	C1-C2-C3	118.7(2)	C2-C3-C4	121.7(2)
	C8-C8'	1.497(3)			C3-C4-C5	118.5(2)	C3-C4-C7	121.1(1)
					C5-C4-C7	120.4(2)	C4-C5-C6	121.1(2)
					C1-C6-C5	119.1(2)	O3-C8-C8'	106.3(1)
(II)	S-O1	1.427(2)	S-O2	1.430(3)	O1-S-O2	119.8(2)	O1-S-O3	103.8(1)
	S-O3	1.577(2)	S-C1	1.750(3)	O1-S-C1	109.7(2)	O2-S-O3	109.1(1)
	O3-C8	1.467(4)	C1-C2	1.387(4)	O2-S-C1	109.3(2)	O3-S-C1	103.9(1)
	C1-C6	1.385(4)	C2-C3	1.374(5)	S-O3-C8	116.8(2)	S-C1-C2	120.0(3)
	C3-C4	1.392(5)	C4-C5	1.391(4)	S-C1-C6	119.5(2)	C2-C1-C6	120.5(3)
	C4-C7	1.497(5)	C5-C6	1.375(5)	C1-C2-C3	119.1(3)	C2-C3-C4	121.7(3)
	C8-C9	1.491(5)	C9-O4	1.404(3)	C3-C4-C5	117.8(3)	C3-C4-C7	121.6(3)
					C5-C4-C7	120.6(3)	C4-C5-C6	121.5(3)
					C1-C6-C5	119.4(3)	O3-C8-C9	107.4(3)
					C8-C9-O4	110.6(3)	C8-C9-O4	108.4(3)
(III)	S-O1	1.43(1)	S-O2	1.44(1)	O1-S-O2	120(1)	O1-S-O3	103(1)
	S-O3	1.58(1)	S-C1	1.75(1)	O1-S-C1	110(1)	O2-S-O3	109(1)
	O3-C8	1.45(1)	O4-C9	1.41(1)	O2-S-C1	110(1)	O3-S-C1	104(1)
	O4-C10	1.45(1)	C1-C2	1.39(1)	S-O3-C8	118(1)	C9-O4-C10	112(1)
	C1-C6	1.36(1)	C2-C3	1.42(1)	S-C1-C2	118(1)	S-C1-C6	120(1)
	C3-C4	1.36(1)	C4-C5	1.42(1)	C2-C1-C6	122(1)	C1-C2-C3	117(1)
	C4-C7	1.50(1)	C5-C6	1.40(1)	C2-C3-C4	122(1)	C3-C4-C5	120(1)
	C8-C9	1.49(1)	C10-C10'	1.51(1)	C3-C4-C7	121(1)	C5-C4-C7	119(1)
					C4-C5-C6	119(1)	C1-C6-C5	121(1)
					O3-C8-C9	108(1)	O4-C9-C8	114(1)
				O4-C10-C10'	105(1)			

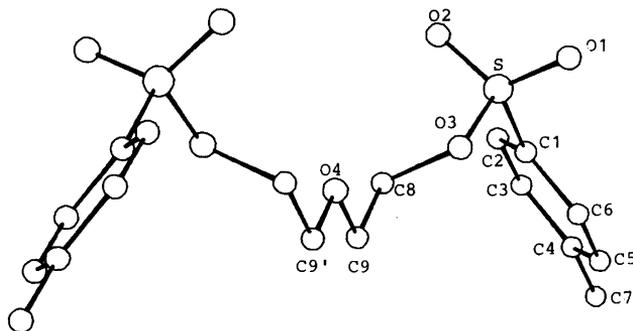


Fig. 2. Schematic drawing of (II) showing the numbering of atoms. The prime corresponds to symmetry operation $1-x, y, \frac{1}{2}-z$.

The crystallographic data for $C_{16}H_{18}O_6S_2$, (I), $C_{18}H_{22}O_7S_2$, (II) and $C_{20}H_{26}O_8S_2$, (III), are given in Table 1. The crystal quality of (III) was poor. Intensity data were collected on an automatic four-circle diffractometer (Syntex PI) at *ca.* -130°C (MoK_α -radiation, $2\theta_{\text{max}}=50^\circ$, ω -scan technique). The scan speed was $3^\circ/\text{min}$ for (I) and (II), and $2^\circ/\text{min}$ for (III). The observed-unobserved cutoff was $2.5\sigma(I)$ for (I) and (II), and $2\sigma(I)$ for (III). No corrections were made for absorption or secondary extinction effects. The structures were solved by direct methods² and refined by full-matrix least squares technique³ (all programs used are included in Ref. 3 except those for phase determination). Weights in least squares were calculated from the standard deviation in intensities, $\sigma(I)$, taken as $\sigma(I)=[C_T+(0.02C_N)^2]^{1/2}$, where C_T is the total number of counts and C_N the net count.

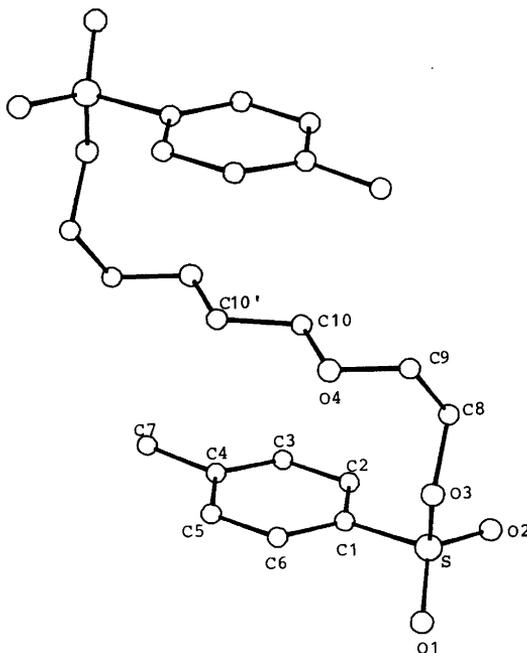


Fig. 3. Schematic drawing of (III) showing the numbering of atoms. The prime corresponds to symmetry operation $-x, 1-y, 1-z$.

Table 4. Some torsion angles with estimated standard deviations

	Dihedral angle	(°)
(I)	C1-S-O3-C8	73.1(1)
	S-O3-C8-C8'	172.9(1)
	O3-C8-C8'-O3'	-67.2(1)
(II)	C1-S-O3-C8	-70.7(3)
	S-O3-C8-C9	179.8(3)
	O3-C8-C9-O4	70.1(3)
	C8-C9-O4-C9'	-177.3(3)
(III)	C1-S-O3-C8	-70(1)
	S-O3-C8-C9	149(1)
	O3-C8-C9-O4	-67(1)
	C10-O4-C9-C8	-74(1)
	C9-O4-C10-C10'	-168(1)

Anisotropic thermal parameters were used for non-hydrogen atoms. Positional parameters for H-atoms were calculated. These atoms were refined with isotropic temperature factors. Maximum r.m.s. amplitudes range from 0.17 to 0.25 Å.

Final fractional coordinates with estimated standard deviations are given in Table 2. The bond distances and angles, given in Table 3, are normal within error limits. Listings of structure factors and thermal parameters are available from the author.

The torsion angles listed in Table 4, show that the conformation of the TsOCH₂CH₂O-unit is *aga* for (I) and (II), while that of (III) may be described as *agg*. It should, however, be pointed out that the *anti* angle deviates considerably from 180°. The conclusions to be drawn from these findings (with regard to the mechanistic proposals) are presented elsewhere.¹ The schematic drawings, Figs. 1, 2 and 3, illustrate the molecules and the numbering of atoms. (I) has a two-fold axis of rotation through the mid point of the C8-C8' bond. (II) has a corresponding axis through O4, while (III) has a centre of symmetry at the mid point of the C10-C10' bond.

1. Dale, J. and Fredriksen, S.B. *Acta Chem. Scand. B* 39 (1985) 511.
2. Germain G., Main, P. and Woolfson, M.M. *Acta Crystallogr. A* 27 (1971) 368.
3. Groth, P. *Acta Chem. Scand.* 27 (1973) 1837.

Received March 22, 1985.