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).

We thank the Fonds der Chemischen Industrie for support.

References

Jones, P. G., Dölle, A., Kirby, A. J. & Parker, J. K. (1992). *Acta Cryst.* C**48**, 835–837.

Jones, P. G., Kirby, A. J. & Parker, J. K. (1992). *Acta Cryst.* C**48**, 852–855.

Kirby, A. J., Parker, J. K. & Raithby, P. R. (1992). *Acta Cryst.* C**48**, 832–834.

Sheldrick, G. M. (1990). *SHELXTL Users Manual.* Revision 4. Nicolet XRD Corporation, Madison, Wisconsin, USA.

Acta Cryst. (1992). C**48**, 841–844

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

By Peter G. Jones

Institut für Anorganische und Analytische Chemie der Technischen Universität, Hagenring 30,
3300 *Braunschweig, Germany*

and Anthony J. Kirby and Jane K. Parker

*University Chemical Laboratory, Cambridge CB*2 1*EW, England*

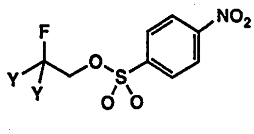
(*Received* 14 *January* 1991; *accepted* 14 *October* 1991)

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}, λ(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}, λ(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

0108-2701/92/050841-04$06.00

previous papers (Jones, Dölle, Kirby & Parker, 1992*a*,*b*) we described five derivatives of 2-fluoro-2-phenylethanol. The C—O*X* bond lengths in these compounds show no simple trend, possibly because of the conformational freedom of this open-chain system. In later papers in this series we report structures of derivatives of 2-fluorocyclohexanol, with fixed conformations. The simplest systems of all are those derived from 2-fluoroethanol, but few useful derivatives are solids at ambient temperatures, and of those we prepared that were solids most gave crystals unsuitable for single-crystal analysis. We report here the structures of two exceptions, the 4-nitrobenzenesulfonates (1) of 2-fluoroethanol itself, and (2) of 2,2,2-trifluoroethanol.



(1) $Y = H$
(2) $Y = F$

Experimental. The esters were prepared 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-Fluoroethyl 4-nitrobenzenesulfonate (1) had m.p. 391–392 K. Single crystals were obtained as orange–yellow prisms by the vapour diffusion technique, using CH_2Cl_2 and hexane.

2,2,2-Trifluoroethyl 4-nitrobenzenesulfonate (2) gave yellow platelets, m.p. 357.5–358 K. Single crystals grown by the liquid diffusion technique, using CH_2Cl_2 and hexane, were yellow tablets.

Data in the following section refer to compound (1), and in most cases apply to (2) also. Where values for (2) are different, they are given in square brackets.

A crystal 0.7 × 0.4 × 0.25 [0.8 × 0.6 × 0.4] mm was mounted in a glass capillary. 3617 [3172] reflections ($\pm h\ +k\ \pm l$ [$+h\ +k\ +l$ and $-h\ -k\ -l$]) were collected on a Siemens *R*3 [Stoe–Siemens] diffractometer using monochromated Mo $K\alpha$ radiation ($2\theta_{\max}$ 50 [55]°). Three check reflections showed no significant intensity change. No absorption correction was applied. Merging equivalents gave 1811 [2521] unique reflections ($R_{\rm int}$ 0.021 [0.016]), index ranges after merging h 0 to 6 [0 to 6], k 0 to 10 [0 to 7], l −24 to 24 [−46 to 46]), of which 1543 [2179] with $F > 4\sigma(F)$ were used for all calculations (program system Siemens *SHELXTL-Plus*; Sheldrick, 1990). The orientation matrix [cell constants] was [were] refined from diffractometer [$\pm\omega$] angles of 32 [52] reflections in the range 2θ 20–24°.

The structures were 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 absolute structure of (2) was determined by an η refinement: $\eta = +0.9\,(2)$. The final *R* was 0.046 [0.046], with *wR* 0.057 [0.053]. The weighting scheme was $w^{-1} = \sigma^2(F) + 0.0002F^2$. 145 [163] parameters; *S* 2.8 [2.1]; max. Δ/σ 0.001 [0.002]; max. $\Delta\rho$ +0.5, −0.41 [+0.42, −0.34] e Å^{-3}. The residual electron density for (1) is higher than usual for a centrosymmetric organic compound, and may indicate slight disorder.

Discussion. Final atom coordinates for (1) and (2) are given in Tables 1 and 3, and derived parameters in Tables 2 and 4. Plots of (1) and (2), showing the atom-numbering schemes, appear as Figs. 1 and 2.* The shortest non-bonded distances (excluding H atoms; symmetry operators refer to the second atoms) are: (1) N···O(3) 3.10 ($-x$, $1-y$, $1-z$); (2) F(2)···F(1) 3.08, F(2)···F(2) 3.12 ($2-x$, $-0.5+y$, $0.5-z$), O(5)···O(4) 3.09, O(4)···N 3.11 Å ($0.5+x$, $0.5-y$, $-z$).

These are simple compounds, with few conformational isomers. The C—F bond in (1) is *gauche* to the C—O bond, as expected and found in all the acylic 2-fluoroethanol derivatives we have examined. (2) adopts the expected staggered conformation; thus one C—F bond is *anti*, and two *gauche* to C—O. The dihedral angle about the C—O bond itself is significantly shorter [S—O(1)—C(1)—C(2) 156.8 (2)° in (1) and 166.5 (2)° in (2)] than in various 2-fluoro-2-phenylethyl esters described previously [dihedral angles generally about 177° (Jones, Dölle, Kirby & Parker, 1992*a*,*b*)], probably for steric reasons.

The C—OS bond length in (1) is 1.463 (4) Å, the same length, within experimental error, as that in the *p*-toluenesulfonate of 2-phenylethanol. Once again there is little evidence that the introduction of the 2-fluorine atom has any significant effect; though one could argue that an increase in bond length corresponding to that observed in going from the tosyl to the 4-nitrobenzenesulfonyl derivative ester of 2-fluoro-2-phenylethanol (Jones, Dölle, Kirby & Parker, 1992*b*) has been neutralized. On the other hand, the high temperature factors associated with this structure could lead to an artificial reduction in apparent bond lengths. However, the introduction of three F atoms clearly has a substantial effect. The C—O bond in the trifluoroethyl derivative (2), is significantly shortened [1.435 (3) Å], compared with the bonds to similar leaving groups discussed above.

---

* Lists of structure factors, H-atom parameters and anisotropic thermal parameters, torsion angles and packing diagrams have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54754 (26 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA0054]

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

	x	y	z	U_{eq}*
S	1947 (1)	5407.4 (8)	3674.4 (3)	42 (1)
O(1)	3538 (3)	6529 (2)	3340 (1)	47 (1)
O(2)	27 (4)	4985 (3)	3220 (1)	60 (1)
O(3)	3463 (4)	4257 (2)	3971 (1)	56 (1)
C(11)	943 (4)	6516 (3)	4310 (1)	37 (1)
C(12)	2299 (5)	6623 (3)	4914 (1)	44 (1)
C(13)	1518 (5)	7450 (3)	5418 (1)	46 (1)
C(14)	− 608 (5)	8148 (3)	5307 (1)	42 (1)
C(15)	− 1958 (5)	8080 (3)	4708 (2)	48 (1)
C(16)	− 1175 (5)	7240 (3)	4205 (1)	46 (1)
N	− 1462 (5)	9015 (3)	5855 (1)	55 (1)
O(4)	− 3359 (5)	9607 (3)	5751 (1)	82 (1)
O(5)	− 239 (5)	9085 (3)	6378 (1)	80 (2)
C(1)	2583 (5)	7599 (4)	2825 (2)	54 (1)
C(2)	4432 (7)	7994 (6)	2433 (2)	86 (2)
F	6200 (5)	8665 (4)	2767 (2)	148 (2)

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

Table 2. *Bond lengths* (Å) *and angles* (°) *for* (1)

S—O(1)	1.555 (2)	S—O(2)	1.417 (2)
S—O(3)	1.422 (2)	S—C(11)	1.766 (3)
O(1)—C(1)	1.463 (4)	C(11)—C(12)	1.387 (3)
C(11)—C(16)	1.382 (4)	C(12)—C(13)	1.372 (4)
C(13)—C(14)	1.377 (4)	C(14)—C(15)	1.375 (4)
C(14)—N	1.480 (4)	C(15)—C(16)	1.377 (4)
N—O(4)	1.218 (4)	N—O(5)	1.212 (4)
C(1)—C(2)	1.454 (5)	C(2)—F	1.306 (5)
O(1)—S—O(2)	110.1 (1)	O(1)—S—O(3)	104.4 (1)
O(2)—S—O(3)	120.3 (1)	O(1)—S—C(11)	104.3 (1)
O(2)—S—C(11)	108.3 (1)	O(3)—S—C(11)	108.2 (1)
S—O(1)—C(1)	120.8 (2)	S—C(11)—C(12)	118.8 (2)
S—C(11)—C(16)	120.0 (2)	C(12)—C(11)—C(16)	121.2 (2)
C(11)—C(12)—C(13)	119.5 (2)	C(12)—C(13)—C(14)	118.6 (2)
C(13)—C(14)—C(15)	122.8 (3)	C(13)—C(14)—N	118.4 (2)
C(15)—C(14)—N	118.8 (2)	C(14)—C(15)—C(16)	118.5 (3)
C(11)—C(16)—C(15)	119.5 (2)	C(14)—N—O(4)	117.5 (3)
C(14)—N—O(5)	118.1 (3)	O(4)—N—O(5)	124.4 (3)
O(1)—C(1)—C(2)	107.3 (3)	C(1)—C(2)—F	114.4 (3)

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

	x	y	z	U_{eq}*
S	3624 (1)	6639 (1)	1368.6 (2)	58 (1)
O(1)	5329 (4)	8346 (3)	1605.4 (5)	60 (1)
O(2)	1862 (5)	8121 (4)	1193.7 (6)	81 (1)
O(3)	2773 (5)	4804 (4)	1600.8 (5)	76 (1)
C(1)	6854 (6)	7394 (5)	1895.8 (7)	63 (1)
C(2)	7702 (9)	9348 (6)	2118.1 (9)	83 (1)
F(1)	8988 (7)	10894 (5)	1934.7 (7)	145 (1)
F(2)	9124 (7)	8662 (5)	2394.8 (7)	154 (1)
F(3)	5835 (9)	10437 (6)	2271.6 (8)	163 (2)
C(11)	5801 (5)	5547 (4)	1045.8 (6)	48 (1)
C(12)	6333 (6)	6822 (5)	728.4 (7)	55 (1)
C(13)	8152 (6)	6046 (5)	492.2 (7)	58 (1)
C(14)	9384 (5)	4001 (5)	572.4 (7)	52 (1)
C(15)	8868 (6)	2689 (5)	875.1 (7)	59 (1)
C(16)	7011 (5)	3476 (5)	1117.5 (7)	55 (1)
N	11455 (5)	3192 (5)	324.3 (7)	68 (1)
O(4)	12166 (5)	4509 (5)	82.8 (6)	87 (1)
O(5)	12302 (5)	1263 (5)	376.5 (7)	98 (1)

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

Table 4. *Bond lengths* (Å) *and angles* (°) *for* (2)

S—O(1)	1.585 (2)	S—O(2)	1.411 (2)
S—O(3)	1.424 (2)	S—C(11)	1.756 (3)
O(1)—C(1)	1.435 (3)	C(1)—C(2)	1.455 (5)
C(2)—F(1)	1.302 (5)	C(2)—F(2)	1.314 (5)
C(2)—F(3)	1.292 (6)	C(11)—C(12)	1.396 (3)
C(11)—C(16)	1.376 (4)	C(12)—C(13)	1.361 (4)
C(13)—C(14)	1.375 (4)	C(14)—C(15)	1.363 (4)
C(14)—N	1.489 (4)	C(15)—C(16)	1.392 (4)
N—O(4)	1.219 (4)	N—O(5)	1.211 (4)
O(1)—S—O(2)	104.0 (1)	O(1)—S—O(3)	108.3 (1)
O(2)—S—O(3)	120.6 (1)	O(1)—S—C(11)	102.5 (1)
O(2)—S—C(11)	110.0 (1)	O(3)—S—C(11)	109.6 (1)
S—O(1)—C(1)	118.7 (2)	O(1)—C(1)—C(2)	106.6 (3)
C(1)—C(2)—F(1)	113.7 (3)	C(1)—C(2)—F(2)	111.6 (3)
F(1)—C(2)—F(2)	107.6 (4)	C(1)—C(2)—F(3)	112.5 (4)
F(1)—C(2)—F(3)	106.5 (3)	F(2)—C(2)—F(3)	104.3 (3)
S—C(11)—C(12)	119.7 (2)	S—C(11)—C(16)	119.0 (2)
C(12)—C(11)—C(16)	121.3 (2)	C(11)—C(12)—C(13)	119.4 (2)
C(12)—C(13)—C(14)	118.5 (2)	C(13)—C(14)—C(15)	123.5 (3)
C(13)—C(14)—N	118.9 (2)	C(15)—C(14)—N	117.5 (3)
C(14)—C(15)—C(16)	118.1 (3)	C(11)—C(16)—C(15)	119.1 (2)
C(14)—N—O(4)	117.8 (3)	C(14)—N—O(5)	117.4 (3)
O(4)—N—O(5)	124.8 (3)		

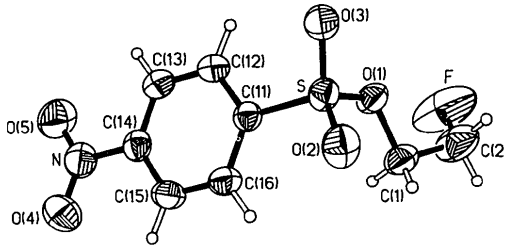


Fig. 1. Molecular structure of (1), showing the atom-numbering scheme.

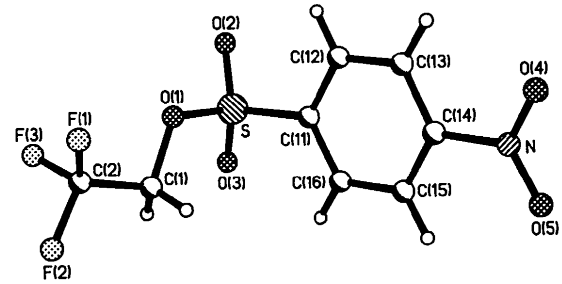


Fig. 2. Molecular structure of (2), showing the atom-numbering scheme.

This is the case also for the C—C single bond, which at 1.455 (5) Å is notably shorter than the 'standard' single-bond length (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987) of 1.530 Å. (Note, however, the high temperature factors associated with the CF_3 group.)

Data for a single compound are not a reliable guide to the significance or otherwise of an effect of this sort. Thus data for the closely related 2,2,3,3,3-pentafluoropropyl 4-chlorobenzoate [C—CO

1.492 (6) Å (Touilloux, Germain, Declercq, Van Meerssche, Wilante & Leroy, 1982)] are not consistent with an important general effect on C—C. The C—O bond length in this pentafluoro compound [1.441 (5) Å] does appear to be shorter than expected for a primary ester [see the plots in the previous papers (Jones, Dölle, Kirby & Parker, 1992*a*,*b*)]. As usual, convincing evidence for a crystal structure correlation requires either the analysis of a large set of relevant data; or the collection of data for a small but homogeneous set of compounds, designed specifically to address a key question. In the following papers we examine the effects of the introduction of a β-fluorine atom on the C—O*X* bond lengths of two homogeneous series of compounds of fixed conformation.

We thank the Fonds der Chemischen Industrie for support.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–S19.

Jones, P. G., Dölle, A., Kirby, A. J. & Parker, J. K. (1992*a*). *Acta Cryst.* C**48**, 838–841.

Jones, P. G., Dölle, A., Kirby, A. J. & Parker, J. K. (1992*b*). *Acta Cryst.* C**48**, 835–837.

Kirby, A. J., Parker, J. K. & Raithby, P. R. (1992). *Acta Cryst.* C**48**, 832–834.

Sheldrick, G. M. (1990). *SHELXTL Users Manual.* Revision 4. Nicolet XRD Corporation, Madison, Wisconsin, USA.

Touilloux, R., Germain, G., Declercq, J.-P., Van Meerssche, M., Wilante, C. & Leroy, G. (1982). *J. Fluorine Chem.* **20**, 3–8.

Acta Cryst. (1992). C**48**, 844–847

Bond Length and Reactivity. Structures of the 4-Phenylbenzoate Esters of *cis*- and *trans*-4-*tert*-Butylcyclohexanol

By Peter G. Jones

Institut für Anorganische und Analytische Chemie der Technischen Universität, Hagenring 30,
3300 *Braunschweig, Germany*

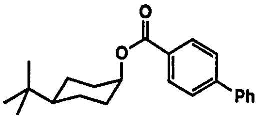
and Anthony J. Kirby and Jane K. Parker

*University Chemical Laboratory, Cambridge CB*2 1*EW, England*

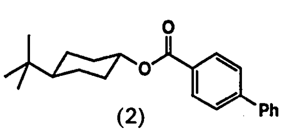
(*Received* 14 *January* 1991; *accepted* 14 *October* 1991)

Abstract. *cis*-4-*tert*-Butylcyclohexyl 4-phenylbenzoate, (1), $C_{23}H_{28}O_2$, $M_r = 336.48$, monoclinic, $P2_1/n$, $a = 6.376$ (2), $b = 14.317$ (7), $c = 21.792$ (8) Å, $\beta = 92.64$ (3)°, $V = 1987$ Å^3, $Z = 4$, $D_x = 1.125$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.07$ mm^{-1}, $F(000) = 728$, $T = 293$ K. Final $R = 0.041$ for 2534 unique observed reflections. *trans*-4-*tert*-Butylcyclohexyl 4-phenylbenzoate, (2), $C_{23}H_{28}O_2$, $M_r = 336.48$, monoclinic, $P2_1/n$, $a = 12.951$ (2), $b = 10.836$ (2), $c = 14.022$ (2) Å, $\beta = 102.66$ (2)°, $V = 1920.1$ Å^3, $Z = 4$, $D_x = 1.164$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.07$ mm^{-1}, $F(000) = 728$, $T = 293$ K. Final $R = 0.041$ for 2351 unique observed reflections. The compounds are axial and equatorial isomers, with closely similar geometries around the ester group. In particular, the ester C—O bonds are almost equal. A standard C—O bond length is defined for equatorial esters, as a function of the strength of the acid involved. The biphenyl unit of (2), unusually, is planar.

Introduction. Our work reported in previous papers of this series (Jones, Dölle, Kirby & Parker, 1992*a*,*b*; Jones, Kirby & Parker, 1992) has shown that the effect on the length of the C—O*X* bond of the introduction of a β-fluorine atom is not large. A complication in a given acyclic system is that the conformation may vary from one derivative to another. So we have prepared a series of derivatives of 2-fluorocyclohexanol, and of its 4-*tert*-butyl derivative, which can be expected to adopt predictable, fixed, conformations. We report here structures for the axial and equatorial isomers, *cis*- and *trans*-4-*tert*-butylcyclohexyl 4-phenylbenzoate (1) and (2).



(1)



(2)

0108-2701/92/050844-04$06.00