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The crystal structure of the organosilicon *p*-toluenesulfonate (Me₃Si)₃CSiPh(H)(OSO₂C₆H₄Me-*p*) *

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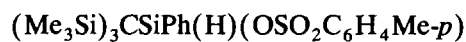
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Abstract

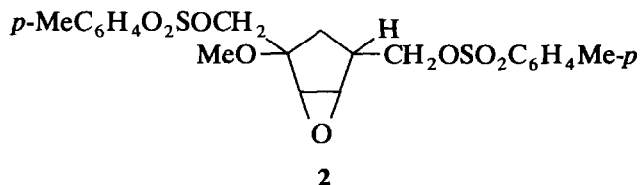
A single crystal X-ray diffraction study of the title compound has shown that the geometry within the OSO₂C₆H₄Me-*p* group is very similar to that in organic tosylates, but the Si–O–S angle (128.0(5)°) is significantly larger than the corresponding C–O–S angle (ca. 118°) in the latter species.

1. Introduction

During a study (not yet complete) of rates of reaction of a range of compounds of the type (Me₃Si)₃CSiPh(H)X, we encountered some unexpectedly large reactivity differences between the compound with X = OSO₂C₆H₄Me-*p* (compound 1) and that with X = OSO₂Me. In order to confirm the identity of the former compound, and perhaps throw light on its properties, we determined its crystal structure. In the event this did not reveal any features that might significantly affect the reactivity of the compound in solution, but since the determination is, as far as we are aware, the first diffraction study of the structure of a silicon sulfonate we present the results below.



1



2. Results and discussion

The tosylate 1 was made, essentially as described previously [1], by treatment of the iodide (Me₃Si)₃CSiPh(H)I with AgOSO₂C₆H₄Me-*p* in CH₂Cl₂.

The unit cell was found to contain two independent molecules, molecule (1) and (2), and bond lengths and angles for both are shown in Table 1. However, since there is no difference of any significance between the geometries of the two molecules, the structure is shown in Fig. 1 only for molecule (1), and in general only the data for this molecule are considered below.

The features of the structure are as follows.

(a) The geometry of the *p*-MeC₆H₄SO₃ group is very similar to that in a range of organic tosylates. For simplicity we make a comparison only with data for compound 2, for which especially accurate results are available [2], but the data for a range of other organic tosylates show no significant variations. (The simplest organic tosylate with which we could make comparison is the cyclohexyl derivative C₆H₁₁OSO₂C₆H₄Me-*p*, but the data for that compound show rather large estimated standard deviations [3]). Some parameters for molecule (1) in 1 and for the left-hand tosylate group in 2 are shown in Table 2, and it will be seen that the two sets are remarkably similar. It is noteworthy that the unexpected difference between the two chemically equivalent O–S = O angles that was commented on in the case of 2 [2] (see also, *e.g.* refs. 3 and 4) is found also for 1.

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* Dedicated to Professor U. Wannagat on the occasion of his 70th birthday on 31 May 1993, in recognition of his important pioneering contributions to organosilicon chemistry.

TABLE 1. Intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses

	Molecule (1)	Molecule (2)		Molecule (1)	Molecule (2)
<i>(a) Bond distances</i>					
Si(1)–O(1)	1.587(8)	1.549(7)	Si(1)–O(2)	1.435(10)	1.442(8)
Si(1)–O(3)	1.426(8)	1.422(10)	Si(1)–C(17)	1.788(8)	1.738(10)
Si(1)–C(1)	1.920(9)	1.932(11)	Si(1)–C(2)	1.877(13)	1.862(14)
Si(1)–C(3)	1.916(14)	1.899(10)	Si(1)–C(4)	1.858(12)	1.868(13)
Si(2)–C(1)	1.925(11)	1.923(11)	Si(2)–C(5)	1.899(11)	1.882(14)
Si(2)–C(6)	1.863(14)	1.883(12)	Si(2)–C(7)	1.891(14)	1.892(10)
Si(3)–C(1)	1.937(10)	1.946(7)	Si(3)–C(8)	1.876(12)	1.914(13)
Si(3)–C(9)	1.882(11)	1.884(13)	Si(3)–C(10)	1.884(12)	1.869(12)
Si(4)–O(1)	1.716(8)	1.718(7)	Si(4)–C(1)	1.857(10)	1.843(10)
Si(4)–C(11)	1.880(11)	1.863(9)	C(11)–C(12)	1.398(11)	1.41(2)
C(11)–C(16)	1.36(2)	1.39(2)	C(12)–C(13)	1.38(2)	1.393(14)
C(13)–C(14)	1.37(2)	1.35(2)	C(14)–C(15)	1.392(13)	1.37(2)
C(15)–C(16)	1.39(2)	1.421(13)	C(17)–C(18)	1.363(13)	1.417(14)
C(17)–C(22)	1.35(2)	1.36(2)	C(18)–C(19)	1.390(14)	1.370(14)
C(19)–C(20)	1.38(2)	1.38(2)	C(20)–C(21)	1.381(13)	1.39(2)
C(20)–C(23)	1.543(14)	1.51(2)	C(21)–C(22)	1.400(13)	1.372(15)
<i>(b) Bond angles</i>					
O(1)–Si(1)–O(2)	104.2(5)	105.5(5)	O(1)–Si(1)–O(3)	107.8(4)	109.0(5)
O(1)–Si(1)–C(17)	104.2(4)	103.7(4)	O(2)–Si(1)–O(3)	121.5(5)	118.9(5)
O(2)–Si(1)–C(17)	108.6(4)	108.1(6)	O(3)–Si(1)–C(17)	109.2(5)	110.4(5)
C(1)–Si(1)–C(2)	112.1(4)	112.7(60)	C(1)–Si(1)–C(3)	112.5(5)	112.2(5)
C(1)–Si(1)–C(4)	114.0(5)	111.6(5)	C(2)–Si(1)–C(3)	105.3(6)	107.1(5)
C(2)–Si(1)–C(4)	105.4(6)	107.2(7)	C(3)–Si(1)–C(4)	107.0(5)	105.7(6)
C(1)–Si(2)–C(5)	111.9(5)	112.4(5)	C(1)–Si(2)–C(6)	113.8(6)	112.7(5)
C(1)–Si(2)–C(7)	112.7(4)	113.6(5)	C(5)–Si(2)–C(6)	105.6(5)	106.8(6)
C(5)–Si(2)–C(7)	105.5(6)	106.4(5)	C(6)–Si(2)–C(7)	106.7(7)	104.4(5)
C(1)–Si(3)–C(8)	112.4(5)	112.5(5)	C(1)–Si(3)–C(9)	113.8(5)	113.4(4)
C(1)–Si(3)–C(10)	111.9(4)	113.1(5)	C(8)–Si(3)–C(9)	105.7(4)	106.8(6)
C(8)–Si(3)–C(10)	105.6(6)	103.9(5)	C(9)–Si(3)–C(10)	106.9(6)	106.6(6)
O(1)–Si(4)–C(1)	105.6(4)	106.5(4)	O(1)–Si(4)–C(11)	107.2(4)	105.7(4)
C(1)–Si(4)–C(11)	122.6(5)	122.2(4)	Si(1)–O(1)–Si(4)	128.0(5)	130.2(5)
Si(1)–C(1)–Si(2)	110.5(5)	111.3(4)	Si(1)–C(1)–Si(3)	109.0(5)	109.8(5)
Si(1)–C(1)–Si(4)	113.6(4)	106.4(5)	Si(2)–C(1)–Si(3)	110.4(3)	109.0(5)
Si(2)–C(1)–Si(4)	106.1(5)	113.8(5)	Si(3)–C(1)–Si(4)	107.2(5)	106.4(4)
Si(4)–C(11)–C(12)	123.8(9)	116.1(8)	Si(4)–C(11)–C(16)	117.0(6)	125.9(8)
C(12)–C(11)–C(16)	119(1)	118.0(9)	C(11)–C(12)–C(13)	120(1)	120(1)
C(12)–C(13)–C(14)	121.0(8)	122(1)	C(13)–C(14)–C(15)	119(1)	121(1)
C(14)–C(15)–C(16)	120(1)	119(1)	C(11)–C(16)–C(15)	120.9(9)	121(1)
Si(1)–C(17)–C(18)	118.5(8)	119.1(9)	Si(1)–C(17)–C(22)	117.8(6)	122.5(8)
C(18)–C(17)–C(22)	123.6(8)	118.4(9)	C(17)–C(18)–C(19)	118(1)	119(1)
C(18)–C(19)–C(20)	121.3(9)	122(1)	C(19)–C(20)–C(21)	119.1(8)	118.8(9)
C(19)–C(20)–C(23)	120.1(9)	122(1)	C(21)–C(20)–C(23)	121(1)	119(1)
C(20)–C(21)–C(22)	120(1)	119(1)	C(17)–C(22)–C(21)	118.1(9)	123(1)

(b) The Si–O–S angle in **1** (128.0(5)°) (130.2(5) in molecule (2)) is distinctly larger than the corresponding C–O–S angle in **2** (118.4(4)°) and other organic tosylates (see *e.g.* ref. 4). It will be recalled that Si–O–C bond angles in, *e.g.* alkoxy silanes are normally substantially larger than C–O–C bond angles in ethers [5].

(c) Somewhat unexpectedly (since it might have been predicted that the aryl groups would lie away from each other in order to relieve steric strain) the two arene rings were found to be fairly close together and almost parallel to each other (the dihedral angle between them is 9(2)°) with a distance of only 3.3 Å

between the centroid of the C(11)–C(16) ring and the plane of the C(17)–C(22) ring. We initially suspected that this might reflect a π – π interaction between the rings, but the view of the molecule shown in Fig. 1 shows that there can be little, if any, such interaction.

(d) The C(1)–Si(4)–C(11) angle, 122.6(5)°, is unusually large, presumably because the aryl group moves away from the (Me₃Si)₃C group to relieve steric strain.

(e) The geometry of the (Me₃Si)₃C group shows the commonly observed feature of long C(1)–SiMe₃ bonds (1.920(9), 1.925(11), and 1.937(10) Å) and substantially shorter Si–Me bonds (mainly in the range 1.86–1.89

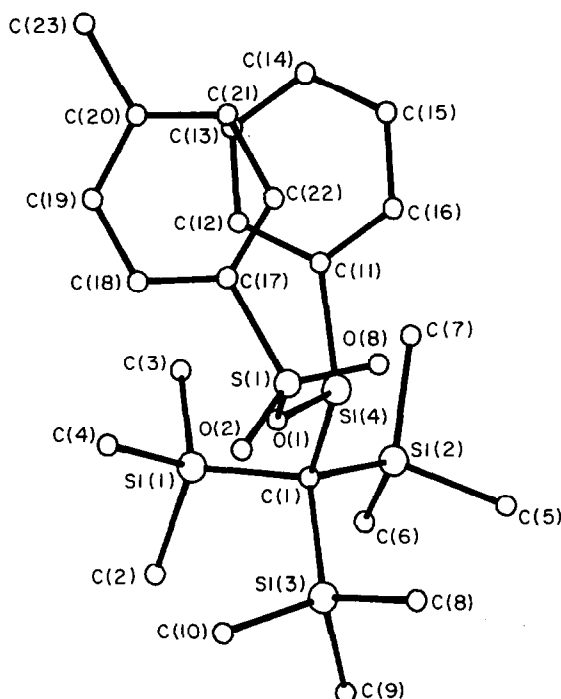


Fig. 1. Molecular structure of compound 1.

Å). The bond between C(1) and Si(4), the silicon of the $SiPh(H)OSO_2C_6H_4Me-p$ group, is markedly shorter, at 1.857(10) Å, than the other bonds to the central carbon (C(1)); this effect has been noticed before in related structures in which a silicon atom attached to the central carbon of a $(Me_3Si)_3C$ group bears an oxygen atom [6].

(f) The O(1) atom lies only 3.250(6) Å (3.281(8) Å in molecule (2)) away from Si(3), and this might be taken to indicate a weak $O \cdots Si$ intramolecular interaction,

TABLE 2. Comparison of some bond lengths (Å) and angles (°) in molecule (1) of 1 with corresponding values for the tosyl group on the left-hand side of 2^a

	1	2
O(1)–S	1.587(8)	1.571(5)
O(2)–S	1.435(10)	1.429(6)
O(3)–S	1.426(8)	1.430(6)
S–C(17)	1.788(8)	1.749(7)
O(1)–S–C(17)	104.2(5)	102.5(3)
O(2)–S–C(17)	108.6(4)	110.3(3)
O(3)–S–C(17)	109.2(5)	108.4(3)
O(2)–S–O(3)	121.5(5)	121.0(4)
O(1)–S–O(2)	104.2(5)	103.4(3)
O(1)–S–O(3)	107.8(4)	109.6(3)

^a The oxygen atoms in 2 corresponding to O(2) and O(3) in 1 are arbitrarily assigned.

TABLE 3. Fractional atomic coordinates ($\times 10^4$) with estimated standard deviations in parentheses

	x	y	z
<i>(a) Molecule (1)</i>			
S(1)	2136.8(35)	2699.4(30)	5698.2(8)
Si(1)	3784.4(41)	1385.6(34)	6860.6(9)
Si(2)	7561.8(39)	3451.1(36)	6661.4(10)
Si(3)	5211.9(38)	5106.3(32)	6693.9(9)
Si(4)	4780.6(35)	2563.8(31)	6128.0(8)
O(1)	2964(7)	2661(7)	6051(2)
O(2)	983(9)	3289(8)	5782(2)
O(3)	3464(9)	3553(8)	5479(2)
C(1)	5301(10)	3083(9)	6587(3)
C(2)	3924(16)	2186(13)	7309(3)
C(3)	4267(14)	–411(11)	6884(3)
C(4)	1529(13)	470(12)	6718(3)
C(5)	9185(14)	5507(14)	6506(4)
C(6)	8189(14)	3509(14)	7113(3)
C(7)	7917(13)	1818(13)	6431(4)
C(8)	5983(13)	6572(11)	6348(3)
C(9)	6523(14)	6324(12)	7084(3)
C(10)	2996(13)	4688(11)	6758(3)
C(11)	4467(11)	566(11)	5915(3)
C(12)	3186(12)	–1000(11)	5987(3)
C(13)	3017(13)	–2397(11)	5811(3)
C(14)	4094(14)	–2280(12)	5567(3)
C(15)	5333(14)	–719(13)	5487(3)
C(16)	5526(13)	685(12)	5669(3)
C(17)	951(11)	566(10)	5550(3)
C(18)	–523(12)	–418(12)	5694(3)
C(19)	–1404(13)	–2081(13)	5580(3)
C(20)	–825(13)	–2707(11)	5328(3)
C(21)	665(12)	–1658(11)	5186(3)
C(22)	1577(12)	17(12)	5300(3)
C(23)	–1806(17)	–4569(13)	5213(3)
<i>(b) Molecule (2)</i>			
S(1a)	2311.9(35)	10275.2(33)	9306.3(8)
Si(1a)	2546.4(40)	5449.5(34)	8312.4(10)
Si(2a)	324.8(38)	7154.3(36)	8138.9(9)
Si(3a)	4217.4(36)	9366.9(33)	8315.2(8)
Si(4a)	1958.6(34)	7439.5(31)	8864.3(8)
O(1a)	2026(8)	9304(6)	8962(2)
O(3a)	3388(9)	9959(9)	9520(2)
O(2a)	2831(10)	11961(8)	9229(2)
C(1a)	2201(10)	7331(10)	8407(2)
C(2a)	2392(16)	4878(14)	7853(4)
C(3a)	959(14)	3530(11)	8517(4)
C(4a)	4662(13)	5856(13)	8479(4)
C(5a)	–500(12)	8530(12)	8317(3)
C(6a)	867(15)	7727(13)	7694(3)
C(7a)	–1530(13)	4980(14)	8092(3)
C(8a)	3793(13)	11191(11)	8273(3)
C(9a)	5213(14)	9174(13)	7919(3)
C(10a)	5896(13)	10113(12)	8662(3)
C(11a)	79(11)	5853(10)	9067(3)
C(12a)	396(13)	4957(12)	9310(3)
C(13a)	–935(14)	3787(12)	9481(3)
C(14a)	–2542(15)	3435(12)	9413(3)
C(15a)	–2902(13)	4312(13)	9186(3)
C(16a)	–1572(12)	5524(11)	9009(3)

TABLE 3 (continued)

C(17a)	307(11)	9436(10)	9459(2)
C(18a)	-133(12)	8291(11)	9713(3)
C(19a)	-1732(13)	7588(11)	9825(3)
C(20a)	-2930(12)	7943(12)	9694(3)
C(21a)	-2482(12)	9088(12)	9448(3)
C(22a)	-880(12)	9790(12)	9336(3)
C(23a)	-4706(14)	7133(15)	9809(3)

but such O...Si distances in systems of this general type are commonly accompanied by equally short intramolecular C...Si distances and probably just reflect the severe crowding [7].

3. Experimental details

3.1. Preparation of 1

A mixture of (Me₃Si)₃CSiPh(H)I [1.38 g, 2.97 mmol] and powdered AgSO₃C₆H₄Me-p (1.2 g, 4.3 mmol) in CH₂Cl₂ (40 cm³) was heated under reflux for 0.5 h and the solvent then evaporated off. The residue was kept for 1 h at 120°C under dried N₂ with exclusion of light, then extracted several times with boiling pentane. The combined extracts were filtered and the solvent was evaporated off. The residue was recrystallized from hexane to give 1 (1.35 g, 89%), m.p. 130–131°C. (lit. [1], 130–131°C). ¹H NMR (CDCl₃): δ 0.20 (Me₃Si); 2.35 (*p*-Me); 5.41 (SiH); 7–8 (aromatic H) (slightly different values were reported previously for a solution in CCl₄). Si NMR (CDCl₃, 360 Hz): δ 0.80 (SiMe₃); 2.14 (SiMe₂O). IR as before [1]: *m/z* 493 (15%, M – Me); 431 (15, M – Ph); 337 (30, M – O₃SC₆H₄Me); 322 (10); 247 (30); 187 (20); 174 (15); 135 (30); 90 (20); 73 (100, SiMe₃). (The main peaks are as before [1] but the relative intensities are somewhat different.)

3.2. Crystal structure determination

Suitable crystals were obtained by recrystallization from hexane. A crystal of dimensions *ca.* 0.4 × 0.3 × 0.1 mm was used.

Crystal data: C₂₃H₄₀Si₄O₃S, *M* = 509, triclinic, *a* = 9.083(3), *b* = 9.232(7), *c* = 39.838(23) Å, α = 92.62(6), β = 91.47(4), γ = 118.94(4)°, *U* = 2915.9 Å³, *Z* = 4, *D_c* = 1.2 g cm⁻³, *F*(000) = 1096, Mo-Kα radiation λ = 0.71069 Å, μ = 2.9 cm⁻¹. Space group *P* $\bar{1}$ from successful structure refinement.

Data were collected on an Enraf-Nonius CAD4

diffractometer. Intensities of 10,188 unique reflections with $\pm h + k \pm l$ and $2 < \theta < 25^\circ$ were measured by a $\theta/2\theta$ scan with scan width $\Delta\theta(0.8 + 0.35 \tan \theta)$ and a maximum scan time of 1 min. Correction was made for Lorentz and polarization effects, and also for crystal decay of 10% during the data collection; 3904 reflections with $|F|^2 > 3\sigma(F^2)$ were used in the structure refinement, where $\sigma(F^2) = [\sigma^2(I) + (0.04I)^2]^{1/2}/L_p$.

Direct methods (MULTAN) were used to find the Si atoms and a difference map to find the C, O, and S atoms, and all these atoms were refined by full-matrix least-squares with anisotropic structure factors. Two independent molecules were found. The hydrogen atoms H(1) and H(1a), connected to Si(4) and Si(4a) respectively, were located on a difference map but not refined. The remaining hydrogen atoms were placed at calculated positions (C–H 0.95 Å). All hydrogen atoms were assigned values of *U*_{iso} equal to 1.3*U*_{eq} for the parent carbon atoms. Refinement converged at *R* = 0.075, *R*' = 0.081, with weighting scheme *w* = 1/σ²*F*. Final shift to error ratios were < 0.71. A final difference map had no peaks of > 1.04 e Å⁻³. The structure solution and refinement were carried out on a Microvax II computer with the Enraf-Nonius Structure Determination Package.

Atomic coordinates are listed in Table 3. Lists of thermal parameters and structure factors are available from PBH.

Acknowledgements

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References

- Z.H. Aiube and C. Eaborn, *J. Organomet. Chem.*, 421 (1991) 159.
- R.D. Guthrie, I.D. Jenkins, R. Yamasaki, B.W. Skelton and A.H. White, *J. Chem. Soc., Perkin Trans.*, 1 (1981) 2328.
- V.J. James and J.F. McConnell, *Tetrahedron*, 27 (1971) 5475.
- Mazar-ul-Hague and A. Freestone, *J. Chem. Soc., Perkin Trans.* 2, (1977) 1509.
- S. Shambayati, J.F. Blake, S.G. Wierschke, W.L. Jorgensen and S.L. Schreiber, *J. Am. Chem. Soc.*, 112 (1990) 697.
- S.S. Al-Juaid, C. Eaborn and P.B. Hitchcock, *J. Organomet. Chem.*, 423 (1992) 5, and references therein.
- N.H. Buttrus, C. Eaborn, P.B. Hitchcock, P.D. Lickiss and S.T. Najim, *J. Chem. Soc., Perkin Trans.* 2, (1987) 1753.