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Bond Length and Reactivity. The Effect of β-Fluorine. Structures of the 4-Methyl-, 4-Chloro- and 4-Nitrobenzenesulfonate Esters of 2-Fluoro-2-phenylethanol

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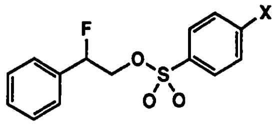
Abstract. 2-Fluoro-2-phenylethyl *p*-toluenesulfonate, (1*a*), $C_{15}H_{15}FO_3S$, $M_r = 294.35$, monoclinic, $P2_1/c$, $a = 11.941$ (3), $b = 7.871$ (3), $c = 15.688$ (3) Å, $\beta = 99.46$ (2)°, $V = 1454.5$ Å^3, $Z = 4$, $D_x = 1.344$ Mg m^{-3}, λ(Cu $K\alpha$) = 1.54179 Å, $\mu = 2.1$ mm^{-1}, $F(000) = 616$, $T = 293$ K. Final $R = 0.074$ for 1509 unique observed reflections. 2-Fluoro-2-phenylethyl 4-chlorobenzenesulfonate, (1*b*), $C_{14}H_{12}ClFO_3S$, $M_r = 314.75$, isostructural with (1*a*), monoclinic, $P2_1/c$, $a = 12.079$ (4), $b = 7.870$ (3), $c = 15.337$ (4) Å, $\beta = 98.90$ (3)°, $V = 1440.5$ Å^3, $Z = 4$, $D_x = 1.451$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.42$ mm^{-1}, $F(000) = 648$, $T = 293$ K. Final $R = 0.053$ for 1752 unique observed reflections. 2-Fluoro-2-phenylethyl 4-nitrobenzenesulfonate, (1*c*), $C_{14}H_{12}FNO_5S$, $M_r = 325.31$, monoclinic, $P2_1/n$, $a = 5.7308$ (8), $b = 24.877$ (5), $c = 10.1784$ (14) Å, $\beta = 91.35$ (2)°, $V = 1450.7$ Å^3, $Z = 4$, $D_x = 1.489$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.25$ mm^{-1}, $F(000) = 672$, $T = 293$ K. Final $R = 0.061$ for 2154 unique observed reflections. The three structures are closely related, with C—F *gauche* to the C—O*X* bond in each case. The terminal C—Ph is either *gauche* [in (1*a*) and (1*b*)] or *anti* [in (1*c*)], and an added complication is positional F disorder for (1*c*). The C—O bond lengths are more sensitive to the 4-substituent than expected. The effect on this bond length of the introduction of the 2-fluorine atom is not clearly defined by the data set available from this and the previous paper.

Introduction. We are interested in the effect on the length of the *R*—O*X* bond of the introduction of a strongly electron-withdrawing substituent on the β-carbon atom of the alkyl group *R*. In the previous paper (Jones, Dölle, Kirby & Parker, 1992) we described two derivatives of 2-fluoro-2-phenylethanol, the 4-nitrophenyl ether and the 4-nitrobenzoate ester, compounds with a moderately poor and a moderately good leaving group XO^-. In this paper we report the structures of three arenesulfonate esters [(1*a*), (1*b*) and (1*c*)] of the same alcohol.



(1*a*) $X = CH_3$
(1*b*) $X = Cl$
(1*c*) $X = NO_2$

Experimental. The esters were prepared from 2-fluoro-2-phenylethanol by the general method described for arenesulfonates in an earlier paper in this series (Kirby, Parker & Raithby, 1992). Purification was by flash column chromatography and recrystallization from CH_2Cl_2–hexane in each case.

2-Fluoro-2-phenylethyl *p*-toluenesulfonate, (1*a*), needles, m.p. 334–335.5 K; and 2-fluoro-2-phenylethyl 4-chlorobenzenesulfonate, (1*b*), platelets, m.p. 336–337 K. In both cases single crystals were grown as irregular colourless blocks by the vapour diffusion technique, using CH_2Cl_2 and hexane.

2-Fluoro-2-phenylethyl 4-nitrobenzenesulfonate, (1*c*), yellow prisms, m.p. 343–345 K. Single crystals obtained by the vapour diffusion technique, using CH_2Cl_2 and hexane, as pale yellow tablets.

(1*a*). A crystal $0.75 \times 0.45 \times 0.35$ mm was mounted in a glass capillary. The crystal was of moderate quality (irregular reflection profiles with imbalanced backgrounds) but no better crystal could be obtained. 4542 reflections ($\pm h$ $+k$ $+l$ and $\pm h$

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$-k$ $-l$) were collected on a Stoe–Siemens diffractometer using monochromated Cu $K\alpha$ radiation ($2\theta_{\max}$ 130°). Three check reflections showed no significant intensity change. No absorption or extinction correction was applied (an attempted absorption correction based on ω scans did not improve the data). Merging equivalents gave 2397 unique reflections ($R_{\rm int}$ 0.048, index ranges after merging h 0 to 13, k 0 to 9, l -18 to 18), of which 1509 with $F > 3\sigma(F)$ were used for all calculations (program system Siemens *SHELXTL-Plus*; Sheldrick, 1990). Cell constants were refined from $\pm\omega$ values of 40 reflections in the 2θ range 61–69°. The structure of (1*a*) was solved by routine direct methods and subjected to anisotropic full-matrix least-squares refinement on F. H atoms were included using a riding model. The final R was 0.074, with wR 0.070. The weighting scheme was $w^{-1} = \sigma^2(F) + gF^2$, with g 0.0003. 181 parameters; S 1.4; max. Δ/σ 0.001; max. $\Delta\rho$ +0.31, -0.34 e Å^{-3}.

(1*b*). As for (1*a*), with the following differences. Crystal 0.6 × 0.4 × 0.4 mm, monochromated Mo $K\alpha$ radiation, $2\theta_{\max}$ 50°, 4399 reflections ($\pm h$ $+k$ $+l$ and some $\pm h$ $-k$ $+l$ equivalents), 2530 unique ($R_{\rm int}$ 0.029), $1752 > 3\sigma(F)$, index ranges h 0 to 14, k 0 to 9, l -18 to 18. Cell constants refined from 52 reflections in the 2θ range 20–24°. R 0.053, wR 0.050, 181 parameters, g 0.00025, S 1.5, max. Δ/σ 0.002; max. $\Delta\rho$ +0.25, -0.37 e Å^{-3}.

(1*c*). As for (1*b*), with the following differences. Crystal 0.9 × 0.6 × 0.15 mm, 5543 reflections ($\pm h$ $+k$ $+l$, $\pm h$ $-k$ $-l$ and some $\pm h$ $-k$ $+l$), 2537 unique ($R_{\rm int}$ 0.016), $2154 > 4\sigma(F)$, index ranges h 0 to 6, k 0 to 29, l -12 to 12. Cell constants from 48 reflections in the 2θ range 20–22°. The CHF group exhibits H/F disorder, with the site occupation factor of the major component 0.783 (6). R 0.061, wR 0.075 for 204 parameters; g 0.00015, S 3.9, max. Δ/σ 0.002; max. $\Delta\rho$ +0.41, -0.29 e Å^{-3}.

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic displacement parameters* (Å$^2 \times 10^3$) *for* (1*a*)

	x	y	z	$U_{\rm eq}$*
C(1)	7945 (5)	−1098 (7)	5078 (3)	59 (2)
O(1)	7684 (3)	596 (5)	5344 (2)	58 (1)
C(2)	7577 (5)	−2356 (8)	5686 (4)	72 (3)
F	6418 (3)	−2291 (6)	5624 (2)	115 (2)
S(1)	8067 (1)	2101 (2)	4805 (1)	59 (1)
O(2)	7783 (4)	3555 (5)	5256 (3)	95 (2)
O(3)	9207 (3)	1834 (5)	4684 (2)	82 (2)
C(11)	7192 (4)	1968 (7)	3797 (3)	48 (2)
C(12)	6077 (4)	2580 (7)	3716 (3)	63 (2)
C(13)	5439 (5)	2626 (8)	2919 (4)	74 (3)
C(14)	5837 (5)	2094 (8)	2187 (4)	72 (3)
C(15)	6956 (5)	1480 (7)	2293 (3)	68 (3)
C(16)	7603 (4)	1420 (6)	3087 (3)	54 (2)
C(17)	5135 (6)	2241 (10)	1304 (4)	113 (3)
C(21)	8120 (4)	−2156 (7)	6628 (3)	52 (2)
C(22)	7650 (5)	−1219 (7)	7202 (4)	62 (2)
C(23)	8151 (6)	−1104 (7)	8047 (4)	71 (3)
C(24)	9165 (6)	−1920 (9)	8322 (4)	75 (3)
C(25)	9647 (5)	−2811 (9)	7743 (5)	84 (3)
C(26)	9132 (5)	−2971 (8)	6904 (4)	67 (2)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic displacement parameters* (Å$^2 \times 10^3$) *for* (1*b*)

	x	y	z	$U_{\rm eq}$*
C(1)	2083 (3)	3871 (4)	4926 (2)	58 (1)
O(1)	2293 (2)	5591 (3)	4648 (1)	55 (1)
C(2)	2451 (3)	2654 (5)	4289 (2)	67 (1)
F	3585 (2)	2729 (4)	4328 (1)	108 (1)
S(1)	1905 (1)	7068 (1)	5215 (1)	52 (1)
O(2)	2134 (2)	8550 (3)	4752 (2)	80 (1)
O(3)	799 (2)	6747 (4)	5378 (2)	74 (1)
C(11)	2815 (2)	6974 (4)	6222 (2)	45 (1)
C(12)	3899 (3)	7572 (5)	6271 (2)	59 (1)
C(13)	4581 (3)	7627 (5)	7070 (3)	68 (2)
C(14)	4183 (3)	7070 (5)	7810 (2)	61 (1)
C(15)	3112 (3)	6454 (5)	7771 (2)	63 (1)
C(16)	2424 (3)	6406 (4)	6970 (2)	55 (1)
Cl	5037 (1)	7196 (2)	8827 (1)	102 (1)
C(21)	1887 (3)	2837 (4)	3349 (2)	51 (1)
C(22)	2344 (3)	3764 (4)	2730 (2)	60 (1)
C(23)	1797 (4)	3882 (5)	1873 (2)	69 (2)
C(24)	785 (3)	3096 (6)	1638 (3)	76 (2)
C(25)	326 (3)	2191 (6)	2240 (3)	82 (2)
C(26)	871 (3)	2051 (5)	3087 (3)	69 (1)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Discussion. Final atom coordinates and derived parameters are given in Tables 1 and 4 for (1*a*), in Tables 2 and 4 for (1*b*) and in Tables 3 and 4 for (1*c*). Plots of (1*a*), (1*b*) and (1*c*), showing the atom-numbering scheme, appear as Figs. 1–3.* The packing shows few unusual features. (1*a*) and (1*b*), however, exhibit short contacts from the H of a CHF group to an O of the SO_2 group [H(2)···O(2) 2.38, 2.40 Å, with corresponding C···O 3.31, 3.34 Å] between molecules related by a y translation. (1*b*) also has a short Cl···F contact of 3.08 Å (F at $1 - x$, $0.5 + y$, $1.5 - z$).

The conformation of the 4-nitro compound (1*c*) resembles those of the 4-nitrophenyl ether and the 4-nitrobenzoate ester described in the previous paper (Jones, Dölle, Kirby & Parker, 1992), with the C—F bond *gauche* and the C—Ph bond *anti* to the C—O*X* bond. Like the 4-nitrobenzoate ester, all three arenesulfonates adopt the extended (*anti*) conformation about the S—O ester bond. However, in the other

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* Lists of structure factors, H-atom parameters and anisotropic thermal parameters, together with complete tables of bond lengths, bond angles and torsion angles, and packing diagrams have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54753 (49 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA0053]

Table 3. *Atomic coordinates* (× 10^4) *and equivalent isotropic displacement parameters* ($Å^2 \times 10^3$) *for* (1*c*)

	x	*y*	*z*	U_{eq}*
S	2297 (2)	2542 (1)	2272 (1)	67 (1)
O(1)	3822 (4)	3051 (1)	2595 (2)	69 (1)
O(2)	−53 (4)	2632 (1)	2622 (3)	91 (1)
O(3)	2837 (5)	2419 (1)	949 (2)	91 (1)
C(11)	3498 (5)	2044 (1)	3323 (3)	52 (1)
C(12)	5553 (5)	1805 (1)	2991 (3)	64 (1)
C(13)	6478 (6)	1407 (1)	3788 (3)	70 (1)
C(14)	5291 (6)	1264 (1)	4893 (3)	66 (1)
C(15)	3234 (6)	1505 (1)	5246 (3)	67 (1)
C(16)	2323 (5)	1904 (1)	4440 (3)	60 (1)
N	6275 (8)	836 (2)	5716 (4)	107 (2)
O(4)	8257 (8)	679 (2)	5488 (4)	163 (2)
O(5)	5166 (7)	687 (2)	6635 (5)	172 (2)
C(1)	4992 (6)	3800 (1)	3910 (3)	76 (1)
C(2)	3605 (7)	3299 (1)	3886 (3)	70 (1)
F	7284 (5)	3707 (2)	3700 (3)	131 (2)
F′	4995 (18)	4004 (4)	2757 (10)	98 (4)
C(21)	4735 (5)	4117 (1)	5144 (3)	59 (1)
C(22)	2777 (6)	4431 (1)	5323 (3)	72 (1)
C(23)	2553 (6)	4738 (1)	6421 (4)	77 (1)
C(24)	4301 (7)	4743 (1)	7369 (3)	78 (1)
C(25)	6240 (7)	4429 (2)	7203 (4)	83 (1)
C(26)	6469 (6)	4110 (1)	6107 (3)	72 (1)

* Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4. *Selected bond lengths* (Å) *and angles* (°) *for* (1*a*)–(1*c*)

Compound (1*a*)			
C(1)—O(1)	1.446 (6)	C(1)—C(2)	1.490 (8)
O(1)—S(1)	1.567 (4)	C(2)—F	1.372 (7)
C(2)—C(21)	1.522 (7)	S(1)—O(2)	1.416 (4)
S(1)—O(3)	1.420 (4)	S(1)—C(11)	1.751 (5)
O(1)—C(1)—C(2)	109.2 (4)	C(1)—O(1)—S(1)	116.5 (3)
C(1)—C(2)—F	109.3 (5)	C(1)—C(2)—C(21)	115.4 (5)
F—C(2)—C(21)	109.2 (5)	O(1)—S(1)—O(2)	103.1 (2)
O(1)—S(1)—O(3)	109.3 (2)	O(2)—S(1)—O(3)	120.0 (3)
O(1)—S(1)—C(11)	105.0 (2)	O(2)—S(1)—C(11)	110.1 (2)
O(3)—S(1)—C(11)	108.3 (2)	S(1)—C(11)—C(12)	118.6 (4)
Compound (1*b*)			
C(1)—O(1)	1.453 (4)	C(1)—C(2)	1.484 (5)
O(1)—S(1)	1.567 (2)	C(2)—F	1.363 (5)
C(2)—C(21)	1.502 (5)	S(1)—O(2)	1.415 (3)
S(1)—O(3)	1.419 (2)	S(1)—C(11)	1.753 (3)
O(1)—C(1)—C(2)	109.0 (3)	C(1)—O(1)—S(1)	116.7 (2)
C(1)—C(2)—F	110.1 (3)	C(1)—C(2)—C(21)	115.6 (3)
F—C(2)—C(21)	109.9 (3)	O(1)—S(1)—O(2)	103.6 (1)
O(1)—S(1)—O(3)	109.6 (1)	O(2)—S(1)—O(3)	119.9 (2)
O(1)—S(1)—C(11)	104.9 (1)	O(2)—S(1)—C(11)	109.4 (1)
O(3)—S(1)—C(11)	108.5 (1)	S(1)—C(11)—C(12)	119.2 (2)
Compound (1*c*)			
S—O(1)	1.569 (2)	S—O(2)	1.419 (3)
S—O(3)	1.422 (2)	S—C(11)	1.766 (3)
O(1)—C(2)	1.459 (4)	C(1)—C(2)	1.477 (5)
C(1)—F	1.355 (5)	C(1)—C(21)	1.493 (5)
C(1)—F′	1.279 (10)		
O(1)—S—O(2)	110.4 (1)	O(1)—S—O(3)	103.8 (1)
O(2)—S—O(3)	120.1 (2)	O(1)—S—C(11)	103.4 (1)
O(2)—S—C(11)	108.5 (2)	O(3)—S—C(11)	109.4 (1)
S—O(1)—C(2)	118.1 (2)	S—C(11)—C(12)	118.7 (2)
C(2)—C(1)—F	112.2 (3)	C(2)—C(1)—C(21)	113.3 (3)
F—C(1)—C(21)	109.7 (3)	O(1)—C(2)—C(1)	108.3 (3)

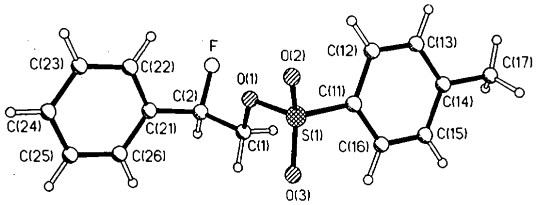

Fig. 1. Molecular structure of (1*a*), showing the atom-numbering scheme.

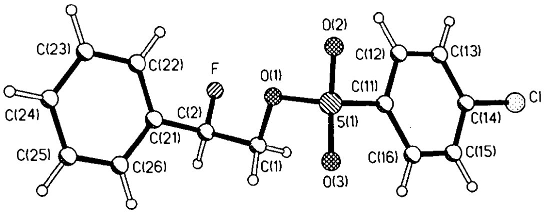

Fig. 2. Molecular structure of (1*b*), showing the atom-numbering scheme.

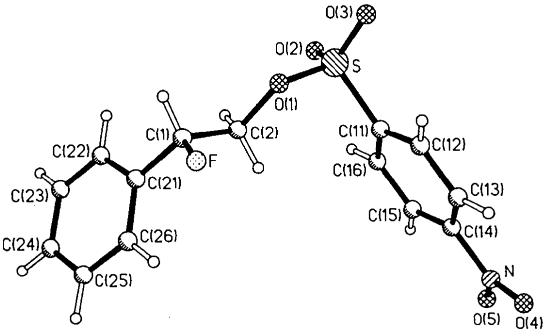

Fig. 3. Molecular structure of (1*c*), showing the atom-numbering scheme.

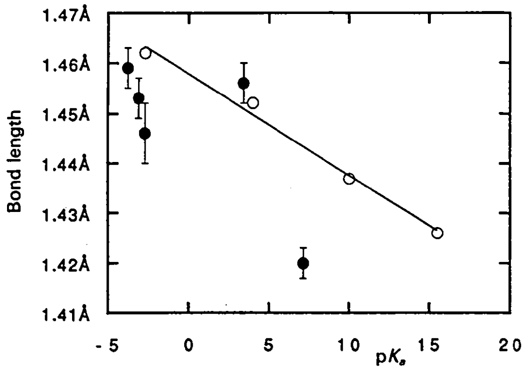

Fig. 4. Plot of C—O*X* bond length for (open circles) aliphatic derivatives RCH_2OX *vs* the pK_a of the conjugate acid (HO*X*) of the leaving group [data from Kirby, Parker & Raithby (1992)]. The filled circles represent the same parameters for derivatives of 2-fluoro-2-phenylethanol, taken from this and the preceding paper (Jones, Dölle, Kirby & Parker, 1992): error bars show bond-length e.s.d.

two arenesulfonates [(1*a*) and (1*b*)] *both* the C—F and the C—Ph bonds are *gauche* to C—OTs in the crystal. It is a reasonable assumption that this reflects packing forces. Alternative explanations, including a possible through-space π–$\sigma^*_{\mathrm{C—O}}$ interaction for the most reactive 4-nitrobenzenesulfonyl compound, are not supported by a detailed examination of the data. Note also that the conformation remains extended enough to keep apart the aromatic rings at the two ends of the molecules.

The C—OSO_2Ar bond lengths, of particular interest for this investigation, do not fit easily into a larger pattern. In particular it is not possible to decide whether the introduction of the β-fluorine atom has a significant effect on the C—O bond length. The available data are compared in Fig. 4. This shows the C—O*X* bond-length data for five derivatives of 2-fluoro-2-phenylethanol (filled circles), taken from this and the preceding paper, on a plot illustrating the least-squares correlation between bond length and leaving group observed for similar primary systems lacking β-F (open circles; Kirby, Parker & Raithby, 1992).

These derivatives of 2-fluoro-2-phenylethanol evidently form a far-from-homogeneous set. The dependence on leaving group pK_a is irregular, and although on average the C—O*X* bond length is shorter in the fluorinated system, it is impossible to quantify any effect, though we can conclude that it is not large. We have found this sort of result previously in systems where the conformation can vary. So we go on to look at the effect of β-fluorine in systems where the conformation is fixed (Jones, Kirby & Parker, 1992).

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Bond Length and Reactivity. The Effect of β-Fluorine. Structures of the 4-Nitrobenzenesulfonate Esters of 2-Fluoroethanol and 2,2,2-Trifluoroethanol

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Abstract. 2-Fluoroethyl 4-nitrobenzenesulfonate, (1), $C_8H_8FNO_5S$, $M_r = 249.22$, monoclinic, $P2_1/c$, $a = 5.842\ (2)$, $b = 8.666\ (3)$, $c = 20.361\ (6)$ Å, $\beta = 96.60\ (2)°$, $V = 1024.0$ Å^3, $Z = 4$, $D_x = 1.616$ Mg m^{-3}, $\lambda(\mathrm{Mo}\ K\alpha) = 0.71069$ Å, $\mu = 0.32$ mm^{-1}, $F(000) = 512$, $T = 293$ K. Final $R = 0.046$ for 1543 unique observed reflections. 2,2,2-Trifluoroethyl 4-nitrobenzenesulfonate, (2), $C_8H_6F_3NO_5S$, $M_r = 285.20$, orthorhombic, $P2_12_12_1$, $a = 5.2568\ (9)$, $b = 5.7559\ (9)$, $c = 36.385\ (7)$ Å, $V = 1100.9$ Å^3, $Z = 4$, $D_x = 1.721$ Mg m^{-3}, $\lambda(\mathrm{Mo}\ K\alpha) = 0.71069$ Å, $\mu = 0.34$ mm^{-1}, $F(000) = 576$, $T = 293$ K. Final $R = 0.046$ for 2179 unique observed reflections. The two related structures have closely similar conformations; C—F is *gauche* to the C—O*X* bond in (1). The C—O*X* bond length [1.463 (4) Å] is substantially longer in the monofluoro compound (1), where it shows little or no effect of the β-fluorine atom; but in the trifluoroethyl derivative (2) there is significant shortening of C—O [1.435 (3) Å], and also of C—C [1.455 (5) Å].

Introduction. We are interested in the effect on the length of the *R*—O*X* bond of the introduction of a strongly electron-withdrawing substituent on the β-carbon atom of the alkyl group *R*. In the two

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