Jones, P. G., Kirby, A. J. & Parker, J. K. (1992*d*). *Acta Cryst.* C48, 849–851.
Jones, P. G., Kirby, A. J. & Parker, J. K. (1992*e*). *Acta Cryst.* C48, 852–855.
Jones, P. G., Kirby, A. J. & Parker, J. K. (1992*f*). *Acta Cryst.* C48, 864–866.
Jones, P. G., Kirby, A. J. & Parker, J. K. (1992*g*). *Acta Cryst.* C48, 824–826.
Kirby, A. J., Parker, J. K. & Raithby, P. R. (1992). *Acta Cryst.* C48, 832–834.
Sheldrick, G. M. (1990). *SHELXTL Users Manual.* Revision 4. Nicolet XRD Corporation, Madison, Wisconsin, USA.

Acta Cryst. (1992). C48, 864–866

Bond Length and Reactivity. The Effect of β-Fluorine. Structure of the Methanesulfonate Ester of *trans,trans*-5-*tert*-Butyl-2-fluorocyclohexanol

By Peter G. Jones

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

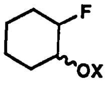
and Anthony J. Kirby and Jane K. Parker

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

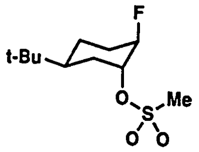
(*Received* 14 *January* 1991; *accepted* 14 *October* 1991)

Abstract. (1*RS*,2*RS*,5*SR*)-5-*tert*-Butyl-2-fluorocyclohexyl methanesulfonate, $C_{11}H_{21}FO_3S$, $M_r = 252.35$, orthorhombic, *Pbca*, $a = 10.249$ (2), $b = 8.853$ (2), $c = 29.687$ (4) Å, $V = 2693$ Å^3, $Z = 8$, $D_x = 1.245$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.23$ mm^{-1}, $F(000) = 1088$, $T = 293$ K. Final $R = 0.058$ for 1623 unique observed reflections. The compound is an isomer of the sulfonate ester described in the previous paper [Jones, Kirby & Parker (1992). *Acta Cryst.* C48, 859–864] with the axial fluorine and mesylate substituents reversed. It is thus a second compound strengthening the data on the effect on C—O*X* bond length of an antiperiplanar β-fluorine. Both the absolute length of the C—O*X* bond, and its sensitivity to electron-withdrawal in *X*, are reduced when the fluorine is present.

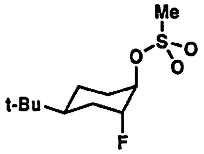
Introduction. In the previous papers in this series we have reported the structures of a total of nine derivatives (1) of cyclohexanol with fluorine in the 2-position in a geometrically defined, *gauche* or antiperiplanar relationship to the C—O*X* bond. The introduction of the 2-fluorine substituent has little or no effect on the length of the C—O*X* bond in the carboxylic or phosphate esters, but a significant shortening is observed for sulfonates. We report here the structure of the tenth, and last, compound in the series, the mesylate (2). This is isomeric with the *cis,trans*-4-*tert*-butyl-2-fluorocyclohexyl methanesulfonate (3) described in the previous paper, with the axial mesylate and fluorine substituents reversed, so is expected to have similar structural parameters in the region of interest.



(1)



(2)



(3)

Experimental. *trans,trans*-5-*tert*-Butyl-2-fluorocyclohexanol was prepared, as a mixture with *cis,trans*-4-*tert*-butyl-2-fluorocyclohexanol, as described in a previous paper (Jones, Kirby & Parker, 1992*b*). The mixture of mesylates (Jones, Kirby & Parker, 1992*a*) was separated by recrystallization, with the *cis,trans* isomer (3) crystallizing first, from CH_2Cl_2–hexane. The remaining yellow oil solidified on standing under pentane at 268 K. Recrystallization from CH_2Cl_2–pentane at 268 K gave *trans,trans*-5-*tert*-Butyl-2-fluorocyclohexyl methanesulfonate (2), m.p. 331–335 K. Single crystals were obtained as colourless tablets by diffusing liquid pentane into a solution in CH_2Cl_2.

A crystal 0.7 × 0.4 × 0.2 mm was mounted in a glass capillary. 3100 reflections ($+h$ $+k$ $\pm l$ and some $-h$ $-k$ $+l$ equivalents) were collected on a Stoe–Siemens diffractometer using monochromated Mo $K\alpha$ radiation ($2\theta_{\max}$ 50°). Three check reflections showed no significant intensity change. No absorption or extinction correction was applied. Merging

0108-2701/92/050864-03$06.00

equivalents gave 2366 unique reflections (R_{int} 0.017, index ranges after merging h 0 to 12, k 0 to 10, l 0 to 35), of which 1623 with $F > 4\sigma(F)$ were used for all calculations (program system Siemens *SHELXTL-Plus*; Sheldrick, 1990). Cell constants were refined from $\pm\,\omega$ values of 50 reflections in the range 20–30°. The structure 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 0.058, with wR 0.057. The weighting scheme was $w^{-1} = \sigma^2(F) + 0.0003F^2$. 145 parameters; S 1.8; max. Δ/σ 0.001; max. $\Delta\rho$ +0.36, −0.33 e Å^{-3}.

Discussion. Final atomic coordinates for (2) are given in Table 1,* and derived parameters in Table 2. A plot of (2), showing the atom-numbering scheme, appears as Fig. 1. Short (< 3.3 Å) non-bonded contacts between non-H atoms are: O(3)···O(2) 3.28 (second atom at $0.5 + x$, y, $1.5 - z$), C(11)···O(3) 3.26 Å ($1 - x$, $0.5 + y$, $1.5 - z$).

The axial F atom shows no positional disorder in this compound, which has a fundamentally different geometry from our other structures with axial F, described in the two previous papers (Jones, Kirby & Parker, 1992*a,b*).

As in (3), the C—F bond is fixed antiperiplanar to C—O by the chair conformation of the ring [dihedral angle C—C—C—F −172.1 (2)°], with the chair flattening slightly to relieve 1,3-diaxial interactions. The geometry and conformation of the mesylate group are closely similar to those observed for the same group in (3) (Jones, Kirby & Parker, 1992*a*) and in the parent compound, *cis*-4-*tert*-butylcyclohexyl mesylate (Jones, Kirby & Parker, 1992*c*). The measured C—F bond lengths do not differ significantly in the two compounds [1.413 (4) Å in (2), 1.406 (2) Å in (3)], supporting our conclusion that the positional disorder of F in (3) and other derivatives of the same alcohol does not have a measurable effect on the observed bond lengths.

The C—OX bond length in (2) is 1.475 (4) Å, a value larger by just over two standard deviations than that [1.465 (5) Å] measured for the corresponding bond in (3). So we take the mean, 1.470 (5) Å, as our best value for the length of the axial C—O bond in a cyclohexyl sulfonate ester with an antiperiplanar F atom in the 2-position.

We can now compare C—OX bond lengths for the series of four different leaving groups OX, using the data for the five diaxial compounds measured in this and the previous paper (Jones, Kirby & Parker, 1992*a*). This bond length depends, as expected (Jones & Kirby, 1979, 1984), on the electron-withdrawing capability of the group X. The plot of the length of the C—OX bond *vs* the pK_a of the conjugate acid,

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

	x	y	z	U_{eq}*
S	3237.5 (7)	3621 (1)	7665.6 (3)	42 (1)
O(1)	3605 (2)	4527 (3)	8100.5 (7)	46 (1)
O(2)	1855 (2)	3511 (3)	7685.1 (8)	57 (1)
O(3)	3992 (2)	2273 (3)	7638.7 (8)	60 (1)
F	6324 (2)	6667 (3)	8494.2 (8)	87 (1)
C(1)	4989 (3)	4744 (5)	8220 (1)	47 (1)
C(2)	4995 (3)	6304 (5)	8429 (1)	62 (1)
C(3)	4308 (4)	6315 (5)	8873 (1)	71 (2)
C(4)	4787 (4)	5094 (5)	9193 (1)	64 (1)
C(5)	4689 (3)	3523 (4)	8986 (1)	46 (1)
C(6)	5441 (3)	3530 (4)	8537 (1)	46 (1)
C(7)	5082 (4)	2224 (5)	9304 (1)	62 (1)
C(8)	6480 (4)	2425 (7)	9483 (1)	94 (2)
C(9)	4138 (5)	2187 (6)	9702 (1)	96 (2)
C(10)	5020 (6)	721 (5)	9060 (2)	105 (2)
C(11)	3673 (3)	4813 (4)	7227 (1)	49 (1)

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

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

S—O(1)	1.566 (2)	S—O(2)	1.422 (2)
S—O(3)	1.424 (2)	S—C(11)	1.734 (3)
O(1)—C(1)	1.475 (4)	F—C(2)	1.413 (4)
C(1)—C(2)	1.513 (6)	C(1)—C(6)	1.502 (5)
C(2)—C(3)	1.495 (5)	C(3)—C(4)	1.521 (6)
C(4)—C(5)	1.525 (5)	C(5)—C(6)	1.538 (4)
C(5)—C(7)	1.541 (5)	C(7)—C(8)	1.538 (6)
C(7)—C(9)	1.527 (6)	C(7)—C(10)	1.516 (6)

O(1)—S—O(2)	104.0 (1)	O(1)—S—O(3)	110.2 (1)
O(2)—S—O(3)	119.1 (2)	O(1)—S—C(11)	104.2 (1)
O(2)—S—C(11)	109.2 (2)	O(3)—S—C(11)	109.1 (2)
S—O(1)—C(1)	119.8 (2)	O(1)—C(1)—C(2)	102.8 (3)
O(1)—C(1)—C(6)	110.7 (3)	C(2)—C(1)—C(6)	113.3 (3)
F—C(2)—C(1)	105.5 (3)	F—C(2)—C(3)	109.3 (3)
C(1)—C(2)—C(3)	111.4 (3)	C(2)—C(3)—C(4)	113.2 (3)
C(3)—C(4)—C(5)	112.0 (3)	C(4)—C(5)—C(6)	108.2 (3)
C(4)—C(5)—C(7)	114.5 (3)	C(6)—C(5)—C(7)	113.7 (3)
C(1)—C(6)—C(5)	113.0 (3)	C(5)—C(7)—C(8)	111.7 (3)
C(5)—C(7)—C(9)	109.0 (3)	C(8)—C(7)—C(9)	108.9 (3)
C(5)—C(7)—C(10)	110.6 (3)	C(8)—C(7)—C(10)	107.8 (4)
C(9)—C(7)—C(10)	108.9 (4)		

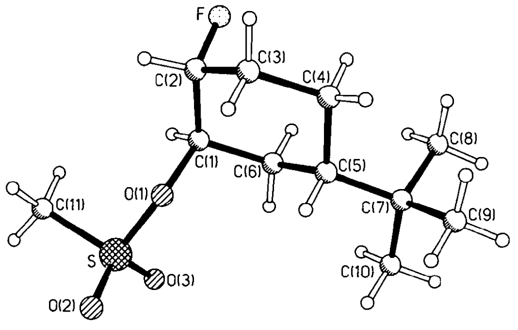


Fig. 1. Molecular structure of (1), showing the atom-numbering scheme.

---

* Lists of structure factors, H-atom parameters and anisotropic thermal parameters, torsion angles and the packing diagram have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54761 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA0061]

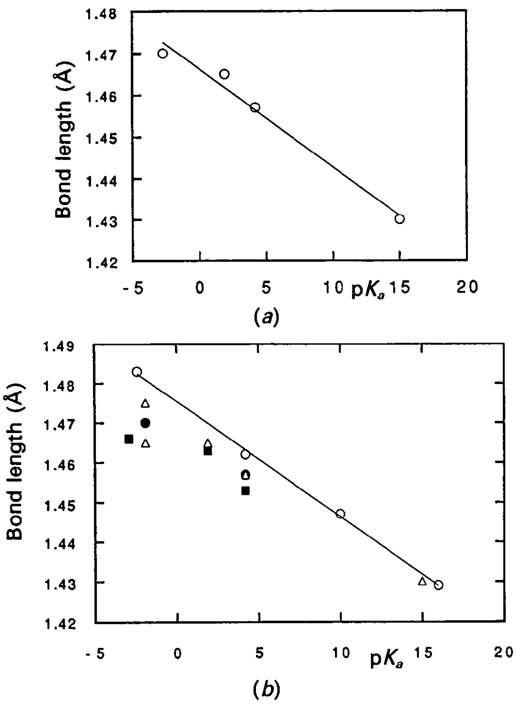


Fig. 2. (a) Plot of the C—O*X* bond length for compounds (1), with F and O*X* *trans* diaxial, *vs* the pK_a of the conjugate acid (HO*X*) of the leaving group. Data for compounds (1)–(3) of the previous paper (Jones, Kirby & Parker, 1992*a*), and for the two mesylates (2) and (3) (mean value, see text). The (least-squares) line drawn fits the equation:

$$\text{Bond length (Å)} = 1.466 - 2.35 \times 10^{-3}\text{p}K_a,$$

with a correlation coefficient, $r = 0.990$. (b) Plot of C—O*X* bond length for derivatives R_2CHO*X* of cyclohexanol *vs* the pK_a of the conjugate acid (HO*X*) of the leaving group. Open circles represent data for unsubstituted compounds. Other symbols represent the same parameter for derivatives of 2-fluorocyclohexanol; open triangles for diaxial compounds (data from this and the previous paper): filled symbols for equatorial O*X* (data from Jones, Kirby & Parker, 1992*b*,*d*). The F atom is either axial (circles) or equatorial (squares), and thus *gauche* to C—O*X*.

HO*X*, of the leaving group gives a good straight line (Fig. 2*a*). Both the intercept and the slope of this correlation are significantly smaller than those found for equatorial derivatives of cyclohexanol (Jones, Kirby & Parker, 1992*c*). The comparison of these correlations is a more reliable guide than comparing individual structures: Fig. 2(*b*) shows all our data, plotted as for Fig. 2(*a*), for nine axial and equatorial 2-fluorocyclohexanol derivatives, taken from this and the previous three papers, compared with bond-length data for the same range of derivatives of the non-fluorinated parent systems. Clearly the effect of β-fluorine, though generally small, is real and, furthermore, it is independent of geometry, as suggested in the previous paper (Jones, Kirby & Parker, 1992*a*). These effects will be discussed in a more general context elsewhere (Amos, Handy, Jones, Kirby, Parker, Percy & Su, 1992).

We thank the Fonds der Chemischen Industrie for support. The crystallographic work on (2) was carried out in Göttingen, at the Institut für Anorganische Chemie der Universität.

References

Amos, R. D., Handy, N. C., Jones, P. G., Kirby, A. J., Parker, J. K., Percy, J. M. & Su, M. D. (1992). *J. Chem. Soc. Perkin Trans.* 2. In the press.
Jones, P. G. & Kirby, A. J. (1979). *J. Chem. Soc. Chem. Commun.* pp. 288–289.
Jones, P. G. & Kirby, A. J. (1984). *J. Am. Chem. Soc.* **106**, 6207.
Jones, P. G., Kirby, A. J. & Parker, J. K. (1992*a*). *Acta Cryst.* C**48**, 859–864.
Jones, P. G., Kirby, A. J. & Parker, J. K. (1992*b*). *Acta Cryst.* C**48**, 855–858.
Jones, P. G., Kirby, A. J. & Parker, J. K. (1992*c*). *Acta Cryst.* C**48**, 849–851.
Jones, P. G., Kirby, A. J. & Parker, J. K. (1992*d*). *Acta Cryst.* C**48**, 852–855.
Sheldrick, G. M. (1990). *SHELXTL Users Manual.* Revision 4. Nicolet XRD Corporation, Madison, Wisconsin, USA.

Acta Cryst. (1992). C**48**, 866–868

Bond Length and Reactivity. The Effect of β-Silicon. Structure of the 4-Phenylbenzoate Ester of 2-Trimethylsilylethanol

By Michael J. Doyle, Anthony J. Kirby, Jonathan M. Percy and Paul R. Raithby

University Chemical Laboratory, Cambridge CB2 1EW, England

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

Abstract. 2-Trimethylsilylethyl 4-phenylbenzoate, $C_{18}H_{22}O_2Si$, $M_r = 299.47$, monoclinic, $P2_1/c$, $a = 6.256\,(1)$, $b = 16.608\,(3)$, $c = 17.012\,(4)$ Å, $\beta = 94.49\,(2)°$, $V = 1762.12$ Å^3, $Z = 4$, $D_x = 1.129$ Mg m^{-3}, $\lambda(\text{Cu } K\alpha) = 1.54178$ Å, $\mu = 1.17$ mm^{-1}, $F(000) = 640$, $T = 293$ K. Final $R =$

0108-2701/92/050866-03$06.00