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p-Toluenesulfonyl esters of perfluorinated tertiary alcohols: crystal structure determination of the absolute configuration of $C_6F_5(CF_3)_2COSO_2C_6H_4CH_3$

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Abstract

Selected perfluorinated tertiary alcohols can be reacted with p-toluenesulfonyl chloride to form their p-toluenesulfonyl esters $C_6F_5(CF_3)_2COSO_2C_6H_4CH_3$ (**1**), $CF_3C_6F_4OC_6F_4(C_3F_7)(C_8F_{17})COSO_2C_6H_4CH_3$ (**2**) and $(CF_3C_6F_4OC_6F_4)_2(C_7F_{15})COSO_2C_6H_4CH_3$ (**3**). The absolute configuration of **1** is established by X-ray diffraction. © 1998 Elsevier Science S.A. All rights reserved.

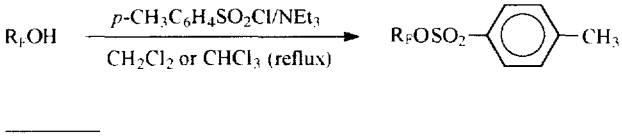
Keywords: Perfluorinated tertiary alcohols; p-Toluenesulfonyl esters; p-Toluenesulfonyl chloride

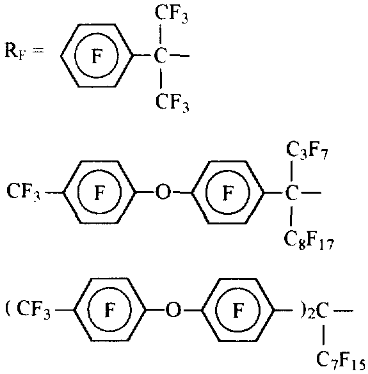
1. Introduction

Perfluorinated tertiary alcohols represent an interesting class of compounds. The increased acidity of the OH hydrogen enables them to be important precursors to a variety of compounds. The fact that they normally exist as liquids, viscous oils or noncrystalline solids, precludes studies in the solid state. p-Toluenesulfonyl esters of alcohols are easily prepared solids [1], and usually form crystalline materials. The ester derivatives also provide enhanced solubility of these highly fluorinated alcohols in common organic solvents. The alcohols usually show decreasing solubility or miscibility in organic solvents as a function of fluorine content, i.e., the number of CF_2 groups present.

2. Results and discussion

The derivatization of selected perfluorinated tertiary alcohols [2,3] to form their p-toluenesulfonyl esters is achieved by heating the alcohols in the presence of triethylamine and an excess of p-toluenesulfonyl chloride.





Unfortunately, ester **2** (highly viscous oil) and **3** (powder) do not form any crystalline materials.

2.1. Crystal structure of $C_6F_5(CF_3)_2COSO_2C_6H_4CH_3$ (1)

The isolation of diffraction quality crystals for **1** allowed us to carry out its single crystal X-ray structural analysis and compare its structure to other p-toluenesulfonyl esters of fluorinated secondary and tertiary alcohols [4,5] which were characterized by X-ray diffraction. Because **1** crystallizes in the non-centrosymmetric space group $Pna2_1$, an attempt was made to determine its absolute configuration. Initial refinement of Flack's parameter required inversion of the atomic coordinates. Upon inversion, Flack's parameter refined to 0.1(2) which suggests the correctness of the absolute configuration.

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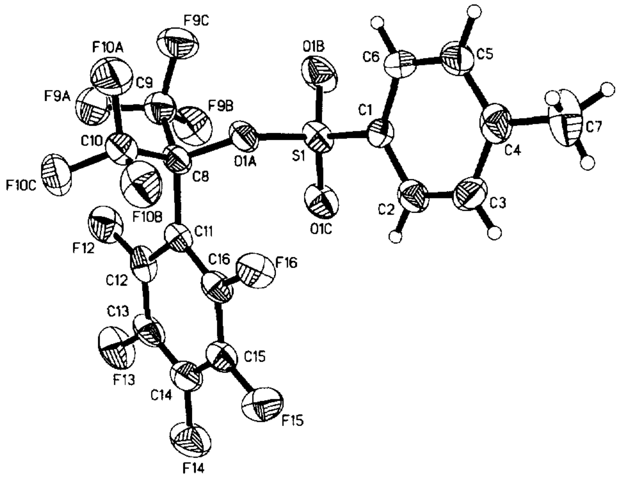

Fig. 1. Crystal structure of $C_6F_5(CF_3)_2COSO_2C_6H_4CH_3$ (**1**) with 50% thermal ellipsoids.

Table 1
Selected bond lengths [Å] and angles [°] for **1**

S(1)–O(1A)	1.633(5)	O(1B)–S(1)–O(1C)	120.2(3)
S(1)–O(1B)	1.414(5)	O(1B)–S(1)–O(1A)	107.1(3)
S(1)–O(1C)	1.419(5)	O(1C)–S(1)–O(1A)	108.1(2)
S(1)–C(1)	1.743(6)	O(1A)–S(1)–C(1)	98.1(3)
O(1A)–C(8)	1.431(7)	O(1B)–S(1)–C(1)	109.8(3)
C(1)–C(6)	1.366(8)	O(1C)–S(1)–C(1)	111.2(3)
C(4)–C(7)	1.508(12)	C(8)–O(1A)–S(1)	124.9(4)
C(5)–C(6)	1.373(9)	C(2)–C(1)–S(1)	120.3(5)
C(8)–C(9)	1.565(10)	C(6)–C(1)–S(1)	119.3(5)
C(8)–C(10)	1.539(11)	C(6)–C(1)–C(2)	120.3(6)
C(8)–C(11)	1.539(8)	O(1A)–C(8)–C(9)	106.9(5)
C(9)–F(9B)	1.307(9)	O(1A)–C(8)–C(10)	102.5(5)
C(10)–F(10B)	1.313(9)	O(1A)–C(8)–C(11)	112.3(5)
C(16)–F(16)	1.346(6)	C(10)–C(8)–C(9)	109.9(7)
		C(11)–C(8)–C(9)	115.5(6)
		C(11)–C(8)–C(10)	108.9(5)
		C(16)–C(11)–C(8)	120.1(5)
		C(16)–C(11)–C(12)	114.3(5)
		F(9B)–C(9)–F(9A)	109.2(8)
		F(16)–C(16)–C(11)	122.0(5)

Fig. 1 shows the molecular structure of **1**. The *p*-toluenesulfonyl and the pentafluorophenyl group are not present in the expected anti position, as is the case for $C_6H_5(CF_3)(R)COSO_2C_6H_4CH_3$ [4] (R=H (**A1**), CH_3 (**A2**), CN (**A3**) and CF_3 (**A4**)) where an anti-conformation exists. Furthermore, a mean plane least square analysis reveals that the aryl groups in **1** are almost coplanar (5.3(3)°). Table 1 lists selected bond lengths and bond angles for **1**. All C–F distances are in the range of 1.307(9)–1.346(6) Å. The C–CF_3 bond distances, i.e., C8–C9 and C8–C10 are 1.565(10) and 1.539(11) Å, are similar to those found in **A4** (1.559(9) and 1.536(9) Å). The C8–C11 bond length of 1.539(8) Å in **1** is longer than the non-fluorinated phenyl analogue **A4** (1.510(8) Å) probably resulting because of steric crowding from the fluorine atoms on the phenyl group and/or repulsive effects between the aromatic fluorine atoms in the *ortho*-position and the CF_3 groups. The C–O bond length of 1.431(7) Å is similar to the bond lengths found in **A3** and **A4** but shorter than in **A1** and **A2**, and in (2-norbornenyl-)(C_2F_5)$COSO_2C_6H_4H_3$ [5]. The S1–O1A bond length of 1.633(5) Å in **1** is longer than the bond lengths observed in **A3** and **A4** (~1.62 Å). This can be attributed to the presence of a more electron deficient tertiary carbon bearing three electron withdrawing groups and to a partially eclipsed conformation with respect to S–O and S–C bonds. In the case where the conformation is staggered as in **A1** and **A2**, the S–O bond length is comparatively shorter at ~1.58 Å.

The geometry around the tertiary carbon atom, C8, deviates from tetrahedral geometry. The most compressed angle is O1A–C8–C10 (102.5(5)°), and the difference between the largest and the smallest angle around C8 is 13.0°. By comparison, this difference is in **A1** 9.6°, **A2** 13.5°, **A3** 11.5° and **A4** 13.4°. Substitution of the phenyl group in **A4** by a pentafluorophenyl group in **1** causes a decrease in the Ph–O–$SO_2C_6H_4CH_3$ angle. This results from a reduction in interatomic repulsions around the sterically crowded C8, thereby bending the *ipso*-carbon of the pentafluorophenyl group, C11, towards the *p*-toluenesulfonyl group. Consequently, some repulsive interactions between the two CF_3 groups are relieved and the CF_3–C8–CF_3 angle in **1** is increased to 109.9(7)° from 107.5(6)° in **A4**.

The packing diagram for **1** along the *c*-axis is shown in Fig. 2. There is a stacking of the pentafluorophenyl groups in the *ab* plane. There are two hydrogen fluorine/oxygen interactions seen in the crystal lattice, i.e., $H7C\cdots F9^a = 2.535$ Å ($a = x, y-1, z$) and $H5\cdots O1B^b = 2.559$ Å ($b = 1-x, 1-y, -1/2+z$), leading to the formation of a chiral crystal structure.

2.2. *Supplementary material available*

Tables listing full data collection and processing parameters, bond distances and bond angles, atomic coordinates, equivalent isotropic and anisotropic displacement coefficients, hydrogen atom coordinates and isotropic displacement coefficients, observed and calculated structure factors, are available from the authors upon request.

3. Experimental

3.1. *General procedures*

Infrared spectra are recorded on a Perkin-Elmer 1710 FT-IR spectrometer between KBr plates as neat liquids or solids as nujol mulls. ^1H and ^{19}F NMR spectra are obtained on a Bruker AC200 FT-NMR instrument using $CDCl_3$ as solvent. Chemical shifts are reported with respect to $(CH_3)_4Si$ or $CFCl_3$. Mass spectra are obtained with a Varian VG 7070 HS mass spectrometer using electron impact (EI) techniques. Elemental analyses are performed by Beller Mikroanalytisches Laboratorium, Göttingen, Germany. *p*-Toluenesulfonyl chloride is recrystallized from petroleum ether, and

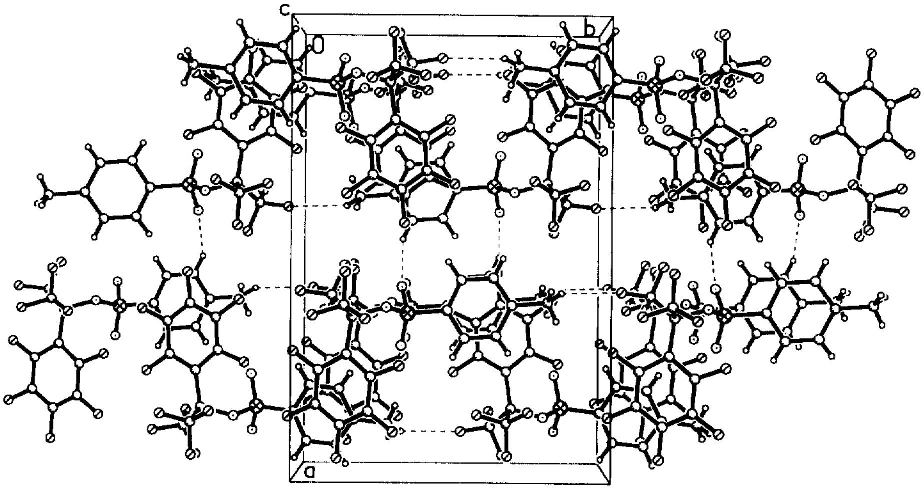

Fig. 2. Crystal packing diagram of $C_6F_5(CF_3)_2COSO_2C_6H_4CH_3$ (**1**) along the *c*-axis.

triethylamine is distilled prior to use. The tertiary alcohols R_FOH are prepared according to literature methods [2,3].

3.2. Preparation and characterization of p-toluenesulfonyl esters $R_FOSO_2C_6H_4CH_3$

3.2.1. $R_F = C_6F_5(CF_3)_2C$ (1)

A mixture consisting of 2.4 mmol $C_6F_5(CF_3)_2COH$ [2], 3.7 mmol *p*-toluenesulfonyl chloride and 7.5 mmol triethylamine in 30 ml dichloromethane is heated under reflux for 3 days. The reaction is monitored by ^{19}F NMR. After removal of all volatile materials, the residue is dissolved in ether and extracted several times with water. The ether layer is then dried over anhydrous Na_2SO_4. Recrystallization from petroleum ether and pumping for 24 h under high vacuum to remove residual *p*-toluenesulfonyl chloride gives colorless crystals of (**1**) (77%, m.p. 95–97°C).

Spectral data are as follows for $C_6F_5(CF_3)_2COSO_2$-$C_6H_4CH_3$ (**1**). IR (Nujol/KBr) 3104w, 1652m, 1597m, 1532s, 1495s, 1386s, 1276s, 1236s br, 1198s, 1185s, 1139s, 1095m, 1049s, 1025m, 997s, 963s, 826s, 785m, 757s, 747m, 724s, 675m, 637w, 598m, 577m, 554m, 545m, 536m, 518m, 456m cm^{-1}; ^{19}F NMR δ 71.3 (CF_3, t, 6F, $^{5}J_{\mathrm{F-F}} = 17.8$ Hz), -131.3 (2-F, m, 2F), -147.2 (4-F, tt, 1F, $^{3}J_{\mathrm{F-F}} = 21.6$ Hz, $^{4}J_{\mathrm{F-F}} = 6.4$ Hz), -159.7 (3-F, m, 2F); ^{1}H NMR δ 7.82 (2-H, d, 2H, $^{3}J_{\mathrm{H-H}} = 8.2$ Hz), 7.38 (3-H, d, 2H), 2.47 (4-CH_3, s, 3H) ppm; MS (EI) |*m/e* (species) intensity| 488 (M^{+}) 14, 317 ($C_6F_5(CF_3)_2C^{+}$) 4. 298 ($C_6F_4(CF_3)_2C^{+}$) 1, 262 ($C_3F_4(CF_3)_2C^{+}$) 7, 217 ($C_7F_7^{+}$) 6, 195 ($C_6F_5CO^{+}$) 9, 167 (C_6F^{+}) 3, 155 ($C_5F_5^{+}$) 95, 139 ($CH_3C_6H_4SO^{+}$) 2, 117 ($C_5F_3^{+}$) 2, 91 ($CH_3C_6H_4^{+}$) 100, 69 (CF_3^{+}) 6. 65 (HSO_2^{+}) 23. Anal. Calcd. for $C_{16}H_7F_{11}O_3S$: C, 39.35; H. 1.45. Found: C, 39.05; H. 1.60.

3.2.2. $R_F = CF_3C_6F_4OC_6F_4(C_3F_7)(C_8F_{17})C$ (2), $(CF_3C_6F_4OC_6F_4)_2(C_7F_{15})C$ (3)

A mixture consisting of 0.2 mmol R_FOH [3], 1.5 mmol *p*-toluenesulfonyl chloride and 1.0 mmol triethylamine in 5 ml chloroform is heated under reflux for 3 days. The reaction is monitored by ^{19}F NMR until complete. After removal of all volatile materials, the residue is dissolved in ether and extracted several times with water. The ether layer is then dried over anhydrous Na_2SO_4. The crude product is repeatedly purified by column chromatography using dichloromethane/hexane mixtures as eluent on silica gel (70–230 mesh). Yields are 65% (**2**) (colorless viscous oil); 67% (**3**) (m.p. 44–46°C, colorless powder).

Spectral data are as follows for $CF_3C_6F_4OC_6F_4(C_3F_7)$-$COSO_2C_6H_4CH_3$ (**2**). IR (liquid/KBr) 3076w, 2962w, 2935m, 1661m, 1641s, 1600m, 1516s, 1488s, 1432m, 1397s, 1345s, 1223s br, 1145s br, 1074m, 1050m, 1000m, 977m, 905w, 877m, 826m, 718m, 705m, 667m, 613w, 557m, 530m cm^{-1}; ^{19}F NMR δ 56.3 (4′-CF_3, t, 3F, $^{4}J_{\mathrm{F-F}} = 22.3$ Hz), -80.8 (CF_3, t, 3F, $^{4}J_{\mathrm{F-F}} = 11.4$ Hz), -81.1 (CF_3, t, 3F, $^{4}J_{\mathrm{F-F}} = 8.9$ Hz), -105.9 (CF_2, br, 2F), -108.0(CF_2, br, 2F), -117.8 (CF_2, br, 2F), -121.5 (CF_2, br, 2F), -121.8 (CF_2, br, 2F), -122.1 (CF_2, br, 2F), -123.0 (CF_2, br, 2F), -126.4 (CF_2, br, 2F), -127.2 (CF_2, br, 2F), -128.7 (2-F, br, 2F), -139.3 (3′-F, m, 2F), -154.5 (3-F, m, 2F), -154.6 (2′-F, br, 2F); ^{1}H NMR δ 7.84 (2-H, d, 2H. $^{3}J_{\mathrm{H-H}} = 8.3$ Hz), 7.36 (3-H, d, 2H), 2.45 (4-CH_3, s, 3H) ppm; MS (EI) [*m/e* (species) intensity| 1151 (M^{+}–H) 5, 1133 (M^{+}–F) 70, 1019 (M^{+}–HF–O–CO–CF_3) 24, 982 (M^{+}–H–C_3F_7) 100, 963 (M^{+}–HF–C_3F_7) 11, 945 (M^{+}–2F–C_3F_7) 7, 814 (M^{+}–F–C_6F_{13}) 21, 409 ($CF_3C_6F_4OC_6F_4CO^{+}$)78, 155 ($C_5F_5^{+}$) 95, 91 ($CH_3C_6H_4^{+}$) 92. Anal. Calcd. for $C_{32}H_7F_{35}O_4S$: C. 33.35; H, 0.61. Found: C, 30.79; H, 0.66.

Spectral data are as follows for $(CF_3C_6F_4OC_6F_4)_2$-$(C_7F_{15})COSO_2C_6H_4CH_3$ (**3**). IR (Nujol/KBr) 1656w, 1645m, 1600w, 1515s, 1488s, 1345s, 1226s br, 1147s, 1077w, 999m, 972m, 877m, 834m, 816w, 772w, 717m, 668m, 618w, 563m, 550m cm^{-1}; ^{19}F NMR δ 56.3 (4′-CF_3, t, 6F, $^{4}J_{\mathrm{F-F}} = 22.3$ Hz), -81.1 (CF_3, t, 3F, $^{4}J_{\mathrm{F-F}} = 9.5$ Hz), -111.0 (CF_2, br, 2F), -116.7 (CF_2, br, 2F), -122.0 (CF_2, br. 4F), -123.0 (CF_2, br, 2F), -126.4 (CF_2, br, 2F), -134.0 (2-F, br, 4F), -139.3 (3′-F, m, 4F), -154.0 (2′-

F, br, 4F), −154.6 (3-F, m, 4F); ^{1}H NMR δ 7.70 (2-H, d, 2H, $^3J_{H-H}$ = 8.3 Hz), 7.34 (3-H, d, 2H), 2.45 (4-CH_3, s, 3H) ppm; MS (EI) [*m/e* (species) intensity] 1295 (M^+–F) 7, 1166 (M^+–3F–$C_6H_4CH_3$) 13, 1143 (M^+–$OSO_2C_6H_4CH_3$) 55, 1124 (M^+–F–$OSO_2C_6H_4CH_3$) 100, 1105 (M^+–2F–$OSO_2C_6H_4CH_3$) 81, 907 (M^+–2F–C_7F_{15}) 16, 856 (M^+–HF–CF_3–C_7F_{15}) 74, 855 (M^+–H–HF–CF_3–C_7F_{15}) 98, 824 (M^+–C_6F_{13}–$OSO_2C_6H_4CH_3$) 39, 409 ($CF_3C_6F_4OC_6F_4$-CO^+) 34, 155 ($C_5F_5^+$) 50, 91 ($CH_3C_6H_4^+$) 48. Anal. Calcd. for $C_{41}H_7F_{37}O_5S$: C, 37.46; H, 0.54. Found: C, 37.51; H, 0.54.

3.3. X-ray crystallographic analysis

The X-ray diffraction data for **1** are collected at 299(2) K on a Siemens 3-circle diffractometer (χ-axis is fixed at 54.74°) equipped with a CCD detector maintained at −54.4(2)°C, using the ω-scan technique [6]. The initial cell constants are determined from reflection data obtained by collecting 60 ten-second frames at a detector resolution of 512×512 pixels. However, the final unit-cell values are based on the least square refinement of all of the observed reflections. A complete hemisphere of data is scanned on omega (0.3°) with a run time of ten-second frames for a total of 1271 frames collected in three sets plus a final set of 50 frames using the SMART software [7]. The crystal decay is monitored from reflection data from 50 frames collected at the beginning and at the end of data collection. Data reduction is accomplished by processing the frames data using SAINT [8] software to give the raw file corrected for Lp/decay. Since the raw file contains information about directional cosines, it is used for empirical absorption correction. The structure is solved by direct methods using SHELXS-90 [9] and refined by the full-matrix least-squares method using SHELXTL Version 5.03 [10]. The final data collection and refinement parameters are listed in Table 2. Determination of the absolute structure is also carried out since this compound crystallizes in the polar space group *Pna*2$_1$. The Flack's parameter refined to 0.1(2) thereby resulting in an accurate determination of the absolute configuration of the crystal structure of **1**. Hydrogen atoms are located from difference Fourier electron density maps and refined with isotropic temperature factors.

Table 2
X-ray crystallographic parameters for **1**

Crystal data	Compound **1**
Empirical formula	$C_{16}H_7F_{11}O_3S$
Formula weight	488.28
Color	Colorless
Crystal size (mm)	0.25 × 0.10 × 0.10
Crystal system	Orthorhombic
Space group	*Pna*2$_1$
Unit cell dimensions (Å)	a = 18.843(2)
	b = 13.0099(13)
	c = 7.4446(8)
Volume (Å^3)	1825.0(3)
Z	4
ρ_{calc} (g cm^{-3})	1.777
F(000)	968
Absorption coefficient (mm^{-1})	0.303
Data Collection	
Radiation employed, λ (Å)	Mo Kα (0.71073)
θ_{max} (°)	23.34
Index ranges	$-20 \le h \le 19$
	$-13 \le k \le 14$
	$-5 \le l \le 8$
No. of data collected	6421
No. of unique data	2174 (R_{int} = 0.0436)
Data with $I > 2\sigma(I)$	1853
$T_{max/min}$	0.9745/0.8955
Solution and refinement	
Parameters refined	309
R, wR (2σ data)	0.0562 (0.0914)
R, wR (all data)	0.0708 (0.0973)
Goodness-of-fit	1.301
Flack's parameter	0.1(2)
Largest difference peak (eA^{-3})	0.170
Largest difference hole (eA^{-3})	−0.176

Acknowledgements

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